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van der Veen, Ike

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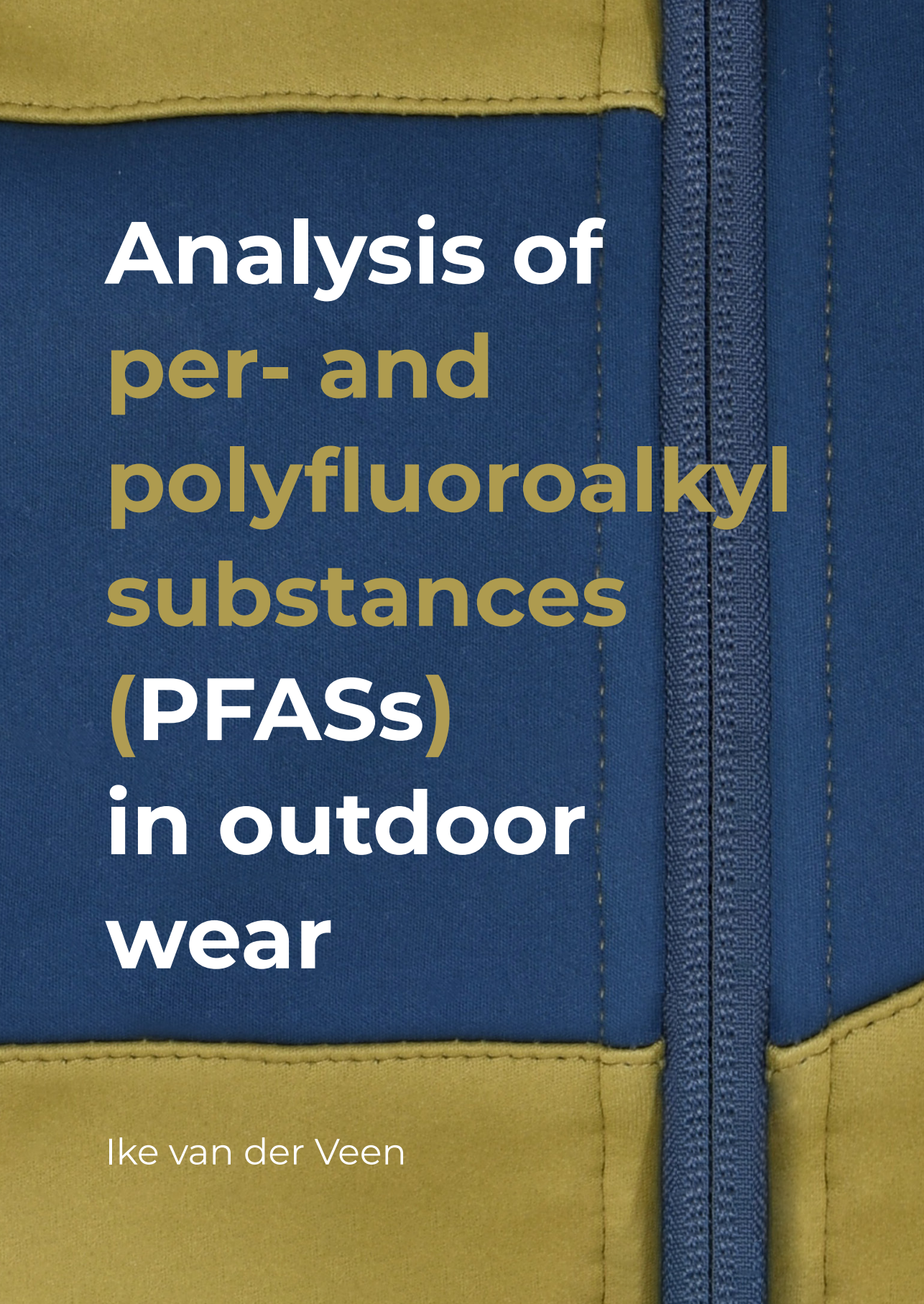

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VRIJE UNIVERSITEIT

ANALYSIS OF PER- AND POLYFLUOROALKYL SUBSTANCES (PFASS) IN OUTDOOR WEAR

ACADEMISCH PROEFSCHRIFT

ter verkrijging van de graad Doctor of Philosophy
aan de Vrije Universiteit Amsterdam,
op gezag van de rector magnificus
prof.dr. J.J.G. Geurts,
in het openbaar te verdedigen
ten overstaan van de promotiecommissie
van de Faculteit der Bètawetenschappen
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door

Ike van der Veen

geboren te Harlingen

promotoren:	prof.dr. J. de Boer prof.dr. P.E.G. Leonards
copromotor:	dr. J.M. Weiss
promotiecommissie:	prof.dr. M.H. Lamoree prof.dr. A.P. van Wezel prof.dr. R.J. Letcher dr. T.P. Traas dr. M. Ricci

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Contents

Abbreviations

AFFF	aqueous film-forming foam
AV	assigned value
BFRs	brominated flame retardants
br-PFOS	branched-perfluorooctane sulfonate anion
bw	body weight
CAS No.	chemical abstract system number
CEE	Central and Eastern Europe
CIC	combustion ion chromatography
CV	coefficient of variation
DDT	dichloro-diphenyltrichloroethane
dl-PCB	dioxin-like PCB
DWR	durable water repellency/durable water repellent
EDI	estimated daily intake
EFSA	European Food Safety Authority
EN	electronegativity
EPA	Environmental Protection Agency
EtFOSA	N-ethyl perfluorooctane sulfonamide
EtFOSE	N-ethyl perfluorooctane sulfonamidoethanol
FBSA	perfluorobutane sulfonamide
FC	fluorine chemistry
FC-4 DWR coating	DWR coatings based on perfluorobutane-based SFPs
FC-6 DWR coating	DWR coatings based on perfluorohexane-based SFPs
FC-8 DWR coating	DWR coatings based on perfluorooctane-based SFPs
FORMAS	Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning
FOSA	perfluorooctane sulfonamide
FTAC	fluorotelomer acrylate
FTMAC	fluorotelomer methacrylate
FTOH	fluorotelomer alcohol
FTP	fluorotelomer-based polymer
FTSA	fluorotelomer sulfonic acid
GC/EI-MS	gas chromatography/electron impact-mass spectrometry
GEF	Global Environment Facility
GenX	2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoic acid

GMP	Global Monitoring Plan
GRULAC	Group of Latin America and the Caribbean
HBCD	hexabromocyclododecane
HDPE	high-density polyethylene
HFPO-DA	2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoic acid
HFPO-TA	ammonium perfluoro-2-[(propoxy) propoxy]-1-propanoate
HxBB	hexabromobiphenyl
ILS	interlaboratory comparison study
INAA	instrumental neutron activation analysis
IS	internal standard
LC	liquid chromatography
LCV	left-censored values
LOD	limit of detection
LOQ	limits of quantification
L-PFBS	linear-perfluorobutane sulfonic acid
L-PFDS	linear-perfluorodecane sulfonic acid
L-PFHxS	linear-perfluorohexane sulfonate anion
L-PFOS	linear-perfluorooctane sulfonate anion
LSE	liquid-solid extraction
MeFBSA	N-methyl perfluorobutane sulfonamide
MeFBSAA	N-methyl perfluorobutane sulfonamidoacetic acid
MeFOSA	N-methyl perfluorooctane sulfonamide
MeFOSE	N-methyl perfluorooctane sulfonamidoethanol
MS/MS	tandem mass spectrometry/tandem mass spectrometric
MTM	Man-Technology-Environment Research Center
N	noise
na	not available
nr	not reported
NAV	no assigned value
NEOF	non-extractable organic fluorine
OCP	organochlorine pesticide
PA	polyamide
PBDE	polybrominated diphenyl ether

PBNS	perfluorobutane sulphonic acid
PBT	persistent bioaccumulative and toxic
PCB	polychlorinated biphenyl
PCDD	polychlorinated dibenzo-*p*-dioxin
PCDF	polychlorinated dibenzofuran
PDF	probability density function
PES	polyester
PFAA	perfluoroalkyl acid
PFAS	per- and polyfluoroalkyl substance
PFBA	perfluorobutanoic acid
PFBS	perfluorobutane sulfonate anion
PFCA	perfluoroalkyl carboxylic acid
PFDA	perfluorodecanoic acid
PFDoDA	perfluorododecanoic acid
PFHpA	perfluoroheptanoic acid
PFHpS	perfluoroheptane sulfonate anion
PFHxA	perfluorohexanoic acid
PFHxS	perfluorohexane sulfonate anion
PFNA	perfluorononanoic acid
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonate anion
PFPeA	perfluoropentanoic acid
PFSA	perfluoroalkane sulfonic acid
PFTeDA	perfluorotetradecanoic acid
PFTrDA	perfluorotridecanoic acid
PFUnDA	perfluoroundecanoic acid
PIGE	particle induced γ-ray emission
POP	persistent organic pollutant
pp	polypropylene
PPA	polymerization processing aid
PTFE	polytetrafluoroethylene
PUF	polyurethane foam
QA	quality assurance
QC	quality control
REACH	Registration, Evaluation and Authorization of Chemicals
Rec	recovery
RIVM	National Institute for Public Health and the Environment

RPF	relative potency factor
RSD	relative standard deviation
SFP	side-chain fluorinated polymer
SI	supporting information
SPE	solid phase extraction
SUPFES	Substitution in Practice of Prioritized Fluorinated Chemicals to Eliminate Diffuse Sources
SVHC	substances of very high concern
TDI	tolerable daily intake
TEF	toxic equivalency factor
TEQ	toxic equivalent
ToF-MS	time-of-flight mass spectrometer
TOP	total oxidizable precursor
TWI	tolerable weekly intake
UNEP	United Nations Environment Programme
UV	ultra violet
VU	Vrije Universiteit Amsterdam
WEOG	Western European and other groups
WEPAL	Wageningen Evaluating Programmes for Analytical Laboratories

Contributions to publications in this thesis

Chapter 2:

Van der Veen, I.; Weiss, J. M.; Hanning, A.; de Boer, J.; Leonards, P. E. G., Development and validation of a method for the quantification of extractable perfluoroalkyl acids (PFAAs) and perfluorooctane sulfonamide (FOSA) in textiles. *Talanta* 2016, 147, 8-15.

(Co)- Author		Contribution
Van der Veen, I.	:	Conceptualization, execution, analyses, data generation, data interpretation, validation, writing
Weiss, J.	:	Supervision, review & editing
Hanning, A.	:	Execution
De Boer, J.	:	Supervision, review & editing
Leonards, P. E. G.	:	Conceptualization, supervision, review & editing

Chapter 3:

Van der Veen, I.; Fiedler, H.; de Boer, J., Assessment of the per- and polyfluoroalkyl substances analysis under the Stockholm Convention – 2018/2019. Submitted to *Chemosphere*.

(Co)- Author		Contribution
Van der Veen, I.	:	Conceptualization, execution, data interpretation, writing
Fiedler, H.	:	Conceptualization, execution, supervision, review & editing
De Boer, J.	:	Conceptualization, supervision, review & editing

Chapter 4:

Van der Veen, I.; Hanning, A.; Stare, A.; Leonards, P. E. G.; de Boer, J.; Weiss, J. M., The effect of weathering on per- and polyfluoroalkyl substances (PFASs) from durable water repellent (DWR) clothing. *Chemosphere* 2020, 249, 126100.

(Co)- Author		Contribution
Van der Veen, I.	:	Conceptualization, execution, analyses, data generation, data interpretation, validation, writing
Hanning, A.	:	Conceptualization, execution
Stare, A.	:	Execution
Leonards, P. E. G.	:	Conceptualization, supervision, review & editing.
De Boer, J.	:	Supervision, review & editing
Weiss, J.	:	Supervision, review & editing

Chapter 5:

Van der Veen, I.; Schellenberger, S.; Hanning, A.; Stare, A.; de Boer, J.; Weiss, J. M.; Leonards, P. E. G., The fate of per- and polyfluoroalkyl substances (PFASs) from durable water repellent (DWR) clothing during use. Submitted to *Environmental Science & Technology*.

(Co)- Author		Contribution
Van der Veen, I.	:	Conceptualization, execution, analyses, data generation, data interpretation, validation, writing
Schellenberger, S.	:	Conceptualization, execution, review & editing
Hanning, A.	:	Conceptualization, execution
Stare, A.	:	Execution
De Boer, J.	:	Supervision, review & editing
Weiss, J.	:	Review & editing
Leonards, P. E. G.	:	Conceptualization, supervision, review & editing.

Chapter 1.

General introduction

1.1. Halogenated compounds

The world around us is made up of countless different chemicals. A number of these are naturally occurring, but a significant proportion are manmade (synthetic) chemicals. Those manmade chemicals were synthesized because of their great benefits, or they were just coincidently synthesized, while the benefit of the chemical was discovered later. In many cases this resulted in large production volumes and intense use of those chemicals. An example is dichloro-diphenyltrichloroethane (DDT). This compound was already synthesized for the first time in 1873 by Othmar Zeidler, but not earlier than 1939 the usefulness of the substance as an insecticide was discovered and demonstrated by Paul Hermann Müller[1, 2]. He received the Nobel Prize in 1948 because DDT proved to be of great value in the fight against typhoid and malaria.

Like DDT, a lot of other organochlorine pesticides like dieldrin, heptachlor, toxaphene and other chlorine-containing organic compounds have been produced, like for example polychlorinated biphenyls (PCBs). These were produced since the late 1920s[3] for their functionality as an isolation fluid, hydraulic fluid, cooling liquid, lubricant, etc. PCBs have also been used as flame-retardants. In the 1970s other types of halogen-containing organic flame-retardants were introduced at the market, namely the brominated flame retardants (BFRs), which are mainly used in electronics and furniture. Nowadays ca. 75 types of brominated organic compounds are being synthesized and marketed.

Besides the aforementioned chlorinated and brominated organic compounds, a third group of halogenated organic substances, the per- and polyfluoroalkyl substances (PFASs), entered the market in the 1950s. PFASs are also manmade chemicals. They have a great functionality in a wide range of consumer products, e.g. as aqueous film-forming foam (AFFF) in firefighting foams, as water and dirt repellent on outdoor wear and furniture, in food wrapping paper, etc. Some are being used as intermediates in the Teflon® production, which is among other used in non-stick coatings in cooking pans.

All those halogen-containing organic compounds have been widely used and applied and have been praised for their good functionality. However, nowadays much more knowledge has become available about the negative side effects of these halogen containing chemicals. The once highly acclaimed DDT turned out to be a highly toxic substance, which, due to its frequent use and persistence, disappears only very slowly from the environment. Like DDT, PCBs are nowadays classified as persistent, bioaccumulative and toxic (PBT) substances. Some of the PCBs have been proven

to have toxic properties comparable to those of dioxins. Polychlorinated dibenzo-*p*-dioxins (PCDDs) and furans can be formed in aging PCB oil, and also be formed from combustion of chlorinated organic compounds, such as PCBs, at temperatures below 1000°C. Also, many BFRs are persistent, toxic and accumulative. All those chlorinated, and brominated compounds are highly lipophilic. When they end up in the environment, they can be found in sediments, as well as in biota, while biomagnification takes place in the food-chain. As a result, those compounds can also be found in the human body, where they are mostly stored in the fat tissue.

1.2. PFAS

The PFASs show a different behavior than the chlorinated and brominated compounds. PFASs consist of a polar functional group like a carboxylic acid, sulfonic acid, alcohol, etc. and a carbon backbone, which varies in carbon chain length from three to more than 20 carbon atoms, of which at least one is fully fluorinated.

In Figure 1-1 the molecular structure of one of the PFASs, perfluorooctane sulfonic acid (PFOS), is given as an example. PFOS has a carbon chain of eight carbon atoms, a sulfonic acid functional group, and all the carbon atoms are fully fluorinated.

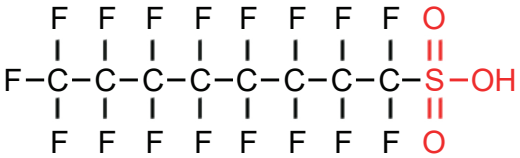

Figure 1-1 Molecular structure of perfluorooctane sulfonic acid (PFOS).

The functional groups of PFASs are polar, while the carbon backbone is a nonpolar chain. However, due to the strong electronegative character of the fluorine atoms (EN= 3.98), the electron cloud within the C-F bonds is very strongly drawn towards the fluorine atoms. This ensures that the carbon chain is neither nonpolar nor polar. This gives the PFASs their unique properties. In the human body PFASs bind in particular to the protein albumin[4] in blood while they are less accumulated in the fat tissue. They are therefore found in whole blood, and not only in the serum. They accumulate in the liver, kidney, brain, lung, and bones[5].

There are several production methods for PFASs, but the main manufacturing processes are electrochemical fluorination (ECF), and telomerization[6]. The PFAS product is dependent of the manufacturing process. The products of telomerization contain mainly PFASs with a linear carbon chain, consisting of an even number of C-atoms, while with ECF PFASs with even as well as odd carbon chain lengths are produced. With ECF a mixture of 70% linear and 30 % branched PFAS isomers is produced.

As can be observed in Figure 1-1, PFASs contain a large number of C-F bonds. The covalent bond between a fluorine atom and a carbon atom is one of the strongest single bonds in organic chemistry. The fluorine atom is the most electronegative atom of all elements in the periodic table, and hence the most electronegative of the halogen atoms. Due to the high electronegativity of the fluorine atom (EN=3.98) compared to the electronegativity of carbon (EN=2.55) the electrons of the C-F bond are drawn towards the fluorine atom, resulting in a high density of electrons around the fluorine atom, and a low density around the carbon atom, which makes both atoms partially charged. This results in a very strong bond between the fluorine and the carbon with a dissociation energy up to 536 kJ/mol. Due to those strong C-F bonds, PFASs are extremely persistent. In comparison, the dissociation energy of the C-Cl bond is 397 kJ/mol and of the C-Br bond 280 kJ/mol. PCBs and many BFRs, which are classified as persistent organic pollutants (POPs), have half-lives of some decades. The PFASs on the other hand are classified as “forever chemicals”, since they are resistant to complete mineralization under natural conditions[7]. Although a variety of studies are being conducted on remediation, at this moment the only way to clean up PFASs is to burn them at high temperatures (> 900°C), at which PFASs break down. Huang and Jaffé (2019)[8] discovered acidimicrobium Sp. autotroph bacteria, who were supposed to degrade PFASs. However, the conditions are so specific (presence of ammonium and high iron concentrations) that this does not work in practice or only at very specific locations. No other bacteria have been identified to attack the C-F bond. Therefore, bioremediation of PFASs-contaminated sites is, until now, no feasible option.

Unfortunately, PFASs are also very mobile. Some of the PFASs are more water soluble, such as perfluorooctanoic acid (PFOA), and will be distributed by surface water up to hundreds of kilometers from the point source[9]. They can also transported to and by the groundwater. Some other PFASs are more volatile, and due to the grasshopper effect, they even end up at the North and South pole[10-12].

Like the chlorinated, and the brominated organic compounds, PFASs were, and still are praised for their good functionality. For example, the non-stick coating in pans

appeared to be a great invention. Also the water and dirt repellence of the PFASs is one of the very popular properties for their use in jackets, shoes and furniture. In firefighting foams the PFASs are very much needed because of the very good film forming foam properties of PFASs. Their fire-extinguishing abilities cannot be reached with any other non-PFASs containing firefighting foam. This is especially true for fires in large atmospheric storage tanks.

Nowadays, it is known that PFASs, like the other organohalogen compounds mentioned above, do not only possess beneficial properties. They are very persistent and very mobile and harmful to the environment and human health.

Since 1951, a factory of Dupont in Parkersburg (West Virginia) used PFOA, which is one of the PFASs, for the production of polytetrafluoroethylene (PTFE or Teflon®). Since the late 1980s a high percentage of employees of Dupont who worked in the factory were diagnosed with cancer and leukemia[13, 14]. In the neighborhood of the Teflon plant, a remarkable number of miscarriages, deformities, kidney and liver cancers and lung diseases appeared. Cows became aggressive, and a high death rate among cattle was observed. People in the surroundings of the plant called this the Teflon disease. Later on it was found out that Dupont discharged enormous amounts of PFOA powder into the Ohio river, and dumped tons of sludge, contaminated with PFOA, into the environment. The environmental lawyer Robert Bilott started to study the observed health issues in relation with PFOA pollution and exposure of the cattle, the citizens of Parkersburg and the employees of Dupont. He filed a federal suit against Dupont for the first time in the summer of 1999[15]. Finally, in 2005 DuPont settled with the United States Environmental Protection Agency (US-EPA) for 16.5 million dollar, because of being accused of withholding information on the toxicity of PFOA and the environmental pollution. As part of the settlement agreement, the C8 Health Project was set up, authorized, and funded. Within the C8 Health Project, the amounts of PFOA and PFOS were determined in blood samples and health data was collected by questionnaires and blood tests. This resulted in more knowledge on the harmfulness of PFOS and PFOA. Partly due to the Parkersburg case PFASs have attracted attention, and more projects and research on the health effects of PFASs have been conducted since.

For PFOS and PFOA more knowledge is now available on possible negative health outcomes caused by exposure to those compounds. Also for some other PFASs, like perfluorohexane sulfonic acid (PFHxS), some studies have already been conducted on possible negative health effects after exposure to those PFASs. For other PFASs it is still unclear, and more research is needed here. Despite this data gap in knowledge, because of the persistence and mobility of PFASs, and the ability of non-persistent

PFASs to degrade or transform into the persistent and harmful PFASs, like the perfluoroalkyl carboxylic acids (PFCAs), and perfluoroalkane sulfonic acids (PFSAs), the use of PFASs is more and more restricted, and safety norms are regularly adjusted to a decreased value.

1.3. Safety and legislation

Partly due to the "Parkersburg case", authorities and companies became aware of the drawbacks of using PFOA, and other PFASs, which resulted in legislation for some of the PFASs. Within the EU, the first PFAS of which the production and use was regulated was PFOS in 2006. In Antwerp, Belgium, the 3M company voluntarily stopped their production of PFOS in 2000, although leaving behind a highly polluted site, at which other PFASs are still being produced. Nowadays, PFOS, and PFOA are included in the Stockholm Convention list of persistent organic pollutants (POPs)[16-18], PFHxS is recommend to be considered for listing in Annex A of the Convention[19, 20], and long-chain PFCAs are proposed for listing under this Convention[21]. In October 2020 the European Commission published a strategy for sustainable chemistry management[22]. Besides other actions, the EU intends to phase out the production and use of PFASs in the EU, unless their use is essential and alternatives are not available.

Because PFOS and PFOA were increasingly found in the environment, in 2008 the European Food Safety Authority (EFSA) evaluated the importance of food to human exposure to those compounds, and established a tolerable daily intake (TDI) for PFOS of 150 ng/kg body weight (bw) per day and for PFOA 1.5 µg/kg bw/d, stating that the general population would not have any negative health effects, i.e. liver damage and developmental and reproductive problems, when exposed by food intake below those TDIs[23].

Since then, the EFSA has lowered the TDIs for PFOS and PFOA several times, after toxicological effect data became gradually available. In 2018, for the first time tolerable weekly intakes (TWIs) were set instead of TDIs. For both PFOS and PFOA, the new TWI (PFOS: 13 ng/kg bw/week, PFOA: 6 ng/kg bw/wk) were, besides other effects as reduced birth weight, based on the risk of an elevated cholesterol level as most critical effect[24].

In 2020 the EFSA drastically lowered the tolerable intake of PFASs again. This time the calculation of the new TWI was based on the decrease in immune response after vaccination[25, 26], which occurs at much lower PFAS concentrations than an increase in cholesterol level. For the first time the TWI was not based on a single compound, but

on the sum of four PFASs, since PFASs often co-occur in food and drinking water[27]. The TWI for the sum of the intake of PFOA, PFOS, perfluorononanoic acid (PFNA), and PFHxS was set at 4.4 ng/kg bw/wk. The RIVM used this TWI to estimate the exposure and risk of the Dutch population. Based on available data of Dutch food intake and drinking water intake, they concluded that people in the Netherlands on average exceed this TWI. The exposure by food was estimated at 83-98% of the TWI and that of drinking water is 2-17%. Interestingly, exposure to indoor dust was not calculated. Levels of several PFASs are, however, quite elevated compared to those in other countries and may contribute to the daily intake[28.] For example, in ten house and office dust samples the average PFOS concentration was 35 µg/kg, and the perfluorobutane sulphonic acid (PBNS) concentration 351 µg/kg. These levels are much higher than the maximum concentrations proposed for PFASs in soil, which are 3 µg/kg for PFOS, 7 µg/kg for PFOA and 3 µg/kg for all other PFASs, for use for building activities. Also, the average intake of indoor dust, 20 mg/d, is much higher than a possible intake of outdoor soil[29, 30]. Currently, several thousands of different PFASs exist, which all have different properties, due to their differences in carbon chain length, functional group, branching, and fluorination degree. Individual PFASs are, therefore, not equally persistent. Some PFASs do (bio)degrade or transform into the not (bio)degradable PFCAs, and PFSAs. The toxicity, risk and harmfulness of the PFCAs and PFSAs also differ per compound. This is partly due to the fact that the short-chain PFASs are much more water-soluble and will therefore be found more often in water, while longer-chain PFASs are detected more often in sediments and biota. All PFASs present in the environment or in organisms can have a toxic effect, although not equal per compound. An extreme example is perfluoro iso-butene[31], which is acutely toxic[32, 33], but was nevertheless legally discharged by the Teflon plant of Chemours in Dordrecht, The Netherlands[34]. The permit has been reduced in 2013 to 28 kg/yr[35, 36]. From 1 January 2025 this permit will be reduced to 0.28 kg/yr[36].

A proposal has now been made by Bil et al. (2021)[27] to express the toxicity of individual PFASs based on a relative potency factor (RPF) methodology equal to the toxic equivalency factor (TEF) system for dioxins. With the TEF system a multiplication factor is established for each dioxin compound, based on a comparison with the most toxic dioxin, which is 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD). For determining the mixture effect of dioxins present in a sample, total concentrations of dioxins are not expressed in mass units, but in Toxic Equivalents (TEQ), which is the sum of the concentrations of individual dioxins multiplied by their TEF values.

For determining the RPF of PFASs, PFOA is used as the index compound and set at one. PFASs which are less toxic than PFOA will have a RPF lower than one, and compounds which are more toxic will have a value higher than one.

Bil et al.[27] derived the RPFs of 16 PFASs based on liver effects, and of seven PFASs based on read across. The RPFs range from 0.001 for PFBS up to 10 for PFNA. The RPFs could have had different values when another endpoint was chosen, like developmental toxicity or immunotoxicity.

1.4. Consequences of legislation and setting safety standards

Legislation of (some) PFASs, and setting safety standards, have consequences and impact on various social, and economic aspects of our society. One example of this was the standard set in the Netherlands for PFASs in soil of construction land. Because of the knowledge on health effects of PFASs, in 2019 the Dutch Government, advised by the Dutch National Institute for Public Health and the Environment (RIVM), set an admissible norm for PFASs of maximum 0.1 µg/kg for soil of construction land. This was an extremely low level. It was basically the implementation of the precautionary principle[37] and based on the detection limits of the analytical method for quantification of PFASs in soil[38, 39]. Since PFASs have been, and are, so widely used and are, in addition to being PBT substances, also mobile, PFASs are detected everywhere in the environment. As a consequence hardly anywhere in the Netherlands soil can be found with PFOA concentrations below this standard. As a result, construction in the Netherlands came to a standstill for several weeks in 2019, with dramatic economic consequences. Therefore, and following protests of building companies, a new standard was temporarily installed, being 7 µg/kg for PFOA, and 3 µg/kg for every other individual PFAS. This made that the construction projects could continue again[40, 41]. At the moment a final standard for PFASs in soil is being discussed.

Another example of the consequences of legislation of some of the PFASs, is the substitution by one or more other harmful compounds, which is called regrettable substitution. In a fluoropolymer production factory in Dordrecht (The Netherlands) PFOA was used as polymerization processing aid (PPA) until 2012. Since PFOA was labeled as a POP under the Stockholm Convention, the production plant in Dordrecht stopped using PFOA, and switched to the use of the ammonium salt of 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoic acid (HFPO-DA) (see Figure 1-2), also called GenX, as alternative chemical for PFOA.

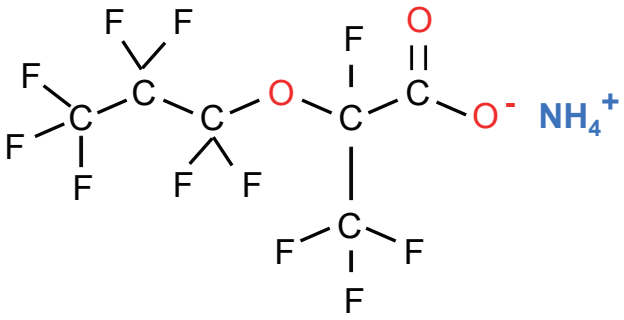

Figure 1-2 Molecular structure of ammonium salt of 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy) propanoic acid (HFPO-DA), also called GenX.

GenX showed to be less bioaccumulative than PFOA. However, GenX is expected to be just as persistent and to have a comparable toxic potency to PFOA, which was determined in a toxicokinetic model study for male rats[42]. GenX is a more water soluble compound than PFOA, and hence more mobile in surface- and groundwater. As a result GenX ends up in drinking water, much more than PFOA[42]. In this way one hazard of PFOA – bioaccumulation in fish – was replaced by another hazard of PFOA in drinking water, of which each citizen consumes ca. 2 L per day. Several other alternatives for PFOA are being used worldwide, such as the use of ammonium perfluoro-2-[(propoxy) propoxy]-1-propanoate (HFPO-TA) in China[43]. This compound was found in surface water collected from the Xiaoqing River (5200–68500 ng/L) and in residents (mean 2.9 ng/mL blood) residing near a fluoropolymer production plant in Huantai County, China. These examples show that banning one compound leads to the introduction of alternatives that are often not much better in environmental behavior.

An additional example of the impact of legislation of PFASs on social and economic aspects of society, is the regulation on PFASs in products. Within the EU, the first PFAS of which the production and use was regulated was PFOS in 2006. Among others this had quite an impact for fire fighters. The use of PFOS in firefighting foam provided a solid foam layer with a strong extinguishing capability. Prohibiting the use of PFOS containing fire-fighting foams created the need for alternative chemicals. However, no other chemicals than PFASs with the quality in functionality as PFOS currently exist. As alternative, firefighting foams were produced which contained 6:2 fluorotelomer sulfonic acid (6:2 FTSA), although the fire-extinguishing quality was less good then those of PFOS-containing firefighting foams. 6:2 FTSA has the same structure as PFOS, except for two carbon atoms nearest to the functional group that are not fluorinated (see Figure 1-3).

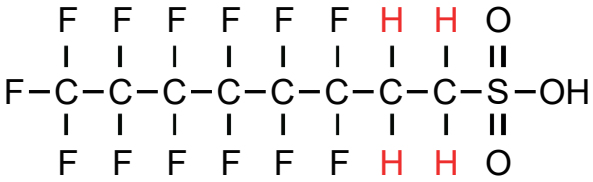

Figure 1-3 Molecular structure of 6:2 fluorotelomer sulfonic acid (6:2 FTSA).

In addition, in the environment 6:2 FTSA can transform into the very persistent PFPeA, and PFHxA[44]. Since legislation in the Netherlands and in the EU is nowadays moving towards not using PFASs at all, or only in essential applications for which no alternative is present, there is a need for PFAS-free alternatives, which are now becoming available for firefighting foams[45].

1.5. PFASs in outdoor clothing

In outdoor clothing, fluorotelomer based polymers (FTPs) with side-chains of long-chain PFASs are used for their water and dirt repellent properties. Because of the regulation of some PFASs and because of the increasing knowledge on the adverse effects of especially the long-chain PFASs, industries started to phase out the use of long-chain PFASs, and started to use alternative chemicals. Those alternative chemicals in outdoor clothing and uniforms were i) FTPs with side-chains of short-chain PFASs, ii) silicon-based polymers or iii) hydrocarbon based polymers[46]. To avoid regrettable substitutions, like the use of GenX instead of PFOA, and water and fat repellence should be maintained as desired properties in outdoor clothing, the Substitution in Practice of Prioritized Fluorinated Chemicals to Eliminate Diffuse Sources (SUPFES)[47] project was set up in 2013. The project team consisted of a consortium of three universities (Stockholm University, Chalmers University of Technology, and the Vrije Universiteit Amsterdam), the outdoor company Haglöfs, the wastewater treatment association Käppala and the Research Institute of Sweden (RISE). The project was financed by the Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning (FORMAS), and ended officially in 2020. The aim of SUPFES was to characterize the diffuse emissions of PFASs from consumer products, such as textiles. In the SUPFES project, alternatives to the long-chain PFASs (FTPs with side-chains of short-chain PFASs, silicon-based polymers, and hydrocarbon based polymers), which were already on the market were assessed in comparison with the long-chain PFASs. The functionality, the toxicity and the emissions of the alternatives during use of the outdoor clothing were examined.

1.6. Scope and outline of the thesis

The work described in this thesis is largely resulting from the SUPFES project and focused on the behavior of PFASs in, and the emission of PFASs from, textiles of outdoor clothing and uniforms during use. The objectives of the study were first to set up extraction and analyses methods for the analyses for ionic as well as volatile PFASs in textiles with a durable water repellence (DWR) coating, with a good quality assurance and quality control. A second objective of the study was to determine the effect of weather conditions on PFASs used in outdoor clothing with a DWR coating, and the final objective was to determine the emissions of PFASs during the use phase of outdoor clothing coated with a DWR based on long-chain PFASs in comparison with outdoor clothing coated with DWR based on alternative shorter-chain PFASs.

1.6.1. Quality assurance and quality control in PFAS analyses

In 2006 a maximum level of 1 µg/m^2 for PFOS in textiles was set by the European[48] while a maximum of 1 µg/m^2 for PFOA was set in 2014 in Norway, being the first country setting a limit for PFOA[49]. To determine whether a textile meets these requirements, there is a demand for good quality assurance (QA) and quality control (QC) for the analysis of PFASs in textile, to avoid that reported concentrations would depend of the quality of the analyzing laboratory.

Various methods have already been developed and described for the analysis of ionic PFASs in sediment, food, fish, water etc. However, no validated methods have been described for the extraction of PFASs from DWR-coated textiles. For this reason, the development, optimization and validation of an extraction and analysis method for ionic PFASs from DWR-coated textiles was developed, optimized and validated (Chapter 2).

Although nowadays PFAS analyses are performed in many laboratories, the analysis remains a challenge, and there is a need for (more) interlaboratory comparison studies (ILSs) to evaluate the comparability of laboratories, especially since some of the PFASs, like PFOS and PFOA, have now been added to the POP list of the Stockholm Convention. Countries that signed the Stockholm Convention are obliged to properly analyse these compounds in certain matrices like air, sediment, and biota. Chapter 3 reports on the organization and evaluation of such a worldwide ILS that was organized in 2018/2019.

1.6.2. Effect of weather conditions on PFASs used in outdoor clothing with a DWR coating

Chapter 4 describes the change in PFAS levels after exposure of commercially available DWR-coated textiles of outdoor clothing to elevated ultra violet (UV) radiation, humidity, and temperature in an aging device. To assess the influence of weathering on PFASs in DWR-treated outdoor clothing, the concentrations of PFASs in the textiles were determined before and after weathering. The hypothesis was that PFASs used in the DWR-treated outdoor clothing are a relevant source of environmental pollution and human exposure due to emission of PFASs during usage.

1.6.3. Emissions of PFASs during the use phase of outdoor clothing

Commercially available textiles of outdoor wear are less suitable to make a good comparison between different DWR chemistries, because it is unknown what type of DWR chemistry was applied on the textiles, and which other additives would possibly be present. Therefore, in the SUPFES project two fabrics, a polyamide (PA) and a polyester (PES) textile, have been coated with different fluorochemistry DWR formulations. Chapter 5 describes the comparison of the effect of washing, tumble drying, and aging on the PFAS concentrations in the DWR of the C_6-based side-chain fluorinated polymers (SFPs) coated textiles compared to the 'old fashioned' C_8-based SFP coated textiles. A comparison was made between the concentrations and the identities of PFASs before and after aging, washing and tumble drying cycles.

In Chapter 6 the results of the research as described in chapters 2 to 5 are discussed, followed by conclusions and recommendations.

References

1. Metcalf, R. L., Century of DDT. *Journal of Agricultural and Food Chemistry* 1973, 21, 511.
2. Dash, A. P.; Raghavendra, K.; Pillai, M. K. K., Resurrection of DDT : A critical appraisal. *Indian Journal of Medical Research* 2007, 126, 1.
3. Bergman, Å.; Rydén, A.; Law, R. J.; de Boer, J.; Covaci, A.; Alaee, M.; Birnbaum, L.; Petreas, M.; Rose, M.; Sakai, S.; Van den Eede, N.; van der Veen, I., A novel abbreviation standard for organobromine, organochlorine and organophosphorus flame retardants and some characteristics of the chemicals. *Environment International* 2012, 49, 57-82.
4. Fedorenko, M.; Alesio, J.; Fedorenko, A.; Slitt, A.; Bothun, G. D., Dominant entropic binding of perfluoroalkyl substances (PFASs) to albumin protein revealed by 19F NMR. *Chemosphere* 2021, 263, 128083.
5. Pérez, F.; Nadal, M.; Navarro-Ortega, A.; Fàbrega, F.; Domingo, J. L.; Barceló, D.; Farré, M., Accumulation of perfluoroalkyl substances in human tissues. *Environment International* 2013, 59, 354-362.
6. Interstate technology regulatory council (ITRC), History and use of per- and polyfluoroalkyl substances (PFAS), Washington, USA, April 2020. https://pfas-.itrcweb.org/fact_sheets_page/PFAS_Fact_Sheet_History_and_Use_April2020.pdf.
7. Cousins, I. T.; DeWitt, J. C.; Glüge, J.; Goldenman, G.; Herzke, D.; Lohmann, R.; Ng, C. A.; Scheringer, M.; Wang, Z., The high persistence of PFAS is sufficient for their management as a chemical class. *Environmental Science: Processes & Impacts* 2020, 22, 2307-2312.
8. Huang, S.; Jaffé, P. R., Defluorination of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) by Acidimicrobium SP. Strain A6. *Environmental Science & Technology* 2019, 53, 11410-11419.
9. Joerss, H.; Xie, Z.; Wagner, C. C.; von Appen, W.-J.; Sunderland, E. M.; Ebinghaus, R., Transport of legacy perfluoroalkyl substances and the replacement compound HFPO-DA through the Atlantic gateway to the Arctic Ocean—Is the Arctic a sink or a source? *Environmental Science & Technology* 2020, 54, 9958-9967.
10. Garnett, J.; Halsall, C.; Vader, A.; Joerss, H.; Ebinghaus, R.; Leeson, A.; Wynn, P. M., High concentrations of perfluoroalkyl acids in Arctic seawater driven by early thawing sea ice. *Environmental Science & Technology* 2021, 55, 11049-11059.
11. Shoeib, M.; Harner, T.; Vlahos, P., Perfluorinated chemicals in the Arctic atmosphere. *Environmental Science & Technology* 2006, 40, 7577-7583.
12. Lowther, N., Emerging contaminants in the Antarctic - A review, University of Canterbury, UK, 2015. http://hdl.handle.net/10092/14112.
13. Andrews;, D.; Walker, B., Poisoned legacy, Ten years later, chemical safety and justice for duponts teflon victims remain elusive, Environmental working group Washington, April 2015. www.ewg.org.
14. Northeastern University, Social Science Environmental Helath Research Institute, The PFAS Project Lab, Parkersburg, West Virginia, USA. https://pfasproject.com/parkersburg-west-virginia/ (Accessed: 12 October 2021).
15. Rich, N., The lawyer who became DuPont's worst nightmare, The New York Times Magazine, 6 January, 2016.

https://www.nytimes.com/2016/01/10/magazine/the-lawyer-who-became-duponts-worst-nightmare.html.
16. UNEP, Decision SC-4/17. Listing of perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride. UNEP-POPS-COP.4-SC-4-17, Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants: Geneva, Switzerland, 2009. http://chm.pops.int/TheConvention/ConferenceoftheParties/ReportsandDecisions/tabid/208/Default.aspx.
17. UNEP, Decision: SC-9/12. Listing of perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds. UNEP-POPS-COP.9-SC-9-12, Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants: Geneva, Switzerland, 2019. http://chm.pops.int/TheConvention/ConferenceoftheParties/Meetings/COP9/tabid/7521/ItemId/7235/Default.aspx.
18. UNEP, Guidance on the Global Monitoring Plan for Persistent Organic Pollutants. UNEP/POPS/COP.7/INF/39, Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants: Geneva, Switzerland, 2015; p 168. https://www.unitar.org/media/2673.
19. UNEP, Perfluorohexane sulfonic acid (PFHxS), its salts and PFHxS-related compounds. UNEP-POPS-POPRC.15-POPRC-15-1, Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants: Rome, Italy, 2019. http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC15/Overview/tabid/8052/Default.aspx.
20. UNEP, Report of the Persistent Organic Pollutants Review Committee on the work of its fifteenth meeting. UNEP/POPS/POPRC.15/7/Add.1, Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants: Rome, Italy, 2019. http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC15/Overview/tabid/8052/Default.aspx.
21. UNEP, Proposal to list long-chain perfluorocarboxylic acids, their salts and related compounds in Annexes A, B and/or C to the Stockholm Convention on Persistent Organic Pollutants. UNEP/POPS/POPRC.17/7, Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants: Geneva, Switzerland, 2021. http://chm.pops.int/Convention/POPsReviewCommittee/Chemicals/tabid/243/Default.aspx.
22. European Commision, communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions, Chemicals Strategy for Sustainability towards a Toxic-Free Environment, Brussels, Belgium, 14 October 2020. https://ec.europa.eu/environment/strategy/chemicals-strategy_en.
23. EFSA, European Food Safety Authority, EFSA opinion on two environmental pollutants (PFOS and PFOA) present in food. https://www.efsa.europa.eu/en/news/efsa-opinion-two-environmental-pollutants-pfos-and-pfoa-present-food (21 July 2008).
24. EFSA, European Food Safety Authority, Risk to human health related to the presence of perfluorooctane sulfonic acid and perfluorooctanoic acid in food. https://efsa.onlinelibrary.wiley.com/doi/epdf/10.2903/j.efsa.2018.5194 (22 March 2018).

25. Grandjean, P.; Heilmann, C.; Weihe, P.; Nielsen, F.; Mogensen, U. B.; Timmermann, A.; Budtz-Jørgensen, E., Estimated exposures to perfluorinated compounds in infancy predict attenuated vaccine antibody concentrations at age 5-years. *Journal of immunotoxicology* 2017, 14, 188-195.
26. Abraham, K.; Mielke, H.; Fromme, H.; Völkel, W.; Menzel, J.; Peiser, M.; Zepp, F.; Willich, S. N.; Weikert, C., Internal exposure to perfluoroalkyl substances (PFASs) and biological markers in 101 healthy 1-year-old children: associations between levels of perfluorooctanoic acid (PFOA) and vaccine response. *Archives of Toxicology* 2020, 94, 2131-2147.
27. Bil, W.; Zeilmaker, M.; Fragki, S.; Lijzen, J.; Verbruggen, E.; Bokkers, B., Risk assessment of per- and polyfluoroalkyl substance mixtures: A relative potency factor approach. *Environmental Toxicology and Chemistry* 2021, 40, 859-870.
28. Harrad, S.; Wemken, N.; Drage, D. S.; Abdallah, M. A.-E.; Coggins, A.-M., Perfluoroalkyl substances in drinking water, indoor air and dust from Ireland: implications for human exposure. *Environmental Science & Technology* 2019, 53, 13449-13457.
29. Jones-Otazo, H. A.; Clarke, J. P.; Diamond, M. L.; Archbold, J. A.; Ferguson, G.; Harner, T.; Richardson, G. M.; Ryan, J. J.; Wilford, B., Is house dust the missing exposure pathway for PBDEs? An analysis of the urban fate and human exposure to PBDEs. *Environmental Science & Technology* 2005, 39, 5121-5130.
30. Canada, H., Canadian Environmental Protection Act: Human health risk assessment for priority substances, Ottawa, Canada 1994. https://publications.gc.ca/collections/collection_2018/eccc/En40-215-41-eng.pdf.
31. Weigert, F. J., Interaction of perfluorocarbons with carbon. *Journal of Fluorine Chemistry* 1993, 65, 67-71.
32. US-EPA, Environmental Protection Agency, About Acute Exposure Guidline Levels (AEGLs); 22/11/2017. https://www.epa.gov/aegl/about-acute-exposure-guideline-levels-aegls.
33. TOXNET, Toxicology Data Network, Perfluoroisobutylene Casnr: 382-21-8. https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+7708 (10-6-2017).
34. MOB, Mobilisation for the environment, Advies met betrekking tot "Aanvraag revisievergunning Wabo/Aanvraag Watervergunning Chemours Netherlands B.V. 30 maart 2018, Nijmegen, 16 mei 2018. https://api1.ibabs.eu/publicdownload.aspx?site=sliedrecht&id=dff3fb96-e96c-4a7c-956c-51973f345eb5 (14-01-2022).
35. Omgevingsdienst Zuid-Holland, Zaaknummer 0080010, Kenmerk 2013023603, Besluit van Gedeputeerde Staten van Zuid-Holland. http://docplayer.nl/12942824-Ontwerpbeschikking-besluit-van-gedeputeerde-staten-van-zuid-holland-algemeen.html (14-2-2022).
36. DCMN milieudienst Rijnmond, Beschikking, Besluit van Gedeputeerde Staten van Zuid-Holland, Kenmerk 999998149_9999638428, 16 december 2019. https://www.papendrecht.nl/Inwoners/Overzicht_Inwoners/Nieuws_en_bekendmakingen/Nieuws_over_Chemours_Dupont/Archief/Artikelen_2019/Uitstoot_PFAS_verbindingen_Chemours_verder_verlaagd/Brief_van_de_Gedeputeerden_Vermeulen_en_Bom_Lemstra_Verdere_verlaging_PFAS_emissies_Chemours_naar_lucht_en_water (14-2-2022).

37. Kriebel, D.; Tickner, J.; Epstein, P.; Lemons, J.; Levins, R.; Loechler, E. L.; Quinn, M.; Rudel, R.; Schettler, T.; Stoto, M., The precautionary principle in environmental science. *Environmental Health Perspectives* 2001, 109, 871-876.
38. RIVM, Rijksinstituut voor Volksgezondheid en Milieu, Vragen en antwoorden PFAS in grond en bagger. https://www.rivm.nl/pfas/bodem/vragen-en-antwoorden-pfas-in-grond-en-bagger (Access data: 5 July 2021).
39. Ministerie van Infrastructuur en Waterstaat, The Hague, the Netherlands, Brief aan De voorzitter van de Tweede Kamer der Staten-Generaal, Beantwoording Kamervragen van het lid Von Martels (CDA) over het bericht baggersector ligt goeddeels stil door strengere norm chemische stoffen PFAS. https://www.rijksoverheid.nl/documenten/kamerstukken/2019/10/29/beantwoording-kamervragen-van-het-lid-von-martels-cda-over-het-bericht-baggersector-ligt-goeddeels-stil-door-strengere-norm-chemische-stoffen-pfas (29 oktober 2019).
40. Ministerie van Infrastructuur en Waterstaat, The Hague, the Netherlands, Brief aan De voorzitter van de Tweede Kamer der Staten-Generaal, Aanpassingen beleid PFAS. https://www.rijksoverheid.nl/documenten/kamerstukken/2020/07/01/aanpassingen-beleid-pfas (1 juli 2020).
41. Rijksoverheid, Ministerie van Infrastructuur en Waterstaat, The Hague, the Netherlands, Tijdelijk handelingskader voor hergebruik van PFAS-houdende grond en baggerspecie Geactualiseerde versie 2 juli 2020. https://www.rijksoverheid.nl/documenten/rapporten/2020/07/03/bijlage-geactualiseerd-tijdelijk-handelingskader (2 July 2020).
42. Brandsma, S. H.; Koekkoek, J. C.; van Velzen, M. J. M.; de Boer, J., The PFOA substitute GenX detected in the environment near a fluoropolymer manufacturing plant in the Netherlands. *Chemosphere* 2019, 220, 493-500.
43. Pan, Y.; Zhang, H.; Cui, Q.; Sheng, N.; Yeung, L. W. Y.; Guo, Y.; Sun, Y.; Dai, J., First Report on the Occurrence and Bioaccumulation of Hexafluoropropylene Oxide Trimer Acid: An Emerging Concern. *Environmental Science & Technology* 2017, 51, 9553-9560.
44. Zhang, S.; Lu, X.; Wang, N.; Buck, R. C., Biotransformation potential of 6:2 fluorotelomer sulfonate (6:2 FTSA) in aerobic and anaerobic sediment. *Chemosphere* 2016, 154, 224-230.
45. Fluorine-free firefighting foams (3F) viable alternatives to fluorinated aqueous film-forming foams (AFFF), Independent Expert Panel Convened by IPEN Stockholm Convention POPRC-14, , Rome, Italy, September 2018. https://ipen.org/sites/default/files/documents/IPEN_F3_Position_Paper_POPRC-14_12September2018d.pdf.
46. Holmquist, H.; Schellenberger, S.; van der Veen, I.; Peters, G. M.; Leonards, P. E. G.; Cousins, I. T., Properties, performance and associated hazards of state-of-the-art durable water repellent (DWR) chemistry for textile finishing. *Environment International* 2016, 91, 251-264.
47. SUPFES, Substitution in Practice of Prioritized Fluorinated Chemicals to Eliminate Diffuse Sources. Formas 2012-11652-24486-65. https://www.ri.se/en/what-we-do/projects/supfes (22-05-2021).

48. EU, Directive 2006/122/EC of the European Parliament and of the Council of 12 December 2006. *Official Journal of the European Union* 2006, L 372/32, 32-34.
49. Lovdata, PFOA-Restriction in Norway, Forskrift om begrensning i bruk av helse- og miljøfarlige kjemikalier og andre produkter (produktforskriften), Product regulation FOR 2004-06-01 Nr. 922, § 2-32. http://lovdata.no/dokument/SF/forskrift/2004-06-01-922/KAPITTEL_2#§2-32 (12-3-2015).

Chapter 2.

Ike van der Veen[a]

Jana M. Weiss[a]

Anne-Charlotte Hanning[b]

Jacob de Boer[a]

Pim E.G. Leonards[a]

[a] Vrije Universiteit, Institute for Environmental Studies (IVM), De Boelelaan 1087, 1081 HV, Amsterdam, The Netherlands
[b] Swerea IVF, Argongatan 30,SE-431 53, Mölndal, Sweden

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Development and validation of a method for the quantification of extractable perfluoroalkyl acids (PFAAs) and perfluorooctane sulfonamide (FOSA) in textiles

Abstract

In textiles, like outdoor clothing, per- and polyfluoroalkyl substances (PFASs) are often used for durable water repellency (DWR) of the final products. The analytical performance to determine the concentration of these chemicals available for exposure to humans and to the environment need to be established. Here a method for the extraction and analysis of one class of PFASs, namely perfluoroalkyl acids (PFAAs), in outdoor clothing was developed and validated. The PFAAs which were validated, included perfluoroalkyl carboxylic acids (PFCAs) (C_4-C_{14}), and perfluoroalkane sulfonic acids (PFSAs) (C_4, C_6, C_7, C_8). In addition, perfluorooctane sulfonamide (FOSA) was included in this study. The method was based on an organic solvent extraction and analysis by high-performance liquid chromatography-tandem mass spectrometry (LC-MS/MS). No further cleaning was needed. Two commonly used organic solvent compositions were evaluated for the optimal extraction, i.e. methanol and acetone/acetonitrile (80:20, v/v), and the number and duration of the sequential extractions were optimized. Results showed that two sequential extractions with 5 mL methanol and an extraction time of 30 min gave an optimal performance with an extraction efficiency of > 90%. The influence of matrix on the quantification of PFAAs was studied. This indicated ion suppression due to different matrix effects or sorption behavior to specific textile samples. Validation of the entire method showed overall recoveries of > 80% and relative standard deviations (RSDs) of < 9% (n=3) for repeatability and < 20% (n=3) for reproducibility. This is the first validation of an analytical method for the analysis of extractable PFCAs, PFSAs and FOSA associated to textiles, which is of high importance due to the regulation of PFAAs in textile.

2.1. Introduction

Per- and polyfluoroalkyl substances (PFASs) are a class of chemicals which consist of a non-polar perfluoroalkyl chain and a polar end-group[1]. This unique combination of physical properties provides both oil and water repellency. Since the 1950s(Buck et al., 2011) polymers with PFAS side-chains have therefore been used in a wide range of consumer products like textiles[2]. Those polymers can degrade to perfluoroalkyl acids (PFAAs) like perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), and contain PFAA impurities[3]. These PFAAs can reach air, water, soil and biota and are hence globally detected in a wide range of environmental matrices[4-7].

Since certain PFAAs are known to cause adverse effects to organisms including humans[8, 9], to be persistent[10] and bioaccumulative[11, 12], industry voluntarily started to phase out the production of PFOS and PFOS-based compounds in 2000[13]. Nowadays, PFOS and its salts are listed as persistent organic pollutants (POPs) under the Stockholm Convention[14] and, consequently, restricted in use in many countries. Some of the longer chain perfluoroalkyl carboxylic acids (PFCAs) (C_8, C_{11}–C_{14}) are included in the Candidate List of Substances of Very High Concern under REACH (Registration, Evaluation and Authorization of Chemicals)[15]. Therefore, industry has started to search for more environmentally friendly alternatives[16-19]. A maximum level of 1 µg/m² for PFOS in textiles was set by the European Union in 2006[20] and a maximum of 1 µg/m² for PFOA was set in 2014 in Norway, as the first country setting a limit for PFOA[21, 22].

Only two analytical methods developed for PFOA analysis in textiles are known[23, 24]. To the best of our knowledge no peer reviewed validation data has been published so far for the determination of the other PFAAs in textiles, although Knepper et al.[25] presented a method for PFAA analysis in textiles in a non-peer review report. Liquid-solid extraction (LSE) with acetone/acetonitrile (80:20, v/v) was used without any purification step. Analysis was performed with high-performance liquid chromatography-tandem mass spectrometry (LC-MS/MS). For a method to be validated the precision, which is generally accepted as repeatability and reproducibility, the accuracy, which is often evaluated by repetitively spiking the matrix, and the limit of detection (LOD) need to be determined as a minimum requirement[26-28]. In the study of Knepper et al.[25] PFAA recoveries of a spiking experiment were generally between 70-130%, except for perfluorotridecanoic acid (PFTrDA) and perfluorotetradecanoic acid (PFTeDA) (< 50%). Repeatabilities were < 20% and no reproducibility or LOD results were reported for PFAAs in outdoor jackets, although LOQs were reported (0.01-0.4 µg/m²).

There are a number of non-peer reviewed studies reporting concentrations of PFAAs in outdoor clothing[29-38]. On the concentration of PFAAs in other types of textiles, like upholstery and table-cloths, two more peer reviewed studies were reported[39, 40]. Vestergren et al.[39] analysed 45 different types of consumer products, including upholstery, carpets, cotton and leather clothes, and food contact materials. Herzke et al.[40] analysed 30 consumer products, including two carpets, one pooled sample of table-cloths and one pooled sample of office furniture textiles. In both studies PFAAs were extracted by LSE with methanol, followed by a purification step with envicarb. In the study of Vestergren et al.[39] seven isotope-labeled PFCAs and two isotope-labeled perfluoroalkane sulfonic acids (PFSAs) were used as internal standards (ISs). Average recoveries ranged from 46 to 108%. Repeatabilities of triplicate extractions and analyses were ⩽ 44%. In the study of Herzke et al.[40] only two ISs were used ($^{13}C_4$-PFOA and $^{13}C_4$-PFOS) for the quantification of 11 PFCAs and six PFSAs. Average recoveries varied between 64 and 126%. No repeatability, reproducibility or LOD results were given.

The aim of the present study was to develop and validate a method for the determination of PFCAs (C_4-C_{14}), PFSAs (C_4, C_6, C_7, C_8) and perfluorooctane sulfonamide (FOSA) in textile samples. In short, the method is based on extraction with an organic solvent and no further cleaning. The goals of the optimization of the extraction solvent composition and the number of sequential extractions were i) to achieve that more than 90% of the analytes are extracted from the samples, ii) although ionization suppression and enhancement in LC–MS ion source due to matrix effects have not been taken into account in validation guides[41], a goal is set to obtain more than 30% recovery *of* the isotope-labeled ISs*,* which equals the regulation of the European Union for the analyses of dioxins by GC-MS[42], and which enables quantification of a compound above the LOQ, and below the limit of 1 µg/m^2 for textiles[20-22], and iii) to achieve the first two goals in the minimum number of extraction steps possible. For the chemical analysis a previously described method based on LC-MS/MS was used[43]. Twelve isotope-labeled PFAAs were used as ISs.

2.2. Material and methods

2.2.1. Chemicals and reagents

All validated PFAAs and isotope-labeled PFAAs are listed in Table S2-1 of the Supporting Information (SI), including their abbreviations according to Buck et al.[2], chemical formula, and chemical abstract system numbers (CAS No.). All PFAAs and isotope-labeled PFAAs were purchased from Greyhound Chromatography

(Merseyside, UK) in solutions of 50 µg/mL in methanol and with a purity of > 98%. The isotope purity of $^{18}O_2$-PFHxS was >94%, and the isotope purity of all other isotope-labeled PFAAs was >99%. HPLC grade methanol (J.T. Baker, 8402), and acetone (J.T. Baker, 9254) were purchased from Boom (Meppel, The Netherlands). Acetonitrile (Chromasolve, 34851) and ammonium formate (Bio ultra, 09735) were obtained from Sigma Aldrich (Zwijndrecht, The Netherlands). Ultrapure water was supplied by a Milli-Q system from Millipore (Watford, UK). Glass fiber filters (GF/F, pore size 0.42µm) for filtering of the mobile phase, were purchased from Whatman (Maidstone, UK).

2.2.2. Textile samples

Pieces of outdoor clothing (three jackets and three fabrics for outdoor clothes), supplied by six different suppliers from the outdoor textile industry in Sweden, were provided by SWEREA IVF (Mölndal, Sweden). Circular pieces with a diameter of 35.3 mm (equals 9.79 cm^2) were cut from the outdoor clothes samples by a bore (Cordia Matic, 270 rpm) for analysis. The known details of the textile samples are given in Table S2-2. Some of the textile samples were laminated with a membrane on one side of the fabric.

2.2.3. Extraction procedure

The cut samples (9.79 cm^2) were weighed into 15 mL polypropylene (pp) tubes. Prior to extraction dust particles were rinsed from the samples by adding 5 mL water to the pp tubes and transferring the samples immediately into fresh 15 mL pp-tubes. The samples were fortified with 50 µL of an IS solution (mixture of isotope-labeled PFAAs, approx. 100 ng/mL each in methanol, which equals a concentration of 5 µg/m^2), added directly onto the samples and left to equilibrate for 1 h. PFAAs were extracted from the samples by LSE. Different extraction variables such as solvent composition, extraction time on a shaking device (Edmund Bühler GmbH, *Hechingen, Germany)*, and number of sequential extractions were optimized. After extraction, the solvent was evaporated till dryness by a gentle stream of nitrogen at 40°C. The extracts were reconstituted in 200 µL methanol: water (1:1, v/v). After centrifugation (10 min, 3000 rpm) the extracts were transferred into 0.3 mL pp micro vials (VWR International BV, Amsterdam, The Netherlands).

2.2.4. Extraction method development

To develop and optimize the analytical method, extraction solvents, the number of sequential extractions and the extraction time were evaluated on 5 samples (Table 2-1). Methanol has been used successfully to extract PFAAs from several matrixes[1, 44-47], including textiles[23, 24, 29, 33, 34, 38, 40]. One group used acetone/acetonitrile (80:20, v/v)[25], therefore both methanol and acetone/acetonitrile were included in the

evaluation. To assess the extraction time and the number of successive extractions needed to achieve an extraction efficiency of > 90% with either methanol or acetone/acetonitrile three experiments were performed, in which sequential extractions were made from 5 samples with 5 mL extraction solvent each (Table 2-1). Prior to all sequential extractions, additional ISs were added to the samples before extraction. The extraction efficiency per sequential extraction is calculated as the percentage of the sum of quantified concentrations over the successive extractions.

Table 2-1 Experiments performed to optimize and validate the extraction method for analyses of PFAAs and FOSA in textiles.

Experiment		Sample No.	Number of replicates	Extraction solvent	Number and time of successive extractions
Optimization					
Experiment 1		1-5	1	Acetone/ acetonitrile (80:20, v/v)	a: 1 h b: 1 h c: 24 h d: 6 d
Experiment 2		1-5	1	Acetone/ acetonitrile (80:20, v/v)	a: 30 min b: 30 min c: 30 min d: 30 min
Experiment 3		1-5	1	Methanol	a: 30 min b: 30 min c: 30 min d: 30 min e: 4 d
Validation					
Recovery assessment	1 µg/m^2	1, 2	3	Methanol	2* 30 min
	10 µg/m^2	1, 2	3	Methanol	2* 30 min
Repeatability assessment		1, 2, 6	3	Methanol	2* 30 min
Reproducibility assessment		1, 2, 6	3	Methanol	2* 30 min

2.2.5. Instrumental analysis and quantification

The extracts were analysed by an Agilent 6410 Triple Quad LC-MS/MS (Agilent Technologies, Amstelveen, The Netherlands) operating in electrospray negative ionization mode according to a previously described method[43]. Briefly, separation was performed on a FluoroSep-RP Octyl column (150 mm length x 2.1 mm i.d., 5 µm; ES Industries, Bellefonte, Pennsylvania, USA) with a Symmetry C_{18} guard column (20 mm x 3.9 mm, 5 µm; Waters Corporation, Milford, Massachusetts, USA). To retain contaminants leaching out of the HPLC and the mobile solvents, an extra column

(Symmetry C_{18}, 150 mm length x 2.1 mm i.d., 5 µm; Waters Corporation) was installed between the pump and the autosampler. Mobile phase solvents used were 5 mM ammonium formate in water (solvent A) and methanol (solvent B) with a flow rate of 300 µL/min. Injection volume was 20 µL. The gradient started at 35% methanol for 2 min, increased to 75% in 3 min, which was followed by an increase to 95% in 20 min. After 10 min the mobile phase composition was returned to 35% methanol in 0.5 min and held constant for 10 min until the next injection. Quantification was performed against five calibration solutions (0.1, 0.5, 2, 10, 50 ng/mL) in methanol: water (1:1, v/v) prepared from a single stock solution and the isotope-labeled ISs (Table S2-3). For quantification the software Masshunter Workstation software, Quantitative analysis for QQQ of Agilent Technologies was used with quadratic curves and a curve fit weight of 1/x, with x being the relative analyte concentration. Procedure solvent blanks were analyzed alongside the samples and subtracted from the final results. LODs were calculated per sample as the concentration of a peak area three times greater than the noise divided by the sample intake and the recovery. Limits of quantification (LOQs) were calculated as 3.3 times the LOD.

2.2.6. Validation of the method

The selected method was validated by a recovery assessment, by assessment of the repeatability, and the determination of the reproducibility (Table 2-1). All samples of the recovery assessment and repeatability assessment were extracted and analysed in the same series and for both assessments the same calibration curves were used.

To assess the recovery of the developed extraction method with methanol two samples in triplicate were fortified with native PFAAs at two different levels (1 and 10 µg/m^2). Two solutions, containing all the native PFAAs and FOSA (Table S2-1) were prepared in methanol (20 and 200 ng/mL), which equals a concentration of 1 µg/m^2 and 10 µg/m^2 respectively. After sample intake, the samples were fortified with 50 µL of the solutions by placing different spots on the textile samples. After three days, the samples were extracted according to the aforementioned procedure. To calculate the recoveries, the average PFAA concentrations of the three fortified repeatability samples were subtracted from the concentrations of the unfortified samples. The concentrations calculated were divided by the fortified concentrations.

To assess the repeatability of the developed extraction method, three samples were extracted in triplicate on the same day. For the reproducibility assessment, the three samples were each extracted and analysed on three different days.

To confirm that the extraction using methanol is exhaustive, the samples of the recovery and repeatability assessment were re-extracted using 5 mL acetone/

acetonitrile (80:20, v/v), which is a less polar solvent. Before re-extraction the samples were fortified with 50 µL IS mixture (approx. 100 ng/mL) which equals a concentration of 5 µg/m^2.

2.3. Result and discussion

2.3.1. Method development

The majority of the PFAAs were extracted during the first extraction (85-100% of the sum of concentrations of the sequential extractions) in experiment 1 where acetone/acetonitrile as extraction solvent was evaluated (Table 2-1 and Table S2-4). The first and second extractions together resulted in a median extraction efficiency of 100% for PFAAs in the five samples. Only minor amounts (< 0.15 µg/m^2, < LOQ) of PFAAs in samples 2 (PFDA, PFDoDA) and 3 (PFHxA, PFHpA, PFDA, PFDoDA) were extracted in the third (0-4%), and fourth (0-3%) sequence.

Results of experiment 2 were comparable with results obtained in experiment 1, using the same extraction solvent but where 30 min extraction cycles were used instead of 1 hour cycles in experiment 1 (Table S2-5). The majority of the PFAAs (83-100%) were extracted during the first extraction and the first and second extraction together resulted in a median extraction efficiency of 100%. Again, minor amounts (< 0.15 µg/m^2, < LOQ) of the PFAAs were detected in samples 2 and 3.

In experiment 3, where methanol was evaluated as extraction solvent, the extraction efficiency of the first sequential extraction was a little lower (77-100%) than those of experiments 1 and 2, but also with methanol the first and second extraction together resulted in an median extraction efficiency of 100% (Table S2-6). Again, only in sample 2 and 3, with higher PFAA concentrations determined, some PFAAs could be detected in the third and fifth extract above LOD but below LOQ.

High concentrations of PFOA, with unclear origin, were detected in the method blank samples, which were extracted and analysed alongside the five samples of experiment 1 and 2. Therefore, the PFOA results of experiments 1 and 2 were considered not reliable and excluded. No PFOA was detected in the blank sample of experiment 3.

The extraction efficiencies of all three experiments are comparable, independent of the extraction solvent and extraction time. Therefore, it is concluded that two sequential extractions with either acetone/acetonitrile or methanol and an extraction time of 30 min for each extraction cycle results in a sufficient extraction efficiency of > 90%.

It is commonly known that ion suppression or enhancement caused by matrix effects can occur in the analysis with LC-MS/MS[48, 49]. This is why the use of isotope-labeled ISs is required in LC-MS/MS quantification. Although the loss of abundance caused by ion suppression will be compensated for by the use of isotope-labeled ISs, the LODs and LOQs will be higher if ion suppression occurs resulting in a decreased method performance. A minimum of 30% recovery of ISs was set by the authors for the analysis of PFAAs in textiles to enable quantification of a compound above the LOQ. The aim was to perform analysis with LOQ below the limit of 1 µg/m^2 for textiles, as set by the European Union[20] for PFOS and by Norway for PFOA[21, 22]. For all extracts measured in the aforementioned experiments the recoveries of the isotope-labeled ISs were calculated by dividing the abundance of the signal of the isotope-labeled ISs by the average abundance of the signals of the isotope-labeled ISs which were added to the five calibration solutions. The results of those calculations are shown in Figure 2-1. As can be observed the extraction with methanol resulted in higher recoveries (33-149%, average 97%) of isotope-labeled PFAA ISs compared to the extraction with acetone/acetonitrile (2-147%, average 66%). Also the recovery of $^{13}C_8$-FOSA is higher with methanol extraction (10-98%, average 45%) than with acetone/acetonitrile (3-55%, average 30%). It is to be expected that with the less polar solvent acetone/acetonitrile (dipole moment 2.88 D and 3.92 D, respectively [50]), more non-polar compounds, which can interfere during the LC-MS/MS analysis, are extracted from the matrix than with methanol (dipole moment 1.70 D [50]). It was observed that IS recoveries for the first sequential extractions (a) with acetone/acetonitrile are lower than IS recoveries for the following sequential extractions (b-d). This might be an indication of lower IS recoveries caused by ion suppression due to matrix effects, since the majority of the extractable matrix is expected to be extracted in the first extraction.

To confirm the influence of matrix on IS recovery, a mixture of $^{13}C_5$-PFHxA, $^{13}C_8$-PFOA, $^{13}C_7$-PFUnDA and $^{13}C_8$-PFOS in methanol was added to the first sequential extraction of sample 1 at a final concentration of 15 ng/mL The recovery of those compounds showed that the matrix was responsible for a signal loss of IS of 33% for PFHxA, 34% for PFOA, 25% for PFUnDA, and 36% for PFOS.

Given the lower recoveries of ISs obtained by extraction with acetone/acetonitrile, methanol was selected as the optimal solvent for extraction. Therefore, the recommended method for the determination of PFAA and FOSA concentrations in textiles is to use two sequential extraction cycles of 30 min each, and methanol as extraction solvent.

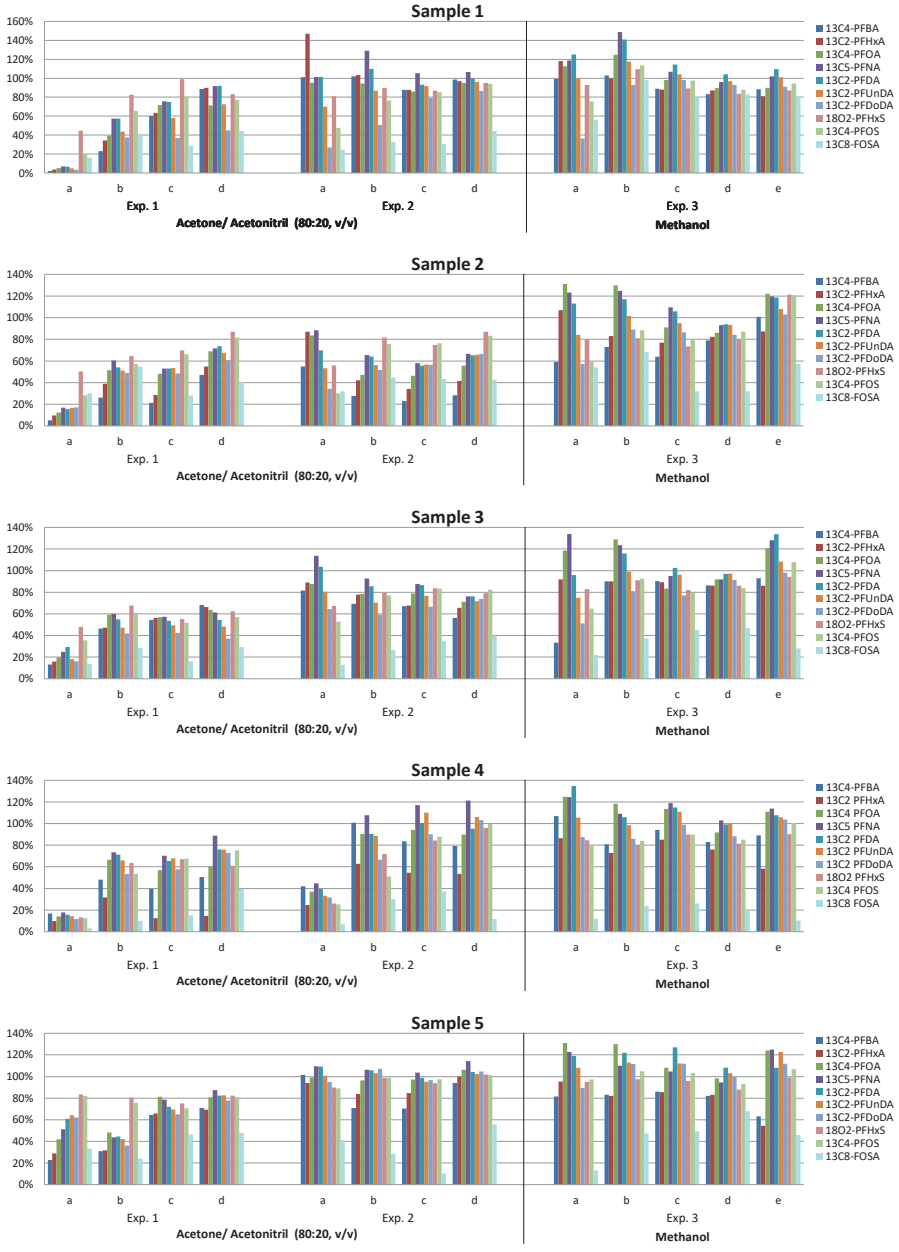

Figure 2-1 Recoveries (%) of ISs added to five different textile samples after sequential extractions (according to Table 2-1) with acetone/acetonitrile or methanol for the quantification of PFAAs and FOSA.

2.3.2. Validation of PFAA and FOSA extraction method with methanol

Recovery assessment

Extraction with methanol of the two fortified samples (textile sample 1 and 2) analysed in triplicate gave satisfactory recoveries (80-120%) for all but two PFAAs, PFTrDA (49-65%) and PFTeDA (31-59%) in sample 2. As can be observed in Figure 2-2, the recoveries for PFTrDA and PFTeDA are normal for sample 1, but on the low side for sample 2. This might be caused by either ion suppression in the LC-MS/MS analysis or by a stronger adsorption to the specific textile material. Both would normally be compensated for by the ISs, but since no isotope-labeled PFTrDA or PFTeDA were available, those two compounds were calculated against $^{13}C_2$-PFUnDA and $^{13}C_2$-PFDoDA, respectively, which might not compensate properly for the ion suppression or the adsorption. In the study of Knepper et al.[25] comparable results were shown for the recovery of PFTrDA and PFTeDA. In their study $^{13}C_2$-PFDoDA was used as IS for the quantification of PFTrDA and PFTeDA. The recoveries of PFTrDA and PFTeDA varied between approximately 40 and 100%, depending on the sample.

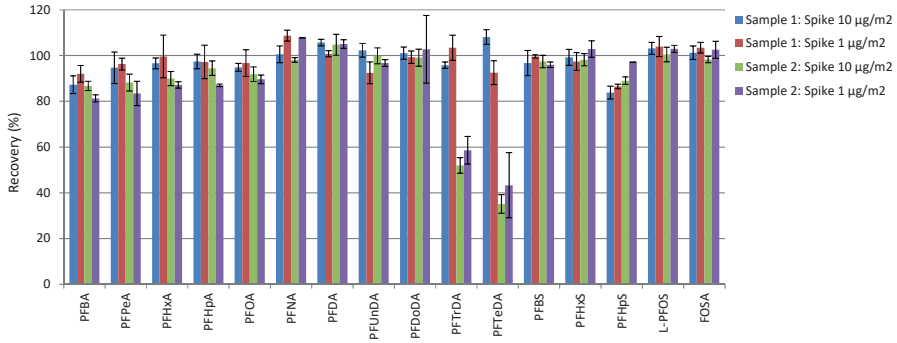

Figure 2-2 Recoveries of PFAAs and FOSA in a recovery assessment in which two samples in triplicate were fortified at two different concentration levels (1 µg/m^2 and 10 µg/m^2).

Repeatability assessment

The calculated relative standard deviation (RSD) of the quantified PFAA concentrations in three samples extracted in triplicate, showed acceptable repeatabilities for all detected PFAAs (0.1-8.7%) (data not shown). The repeatabilities of PFTrDA, PFHpS, L-PFOS and FOSA could not be determined in the unfortified samples of this validation assignment as the concentrations were < LOD in all three samples. However, the RSDs of the calculated recoveries of the fortified samples in the recovery study were well below 10%, except for three PFAAs in sample 2 fortified

at level 1 µg/m², and one PFAA in sample 2 fortified at level 10 µg/m² (Table S2-7 and error bars in Figure 2-3). Those higher RSDs were all caused by the third replicate, of which the quantified concentrations are higher than the concentrations in the other two replicates. No explanation other than a possible incidental contamination was found for the higher results obtained for this replicate.

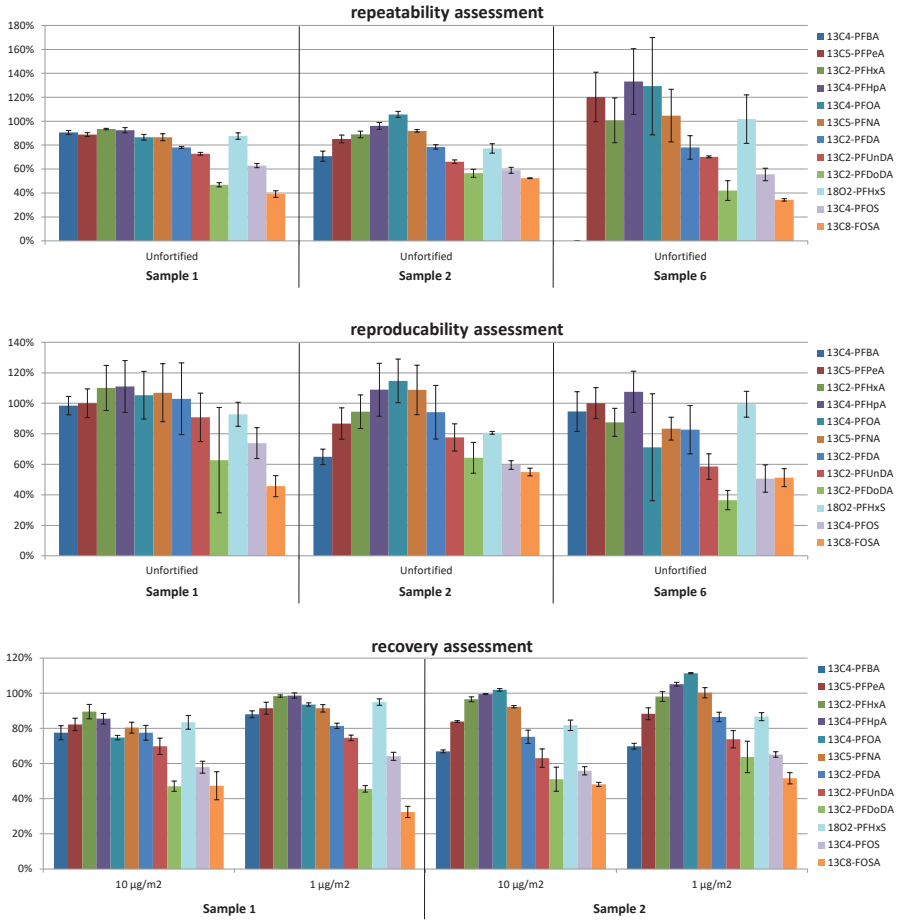

Figure 2-3 Recoveries of the internal standards added to the textile samples of the repeatability, reproducibility and recovery assessment, to study possible matrix effects for PFAAs and FOSA.

Reproducibility assessment

Acceptable RSD for the reproducibilities were calculated for all detected PFAAs (2-20%) in samples 1, 2 and 6 extracted and analysed over three executive days (Table S2-8). The reproducibility was not reported by Knepper et al.[25] on the extraction of PFAAs from textile samples, except for the RSDs of the analyses of a fortified extract on two different days (0.2-5.1%). Stadalius et al.[24] calculated a reproducibility of PFOA in samples fortified at three different levels, which were extracted on three different days. RSDs were 2.5% (fortified at 5 ng/g), 4.0% (fortified at 50 ng/g) and 3.9% (fortified at 200 ng/g), which is better than the reproducibility of PFOA in the present study for the unfortified samples No. 1 (17.5%), No. 2 (8.9%) and No. 6 (5.3%). A reasonable explanation of the higher RSD for sample No. 1 might be the 5-fold lower concentration of the sample (approximately 1 ng/g) than in the Stadalius study. For all three samples the higher RSDs might be explained by the fact that the samples were unfortified. To the best of our knowledge no reproducibility data have been published on the extraction of the other PFAAs in textiles. In an interlaboratory comparison study (ILS) from 2011 between-laboratory coefficient of variations (CVs) were 12-31% for the analysis of PFAAs in a standard solution[44]. Since the standard solution contained PFAAs in concentrations comparable to those of the final extracts of the present study, it was expected that the extraction and analyses of a textile would give higher RSDs, due to the additional extraction procedure and due to additional matrix. However, the RSDs obtained in the present study are < 20% and hence satisfactory.

Matrix effects

To examine the influence of matrix effects on the quantification of PFAAs and FOSA when using the validated method, in which two extracts are combined, the recoveries of the isotope-labeled standards in the extracts of the validation samples were determined. The results are shown in Figure 2-3. Although all recoveries of the ISs were higher than the limit of 30%, which was set by the authors, the recoveries of $^{13}C_8$-FOSA (average 46%, range 30-58%) were substantial lower than the recoveries of the other ISs (average 84%, range 30-175%). The low recoveries of FOSA are comparable to those obtained in the validation of the method used by Knepper et al.[25] with acetone/acetonitrile as extraction solvent (<33%). Knepper et al.[25] explained the low recovery by evaporation of FOSA during the evaporation of the extraction solvent at elevated temperatures (40°C). Another method developed by Knepper et al.[25] based on extraction with hexane and concentration by solid phase extraction (SPE) showed slightly better recoveries of 49%. As can be observed from Figure 2-3 all replicates of a sample, fortified as well as unfortified, have the same pattern of IS recovery, while the patterns between the three different samples slightly differ from each other. This might be an indication of ion suppression due to different matrix effects or sorption behavior to specific textile samples.

Confirmation of completion of extraction (recovery and repeatability samples)
To confirm that the extraction efficiency of the methanol extraction is sufficient in comparison with acetone/acetonitrile extraction, the samples of the repeatability and recovery assessment were re-extracted with acetone/acetonitrile after the methanol extraction for 30 min. Except for PFBS in the first replicate of sample 6 (2%), all PFAAs in the acetone/acetonitrile extracts of the repeatability assessment were below the LODs. Samples from the recovery assessment showed that all PFAA concentrations in the acetone/acetonitrile extracts were ⩽ 5%, with the exception of PFTeDA (0-8%, average 4%) and PFBS (0-11%, average 4%), which are both compounds without an isotope-labeled homologue. This shows that using methanol as extraction solvent results in an extraction efficiency of > 90%.

Expression of concentration unit: µg/m² vs ng/g
Although Guo et al.[29], Stadalius et al.[24] and Mawn et al.[23] expressed the PFAA concentration in textile samples in ng/g, the unit predominantly used for expression of the concentration of PFAAs in textiles is µg/m² [25, 39, 40, 51]. The average sample intakes (*9.79 cm*²) for sample 1, 2 and 6 for the repeatability and recovery assessment were 143.3, 179.6 and 143.9 mg, respectively. As the RSDs of the sample intake for sample 1, 2 and 6, expressed in mg were low (3.1, 1.9 and 0.4%, respectively) the results of the repeatability and reproducibility assessments also apply when the PFAA concentrations are expressed in ng/g instead of µg/m². Since all textile samples differ from each other in thickness and fiber material, we suggest that authors report both in ng/g and in µg/m².

Limit of detection
The LODs varied between samples mainly due to differences in IS recoveries. The LODs per compound at 100% recovery of IS were 0.02-0.10 µg/m² for all analyses performed in this study (Table S2-9). The LODs were lower than or equal to those reported by Brigden et al.[33] (0.049-2.424 µg/m²) and by Brigden et al.[34] (0.092-0.184 µg/m²), but slightly higher than those reported by Vestergren et al.[39] (0.005-0.010 µg/m²), what could be explained by the 10-fold higher sample intake used by Vestergren et al.[39]. LOQs, calculated as 3.3* LOD, were in the same range as LOQs reported by Knepper et al.[25] (0.01-0.4 µg/m²), although the sample intake in the present study was 5-fold lower.

LODs expressed in ng/g varied between 0.15 and 3.7 ng/g depending on the mass of the sample intake (0.14-0.19 g) for all PFAAs, which was equal to or better than the LODs reported by Guo et al.[29] (1-3.9 ng/g). For the analysis of PFOA, LODs and LOQs varied depending on the weight of the sample intake and the recovery of the ISs between 0.15 and 0.74 ng/g, and between 0.48 and 2.4 ng/g, respectively, which was

equal to or better than the LOD reported by Stadalius et al.[24] for PFOA (1 ng/g) and the LOQ reported by Mawn et al.[23] for PFOA (2.5 ng/g). In the studies of Berger and Herzke[38] and Herzke et al.[40] no LODs or LOQs were reported.

2.4. Conclusions

For the first time a validation of an analytical method for the extraction and quantification of a set of PFAAs in textile samples was reported. Extraction efficiencies of > 90% and LODs between 0.02-0.10 µg/m^2 were achieved using a two-step sequential extraction (2x5 mL methanol) and extraction times of 30 min each. Validation of the method based on three replicate extractions of three different samples on either the same day or on three different days results in repeatabilities of < 9% and reproducibilities of < 20%. Two samples fortified at two different levels showed recoveries > 80% for all PFAAs for which an isotope-labeled IS was available. The developed method is able to detect PFOS and PFOA below the set of European maximum allowable levels in textile.

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References

1. de Voogt, P.; Sáez, M., Analytical chemistry of perfluoroalkylated substances. *Trends in Analytical Chemistry* 2006, 25, 326-342.
2. Buck, R. C.; Franklin, J.; Berger, U.; Conder, J. M.; Cousins, I. T.; de Voogt, P.; Jensen, A. A.; Kannan, K.; Mabury, S. A.; van Leeuwen, S. P. J., Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. *Integrated Environmental Assessment and Management* 2011, 7, 513-541.
3. Prevedouros, K.; Cousins, I. T.; Buck, R. C.; Korzeniowski, S. H., Sources, fate and transport of perfluorocarboxylates. *Environmental Science & Technology* 2005, 40, 32-44.
4. Butt, C. M.; Berger, U.; Bossi, R.; Tomy, G. T., Levels and trends of poly- and perfluorinated compounds in the arctic environment. *Science of The Total Environment* 2010, 408, 2936-2965.
5. Rotander, A.; Kärrman, A.; Bavel, B. v.; Polder, A.; Rigét, F.; Auðunsson, G. A.; Víkingsson, G.; Gabrielsen, G. W.; Bloch, D.; Dam, M., Increasing levels of long-chain perfluorocarboxylic acids (PFCAs) in Arctic and North Atlantic marine mammals, 1984–2009. *Chemosphere* 2012, 86, 278-285.
6. Yoo, H.; Kannan, K.; Kim, S. K.; Lee, K. T.; Newsted, J. L.; Giesy, J. P., Perfluoroalkyl acids in the egg yolk of birds from Lake Shihwa, Korea. *Environmental Science & Technology* 2008, 42, 5821-5827.
7. Kwadijk, C. J. A. F.; Korytár, P.; Koelmans, A. A., Distribution of perfluorinated compounds in aquatic systems in The Netherlands. *Environmental Science & Technology* 2010, 44, 3746-3751.
8. Liu, C.; Chang, V. W. C.; Gin, K. Y. H., Oxidative toxicity of perfluorinated chemicals in green mussel and bioaccumulation factor dependent quantitative structure–activity relationship. *Environmental Toxicology and Chemistry* 2014, 33, 2323-2332.
9. Corsini, E.; Sangiovanni, E.; Avogadro, A.; Galbiati, V.; Viviani, B.; Marinovich, M.; Galli, C. L.; Dell'Agli, M.; Germolec, D. R., In vitro characterization of the immunotoxic potential of several perfluorinated compounds (PFCs). *Toxicology and Applied Pharmacology* 2012, 258, 248-255.
10. US-EPA, Environmental Protection Agency, America's children and the environment, Third Edition, January 2013, 2013; p 504. http://www.epa.gov/ace/pdfs/ACE3_2013.pdf.
11. Stahl, T.; Mattern, D.; Brunn, H., Toxicology of perfluorinated compounds. *Environmental Sciences Europe* 2011, 23, 38.
12. de Vos, M. G.; Huijbregts, M. A. J.; van den Heuvel-Greve, M. J.; Vethaak, A. D.; Van de Vijver, K. I.; Leonards, P. E. G.; van Leeuwen, S. P. J.; de Voogt, P.; Hendriks, A. J., Accumulation of perfluorooctane sulfonate (PFOS) in the food chain of the Western Scheldt estuary: Comparing field measurements with kinetic modeling. *Chemosphere* 2008, 70, 1766-1773.
13. Schultz, M. M.; Barofsky, D. F.; Field, J. A., Fluorinated Alkyl Surfactants. *Environmental Engineering Science* 2003, 20, 487-501.
14. UNEP, United Nations Environment Programme, Stockholm Convention on Persistent Organic Pollutants: Guidance on alternatives to perfluorooctane sulfonic acid, its salts, perfluorooctane sulfonyl fluoride and their related

chemicals. UNEP/POPS/POPRC.9/INF/11/Rev.1,, United Nations Environment Programme, UNEP/POPS/POPRC.9/INF/11/Rev.1,: Rome, 2013; p 63. http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC9/Documents/tabid/3281/Default.aspx.
15. ECHA, European Chemical Agency, Candidate list of substances of very high concern for authorisation. http://echa.europa.eu/web/guest/candidate-list-table (17-12-2014).
16. SUPFES, Substitution in Practice of Prioritized Fluorinated Chemicals to Eliminate Diffuse Sources. Formas 2012-11652-24486-65. https://www.ri.se/en/what-we-do/projects/supfes (22-05-2021).
17. Poulsen, P. B.; Jensen, A. A.; Wallström, E., Danish Environmental Protection Agency, More environmentally friendly alternatives to PFOS-compounds and PFOA, Danish Environmental Protection Agency, 2005; p 162. http://www2.mst.dk/common/Udgivramme/Frame.asp?http://www2.mst.dk/Udgiv/publications/2005/87-7614-668-5/html/default_eng.htm.
18. UNEP, United Nations Environment Programme, Technical paper on the identification and assessment of alternatives to the use of perfluorooctane sulfonic acid in open applications. UNEP/POPS/POPRC.8/INF/17, Geneva, 2012; p 48. http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC8/MeetingDocuments/tabid/2801/Default.aspx.
19. Wang, Z.; Cousins, I. T.; Scheringer, M.; Hungerbühler, K., Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and their potential precursors. *Environment International* 2013, 60, 242-248.
20. EU, Directive 2006/122/EC of the European Parliament and of the Council of 12 December 2006. *Official Journal of the European Union* 2006, L 372/32, 32-34.
21. Bureau Veritas, Norways Bans PFOA in concumer products. http://www.bureauveritas.com/wps/wcm/connect/bf2081c9-fc83-4d28-89d2-1602e72a9af8/Newsbyte_13NB-045.pdf?MOD=AJPERES (7-11-2014).
22. Lovdata, PFOA-Restriction in Norway, Forskrift om begrensning i bruk av helse- og miljøfarlige kjemikalier og andre produkter (produktforskriften), Product regulation FOR 2004-06-01 Nr. 922, § 2-32. http://lovdata.no/dokument/SF/forskrift/2004-06-01-922/KAPITTEL_2#§2-32 (12-3-2015).
23. Mawn, M. P.; McKay, R. G.; Ryan, T. W.; Szostek, B.; Powley, C. R.; Buck, R. C., Determination of extractable perfluorooctanoic acid (PFOA) in water, sweat simulant, saliva simulant, and methanol from textile and carpet samples by LC/MS/MS. *Analyst* 2005, 130, 670-8.
24. Stadalius, M.; Connolly, P.; L'Empereur, K.; Flaherty, J. M.; Isemura, T.; Kaiser, M. A.; Knaup, W.; Noguchi, M., A method for the low-level (ng g−1) determination of perfluorooctanoate in paper and textile by liquid chromatography with tandem mass spectrometry. *Journal of Chromatography A* 2006, 1123, 10-14.
25. Knepper, T. P.; Frömel, T.; Gremmel, C.; Driezum, I. v.; Weil, H.; Vestergren, R.; Cousins, I., UMWELTBUNDESAMT (UBA), Understanding the exposure pathways of per- and polyfluoralkyl substances (PFASs) via use of PFASs-Containing products – risk estimation for man and environment, (UBA-FB) 001935/E 47/2014, UMWELTBUNDESAMT (UBA), Dessau-Roßlau, July 2014, 2014; p 133.

https://www.umweltbundesamt.de/sites/default/files/medien/378/publikationen/texte_47_2014_understanding_the_exposure_pathways_of_per-_and_polyfluoralkyl_substances_pfass_0.pdf.

26. UNIDO, United Nations Industrial Development Organization, Complying with iso 17025. A practical guidebook for meeting the requirements of laboratory accreditation schemes based on ISO 1705:2005 or equivalent national standards, Vienna, Austria, 2009, 2009; p 108. https://www.unido.org/fileadmin/user_media/Publications/Pub_free/Complying_with_ISO_17025_A_practical_guidebook.pdf.
27. ALACC, Analytical Laboratory Accreditation Criteria Committee, AOAC International, How to Meet ISO 17025. Requirements for Method Verification, Gaithersburg, USA, 2007, 2007; p 18. http://www.aoac.org/imis15_prod/AOAC_Docs/LPTP/alacc_guide_2008.pdf.
28. EU, Commision Decision of 12 august 2002, implementing Council Directive 96/23/EC concerning the performance of analytical methods and the interpretation of results. *Official Journal of the European Communities* 2002, L 221/8, 8-36.
29. Guo, Z.; Liu, X.; Krebs, K. A.; Roache, N. F., Perfluorocarboxylic acid content in 116 articles of commerce, EPA/600/R-09/033, US-EPA (Environmental Protection Agency), March 2009, p 51. http://www.oecd.org/env/48125746.pdf.
30. SFT, Kartlegging av perfluoralkylstoffer (PFAS) i utvalgte tekstiler, ISBN 82-7655-285-4, TA-2173/2006, Oslo, April 2006, 2006; p 61. http://www.miljodirektoratet.no/old/klif/publikasjoner/kjemikalier/2173/ta2173.pdf.
31. Santen, M.; Kallee, U., Chemistry for any weather – Greenpeace tests outdoor clothes for perfluorinated toxins, Greenpeace, Hamburg, 2012, p 44. http://www.greenpeace.org/romania/Global/romania/detox/Chemistry%20for%20any%20weather.pdf.
32. Greenpeace, A Little Story about the Monsters in Your Closet, Greenpeace International, Beijing, 2014, 2014; p 40. http://www.greenpeace.org/eastasia/Global/eastasia/publications/reports/toxics/2013/A%20Little%20Story%20About%20the%20Monsters%20In%20Your%20Closet%20-%20Report.pdf.
33. Brigden, K.; Hetherington, S.; Wang, M.; Santillo, D.; Johnston, P., Greenpeace, Hazardous chemicals in branded textile products on sale in 25 countries/regions during 2013, Technical Report 06/2013, Greenpeace Research Laboratories, Exeter, UK, December 2013, 2013; p 47. http://www.greenpeace.org/eastasia/Global/eastasia/publications/reports/toxics/2013/A%20Little%20Story%20About%20the%20Monsters%20In%20Your%20Closet%20-%20Technical%20Report.pdf.
34. Brigden, K.; Hetherington, S.; Wang, M.; Santillo, D.; Johnston, P., Greenpeace, Hazardous chemicals in branded luxury textile products on sale during 2013, Technical Report 01/2014, Greenpeace Research Laboratories, Exeter, UK, February 2014; p 32. http://www.greenpeace.org/international/Global/international/publications/toxics/2014/Technical-Report-01-2014.pdf.
35. Kallee, U.; Santen, M., Chemistry for any weather – Part II, Executive summary – Outdoor report 2013, 12/2013, Greenpeace, Hamberg, 2013, p 11. http://m.greenpeace.org/italy/Global/italy/report/2013/toxics/ExecSummary_Greenpeace%20Outdoor%20Report%202013_1.pdf.

36. SNCS, Fluorerade miljögifter i allvädersklädеr, Report 2006 (In Swedish), 26. http://naturvernforbundet.no/getfile.php/Dokumenter/Rapporter%20og%20faktaark/2008-2007/fluormiljogifter%20Impregneringsmiddel%20naturskyddforeningen.pdf.
37. KEMI, Swedish Chemicals Agency, Perfluorinated substances and their uses in Sweden, ISSN: 0284-1185, Swedish Chemicals Agency, ISSN: 0284-1185, 7/06, Stockholm, November 2006, p 60. http://www.kemi.se/Documents/Publikationer/Trycksaker/Rapporter/Report7_06.pdf.
38. Berger, U.; Herzke, D., Per- and polyfluorinated alkyl substances (PFAS) extracted from textile samples. *Organohalogen compounds* 2006, 68, 2023-2026.
39. Vestergren, R.; Herzke, D.; Wang, T.; Cousins, I. T., Are imported consumer products an important diffuse source of PFASs to the Norwegian environment? *Environmental Pollution* 2015, 198, 223-230.
40. Herzke, D.; Olsson, E.; Posner, S., Perfluoroalkyl and polyfluoroalkyl substances (PFASs) in consumer products in Norway – A pilot study. *Chemosphere* 2012, 88, 980-987.
41. Kruve, A.; Rebane, R.; Kipper, K.; Oldekop, M.-L.; Evard, H.; Herodes, K.; Ravio, P.; Leito, I., Tutorial review on validation of liquid chromatography–mass spectrometry methods: Part I. *Analytica Chimica Acta* 2015, 870, 29-44.
42. EU, Commission regulation (EU) No 252/2012 of 21 March 2012. *Official Journal of the European Union* 2012, L 84.
43. Ballesteros-Gómez, A.; Rubio, S.; van Leeuwen, S., Tetrahydrofuran–water extraction, in-line clean-up and selective liquid chromatography/tandem mass spectrometry for the quantitation of perfluorinated compounds in food at the low picogram per gram level. *Journal of Chromatography* A 2010, 1217, 5913-5921.
44. Weiss, J. M.; van der Veen, I.; de Boer, J.; van Leeuwen, S. P. J.; Cofino, W.; Crum, S., Analytical improvements shown over four interlaboratory studies of perfluoroalkyl substances in environmental and food samples. *Trends in Analytical Chemistry* 2013, 43, 204-216.
45. Backe, W. J.; Day, T. C.; Field, J. A., Zwitterionic, Cationic, and Anionic Fluorinated Chemicals in Aqueous Film Forming Foam Formulations and Groundwater from U.S. Military Bases by Nonaqueous Large-Volume Injection HPLC-MS/MS. *Environmental Science & Technology* 2013, 47, 5226-5234.
46. Wang, F.; Lu, X.; Shih, K. M.; Wang, P.; Li, X., Removal of perfluoroalkyl sulfonates (PFAS) from aqueous solution using permanently confined micelle arrays (PCMAs). *Separation and Purification Technology* 2014, 138, 7-12.
47. van Leeuwen, S. P. J.; van Velzen, M. J. M.; Swart, C. P.; van der Veen, I.; Traag, W. A.; de Boer, J., Halogenated Contaminants in Farmed Salmon, Trout, Tilapia, Pangasius, and Shrimp. *Environmental Science & Technology* 2009, 43, 4009-4015.
48. Annesley, T. M., Ion Suppression in Mass Spectrometry. *Clinical Chemistry* 2003, 49, 1041-1044.
49. Jessome, L. L.; Volmer, D. A., Ion suppression: A major concern in mass spectrometry. LCGC North America 2006, 24, 498-510.
50. Sigma-Aldrich, Solvent center. http://www.sigmaaldrich.com/chemistry/solvents.html (10-03-2015).
51. EU, Commision Regulation (EU) No 757/2010 of 24 August 2010. *Official Journal of the European Union* 2010, L 223/29, 29-36.

Supporting Information

Table S2-1 Full names, acronyms, chemical formula and CAS numbers of compounds analysed in this study and their isotope-labeled ISs.

Compounds	Abbreviation	Formula	CAS No.
Perfluorobutanoic acid	PFBA	C_3F_7COOH	375-22-4
Perfluoropentanoic acid	PFPeA	C_4F_9COOH	2706-90-3
Perfluorohexanoic acid	PFHxA	$C_5F_{11}COOH$	307-24-4
Perfluoroheptanoic acid	PFHpA	$C_6F_{13}COOH$	375-85-9
Perfluorooctanoic acid	PFOA	$C_7F_{15}COOH$	335-67-1
Perfluorononanoic acid	PFNA	$C_8F_{17}COOH$	375-95-1
Perfluorodecanoic acid	PFDA	$C_9F_{19}COOH$	335-76-2
Perfluoroundecanoic acid	PFUnDA	$C_{10}F_{21}COOH$	2058-94-8
Perfluorododecanoic acid	PFDoDA	$C_{11}F_{23}COOH$	307-55-1
Perfluorotridecanoic acid	PFTrDA	$C_{12}F_{25}COOH$	72629-94-8
Perfluorotetradecanoic acid	PFTeDA	$C_{13}F_{27}COOH$	376-06-7
Perfluorobutane sulfonate anion	PFBS	$C_4F_9SO^3$-	45187-15-3
Perfluorohexane sulfonate anion	PFHxS	$C_6F_{13}SO^3$-	108427-53-8
Perfluoroheptane sulfonate anion	PFHpS	$C_7F_{1S}SO_3^-$	375-92-8
Perfluorooctane sulfonate anion	PFOS	$C_8F_{17}SO_3^-$	45298-90-6
Perfluorooctane sulfonamide	FOSA	$C_8F_{17}SO_2NH_2$	754-91-6
Isotope-Labeled PFAAs			
Perfluoro-n-[1,2,3,4-$^{13}C_4$]butanoic acid	$^{13}C_4$-PFBA	[2,3,4-$^{13}C_3$]$F_7{}^{13}COOH$	na
Perfluoro-n-[1,2,3,4,5-$^{13}C_5$]pentanoic acid	$^{13}C_5$-PFPeA	[2,3,4,5-$^{13}C_4$]$F_9{}^{13}COOH$	na
Perfluoro-n-[1,2-$^{13}C_2$]hexanoic acid	$^{13}C_2$-PFHxA	C_4F_9[2-^{13}C]$F_2{}^{13}COOH$	na
Perfluoro-n-[1,2,3,4-$^{13}C_4$]heptanoic acid	$^{13}C_4$-PFHpA	C_3F_7[2,3,4-$^{13}C_3$] $F_6{}^{13}COOH$	na
Perfluoro-n-[1,2,3,4-$^{13}C_4$]octanoic acid	$^{13}C_4$-PFOA	C_4F_9[2,3,4-$^{13}C_3$] $F_6{}^{13}COOH$	na
Perfluoro-n-[1,2,3,4,5-$^{13}C_5$]nonanoic acid	$^{13}C_5$-PFNA	C_4F_9[2,3,4,5-$^{13}C_4$]$F_8{}^{13}COOH$	na
Perfluoro-n-[1,2-$^{13}C_2$]decanoic acid	$^{13}C_2$-PFDA	C_8F_{17}[2-^{13}C]$F_2{}^{13}COOH$	na
Perfluoro-n-[1,2-$^{13}C_2$]undecanoic acid	$^{13}C_2$-PFUnDA	C_9F_{19}[2-^{13}C]$F_2{}^{13}COOH$	na
Perfluoro-n-[1,2-$^{13}C_2$]dodecanoic acid	$^{13}C_2$-PFDoDA	$C_{10}F_{21}$[2-^{13}C]$F_2{}^{13}COOH$	na
Perfluoro-1-hexane[$^{18}O_2$]sulfonate anion	$^{18}O_2$-PFHxS	$C_6F_{13}S[^{18}O_2]O^-$	na
Perfluoro-1-[1,2,3,4-$^{13}C_4$]octane sulfonate anion	$^{13}C_4$-PFOS	C_4F_9[1,2,3,4-$^{13}C_4$]$F_8SO_3^-$	na
Perfluoro-1-[$^{13}C_8$]octane sulfonamide	$^{13}C_8$-FOSA	$^{13}C_8F_{17}SO_2NH_2$	na

na = not available

Table S2-2 Details of outdoor clothing samples.

Sample No.	Sample type	Sample color	Year of manufacturing	Material	Membrane
1	Fabric for outdoor clothes	Red	n.r.*	100% recycled polyester	Transparent layer, polyethylene
2	Jacket	Yellow	2013	100% polyester	White layer, unknown**
3	Jacket	Yellow	2012-2013	100% polyester	White layer, unknown**
4	Fabric for outdoor clothes	Black	2013	92% polyester, 8% elastan	Not**
5	Fabric for outdoor clothes	Turquois blue	2013	100% nylon	Not**
6	Jacket	Black	n.r.*	100% polyester	Thick white layer, unknown**

n.r. : not reported; * information given by supplier; ** visually observed

Table S2-3 Instrumental settings for PFAAs and FOSA analyses.

Abbreviation	MS/MS mass transition (m/z-> m/z)	Fragmentor voltage (V)	Collision energy (V)	Ionization mode	Isotope-labeled standard
PFBA	213.0 → 169.0	60	3	Negative	$^{13}C_4$-PFBA
PFPeA	263.0 → 219.0	60	3	Negative	$^{13}C_5$-PFPeA
PFHxA	313.0 → 269.0	80	3	Negative	$^{13}C_2$-PFHxA
PFHpA	363.1 → 319.0	80	4	Negative	$^{13}C_4$-PFHpA
PFOA	413.0 → 369.0	80	4	Negative	$^{13}C_4$-PFOA
PFNA	463.0 → 419.0	100	5	Negative	$^{13}C_5$-PFNA
PFDA	513.0 → 468.9	100	5	Negative	$^{13}C_2$-PFDA
PFUnDA	562.9 → 518.9	100	6	Negative	$^{13}C_2$-PFUnDA
PFDoDA	613.0 → 568.9	100	7	Negative	$^{13}C_2$-PFDoDA
PFTrDA	663.0 → 618.9	100	7	Negative	$^{13}C_2$-PFUnDA
PFTeDA	712.9 → 668.9	120	4	Negative	$^{13}C_2$-PFDoDA
PFBS	299.0 → 80.0	150	35	Negative	$^{18}O_2$-PFHxS
PFHxS	399.0 → 80.0	200	48	Negative	$^{18}O_2$-PFHxS
PFHpS	449.0 → 80.0	150	45	Negative	$^{18}O_2$-PFHxS
PFOS	499.0 → 80.0	200	48	Negative	$^{13}C_4$-PFOS
FOSA	498.1 → 78.0	200	35	Negative	$^{13}C_8$-FOSA
$^{13}C_4$-PFBA	217.0 → 172.0	60	3	Negative	
$^{13}C_5$-PFPeA	268.0 → 222.9	60	3	Negative	
$^{13}C_2$-PFHxA	315.0 → 270.0	80	3	Negative	
$^{13}C_4$-PFHpA	367.0 → 321.9	80	4	Negative	
$^{13}C_4$-PFOA	416.9 → 371.9	80	4	Negative	
$^{13}C_5$-PFNA	468.0 → 423.0	100	5	Negative	
$^{13}C_2$-PFDA	515.0 → 470.0	100	5	Negative	
$^{13}C_2$-PFUnDA	565.0 → 520.0	100	6	Negative	
$^{13}C_2$-PFDoDA	615.0 → 569.9	100	7	Negative	
$^{18}O_2$-PFHxS	403.0 → 84	200	48	Negative	
$^{13}C_4$-PFOS	503.0 → 80	200	48	Negative	
$^{13}C_8$-FOSA	506.1 → 78	200	35	Negative	

Table S2-4 PFAA concentrations > LOD in extracts of four sequential extractions with acetone/acetonitrile as extraction solvent and varying extraction times (µg/m²) (Experiment 1).

Sample No.	Sequential extraction	Extraction time	PFBA	PFPeA	PFHxA	PFHpA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	PFBS	PFHxS	PFHpS	L-PFOS	FOSA
1	a	1 h			0.90*			0.14*					0.04*			0.74	
	b	1 h															
	c	24 h															
	d	6 d															
2	a	1 h			0.44*	0.17*	0.09*	1.26		1.29		0.39		0.15			
	b	1 h						0.11		0.12		0.03*					
	c	24 h						0.05*		0.02*							
	d	6 d						0.02*		0.02*							
3	a	1 h	1.03	1.61*	3.87	1.33	0.10*	1.01	0.03*	0.53		0.10				0.14*	
	b	1 h	0.14	0.23*	0.44	0.16		0.09		0.05							
	c	24 h			0.15*	0.06*		0.03*		0.01*							
	d	6 d			0.07*			0.04*									
4	a	1 h						0.12									
	b	1 h															
	c	24 h															
	d	6 d															
5	a	1 h															
	b	1 h															
	c	24 h															
	d	6 d															

NB: Since high concentrations of PFOA, with unclear origin, were detected in the blank samples which were extracted and analysed alongside the samples, results for PFOA are not reliable and therefore excluded.
* Concentration between LOD and LOQ.

Table S2-5 PFAA concentrations >LOD in extracts of four sequential extractions with acetone/acetonitrile as extraction solvent (µg/m^2) and extraction times of 30 min (Experiment 2).

Sample No.	Sequential extraction	Extraction time	PFBA	PFPeA	PFHxA	PFHpA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	PFBS	PFHxS	PFHpS	L-PFOS	FOSA
1	a	30 min	0.24	0.09*	0.30	0.04*	0.02*	0.05*								0.02*	
	b	30 min			0.02*												
	c	30 min															
	d	30 min															
2	a	30 min	0.22		0.32	0.10	0.07	1.29	0.04	1.32		0.27		0.22		0.02*	
	b	30 min			0.04*			0.10		0.11*				0.03*			
	c	30 min						0.05*									
	d	30 min															
3	a	30 min	0.67	1.41	3.39	1.53	0.09	1.03	0.03	0.53		0.04					
	b	30 min	0.14	0.17*	0.45	0.21	0.02*	0.09		0.05							
	c	30 min			0.15*	0.05*		0.02*									
	d	30 min			0.07*												
4	a	30 min				0.04*		0.08									
	b	30 min						0.02*									
	c	30 min															
	d	30 min															
5	a	30 min															
	b	30 min															
	c	30 min															
	d	30 min															

NB: Since high concentrations of PFOA, with unclear origin, were detected in the blank samples which were extracted and analysed alongside the samples, results for PFOA are not reliable and therefore excluded.
* Concentration between LOD and LOQ.

Table S2-6 PFAA concentrations > LOD in extracts of five sequential extractions with methanol as extraction solvent (µg/m²) and different extraction times (Experiment 3).

Sample No.	Sequential extraction	Extraction time	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	PFBS	PFHxS	PFHpS	L-PFOS	FOSA
1	a	30 min	0.17	0.14*	0.28	0.03*	0.19		0.05									
	b	30 min	0.03*		0.03*													
	c	30 min																
	d	30 min																
	e	4 d																
2	a	30 min	0.14*	0.11*	0.29	0.09	0.79	0.07	0.94	0.04*	1.07		0.24		0.15			
	b	30 min			0.04*		0.05*	0.02*	0.07		0.08		0.03*		0.02*			
	c	30 min									0.02*							
	d	30 min																
	e	4 d									0.01*							
3	a	30 min	0.69	1.06	3.99	1.42	2.81	0.11	0.81	0.02*	0.41		0.03*					
	b	30 min	0.02*	0.13*	0.35	0.09	0.17	0.03*	0.10		0.05							
	c	30 min			0.04*		0.02*		0.02*		0.02*							
	d	30 min																
	e	4 d							0.02*		0.03*							
4	a	30 min			0.07*	0.02*	0.23	0.05	0.08		0.02*							
	b	30 min					0.07		0.02*									
	c	30 min																
	d	30 min																
	e	4 d																
5	a	30 min			0.04*													
	b	30 min																
	c	30 min																
	d	30 min																
	e	4 d																

* Concentration between LOD and LOQ.

Table S2-7 Recoveries (%) and RSDs of fortified textile samples (n=3) extracted and analysed to validate a method for PFAAs and FOSA analysis.

Sample	Spiking level	Replicate	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	PFBS	PFHxS	PFHpS	L-PFOS	FOSA
1	10 µg/m²	Rep.1	87	97	96	97	94	100	106	105	102	97	104	98	98	85	102	103
		Rep.2	84	87	95	94	94	97	104	99	98	95	109	91	96	81	102	98
		Rep.3	91	100	99	101	97	105	107	103	103	96	110	102	103	86	106	103
		RSD (%)	*4.5*	*7.2*	*2.4*	*3.3*	*1.8*	*3.7*	*1.4*	*2.9*	*2.6*	*1.4*	*3.0*	*5.7*	*3.5*	*3.4*	*2.5*	*2.9*
1	1 µg/m²	Rep.1	91	93	103	102	99	111	100	95	96	99	87	100	102	85	99	101
		Rep.2	96	98	107	101	101	109	102	96	101	109	96	100	95	87	106	104
		Rep.3	89	98	89	89	90	106	100	87	100	102	96	99	96	87	107	106
		RSD (%)	*4.0*	*2.7*	*9.4*	*7.5*	*6.0*	*2.2*	*1.3*	*5.2*	*2.7*	*5.3*	*5.6*	*0.7*	*3.9*	*1.2*	*4.2*	*2.3*
2	10 µg/m²	Rep.1	84	84	87	91	88	97	100	97	95	56	36	95	95	91	99	97
		Rep.2	87	90	93	95	94	98	105	99	101	52	31	100	101	88	98	98
		Rep.3	88	91	91	98	93	99	109	104	102	49	39	97	99	88	104	100
		RSD (%)	*2.4*	*4.2*	*3.4*	*3.4*	*3.4*	*1.0*	*4.4*	*3.5*	*3.8*	*6.6*	*11.6*	*2.8*	*2.8*	*1.8*	*3.2*	*1.4*
2	1 µg/m²	Rep.1	80	80	87	86	89	108	107	97	93	54	32	97	103	97	102	105
		Rep.2	81	90	89	88	92	108	103	95	95	57	38	97	107	97	103	104
		Rep.3	83	91	86	87	88	108	105	98	120	65	59	95	99	97	105	98
		RSD (%)	*1.9*	*6.4*	*1.6*	*0.6*	*2.1*	*0.1*	*1.8*	*1.6*	*14.4*	*10.3*	*32.9*	*1.3*	*3.5*	*0.1*	*1.5*	*3.6*

Table S2-8 Concentrations (µg/m²) and reproducibilities (%) of three textile samples extracted and analysed on three different days to validate a method for PFAAs and FOSA analysis.

Sample number		PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	PFBS	PFHxS	PFHpS	L-PFOS	FOSA
1	Rep.1	0.20	0.14*	0.30	0.03*	0.19		0.05*									
	Rep.2	0.20	0.13*	0.36	0.03*	0.14		0.03*									
	Rep.3	0.18	0.12*	0.35	0.02*	0.14	0.01*	0.04*									
	RSD (%)	*4.2*	*5.4*	*9.4*	*13.5*	*17.5*		*13.7*									
2	Rep.1	0.14*	0.11*	0.33	0.09	0.83	0.09	1.01	0.04*	1.15		0.27		0.17			
	Rep.2	0.11*		0.32	0.08	0.71	0.07	1.13	0.03*	1.29		0.21		0.14			
	Rep.3	0.14*	0.08*	0.31	0.08	0.84	0.08	1.28	0.04*	1.56		0.26		0.11		0.02*	
	RSD (%)	*13.1*		*2.4*	*3.1*	*8.9*	*10.2*	*11.8*	*8.0*	*15.4*		*13.0*		*19.8*			
6	Rep.1	1.68	0.61	1.35	1.14	2.26	0.95	0.85	0.22*	0.31*			1.60				
	Rep.2	1.53	0.60	1.20	1.02	2.16	0.81	0.88	0.24*	0.25*			1.50				
	Rep.3	1.51	0.57	1.19	1.01	2.40	0.83	0.88	0.22*	0.23*			1.46				
	RSD (%)	*5.9*	*3.3*	*7.1*	*6.5*	*5.3*	*8.5*	*1.5*	*4.8*	*14.4*			*4.8*				

* Concentration between LOD and LOQ

Table S2-9 LODs and LOQs per compound for the analyses of PFAAs and FOSA in textiles at a IS recovery of 100%.

	LOD	**LOQ**
	(µg/m2)	*(µg/m2)*
PFBA	0.04	0.13
PFPeA	0.10	0.34
PFHxA	0.03	0.10
PFHpA	0.02	0.07
PFOA	0.02	0.07
PFNA	0.02	0.07
PFDA	0.02	0.07
PFUnDA	0.02	0.07
PFDoDA	0.02	0.07
PFTrDA	0.02	0.07
PFTeDA	0.03	0.10
PFBS	0.02	0.07
PFHxS	0.02	0.07
PFHpS	0.02	0.07
L-PFOS	0.02	0. 07
FOSA	0.02	0.07

Chapter 3.

Ike van der Veen [a]

Heidelore Fiedler [b]

Jacob de Boer [a]

[a] Vrije Universiteit, De Boelelaan 1085, 1081 HV, Amsterdam, The Netherlands

[b] Örebro University, School of Science and Technology, MTM Research Centre, SE-701 82, Örebro, Sweden

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Assessment of the per- and polyfluoroalkyl substances analysis under the Stockholm Convention – 2018/2019

Abstract

The comparability of laboratories for the analysis of per- and polyfluoroalkyl substances (PFASs) was assessed in the fourth round (2018/2019) of a series of interlaboratory comparison studies (ILSs) coordinated by the United Nations Environment Programme (UNEP) in support of the Stockholm Convention quality assurance activities as to persistent organic pollutants (POPs) laboratories reporting data under this Convention. The participating laboratories were asked to analyse PFAS concentrations in a test solution of the target compounds, in the four core matrices of the global monitoring plan (GMP), human milk, human plasma, an air extract, and water, and in a sediment and a fish matrix. 39 participating laboratories submitted PFAS data for one or more test materials. The majority of the participating laboratories originated from the Asia-Pacific region, and from the Western European and other groups (WEOG). Only one laboratory out of the group of Latin America and Caribbean (GRULAC), and two out of the Central and Eastern Europe (CEE) region submitted results. None of the African laboratories submitted data. The coefficients of variation (CVs) varied from 7% to 24% (mean 14%) for the test solution. Mean CVs for all matrices, except for the human plasma test material (18%), were above the satisfactory limit of 25%. The highest mean CV was found for human milk (61%). In total 1457 z- scores were assigned for PFASs in this round of which 64% were satisfactory ($|z| < 2$). Instrumentation used was mainly high performance liquid chromatography (HPLC), in combination with various mass spectrometric (MS) techniques, in most cases tandem MS (MS/MS). Additional PFASs beyond perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) which are listed at the Stockholm Convention POPs list, as well as water as a matrix only for PFASs and human plasma were added as a service for the laboratories.

3.1. Introduction

Per- and polyfluoroalkyl substances (PFASs) are gaining increasing attention from a human health as well as from an environmental perspective. Legislation for those compounds started in 2006 with perfluorooctane sulfonic acid (PFOS) as the first PFAS regulated by the European Commission (Regulation Directive 2006/122/EC)[1]. In 2009, PFOS was listed under the Stockholm Convention on Persistent Organic Pollutants (POPs) and perfluorooctanoic acid (PFOA) in 2019[2-4]. Perfluorohexane sulfonic acid (PFHxS) is proposed for listing under the Convention[5]. It can be foreseen that in the near future, wider regulation of PFASs will occur. The Stockholm Convention plans to include long-chain perfluorocarboxylic acids, their salts and related compounds[6].The new advisory values of the European Food Safety Authority (EFSA) with a maximum uptake of 4.4 ng/kg bodyweight (bw) per week[7] for the sum of four compounds (PFOS, PFOA, PFHxS and perfluorononanoic acid (PFNA)), further emphasizes the high toxicity of PFASs and the need for reliable analytical methods for PFASs.

Since 2005, as part of the United Nations Environment Programme's (UNEP) capacity building projects for laboratories, a worldwide interlaboratory comparison study (ILS) for analysing POPs was initiated[8-10]. In the second round of the UNEP-coordinated biennial ILS (IL2) (2012/2013)[11], PFASs were included in the study for the first time[11]. In this IL2, and in the following two rounds, IL3 (2016/2017)[12, 13], and the here described IL4 (2018/2019)[14, 15], participating laboratories were offered reporting PFAS concentrations in a test solution of the target compounds, and in the four core matrices of the global monitoring plan (GMP) (human milk, human plasma, air extract, water). In addition, participants had the possibility reporting PFAS concentrations in sediment and fish samples, which were included in the assessments due to large interest by countries and authorities for reasons such as mentioned before. For the other matrices the list was extended in the here described IL4. In this paper we present the results of the PFAS analyses of the fourth round (2018/2019) and assess if the participating laboratories are able to deliver good quality data in the core matrices of the GMP and others. We compare them with the results of the previous rounds[11-13] to assess progress and with other PFAS proficiency tests.

3.2. Material and methods

3.2.1. Design of the Assessment

This IL*4* followed the structure of IL3[12, 13]. In April 2018, POPs laboratories were invited to register for the fourth Bi-ennial Global ILS on POPs. In September 2018, sediment, fish and water test materials were dispatched by the Department of Environment & Health of the Vrije Universiteit Amsterdam (VU), the Netherlands. The mixture of PFASs in an inert solution (TS), human milk, human plasma, and air extract test materials were dispatched by the Man-Technology-Environment (MTM) Research Center, School of Science and Technology at the University of Örebro, Sweden. Detailed instructions, including information on the nature of the test matrices, the storage conditions, and the requested reporting units, and an MS Excel reporting form were sent to the participants by e-mail. Participants were requested to report the concentrations of PFASs using their in-house methods. In addition, participants were asked to provide information on the method of extraction, clean-up and instrumental analyses used. The deadline for reporting was 15 January 2019.

Data evaluation was performed by using Cofino statistics[16, 17]. In brief, this model is based on observations of the entire data set and the determination of a probability density function. An example of the four plots used in the statistical evaluation is given in Figure 3-1. The upper left plot provides an impression of the probability density function (PDF) for all data (black) and for the first mode (blue dotted) (PMF1) of the data. Superimposed on these PDFs is a histogram of the individual measurements, given in grey. This plot shows the distribution of the data as a whole, and of the data in the main mode (PMF1) on which the assigned value (AV) is based. The “Kilt Plot” (overlap matrix) (upper right plot) provides an overview of the degree of overlap of each pair of data. It gives a clear indication of the degree of homogeneity of the data. As a key, the white areas indicate maximum overlap of the PDFs and, therefore, highest agreement (an overlap of one implies that the two laboratories of the pair report exactly the same results), while the black area show the pairs in poor agreement. The lower left plot in Figure 3-1 is a ranked overview of all data with an error bar of ± 2 standard deviation (SD). The numerical values are given in blue and the left censored values (LCVs), which are the values below the limit of detection (LOD), are given in red. The ranked z-score plot (lower right) is based on the mean of the data, which is normally also the AV. However, if there is any adjustment required to the AV as a result of the assessment, e.g., use of the nominal concentration or a trimmed value, the final z-score given in the z-score histograms will reflect these changes. In this assessment, no such adjustments are made and therefore, the z-score plot (lower right) is the definite plot for obtaining the individual lab z-scores. As mentioned

above |z|=2 is set as the maximum allowable variability in the data. In case |z|< 2, the performance was considered to be satisfactory (S), when 2 < |z| < 3, the performance was questionable (Q), and if |z| > 3, the performance was unsatisfactory (U). LCVs were assigned to be either consistent (C) (LCV/2 < concentration corresponding to |z|=3) or inconsistent (I) (LCV/2 > concentration corresponding to |z|=3).

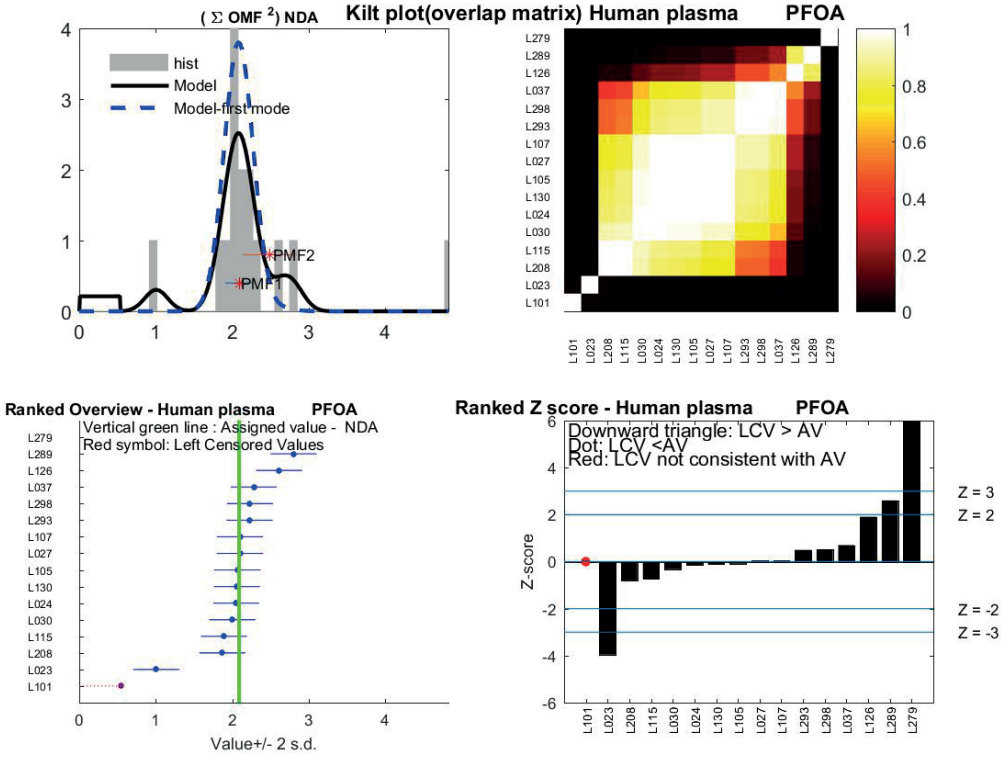

Figure 3-1 Graphical output of the Cofino model statistics for PFOA in the human plasma test material. PMF is probability main mode; NDA is normal distribution assumption.

3.2.2. Test Materials for PFAS Analyses

Sediment

The sediment test material originated from Rotterdam harbor (The Netherlands). HDPE plastic containers containing 150 g of dried (at 40°C) and sieved (0.5 mm pore size) sediment, obtained from the Wageningen Evaluating Programmes for Analytical Laboratories (WEPAL, Wageningen, The Netherlands). The test material was stored at room temperature until shipment.

Fish

The fish test material consisted of pike perch (*Stizostedion lucioperca*) originating from the river Amer (Rhine/Meuse estuary), the Netherlands. After filleting, cutting and homogenizing, glass jars were filled with ca. 40 g of the homogenate. The jars were sterilized by autoclaving, which enabled storage and transport of the material at room temperature. Homogeneity of the material was confirmed by performing a homogeneity test of PFOS on 7 randomly selected jars. More information on the results of the homogeneity testing is given in Chapter S3-4 of the Supporting Information (SI).

Human Milk

The human milk test material consisted of a pooled sample from human milk banks in the Örebro region, Sweden. To reach the sample volume needed to serve all participants in the ILS, 1.5 L of cows' milk from Sweden (approx. 25% of total volume) was added. Fifty mL milk were packed in polypropylene bottles and frozen (-20°C) prior to shipment.

Human Plasma

The human plasma test material was a homogenized pooled human blood plasma of individuals in Sweden including some with potential exposure to PFASs. The samples were stored in high-density polyethylene (HDPE) vials and kept frozen (-20 °C). Ice pads were used for the dispatch, both for the human plasma and the human milk test materials.

Air Extract

The air extract was a methanol extract of polyurethane foam (PUF) filters from active air sampling, exposed in Örebro, Sweden, during spring 2018, mixed with remaining extracts from previous ILS (at that time spiked with native PFOS and PFOS precursor compounds) [12, 13]. The extract was ampouled into 1.2 mL brown glass vials and kept in a fridge until shipment.

Water

The water test material was a combined surface water sample taken from different locations in the Netherlands. After bottling in HDPE bottles (250 mL), the material was sterilized by irradiation and kept at room temperature until shipment.

Test Solution

The PFAS test solution consisted of a mixture of perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs), perfluorooctane sulphonamides (FOSAs), and perfluorooctane sulfonamidoethanols (FOSEs) in methanol with

concentrations between 10 ng/g and 300 ng/g. The solution was prepared, ampouled and labelled by Wellington Laboratories (Guelph, Ontario, Canada).

3.2.3. Target Compounds for Analysis

The protocol allowed reporting of 22 PFASs for the test solution, and for the core matrices human plasma, and the air extract, and 17 PFASs for fish and sediment and for the core matrices human milk and water. The PFASs to report on were: perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, PFNA, perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA), perfluorotridecanoic acid (PFTrDA), and perfluorotetradecanoic acid (PFTeDA), linear-perfluorobutane sulfonic acid (L-PFBS), L-PFHxS, L-PFOS, branched-PFOS (br-PFOS), L-perfluorodecane sulfonic acid (L-PFDS), and 6:2 fluorotelomer sulfonic acid (6:2 FTSA) in all test materials. The PFOS precursors FOSAs and FOSEs (including FOSA, N-methyl perfluorooctane sulfonamide (MeFOSA), N-ethyl perfluorooctane sulfonamide (EtFOSA), N-methyl perfluorooctane sulfonamidoethanol (MeFOSE), N-ethyl perfluorooctane sulfonamidoethanol (EtFOSE)) were to be reported for human plasma, the air extract and the test solution.

Of all PFASs only the concentration of the linear isomer could be reported, except for PFOS. Total-PFOS (tot-PFOS) concentrations were either submitted by the participants or were calculated as the sum of L-PFOS and br-PFOS, with a lower-bound value (LB) calculated as <LOD=0, and an upper-bound value (UB) calculated as n<LOD=LOD.

3.3. Results

3.3.1. Participation

In total, 148 laboratories from 62 countries representing all five UN regions, Africa, Asia-Pacific, Central and Eastern Europe (CEE), group of Latin America and Caribbean (GRULAC), and Western European and other groups (WEOG) registered for this ILS. Among these laboratories, 53 registered for the analyses of PFASs in one or more test materials. Finally, 39 laboratories submitted results. None of the three registered laboratories from Africa submitted results. Only one of the five laboratories in the GRULAC region submitted results, and only for three test materials, while 25 of the 28 (89%) laboratories from the WEOG submitted data (Table 3-1).

Table 3-1 Number of participants that registered for the analyses of PFASs in IL4 per matrix and the number of participants which submitted results for PFASs per matrix.

	Number of participants											
	Registered						Submitted results					
Matrix	*Total*	*Africa*	*Asia-Pacific*	*CEE*	*GRULAC*	*WEOG*	*Total*	*Africa*	*Asia-Pacific*	*CEE*	*GRULAC*	*WEOG*
Total	**53**	**3**	**15**	**2**	**5**	**28**	**39**	**0**	**11**	**2**	**1**	**25**
Test solution	40	1	10	2	4	23	29	0	7	2	1	19
Sediment	22	1	10	1	1	9	13	0	5	1	0	7
Fish	34	1	12	1	1	19	25	0	7	1	0	17
Human milk	27	0	8	1	1	17	18	0	6	1	0	11
Human plasma	23	1	8	2	0	12	16	0	5	2	0	9
Air extract	23	1	10	1	1	10	18	0	7	1	1	9
Water	33	3	13	1	2	14	22	0	8	1	1	12

CEE = Central and Eastern Europe; GRULAC= Group of Latin America and Caribbean; WEOG = Western European and other groups

Of the 39 laboratories that submitted results, 38 provided information on instrumentation and methods used for the PFAS analysis. All laboratories reported the use of liquid chromatography (LC). The vast majority reported tandem mass spectrometric (MS/MS) detection. Three laboratories used an Orbitrap instrument and one laboratory used a time-of-flight mass spectrometer (ToF-MS) for detection.

3.3.2. Results

Detailed results as submitted by the 39 laboratories are given in the SI (Tables S3-1.1-S3-1.7) and are summarized in Tables S3-2.1-S3-2.7. The laboratory performances of all compounds in all test matrices are given in Tables S3-3.1-S3-3.7, and are summarized in Table 3-2. In Table 3-3 a summary is given of all submitted results for PFOS, and the laboratory performance for PFOS in all test matrices.

Table 3-2 Summary of statistical results.

	Between lab CV (%)							Percentage of satisfactory z-scores |z|<2						
Analyte	*Test Solution*	*Sediment*	*Fish*	*Human milk*	*Human plasma*	*Air extract*	*Water*	*Test Solution*	*Sediment*	*Fish*	*Human milk*	*Human plasma*	*Air extract*	*Water*
L-PFOS anion	16	23	11	40	9	21	33	75	67	90	40	71	65	53
br-PFOS anion	32	45	32	105	38	NAV	40	58	57	69	42	50		43
tot-PFOS LB	*18*	*32*	*14*	*59*	*22*	*21*	*42*	*79*	*77*	*84*	*39*	*88*	*67*	*48*
tot-PFOS UB	*18*	*30*	*16*	*103*	*9*	*26*	*33*	*80*	*67*	*88*	*47*	*92*	*73*	*56*
FOSA	17				NAV	23		80					60	
MeFOSA	8				NAV	6		86					78	
EtFOSA	16				NAV	10		79					67	
MeFOSE	7				NAV	28		77					50	
EtFOSE	11				NAV	4		85					70	
PFBA	11	NAV	NAV	NAV	NAV	41	34	83					38	63
PFPeA	12	NAV	NAV	NAV	NAV	34	36	80					46	38
PFHxA	15	26	NAV	NAV	NAV	22	17	93	45				60	78
PFHpA	15	17	NAV	NAV	NAV	27	19	86	36				57	67
PFOA	12	23	NAV	38	9	25	23	83	50		36	75	63	58
PFNA	15	34	38	NAV	12	21	16	89	55	29		67	64	44
PFDA	10	53	13	NAV	10	21	14	93	36	62		64	67	41
PFUnDA	16	41	34	NAV	16	30	224	86	36	48		60	57	0
PFDoDA	13	17	16	NAV	47	30	115	75	64	71		36	62	0
PFTrDA	19	21	41	NAV	NAV	55	NAV	74	45	50			43	
PFTeDA	12	45	52	NAV	NAV	56	NAV	89	36	33			31	
L-PFBS	17	51	NAV	NAV	NAV	26	24	89	36				60	67
L-PFHxS	12	20	81	NAV	7	19	16	79	55	20		73	60	61
L-PFDS	15	NAV	NAV	NAV	NAV	35	NAV	81					64	
6:2 FTSA	22	2	NAV	NAV	NAV	51	31	79	50				44	56

CV = Coefficient of variation; NAV: No assigned value; LB = Lower-bound value; UB = Upper-bound value

Table 3-3 Summary of PFOS results.

	N			Theoretical conc.	AV	Median	Min	Max	Between lab CV	Inclusion rate	Satisfactory z-scores (%)	Questionable z-scores (%)	Unsatisfactory z-scores (%)	Extreme z-scores (%)
	Total	Numerical	LCV	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(%)	(%)	z|>3	|z|<2	3>|z|>2	z|>6
Test solution														
L-PFOS	28	28	0	58.7	61.4	60.8	31.8	103	16	69	14	75	11	14
Br-PFOS	19	18	1	15.8	12.3	12.7	7.4	23.4	32	71	11	58	16	11
tot-PFOS LB	29	29	0	71.5	69.7	70.0	40.9	103	18	72	17	79	3	17
tot-PFOS UB	20	20	0	71.5	68.8	68.8	40.9	99.0	18	71	15	80	5	15
Sediment														
L-PFOS	12	12	0		3.8	3.8	2.3	8.0	23	71	16	67	17	16
Br-PFOS	7	5	2		0.51	0.55	0.39	0.93	45	68	14	57	0	14
tot-PFOS LB	13	13	0		4.0	4.3	2.3	8.0	32	80	15	77	0	15
tot-PFOS UB	9	9	0		4.1	4.3	2.3	5.9	30	81	22	67	11	22
Fish														
L-PFOS	21	21	0		8.5	8.6	6.6	48.6	11	71	10	90	0	10
Br-PFOS	13	12	1		0.52	0.53	0.00	0.68	32	78	8	69	15	8
tot-PFOS LB	25	25	0		8.7	8.9	6.8	48.6	14	70	0	84	4	0
tot-PFOS UB	16	16	0		8.7	8.8	6.8	24.5	16	76	0	88	6	0
Human milk														
L-PFOS	15	9	6		0.02	0.03	0.02	7.5	40	61	20	40	0	20
Br-PFOS	12	8	4		0.02	0.02	0.005	0.58	105	60	8	42	0	8
tot-PFOS LB	18	12	6		0.03	0.04	0.00	8.0	59	56	0	39	0	0
tot-PFOS UB	15	15	0		0.07	0.08	0.03	8.0	103	64	27	47	7	27
Human plasma														
L-PFOS	14	14	0		14.7	14.4	0.50	24.5	9	59	21	71	7	21
Br-PFOS	10	10	0		5.4	5.1	0.60	10.3	38	65	20	50	10	20
tot-PFOS LB	16	16	0		19.8	19.5	1.1	24.5	22	77	6	88	0	6
tot-PFOS UB	12	12	0		20.1	19.9	1.1	23.8	9	62	0	92	0	0
Air extract														
L-PFOS	17	17	0		4.2	4.5	2.5	14.2	21	67	24	65	12	24
Br-PFOS	10	5	5		NAV	0.16	0.07	1.7	99	56	0	0	0	0
tot-PFOS LB	18	18	0		4.1	4.4	2.5	14.2	21	63	11	67	6	11
tot-PFOS UB	11	11	0		4.1	4.1	2.7	9.4	25	74	9	73	9	9
Water														
L-PFOS	19	18	1		2.4	2.5	0.001	2294	33	70	32	53	11	32
Br-PFOS	14	14	0		2.0	1.9	0.37	2162	33	70	21	43	14	21
tot-PFOS LB	21	20	1		3.9	4.2	0.0	4456	42	66	24	48	5	24
tot-PFOS UB	16	16	0		4.3	4.6	1.7	4456	33	67	19	56	6	19

AV: Assigned value; CV = Coefficient of variation; LB = Lower-bound value; UB = Upper-bound value

In total 1457 z-scores could be assigned for the results of the individual PFASs (tot-PFOS UB, and LB are not included) (Table 3-4). Of the z-scores, 939 were satisfactory, corresponding to 64% of all z-scores assigned for the PFASs. 232 (16%) were unsatisfactory, and 147 (10%) were questionable. For 9% of the data no z-score could be calculated since those results were either C or I. One laboratory, which only submitted results for the human plasma test material, had 100% satisfactory z-scores. Three laboratories had only unsatisfactory results (L259, L279 and L287). Those laboratories analysed one (L259), two (L287) or three (L279) test materials. For the test solution, seven participants (L027, L117, L124, L224, L242, L276, and L293) out of 29, obtained 100% satisfactory results, although only two of those laboratories (L027 and L276) reported on all PFASs.

Table 3-4 Summary of performance of all laboratories submitting results for PFASs (all individual PFASs and all matrices included).

Interlab assessment	*Number of z-scores*						*Percentages of z-scores*				
	# S	*# Q*	*# U*	*# C*	*# I*	**Total**	*% S*	*% Q*	*% U*	*% C*	*% I*
IL4	939	147	232	63	76	**1457**	64	10	16	4	5

S= satisfactory: |z| < 2; Q= Questionable: 2 < |z| < 3; U= Unsatisfactory: |z| > 3; C= Consistent: LCV/2 < concentration corresponding to |z|=3 ; I= Inconsistent: LCV/2 > concentration corresponding to |z|=3.

22 determinants were reported for the test solution. The AVs are shown in Table S3-2.1; there were no LCVs. The coefficients of variation (CVs) were between 7% and 32% (mean 14%) (Figure 3-2, Table 3-2 and Table S3-2.1). The differences between the theoretical values and the AVs for the PFASs in the test solution were less than 7% except for br-PFOS (22%), and 6:2 FTSA (16%) (Table S3-2.1).

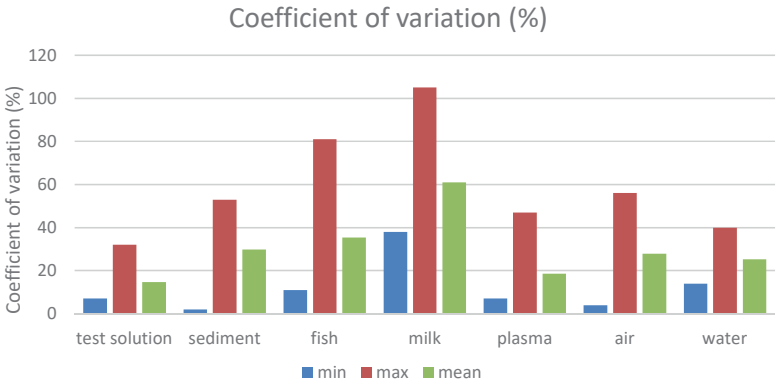

Figure 3-2 Coefficients of variation (CVs) (%) in IL4 for PFAS analyses per matrix for compounds for which an assigned value (AV) could be calculated.

Only a small percentage of the participants reported all requested PFASs (test solution, 31%; human plasma, 6%; air extract, 17%; human milk, 6%; water 23%; sediment, 31%; fish, 20%). PFOS (either L-PFOS, total-PFOS or both), which is one of the listed POPs, was reported by all participants but one in all matrices. This participant did not report PFOS in the water test material, although it was reported in fish (Table S3-1.3). PFOA concentration were reported by the majority of the participants for the core matrices (human plasma 16 of 16 participants; air extract 16 of 18; human milk, 14 of 18; water 19 of 22). For the relevant compounds in air, the PFOS precursors (FOSAs, and FOSEs), ten out of 18 participants reported concentrations.

3.4. Discussion

3.4.1. Participation

Since the introduction of PFASs in the UNEP ILS the number of participants for PFAS analyses has increased from 25 laboratories in IL2 to 39 in the present study. This is partly due to the participation of food labs, which participate because no other ILSs for food were organized, while EFSA recommended a new safety norm for the tolerably weekly intake (TWI) of the sum of four PFASs (PFOA, PFNA, PFOS, and PFHxS)[7]. This shows the rising interest in PFAS analysis. However, striking is the entire lack of participation by laboratories from Africa, and the low participation degree in the GRULAC region (Table 3-1). This is more or less in line with the participation in IL2 (Africa: 0, GRULAC: 0) and IL3 (Africa: 2, GRULAC: 1)[12]. The initial registration of 53 laboratories also shows that the ambition of the laboratories is often high, but then hindered by practical conditions. Three labs which did not report results did not receive the test materials. Sending and receiving packages with biota or environmental samples has become more difficult in the past few years. Regulations for the import and export of environmental and biological materials are becoming increasingly strict in various countries, and for some countries it is even impossible to receive certain types of matrices like e.g. fish in Japan or Cameroon. For other countries import permits are required. Laboratories participating in the UNEP ILS had to arrange their own import permits in time, which they did not always manage. Then test materials stay too long in customs. The reasons of the other 11 laboratories which did not manage to submit data remain unclear. These could be lack of facilities, lack of consumables, difficulties with ordering analytical standards abroad, or others. The gap between the working conditions in laboratories in developing countries and those in the WEOG region is still substantial.

3.4.2. Laboratory performance

The mean CVs for all PFASs for which an AV could be calculated in other matrices, except the human plasma test material (18%), were above the desired maximum of 25%[18] (Figure 3-2). Since the inclusion of PFASs in the second round of the UNEP IL, L-PFOS could be reported for all test materials. For the analyses of L-PFOS in the present round, the CV values fulfilled the criteria of 25% for all matrices except for the water (33%), and the human milk (40%) (Table 3-3). The concentration of L-PFOS in the water test material was more than 3 times higher than in the previous rounds, but the performance was equal to the performance on L-PFOS in IL3, although a higher percentages of satisfactory z-scores was assigned in this fourth round (IL3: 45%, IL4: 53%) (Figure 3-3). In IL2 the performance was better (CV: 21%) and 70% of the participants received a satisfactory z-score.

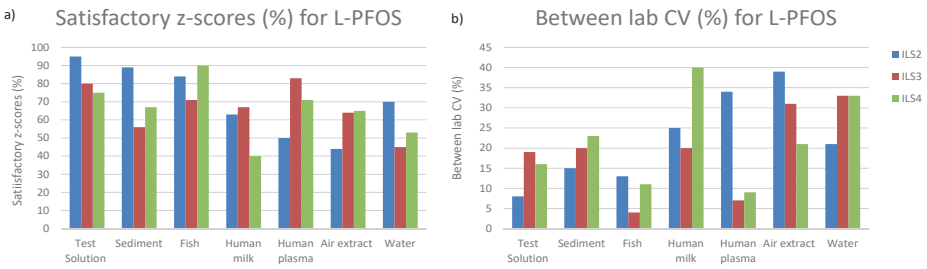

Figure 3-3 Statistical evaluation of L-PFOS results in all matrices in the last three rounds of the UNEP ILS. Percentage of satisfactory z-scores, b) percentage of between lab CV.

Figure 3-4 shows that WEOG laboratories performed better than Asian laboratories on L-PFOS in the water test material, which is one of the core matrices of the GMP. Of the WEOG laboratories only two participants received unsatisfactory z-scores (-3.4 and 4.4), while of the Asian laboratories only two participants managed to receive satisfactory z-scores, two laboratories obtained very extreme positive z-scores (822 and 7215) and one laboratory received an extreme negative z-score (-7.7). The same figure also shows the low participation of laboratories from the other three regions.

Not only L-PFOS, but also the analyses of the other PFASs in the human milk test material posed some problems to the laboratories; possibly due to the low concentrations (20 pg/g wet weight for L-PFOS) (Table 3-2). Sensitivity is always a difficulty for laboratories, especially when the matrix has a relatively high fat content. For most of the analytes, it was not possible to calculate an AV. For the PFASs for which an AV could be assigned, the variation was quite high (CV values from 38%

for PFOA to more than 100 for br-PFOS, and PFHxS). Even higher CV values were obtained for PFNA (CV: 611%) and PFUnDA (CV: 231%) (Table S3-2.4).

Although the PFAS concentrations in the sediment test material were on the low side for most of the compounds, only for three compounds (PFBA, PFPeA, L-PFDS) no AV could be calculated. For the other compounds the CV values ranged from 2% (6:2 FTSA) to 53% (PFDA), with a mean of 30%.

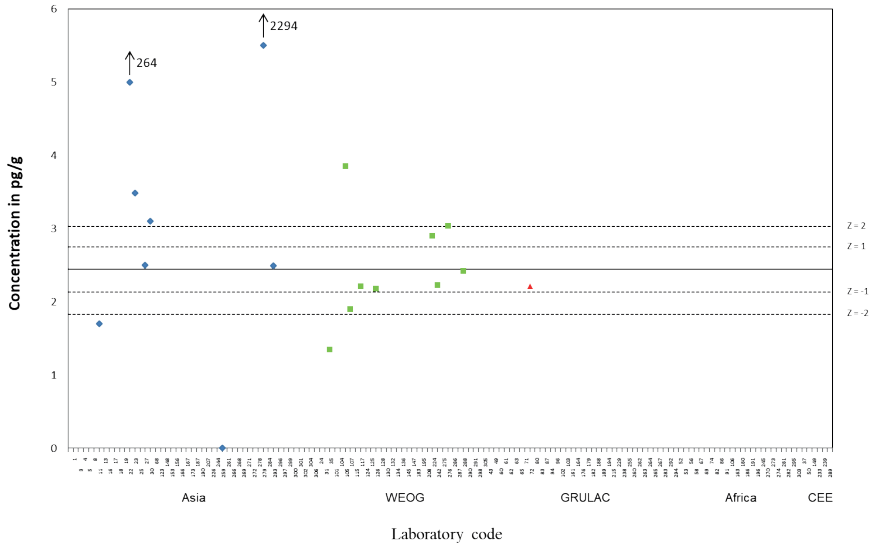

Figure 3-4 Results for L-PFOS anion in the water test material in IL4. Laboratory code on the x-axis, concentration in pg/g on the y-axis. The assigned value is given by the straight line, z = ± 1 (12.5%) and z = ± 2 (25%) are given by the dotted lines. The blue ♦ symbols represent Asia, the green ■ symbols represent WEOG, the red ▲ symbols represent GRULAC. Note: None of the laboratories from Africa and CEE submitted results.

AVs could be calculated for nine of the 17 compounds in the fish test material (Table S3-2.3). The other PFASs, except L-PFDS, all contained a maximum of eight carbon atoms. Short-chain PFASs are more water soluble, and hence less present in fish. As a result, the low concentrations of those PFASs caused the majority of participants reporting an LCV for short-chain PFASs.

In the fish material the sum of the concentrations of PFOA (NAV: median: 0.06 ng/g), PFNA (AV: 0.04 ng/g), L-PFOS (AV: 8.5 ng/g), and PFHxS (AV: 0.05 ng/g) was 8.65 ng/g (Table S3-2.3). With an average fish consumption of 22 kg/y[19] per person in the

Netherlands, and an average bodyweight of an adult of approx. 80 kg, this would be a weekly intake of the sum of four PFASs of 45 ng/kg bw/w, which is about 10 times higher than the TWI (4.4 ng/kg bw/w) set by EFSA[7]. This high concentration was mainly due to the high concentration of L-PFOS (AV: 8.5 ng/g). The CV for L-PFOS in this material was excellent (11%) (Table S3-2.3), with 90% of the participants receiving a satisfactory z-score (Table S3-3.3). Analyzing samples with higher concentrations results mostly in a better performance since the matrix is much more diluted, and the analysis is less disturbed by fat. However, the concentrations of PFOA, PFNA and L-PFHxS were much lower (0.15 ng/g) and together responsible for approx. 0.79 ng/kg bw/w (Table S3-2.3). Those low concentration resulted for PFOA in 16 of 22 participants reporting a LCV, and hence that no AV could be calculated, and a laboratory performance which was extreme high (CV: 174%). Also the performance on L-PFHxS was high (CV: 81%) with 20% of the participants receiving a satisfactory z-score (Tables S3-2.3, and S3-3.3). The performance on PFNA in the fish was slightly better (CV: 38%), with 29% of the participants obtaining a satisfactory z-score.

The performance for PFDA (CV: 13%), and PFDoDA (CV: 16%) was also very good. The CVs of the other six compounds for which an AV could be calculated was a bit higher (32%- 81%, mean 46%). Of those compounds, only for br-PFOS the majority (69%) of the participants was able to receive a satisfactory z-score. The better performance of the laboratories in fish is due to a combination of higher PFOS concentration and a lower fat percentage of the fish species (pike perch) used.

Except for the fish, and the human milk test materials, an AV could be calculated for all matrices for PFOA (CV: 9%-25%), PFNA (CV: 12%-34%), PFDA (CV: 10%-53%), L-PFHxS (CV: 7%-20%), L-PFOS (CV: 9%-33%) and also for br-PFOS (CV: 32%-99%).

The relatively poor performance of a number of labs for the standard solution is most likely due to the lack of experience of laboratories in analyzing such solutions. Laboratories analyse samples – fish, sediment, food, etc., but normally not standard solutions. Therefore mistakes are more easily made. The phenomenon has been observed in many other ILSs[20, 21]. This emphasizes again the essence of experience in this type of complex analysis.

The performance of PFOA, which is listed as POP at the Stockholm Convention met the criterion (max CV: 25%[18]) set in the GMP for the core matrices human plasma (CV: 9%), air extract (CV: 25%), and water (CV: 23%), with 75%, 63%, and 58% respectively of the participants obtaining a satisfactory z-score. For the human milk, which is also one of the core matrices, this criteria was not met (CV: 38%), with 36% receiving a satisfactory z-score (Tables S3-2.4 – S3-2.7, and Tables S3-3.4- S3-3.7).

For PFHxS, which is recommend to be considered for listing in Annex A of the Convention[5], the performance was very good for four of the test matrices (sediment CV: 20%, plasma CV: 7%, air extract CV: 19%, and water CV: 16%), and for the test solution (CV: 12%). However, extreme high CVs were calculated for the fish (81%) and human milk (113%), which is most likely due to the low contamination of those materials, resulting the majority of participant reporting an LCV (65% for fish, and 67% for human milk).

FOSAs and FOSEs could only be reported for the test solution, the human plasma test material, and the air extract. The performance for those compounds in the test solution (CV: 7%-17%) and the air extract (CV: 4%-28%) was extremely good, with more than 77% (77%-86%, mean 81%) of the participant receiving a satisfactory z-score for the test solution, and more than 50% (50%-78%, mean 65%) receiving it for the air extract. This was a clear improvement in comparison with IL3. In that ILS the concentrations in the test solution were up to 5 times higher and the CVs for the test solution were 27%-51% (mean 33%), while no AV could be calculated for any of the FOSAs in the air extract.

For eight PFASs in human plasma an AV could be calculated. The performance on six of those compounds was very good (CV: 7%-16%) with more than 60% (60%-75%) of the results being satisfactory (Table 3-2). As an example of the good agreement between the participants the graphical output of the Cofino model statistics for PFOA in the human plasma test material is given in Figure 3-1. For br-PFOS (CV: 38%) and PFDoDA (CV: 47%) the performance was less good, which might for PFDoDA have been caused by the very low concentration in the plasma (AV: 0.07 ng/g).

3.4.3. Analytical methods

All laboratories, which reported on their analytical methods (n=38) used LC for the separation of PFASs, and only one laboratory reported to have used gas chromatography (GC) for the separation of PFOS precursors. For the separation of traditional POPs, like PCBs and PBDEs mostly GC is used. This is why traditional POP laboratories do own a GC, but not always possess an HPLC, which is needed for the PFAS analyses. This might explain, the low participation degree in the GRULAC region and Africa. Also the extraction solvents needed for PFASs are different than those for traditional POPs. The majority of the participants used methanol (70%), and acetonitrile was used in 8.8% of the samples. An additional column was used by 43.6% of the laboratories between the pump and the injector of the HPLC, in order to retain PFASs which leach out of the HPLC system. 56.4% of the participants did not use such column. It was not reported by those laboratories if their systems contained polytetrafluoroethylene (PTFE) parts.

For all test materials results on the analyses of br-PFOS are worse than results obtained for L-PFOS (Table 3-2). It was not investigated in this study how participants performed the calculations for the br-PFOS and the L-PFOS. However, quantification of L-PFOS is often based on calibration standards consisting of 100% of the linear isomer. The quantification of the br-PFOS is often based on calibration standards of a technical mixture of PFOS isomers. Since all isomers have a different fragmentation ratio for the m/z 80 and the m/z 99 fragments, and the ration is also depended on the analytical instrument which is used, this can result in a higher CV. The laboratory performance on tot-PFOS was worse than the performance on L-PFOS for all matrices, except for tot-PFOS UB in the human plasma, and water, and tot-PFOS LB in in the air extract, for which all less satisfactory z-scores were obtained than for L-PFOS (Table 3-3). This results can partly be explained by the performance on br-PFOS, However, the assessment of the laboratory performance on tot-PFOS was not reliable, since some laboratories reported the concentration of tot-PFOS, while for other participants the LB and UB of tot-PFOS was calculated as the sum of L-PFOS and br-PFOS, while not all participant reported on both compounds.

3.4.4. Comparison with other ILSs

In comparison with previous ILSs[11-13], more PFAS laboratories participated in this IL4 and more determinants were included; both resulting in a larger number of z-scores that could be calculated (sums of PFASs not included)[12] (Table 3-4). It must be noted that the performance decreased from 86% satisfactory results in IL2 to 64% in IL4.

The same sediment test material of our study was also analysed in a small intercomparison study organized by WEPAL in commission of the Dutch National Institute for Public Health and the Environment (RIVM) in 2019[22]. In that exercise nine laboratories participated. All compounds which could be reported in our study could also be reported in the study of WEPAL. For four compounds (PFHpA, PFNA, PFDoDA, PFHxS) no AV could be calculated in the WEPAL study, while it could in our study. The number of participants analyzing those compounds was almost similar, but in the WEPAL study more reported an LCV value. For PFOS, and PFOA the performance was similar, but for all other compounds (except 6:2 FTSA) the performance was better in the WEPAL study (4%-30%, mean 16%) compared to our study (21%-53%, mean 39%). Most likely this can be explained by the fact that in our study a number of participants are less experienced in the analyses of PFASs, other than PFOA and PFOS, while in the WEPAL study only experienced labs were invited to participate. In 2006 the first ILS was organized on the analyses of PFASs in environmental and human samples[23]. This ILS was followed by four other ILSs on PFASs of which the last was organized in 2011 on PFASs in food and environmental samples[24]. The performance over the ILSs increased, for the analyses of PFASs in water and fish, mainly due to the

availability of labeled internal standards in the later study[24]. In the study of Weiss et al.[24], besides other matrices, two fish test materials, and a drinking water test material were analysed,. The performance on the water test material was a little better in the current study (mean CV 25% vs 28% for all PFASs with an AV in both studies). For the fish material the performance in the current study was equal to the performance on the low contaminated fish of the study of Weiss et al.[24]. Over the last years more is known on the analyses of PFASs, more labeled standards have come available, and more sensitive mass spectrometers are on the market, so it would be expected that the performance would have improved compared to 2011.

Although results of individual laboratories have improved in various cases, the results of the UNEP ILSs show a varying performance of individual participants. 24 laboratories participated, and received z-scores in two or three of the UNEP ILSs (IL2, IL3, and IL4) for the same compounds in the same matrix types. Those z-scores are given per laboratory in Table S3-5.1 of the SI. Two of those laboratories (L124 and L224) received only satisfactory z-scores for the compounds for which z-scores were assigned in both ILSs they participated in. Some other laboratories performed equal or almost equal in two (L002, L027, L130, L195) or three of the ILSs (L001, L030, L117). For some laboratories the performance was worse in the later ILSs (L023, L035, L107, L129), while the performance of some other laboratories (slightly) improved (L022, L221, L128).

To the best of our knowledge no more recent ILSs were organized on the analyses of PFASs, except IL2 and IL3 of the UNEP IL, although it would be recommended to laboratories to regularly test their performance in an intercomparison exercise to validate their method.

3.5. Conclusions

The percentage of assigned satisfactory z-scores decreased compared to previous rounds of the UNEP ILSs. The overall laboratory performance in this ILS showed that laboratories in general are not yet able to deliver good quality data (CV<25%) for the GMP for human milk, air extract, and water. However, the results on human plasma (CV: 18%) fulfilled the criterion.

Naturally contaminated test materials, which contain target compounds above LOD, are required for an IL, but not always available. In future ILSs it should be considered in case those materials are not available to fortify materials with the target compounds, on a realistic level above LOD, in order to enable participants to report

on all requested compounds. For future ILSs it should also be considered to encourage participants on forehand to make arrangements for import permits in time in case needed, in order to avoid packages to be left at customs for a couple of weeks. In future ILSs it is recommended to request participants to report on the concentration of L-PFOS, br-PFOS, and tot-PFOS separately, in order to make a reliable assessment on the laboratory performance of either reported tot-PFOS, or the calculated sum of L-PFOS and br-PFOS.

Although the performance of individual participants in the UNEP ILSs varies, it is recommended that laboratories carry out PFAS analyses on a regular basis in order not to lose the built-up knowledge. Governments should support their laboratories herein, as only participation in this ILS and occasional training will not be enough to guarantee reliable analytical results for POPs. The recently introduced new safety limits of EFSA for PFASs (TWI of 4.4 ng/kg bw/w for the sum of four PFASs) also includes PFNA[7]. At this moment PFNA is not yet listed as a POP. However, it is encouraging to see that the PFNA results belonged to the better ones in terms of CV values. Assuring the quality of PFAS analysis by regularly carrying out analyses, including the use of quality control (QC) charts, the analyses of certified reference materials, and the regular participation in ILSs will help to produce reliable results.

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References

1. EU, Directive 2006/122/EC of the European Parliament and of the Council of 12 December 2006. *Official Journal of the European Union* 2006, L 372/32, 32-34.
2. UNEP, Decision SC-4/17. Listing of perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride. UNEP-POPS-COP.4-SC-4-17, Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants: Geneva, Switzerland, 2009. http://chm.pops.int/TheConvention/ConferenceoftheParties/ReportsandDecisions/tabid/208/Default.aspx.
3. UNEP, Decision SC-9/4. Perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride. UNEP-POPS-COP.9-SC-9-4, Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants: Geneva, Switzerland, 2019. http://www.pops.int/Implementation/IndustrialPOPs/PFOS/Decisions/tabid/5222/Default.aspx
4. UNEP, Decision: SC-9/12. Listing of perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds. UNEP-POPS-COP.9-SC-9-12, Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants: Geneva, Switzerland, 2019. http://chm.pops.int/TheConvention/ConferenceoftheParties/Meetings/COP9/tabid/7521/ItemId/7235/Default.aspx.
5. UNEP, Perfluorohexane sulfonic acid (PFHxS), its salts and PFHxS-related compounds. UNEP-POPS-POPRC.15-POPRC-15-1, Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants: Rome, Italy, 2019. http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC15/Overview/tabid/8052/Default.aspx.
6. UNEP, Proposal to list long-chain perfluorocarboxylic acids, their salts and related compounds in Annexes A, B and/or C to the Stockholm Convention on Persistent Organic Pollutants. UNEP/POPS/POPRC.17/7, Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants: Geneva, Switzerland, 2021. http://chm.pops.int/Convention/POPsReviewCommittee/Chemicals/tabid/243/Default.aspx.
7. EFSA, EFSA Panel on Contaminants in the Food Chain, Scientific Opinion on the risk to human health related to the presence of perfuoroalkyl substances in food. *EFSA Journal* 2020, 18 (9), 6223.
8. UNEP, Report of the final results workshop of first worldwide` UNEP intercalibration study on POPs – Asia Region, Hong Kong, People's Republic of China, 26-28 February 2010, 2010. https://wedocs.unep.org/bitstream/handle/20.500.11822/22163/POPs%20IA%201st%20round_Report%20of%20the%20Final%20Results%20Workshop-%20Asia%20Region_May%202010.pdf?sequence=1&isAllowed=yx.
9. UNEP, van Bavel, B., van Leeuwen, S., de Boer, J., Bi-ennial global interlaboratory assessment on persistent organic pollutants – First Round 2010/2011, United Nations Environment Programme (UNEP), Geneva, Switzerland, 2011.

10. Fiedler, H.; van der Veen, I.; de Boer, J., Assessment of four rounds of interlaboratory tests within the UNEP-coordinated POPs projects. *Chemosphere* 2021, 132441.
11. UNEP, Nilsson, H., van Bavel, B., van der Veen, I., de Boer, J., Fiedler, H., Bi-ennial global interlaboratory assessment on persistent organic pollutants – Second Round 2012/2013, United Nations Environment Programme (UNEP), Geneva, Switzerland, 2014.
12. Fiedler, H.; van der Veen, I.; de Boer, J., Global interlaboratory assessments of perfluoroalkyl substances under the Stockholm Convention on persistent organic pollutants. *Trends in Analytical Chemistry* 2020, 124, 115459.
13. UNEP, Fiedler, H., van der Veen, I., de Boer, J., Bi-ennial global interlaboratory assessment on persistent organic pollutants – Third Round 2016/2017, United Nations Environment Programme (UNEP), Geneva, Switzerland, 2017; p 100.
14. UNEP, Fiedler, H., van der Veen, I., de Boer, J., Bi-ennial global interlaboratory assessment on persistent organic pollutants – Fourth Round 2018/2019, United Nations Environment Programme (UNEP), Geneva, Switzerland, 2021; p 100.
15. Fiedler, H.; van der Veen, I.; de Boer, J., Interlaboratory assessments for dioxin-like POPs (2016/2017 and 2018/2019). *Chemosphere* 2022, 288, 132449.
16. Cofino, W. P.; van Stokkum, I. H. M.; Wells, D. E.; Ariese, F.; Wegener, J.-W. M.; Peerboom, R. A. L., A new model for the inference of population characteristics from experimental data using uncertainties. Application to interlaboratory studies. *Chemometrics and Intelligent Laboratory Systems* 2000, 53, 37-55.
17. Cofino, W. P.; Molenaar, J.; Torfs, P., Proficiency tests, Evaluating. *Wiley StatsRef: Statistics Reference Online, doi:10.1002/9781118445112.stat04068.pub2* 2017, 1-8.
18. UNEP, Guidance on the global monitoring plan for persistent organic pollutants. UNEP/POPS/COP.9/INF/36, Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants: Geneva, Switzerland, 2019; p 149. http://www.brsmeas.org/Decisionmaking/COPsandExCOPs/2019COPs/MeetingDocuments/tabid/7832/ctl/Download/mid/21620/language/en-US/Default.aspx?id=72&ObjID=26562
19. EU, Data News Hub, Food consumption in the EU. https://ednh.news/food-consumption-in-the-eu/ (20 October 2021).
20. de Boer, J.; Wells, D. E., Pitfalls in the analysis of brominated flame retardants in environmental, human and food samples – including results of three international interlaboratory studies. *Trends in Analytical Chemistry* 2006, 25, 364-372.
21. Su, Y.; Hung, H., Inter-laboratory comparison study on measuring semi-volatile organic chemicals in standards and air samples. *Environmental Pollution* 2010, 158, 3365-3371.
22. Van Vark, W., Per- and Polyfluoro Alkyl Substances, Report 2019, Nederlandse versie no 2 Wageningen Evaluating Programmes for Analytical Laboratories (WEPAL), 2019, 2019; p 168. https://www.rijksoverheid.nl/documenten/rapporten/2020/04/15/resultaten-ringonderzoek-pfas.
23. van Leeuwen, S. P. J.; Kärrman, A.; van Bavel, B.; de Boer, J.; Lindström, G., Struggle for Quality in Determination of Perfluorinated Contaminants in Environmental and Human Samples. *Environmental Science & Technology* 2006, 40, 7854-7860.

24. Weiss, J. M.; van der Veen, I.; de Boer, J.; van Leeuwen, S. P. J.; Cofino, W.; Crum, S., Analytical improvements shown over four interlaboratory studies of perfluoroalkyl substances in environmental and food samples. *Trends in Analytical Chemistry* 2013, 43, 204-216.

Supporting Information

S3-1. Final data as submitted by participating laboratory

Table S3-1.1 Test solution (ng/g).

Test solution	**L001**	**L011**	**L023**	**L024**	**L027**	**L030**	**L035**	**L037**	**L072**	**L101**	**L104**	**L105**	**L107**	**L115**
Region[a]	*Asia*	*Asia*	*Asia*	*WEOG*	*Asia*	*Asia*	*WEOG*	*CEE*	*GRU-LAC*	*WEOG*	*WEOG*	*WEOG*	*WEOG*	*WEOG*
PFOS														
L-PFOS anion	54.305	79	103.1826681	52	62	64	33.47	31.79	55.4	96.23	69	56.84684932	43	78.39724867
br-PFOS anion	9.365	NA	NA	13	15	21	7.42	9.62	12.1	NA	NA	<5	11	NA
tot-PFOS Lower Bound (ND=0)	63.67	79	103.1826681	65	77	85	40.88	41.41	67.5	96.23	69	56.84684932	54	78.39724867
tot-PFOS Upper Bound (ND=LOD)	63.67	NA	NA	65	77	85	40.88	41.41	67.5	NA	NA	61.84684932	54	NA
PFOS precursors														
FOSA	63.775	62	NA	52	63	NA	117.59	NA	56.8	203.45	38	53.50684932	44	NA
MeFOSA	132.374	122	NA	133	130	NA	113.18	NA	132	NA	127	51.52767123	97	NA
EtFOSA	205.725	161	NA	261	190	NA	149.28	NA	200	NA	190	98.0460274	130	NA
MeFOSE	NA	154	NA	127	130	NA	NA	NA	128	NA	130	95.57232877	88	NA
EtFOSE	NA	156	NA	104	130	NA	NA	NA	137	NA	132	69.78821918	86	NA
PFCAs and PFSAs														
PFBA	60.455	65	94.02861968	50	64	NA	33.69	50.54	57.6	NA	63	71.45013699	45	77.95710135
PFPeA	49.597	75	87.57426368	57	61	NA	45.18	43.88	60.6	64.82	61	68.43753425	45	78.10631903
PFHxA	62.668	113	113.5510136	80	95	93	78.29	73.61	89.4	91.81	98	103.8186301	68	102.493277
PFHpA	50.512	72	78.13210956	61	64	58	33.78	52.48	54.8	70.17	66	64.94	45	81.4798944
PFOA	58.475	72	72.38596718	57	63	66	31.98	53.01	51.9	48.88	65	56.40630137	43	111.1884347
PFNA	104.302	129	150.2182829	115	130	130	60.37	105.28	110	116.83	129	109.6158904	88	102.4059967
PFDA	61.233	69	74.18581923	57	65	61	39.09	50.25	60.6	67.34	63	63.87671233	38	74.04045688
PFUnDA	51.178	71	68.07865085	59	66	62	38.82	51.16	49.7	65.25	65	101.1764384	45	68.87668324
PFDoDA	165.429	227	237.9328096	181	180	180	95.47	146	172	228.73	186	184.1452055	130	160.4057836
PFTrDA	73.327	86	80.31948641	65	55	66	50.45	58.56	96.7	102.36	64	79.24246575	52	47.91046064
PFTeDA	61.167	78	75.84173778	63	65	70	51.5	62.63	72.7	54.67	67	64.62821918	40	51.52958535
L-PFBS	85.007	82	118.3843557	73	100	NA	94.93	73.57	78.5	98.27	96	70.80438356	61	51.52958535
L-PFHxS	57.472	72	87.58182073	47	65	63	33.08	49.1	56	82.35	65	62.71835616	43	99.70728823
L-PFDS	58.596	78	83.47494494	57	67	63	40.25	43.88	71.6	49.38	70	NA	42	78.40361447
6:2 FTSA	68.424	56	NA	64	NA	NA	NA	NA	44	NA	NA	47.24986301	40	39.43708946

a WEOG = Western European and other groups , CEE = Central and Eastern Europe, GRULAC= group of Latin America and Caribbean

Test solution	**L117**	**L124**	**L126**	**L128**	**L190**	**L195**	**L208**	**L224**	**L242**	**L276**	**L288**	**L289**	**L290**	**L293**	**L298**
Region[a]	*WEOG*	*WEOG*	*WEOG*	*WEOG*	*Asia*	*WEOG*	*WEOG*	*WEOG*	*WEOG*	*WEOG*	*WEOG*	*CEE*	*WEOG*	*Asia*	*WEOG*
PFOS															
L-PFOS anion	59.8	64.9	60.7	67.67	71.8	66	65	60.8	51.04	59	75.61534793	NA	60.2	59.556	52.6
br-PFOS anion	12.7	NA	12.9	21.68	NA	NA	16	11.2	12.74	11	23.37609917	NA	16.3	NA	7.82
tot-PFOS Lower Bound (ND=0)	72.5	64.9	73.6	89.35	71.8	66	81	72	63.78	70	99	53	76.5	59.556	60.42
tot-PFOS Upper Bound (ND=LOD)	72.5	NA	73.6	89.35	NA	NA	81	72	63.78	70	99	53	76.5	NA	60.42
PFOS precursors															
FOSA	NA	67.63	65.1	NA	65.6	65	49	61	53.79	63	71.71	NA	NA	NA	49.3
MeFOSA	NA	138.9	179	NA	124	115	NA	NA	NA	120	NA	NA	NA	NA	NA
EtFOSA	NA	187.1	210	NA	158	170	NA	NA	NA	200	NA	NA	NA	NA	NA
MeFOSE	NA	121.8	128	NA	152	72	NA	NA	NA	130	NA	NA	NA	NA	104.62
EtFOSE	NA	130.2	150	NA	156	121	NA	NA	NA	130	NA	NA	NA	NA	121.1
PFCAs and PFSAs															
PFBA	54.8	66.57	55.8	NA	66.6	65	62	NA	57.47	64	63	NA	60.1	63.982	57.13
PFPeA	56.1	67.36	65.9	NA	74.2	60	61	60.4	54.77	62	56.5	NA	NA	62.564	59.08
PFHxA	85.3	97.62	92.5	99.95	107	92	109	88.5	80.38	98	108.1	NA	83.5	90.911	81.49
PFHpA	57.3	70.06	68	63.16	71.7	61	54	59.4	56.43	64	72.6	NA	57.7	60.215	52.29
PFOA	55.4	66.33	58.3	65.27	72.4	58	66	59.2	55.31	61	77.4	98	56.1	61.048	64.78
PFNA	116	130.8	131	103.06	129	121	124	116.1	105.4	130	143.5	NA	106.5	123.595	103.72
PFDA	59	65.37	61	56.61	68.1	60	67	59.7	53.96	68	73.6	NA	58.5	61.77	53.23
PFUnDA	56	64.81	60.2	70.37	75	60	72	58.2	54.21	65	79.7	NA	56.3	59.94	51.85
PFDoDA	167	202.9	171	249.36	235	181	203	169.8	156.9	172	213.5	NA	176.2	173.196	138.83
PFTrDA	56.7	63.57	67.7	98.45	86.6	66	68	63.6	68.48	55	NA	NA	60.8	64.296	24.06
PFTeDA	58.1	64.16	60.8	68.93	82.9	85	62	57.4	67.66	66	NA	NA	58.9	64.635	53.28
L-PFBS	76.2	85.37	78	72.24	101	94	79	91.6	75.29	91	102.2	NA	83.9	81.349	93.93
L-PFHxS	51.5	65.38	60.1	60.87	72.1	62	60	54.4	52.1	64	81.4	NA	57.9	58.153	64.85
L-PFDS	57	62.83	60.8	81.06	71.2	57	67	NA	70.39	62	64.8	NA	56.8	63.455	60.91
6:2 FTSA	50.7	61.54	57.7	115.46	61.7	NA	NA	NA	NA	58	NA	NA	NA	NA	40.51

Table S3-1.2 Received results per participant, sediment (ng/g).

Sediment	**L011**	**L022**	**L023**	**L024**	**L027**	**L101**	**L105**	**L107**	**L115**	**L117**	**L126**	**L190**	**L289**
Region[a]	Asia	Asia	Asia	WEOG	Asia	WEOG	WEOG	WEOG	WEOG	WEOG	WEOG	Asia	CEE
PFOS													
L-PFOS anion	4.4	5.005	2.300946785	3.2	4.4	7.97	3.68532374	3.2	3.7462	2.9	3.86	4.86	NA
br-PFOS anion	NA	0.9327	NA	<0.3	0.39	NA	0.654968455	<1	NA	0.4	0.55	NA	NA
tot-PFOS Lower Bound (ND=0)	*4.4*	*5.9377*	*2.300946785*	*3.2*	*4.79*	*7.97*	*4.340292196*	*3.2*	*3.7642*	*3.3*	*4.41*	*4.86*	*3.4*
tot-PFOS Upper Bound (ND=LOD)	*NA*	*5.9377*	*2.300946785*	*3.5*	*4.79*	*NA*	*4.340292196*	*5.2*	*NA*	*3.3*	*4.41*	*NA*	*3.4*
PFCAs and PFSAs													
PFBA	<0.06	NA	<0.02	<1	<0.05	NA	0.177687205	<5	0.106195143	0.276	<0.01	<0.06	NA
PFPeA	<0.06	NA	<0.05	<0.5	<0.05	<0.5	0.086546925	<1	<0.1	<0.215	0.13	<0.02	NA
PFHxA	0.28	NA	0.18600048	<0.5	0.18	1.53	0.170516552	<1	0.173484343	<0.215	0.23	0.331	NA
PFHpA	<0.09	NA	0.042477877	<0.5	0.053	<0.5	0.054498485	<1	<0.1	<0.215	0.07	<0.02	NA
PFOA	0.83	NA	0.266175683	0.52	0.45	4.31	0.444965227	<1	0.520510314	0.31	0.5	0.824	0.54
PFNA	0.12	NA	0.081223219	<0.5	0.059	<0.5	0.064832294	<1	<0.1	<0.215	0.08	0.123	NA
PFDA	0.5	NA	0.165188615	<0.5	0.25	6.63	0.249228486	<1	0.374868826	<0.215	0.26	0.484	NA
PFUnDA	0.41	NA	0.182944934	<0.5	0.27	<0.5	0.277607041	<1	0.423230434	0.24	0.2	0.472	NA
PFDoDA	0.32	NA	0.274046771	<0.5	0.35	<0.5	0.266962234	<1	0.380481881	0.282	<0.01	0.348	NA
PFTrDA	0.091	NA	0.097747597	<0.5	0.13	<0.5	0.097517669	<1	0.148817907	<0.215	<0.01	0.0782	NA
PFTeDA	0.072	NA	<0.05	<0.5	0.11	<0.5	0.098460738	<1	<0.1	<0.215	<0.01	0.0449	NA
L-PFBS	0.18	NA	0.16737036	<0.5	0.14	2.41	0.068636559	<1	<0.1	<0.323	0.09	0.215	NA
L-PFHxS	0.09	NA	0.094976336	<0.5	0.052	0.94	0.057468336	<1	0.100213818	<0.323	<0.01	0.08	NA
L-PFDS	0.092	NA	<0.05	<1	0.26	<0.5	NA	<1	<0.1	<0.323	<0.01	0.0884	NA
6:2 FTSA	0.69	NA	NA	0.87	NA	NA	0.436121162	<1	<0.1	<0.323	0.68	0.698	NA

[a] WEOG = Western European and other groups , CEE = Central and Eastern Europe, GRULAC= group of Latin America and Caribbean

Table S3-1.3 Received results per participant, fish (ng/g).

Fish	L001	L011	L022	L023	L024	L027	L031	L101	L105	L107	L115	L117	L124	L126	L134	L190	L208	L224	L286	L287	L288	L289	L290	L291	L293
Region[a]	Asia	Asia	Asia	Asia	WEOG	Asia	WEOG	WEOG	WEOG	WEOG	WEOG	WEOG	WEOG	WEOG	WEOG	Asia	WEOG	WEOG	WEOG	WEOG	WEOG	CEE	WEOG	WEOG	Asia
PFOS																									
L-PFOS anion	8.408	45	9.4072	8.669010486	7.2	9.1	NA	10.4	8.282208282	8.6	8.087	8.26	7.87	9.97	NA	48.6	7.76	8.66	9.65	NA	7.94	NA	6.57	9	8.106
br-PFOS anion	0.329	NA	0.5933	NA	0.41	0.64	NA	NA	0.662024711	0.43	NA	0.46	NA	0.68	NA	0	0.59	0.6	NA	NA	0.12	NA	0.38	NA	NA
tot-PFOS Lower Bound (ND=0)	*8.737*	*45*	*10.0005*	*8.669010486*	*7.6*	*9.74*	*7.73*	*10.4*	*8.944232993*	*9.03*	*8.087*	*8.72*	*7.87*	*10.7*	*11*	*48.6*	*8.35*	*9.26*	*9.65*	*24.48*	*8.07*	*6.8*	*6.95*	*9*	*8.106*
tot-PFOS Upper Bound (ND=LOD)	*8.737*	*NA*	*10.0005*	*NA*	*7.6*	*9.74*	*7.73*	*NA*	*8.944232993*	*9.03*	*NA*	*8.72*	*NA*	*10.7*	*11*	*NA*	*8.35*	*9.26*	*NA*	*24.48*	*8.07*	*6.8*	*6.95*	*NA*	*NA*
PFCAs and PFSAs																									
PFBA	NA	<0.06	NA	<0.02	<1	<0.1	NA	NA	<0.02	<0.25	<0.1	<0.207	<1	<0.01	NA	<0.06	<0.2	NA	NA	NA	<0.47	NA	<0.5	1.4	NA
PFPeA	NA	<0.06	NA	0	<0.5	<0.1	NA	<0.02	<0.02	<0.25	<0.1	<0.207	<2	<0.01	NA	<0.02	<0.05	<0.1	<0.8	NA	<0.24	NA	NA	NA	NA
PFHxA	NA	<0.08	NA	<0.02	<0.5	<0.02	NA	0.27	<0.005	<0.25	<0.1	<0.207	<1	<0.01	<1	<0.081	<0.05	<0.1	<0.2	NA	<0.05	NA	<0.1	<0.5	NA
PFHpA	NA	<0.09	NA	<0.01	<0.5	<0.02	NA	<0.01	<0.005	<0.25	<0.1	<0.207	<1	<0.01	<0.1	<0.02	<0.05	<0.1	<0.2	NA	<0.05	NA	<0.1	0.3	NA
PFOA	0.03	<0.01	NA	0.092195282	<0.3	<0.02	NA	<0.01	0.006371516	<0.25	0.225980394	<0.207	<1	0.03	<0.1	<0.011	<0.05	<0.1	<0.2	0.21	<0.05	<0.15	<0.1	<0.6	NA
PFNA	0.03	0.29	NA	<0.04	<0.5	0.045	NA	<0.01	0.03995865	<0.25	<0.1	<0.207	<1	0.05	<0.1	0.285	0.039	<0.1	<0.2	0.51	0.06	NA	<0.1	<0.2	NA
PFDA	0.785	5.5	NA	0.74713885	0.84	0.81	NA	1.55	0.821537911	0.84	1.097322238	0.649	0.808	0.82	1.5	5.45	0.85	0.74	0.9	4.62	0.76	NA	0.57	<0.6	NA
PFUnDA	0.399	3.1	NA	0.391581763	<0.5	0.5	NA	0.072	0.190970538	0.49	0.777117123	0.518	0.594	0.4	0.89	3.08	0.404	<0.1	0.54	3.28	0.42	NA	0.32	<0.2	NA
PFDoDA	0.921	3.4	NA	0.819994259	1.1	0.94	NA	0.14	0.791650393	1	0.847727675	0.74	0.892	1.07	1.3	3.55	0.88	0.82	0.94	2.99	0.89	NA	0.58	0.8	NA
PFTrDA	0.696	1.8	NA	0.370769859	0.56	0.6	NA	0.54	0.425640064	0.88	0.540198993	0.454	0.591	<0.01	NA	1.81	0.32	0.34	0.49	NA	NA	NA	0.82	0.3	NA
PFTeDA	0.762	1.8	NA	0.268223225	0.8	0.61	NA	<0.05	0.597477001	0.8	0.475189443	0.708	0.624	<0.01	NA	1.71	0.22	0.38	0.3	NA	NA	NA	<0.5	0.4	NA
L-PFBS	NA	0.045	NA	<0.03	<0.5	0.021	NA	<0.002	<0.005	<0.25	0.475189443	<0.311	<1	<0.01	<0.1	0.0517	<0.05	<0.1	<0.2	0.28	<0.01	NA	<0.1	<1	NA
L-PFHxS	NA	0.18	NA	0.064028065	<0.5	0.054	NA	<0.01	0.036915033	<0.25	<0.1	<0.311	<1	0.05	<0.1	0.185	<0.05	<0.1	<0.2	0.12	<0.04	NA	<0.1	<1	NA
L-PFDS	0.026	0.17	NA	<0.05	<1	0.044	NA	<0.06	NA	<0.25	<0.1	<0.311	<1	<0.01	NA	0.167	<0.05	NA	<0.2	NA	<0.02	NA	<0.1	<0.2	NA
6:2 FTSA	0.05	0.14	NA	NA	<0.5	NA	NA	NA	<0.01	<0.25	<0.1	<0.311	<2	<0.01	NA	0.143	NA	NA	NA	NA	NA	NA	NA	NA	NA

a WEOG = Western European and other groups , CEE = Central and Eastern Europe, GRULAC= group of Latin America and Caribbean

Table S3-1.4 Received results per participant, human milk (ng/g).

Human milk	**L001**	**L022**	**L027**	**L030**	**L031**	**L101**	**L105**	**L107**	**L126**	**L208**	**L279**	**L286**	**L287**	**L288**	**L289**	**L290**	**L293**	**L298**
Region[a]	*Asia*	*Asia*	*Asia*	*Asia*	*WEOG*	*WEOG*	*WEOG*	*WEOG*	*WEOG*	*WEOG*	*Asia*	*WEOG*	*WEOG*	*WEOG*	*CEE*	*WEOG*	*Asia*	*WEOG*
PFOS																		
L-PFOS anion	0.024	7.5402	0.02	0.089	NA	<0.05	<0.04	<0.1	0.022	<0.02	0.456	<0.05	NA	0.027	NA	0.02	0.027	<0.08
br-PFOS anion	0.005	0.4697	0.016	0.076	NA	NA	<0.04	<0.1	0.011	<0.02	0.582	NA	NA	0.022	NA	0.02	NA	<0.08
tot-PFOS Lower Bound (ND=0)	*0.029*	*8.0099*	*0.036*	*0.165*	*0.16*	*0*	*0*	*0*	*0.033*	*0*	*1.038*	*0*	*0.54*	*0.049*	*0.028*	*0.04*	*0.027*	*0*
tot-PFOS Upper Bound (ND=LOD)	*0.031*	*8.0099*	*0.036*	*0.165*	*0.16*	*NA*	*0.08*	*0.2*	*0.033*	*0.04*	*1.038*	*NA*	*0.54*	*0.049*	*0.028*	*0.04*	*NA*	*0.16*
PFCAs and PFSAs																		
PFBA	NA	NA	<0.01	NA	NA	NA	<0.09	<0.1	<0.01	2.81	20.3504	NA	NA	<0.66	NA	<0.05	NA	NA
PFPeA	NA	NA	<0.01	NA	NA	<0.5	<0.09	<0.1	<0.01	<0.02	NA	<0.2	NA	<0.2	NA	NA	NA	NA
PFHxA	NA	NA	<0.01	0.13	NA	<0.5	<0.02	<0.1	<0.01	<0.02	NA	<0.05	NA	NA	NA	<0.01	NA	NA
PFHpA	NA	NA	<0.01	<0.11	NA	<0.5	<0.02	<0.1	<0.01	<0.02	NA	<0.05	NA	<0.007	NA	<0.01	NA	NA
PFOA	0.032	NA	0.025	<0.086	NA	22.31	<0.02	<0.1	0.029	0.024	14.6115	<0.25	0.85	0.029	<0.15	0.07	NA	NA
PFNA	0.003	NA	<0.01	<0.053	NA	<0.5	<0.02	<0.1	<0.01	<0.02	2.9857	<0.05	0.74	<0.007	NA	<0.01	NA	NA
PFDA	0.007	NA	<0.01	<0.085	NA	<0.5	<0.02	<0.1	<0.01	<0.02	NA	<0.05	1.07	<0.02	NA	<0.01	NA	NA
PFUnDA	NA	NA	<0.01	<0.088	NA	1.02	<0.02	<0.1	<0.01	<0.02	2.6479	<0.05	0.7	<0.02	NA	<0.05	NA	NA
PFDoDA	NA	NA	<0.01	<0.091	NA	<0.5	<0.09	<0.1	<0.01	<0.02	NA	<0.05	1.4	NA	NA	<0.05	NA	NA
PFTrDA	NA	NA	<0.01	<0.079	NA	<0.5	<0.09	<0.1	<0.01	<0.02	NA	<0.05	NA	NA	NA	<0.05	NA	NA
PFTeDA	NA	NA	<0.01	<0.13	NA	<0.5	<0.09	<0.1	<0.03	<0.02	NA	<0.05	NA	NA	NA	<0.05	NA	NA
L-PFBS	NA	NA	<0.01	NA	NA	<0.5	<0.02	<0.1	NA	<0.02	<2	<0.05	0.9	<0.002	NA	<0.01	NA	NA
L-PFHxS	NA	NA	0.013	<0.063	NA	<0.5	0.040680713	<0.1	<0.01	<0.02	<2	<0.05	0.22	0.017	NA	<0.01	NA	NA
L-PFDS	NA	NA	<0.01	<0.048	NA	<0.5	NA	<0.1	<0.01	<0.02	NA	<0.05	NA	<0.001	NA	<0.05	NA	NA
6:2 FTSA	0.007	NA	NA	NA	NA	NA	<0.09	<0.1	NA	NA	2.7458	NA	NA	NA	NA	NA	NA	NA

[a] WEOG = Western European and other groups , CEE = Central and Eastern Europe, GRULAC= group of Latin America and Caribbean

Table S3-1.5 Received results per participant, human plasma (ng/g).

Human plasma	L023	L024	L027	L030	L037	L101	L105	L107	L115	L126	L130	L208	L279	L289	L293	L298
Region[a]	*Asia*	*WEOG*	*Asia*	*Asia*	*CEE*	*WEOG*	*WEOG*	*WEOG*	*WEOG*	*WEOG*	*WEOG*	*WEOG*	*Asia*	*CEE*	*Asia*	*WEOG*
PFOS																
L-PFOS anion	7.705849354	10.6	14	15	14.51	24.45	13.50101754	14	15.40875181	14.2	NA	14.7	0.4998	NA	16.876	17.03
br-PFOS anion	NA	4.57	4.4	8.2	4.68	NA	10.34407119	6.2	NA	5.61	NA	8.8	0.602	NA	NA	3.68
tot-PFOS Lower Bound (ND=0)	*7.705849354*	*15.2*	*18.4*	*23.2*	*19.19*	*24.45*	*23.84508873*	*20*	*15.40875181*	*19.8*	*20*	*23.5*	*1.1018*	*19*	*16.876*	*20.71*
tot-PFOS Upper Bound (ND=LOD)	*NA*	*15.2*	*18.4*	*23.2*	*19.19*	*NA*	*23.84508873*	*20*	*NA*	*19.8*	*20*	*23.5*	*1.1018*	*19*	*NA*	*20.71*
PFOS precursors																
FOSA	NA	<1	<0.1	NA	NA	<0.125	<0.5	<0.1	NA	<0.03	NA	<0.2	NA	NA	NA	NA
MeFOSA	NA	NA	<0.1	NA	NA	NA	<0.5	<0.1	NA	NA	NA	NA	NA	NA	NA	NA
EtFOSA	NA	NA	<0.1	NA	NA	NA	<0.5	<0.1	NA	NA	NA	NA	NA	NA	NA	NA
MeFOSE	NA	NA	<0.1	NA	NA	NA	<0.5	<0.1	NA	NA	NA	NA	NA	NA	NA	NA
EtFOSE	NA	NA	<0.1	NA	NA	NA	<0.5	<0.1	NA	NA	NA	NA	NA	NA	NA	NA
PFCAs and PFSAs																
PFBA	0.144505782	<0.5	<0.5	NA	<0.01	NA	<0.09	<0.1	0.1086	<0.03	NA	<0.2	14.486	NA	<0.3	<0.09
PFPeA	<0.33	<0.5	<0.5	NA	<0.01	<3.66	<0.09	<0.1	<0.1	<0.03	NA	<0.05	NA	NA	<0.1	0.64
PFHxA	<0.17	<0.5	<0.1	<0.086	<0.01	<0.69	<0.02	<0.1	<0.1	<0.03	NA	<0.05	NA	NA	<0.5	<0.17
PFHpA	<0.09	<0.5	<0.1	<0.11	<0.004	<0.53	0.028201168	<0.1	<0.1	<0.03	NA	0.18	NA	NA	<0.1	<0.15
PFOA	1.005363478	2.05	2.1	2	2.28	<0.54	2.063795354	2.1	1.890546358	2.61	2.06	1.87	11.8114	2.8	2.224	2.23
PFNA	0.409607203	0.89	0.96	0.93	1.08	<0.95	0.859133883	1	0.623204434	1.24	0.89	0.87	3.2442	NA	1.093	0.96
PFDA	0.288392706	<0.5	0.49	0.54	0.701	<0.42	0.51306238	0.43	<0.1	0.58	0.64	0.52	NA	NA	0.519	0.55
PFUnDA	<0.21	<0.5	0.48	0.5	0.657	<2.41	0.591241576	0.44	<0.1	0.57	0.43	0.34	2.5661	NA	0.462	0.48
PFDoDA	<0.15	<0.5	<0.1	0.13	0.051	<1.07	<0.09	<0.1	0.722363077	0.08	0.07	0.054	NA	NA	<0.1	0.08
PFTrDA	<0.33	<0.5	<0.1	<0.079	0.15	<1.53	<0.09	<0.1	<0.1	<0.23	NA	0.034	NA	NA	<0.1	<0.17
PFTeDA	<0.35	<0.5	<0.1	<0.13	<0.04	<1.07	<0.09	<0.1	<0.1	<0.03	NA	<0.05	NA	NA	<0.1	<0.33
L-PFBS	0.470146113	<0.5	<0.1	NA	<0.04	<0.32	<0.02	<0.1	<0.1	<0.03	NA	<0.05	<2	NA	<0.1	<0.1
L-PFHxS	2.951041916	4.72	6.3	6.4	6.24	6.71	6.569795046	6.2	<0.1	6.56	5.9	4.7	<2	NA	6.006	6.33
L-PFDS	<0.41	<0.5	<0.1	8.2	0.012	<0.45	NA	<0.1	5.936876839	<0.03	NA	<0.05	NA	NA	<0.1	<0.18
6:2 FTSA	NA	<1	NA	NA	NA	NA	<0.09	<0.1	<0.1	<0.03	NA	NA	1.9644	NA	NA	<0.31

a WEOG = Western European and other groups , CEE = Central and Eastern Europe, GRULAC= group of Latin America and Caribbean

Table S3-1.6 Received results per participant, air extract (ng/g).

Air extract	**L011**	**L017**	**L022**	**L023**	**L024**	**L027**	**L072**	**L101**	**L104**	**L105**	**L107**	**L126**	**L128**	**L190**	**L195**	**L289**	**L293**	**L298**
Region[a]	*Asia*	*Asia*	*Asia*	*Asia*	*WEOG*	*Asia*	*GRULAC*	*WEOG*	*WEOG*	*WEOG*	*WEOG*	*WEOG*	*WEOG*	*Asia*	*WEOG*	*CEE*	*Asia*	*WEOG*
PFOS																		
L-PFOS anion	14	3.87	7.7573	2.90161027	4.5	4.7	4.77	4.93	4.3	2.512672986	3.1	3.71	5.18	14.2	4.2	NA	4.517	3.93
br-PFOS anion	NA	<0.12	1.6736	NA	<0.3	0.16	0.12	NA	NA	<0.2	<0.1	0.07	0.576	NA	NA	NA	NA	<0.18
tot-PFOS Lower Bound (ND=0)	*14*	*3.87*	*9.4309*	*2.90161027*	*4.5*	*4.86*	*4.89*	*4.93*	*4.3*	*2.512672986*	*3.1*	*3.78*	*5.76*	*14.2*	*4.2*	*3.4*	*4.517*	*3.93*
tot-PFOS Upper Bound (ND=LOD)	*NA*	*3.99*	*9.4309*	*NA*	*4.8*	*4.86*	*4.89*	*NA*	*NA*	*2.712672986*	*3.3*	*3.78*	*5.76*	*NA*	*NA*	*3.4*	*NA*	*4.11*
PFOS precursors																		
FOSA	71	NA	NA	NA	52	53	56.1	NA	32	NA	19	42.2	NA	70.3	45	NA	NA	43.05
MeFOSA	181	NA	NA	NA	233	170	175	NA	174	NA	59	138	NA	187	166	NA	NA	NA
EtFOSA	176	NA	NA	NA	325	190	172	NA	193	NA	46	108	NA	173	180	NA	NA	NA
MeFOSE	258	NA	NA	NA	108	93	89.9	NA	87	NA	39	96.1	NA	255	55	NA	NA	74.88
EtFOSE	194	NA	NA	NA	89	93	89.7	NA	90	NA	33	94.4	NA	204	100	NA	NA	89.27
PFCAs and PFSAs																		
PFBA	9.5	NA	NA	3.95383604	6.5	5	8.05	NA	8.3	3.527809491	4.6	4.61	NA	9.35	6.6	NA	5.815	8.39
PFPeA	4.4	NA	NA	2.068221116	4.1	3.6	<3.58	NA	2.9	1.758802374	2.5	3.27	NA	4.41	2.2	NA	3.453	2.78
PFHxA	12	NA	NA	3.622684491	7.2	6.9	6.5	4.51	6.6	4.077229827	5.6	6.33	8.69	11.4	6.3	NA	5.482	7.13
PFHpA	5.9	NA	NA	1.743353657	3.9	3.5	3.35	NA	3.4	2.300996601	2.7	3.12	3.656	5.98	2.2	NA	3.337	4.08
PFOA	5.5	3.57	NA	1.798779942	4	3.7	3.46	NA	3.4	2.407222124	2.7	3.29	4.09	5.49	2.4	5.5	3.768	3.01
PFNA	4.7	NA	NA	1.733096857	4	3.5	3.39	NA	3.1	2.149361369	2.5	2.91	2.66	4.28	3.1	NA	3.339	2.97
PFDA	10	NA	NA	3.920223822	6.9	6.9	7.36	9.64	6.4	4.341101913	5.3	5.6	6.58	10.3	5.7	NA	6.683	6.33
PFUnDA	5.3	NA	NA	1.837274551	3.5	3.5	2.9	1.62	3.3	2.918897707	1.9	2.74	4.43	5.56	2.4	NA	NA	2.98
PFDoDA	5.9	NA	NA	2.046615086	3.6	3.3	3.47	NA	3	1.748036125	2.7	2.64	4.89	6.03	2.2	NA	NA	2.94
PFTrDA	3.3	NA	NA	1.063030857	3.5	3.1	4.47	5.69	5.1	1.5262844	1.5	2.12	3.48	3.28	3.4	NA	NA	1.38
PFTeDA	1.5	NA	NA	<0.69	3.8	3.4	3.84	NA	5.8	1.90260714	1.2	2.4	4.796	1.49	3.9	NA	NA	3.33
L-PFBS	11	NA	NA	5.682206381	7	7.7	7.67	4.53	7.5	3.715483506	5.1	6.31	10.09	12	7.6	NA	7.454	8.14
L-PFHxS	7.7	NA	NA	2.770418331	4.2	4.9	4.33	10.51	4.3	2.73081575	3	3.75	4.67	7.19	4.2	NA	4.294	3.94
L-PFDS	3.4	NA	NA	0.828970244	4.6	5.3	4.34	NA	3.5	NA	1.3	NA	4.43	3.33	3	NA	NA	5.22
6:2 FTSA	2	NA	NA	NA	<1	NA	0.38	NA	NA	0.196108437	0.22	0.22	0.416	1.7	NA	NA	NA	0.2

a WEOG = Western European and other groups , CEE = Central and Eastern Europe, GRULAC= group of Latin America and Caribbean

Table S3-1.7 Received results per participant, water (pg/g).

Water	**L011**	**L022**	**L023**	**L027**	**L030**	**L031**	**L035**	**L072**	**L101**	**L105**	**L107**	**L117**	**L126**	**L224**	**L242**	**L259**	**L276**	**L279**	**L288**	**L289**	**L291**	**L293**
Region[a]	*Asia*	*Asia*	*Asia*	*Asia*	*Asia*	*WEOG*	*WEOG*	*GRULAC*	*WEOG*	*WEOG*	*WEOG*	*WEOG*	*WEOG*	*WEOG*	*WEOG*	*Asia*	*WEOG*	*Asia*	*WEOG*	*CEE*	*WEOG*	*Asia*
PFOS																						
L-PFOS anion	1.7	263.6	3.487793179	2.5	3.1	NA	1.35	2.21	<130	3.849980823	1.9	2.21	2.18	2.9	2.231	0.0013	3.04	2294	2.42	NA	NA	2.491
br-PFOS anion	NA	12.8	NA	1.9	3.2	NA	0.37	1.39	NA	2.752744903	1.5	1.96	1.44	2.8	2.485	NA	1.65	2162	1.85	NA	NA	NA
tot-PFOS Lower Bound (ND=0)	*1.7*	*276.4*	*3.487793179*	*4.4*	*6.3*	*28.32*	*1.72*	*3.6*	*0*	*6.602725726*	*3.4*	*4.17*	*3.62*	*5.7*	*4.716*	*0.0013*	*4.69*	*4456*	*4.27*	*3.7*	*NA*	*2.491*
tot-PFOS Upper Bound (ND=LOD)	*NA*	*276.4*	*NA*	*4.4*	*6.3*	*28.32*	*1.72*	*3.6*	*NA*	*6.602725726*	*3.4*	*4.17*	*3.62*	*5.7*	*4.716*	*NA*	*4.69*	*4456*	*4.27*	*3.7*	*NA*	*NA*
PFCAs and PFSAS																						
PFBA	12	NA	7.653893364	8.5	NA	NA	4.77	25.35	NA	7.27004908	7.5	7.89	5.89	NA	5.278	0.0059	7.9	64430	5.74	NA	18	6.185
PFPeA	4.8	NA	8.055626351	<0.4	NA	NA	3.61	<11	<3800	6.007154891	5.8	4.84	5.78	4.6	3.61	0.0092	7.2	NA	8.62	NA	NA	7.265
PFHxA	7.7	NA	8.467919779	7.9	8.7	NA	4.66	8.8	<5000	7.234110036	7.5	5.44	7.7	8.7	6.929	0.0065	9.4	NA	8.57	NA	6	8.69
PFHpA	8.7	NA	5.411908326	3.4	4.3	NA	1.97	4.02	<1700	3.246290982	3.5	2.95	3.55	4.3	3.528	0.0029	3.8	NA	3.76	NA	5	3.757
PFOA	11	NA	10.19214279	11	11	NA	5.49	8.33	<280	8.764042856	9.1	6.65	9.53	13.9	7.918	0.01	13	17928	11.37	13	NA	9.968
PFNA	1.2	NA	<1.9	0.63	0.58	NA	0.35	<1.44	<630	0.331886534	<1	<1	0.48	0.6	0.4936	0.0003	0.54	3217	0.55	NA	NA	0.525
PFDA	0.71	NA	<1.24	<0.4	0.32	NA	0.36	<1.18	751.42	0.242174913	<1	<1	0.33	<1	<0.0739	0.0002	0.33	NA	0.38	NA	NA	0.38
PFUnDA	<0.6	NA	<1.53	<0.4	<0.29	NA	0.27	<1.04	<390	<0.5	<1	<1	<0.042	<1	<0.0431	<0.0003	<0.3	2514	<0.1	NA	NA	0.072
PFDoDA	<0.7	NA	<1.11	<0.4	<0.29	NA	0.2	1.79	<1200	<0.5	<1	<1	0.07	<1	<0.1008	<0.0001	<0.3	NA	<0.1	NA	NA	<0.1
PFTrDA	<0.03	NA	<2.44	<0.4	NA	NA	<0.1	<1.35	<3300	<0.5	<1	<1	<0.026	<1	<0.1034	<0.0007	<0.3	NA	NA	NA	NA	<0.1
PFTeDA	<0.03	NA	<2.61	<0.4	NA	NA	0.06	<1.26	<1100	<0.5	<1	<1	0.11	<1	<0.1341	<0.00004	<0.3	NA	NA	NA	NA	<0.1
L-PFBS	8.8	NA	10.50740196	7.9	NA	NA	6.73	6.66	<820	4.912787427	6	5.5	6.43	8	7.536	0.0095	8.7	2351	6.1	NA	12	6.822
L-PFHxS	2.2	NA	3.46524501	1.5	1.6	NA	1.1	1.35	464.16	0.900323273	1.4	<1.5	1.36	1.4	1.263	0.0017	1.5	<2000	1.65	NA	NA	1.454
L-PFDS	<7.09	NA	<3	<0.4	<0.34	NA	<0.005	<0.17	<120	NA	<1	<1.5	<0.004	NA	<0.0139	<0.0006	<0.3	NA	<0.02	NA	NA	<0.1
6:2 FTSA	42	NA	NA	NA	NA	NA	NA	13	NA	15.73267327	18	2.15	16.5	NA	NA	0.015	18	21490	NA	NA	NA	NA

a WEOG = Western European and other groups , CEE = Central and Eastern Europe, GRULAC= group of Latin America and Caribbean

S3-2 . Summary of assessment

Table S3-2.1 Summary results test solution (ng/g).

Test solution	n					Difference theoretical conc. and					Between lab CV	Inclusion rate
Analyte	Total	Numerical	LCV	Theoretical conc.	AV	AV (%)	Median	Mean	Min	Max	(%)	(%)
PFOS												
L-PFOS anion	28	28	0	58.7	61.4	4.5	60.8	61.4	31.8	103	16	69
br-PFOS anion	19	18	1	15.8	12.3	22	12.7	12.3	7.4	23.4	32	71
tot-PFOS LB	*29*	*29*	*0*	*71.5*	*69.7*	*2.5*	*70.0*	*69.7*	*40.9*	*103*	*18*	*72*
tot-PFOS UB	*20*	*20*	*0*	*71.5*	*68.8*	*3.8*	*68.8*	*68.8*	*40.9*	*99.0*	*18*	*71*
PFOS precursors												
FOSA	20	20	0	63.2	59.2	6.3	62.5	59.2	38.0	203	17	73
MeFOSA	14	14	0	126	126	0.0	126	126	51.5	179	8	66
EtFOSA	14	14	0	190	183	3.9	189	183	98.0	261	16	71
MeFOSE	13	13	0	126	128	1.6	128	128	72.0	154	7	54
EtFOSE	13	13	0	126	132	4.9	130	132	69.8	156	11	61
PFCAs and PFSAs												
PFBA	24	24	0	63.2	61.4	2.9	62.5	61.4	33.7	94.0	11	69
PFPeA	25	25	0	63.2	60.7	3.9	61.0	60.7	43.9	87.6	12	69
PFHxA	28	28	0	94.8	92.9	2.0	92.3	92.9	62.7	114	15	78
PFHpA	28	28	0	63.2	61.8	2.1	61.0	61.8	33.8	81.5	15	77
PFOA	29	29	0	63.2	60.6	4.1	61.0	60.6	32.0	111	12	67
PFNA	28	28	0	126	118	6.1	116	118	60.4	150	15	81
PFDA	28	28	0	63.2	62.4	1.2	61.1	62.4	38.0	74.2	10	72
PFUnDA	28	28	0	63.2	61.4	2.8	61.1	61.4	38.8	101	16	76
PFDoDA	28	28	0	190	177	6.9	178	177	95.5	249	13	66
PFTrDA	27	27	0	63.2	64.8	2.5	65.0	64.8	24.1	102	19	70
PFTeDA	27	27	0	63.2	63.4	0.4	64.2	63.4	40.0	85.0	12	72
L-PFBS	27	27	0	83.9	84.8	1.0	83.9	84.8	51.5	118	17	79
L-PFHxS	28	28	0	59.8	60.3	0.9	61.4	60.3	33.1	99.7	12	62
L-PFDS	26	26	0	60.9	63.7	4.6	62.9	63.7	40.3	83.5	15	70
6:2 FTSA	14	14	0	63.2	53.3	16.6	56.9	53.3	39.4	115.5	22	76

NAV: No assigned value: LB = Lower Bound: non detect = 0: UB = Upper Bound: non detect = limit of detection

Table S3-2.2 Summary results sediment (ng/g).

Sediment	n			AV	Median	Mean	Min	Max	Between lab CV (%)	Inclusion rate (%)
Analyte	**Total**	**Numerical**	**LCV**							
PFOS										
L-PFOS anion	12	12	0	3.8	3.8	3.8	2.3	8.0	23	71
br-PFOS anion	7	5	2	0.51	0.55	0.51	0.39	0.93	45	68
tot-PFOS LB	*13*	*13*	*0*	*4.0*	*4.3*	*4.0*	*2.3*	*8.0*	*32*	*80*
tot-PFOS UB	*9*	*9*	*0*	*4.1*	*4.3*	*4.1*	*2.3*	*5.9*	*30*	*81*
PFCAs and PFSAs										
PFBA	10	3	7	NAV	0.18	0.04	0.11	0.28	157	51
PFPeA	11	2	9	NAV	NAV	NAV	0.09	0.13	NAV	NAV
PFHxA	11	8	3	0.20	0.21	0.20	0.17	1.5	26	65
PFHpA	11	4	7	0.05	0.05	0.05	0.04	0.07	17	58
PFOA	12	11	1	0.47	0.52	0.47	0.27	4.3	23	59
PFNA	11	6	5	0.08	0.08	0.08	0.06	0.12	34	77
PFDA	11	8	3	0.30	0.32	0.30	0.17	6.6	53	68
PFUnDA	11	8	3	0.30	0.27	0.30	0.18	0.47	41	79
PFDoDA	11	7	4	0.32	0.32	0.32	0.27	0.38	17	73
PFTrDA	11	6	5	0.10	0.10	0.10	0.08	0.15	21	59
PFTeDA	11	4	7	0.07	0.09	0.07	0.04	0.11	45	54
L-PFBS	11	7	4	0.13	0.17	0.13	0.07	2.4	51	66
L-PFHxS	11	7	4	0.08	0.09	0.08	0.05	0.94	20	51
L-PFDS	10	3	7	NAV	0.09	0.09	0.09	0.26	5	38
6:2 FTSA	8	5	3	0.69	0.69	0.69	0.44	0.87	2	39

NAV: No assigned value: LB = Lower Bound: non detect = 0: UB = Upper Bound: non detect = limit of detection

Table S3-2.3 Summary results fish (ng/g).

Fish		n							Between lab CV	Inclusion rate
Analyte	Total	Numerical	LCV	AV	Median	Mean	Min	Max	(%)	(%)
PFOS										
L-PFOS anion	21	21	0	8.5	8.6	8.5	6.6	48.6	11	71
br-PFOS anion	13	12	1	0.52	0.53	0.52	0.00	0.68	32	78
tot-PFOS LB	*25*	*25*	*0*	*8.7*	*8.9*	*8.7*	*6.8*	*48.6*	*14*	*70*
tot-PFOS UB	*16*	*16*	*0*	*8.7*	*8.8*	*8.7*	*6.8*	*24.5*	*16*	*76*
PFCAs and PFSAs										
PFBA	15	1	14	NAV	NAV	NAV	1.4	1.4	NAV	NAV
PFPeA	16	0	16	NAV	NAV	NAV	0.00	0.00	NAV	NAV
PFHxA	19	1	18	NAV	NAV	NAV	0.27	0.27	NAV	NAV
PFHpA	19	1	18	NAV	NAV	NAV	0.30	0.30	NAV	NAV
PFOA	22	6	16	NAV	0.06	0.02	0.01	0.23	174	49
PFNA	21	9	12	0.04	0.05	0.04	0.03	0.51	38	52
PFDA	21	20	1	0.80	0.83	0.80	0.57	5.5	13	58
PFUnDA	21	18	3	0.44	0.50	0.44	0.07	3.3	34	54
PFDoDA	21	21	0	0.88	0.89	0.88	0.14	3.6	16	63
PFTrDA	18	17	1	0.51	0.54	0.51	0.30	1.8	41	70
PFTeDA	18	15	3	0.52	0.61	0.52	0.22	1.8	52	63
L-PFBS	20	5	15	NAV	0.05	0.01	0.02	0.48	167	42
L-PFHxS	20	7	13	0.05	0.06	0.05	0.04	0.19	81	53
L-PFDS	17	4	13	NAV	0.11	0.04	0.03	0.17	121	58
6:2 FTSA	10	3	7	NAV	0.14	0.01	0.05	0.14	166	37

NAV: No assigned value: LB = Lower Bound: non detect = 0: UB = Upper Bound: non detect = limit of detection

Table S3-2.4 Summary results human milk (product basis) (ng/g).

Human milk		n							Between lab CV	Inclusion rate
Analyte	**Total**	**Numerical**	**LCV**	**AV**	**Median**	**Mean**	**Min**	**Max**	**(%)**	**(%)**
PFOS										
L-PFOS anion	15	9	6	0.02	0.03	0.02	0.02	7.5	40	61
br-PFOS anion	12	8	4	0.02	0.02	0.02	0.005	0.58	105	60
tot-PFOS LB	*18*	*12*	*6*	*0.03*	*0.04*	*0.03*	*0.00*	*8.0*	*59*	*56*
tot-PFOS UB	*15*	*15*	*0*	*0.07*	*0.08*	*0.07*	*0.03*	*8.0*	*103*	*64*
PFCAs and PFSAs										
PFBA	8	2	6	NAV	NAV	NAV	2.8	20.4	NAV	NAV
PFPeA	8	0	8	NAV	NAV	NAV	0.00	0.00	NAV	NAV
PFHxA	9	1	8	NAV	NAV	NAV	0.13	0.13	NAV	NAV
PFHpA	10	0	10	NAV	NAV	NAV	0.00	0.00	NAV	NAV
PFOA	14	9	5	0.03	0.03	0.03	0.02	22.3	38	51
PFNA	13	3	10	NAV	0.7	0.01	0.003	3.0	611	48
PFDA	12	2	10	NAV	NAV	NAV	0.007	1.1	NAV	NAV
PFUnDA	12	3	9	NAV	1.0	0.0	0.70	2.6	231	51
PFDoDA	10	1	9	NAV	NAV	NAV	1.4	1.4	NAV	NAV
PFTrDA	9	0	9	NAV	NAV	NAV	0.00	0.00	NAV	NAV
PFTeDA	9	0	9	NAV	NAV	NAV	0.00	0.00	NAV	NAV
L-PFBS	10	1	9	NAV	NAV	NAV	0.90	0.90	NAV	NAV
L-PFHxS	12	4	8	NAV	0.03	0.01	0.01	0.22	113	56
L-PFDS	9	0	9	NAV	NAV	NAV	0.00	0.00	NAV	NAV
6:2 FTSA	4	2	2	NAV	NAV	NAV	0.007	2.7	NAV	NAV

NAV: No assigned value: LB = Lower Bound: non detect = 0: UB = Upper Bound: non detect = limit of detection

Table S3-2.5 Summary results human plasma (product basis) (ng/g).

Human plasma	n								Between lab CV	Inclusion rate
Analyte	Total	Numerical	LCV	AV	Median	Mean	Min	Max	(%)	(%)
PFOS										
L-PFOS anion	14	14	0	14.7	14.4	14.7	0.50	24.5	9	59
br-PFOS anion	10	10	0	5.4	5.1	5.4	0.60	10.3	38	65
tot-PFOS LB	*16*	*16*	*0*	*19.8*	*19.5*	*19.8*	*1.1*	*24.5*	*22*	*77*
tot-PFOS UB	*12*	*12*	*0*	*20.1*	*19.9*	*20.1*	*1.1*	*23.8*	*9*	*62*
PFOS precursors										
FOSA	7	0	7	NAV	NAV	NAV	0.00	0.00	NAV	NAV
MeFOSA	3	0	3	NAV	NAV	NAV	0.00	0.00	NAV	NAV
EtFOSA	3	0	3	NAV	NAV	NAV	0.00	0.00	NAV	NAV
MeFOSE	3	0	3	NAV	NAV	NAV	0.00	0.00	NAV	NAV
EtFOSE	3	0	3	NAV	NAV	NAV	0.00	0.00	NAV	NAV
PFCAs and PFSAs										
PFBA	12	3	9	NAV	0.14	0.05	0.11	14.5	83	50
PFPeA	12	1	11	NAV	NAV	NAV	0.64	0.64	NAV	NAV
PFHxA	13	0	13	NAV	NAV	NAV	0.00	0.00	NAV	NAV
PFHpA	13	2	11	NAV	NAV	NAV	0.03	0.18	NAV	NAV
PFOA	16	15	1	2.1	2.1	2.1	1.0	11.8	9	60
PFNA	15	14	1	0.95	0.95	0.95	0.41	3.2	12	63
PFDA	14	11	3	0.53	0.52	0.53	0.29	0.70	10	47
PFUnDA	15	11	4	0.48	0.48	0.48	0.34	2.6	16	55
PFDoDA	14	7	7	0.07	0.08	0.07	0.05	0.72	47	74
PFTrDA	13	2	11	NAV	NAV	NAV	0.03	0.15	NAV	NAV
PFTeDA	13	0	13	NAV	NAV	NAV	0.00	0.00	NAV	NAV
L-PFBS	13	1	12	NAV	NAV	NAV	0.47	0.47	NAV	NAV
L-PFHxS	15	13	2	6.3	6.2	6.3	3.0	6.7	7	61
L-PFDS	12	3	9	NAV	5.9	0.08	0.01	8.2	351	49
6:2 FTSA	7	1	6	NAV	NAV	NAV	2.0	2.0	NAV	NAV

NAV: No assigned value: LB = Lower Bound: non detect = 0: UB = Upper Bound: non detect = limit of detection

Table S3-2.6 Summary results air extract (ng/g).

Air extract		n							Between lab CV	Inclusion rate
Analyte	**Total**	**Numerical**	**LCV**	**AV**	**Median**	**Mean**	**Min**	**Max**	**(%)**	**(%)**
PFOS										
L-PFOS anion	17	17	0	4.2	4.5	4.2	2.5	14.2	21	67
br-PFOS anion	10	5	5	NAV	0.16	0.09	0.07	1.7	99	56
tot-PFOS LB	*18*	*18*	*0*	*4.1*	*4.4*	*4.1*	*2.5*	*14.2*	*21*	*63*
tot-PFOS UB	*11*	*11*	*0*	*4.1*	*4.1*	*4.1*	*2.7*	*9.4*	*25*	*74*
PFOS precursors										
FOSA	10	10	0	48.9	48.5	48.9	19.0	71.0	23	64
MeFOSA	9	9	0	175	174	175	59.0	233	6	59
EtFOSA	9	9	0	180	176	180	46.0	325	10	63
MeFOSE	10	10	0	84.9	91.5	84.9	39.0	258	28	64
EtFOSE	10	10	0	91.1	91.5	91.1	33.0	204	4	56
PFCAs and PFSAs										
PFBA	13	13	0	6.4	6.5	6.4	3.5	9.5	41	84
PFPeA	13	12	1	3.1	3.1	3.1	1.8	4.4	34	81
PFHxA	15	15	0	6.2	6.5	6.2	3.6	12.0	22	66
PFHpA	14	14	0	3.2	3.4	3.2	1.7	6.0	27	71
PFOA	16	16	0	3.4	3.5	3.4	1.8	5.5	25	67
PFNA	14	14	0	3.1	3.1	3.1	1.7	4.7	21	69
PFDA	15	15	0	6.3	6.6	6.3	3.9	10.3	21	68
PFUnDA	14	14	0	2.9	2.9	2.9	1.6	5.6	30	67
PFDoDA	13	13	0	2.9	3.0	2.9	1.7	6.0	30	68
PFTrDA	14	14	0	3.0	3.3	3.0	1.1	5.7	55	82
PFTeDA	13	12	1	3.0	3.4	3.0	1.2	5.8	56	76
L-PFBS	15	15	0	7.1	7.5	7.1	3.7	12.0	26	70
L-PFHxS	15	15	0	4.1	4.3	4.1	2.7	10.5	19	64
L-PFDS	11	11	0	3.9	3.5	3.9	0.83	5.3	35	76
6:2 FTSA	9	8	1	0.26	0.30	0.26	0.20	2.0	51	66

NAV: No assigned value: LB = Lower Bound: non detect = 0: UB = Upper Bound: non detect = limit of detection

Table S3-2.7 Summary results water (pg/g).

Water		n							Between lab CV (%)	Inclusion rate (%)
Analyte	**Total**	**Numerical**	**LCV**	**AV**	**Median**	**Mean**	**Min**	**Max**		
PFOS										
L-PFOS anion	19	18	1	2.4	2.5	2.4	0.001	2294	33	70
br-PFOS anion	14	14	0	2.0	1.9	2.0	0.37	2162	40	67
tot-PFOS LB	*21*	*20*	*1*	*3.9*	*4.2*	*3.9*	*0.0*	*4456*	*42*	*66*
tot-PFOS UB	*16*	*16*	*0*	*4.3*	*4.6*	*4.3*	*1.7*	*4456*	*33*	*67*
PFCAs and PFSAs										
PFBA	16	16	0	6.9	7.6	6.9	0.006	64430	34	66
PFPeA	15	13	2	5.7	5.8	5.7	0.009	8.6	36	71
PFHxA	17	17	0	7.9	7.7	7.9	0.007	9.4	17	76
PFHpA	17	17	0	3.7	3.8	3.7	0.003	8.7	19	68
PFOA	19	18	1	10.1	10.1	10.1	0.01	17928	23	68
PFNA	18	13	5	0.53	0.54	0.53	0.0003	3217	16	58
PFDA	17	10	7	0.34	0.35	0.34	0.0002	751	14	52
PFUnDA	18	3	15	NAV	0.27	0.05	0.07	2514	224	43
PFDoDA	16	3	13	NAV	0.20	0.06	0.07	1.8	115	53
PFTrDA	14	0	14	NAV	NAV	NAV	0.00	0.00	NAV	NAV
PFTeDA	14	2	12	NAV	NAV	NAV	0.06	0.11	NAV	NAV
L-PFBS	18	17	1	7.1	6.8	7.1	0.010	2351	24	68
L-PFHxS	17	16	1	1.4	1.4	1.4	0.002	464	16	63
L-PFDS	15	0	15	NAV	NAV	NAV	0.000	0.000	NAV	NAV
6:2 FTSA	9	9	0	15.7	16.5	15.7	0.02	21490	31	54

NAV: No assigned value: LB = Lower Bound: non detect = 0: UB = Upper Bound: non detect = limit of detection

S3-3 . Summary of laboratory performance

Table S3-3.1 Summary of laboratory performance PFASs, test solution.

Test solution	% of z-scores |z|<2	% of z-scores 3>|z|>2	% of z-scores 6>|z|>3	% of z-scores |z|>6
Analyte	**Satisfactory**	**Questionable**	**Unsatisfactory**	**Extreme**
L-PFOS anion	75	11	14	0
br-PFOS anion	58	16	11	11
tot-PFOS LB	*79*	*3*	*17*	*0*
tot-PFOS UB	*80*	*5*	*15*	*0*
FOSA	80	10	0	10
MeFOSA	86	0	14	0
EtFOSA	79	7	14	0
MeFOSE	77	15	8	0
EtFOSE	85	8	8	0
PFBA	83	8	8	0
PFPeA	80	16	4	0
PFHxA	93	7	0	0
PFHpA	86	11	4	0
PFOA	83	7	7	3
PFNA	89	7	4	0
PFDA	93	4	4	0
PFUnDA	86	11	4	0
PFDoDA	75	18	7	0
PFTrDA	74	11	15	0
PFTeDA	89	11	0	0
L-PFBS	89	4	7	0
L-PFHxS	79	11	11	0
L-PFDS	81	19	0	0
6:2 FTSA	79	14	0	7

Table S3-3.2 Summary of laboratory performance PFASs, sediment.

Sediment	% of z-scores	% of z-scores	% of z-scores	% of z-scores
	|z|<2	3>|z|>2	6>|z|>3	|z|>6
Analyte	Satisfactory	Questionable	Unsatisfactory	Extreme
L-PFOS anion	67	17	8	8
br-PFOS anion	57	0	14	0
tot-PFOS LB	*77*	*0*	*15*	*8*
tot-PFOS UB	*67*	*11*	*22*	*0*
PFBA	0	0	0	0
PFPeA	0	0	0	0
PFHxA	45	9	9	9
PFHpA	36	0	0	0
PFOA	50	17	17	8
PFNA	55	0	0	0
PFDA	36	9	18	9
PFUnDA	36	27	9	0
PFDoDA	64	0	0	0
PFTrDA	45	9	0	0
PFTeDA	36	0	0	0
L-PFBS	36	18	0	9
L-PFHxS	55	0	0	9
L-PFDS	0	0	0	0
6:2 FTSA	50	13	0	0

Table S3-3.3 Summary of laboratory performance PFASs, fish.

Fish Analyte	% of z-scores |z|<2 Satisfactory	% of z-scores 3>|z|>2 Questionable	% of z-scores 6>|z|>3 Unsatisfactory	% of z-scores |z|>6 Extreme
L-PFOS anion	90	0	0	10
br-PFOS anion	69	15	8	0
tot-PFOS LB	*84*	*4*	*0*	*12*
tot-PFOS UB	*88*	*6*	*0*	*6*
PFBA	0	0	0	0
PFPeA	0	0	0	0
PFHxA	0	0	0	0
PFHpA	0	0	0	0
PFOA	0	0	0	0
PFNA	29	0	0	14
PFDA	62	10	0	24
PFUnDA	48	5	14	19
PFDoDA	71	5	5	19
PFTrDA	50	22	11	11
PFTeDA	33	11	28	11
L-PFBS	0	0	0	0
L-PFHxS	20	0	5	10
L-PFDS	0	0	0	0
6:2 FTSA	0	0	0	0

Table S3-3.4 Summary of laboratory performance PFASs, human milk.

Human milk Analyte	% of z-scores |z|<2 Satisfactory	% of z-scores 3>|z|>2 Questionable	% of z-scores 6>|z|>3 Unsatisfactory	% of z-scores |z|>6 Extreme
L-PFOS anion	40	0	7	13
br-PFOS anion	42	0	8	17
tot-PFOS LB	*39*	*0*	*0*	*28*
tot-PFOS UB	*47*	*7*	*27*	*20*
PFBA	0	0	0	0
PFPeA	0	0	0	0
PFHxA	0	0	0	0
PFHpA	0	0	0	0
PFOA	36	7	0	21
PFNA	0	0	0	0
PFDA	0	0	0	0
PFUnDA	0	0	0	0
PFDoDA	0	0	0	0
PFTrDA	0	0	0	0
PFTeDA	0	0	0	0
L-PFBS	0	0	0	0
L-PFHxS	0	0	0	0
L-PFDS	0	0	0	0
6:2 FTSA	0	0	0	0

Table S3-3.5 Summary of laboratory performance PFASs, human plasma.

Human plasma Analyte	% of z-scores |z|<2 Satisfactory	% of z-scores 3>|z|>2 Questionable	% of z-scores 6>|z|>3 Unsatisfactory	% of z-scores |z|>6 Extreme
L-PFOS anion	71	7	14	7
br-PFOS anion	50	10	20	20
tot-PFOS LB	*88*	*0*	*6*	*6*
tot-PFOS UB	*92*	*0*	*0*	*8*
FOSA	0	0	0	0
MeFOSA	0	0	0	0
EtFOSA	0	0	0	0
MeFOSE	0	0	0	0
EtFOSE	0	0	0	0
PFBA	0	0	0	0
PFPeA	0	0	0	0
PFHxA	0	0	0	0
PFHpA	0	0	0	0
PFOA	75	6	6	6
PFNA	67	13	7	7
PFDA	64	7	7	0
PFUnDA	60	7	0	7
PFDoDA	36	7	0	7
PFTrDA	0	0	0	0
PFTeDA	0	0	0	0
L-PFBS	0	0	0	0
L-PFHxS	73	7	7	0
L-PFDS	0	0	0	0
6:2 FTSA	0	0	0	0

Table S3-3.6 Summary of laboratory performance PFASs, air extract.

Air extract	% of z-scores	% of z-scores	% of z-scores	% of z-scores
	|z|<2	3>|z|>2	6>|z|>3	|z|>6
Analyte	Satisfactory	Questionable	Unsatisfactory	Extreme
L-PFOS anion	65	12	6	18
br-PFOS anion	0	0	0	0
tot-PFOS LB	*67*	*6*	*11*	*17*
tot-PFOS UB	*73*	*9*	*9*	*9*
FOSA	60	10	30	0
MeFOSA	78	11	11	0
EtFOSA	67	0	22	11
MeFOSE	50	20	10	20
EtFOSE	70	0	10	20
PFBA	38	31	31	0
PFPeA	46	23	23	0
PFHxA	60	13	13	13
PFHpA	57	21	7	14
PFOA	63	13	25	0
PFNA	64	21	14	0
PFDA	67	13	20	0
PFUnDA	57	14	14	14
PFDoDA	62	8	15	15
PFTrDA	43	7	43	7
PFTeDA	31	23	31	8
L-PFBS	60	13	27	0
L-PFHxS	60	20	0	20
L-PFDS	64	18	9	9
6:2 FTSA	44	11	11	22

Table S3-3.7 Summary of laboratory performance PFASs, water.

Water	% of z-scores	% of z-scores	% of z-scores	% of z-scores
	|z|<2	3>|z|>2	6>|z|>3	|z|>6
Analyte	Satisfactory	Questionable	Unsatisfactory	Extreme
L-PFOS anion	53	11	16	16
br-PFOS anion	43	14	21	21
tot-PFOS LB	*48*	*5*	*24*	*19*
tot-PFOS UB	*56*	*6*	*19*	*19*
PFBA	63	6	6	25
PFPeA	38	25	13	6
PFHxA	78	6	6	6
-PFHpA	67	6	11	11
PFOA	58	21	5	11
PFNA	44	11	0	17
PFDA	41	0	0	18
PFUnDA	0	0	0	0
PFDoDA	0	0	0	0
PFTrDA	0	0	0	0
PFTeDA	0	0	0	0
L-PFBS	67	6	11	11
L-PFHxS	61	6	6	17
L-PFDS	0	0	0	0
6:2 FTSA	56	0	0	44

S3-4. Homogeneity of the fish test material

After filleting, cutting and homogenizing of the pike perch, 320 glass jars were filled with ca. 40 g of the homogenate. After sterilization of the jars by autoclaving, the homogeneity of the material was confirmed by performing a homogeneity test of PFOS on 7 randomly selected jars which were analysed in duplicate. Results of the homogeneity test are given in Table S3-4.1 and are shown in Figure S3-4.1.

Table S3-4.1 Results of the homogeneity test of PFOS (µg/kg ww) in the fish test material.

Measurements							
Jar number	*Analysis #1*		*Analysis #2*		*Mean*		*St.Dev.*
33	9.952		12.710		11.331		1.950
74	11.875		11.168		11.522		0.500
120	10.139		11.654		10.897		1.071
177	10.296		10.331		10.314		0.025
231	9.542		9.697		9.620		0.110
296	9.504		11.363		10.434		1.315
317	8.832		10.806		9.819		1.396
Statistics							
Mean of all	10.562				Mean of means		10.562
STDev	1.080				STDev		0.724
CV (%)	10.23				CV (%)		6.85
n	14				n		7
ANOVA Table							
Source of variation	SS	d.f.	MS	St.Dev.	F	F-crit 95%	F-crit 99%
Between units	6.285	6	1.048	MSB<MSW	0.83	3.87	7.19
Within units	8.890	7	1.270	1.127			
Snedecor F-Test							
Differences between units statistically significant? (a=95%):							No
Differences between units statistically significant? (a=99%):							No

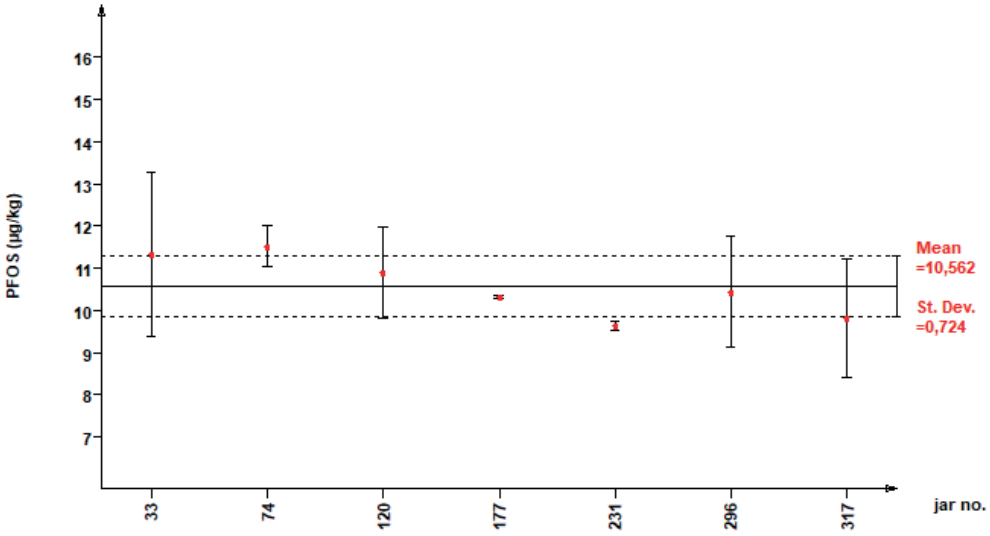

Figure S3-4.1 PFOS (µg/kg) concentrations in 7 jars of fish test material analysed in duplicate for the homogeneity testing of the material.

S3-5. Performance of individual laboratories over three ILSs

Table S3-5.1 z-scores assigned for compounds in multiple ILSs per laboratory.

	L001			L002		L004		L011			L017			L022		L023		L024		L027		L030			L035			L072	
Determinand	**IL2**	**IL3**	**IL4**	**IL2**	**IL3**	**IL2**	**IL3**	**IL2**	**IL3**	**IL4**	**IL2**	**IL3**	**IL4**	**IL3**	**IL4**	**IL3**	**IL4**	**IL3**	**IL4**	**IL2**	**R4**	**IL2**	**IL3**	**IL4**	**IL2**	**IL3**	**IL4**	**IL3**	**IL4**
Test Solution																													
L-PFOS	-0.23	0.23	-0.92	-0.12	0.22	-1.16	-1.09	-0.98	2.43	2.30						-0.82	5.44	-2.50	-1.22	0.21	0.08	0.44	-0.72	0.34		0.27	-3.63	1.30	-0.78
br-PFOS		-0.71	-1.89															-2.61	0.46							1.04	-3.14		
FOSA								-1.13	-1.43	0.38								-2.24	-0.97	-0.51	0.51					3.95	7.88	1.78	-0.32
PFBA						-0.90	-1.24	-0.35	4.31	0.47						-0.98	4.25	-1.57	-1.48	-0.11	0.34					1.08	-3.60		
PFPeA						-1.43	-0.12	-0.88	2.51	1.88						-1.22	3.53	-1.69	-0.49	-0.63	0.04					5.63	-2.04		
PFHxA	0.04	-2.03	-2.60	0.11	-2.02	-1.09	-0.86	-0.17	1.71	1.73						-0.74	1.78	-1.04	-1.11	-0.60	0.18		0.96	0.01		0.65	-1.25		
PFHpA	-0.50	-2.17	-1.46	-0.28	-2.20	-1.39	-1.25	-1.13	1.41	1.31						-0.86	2.10	-0.07	-0.11	0.64	0.28		-1.68	-0.50		3.26	-3.62		
PFOA	-0.34	0.10	-0.28	-0.27	0.07	-1.39	-1.41	-0.70	2.55	1.50						-1.32	1.55	-2.27	-0.48	0.11	0.31	0.79	-0.30	0.71		0.71	-3.77		
PFNA	-0.20	0.44	-0.95	-0.30	0.42	-1.50	2.94	0.66	1.09	0.72						-0.65	2.16	-1.26	-0.22	-0.57	0.79		-0.48	0.79		0.35	-3.91		
PFDA	0.21	0.03	-0.16	0.14	0.02	-0.87	1.94	0.34	1.41	0.84						-0.78	1.50	-0.89	-0.70	0.10	0.33		-0.55	-0.19		0.71	-2.99		
PFUnDA	-0.22		-1.33					1.35		1.25										-0.28	0.60								
PFDoDA	-0.44		-0.52					-0.04		2.26										-0.48	0.14								
PFTrDA	-0.01		1.06					0.10		2.62										-0.65	-1.20								
PFTeDA	0.16		-0.28					-0.96		1.84										-0.38	0.20								
L-PFBS						0.35	-0.74	-0.92	1.73	-0.26						-0.66	3.17	-1.66	-1.11	0.17	1.43					10.25	0.96		
L-PFHxS	-0.16	0.59	-0.38	-0.10	0.60	-1.00	-1.76	0.42	1.85	1.55						-0.81	3.61	-1.76	-1.76	0.29	0.62		-0.37	0.35		0.36	-3.61		
L-PFDS	0.17		-0.64					-0.13		1.80										-0.58	0.42								
MeFOSA	0.30		0.40					-1.71	0.19	-0.26										4.88	0.25					-1.03	-0.82		
MeFOSE									1.33	1.62																			
EtFOSE									1.71	1.44																			
Sediment																													
L-PFOS						-1.23	-1.26	1.96	5.37	1.24	-0.44	1.52		8.38	2.48	-2.05	-3.07	0.00	-1.23										
br-PFOS														61.87	5.54														
Fish																													
L-PFOS	-0.08	0.05	-0.07	-0.73	0.05			1.02	8.10	34.03				-7.01	0.86	-0.68	0.17	-0.07	-1.20	0.95	0.57								
br-PFOS		-1.33	-2.47											36.41	0.94			4.10	-1.42										
Human milk																													
L-PFOS	1.27	-0.05	0.12	0.56	-0.02															-1.40	-0.14								
Human serum/plasma																													
L-PFOS	4.62	0.26		4.28	0.17	-2.06	-0.87									-0.08	-3.77	2.16	-2.20			-0.19	-0.37	0.19					
br-PFOS																		0.74	-1.23										
PFOA	-0.22	-0.29		-0.39	-0.28	-0.18	-4.74									-0.74	-3.96	4.30	-0.14			0.37	-0.47	-0.32					
PFNA	-0.08	1.00		-0.09	1.09	0.13	-2.63									-1.06	-4.11	6.41	-0.44				-0.29	-0.13					
PFDA	-0.33	0.46		-0.37	0.28	-0.63	-0.90																-0.01	0.19					
PFUnDA	-0.81	0.12		-0.71	0.02																		-1.21	0.21					
PFDoDA																													
L-PFHxS	-0.97	-0.41		-0.26	-0.41	1.51	-1.64									-0.93	-1.99												
Air extract																													
L-PFOS									15.60	18.25		0.09	-0.61			-1.62	-2.41	-0.51	0.56	0.92	0.94							5.89	1.07
FOSA																				-0.49	0.67								
Water																													
L-PFOS								-0.65	37.53	-2.33	-0.21	14.60		2.16	822	-1.00	3.30			-0.14	0.19	0.23	0.68	2.08	4.92	-0.48	-3.43	7.00	-0.73

	L104		L105			L107		L117			L121		L124		L126			L128			L129		L130		L195		L224	
Determinand	**IL3**	**IL4**	**IL2**	**IL3**	**IL4**	**IL2**	**IL4**	**IL2**	**IL3**	**IL4**	**IL2**	**IL3**	**IL3**	**IL4**	**IL2**	**IL3**	**IL4**	**IL2**	**IL3**	**IL4**	**IL2**	**IL3**	**IL2**	**IL4**	**IL3**	**IL4**	**IL3**	**IL4**
Test Solution																												
L-PFOS	-0.29	0.99	-0.83	-0.48	-0.59	0.30	-2.39	-1.07	0.38	-0.20	0.41	1.53	-1.05	0.46	0.07	0.38	-0.09	-0.42	1.53	0.82	-0.15	0.21			-1.68	0.60	1.43	-0.07
br-PFOS									2.67	0.27						2.01	0.40		7.67	6.07							0.25	-0.70
FOSA	0.75	-2.86	0.05	-7.76	-0.77	0.04	-2.05	0.32	1.09		-0.22				0.19	1.49	0.79	3.14	10.1		-0.03	-3.81			-2.38	0.78	0.40	0.24
PFBA	0.07	0.21	-0.70	-0.50	1.31			-0.64	0.21	-0.85	-0.17	1.95	-0.48	0.68	0.48	1.11	-0.72	0.61	890						-0.97	0.47		
PFPeA	-0.75	0.04	-0.83	-0.41	1.02			-0.08	-0.15	-0.61	0.92	1.05	-0.75	0.87	1.21	1.45	0.68								-1.80	-0.09	0.78	-0.04
PFHxA	-0.72	0.44	-0.19	-0.29	0.94	1.13	-2.14	-0.48	0.50	-0.65	-0.04	1.68	-0.33	0.41	-0.03	1.03	-0.03	0.06	2.93	0.61	-0.06	-4.09			-0.83	-0.07	1.36	-0.38
PFHpA	0.77	0.54	-0.13	-0.62	0.40	0.46	-2.18	-0.34	0.98	-0.59	8.28	1.55	-0.56	1.06	0.83	8.91	0.79	-0.19	2.41	0.17	-0.16	-2.80			-0.77	-0.11	0.56	-0.32
PFOA	-0.10	0.58	-0.42	-0.46	-0.56	0.54	-2.32	-0.83	0.21	-0.69	0.41	1.24	-0.83	0.75	-0.14	1.21	-0.31	-0.55	2.36	0.61	-0.39	-1.07			-1.27	-0.35	0.04	-0.19
PFNA	0.48	0.72	-0.63	-0.04	-0.59	0.67	-2.05	-0.94	0.00	-0.15	-0.27	1.71	-0.48	0.85	-0.20	1.02	0.86	-2.27	0.11	-1.03	0.24	-1.16			-1.26	0.18	0.61	-0.15
PFDA	-0.62	0.07	-0.32	-0.92	0.18	0.91	-3.13	-0.32	-0.15	-0.44	-0.07	1.55	-0.75	0.37	-0.06	1.68	-0.19	-0.66	1.26	-0.75	-0.55	-2.92			-1.03	-0.31	0.67	-0.35
PFUnDA			-0.26		5.17	0.87	-2.14	-0.73		-0.70					-0.22		-0.16	0.11		1.16								
PFDoDA			1.27		0.33	1.02	-2.12	-0.73		-0.45					-0.36		-0.27											
PFTrDA			-3.23		1.79	1.06	-1.57	-0.47		-0.99					0.08		0.36											
PFTeDA			-1.81		0.15	1.32	-2.95	1.15		-0.67					0.21		-0.33											
L-PFBS	0.18	1.06	-1.51	0.05	-1.32	0.71	-2.24	-0.53	-0.49	-0.81	-4.30	2.01	-0.21	0.06	-0.17	0.73	-0.64	-0.06	0.18	-1.18	-0.17	0.23			-0.32	0.87	1.23	0.64
L-PFHxS	-0.23	0.62	-1.44	-0.13	0.32	0.20	-2.29	-0.91	0.04	-1.17	0.43	2.19	-0.44	0.67	-0.58	1.01	-0.03	-0.25	1.76	0.07	-0.45	-3.84			-0.86	0.22	-0.02	-0.78
L-PFDS						-0.44	-2.72	-0.58		-0.84					-0.02		-0.36											
MeFOSA	-2.83	0.06	-3.15	-3.07	-4.73											0.38	3.36								2.40	-0.70		
MeFOSE	-2.33	0.12		-0.77	-2.03											4.72	0.00								1.81	-3.50		
EtFOSE	-3.23	-0.01		-1.09	-3.77											1.74	1.08								1.07	-0.68		
Sediment																												
L-PFOS			-0.64	-0.33	-0.23	0.90	-1.23	-1.97		-1.84					-0.19	0.34	0.13	3.72	0.63		-0.69	-0.51						
br-PFOS				-0.47	1.90																							
Fish																												
L-PFOS			-0.78	-0.20	-0.19	-0.83	0.11	-1.90	0.01	-0.21					-0.24	0.38	1.38				-0.65	1.66					0.21	0.16
br-PFOS				4.81	1.83				-0.46	-0.78							2.06											
Human milk																												
L-PFOS			-5.59	-0.92											-0.51	2.66	-0.01											
Human serum/ plasma																												
L-PFOS			-2.36	-0.31	-0.62	0.11	-0.35								-1.49	0.30	-0.25											
br-PFOS				-2.52	7.13											-1.51	0.27											
PFOA			-2.43	-1.49	-0.09	0.15	0.04								0.80	1.41	1.91						0.37	-0.10				
PFNA			-0.04	-1.07	-0.67	2.05	0.40								0.87	0.27	2.24						2.49	-0.44				
PFDA			-0.09	-0.39	-0.16	2.62	-1.22								0.81	2.35	0.70						0.81	1.47				
PFUnDA			0.42	-0.45	1.46	2.52	-0.61								1.32		1.16						0.12	-0.75				
PFDoDA															0.55		0.32						-0.91	-0.14				
L-PFHxS			-0.39	-0.18		2.39	-0.14								0.79	0.26	0.30						-0.80	-0.52				
Air extract																												
L-PFOS	1.99	0.19	0.77	-0.59	-3.14	1.66	-2.04	-4.43	-1.49							7.24	-0.91	0.05		1.83					-1.59	0.00		
FOSA						0.86	-4.88								-7.69		-1.09											
Water																												
L-PFOS			-0.40	-0.96	4.44	-1.97	-1.70	-0.91	-0.17	-0.73	-0.38	-0.91				39.78	-0.82				3.70	5.07					-1.14	1.45

= satisfactory: |z| < 2; = Questionable: 2 < |z| < 3; = Unsatisfactory: |z| > 3

Chapter 4.

Ike van der Veen[a]

Anne-Charlotte Hanning[b]

Ann Stare[b]

Pim E.G. Leonards[a]

Jacob de Boer[a]

Jana M. Weiss[c]

[a] Vrije Universiteit, De Boelelaan 1085, 1081 HV, Amsterdam, The Netherlands
[b] RISE IVF AB, Argongatan 30, SE-431 53, Mölndal, Sweden
[c] Department of Environmental Science, Stockholm University, Svante Arrheniusv. 8, SE-11418 Stockholm, Sweden

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The effect of weathering on per- and polyfluoroalkyl substances (PFASs) from durable water repellent (DWR) clothing

Abstract

To assess the effects of weathering on per- and polyfluoroalkyl substances (PFASs) from durable water repellent (DWR) clothing, thirteen commercial textile samples were exposed to elevated ultra violet (UV) radiation, humidity, and temperature in an aging device for 300 h, which mimics the lifespan of outdoor clothing. Before and after aging, the textile samples were extracted and analysed for the ionic PFASs (perfluoroalkyl acids (PFAAs), perfluorooctane sulfonamide (FOSA)) and volatile PFASs (fluorotelomer alcohols (FTOHs), acrylates (FTACs) and methacrylates (FTMACs)). Results showed that weathering can have an effect on PFASs used in DWR of outdoor clothing, both on the PFAS profile and on the measured concentrations. In most weathered samples the PFAA concentrations increased by 5- to more than 100-fold, while PFAAs not detected in the original textiles were detected in the weathered samples. DWR chemistries are based on side-chain fluorinated polymers. A possible explanation for the increase in concentration of the PFAAs is hydrolysis of the fluorotelomer based polymers (FTPs), or degradation of the FTOHs, which are used in the manufacturing of the FTPs. The concentrations of volatile PFASs also increased, by a factor up to 20. Suggested explanations are the degradation of the DWR polymers, making non-extractable fluorines extractable, or the transformation or degradation of unknown precursors. Further research is needed to unravel the details of these processes and to determine the transformation routes. This study shows that setting maximum tolerance limits only for a few individual PFASs is not sufficient to control these harmful substances in outdoor clothing.

4.1. Introduction

Per- and polyfluoroalkyl substances (PFASs) are a class of man-made chemicals, which do not occur in nature. Nowadays, they are ubiquitously present in water, soil, air and biota, and also in human blood and mother's milk[1-7]. PFASs are used in a wide range of consumer products such as in firefighting foams, cooking pans, carpets and food wrapping paper. Among the multitude of applications, PFASs are also used in textiles for outdoor clothing[8] in order to obtain the desired durable water repellence (DWR). DWR chemistries are based on side-chain fluorinated polymers[9]. PFASs are divided into short-chain, and long-chain PFASs by their alkyl chain length (C_nF_{2n+1}), with $n \geqslant 6$ for long-chain perfluoroalkane sulfonic acids (PFSAs), and $n \geqslant 7$ for long-chain perfluoroalkyl carboxylic acids (PFCAs)[8, 9]. Since it was revealed that some of the PFASs are very persistent in the environment[10], bioaccumulative[1, 12] and (eco) toxic[13-17], the use and production of some PFASs was regulated. In 2006 the European Commission regulated the level of perfluorooctane sulfonate (PFOS) in consumer products (Regulation Directive 2006/122/EC)[18]. In June 2017, perfluorooctanoic acid (PFOA) and PFOA-related substances, including salts and polymer containing -C_8F_{17} as structural element, have been added to REACH annex XVII restricted substances list (entry 68) by the European Commission[19]. Some of the longer chain PFCAs (C_8, C_{11}–C_{14}) were included in the Candidate List of Substances of Very High Concern (SVHC) under REACH[20], and recently also perfluorohexane sulfonate (PFHxS) was added to that list[21]. In 2009 PFOS and in 2017 PFOA and its salts have been listed in Annex B of the Stockholm Convention (decisions SC-4/17[22] and SC-9/12[23]), which describes the restriction of production and use of the compounds[19, 22-24]. Finally, in 2019 the conference of the parties (COP) decided to list PFOA and its salts in Annex A (decision UNEP/POPS/COP.9/CRP.14)[25, 26]. PFHxS is currently proposed to be listed as a POP under the Stockholm Convention[27]. Nowadays, the textile industry is phasing-out the long-chained PFASs[9] and is replacing those compounds with alternative chemicals that also deliver the desired DWR effect. Those alternative chemicals can be divided in three main groups: fluorocarbon-based, silicon-based and hydrocarbon-based polymers[28]. Hill et al.[29] assessed the repellent performance of some hydrocarbon-based DWRs in comparison with the long-chained PFAS DWR, and within the SUPFES (Substitution in Practice of Prioritized Fluorinated Chemicals to Eliminate Diffuse Sources[30]) project alternative DWRs from all three main groups were assessed in comparison with PFASs with regard to their functionality and their impact on the environment[30, 31].

Some studies have been performed before on the concentrations of PFASs in textiles[32-44]. Gremmel et al.[37] analysed 16 outdoor jackets for the concentrations of 23 PFASs. All jackets contained at least one of the PFASs. Brigden et al.[34] reported the detection of PFASs in 15 articles including seven waterproof garments, and Robel et al.[40] reported the analyses of nine textiles, which included seven garment samples. Not only PFASs in outdoor clothing have been analysed, but also the leaching of PFASs from the garments during washing was investigated. Knepper et al.[45] reported PFAS concentrations in washing water after washing of outdoor jackets. Until now, no studies have been performed on the effect of different weather conditions on PFASs in textiles. As part of the SUPFES project, the present study was conducted with an aim to assess the influence of weathering on PFASs in DWR-treated outdoor clothing. The hypothesis was that PFASs used in the DWR-treated outdoor clothing is a relevant source of environmental pollution and human exposure due to emission of PFASs during usage.

4.2. Material and methods

4.2.1. Chemicals and reagents

All analysed PFASs and isotope-labeled perfluoroalkyl acids (PFAAs), are shown in the Tables S4-1.1 (ionic PFASs) and S4-1.2 (volatile PFASs) of the Supporting Information (SI) according to the terminology of Buck et al.[8]. Three mixtures containing 50 µg mL^{-1} of FTOHs (4:2, 6:2, 8:2, and 10:2), FTACs (6:2, 8:2, 10:2), and FTMACs (6:2, 8:2, 10:2) in methanol, and individual solutions of 50 µg/mL of the isotope labeled D_2-6:2 FTOH, D_3-6:2 FTAC and D_5-6:2 FTMAC in methanol, were purchased from Chiron AS (Trondheim, Norway). The purities of those mixtures were >98%, and the isotope purity of D_2-6:2 FTOH, D_3-6:2 FTAC and D_5-6:2 FTMAC was >99%. All other PFASs (50 µg/mL in methanol, purity of > 98%.) were purchased from Wellington Laboratories (Guelph, ON, Canada). The isotope purity of the isotope-labeled PFAAs was >99%, except for $^{18}O_2$-PFHxS (>94%). HPLC grade methanol (J.T. Baker, 8402), and acetone (J.T. Baker, 9254) were obtained from Boom (Meppel, The Netherlands). Ethylacetate (HPLC, 054006) was purchased from Biosolve Chimie (Dieuze, France). Acetonitrile (Chromasolve, 34851), ammonium formate (Bio ultra, 09735), and Supelclean™ Envi-carb™ (Supelco, 957210-U) were purchased from Sigma Aldrich (Zwijndrecht, The Netherlands). A Milli-Q system from Millipore (Watford, UK) was used to obtain ultrapure water. Glass fiber filters (GF/F, pore size 0.42 µm), purchased from Whatman (Maidstone, UK), were used for filtering of the mobile phase.

4.2.2. Textile samples

Textile samples originating from outdoor clothing (one pair of outdoor trousers, seven jackets, four fabrics for outdoor clothes, and one outdoor overall, Table 4-1), were provided by six different suppliers from the outdoor textile industry in Sweden to SWEREA IVF (Mölndal, Sweden). Two pieces were cut out of each fabric. One of the pieces (9 cm x 12 cm) was exposed in an ATLAS weather-Ometer Ci 3000 to elevated UV radiation, humidity, and temperature for 300 h (Table 4-2), which can be compared to the lifespan of the outdoor clothing[46]. Both pieces of textile, aged and not aged, were analysed for ionic PFAS and volatile PFAS content. Until analyses, all pieces of textile were stored at room temperature in the dark.

Table 4-1 Details of outdoor clothing samples.

Sample No.	Sample type	Sample color	Year of manufacturing*	Fabric*
1	Outdoor trousers	Black	nr	100% recycled polyester
2	Fabric for jacket	Anthracite	nr	80% polyester, 20% cotton
3	Fabric for jacket	Olive	nr	100% polyamide
4	Men's jacket	Brown	2013	100% cotton
5	Men's jacket	Yellow	2013	100% polyester
6	Fabric for outdoor clothes	Yellow	2012	65% cotton, 35% polyester
7	Children's jacket	Brown	2012/2013	100% polyamide
8	Jacket (parka)	Olive	nr	nr
9	Fabric for outdoor clothes	Yellow	nr	100% polyester
10	Fabric for outdoor clothes	Green	nr	nr
11	Fabric for outdoor clothes	Yellow	nr	nr
12	Fabric for outdoor clothes	Light blue	nr	nr
13	Fabric for outdoor clothes	Bright blue	nr	100% polyester

nr: not reported; *: information given by supplier

Table 4-2 Conditions of ATLAS weather-Ometer Ci 3000 for a weathering experiment (total duration 300 h)*.

Method	Exposure cycles	Broadband (300-400 nm) W /m²	Narrowband (340 nm) W /m² nm	Black standard temperature** (˚C)	Chamber temperature (˚C)	Humidity (%)
A1 (ISO 4892-2)	102 min dry 18 min water spray	60 ± 2	0.51 ± 0.02	65 ± 3	38 ± 3	50 ± 10

* Conditions as described in ISO 4892-2 method A1[47], and ISO 105-B10 Exposure method A[46]
** Reference temperature on a black metal plate in the ATLAS weather-Ometer Ci 3000, which characterizes the temperature on the sample surface[48]

4.2.3. Extraction procedure

Ionic PFASs

Circular pieces with a diameter of 35.3 mm (equals 9.79 cm^2) were taken from the aged and unaged outdoor clothes samples by a bore (Cordia Matic, 270 rpm) for analysis of ionic PFASs. Extraction was performed according to the method of Van der Veen et al.[49], which was developed and validated after comprehensive testing of different solvents and exhaustive extraction. In short, dust particles were rinsed from the textile pieces by adding 5 mL water to the test tube and taking the textile piece out immediately afterwards. After adding 150 µL isotope labeled internal standard solution (conc. 100 ng/mL) (Table S4-1.1), the samples were left to equilibrate for one night. Ionic PFASs were extracted with two times shaking the textile pieces in 5 mL methanol for 30 minutes on a shaking device. After concentration until dryness by a gentle stream of nitrogen at 40°C, the extracts were reconstituted in 200 µL methanol: water (1:1, v/v).

Volatile PFASs

Both pieces of textile, aged and not aged, were extracted and analysed for volatile PFAS content in the same series. Because of the limited amount of textile available for the analyses of volatile PFASs, squares of approximately 20 cm^2 were cut with a pair of scissors from each aged and unaged outdoor clothes sample, instead of cutting by a bore.

To enhance extraction performance, each piece of textile was cut into eight smaller pieces, which were all weighed together into a 15 mL polypropylene (pp) tube. The samples were fortified with 50 µL of an IS solution (mixture of 800 ng/mL D_2-6:2 FTOH, 800 ng/mL D_3-6:2 FTAC and 200 ng/mL D_5-6:2 FTMAC in ethylacetate, which equals concentrations of 20, 20 and 5 µg/m^2, respectively), added directly onto the samples and left to equilibrate for one night (IS recoveries are given in Table S4-2.3). Volatile PFASs were extracted from the samples by liquid solid extraction (LSE) with 2 times 5 mL ethylacetate. Extraction was performed by shaking on a shaking device (Edmund Bühler GmbH, Hechingen, Germany) for 30 min. The extracts were concentrated to a volume of approximately 1 mL by a gentle stream of nitrogen at 20°C. The extracts were purified by adding 100 mg Envi-carb™ followed by mixing on a Vortex and centrifugation (10 min, 3000 rpm). The final extracts were concentrated to a volume of 100 µL by a gentle stream of nitrogen at 20°C.

4.2.4. Instrumental analysis and quantification

Ionic PFASs

The extracts were analysed for ionic PFASs by electrospray negative ionization LC-MS/MS as previously described by Van der Veen et al.[49]. Instrumental settings are reported in Table S4-1.3.

Volatile PFASs

Separation and detection of volatile PFASs was carried out by GC/EI-MS (Gas chromatography/ Electron impact-Mass spectrometry) on an Agilent 6890 series GC coupled to a 5973 Network MS (Agilent Technologies, Amstelveen, The Netherlands) equipped with a PTV injector without liner. Separation was performed on a HP-INNOWAX column (30 m x 0.25 mm i.d. x 0.25 µm; Agilent Technologies, Amstelveen, The Netherlands) using the following GC temperature programming: 50°C (held 1 min), ramped at 3°C/min to 130°C (held 10 min), ramped at 20°C/min to 225°C (held 11 min). An injector temperature program was used, with an initial temperature of 50°C (held for 0.1 min), ramped at 5°C/sec to 150°C (held 10 min), ramped at 3.3°C/sec to 220°C (held 1 min). Injection volume was 1 µL in pulsed splitless mode. Helium was employed as the carrier gas. Quantification was performed against three individual calibration curves (FTOHs, FTACs and FTMAC) consisting out of six calibration solutions (5, 10, 25, 50, 100, 500 ng/mL) for FTACs and FTMACs and eight solution for FTOHs (5, 10, 25, 50, 100, 500, 2500, 5000 ng/mL) in ethylacetate, and against the isotope-labeled ISs D_2-6:2 FTOH, D_3-6:2 FTAC and D_5-6:2 FTMAC. Instrumental settings are reported in Table S4-1.4. For quantification MSD Chemstation software (E.02.00.493) of Agilent Technologies (Amstelveen, The Netherlands) was used with quadratic curves.

4.2.5. Quality control

Validation of the extraction and analyses method for volatile PFASs

The extraction and analysis method for the volatile PFASs was validated by assessment of the repeatability and the recovery. All textile samples of the repeatability and recovery assessment were extracted and analysed in the same series. For both assessments the same calibration curves were used. To assess the repeatability of the method, two textile samples were extracted in triplicate on the same day. To assess the recovery of the method, those textiles were fortified with volatile PFASs at two different levels (50 and 500 µg/m^2) in triplicate. Calculations of the repeatability and the recovery are given in Chapter S4-3. The relative

standard deviations for the triplicate analyses of the unfortified samples were 5-17% for PFASs. The relative standard deviations of the fortified textile samples were 0-28%. The recoveries were 60-130% (median 100%) for all compounds except 10:2 FTOH (86-159%, median 98%), and 8:2 FTAC (103-146, median 132%).

Carry-over and blank control

Two textile fabrics (polyamide and polyester) without any DWR-treatment were exposed to UV radiation, humidity, and temperature alongside the cloth samples, to determine any possible carry-over in the aging device. No ionic PFASs were detected in the textiles before and after aging. Only 6:2 FTOH was present of the volatile PFASs before aging in both textiles (9.3 and 13 μg/m^2). After aging the concentration of 6:2 FTOH increased with an average of 5 μg/m^2, and small amounts of 8:2 FTOH (4 μg/m^2), 10:2 FTOH (4 μg/m^2) and 6:2 FTMAC (2 μg/m^2) were detected, which were subtracted from the final results. Only results higher than three times the amount detected in the blank textiles were reported.

Procedure solvent blanks were analysed alongside the samples and subtracted from the final results. Limits of detection (LODs) of the ionic PFASs were between 0.02 and 0.1 μg/m^2, and LODs of the volatile PFASs were 0.3 μg/m^2. The limit of quantification (LOQ) was calculated as 3.3 times the LOD. (Chapter S4-3).

Homogeneity testing of PFAAs in textiles from commercial outdoor clothing

Homogeneity tests of PFAAs have been performed on pieces of textile originating from four fabrics of commercial outdoor clothing, which is described in Chapter S4-4 of the SI. Results showed that the homogeneity differs per fabric, but can also differ per piece of the same material, which is shown for PFOA in Figure 4-1.

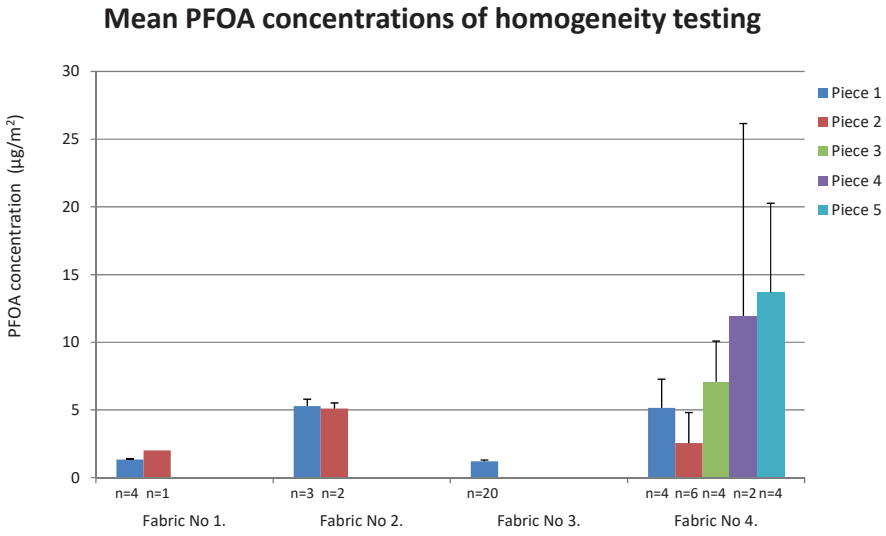

Figure 4-1 Results of homogeneity testing of mean PFOA concentration (+/- 1 sd) (µg/m²) in four fabrics (Fabric No 1 – 4) of commercial outdoor clothing. ('n' represents the number of samples analysed per piece of fabric).

4.3. Results and discussion

4.3.1. Concentrations before weathering

As expected, the fabrics contained a wide range of levels of PFASs with different congener profiles depending on the DWR layer. Tables S4-2.1 and S4-2.2 show the concentrations of ionic PFASs and volatile PFASs in the original samples. Volatile PFASs were present in higher concentrations (median 4.8 µg/m², max. 350 µg/m²) than ionic PFASs (median 0.85 µg/m², max. 45 µg/m²).

Ionic PFASs

In 77% of the samples at least one of the ionic PFASs was detected. PFHxA and PFOA were the most frequently detected PFAAs above limit of quantification (LOQ) (each detected in 62% of the samples). PFTrDA, PFHpS, FOSA, and 4:2 FTSA were not present above the LOQ in any of the samples. The highest concentration was 45 µg/m² for PFBS in one of the samples. This sample also contained a high amount of PFBA (28 µg/m²). For all other PFAAs the concentrations in the unexposed samples ranged from < LOQ to 9.1 µg/m² for 8:2 FTSA. Those concentrations were in the same range as reported by Gremmel et al.[37],

and of Robel et al.[40]. Concentrations of individual PFAAs in 16 outdoor jackets reported by Gremmel et al.[37] ranged up to 9.24 µg/m^2, except for one jacket which contained PFOA in a concentration of 171 µg/m^2. The highest concentration of PFAAs reported by Robel et al.[40] for seven clothing samples was 31 µg/m^2 for PFHxA.

Volatile PFASs

Since volatile PFASs can easily evaporate, concentrations detected in the fabrics in our study might be underestimating the real concentrations present in the fabrics. However, the detected concentrations are in line with the studies of Gremmel et al.[37], and of Robel et al.[40]. The highest concentration quantified for volatile PFASs in our study was 350 µg/m^2 for 6:2 FTOH. Gremmel et al.[37] reported concentrations up to 516 µg/m^2 for individual FTOHs. In all of their samples, except one, 8:2 FTOH was detected, which corresponds to the results from our study. It is remarkable though, that in our study all samples except one contained 6:2 FTOH, while in the study of Gremmel et al.[37] 6:2 FTOH was only quantifiable in two samples. In the study of Robel et al.[40] 6:2 FTOH was detected in four of seven samples. In one of those samples an extremely high concentration (14000 µg/m^2) was found. In our study 10:2 FTOH was found in eleven out of thirteen samples and 6:2 FTMAC in nine samples. 8:2 FTMAC and 10:2 FTMAC were not detected at all. 4:2 FTOH was not detected in any of the samples. Due to the high costs of isotope-labeled standards only D_2-6:2 FTOH was used as internal standard for the quantification of 4:2 FTOH, which might have been insufficient to compensate for eventual losses during extraction and analyses due to the volatility of the short-chain 4:2 FTOH.

4.3.2. Effects of weathering

Ionic PFASs

Weathering increased the concentrations of all ionic PFASs in most samples, by 5-fold to more than 100-fold. Three samples did not contain any ionic PFASs before aging. In one of those samples, no ionic PFASs were found after aging, while in another sample after aging two PFAAs (PFHpA, 0.16 µg/m^2; PFNA 0.13 µg/m^2) appeared. In the third sample six different PFAAs appeared with concentrations of 0.1 µg/m^2 (PFOA) – 7.1 µg/m^2 (PFBA). Tables S4-2.1 and S4.2.2 show all extractable concentrations of ionic PFASs and volatile PFASs in the samples before and after aging, and Figure 4-2 shows four selected samples to illustrate different results. As can be observed, the concentrations of all PFCAs in samples 5 and 6 increased, and the odd-chain length PFASs PFUnDA and PFTrDA appeared. In sample 9 the most abundant ionic PFASs were the compounds with a C4 chain length, PFBA and PFBS, which increased 5 and 8 times, respectively. Sample 13 did not contain any ionic PFASs before aging, while 6 PFASs were detected in the samples after aging. In Figure S4-2.1 the results of all the samples are shown.

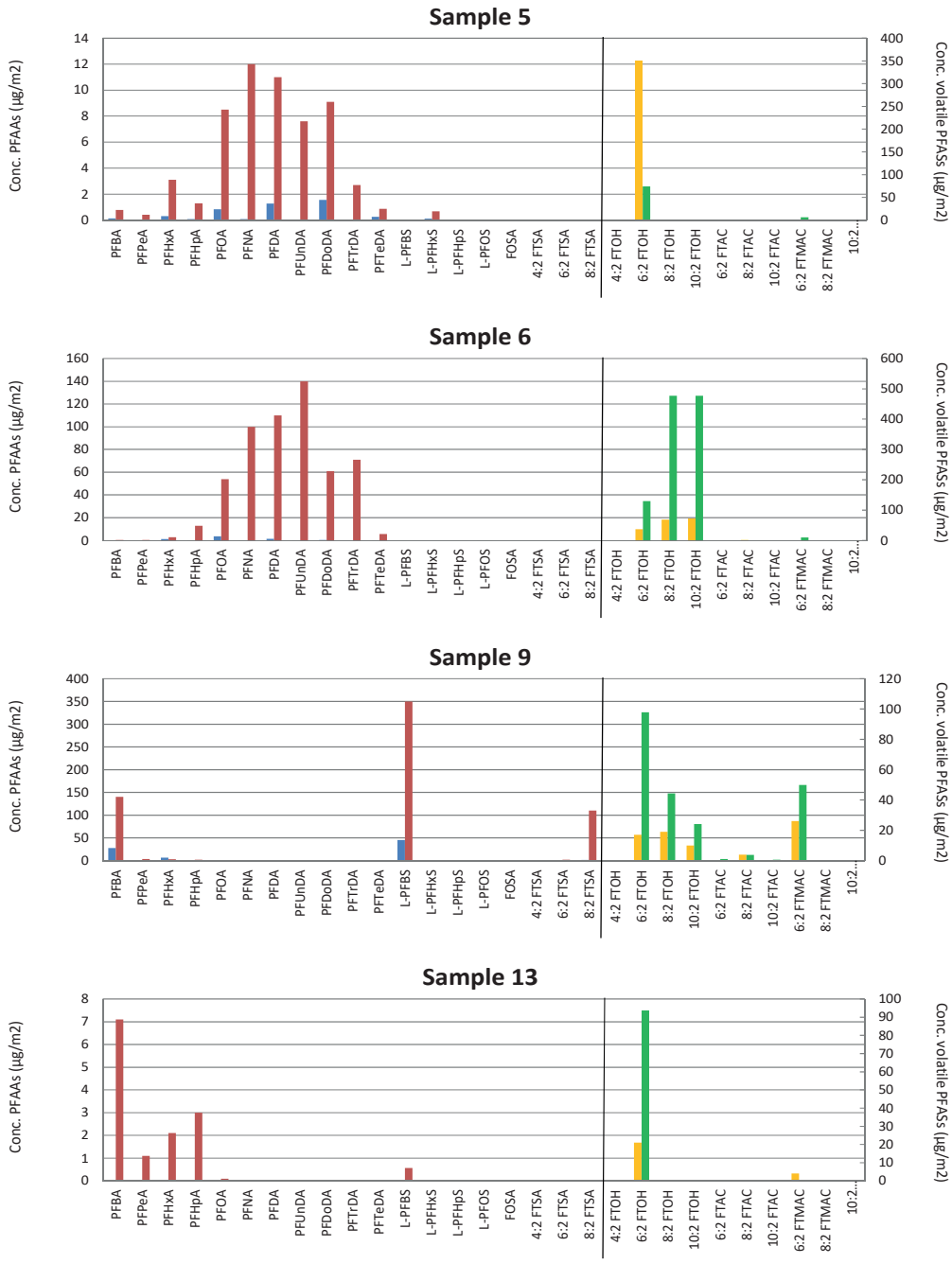

Figure 4-2 PFAS concentrations quantified in four textile samples of outdoor clothing (sample 5, 6, 9 and 13). Concentrations of ionic PFASs (■before; ■after) in µg/m² on the left y-axis. Concentrations of volatile PFASs (■before; ■after) in µg/m² on the right y-axis. The PFAS concentrations in the other textile samples are given in Figure S4-2.1 and Table S4-2.1, and S4-2.2.

Robel et al.[40] performed a study on the mass balance of PFASs. They analysed 77 individual PFASs in nine textiles and eight papers, and analysed the total amount of organic fluor by particle induced gamma ray emission (PIGE) spectroscopy. After extraction the papers and textiles still contained 64 ± 28% to 110 ± 30% of the original concentration, expressed in nmol F/cm^2. The high non-extractable organic fluor (NEOF) fraction was also described by Koch et al.[50], and by Schultes et al.[51]. Within our study the amount of total organic fluorine was not determined, but it is expected that the textiles before aging also contained NEOF. The increase of PFAAs as an effect of the exposure to weather conditions might be explained by the NEOF, which could have become partially extractable due to weather conditions.

Another explanation for the increase in PFAAs as an effect of the exposure to weather conditions, might be the degradation and transformation of the precursors FTOHs, FTACs, and FTMAC, which are used for the formation of the DWR polymers. The degradation and transformation of FTOHs into PFCAs has been described multiple times[8], including aerobic biodegradation[52-56], anaerobic biodegradation[57], metabolic transformation[58], and atmospheric degradation[59, 60]. Photodegradation might be the degradation and transformation route when precursors are exposed to weather conditions. Taniyasu et al.[61] tested the influence of solar irradiation on 21 PFASs in test solutions in a field study, and in a laboratory study in which the solutions were irradiated in an UV chamber. Although results of their study indicated photodegradation of PFOA, PFNA, PFDA, PFOS, PFDS, 4:2 FTOH, 6:2 FTOH, and 8:2 FTOH, the conclusions of their study are being questioned, because of the lack of essential experimental details, the lack of plausible transformation mechanisms, and the inconsistency of results[62]. However, the photodegradation of PFAAs in aqueous solutions under special conditions, with PFAAs decomposing slowly to form F^-, CO_2, and shorter-chain PFCAs, has been described earlier by Hori et al.[63, 64]. Also Kongpran et al.[65] performed experiments that showed photodegradation of FTOHs into PFCAs. Since PFCAs in their study were formed at a very slow rate, the authors concluded that 8:2 FTOH did not degrade to PFCAs directly, but first to some intermediate products[65].

Degradation of the FTOHs, or (part of) the NEOF becoming extractable might not only explain the increase in concentrations of the ionic PFASs in our study, but also the formation of odd-chain length PFASs in some of the samples, which were not present in the original textiles.

Volatile PFASs

If the increase in concentrations of ionic PFASs would only be the result of the transformation of the volatile PFASs into ionic PFASs, it could be expected that the concentrations of volatile PFASs would decrease when exposed to weather conditions.

In contrast with this expectation, the volatile PFASs show an increase in concentrations after aging, by a factor up to 20. No 4:2 FTOH, 8:2 FTMAC and 10:2 FTMAC were formed, while the concentration of 6:2 FTOH increased in all samples except in sample 5 (Figure 4-2, Table S4-2.2). It is possible that sample 5 did not contain any precursors of 6:2 FTOH. However, since in all samples the concentration of 6:2 FTOH increased by a factor of 2.4-16, the decrease in sample 5 might possibly be due to inhomogeneity of the textile (section 4.2.5). Confirmation of this hypothesis was not possible since there was not enough material to perform homogeneity tests on the commercial textile samples, which were used for the aging experiments.

Although concentrations of volatile PFASs could be underestimated due to off-gassing during storage (section 3.1.2), the differences between the concentrations before and after aging could not be explained by this, since all samples were stored at the same temperature, and analysed in the same series.

In the study of Robel et al.[40] where 77 individual PFASs were quantified in paper and textiles, the analyses of the total amount of organic fluor by PIGE spectroscopy showed that only 0-2.2% of the total amount of organic fluor was explained by the analysed volatile PFASs, and only 0-0.41% by the analysed ionic PFASs. The remaining organic fluor in the study of Robel et al.[40] might be in the fluorotelomer based polymers (FTPs). Since nowadays more than 2,000 different PFASs are present on the market[66], part of the remaining organic fluor might also be non-polymeric PFASs that were not included in the analysis. In our study, only 29 individual PFASs were analysed. It is likely that more non-polymeric PFASs were present in the unexposed samples. Possibly, some of the PFASs that were not analysed in this study could have been degraded or transformed into the volatile PFASs, analysed in our study. It cannot be ruled out that more volatile PFASs were formed and emitted to the air, or to the spray water. Further research with e.g. total organic fluorine analyses, and total oxidizable precursor (TOP) assays[67] is needed to complete the balance on PFASs present before and after weathering.

Another explanation for the increase in the concentrations of volatile PFASs as an effect of the exposure to weather conditions might come from the FTPs. DWR chemistries of outdoor clothing are not based on the individual volatile PFASs, like alcohols and acrylates, but are based on side-chain fluorinated polymers[9]. FTPs can degrade to FTOHs and FTACs in the environment[68]. This was also demonstrated by Washington et al.[69]. They reported degradation of two commercial acrylate-linked FTPs in soil and water and monitored 71 analytes. Fifty of those were detected in the final samples, which made the authors conclude that commercial FTPs can degrade under environmental conditions at levels that are detectable. Additional experiments performed by Washington et al.[69] suggested hydrolysis of the ester linkage of the FTP as

a degradation mechanism, and a follow-up study showed not only an increase of FTOH concentrations, but also of PFCAs [70]. The half-lives reported by Washington and Jenkins were 55 years for 8:2 FTOH and 89 years for 10:2 FTOH at 25°C [70]. Considering the black standard temperature (Table 4-2) during aging in our study was 65°C, it is expected that the half-lives in our study would be much shorter [71]. Based on the studies of Li et al.[68], Washington et al.[69], and Washington and Jenskins[70] not only the increase in the concentrations of volatile PFASs in our study may be explained by the degradation of the DWR polymers themselves, or by hydrolysis of the FTPs, but also the increase of ionic PFASs could be explained by hydrolysis of the FTPs.

Finally, the increase of the volatile PFAS concentrations might also be explained by the NEOF becoming extractable under influence of weather conditions, as described in section 4.3.2.

An overview of potential degradation/transformation pathways of PFASs used in the DWR layer of textiles is shown in Figure 4-3. More research is needed to reveal or confirm the processes which are responsible for the increase in concentration of the analysed PFASs.

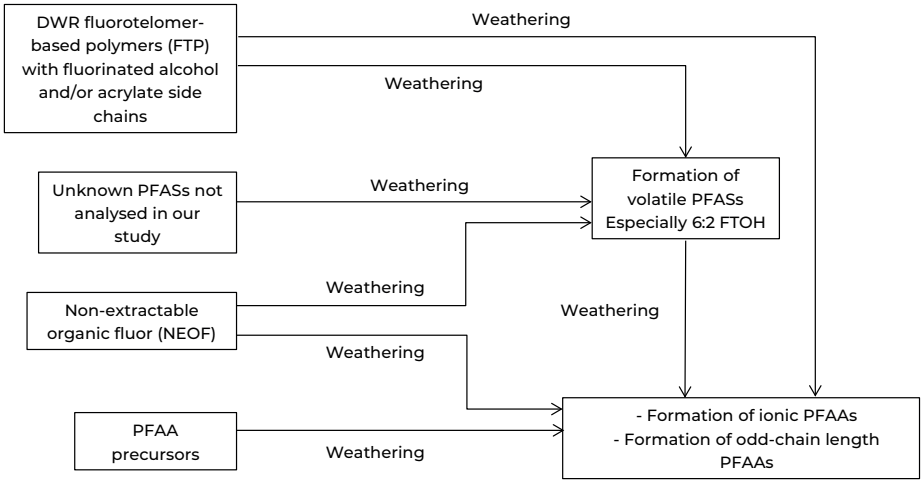

Figure 4-3 Potential degradation pathways of weathering of PFASs used in the DWR layer of textiles.

4.3.3. Implications of weathering

For PFOS and PFOA a content limit is set by the European Commission for products like textiles for outdoor clothing. According to the restriction of PFOS by the European commission in 2006 [18], its concentration in coated materials should be lower than 1 µg/m^2. One of the textiles of our study (Sample No.2) exceeded this limit before weathering, but after aging PFOS was not detected anymore. The EU regulation for PFOA[19] states that, starting 4 July 2023, PFOA and PFOA-related substances shall not be used or placed on the market in textiles used for protective clothing in a concentration equal to or above 25 µg/kg[72]. The original textile products used in this study all fulfilled this criterion for PFOA, but after aging two of the tested fabrics exceeded this limit, with PFOA concentrations of 47 and 170 µg/kg. This means that setting a limit only for PFOA and related substances may not be sufficient to ensure safety. Instead of regulating only PFOA and related substances, all possible precursors of PFOA, including the FTP, should be taken into account when setting criteria.

The leaching of PFASs out of textiles, but also the increase in concentrations of PFOA and other PFASs due to weather conditions might not only have an environmental impact. The use in outdoor clothing may also form a direct exposure route to humans, since there is dermal contact with the textiles. Franko et al.[73] showed in an in vitro study that PFOA can penetrate the human skin. As much as 24% of the applied PFOA dose penetrated the complete skin, and 46% was found in the skin. In an *in vivo* study of mice, Franko et al.[73] also showed that dermal exposure to PFOA caused an increase in PFOA levels in serum. The dermal absorption of PFASs from dust was estimated by Su et al.[74]. They determined an estimated daily intake (EDI) of 0.04-1.79 ng PFOA /kg bw/d for dermal absorption, depending on age. Combining the findings in our study and the dermal uptake determined by Franko et al.*73* a worst case scenario could be calculated for the dermal exposure of humans to PFOA when wearing outdoor clothing.

In our study the highest PFOA concentration detected after aging was 54 µg/m^2 (170 µg/kg). Assuming an average outdoor jacket would consist of approximately 2 m^2 fabric, would result in an absolute amount of 108 µg PFOA in the jacket. In a worst case scenario, a person would be having direct skin contact with the entire fabric of the jacket and all PFOA would be leaching out of the jacket. With 24% of the PFOA penetrating through the skin[73], by wearing this outdoor jacket a person could absorb a maximum of 26 µg PFOA, or ca. 0.4 µg/kg for a person of 70 kg. This is most likely an overestimation as the concentration of leachable PFOA was determined by extracting the material with methanol, whereas leaching of PFOA from the textile in contact with the skin will be much slower.

The health-based safety value for human derived by the Dutch National Institute for Public Health and the Environment (RIVM) is 89 ng/mL PFOA in serum[75], corresponding to 267 µg PFOA in an adult with approximately 3 L serum. The maximum up-take of 26 µg PFOA from wearing the outdoor jacket calculated here would correspond to 10% of this safety limit. Although it is unlikely that a human will be exposed to the total amount of PFOA present in a jacket, and this worst case scenario is also based on the total life time of the jacket, further research is warranted to determine the importance of this possible exposure pathway of PFOA for humans.

4.4. Conclusion

Weather conditions like sunlight, high temperature, or humidity can have an effect on the congener profile and concentrations of PFASs in DWR-treated outdoor clothing. In most samples the PFAA concentrations increased and PFAAs not present in the original textiles were formed during weathering. A possible explanation is degradation of the fluorotelomer alcohols to the PFAAs, or hydrolysis of the FTPs. The concentrations of volatile PFASs also increased. Degradation of the DWR polymers is suggested as one of the possible explanations for this phenomenon. Other possibilities would be non-extractable organic fluor becoming extractable, or unknown precursors degrading or transforming to the analysed volatile PFASs. Further research is needed to unravel the details of these processes and to determine the transformation routes. Total organic fluorine analyses, and TOP assays are suggested to complete the balance on PFASs present before and after weathering. This study shows that setting maximum tolerance limits for a few PFASs alone is not sufficient to control these harmful substances in outdoor clothing.

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References

1. Butt, C. M.; Berger, U.; Bossi, R.; Tomy, G. T., Levels and trends of poly- and perfluorinated compounds in the arctic environment. *Science of The Total Environment* 2010, 408, 2936-2965.
2. Rotander, A.; Kärrman, A.; Bavel, B. v.; Polder, A.; Rigét, F.; Auðunsson, G. A.; Víkingsson, G.; Gabrielsen, G. W.; Bloch, D.; Dam, M., Increasing levels of long-chain perfluorocarboxylic acids (PFCAs) in Arctic and North Atlantic marine mammals, 1984–2009. *Chemosphere* 2012, 86, 278-285.
3. Mørck, T. A.; Nielsen, F.; Nielsen, J. K. S.; Siersma, V. D.; Grandjean, P.; Knudsen, L. E., PFAS concentrations in plasma samples from Danish school children and their mothers. *Chemosphere* 2015, 129, 203-209.
4. Olsen, G. W.; Mair, D. C.; Lange, C. C.; Harrington, L. M.; Church, T. R.; Goldberg, C. L.; Herron, R. M.; Hanna, H.; Nobiletti, J. B.; Rios, J. A.; Reagen, W. K.; Ley, C. A., Per- and polyfluoroalkyl substances (PFAS) in American Red Cross adult blood donors, 2000–2015. *Environmental Research* 2017, 157, 87-95.
5. Cariou, R.; Veyrand, B.; Yamada, A.; Berrebi, A.; Zalko, D.; Durand, S.; Pollono, C.; Marchand, P.; Leblanc, J.-C.; Antignac, J.-P.; Le Bizec, B., Perfluoroalkyl acid (PFAA) levels and profiles in breast milk, maternal and cord serum of French women and their newborns. *Environment International* 2015, 84, 71-81.
6. Yoo, H.; Kannan, K.; Kim, S. K.; Lee, K. T.; Newsted, J. L.; Giesy, J. P., Perfluoroalkyl acids in the egg yolk of birds from Lake Shihwa, Korea. *Environmental Science & Technology* 2008, 42, 5821-5827.
7. Kwadijk, C. J. A. F.; Korytár, P.; Koelmans, A. A., Distribution of perfluorinated compounds in aquatic systems in The Netherlands. *Environmental Science & Technology* 2010, 44, 3746-3751.
8. Buck, R. C.; Franklin, J.; Berger, U.; Conder, J. M.; Cousins, I. T.; de Voogt, P.; Jensen, A. A.; Kannan, K.; Mabury, S. A.; van Leeuwen, S. P. J., Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. *Integrated Environmental Assessment and Management* 2011, 7, 513-541.
9. Holmquist, H.; Schellenberger, S.; van der Veen, I.; Peters, G. M.; Leonards, P. E. G.; Cousins, I. T., Properties, performance and associated hazards of state-of-the-art durable water repellent (DWR) chemistry for textile finishing. *Environment International* 2016, 91, 251-264.
10. US-EPA, America's children and the environment, Third Edition DRAFT Indicators biomonitoring: Perfluorochemicals (PFCs), US-EPA (Environmental Protection Agency), March 2011, 2011; p 38. http://www.epa.gov/ace/ace3draft/draft_pdfs/ACE3PFCsReviewPackage3-02-11.pdf.
11. Stahl, T.; Mattern, D.; Brunn, H., Toxicology of perfluorinated compounds. *Environmental Sciences Europe* 2011, 23, 38.
12. de Vos, M. G.; Huijbregts, M. A. J.; van den Heuvel-Greve, M. J.; Vethaak, A. D.; Van de Vijver, K. I.; Leonards, P. E. G.; van Leeuwen, S. P. J.; de Voogt, P.; Hendriks, A. J., Accumulation of perfluorooctane sulfonate (PFOS) in the food chain of the Western Scheldt estuary: Comparing field measurements with kinetic modeling. *Chemosphere* 2008, 70, 1766-1773.
13. Liu, C.; Chang, V. W. C.; Gin, K. Y. H., Oxidative toxicity of perfluorinated chemicals in green mussel and bioaccumulation factor dependent quantitative structure–

activity relationship. *Environmental Toxicology and Chemistry* 2014, 33, 2323-2332.
14. Olsen, G. W.; Burris, J. M.; Ehresman, D. J.; Froehlich, J. W.; Seacat, A. M.; Butenhoff, J. L.; Zobel, L. R., Half-life of serum elimination of perfluorooctanesulfonate, perfluorohexane-sulfonate, and perfluorooctanoate in retired fluorochemical production workers. *Environmental Health Perspectives* 2007, 115, 1298-1305.
15. Hekster, F. M.; Laane, R. W. P. M.; de Voogt, P., Environmental and toxicity effects of perfluoroalkylated substances. In *Reviews of Environmental Contamination and Toxicology*, Springer New York, New York, NY, 2003, pp 99-121.
16. Lopez-Espinosa, M.-J.; Fletcher, T.; Armstrong, B.; Genser, B.; Dhatariya, K.; Mondal, D.; Ducatman, A.; Leonardi, G., Association of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) with age of puberty among children living near a chemical plant. *Environmental Science & Technology* 2011, 45, 8160-8166.
17. Corsini, E.; Sangiovanni, E.; Avogadro, A.; Galbiati, V.; Viviani, B.; Marinovich, M.; Galli, C. L.; Dell'Agli, M.; Germolec, D. R., In vitro characterization of the immunotoxic potential of several perfluorinated compounds (PFCs). *Toxicology and Applied Pharmacology* 2012, 258, 248-255.
18. EU, Directive 2006/122/EC of the European Parliament and of the Council of 12 December 2006. *Official Journal of the European Union* 2006, L 372/32, 32-34.
19. EU, COMMISSION REGULATION (EU) 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. . *Official Journal of the European Union* 2017, L 150/14.
20. ECHA, European Chemical Agency, Candidate list of substances of very high concern for authorisation. http://echa.europa.eu/web/guest/candidate-list-table (17-12-2014).
21. ECHA, One new substance added to the Candidate List, several entries updated. https://echa.europa.eu/nl/-/one-new-substance-added-to-the-candidate-list (24-07-2017).
22. UNEP, Decision SC-4/17. Listing of perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride. UNEP-POPS-COP.4-SC-4-17, Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants: Geneva, Switzerland, 2009. http://chm.pops.int/TheConvention/ConferenceoftheParties/ReportsandDecisions/tabid/208/Default.aspx.
23. UNEP, Decision: SC-9/12. Listing of perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds. UNEP-POPS-COP.9-SC-9-12, Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants: Geneva, Switzerland, 2019. http://chm.pops.int/TheConvention/ConferenceoftheParties/Meetings/COP9/tabid/7521/ItemId/7235/Default.aspx.
24. UNEP, UNEP, Proposal to list pentadecafluorooctanoic acid (CAS No: 335-67-1, PFOA, perfluorooctanoic acid), its salts and PFOA-related compounds in Annexes A, B and/or C to the Stockholm Convention on Persistent Organic Pollutants, UNEP (United Nations Environment Programme), UNEP/POPS/POPRC.11/5 19–23 October 2015. http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC11/POPRC11Documents/tabid/4573/.

25. EU, COUNCIL DECISION (EU) 2019/639 of 15 April 2019. *Official Journal of the European Union, L 109/22* 24.4.2019.
26. IISD, Summary of the Meetings of the Conferences of the Parties to the Basel, Rotterdam and Stockholm Conventions 29 April – 10 May 2019 | Geneva, Switzerland. *Earth Negotiations Bulletin (ENB)* Volume 15 Number 269, Monday, 13 May 2019.
27. UNEP, UNEP, Proposal to list perfluorohexane sulfonic acid (CAS No: 355-46-4, PFHxS), its salts and PFHxS-related compounds in Annexes A, B and/or C to the Stockholm Convention on Persistent Organic Pollutants, UNEP (United Nations Environment Programme), UNEP/POPS/POPRC.13/4 17–20 October 2017. http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC13/MeetingDocuments/tabid/6024/Default.aspx.
28. Schultz, M. M.; Barofsky, D. F.; Field, J. A., Fluorinated alkyl surfactants. *Environmental Engineering Science* 2003, 20, 487-501.
29. Hill, P. J.; Taylor, M.; Goswami, P.; Blackburn, R. S., Substitution of PFAS chemistry in outdoor apparel and the impact on repellency performance. *Chemosphere* 2017, 181, 500-507.
30. SUPFES, Substitution in Practice of Prioritized Fluorinated Chemicals to Eliminate Diffuse Sources. Formas 2012-11652-24486-65. https://www.ri.se/en/what-we-do/projects/supfes (22-05-2021).
31. Schellenberger, S. The missing links : Towards an informed substitution of durable water repellent chemicals for textiles. Doctoral thesis, comprehensive summary, Department of Environmental Science and Analytical Chemistry, Stockholm University, Stockholm, 2019.
32. SFT, Kartlegging av perfluoralkylstoffer (PFAS) i utvalgte tekstiler, ISBN 82-7655-285-4, TA-2173/2006, Oslo, April 2006, 2006; p 61. http://www.miljodirektoratet.no/old/klif/publikasjoner/kjemikalier/2173/ta2173.pdf.
33. Greenpeace, A little story about the monsters in your closet, Greenpeace International, Beijing, 2014, 2014; p 40. http://www.greenpeace.org/eastasia/Global/eastasia/publications/reports/toxics/2013/A%20Little%20Story%20About%20the%20Monsters%20In%20Your%20Closet%20-%20Report.pdf.
34. Brigden, K.; Hetherington, S.; Wang, M.; Santillo, D.; Johnston, P., Greenpeace, Hazardous chemicals in branded textile products on sale in 25 countries/regions during 2013, Technical Report 06/2013, Greenpeace Research Laboratories, Exeter, UK, December 2013, 2013; p 47. http://www.greenpeace.org/eastasia/Global/eastasia/publications/reports/toxics/2013/A%20Little%20Story%20About%20the%20Monsters%20In%20Your%20Closet%20-%20Technical%20Report.pdf.
35. SNCS, Fluorerade miljögifter i allvädersskläder, 2006.
36. KEMI, Swedish Chemicals Agency, Perfluorinated substances and their uses in Sweden, ISSN: 0284-1185, Swedish Chemicals Agency, ISSN: 0284-1185, 7/06, Stockholm, November 2006, p 60. http://www.kemi.se/Documents/Publikationer/Trycksaker/Rapporter/Report7_06.pdf.
37. Gremmel, C.; Frömel, T.; Knepper, T. P., Systematic determination of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in outdoor jackets. *Chemosphere* 2016, 160, 173-180.

38. Vestergren, R.; Herzke, D.; Wang, T.; Cousins, I. T., Are imported consumer products an important diffuse source of PFASs to the Norwegian environment? *Environmental Pollution* 2015, 198, 223-230.
39. Herzke, D.; Olsson, E.; Posner, S., Perfluoroalkyl and polyfluoroalkyl substances (PFASs) in consumer products in Norway – A pilot study. *Chemosphere* 2012, 88, 980-987.
40. Robel, A. E.; Marshall, K.; Dickinson, M.; Lunderberg, D.; Butt, C.; Peaslee, G.; Stapleton, H. M.; Field, J. A., Closing the mass balance on fluorine on papers and textiles. *Environmental Science & Technology* 2017, 51, 9022-9032.
41. Guo, Z.; Liu, X.; Krebs, K. A.; Roache, N. F., Perfluorocarboxylic acid content in 116 articles of commerce, EPA/600/R-09/033, US-EPA (Environmental Protection Agency), March 2009, p 51. http://www.oecd.org/env/48125746.pdf.
42. Santen, M.; Kallee, U., Chemistry for any weather – Greenpeace tests outdoor clothes for perfluorinated toxins, Greenpeace, Hamburg, 2012, p 44. http://www.greenpeace.org/romania/Global/romania/detox/Chemistry%20for%20any%20weather.pdf.
43. Brigden, K.; Hetherington, S.; Wang, M.; Santillo, D.; Johnston, P., Greenpeace, Hazardous chemicals in branded luxury textile products on sale during 2013, Technical Report 01/2014, Greenpeace Research Laboratories, Exeter, UK, February 2014; p 32. http://www.greenpeace.org/international/Global/international/publications/toxics/2014/Technical-Report-01-2014.pdf.
44. Kallee, U.; Santen, M., Chemistry for any weather – Part II, Executive summary – Outdoor report 2013, 12/2013, Greenpeace, Hamberg, 2013, p 11. http://m.greenpeace.org/italy/Global/italy/report/2013/toxics/ExecSummary_Greenpeace%20Outdoor%20Report%202013_1.pdf.
45. Knepper, T. P.; Frömel, T.; Gremmel, C.; Driezum, I. v.; Weil, H.; Vestergren, R.; Cousins, I., UMWELTBUNDESAMT (UBA), Understanding the exposure pathways of per- and polyfluoralkyl substances (PFASs) via use of PFASs-Containing products – risk estimation for man and environment, (UBA-FB) 001935/E 47/2014, UMWELTBUNDESAMT (UBA), Dessau-Roßlau, July 2014, 2014; p 133. https://www.umweltbundesamt.de/sites/default/files/medien/378/publikationen/texte_47_2014_understanding_the_exposure_pathways_of_per-_and_polyfluoralkyl_substances_pfass_0.pdf.
46. International Standard ISO 105-B10 Exposure method A, Textiles- Test for colour fastness. 2011.
47. International Standard ISO 4892-2, Plastics — Methods of exposure to laboratory light sources — Part 2: Xenon-arc lamps. p 13.
48. ATLAS, Atlas Material Testing Solutions, Weathering Testing Guidebook, Atlas Electric Devices Company. Pub. No. 2062/098/200/AA/03/01. 2001.
49. Van der Veen, I.; Weiss, J. M.; Hanning, A.; de Boer, J.; Leonards, P. E. G., Development and validation of a method for the quantification of extractable perfluoroalkyl acids (PFAAs) and perfluorooctane sulfonamide (FOSA) in textiles. *Talanta* 2016, 147, 8-15.
50. Koch, A.; Aro, R.; Wang, T.; Yeung, L. W. Y., Towards a comprehensive analytical workflow for the chemical characterisation of organofluorine in consumer products and environmental samples. *Trends in Analytical Chemistry* 2019.
51. Schultes, L. Fluorine mass balance in wildlife and consumer products : How much organofluorine are we missing? Doctoral thesis, comprehensive summary,

Department of Environmental Science and Analytical Chemistry, Stockholm University, Stockholm, 2019.
52. Dinglasan, M.J. A.; Ye, Y.; Edwards, E. A.; Mabury, S. A., Fluorotelomer alcohol biodegradation yields poly- and perfluorinated acids. *Environmental Science & Technology* 2004, 38, 2857-2864.
53. Kim, M. H.; Wang, N.; Chu, K. H., 6:2 Fluorotelomer alcohol (6:2 FTOH) biodegradation by multiple microbial species under different physiological conditions. *Applied Microbiology and Biotechnology* 2014, 98, 1831-1840.
54. Wang, N.; Szostek, B.; Buck, R. C.; Folsom, P. W.; Sulecki, L. M.; Gannon, J. T., 8-2 Fluorotelomer alcohol aerobic soil biodegradation: Pathways, metabolites, and metabolite yields. *Chemosphere* 2009, 75, 1089-1096.
55. Wang, N.; Szostek, B.; Buck, R. C.; Folsom, P. W.; Sulecki, L. M.; Capka, V.; Berti, W. R.; Gannon, J. T., Fluorotelomer alcohol biodegradation- direct evidence that perfluorinated carbon chains breakdown. *Environmental Science & Technology* 2005, 39, 7516-7528.
56. Liu, J.; Lee, L. S.; Nies, L. F.; Nakatsu, C. H.; Turco, R. F., Biotransformation of 8:2 fluorotelomer alcohol in soil and by soil bacteria isolates. *Environmental Science & Technology* 2007, 41, 8024-8030.
57. Li, F.; Su, Q.; Zhou, Z.; Liao, X.; Zou, J.; Yuan, B.; Sun, W., Anaerobic biodegradation of 8:2 fluorotelomer alcohol in anaerobic activated sludge: Metabolic products and pathways. *Chemosphere* 2018, 200, 124-132.
58. Russell, M. H.; Himmelstein, M. W.; Buck, R. C., Inhalation and oral toxicokinetics of 6:2 FTOH and its metabolites in mammals. *Chemosphere* 2015, 120, 328-335.
59. Wallington, T. J.; Hurley, M. D.; Xia, J.; Wuebbles, D. J.; Sillman, S.; Ito, A.; Penner, J. E.; Ellis, D. A.; Martin, J.; Mabury, S. A.; Nielsen, O. J.; Sulbaek Andersen, M. P., Formation of C7F15COOH (PFOA) and other perfluorocarboxylic acids during the atmospheric oxidation of 8:2 fluorotelomer alcohol. *Environmental Science & Technology* 2006, 40, 924-930.
60. Ellis, D. A.; Martin, J. W.; De Silva, A. O.; Mabury, S. A.; Hurley, M. D.; Sulbaek Andersen, M. P.; Wallington, T. J., Degradation of fluorotelomer alcohols: A likely atmospheric source of perfluorinated carboxylic acids. *Environmental Science & Technology* 2004, 38, 3316-3321.
61. Taniyasu, S.; Yamashita, N.; Yamazaki, E.; Petrick, G.; Kannan, K., The environmental photolysis of perfluorooctanesulfonate, perfluorooctanoate, and related fluorochemicals. *Chemosphere* 2013, 90, 1686-1692.
62. Wang, Z.; Cousins, I. T.; Scheringer, M., Comment on “The environmental photolysis of perfluorooctanesulfonate, perfluorooctanoate, and related fluorochemicals”. *Chemosphere* 2015, 122, 301-303.
63. Hori, H.; Hayakawa, E.; Einaga, H.; Kutsuna, S.; Koike, K.; Ibusuki, T.; Kiatagawa, H.; Arakawa, R., Decomposition of environmentally persistent perfluorooctanoic acid in water by photochemical approaches. *Environmental Science & Technology* 2004, 38, 6118-6124.
64. Hori, H.; Yamamoto, A.; Koike, K.; Kutsuna, S.; Osaka, I.; Arakawa, R., Photochemical decomposition of environmentally persistent short-chain perfluorocarboxylic acids in water mediated by iron(II)/(III) redox reactions. *Chemosphere* 2007, 68, 572-578.
65. Kongpran, J.; Tanaka, S.; Fujii, S.; Suzuki, Y.; Sakui, N.; Saito, N., Wet deposition and photodegradation of perfluoroalkyl carboxylates and fluorotelomer alcohols:

Distribution pathways from air to water environment. *Journal of Water and Environment Technology* 2014, 12, 481-499.
66. KEMI, Swedish Chemicals Agency, Perfluorinated substances and their uses in Sweden, Occurrence and use of highly fluorinated substances and alternatives, Report from a government assignment, kemi, Stockholm, 2015, 2015; p 114.
67. Zhang, C.; Hopkins, Z. R.; McCord, J.; Strynar, M. J.; Knappe, D. R. U., Fate of Per- and Polyfluoroalkyl Ether Acids in the Total Oxidizable Precursor Assay and Implications for the Analysis of Impacted Water. *Environ. Sci. Tech. Let.* 2019, 6, 662-668.
68. Li, L.; Liu, J.; Hu, J.; Wania, F., Degradation of fluorotelomer-based polymers contributes to the global occurrence of fluorotelomer alcohol and perfluoroalkyl carboxylates: A combined dynamic substance flow and environmental fate modeling analysis. *Environmental Science & Technology* 2017, 51, 4461-4470.
69. Washington, J. W.; Jenkins, T. M.; Rankin, K.; Naile, J. E., Decades-scale degradation of commercial, side-chain, fluorotelomer-based polymers in soils and water. *Environmental Science & Technology* 2015, 49, 915-923.
70. Washington, J. W.; Jenkins, T. M., Abiotic hydrolysis of fluorotelomer-based polymers as a source of perfluorocarboxylates at the global scale. *Environ. Sci. Technol.* 2015, 49, 14129.
71. Tebes-Stevens, C.; Patel, J. M.; Jones, W. J.; Weber, E. J., Prediction of hydrolysis products of organic chemicals under environmental pH conditions. *Environmental Science & Technology* 2017, 51, 5008-5016.
72. ChemsafetyPRO, Perfluorooctanoic acid (PFOA), its salts and PFOA-related substances. http://www.chemsafetypro.com/Topics/Restriction/Perfluorooctanoic_acid_PFOA_its_salts_and_related_substances.html (24-07-2017).
73. Franko, J.; Meade, B. J.; Frasch, H. F.; Barbero, A. M.; Anderson, S. E., Dermal penetration potential of perfluorooctanoic acid (PFOA) in human and mouse skin. *Journal of Toxicology and Environmental Health, Part A* 2012, 75, 50-62.
74. Su, H.; Lu, Y.; Wang, P.; Shi, Y.; Li, Q.; Zhou, Y.; Johnson, A. C., Perfluoroalkyl acids (PFAAs) in indoor and outdoor dusts around a mega fluorochemical industrial park in China: Implications for human exposure. *Environment International* 2016, 94, 667-673.
75. Zeilmaker, M. J., Janssen, P., Versteegh, A., van Pul, A., de Vries, W., Bokkers, B., Wuijts, S., Oomen, A., Herremans, J., Risicoschatting emissie PFOA voor omwonenden, Locatie: DuPont/Chemours, Dordrecht, Nederland, Dutch National Institute for Public Health and the Environment (RIVM) 2016, 2016; p 65. https://cms.dordrecht.nl/Dordrecht/up/ZwbbqamJC_ZmbjknlJaB_rivm-briefrapport-2016-0049-risicoschatting-emissie-pfoa-voor-omwonenden.pdf.

Supporting Information

S4-1. PFAS analysis of samples

The data in the Tables S4-1.1 and S4-1.2 show the general information of the compounds analysed in this study. In Table S41.1 the PFAAs are given and in Table S4-1.2 the volatile PFASs are shown. In the Tables S4-1.3 and S4-1.4 the instrumental settings for the analyses are given.

Table S4-1.1 Full names, acronyms, chemical formula and CAS numbers of PFAAs analysed in this study and their isotope-labeled ISs.

Compounds	Abbreviation	Formula	CAS No.
Perfluorobutanoic acid	PFBA	C_3F_7COOH	375-22-4
Perfluoropentanoic acid	PFPeA	C_4F_9COOH	2706-90-3
Perfluorohexanoic acid	PFHxA	$C_5F_{11}COOH$	307-24-4
Perfluoroheptanoic acid	PFHpA	$C_6F_{13}COOH$	375-85-9
Perfluorooctanoic acid	PFOA	$C_7F_{15}COOH$	335-67-1
Perfluorononanoic acid	PFNA	$C_8F_{17}COOH$	375-95-1
Perfluorodecanoic acid	PFDA	$C_9F_{19}COOH$	335-76-2
Perfluoroundecanoic acid	PFUnDA	$C_{10}F_{21}COOH$	2058-94-8
Perfluorododecanoic acid	PFDoDA	$C_{11}F_{23}COOH$	307-55-1
Perfluorotridecanoic acid	PFTrDA	$C_{12}F_{25}COOH$	72629-94-8
Perfluorotetradecanoic acid	PFTeDA	$C_{13}F_{27}COOH$	376-06-7
Perfluorobutane sulfonate anion	PFBS	$C_4F_9SO_3^-$	45187-15-3
Perfluorohexane sulfonate anion	PFHxS	$C_6F_{13}SO_3^-$	108427-53-8
Perfluoroheptane sulfonate anion	PFHpS	$C_7F_{15}SO_3^-$	375-92-8
Perfluorooctane sulfonate anion	PFOS	$C_8F_{17}SO_3^-$	45298-90-6
Perfluorooctane sulfonamide	FOSA	$C_8F_{17}SO_2NH_2$	754-91-6
4:2 Fluorotelomer sulfonic acid	4:2 FTSA	$C_4F_9CH_2CH_2SO_3H$	757124-72-4
6:2 Fluorotelomer sulfonic acid	6:2 FTSA	$C_6F_{13}CH_2CH_2SO_3H$	27619-97-2
8:2 Fluorotelomer sulfonic acid	8:2 FTSA	$C_8F_{17}CH_2CH_2SO_3H$	39108-34-4
Isotope-Labeled PFAAs			
Perfluoro-n-[1,2,3,4-$^{13}C_4$]butanoic acid	$^{13}C_4$-PFBA		na
Perfluoro-n-[1,2,3,4,5-$^{13}C_5$]pentanoic acid	$^{13}C_5$-PFPeA		na
Perfluoro-n-[1,2-$^{13}C_2$]hexanoic acid	$^{13}C_2$-PFHxA		na
Perfluoro-n-[1,2,3,4-$^{13}C_4$]heptanoic acid	$^{13}C_4$-PFHpA		na
Perfluoro-n-[1,2,3,4-$^{13}C_4$]octanoic acid	$^{13}C_4$-PFOA		na
Perfluoro-n-[1,2,3,4,5-$^{13}C_5$]nonanoic acid	$^{13}C_5$-PFNA		na
Perfluoro-n-[1,2-$^{13}C_2$]decanoic acid	$^{13}C_2$-PFDA		na
Perfluoro-n-[1,2-$^{13}C_2$]undecanoic acid	$^{13}C_2$-PFUnDA		na
Perfluoro-n-[1,2-$^{13}C_2$]dodecanoic acid	$^{13}C_2$-PFDoDA		na
Perfluoro-1-hexane[$^{18}O_2$]sulfonate anion	$^{18}O_2$-PFHxS		na
Perfluoro-1-[1,2,3,4-$^{13}C_4$]octane sulfonate anion	$^{13}C_4$-PFOS		na
Perfluoro-1-[$^{13}C_8$]octane sulfonamide	$^{13}C_8$-FOSA		na
$^{13}C_2$ 6:2 Fluorotelomer sulfonic acid	$^{13}C_2$-6:2 FTSA		na

na = not available

Table S4-1.2 Full names, acronyms, chemical formula and CAS numbers of volatile PFASs analysed in this study and their isotope-labeled ISs.

Compounds	Abbreviation	Formula	CAS No.
4:2-Fluorotelomer alcohol	4:2 FTOH	$C_4F_9CH_2CH_2OH$	2043-47-2
6:2-Fluorotelomer alcohol	6:2 FTOH	$C_6F_{13}CH_2CH_2OH$	647-42-7
8:2-Fluorotelomer alcohol	8:2 FTOH	$C_8F_{17}CH_2CH_2OH$	678-39-7
10:2-Fluorotelomer alcohol	10:2 FTOH	$C_{10}F_{21}CH_2CH_2OH$	865-86-1
6:2 Fluorotelomer acrylate	6:2 FTAC	$C_6F_{13}CH_2CH_2OC(O)CH=CH_2$	17527-29-6
8:2 Fluorotelomer acrylate	8:2 FTAC	$C_8F_{17}CH_2CH_2OC(O)CH=CH_2$	27905-45-9
10:2 Fluorotelomer acrylate	10:2 FTAC	$C_{10}F_{21}CH_2CH_2OC(O)CH=CH_2$	17741-60-5
6:2 Fluorotelomer methacrylate	6:2 FTMAC	$C_6F_{13}CH_2CH_2OC(O)C(CH_3)=CH_2$	2144-53-8
8:2 Fluorotelomer methacrylate	8:2 FTMAC	$C_8F_{17}CH_2CH_2OC(O)C(CH_3)=CH_2$	1996-88-9
10:2 Fluorotelomer methacrylate	10:2 FTMAC	$C_{10}F_{21}CH_2CH_2OC(O)C(CH_3)=CH_2$	2144-54-9
Isotope-Labeled volatile PFASs			
6:2 Fluorotelomer alcohol-D2	D_2-6:2 FTOH		na
6:2 Fluorotelomer acrylate-D3	D_3-6:2 FTAC		na
6:2 Fluorotelomer methacrylate-D5	D_5-6:2 FTMAC		na

na = not available

Table S4-1.3 Instrumental settings for PFAAs and FOSA analyses.

Abbreviation	MS/MS mass transition (m/z-> m/z)	Fragmentor voltage (V)	Collision energy (V)	Ionization mode	Isotope-labeled standard
PFBA	213.0 → 169.0	60	3	Negative	$^{13}C_4$-PFBA
PFPeA	263.0 → 219.0	60	3	Negative	$^{13}C_5$-PFPeA
PFHxA	313.0 → 269.0	80	3	Negative	$^{13}C_2$-PFHxA
PFHpA	363.1 → 319.0	80	4	Negative	$^{13}C_4$-PFHpA
PFOA	413.0 → 369.0	80	4	Negative	$^{13}C_4$-PFOA
PFNA	463.0 → 419.0	100	5	Negative	$^{13}C_5$-PFNA
PFDA	513.0 → 468.9	100	5	Negative	$^{13}C_2$-PFDA
PFUnDA	562.9 → 518.9	100	6	Negative	$^{13}C_2$-PFUnDA
PFDoDA	613.0 → 568.9	100	7	Negative	$^{13}C_2$-PFDoDA
PFTrDA	663.0 → 618.9	100	7	Negative	$^{13}C_2$-PFUnDA
PFTeDA	712.9 → 668.9	120	4	Negative	$^{13}C_2$-PFDoDA
PFBS	299.0 → 80.0	150	35	Negative	$^{18}O_2$-PFHxS
PFHxS	399.0 → 80.0	200	48	Negative	$^{18}O_2$-PFHxS
PFHpS	449.0 → 80.0	150	45	Negative	$^{18}O_2$-PFHxS
PFOS	499.0 → 80.0	200	48	Negative	$^{13}C_4$-PFOS
FOSA	498.1 → 78.0	200	35	Negative	$^{13}C_8$-FOSA
4:2 FTSA	327.0 → 307.0	127	20	Negative	$^{13}C_2$-6:2 FTSA
6:2 FTSA	427.0 → 407.0	150	25	Negative	$^{13}C_2$-6:2 FTSA
8:2 FTSA	527.0 → 506.9	157	28	Negative	$^{13}C_2$-6:2 FTSA
$^{13}C_4$-PFBA	217.0 → 172.0	60	3	Negative	
$^{13}C_5$-PFPeA	268.0 → 222.9	60	3	Negative	
$^{13}C_2$-PFHxA	315.0 → 270.0	80	3	Negative	
$^{13}C_4$-PFHpA	367.0 → 321.9	80	4	Negative	
$^{13}C_4$-PFOA	416.9 → 371.9	80	4	Negative	
$^{13}C_5$-PFNA	468.0 → 423.0	100	5	Negative	
$^{13}C_2$-PFDA	515.0 → 470.0	100	5	Negative	
$^{13}C_2$-PFUnDA	565.0 → 520.0	100	6	Negative	
$^{13}C_2$-PFDoDA	615.0 → 569.9	100	7	Negative	
$^{18}O_2$-PFHxS	403.0 → 84	200	48	Negative	
$^{13}C_4$-PFOS	503.0 → 80	200	48	Negative	
$^{13}C_8$-FOSA	506.1 → 78	200	35	Negative	
$^{13}C_2$-6:2 FTSA	429.0 → 408.9	150	25	Negative	

Table S4-1.4 Instrumental settings for volatile PFASs analysed.

Abbreviation	Target ion	Qualifier ion
4:2 FTOH	244.0	263.1
6:2 FTOH	344.1	295.1
8:2 FTOH	405.1	463.1
10:2 FTOH	505.1	563.1
6:2 FTAC	418.1	327.0
8:2 FTAC	518.1	427.1
10:2 FTAC	618.1	527.1
6:2 FTMAC	432.2	327.0
8:2 FTMAC	532.0	427.1
10:2 FTMAC	632.0	527.1
D_2-6:2 FTOH	346.1	314.1
D_3-6:2 FTAC	421.1	420.3
D_5-6:2 FTMAC	437.1	438.2

S4-2. PFAS concentrations

PFAS concentrations are quantified in thirteen textiles of outdoor clothing before and after the textiles have been exposed to radiation, humidity, and temperature in an aging device for 300 h. In Table S4-2.1 the PFAA concentrations before and after exposure are given and in Table S4-2.2 the concentrations of volatile PFASs are shown. In Figure S4-2.1 those concentrations are graphically presented as well.

Table S4-2.1 PFAA concentrations quantified in thirteen textile samples of outdoor clothing before and after aging (µg/m²)*.

Sample No.	aging	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	L-PFBS	L-PFHxS	L-PFHpS	L-PFOS	FOSA	4:2 FTSA	6:2 FTSA	8:2 FTSA
1	before					0,11														
	after					0,28	1,3	0,27	0,69											
2	before			1,3	0,07	2,9	0,05	0,10						0,89		3,24			0,03	
	after	0,67		1,4	2,1	0,22	0,14	0,17												
3	before																			
	after				0,16		0,13													
4	before					0,03														
	after					0,06		0,07												
5	before	0,14		0,31	0,08	0,84	0,08	1,3		1,6		0,26		0,11						
	after	0,79	0,42	3,1	1,3	8,5	12	11	7,6	9,1	2,7	0,88		0,68						
6	before	0,17		1,2	0,38	3,8	0,29	1,5	0,14	0,47		0,12				0,10				0,03
	after	0,57	0,56	2,8	13	54	100	110	140	61	71	5,7				0,11				0,17
7	before																			
	after																			
8	before			1,2	0,89	0,46	1,1	0,85	0,19											
	after		1,2	6,9	8,0	4,5	3,5	1,6												
9	before	28	0,97	6,4	0,88	0,35							45							1,3
	after	140	3,4	2,8	1,9	0,23	0,63	0,55	0,94	0,52	0,46	0,19	350						1,8	110
10	before	6,5	0,29	1,3	0,40								9,6							
	after	190	27	25	32	0,32	0,15	0,13					130						0,1	0,13
11	before	21	1,0	6,4	1,1	0,42		0,27					43							9,1
	after	54	5,8	2,0	1,6	0,26	0,49	0,42	0,81	0,25	0,27		140						1,8	300
12	before	3,2		0,79																
	after	22	11	31	16	0,59	0,11	0,14					1,7			0,36				0,28
13	before																			
	after	7,1	1,1	2,1	3,0	0,10							0,57	NA						

* Empty cells are non-detects

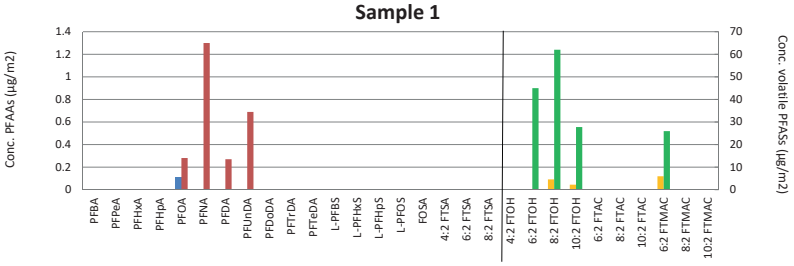
Table S4-2.2 Volatile PFAS concentrations quantified in thirteen textile samples of outdoor clothing before and after aging (µg/m²)*.

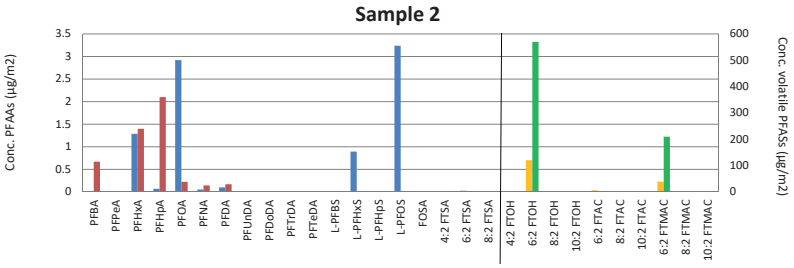
Sample No.	aging	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	6:2 FTAC	8:2 FTAC	10:2 FTAC	6:2 FTMAC	8:2 FTMAC	10:2 FTMAC
1	before			4,6	2,2				6,0		
	after		45	62	28				26		
2	before		120	1,3		6			39		
	after		570						210		
3	before		4,5	0,12	0,38				49		
	after		48						46		
4	before		1,9	2,0	1,6						
	after		31						15		
5	before		350								
	after		74						6,6		
6	before		37	69	73		2,1				
	after		130	477	477				9,9		
7	before		85	14	9,7						
	after		202						38		
8	before		68	18	14				180		
	after		530	69	54				160		
9	before		17	19	10		3,9		26		
	after		98	44	24	1,0	3,7	0,67	50		
10	before		90	2,4	2,7		1,4		4,1		
	after		480				2	2,1	84		
11	before		5,8	2,0	1,8		2,2	0,54	10		
	after		68				2,6		16		
12	before		48	2,5	3,3		1,9	1,1	5,0		
	after		350						37		
13	before		21	0,39	0,53				4,1		
	after		93								

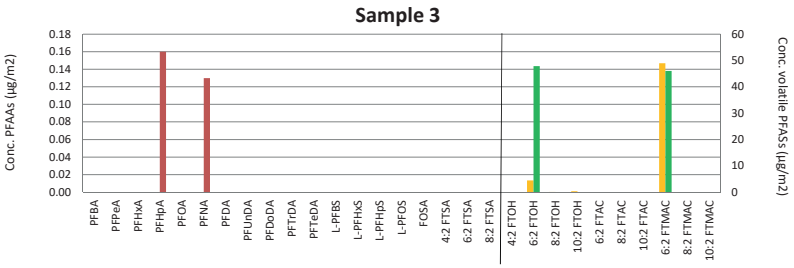
* Empty cells are non-detects

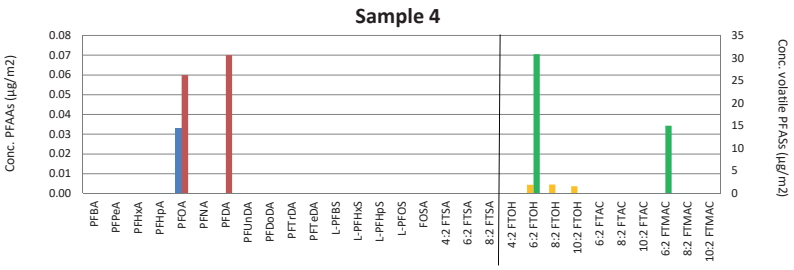
Table S4-2.3 Recoveries of internal standards spiked to the textile samples (%).

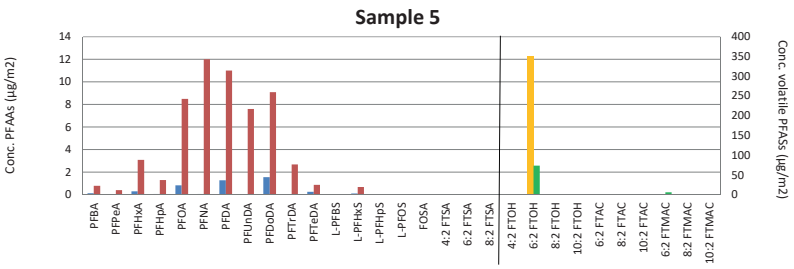
	$^{13}C_4$ PFBA	$^{13}C_5$ PFPeA	$^{13}C_2$ PFHxA	$^{13}C_4$ PFHpA	$^{13}C_4$ PFOA	$^{13}C_5$ PFNA	$^{13}C_2$ PFDA	$^{13}C_2$ PFUnDA	$^{13}C_2$ PFDoDA	$^{18}O_2$ PFHxS	$^{13}C_4$ PFOS	$^{13}C_8$ FOSA	$^{13}C_2$ 6:2 FTSA	D_2-6:2 FTOH	D_3-6:2 FTAC	D_5-6:2 FTM AC
min	13	14	20	24	27	34	32	19	16	40	21	10	49	30	26	31
max	116	130	118	148	203	158	166	131	155	162	128	105	435	173	150	187
median	72	84	86	99	100	95	71	58	46	81	61	29	159	59	55	61

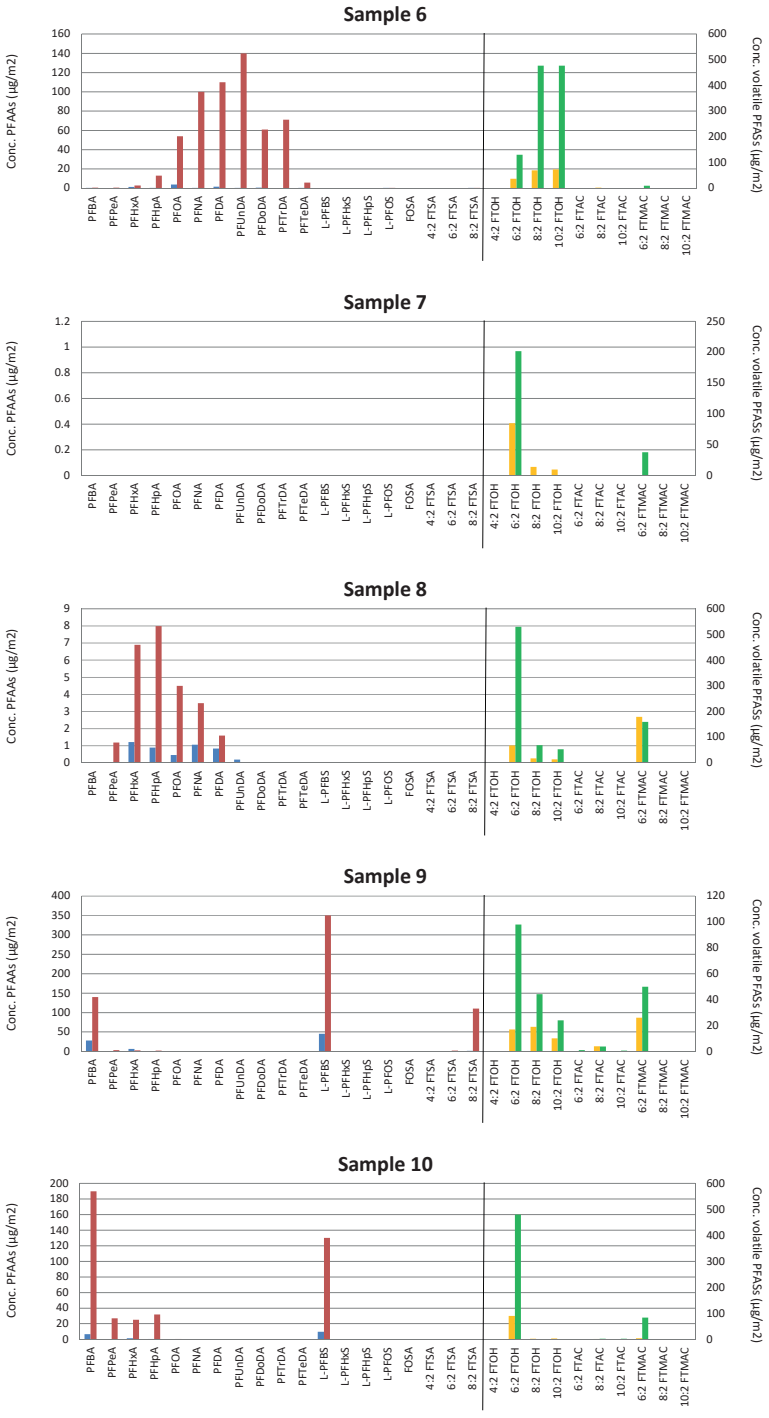

Sample 1
Conc. PFAAs (µg/m2)
Conc. volatile PFASs (µg/m2)
PFBA PFPeA PFHxA PFHpA PFOA PFNA PFDA PFUnDA PFDoDA PFTrDA PFTeDA L-PFBS L-PFHxS L-PFHpS L-PFOS FOSA 4:2 FTSA 6:2 FTSA 8:2 FTSA 4:2 FTOH 6:2 FTOH 8:2 FTOH 10:2 FTOH 6:2 FTAC 8:2 FTAC 10:2 FTAC 6:2 FTMAC 8:2 FTMAC 10:2 FTMAC


Sample 2
Conc. PFAAs (µg/m2)
Conc. volatile PFASs (µg/m2)
PFBA PFPeA PFHxA PFHpA PFOA PFNA PFDA PFUnDA PFDoDA PFTrDA PFTeDA L-PFBS L-PFHxS L-PFHpS L-PFOS FOSA 4:2 FTSA 6:2 FTSA 8:2 FTSA 4:2 FTOH 6:2 FTOH 8:2 FTOH 10:2 FTOH 6:2 FTAC 8:2 FTAC 10:2 FTAC 6:2 FTMAC 8:2 FTMAC 10:2 FTMAC


Sample 3
Conc. PFAAs (µg/m2)
Conc. volatile PFASs (µg/m2)
PFBA PFPeA PFHxA PFHpA PFOA PFNA PFDA PFUnDA PFDoDA PFTrDA PFTeDA L-PFBS L-PFHxS L-PFHpS L-PFOS FOSA 4:2 FTSA 6:2 FTSA 8:2 FTSA 4:2 FTOH 6:2 FTOH 8:2 FTOH 10:2 FTOH 6:2 FTAC 8:2 FTAC 10:2 FTAC 6:2 FTMAC 8:2 FTMAC 10:2 FTMAC


Sample 4
Conc. PFAAs (µg/m2)
Conc. volatile PFASs (µg/m2)
PFBA PFPeA PFHxA PFHpA PFOA PFNA PFDA PFUnDA PFDoDA PFTrDA PFTeDA L-PFBS L-PFHxS L-PFHpS L-PFOS FOSA 4:2 FTSA 6:2 FTSA 8:2 FTSA 4:2 FTOH 6:2 FTOH 8:2 FTOH 10:2 FTOH 6:2 FTAC 8:2 FTAC 10:2 FTAC 6:2 FTMAC 8:2 FTMAC 10:2 FTMAC


Sample 5
Conc. PFAAs (µg/m2)
Conc. volatile PFASs (µg/m2)
PFBA PFPeA PFHxA PFHpA PFOA PFNA PFDA PFUnDA PFDoDA PFTrDA PFTeDA L-PFBS L-PFHxS L-PFHpS L-PFOS FOSA 4:2 FTSA 6:2 FTSA 8:2 FTSA 4:2 FTOH 6:2 FTOH 8:2 FTOH 10:2 FTOH 6:2 FTAC 8:2 FTAC 10:2 FTAC 6:2 FTMAC 8:2 FTMAC 10:2 FTMAC


Sample 6
Sample 7
Sample 8
Sample 9
Sample 10
Conc. PFAAs (µg/m2)
Conc. volatile PFASs (µg/m2)
PFBA
PFPeA
PFHxA
PFHpA
PFOA
PFNA
PFDA
PFUnDA
PFDoDA
PFTrDA
PFTeDA
L-PFBS
L-PFHxS
L-PFHpS
L-PFOS
FOSA
4:2 FTSA
6:2 FTSA
8:2 FTSA
4:2 FTOH
6:2 FTOH
8:2 FTOH
10:2 FTOH
6:2 FTAC
8:2 FTAC
10:2 FTAC
6:2 FTMAC
8:2 FTMAC
10:2 FTMAC

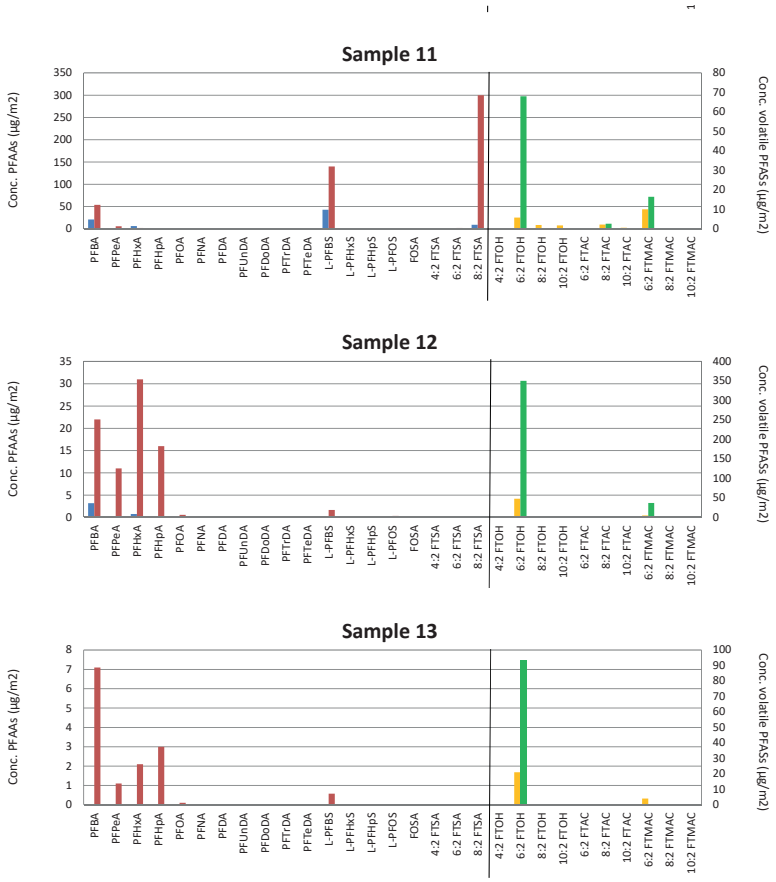


Figure S4-2.1 PFAS concentrations quantified in thirteen textile samples of outdoor clothing. Concentrations of ionic PFASs (■before; ■after) in µg/m² on the left y-axis. Concentrations of volatile PFASs (■before; ■after) in µg/m² on the right y-axis.

S4-3. Quality control

Recovery

To assess the recovery of the method, two textile samples were fortified with volatile PFASs at two different levels (50 and 500 µg/m^2) in triplicate. The unfortified textile samples (in triplicate), and the fortified textiles were extracted and analysed for the concentration of volatile PFASs. Calculation of the recovery of the volatile PFASs is given in Equation 1:

Equation 1: **Recovery= (C_f - C_{Uf})/C_a* 100 %**

C_f	**=**	**Mean PFAS concentration of fortified textile samples (µg/m^2)**
C_{Uf}	**=**	**Mean PFAS concentration of unfortified textile samples (µg/m^2)**
C_a	**=**	**Added PFAS concentration (µg/m^2)**

Repeatability

The unfortified, and fortified textile samples of the recovery assessment were extracted and analyzed in triplicate for the concentration of volatile PFASs. Repeatabilities were given as the relative standard deviation (RSD) of the results of the triplicate analyses as calculated in Equation 2:

Equation 2: **RSD = st.dev./mean * 100 %**

RSD	**=**	**Relative standard deviation**
St.dev.	**=**	**Standard deviation**

LOD/ LOQ

The limit of detection (LOD) was calculated per compound per sample as three times the noise divided by the sample intake and corrected for the recovery of the internal standard as given in Equation 3:

Equation 3: **LOD = (3 * N/rec)/X**

LOD	**=**	**Limit of detection (µg/m^2)**
N	**=**	**noise (µg)**
Rec	**=**	**recovery**
X	**=**	**sample intake (m^2)**

The limit of quantification (LOQ) was calculated as 3.3 times the LOD.

S4-4. Homogeneity of PFASs in commercial textiles

Homogeneity tests of PFAAs have been performed on pieces of textiles originating from four fabrics of commercial outdoor clothing. Results showed that the homogeneity differs per fabric, but can also differ per piece of the same fabric.

Fabric No.1 and No.2 consisted each out of two pieces, which is shown in Figures S4-4.1 and S4-4.3. Fabric No.3 consisted of one piece of textile (Figure S4-4.5), and Fabric No.4 consisted of 5 pieces of textile (Figure S4-4.7), each originating from the same fabric of outdoor clothing. The numbers in the picture represent the positions of which the samples for the homogeneity tests have been taken. The results of the homogeneity testing are shown in Figures S4-4.2, S4-4.4, S4-4.6 and S4-4.8.

Fabric No. 1

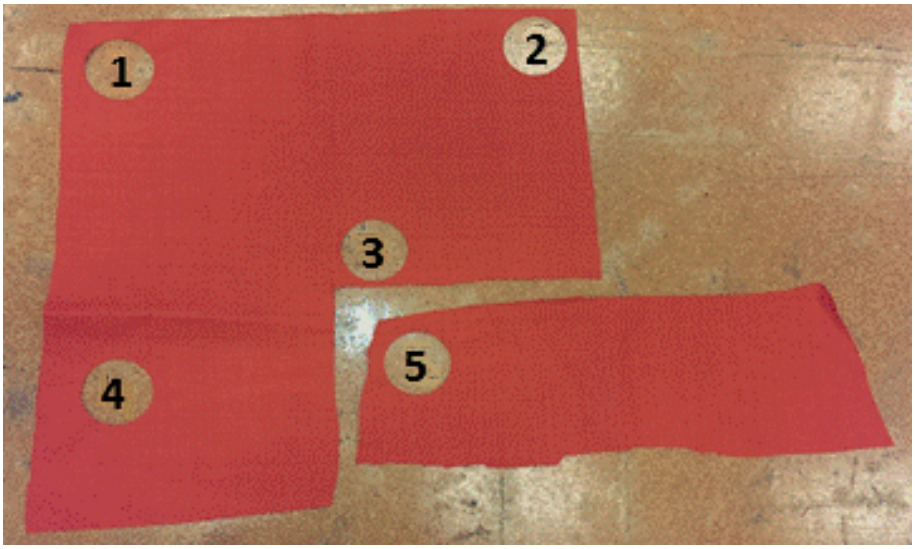


Figure S4-4.1 Picture of Fabric No. 1. The numbers 1-5 represent the positions of which the samples are taken for homogeneity testing.

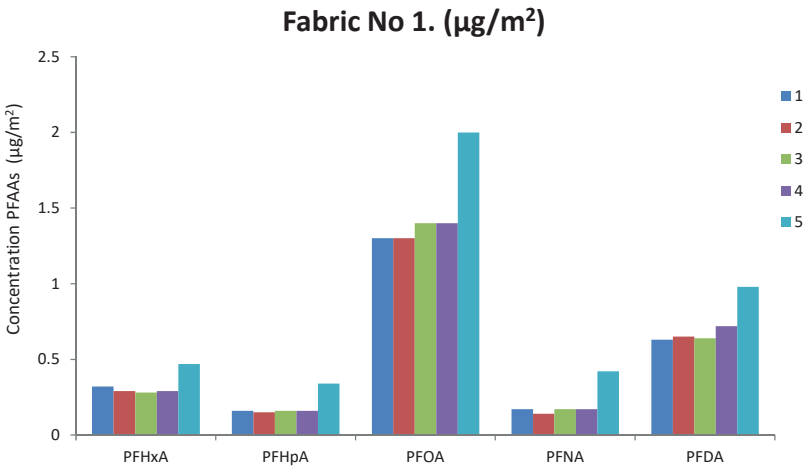


Figure S4-4.2 PFAA concentrations (µg/m²) of Fabric No.1. The numbers 1-5 represent the positions of which the samples are taken for homogeneity testing.

Of Fabric No.1. four samples were analysed out of the first piece and one sample out of the second piece (Figure S4-4.1). The relative standard deviations (RSDs) for the individual PFASs over all samples were 20-54%, with a maximum of a factor 3 between the lowest and highest concentration quantified for an individual PFAS congener. Excluding the second piece of Fabric No.1 (i.e. sample 5) results in RSDs of 3.2-9.2%, and a maximum factor difference of 1.2 between the lowest and highest concentration. Out of this it can be concluded that even though samples out of one piece of fabric can show a certain amount of homogeneity, there can be an inhomogeneity between pieces of fabric, which originate from the same outdoor clothing.

Fabric No. 2

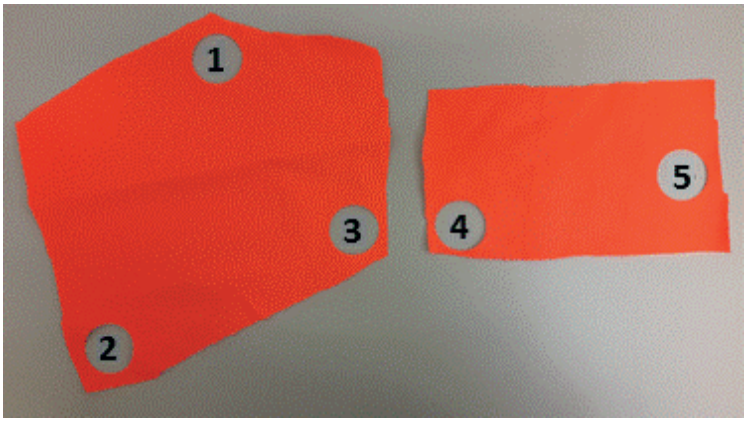


Figure S4-4.3 Picture of Fabric No. 2. The numbers 1-5 represent the positions of which the samples are taken for homogeneity testing.

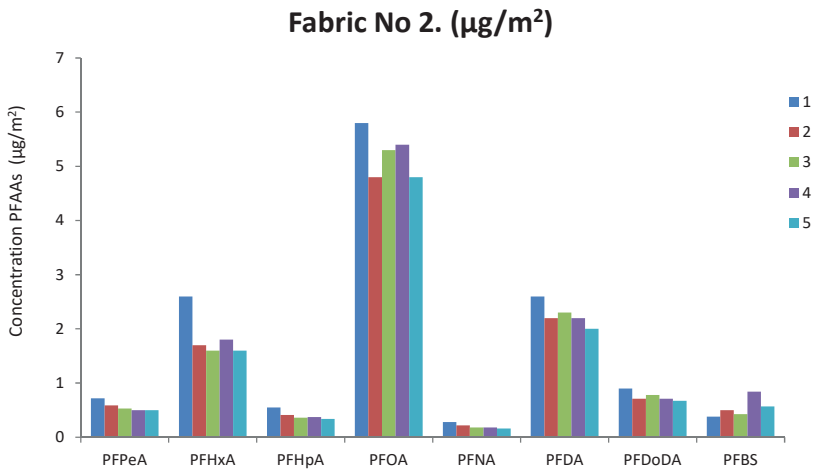


Figure S4-4.4 PFAA concentrations (µg/m²) of Fabric No.2. The numbers 1-5 represent the positions of which the samples are taken for homogeneity testing.

Of Fabric No.2. three samples were analysed out of the first piece and two sample out of the second piece (Figure S4-4.3). The RSDs for the individual PFASs over all samples were 8-33%, with a maximum of a factor 2.2 between the lowest and highest concentration quantified for an individual PFAS congener.

Fabric No. 3

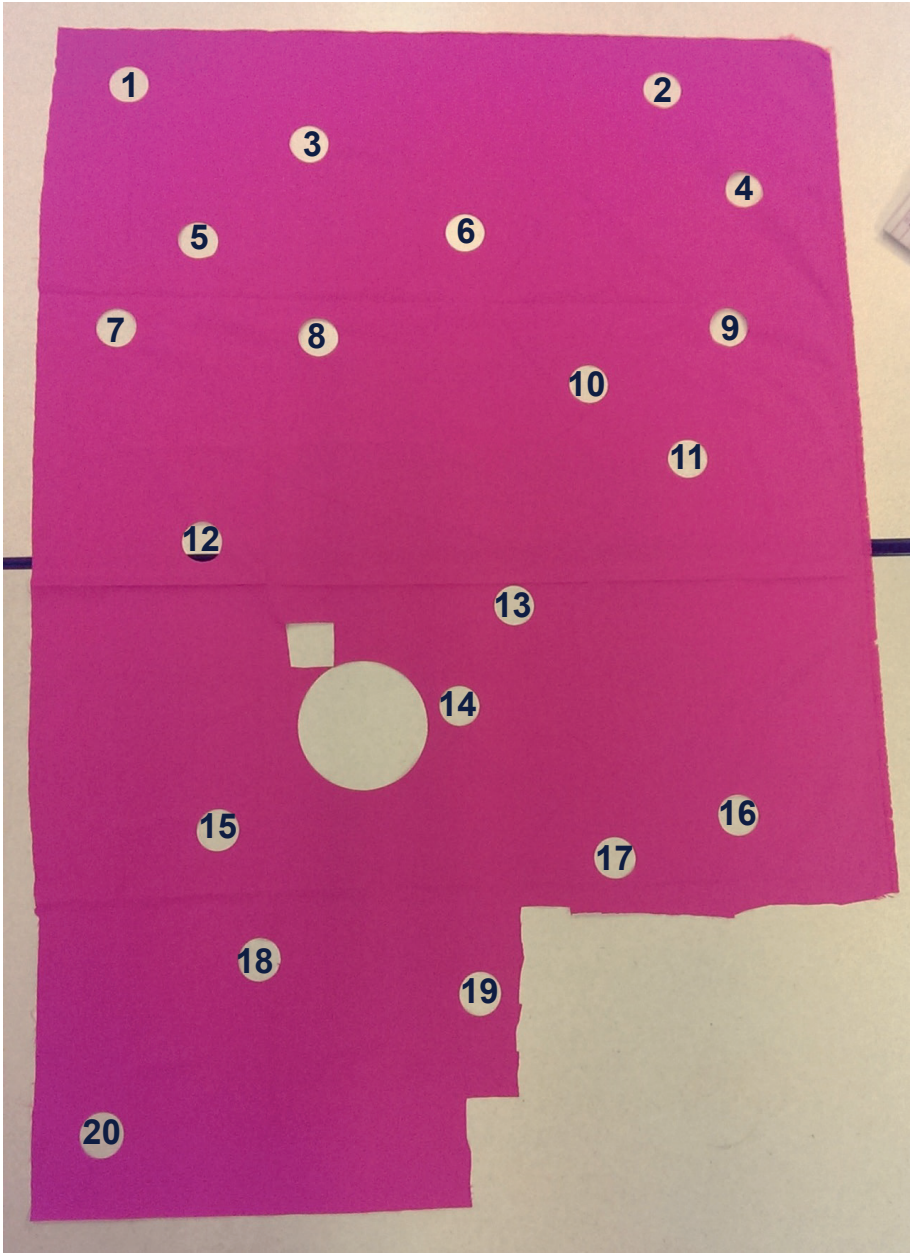


Figure S4-4.5 Picture of Fabric No. 3. The numbers 1-20 represent the positions of which the samples are taken for homogeneity testing.

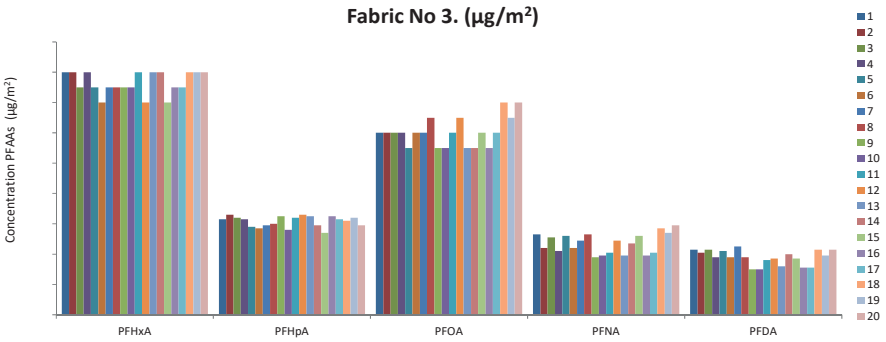


Figure S4-4.6 PFAA concentrations (µg/m²) of Fabric No.3. The numbers 1-20 represent the positions of which the samples are taken for homogeneity testing.

Of Fabric No.3 a bigger piece of textile was available (Figure S4-4.5). Twenty samples were analyses, resulting in RSDs of 4.8-14% for PFASs present > LOQ, with a maximum factor difference of 1.6 between the lowest and highest concentration quantified for an individual PFAS congener.

Fabric No. 4

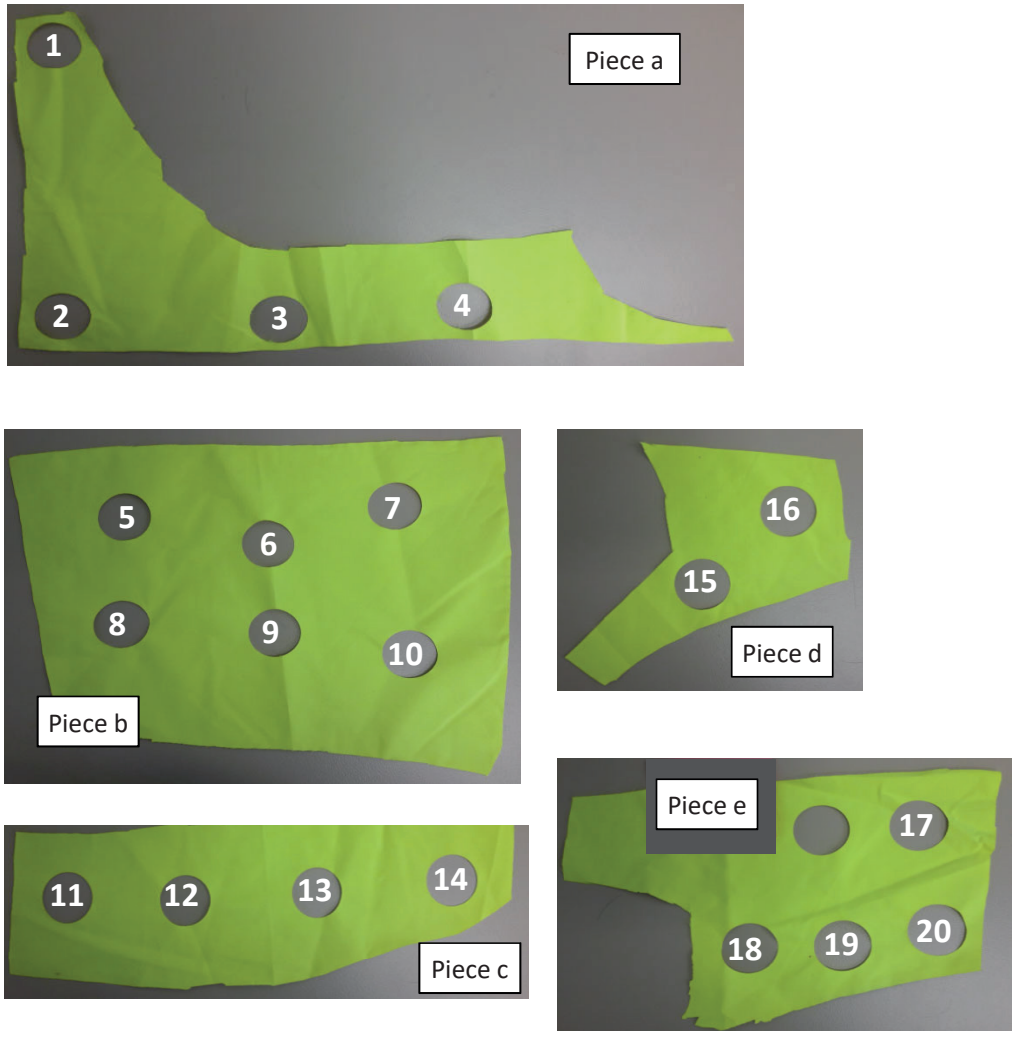


Figure S4-4.7 Picture of Fabric No. 4. The numbers 1-20 represent the positions of which the samples are taken for homogeneity testing.

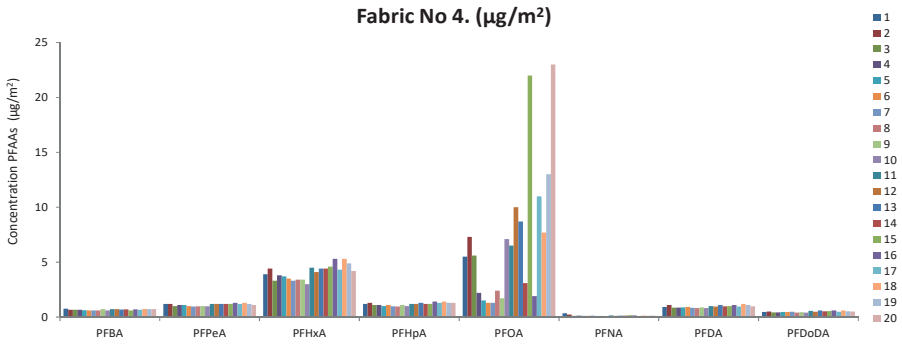


Figure S4-4.8 PFAA concentrations (µg/m²) of Fabric No.4. The numbers 1-20 represent the positions of which the samples are taken for homogeneity testing.

Five pieces were available of Fabric No.4 (Figure S4-4.7), of which 20 samples were taken in total. The fabric appeared to be inhomogeneous for especially PFOA and PFNA with RSDs of 88 and 44% respectively. Concentrations of PFOA in this fabric ranged between 1.3 and 23 µg/m² and concentration of PFNA ranged from 0.09- 0.35 µg/m². For this fabric not only between the five pieces inhomogeneity was shown, but also within the pieces. For example, PFOA concentrations in Piece d (Figure S4-4.7) were 22 µg/m² for sample 15 and 1.9 µg/m² for sample 16.

Chapter 5.

Ike van der Veen[a]

Steffen Schellenberger[b,c]

Anne-Charlotte Hanning[d]

Ann Stare[d]

Jacob de Boer[a]

Jana M. Weiss[b]

Pim E.G. Leonards[a]

[a] Vrije Universiteit, De Boelelaan 1085, 1081 HV, Amsterdam, The Netherlands

[b] Department Environmental Science (ACES), Stockholm University, Svante Arrheniusv. 8, SE-11418 Stockholm, Sweden

[c] RISE, Research Institutes of Sweden, Brinellvägen 68, 100 44 Stockholm, Sweden

[d] RISE IVF AB, Argongatan 30, SE-431 53, Mölndal, Sweden

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The fate of per- and polyfluoroalkyl substances (PFASs) from durable water repellent (DWR) clothing during use

Abstract

To make outdoor clothing water- or dirt-repellent, durable water repellent (DWR) coatings based on side-chain fluorinated polymers (SFPs) are used. During use of the outdoor clothing per- and polyfluoroalkyl substances (PFASs) can be emitted from the DWR to the environment. In this study, the effect of aging, washing and tumble drying on the concentration of extractable PFASs in DWR of perfluorohexane-based short-chain SFPs (FC-6 chemistry) and of perfluorooctane-based SFPs long-chain SFP (FC-8 chemistry) were assessed. For this purpose, polyamide (PA) and polyester (PES) fabrics were coated with FC-6 and FC-8 based DWRs. Results show that aging of the coated fabrics causes an increase in concentration and formation of perfluoroalkyl acids (PFAAs). The effect of aging on the volatile PFASs depends on the type of fabric. Washing causes a decrease in PFAA concentrations, and in general volatile PFASs are partly washed out of the textiles. However, washing can also increase the extractable concentration of volatile PFASs in the fabrics. This effect becomes stronger by a combination of aging and washing. Tumble drying does not affect the PFAS concentrations on textiles. In conclusion aging and washing of fabrics coated with DWR based on SFPs releases PFASs to the environment.

5.1. Introduction

In outdoor clothes and work wear for protection (e.g. for fire fighter, emergency medical service) side-chain fluorinated polymers (SFPs) are being used because of their water- and oil resistant properties. SFPs consist of polymers such as polyurethanes or acrylates with per- and polyfluoroalkyl substances (PFASs) as side-chains. These side-chains stick out like teeth on a comb and are usually bases on fluorotelomer alcohols (FTOHs), fluorotelomer acrylates (FTACs) and fluorotelomer methacrylates (FTMACs)[1, 2]. By abiotic and biotic degradation, FTOHs, FTACs, and FTMAC can degrade and (bio)transform into perfluoroalkyl acids (PFAAs), which are very persistent and very mobile in the environment[3-12]. Some PFASs, such as perfluorooctanoic acid (PFOA), have shown to cause adverse health effects, like liver damage, increased cholesterol levels, and a lower immune response after vaccination[13, 14]. Because of the high persistence of PFASs, industries started to phase out the use of some of longer-chain perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs)[1, 15, 16]. This led to the production and use of alternative compounds to obtain the required durable water repellency (DWR) for outdoor clothing, and work wear. Some of the alternatives now brought to the market were silicones and waxes, but also shorter-chain PFASs[1, 2, 17]. To assess the emissions of DWR components, e.g. old-fashioned but phased out long-chain PFASs, and alternative chemistries to the environment, and to assess the functionality of the alternatives compared to long-chain PFASs the SUPFES (Substitution in Practice of Prioritized Fluorinated Chemicals to Eliminate Diffuse Sources) project was initiated in 2013[18]. After assessing the performance of different types of DWR, it was concluded by Schellenberger et al.[2], that the alternative chemistries, like silicones or waxes, could deliver the desired water repellence. However, it was not possible to achieve the oil- and dirt-repellence properties that PFASs can deliver. Although the DWR coating of fabrics consists mainly of SFPs[1, 19] after coating some unreacted ionic or volatile PFAS residuals or impurities might still be present on the fabrics[20]. Several studies are published on PFAS concentrations in textiles[20-31] and a variety of studies are published on the emission of PFASs to the environment[32-39]. Recently, it has been reported that aging of textiles is one of factors that influence the fate of PFASs in outdoor clothing during use[20]. Aging of textiles with a DWR based PFAS chemistry can lead to an increase in some of the extractable PFAS concentrations. DWRs can contain known and unknown impurities from production which are precursors of PFAAs. A possible explanation of the increase in concentrations of extractable PFASs by aging might be that some of the unknown impurities are transformed, or degraded by aging into some of the target PFASs. Other possibilities for emission is sidechain cleavage of the SFPs, or the release of non-extractable organic fluorine (NEOF). Other factors influencing the fate of PFASs during the use of outdoor clothing are washing

and tumble drying of the clothing. Although the effect of aging on PFASs in DWR of textiles of outdoor clothing has been described previously[20], to the best of our knowledge, the effects of washing and tumble drying in combination with aging on PFASs in DWR coated textiles have not been assessed before. Commercially available textiles of outdoor clothing are less suitable to make a good comparison between different DWR chemistries, because it is often unknown what type of DWR chemistry was applied on those textiles, and which other additives are present. Therefore, in the SUPFES project[18] two fabrics, a polyamide (PA) and a polyester (PES) textile, have been coated with different PFAS based DWR formulations provided by major raw material suppliers of DWR chemicals and by following processes close to conditions used by textile manufactures[2]. In our study, the textiles were subjected to accelerated weathering under laboratory conditions, simulating the outdoor exposure of textiles to weather conditions, and a number of washing plus tumble drying cycles. Within the SUPFES project[18] the functionality of those textiles before and after aging, washing and tumble drying was assessed[2]. The aim of the present study was to assess the effect of washing, tumble drying, and aging on the PFASs in the DWR of perfluorohexane-based short-chain SFP (FC-6 chemistry) coated textiles compared to the effect on the PFASs in the old-fashioned but phased out perfluorooctane-based long-chain SFP (FC-8 chemistry) coated textiles. A comparison was made between the concentration and identity of PFASs before and after aging, washing and tumble drying cycles. A perfluorobutane-based SFP (FC-4 chemistry) coated PES fabric was evaluated for homogeneity to demonstrate the quality of the coating method applied in the project. The studied PFASs are; the ionic PFAAs including the C_4-C_{14} PFCAs, and the C_4, C_6, C_7, and C_8 PFSAs. The volatile PFASs studied are the n:2 FTOHs (4:2, 6:2, 8:2, 10:2), the n:2 FTACs (6:2, 8:2, 10:2), and the n:2 FTMACs (6:2, 8:2, 10:2).

5.2. Materials and methods

The effect of aging, washing and tumble drying on PFASs in DWR coated fabrics was assessed on four DWR coated fabrics. Aging of textiles is time consuming, and can only be performed on small pieces of textiles, which are needed in total for PFAS analysis to meet the limit of detection (LOD). Also, performing multiple washing plus tumble drying cycles according to ISO protocols is time consuming. In addition, the coated fabrics were needed for additional performance testing as well[2]. This together resulted in a limited available amount of treated fabrics. Due to this, the current study was based on single experiments and analyses and statistical evaluations were not possible to perform. However, all treatments were performed according to ISO standards EN-ISO 6330:2012[40], and EN-ISO 4992:2013[41]. In addition, to secure the

same results. the washing machine was calibrated and checked concerning quantity of water and temperature, before performing the washing of the fabrics.

5.2.1. Chemicals and reagents

The PFAAs and volatile PFASs assessed and analysed in this study are given in Tables S5-1.1 (PFAAs) and S5-1.2 (volatile PFASs) of the Supporting information (SI). PFAAs (50 µg/mL in methanol) were obtained from Greyhound Chromatography (Merseyside, UK). Volatile PFASs (50 µg/mL in methanol) were purchased from Chiron AS (Trondheim, Norway). Ultrapure water originated from a Milli-Q system from Millipore (Watford, UK). Ethylacetate (HPLC, 054006) was supplied by Biosolve Chimie (Dieuze, France). Acetonitrile (Chromasolve, 34851), Supelclean™ Envi-carb™ (Supelco, 957210-U), and ammonium formate (Bio ultra, 09735), were purchased from Sigma Aldrich (Zwijndrecht, The Netherlands). HPLC grade acetone (J.T. Baker, 9254) and methanol (J.T. Baker, 8402) were obtained from Boom (Meppel, The Netherlands).

5.2.2. Fabrics

Two types of synthetic fabrics, a PA and a PES fabric, which are regularly used for the production of outdoor clothing, have been provided by FOV AB, Borås, Sweden (Table S5-1.3). To both types of fabrics DWR coatings based on FC-6 chemistry, and FC-8 chemistry have been applied as described by Schellenberger et al.[2], and to the PES fabric FC-4 chemistry DWR coating has been applied (Table S5-1.3).

5.2.3. DWR textile treatments

The effects of aging, washing and tumble drying were assessed on the PA and PES fabrics coated with the FC-6 and FC-8 DWR emulsions. An overview of all treatments and the number of samples analysed per treatment can be found in Table 5-1 and are described below.

Table 5-1 Treatments of PA and PES textiles coated with FC-6 and FC-8 chemistries expressed in numbers of samples analysed.

Sample Code	DWR chemistry	Fabric	No of samples		Aged	Washing*	Tumble drying*
			PFAAs	*Volatile PFASs*			
1-7	FC-6	PA	5	2	No	No	No
8-9	FC-6	PA	1	1	Yes	No	No
10-11	FC-6	PA	1	1	Yes	5 cycles	5 cycles
12-13	FC-6	PA	1	1	Yes	10 cycles	10 cycles
14-15	FC-6	PA	1	1	Yes	5 cycles	No
16-17	FC-6	PA	1	1	No	5 cycles	5 cycles
18-19	FC-6	PA	1	1	No	No	5 cycles
20-26	FC-6	PES	5	2	No	No	No
27-28	FC-6	PES	1	1	Yes	No	No
29-30	FC-6	PES	1	1	Yes	5 cycles	5 cycles
31-32	FC-6	PES	1	1	Yes	10 cycles	10 cycles
33-39	FC-8	PA	5	2	No	No	No
40-41	FC-8	PA	1	1	Yes	No	No
42-43	FC-8	PA	1	1	Yes	5 cycles	5 cycles
44-45	FC-8	PA	1	1	Yes	10 cycles	10 cycles
46-52	FC-8	PES	5	2	No	No	No
53-54	FC-8	PES	1	1	Yes	No	No
55-56	FC-8	PES	1	1	Yes	5 cycles	5 cycles
57-58	FC-8	PES	1	1	Yes	10 cycles	10 cycles

* In case washing and tumble drying both were performed, one cycle consisted of washing followed by tumble drying.

Aging

The fabrics (FC-6 and FC-8 coated PA and PES fabrics) were aged in an ATLAS weather-o-meter Cr 3000 using the method previously described in Van der Veen et al[20] (Table S5-1.4). The fabrics were exposed to elevated temperatures, humidity and UV irradiation for 300 h, which simulates exposure to weather conditions during a life time wear of outdoor clothing.

Washing and Tumble drying

The effect of washing plus tumble drying on the aged FC-6 and FC-8 coated fabrics, was assessed after five and 10 sequential washing plus tumble drying cycles. Washing and tumble drying of the fabrics were performed according to SS-EN ISO 6330:2012[40], and as described by Schellenberger et al.[2] Each type of coated fabric was washed separately at 40°C. Tumble drying was performed at 60°C for 30 min.

Three additional assessments have been performed on the FC-6 coated PA fabric (Table 5-1). For the first assessment, five washing cycles without tumble drying were performed on the aged material. The second assessment contained five sequential washing plus tumble drying cycles on the original, not weathered coated fabric. In the third assessment five sequential tumble drying cycles were performed on the original, not weathered coated material, without washing the fabric.

5.2.4. Extraction and instrumental analyses

After each treatment (Table 5-1) the fabrics were analysed for PFAAs and volatile PFASs. PFAAs were extracted and analysed by the method earlier developed and described by Van der Veen et al.[31] In short, textile samples of approximately 20 cm^2, cut in smaller pieces were extracted with methanol for the determination of PFAAs with an Agilent 6410 Triple Quad liquid chromatography- tandem mass spectrometer (LC-MS/MS, Agilent Technologies, Amstelveen, The Netherlands) in the electrospray negative ionization mode. For extraction and analysis of the volatile PFASs the method described by Van der Veen et al.[20] was used. In short, textile samples of approximately 20 cm^2, were extracted with ethyl acetate. After cleaning the extracts with Envi-carb™, and a concentrating step, the extracts were analysed with gas chromatography/ electron impact-mass spectrometry (GC/EI-MS) on an Agilent 6890 series GC coupled to a 5973 Network MS (Agilent Technologies, Amstelveen, The Netherlands).

5.2.5. Quality control

Homogeneity of PFASs in the DWR coated fabrics

The homogeneity testing of the FC-4 coated PES fabric, and of the FC-6 and FC-8 coated PA and PES fabrics are described in Chapter 2 of the SI. Because of the limited amount of fabric available it was not possible to perform an extensive homogeneity test for each of the coated fabrics of interest in our study. Since FC-6 and FC-8 coatings were applied by the same procedures as the FC-4 coating, it is likely that they were evenly coated as well. Therefore, a general assessment of the distribution of PFAS concentrations in the coated fabrics, and between the coated fabrics, was performed on PFAA concentrations in the PES fabrics coated with the FC-4 emulsion. For this, 20 samples were analysed out of one piece of FC-4 coated PES fabric (40x35 cm), and 10 samples out of another piece (40x35 cm) of FC-4 coated PES fabric (Figure S5-2.1). For the remaining 4 fabrics (FC-6 and FC-8 coated PA and PES fabrics) five samples (approximately 20 cm^2) of each of the fabrics were analysed for PFAAs, and two samples for volatile PFAS concentrations.

Results, as determined with the SoftCRM software[42] showed a homogeneous distribution of perfluorobutanoic acid (PFBA) over both fabrics of the FC-4 coated

PES fabrics at the 99% confidence level (Table S5-2.1). The relative standard deviation (RSD) over 30 measurements was 14%. These results showed that coating fabrics with DWR emulsions based on SFPs by the method of Schellenberger et al.[2], results in fabrics with a homogenous PFAS distribution. This makes the fabrics suitable for the determination of the effect of aging, washing and tumble drying on PFASs in the fabrics. The mean RSDs of all PFASs in the four coated fabrics of interest in our study (FC-6 and FC-8 coated PA and PES fabrics) were 25%. (Figure S5-2.2-S5-2.6). This included the high RSDs of perfluorohexanoic acid (PFHxA) (95%) for the FC-6 coated PES fabric, and of PFOA (63%) and perfluorononanoic acid (PFNA) (57%) for the FC-8 coated PA fabric. The RSDs of these limited homogeneity tests were taken into account in the evaluation of the results obtained from the aging, washing and tumble drying studies.

Carry-over in aging device

In a previous study by Van der Veen et al.[20] the possible carry-over of PFASs between DWR coated fabrics in the aging device was determined. No carry over was observed for PFAAs. Of the volatile PFASs 6:2 FTOH (17 µg/kg), 8:2 FTOH (35 µg/kg), and 10:2 FTOH (35 µg/kg) were detected.

5.3. Results and discussion

5.3.1. Initial PFAS concentrations in DWR coated fabrics before treatments

Detailed information on the PFAS concentrations in the four DWR coated fabrics before and after aging, washing and tumble drying experiments are shown in Table S5-3.1.

PA versus PES fabrics

In Figure 5-1 all PFAS concentrations detected in the coated PA and PES fabrics are given (seven PFAAs and six volatile PFASs). Those concentrations in the coated PA and PES fabrics were different even though the fabrics were coated with the same DWR emulsions. The FC-6 coated PA contained more volatile PFAS congeners than the FC-6 coated PES, and the concentration of the PFASs which were present in both materials were two to six times higher in the FC-6 coated PA. In the FC-8 coated materials the same PFAS congeners were detected in both the PA and the PES fabric. Also, for this formulation the concentrations of all detected volatile PFASs were higher in the PA fabric than in the PES fabric, except for 10:2 FTOH. In conclusion, the coated PA fabrics both contained more PFASs then the PES fabrics. This difference in PFAS concentrations could be explained by the DWR uptake of the fabrics during

the coating process. The PA fabric had a different weave structure (rib-stop pattern) then the PES fabric (plain weave) (Table S5-1.3). Another explanation might be the difference in hydrophobicity of PA compared to PES[43].

Higher PFAS concentrations in PA fabrics compared to PES fabrics was also observed in the results of the studies of Gremmel et al.[27] and of Santen et al.[22] In both studies commercially available outdoor jackets were analysed for their PFAS content. In the study of Gremmel et al.[27] the sum of PFAS concentrations in PES textiles was 0.35- 76.1 µg/kg (median 14.4 µg/kg), and in PA textiles 62.8-500 µg/kg (median 145 µg/kg). In the study of Santen et al.[22] the sum of PFAS concentrations in PES textiles was 2.1- 74 µg/m^2 (median 23 µg/m^2) and in PA textiles 6.7- 421 µg/m^2 (median 37 µg/m^2). In other studies on PFASs in DWR coated fabrics the types of fabrics were either not given[21, 23, 24, 29, 30] or no PA fabric was analysed[28].

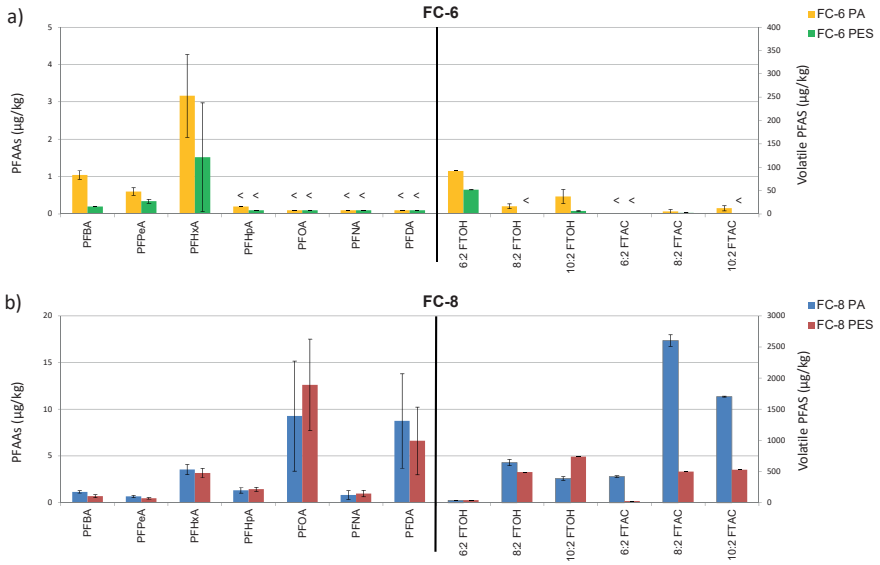

Figure 5-1 PFAS concentration (µg/kg) of relevant PFASs in a PA and a PES fabric applied with a) Fluorcarbon 6 (FC-6) DWR emulsion, b) Fluorcarbon 8 (FC-8) DWR emulsion before aging, washing and tumble drying. <: LOD.

FC-6 versus FC-8 DWR coated fabrics

The FC-8 coated fabrics contained more PFAA congeners (PFBA, perfluoropentanoic acid (PFPeA), PFHxA, perfluoroheptanoic acid (PFHpA), PFOA, PFNA and perfluorodecanoic acid (PFDA)) than the FC-6 coated fabrics, in which only three

PFAA congeners (PFBA, PFPeA, and PFHxA) could be quantified. The highest PFAA concentrations in the FC-6 coated fabrics were found for PFHxA (PA: 3.2 µg/kg; PES 1.5 µg/kg) and the highest volatile PFAS concentrations for 6:2 FTOH (PA: 92 µg/kg; PES 52 µg/kg). This result could be expected since the formulation used to coat the fabrics was based on FC-6 chemistry[2], and after coating some unreacted ionic or volatile FC-6 PFAS residuals or impurities might still be present on the fabrics[20].

In the FC-8 coated fabrics, besides the PFASs with a chain length of 8 carbons (PFOA, 8:2 FTOH, and 8:2 FTAC) PFASs with a chain length of 10 carbons (PFDA, 10:2 FTOH and 10:2 FTAC) were present in comparable concentrations. This might be due to the fact that DWR emulsions used for coating the fabrics often consist of a mixture of the desired SFPs, and fluorinated polymers with shorter- and longer side-chains[19]. Other PFAAs (PFBA, PFPeA, PFHxA, PFHpA, PFNA) and volatile PFASs (6:2 FTOH, 6:2 FTAC) were detected in lower concentration in the FC-8 coated fabrics. The FC-6 coated fabrics contained only two other PFAAs (PFBA and PFPeA). Four of the volatile PFASs (8:2 FTOH, 10:2 FTOH, 8:2 FTAC and 10:2 FTAC) were detected on at least one of the FC-6 coated fabrics, but all in much lower concentrations (2.4-38 µg/kg) than in the FC-8 coated fabrics (26-2600 µg/kg).

5.3.2. The effect of aging, washing and tumble drying on PFASs in DWR coated fabrics

In Figure 5-2, the PFAS concentrations in the FC-6 and the FC-8 coated PA and PES fabrics are shown before the textiles were aged (original), after aging, after aging followed by five times washing plus tumble drying cycles, and after the textiles were aged followed by ten washing plus tumble drying cycles.

The effect of aging on PFAAs

Aging of the FC-6 coated PA increased the concentrations of PFAAs which were present in the original coated fabric (PFBA, PFPeA and PFHxA) with a factor of 3.6-15. In addition, PFHpA was detected in the aged material (7.6 µg/kg), while this compound was not present in the original coated material (Figure 5-2). Also, in the aged FC-6 coated PES fabric the concentration of PFHxA increased, and PFHpA was detected, although both in lower concentrations (2.6 and 1.5 µg/kg respectively) than in the PA fabric.

In the FC-8 coated PA fabric an increase of 3-15 times in concentration of all detected PFAAs was observed after aging, of which especially the odd-chain PFASs were formed with 6.8-15-fold increase, compared to the 1.3-3.4-fold increase of the even-chain PFASs. In the FC-8 coated PES fabric the concentrations of longer-chain PFAAs (>C_9) also increased. However, in this coated fabric the concentrations of shorter-chain

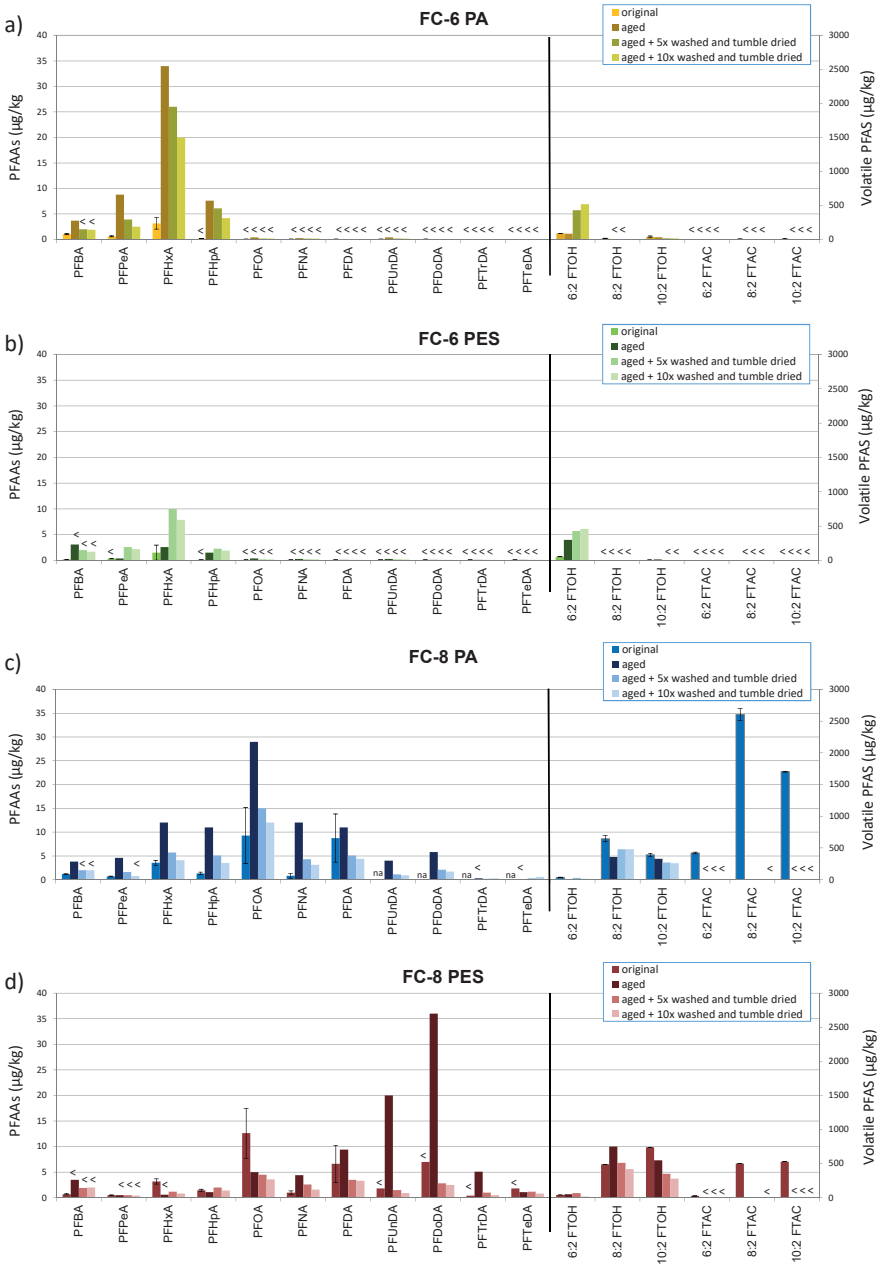

Figure 5-2 Effect of aging, washing and tumble drying on PFAS concentration (µg/kg) in a) a polyamide (PA) fabric applied with FC-6 DWR emulsion, b) a polyester (PES) fabric applied with FC-6 DWR emulsion, c) a PA fabric applied with FC-8 DWR emulsion, d) a PES fabric applied with FC-8 DWR emulsion. (na: not available due to low IS recovery). <: LOD.

PFASs (C_6-C_8) decreased. The increase in PFAA concentrations and the formation of PFAAs by aging was in line with the findings of Van der Veen et al.[20] on the aging of commercial available DWR coated textiles of outdoor clothing. Also, the formation of odd-chain PFASs was observed in two samples in that study. The increase in extractable PFAA concentrations could be explained by atmospheric oxidation of FTOHs which were present in the coated fabrics[9], degradation or transformation of other PFAA precursors, release of NEOF or cleavage of the side-chains of the SFPs[20, 43-45].

There is a difference between the effect of aging on the PFAAs in the FC-6 DWR chemistry and in the FC-8 DWR chemistry. The FC-6 coated materials only contained shorter-chain PFAAs with PFHxA being the PFAA with the longest carbon chain length (C_6). After aging the PFAA with the longest chain length was PFHpA (C_7). In the FC-8 coated fabrics the longest PFAA before aging was PFDA (C_{10}). After aging PFAAs with even longer carbon chain lengths appeared (PA: C_{11} and C_{12}; PES C_{11}- C_{14}).

To summarize, comparison of the PA and PES fabrics showed that aging of the coated PA fabrics resulted in an increase in concentrations of all PFAAs present in the original coated fabrics, and in addition some PFAAs showed up which were not detected before aging. Aging of the coated PES fabrics resulted in a decrease of concentrations, or even absence, of shorter-chain PFAAs, and an increase in concentration, or appearance of PFAAs with a longer carbon chain (for PA: C6 and C7; for PES C9-C14). The results show that shorter-chain PFAA residuals, impurities or degradation products out of the DWR formulations, more easily remained on the original coated and aged PA textiles than on the PES fabrics. The coated PES fabrics on the other hand gained more in concentration of longer-chain PFAAs. The difference in weave structure of the PA fabric and the PES fabric (Table S5-1.3) might have influenced the coating process, and explain this phenomenon. Also the higher hydrophobicity of PES compared to PA[46] might explain those results. The higher hydrophobicity results in lower interaction to more hydrophilic short-chain PFASs. This could results in an easier release during weathering and lower their concentrations.

The effect of aging on volatile PFASs

Aging resulted in the disappearance of all FTACs which were present in the coated fabrics before aging. This disappearance could be explained by atmospheric oxidation of the FTACs by reaction with OH radicals, which results in the formation of PFAAs as described by Butt et al.[47], or by hydrolysis with water, which forms FTOHs[48]. Aging of the FC-6 coated fabrics however, did not have an effect on the concentration of 6:2 FTOH in the PA fabric, but in the PES fabric the concentration of 6:2 FTOH increased from 52 to 300 µg/kg. Also, in the FC-8 coated PES fabric the concentration of the

relevant FTOH (8:2 FTOH) increased from 490 µg/kg up to 750 µg/kg. A decrease of 60% was observed for the concentration of 8:2 FTOH in the PA fabric as effect of aging. Aging can have an effect on the DWR coatings, but it can also degrade PA, and PES at the molecular level, and change the properties of the textiles[49, 50]. Aging in our study could have released the unextractable fraction of 6:2 and 8:2 FTOH in the PES fabrics, while it did not in the PA fabrics. The effects of aging on 6:2 FTOH, and 8:2 FTOH in our study are in agreement with the findings of Van der Veen et al.[20] In that study the concentration of 6:2 FTOH increased in 12 out of 13 textile samples after aging, and the concentration of 8:2 FTOH increased in some of the samples and decreased in other samples.

The effect of washing plus tumble drying

Performing five washing plus tumble drying cycles on the aged fabrics resulted in a decrease in concentration of all extractable PFAAs in all coated fabrics. However, no conclusions can be drawn on the PFDA concentration due to the high variance in the original samples (Figure 5-2). Performing ten washing plus tumble drying cycles on the aged fabrics, resulted in even lower concentrations of extractable PFAAs. The only exceptions to this decrease are PFHxA and PFHpA in the PES fabrics. However, due to the high RSDs detected over the analyses of five untreated coated fabrics, for PFHxA and PFHpA no definitive conclusions can be drawn on the small increase in those two compounds after the first five washing plus tumble drying cycles.

Like the PFAAs, the 10:2 FTOH concentration decreased in all coated fabrics when five washing plus tumble drying cycles were performed after aging, and even further when ten washing plus tumble drying cycles were performed (Figure 5-2). Also 8:2 FTOH in the FC-8 coated PES fabric followed this pattern. However, the concentration of 8:2 FTOH in the FC-8 coated PA fabric increased from 360 µg/kg to 480 µg/kg, and the concentration of 6:2 FTOH in both the FC-6 coated PA, and PES fabrics increased from 87 to 430 µg/kg and from 300 to 430 µg/kg, respectively. This increase could be explained by the hydrolyses of residuals, impurities or SFPs out of the DWR in combination with abrasion of the DWR coating or abrasion of the textile fibers, which occurs during the washing process[48]. An explanation for the difference in observed effects for 8:2 FTOH in the PA and PES fabric might be found in the type of fabric, since the DWR coating on both types of materials was the same. Washing and tumble drying of the aged FC-8 PES fabric most likely washes off the 8:2 FTOH which was released by aging (see above), while washing and tumble drying of the aged FC-8 PA fabric did release more unextractable 8:2 FTOH then the amount of 8:2 FTOH which was washed off. The same phenomenon was observed by the 6:2 FTOH concentrations detected in the FC-6 fabrics. Washing plus tumble drying of the aged PA fabric did release unextractable 6:2 FTOH, or did transform FTOH precursors. Similar to 8:2

FTOH in the FC-8 PES fabric, the concentration of 6:2 FTOH in the FC-6 PES fabric increased after washing and tumble drying of the aged fabric, however not so much as in the PA fabric.

This increase in concentration might be caused by a remainder of the unextractable fraction of 6:2 FTOH which became available by either washing or tumble drying. Another explanation of the further increase might be precursors which could transform into 6:2 FTOH as result of washing plus tumble drying as earlier described by Van der Veen et al.[20] as possible explanation for the observed increase in 6:2 FTOH concentration as an effect of aging, or the cleavage of side-chains of fluorotelomer-based polymer (FTPs).

The effect of aging, washing and tumble drying on PFASs in DWR coated fabrics illustrated by 6:2 FTOH

To assess first whether the increase in 6:2 FTOH after aging, washing and tumble drying was caused by either the effect of washing or the effect of tumble drying, and second to assess whether this increase also appears when to not aged fabric would have been washed and tumble dried, some additional tests were performed on the FC-6 coated PA fabric. All PFAS concentrations detected in the original FC-6 coated PA fabric, and in the aged, washed, and tumble dried FC-6 coated PA fabrics, are shown in Figure S5-3.1. In Figure 5-3a the effects of aging on 6:2 FTOH in the FC-6 coated PA fabric are shown for two different treatments. When the original coated material was aged, no effect was observed in the concentration of 6:2 FTOH (Figure 5-3, Comparison a1). However, washing plus tumble drying of the aged fabric results in a higher concentration of 6:2 FTOH then washing plus tumble drying of the coated fabric which was not aged (Figure 5-3, Comparison a2), showing that aging did have an impact on the compounds in the DWR. In Figure 5-3b the effects of washing on 6:2 FTOH in the FC-6 coated PA fabric are shown for four different treatments. When the original coated material was washed plus tumble dried, the concentration of 6:2 FTOH increased from 92 µg/kg to 150 µg/kg (Figure 5-3, Comparison b1). An increase of the 6:2 FTOH concentration was also observed when the concentration in the aged fabric (87 µg/kg) was compared with the concentration in the aged fabric, which was five times washed afterwards without tumble drying (390 µg/kg) (Figure 5-3, Comparison b2). The third comparison (Figure 5-3, Comparison b3) shows an increase of the 6:2 FTOH concentration between the aged fabric (87 µg/kg), the aged fabric which was five times washed and tumble dried (430 µg/kg), and the aged fabric which was ten times washed and tumble dried (520 µg/kg). Those comparisons show that the increase of the concentration of 6:2 FTOH was caused by the washing process. This was confirmed by the results of the fourth comparison (Figure 5-3, comparison b4), in which the 6:2 FTOH concentration of the FC-6 coated PA fabric which was only

tumble dried (6:2 FTOH 85 µg/kg) is compared with the concentration in the PA fabric when five washing plus tumble drying cycles were performed on the textile (150 µg/kg). The increase in 6:2 FTOH is most likely the result of transformation of FTOH precursors or side-chain cleavage due to e.g. hydrolysis during washing[44, 48].

Tumble drying did not have an effect on the concentration of 6:2 FTOH in the PA fabric, as can be seen in the comparison of the 6:2 FTOH concentration in the original coated fabric with that in the fabric which was five times tumble dried (Figure 5-3, Comparison c1). In the comparison of the concentration of 6:2 FTOH in the aged and washed fabric, which was not tumble dried with the fabric which was aged, washed and tumbled dried (Figure 5-3, Comparison c2) no difference was observed either.

An additional effect was observed for the combination of aging and washing. When five washing plus tumble drying cycles were performed on the original coated material the concentration of 6:2 FTOH increased from 92 µg/kg to 150 µg/kg (Figure 5-3, Comparison b1). When instead the five washing plus tumble drying cycles were performed on the aged fabric (87 µg/kg) the increase in 6:2 FTOH concentration was almost three times higher (430 µg/kg) (Figure 5-3, Comparison b3). As described above, aging by it selves does not release 6:2 FTOH in the PA fabric, but this observation shows that washing does increase the extractable 6:2 FTOH concentration in the PA fabric, and a combination of aging and washing makes the extractable 6:2 FTOH fraction even bigger. One of the mechanisms that could cause this higher increase in extractable 6:2 FTOH concentration is the damaging of either the DWR coating or the fibers of the PA fabric as effect of aging. Washing afterwards causes the release of a larger NEOF fraction. Another mechanism would be the transformation of FTOH precursors by aging (e.g. oxidation) in combination with washing (hydrolyses), which has a large effect on the formation of FTOHs.

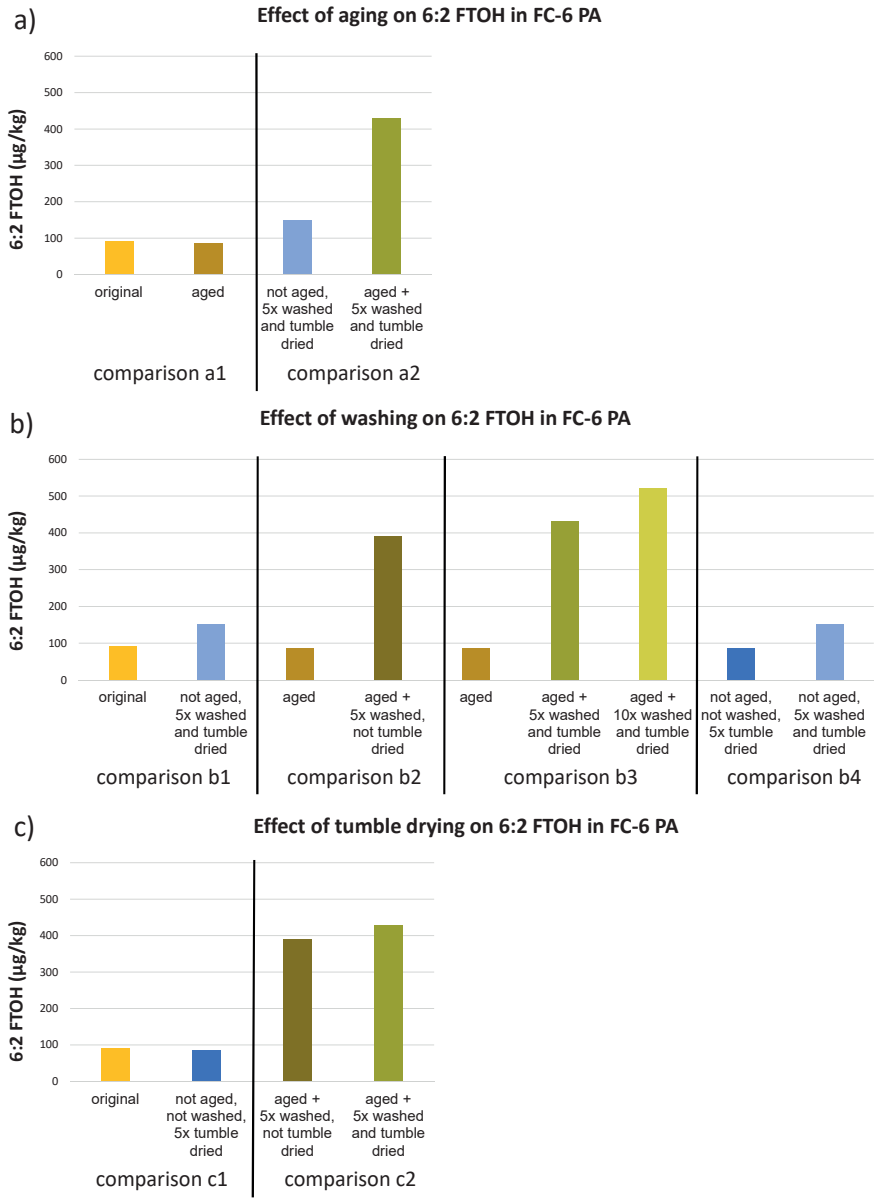

Figure 5-3 The effect of a) aging, b) washing and c) tumble drying on the 6:2 FTOH concentration (µg/kg) in PA fabric coated with FC-6 DWR emulsion. To clearly show the effects of aging, washing and tumble drying different comparisons have been made between the analysed samples. Corresponding colors represent the same analyses.

An overview of all potential mechanisms for the increase of extractable PFAS concentrations in fabrics coated with DWR based on SFPs, and the emissions of PFASs from the fabrics as effect of aging and washing of the fabrics is shown in Figure 5-4.

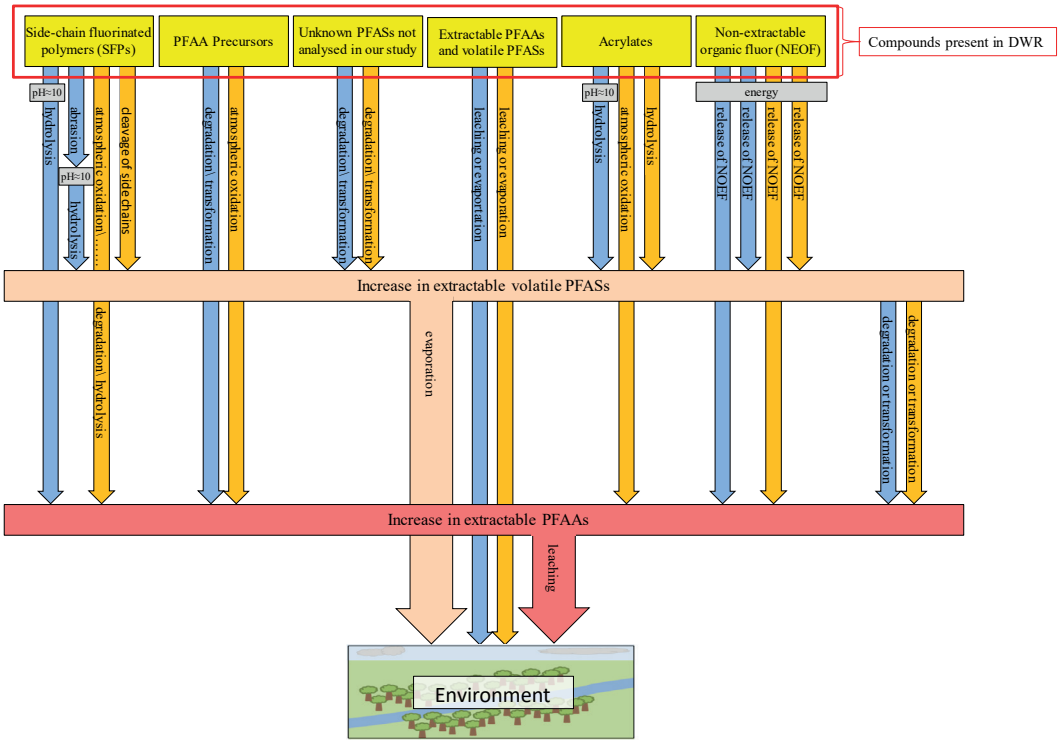

Figure 5-4 Potential mechanisms for the increase of extractable PFAS concentrations in, and the emissions of PFASs from fabrics coated with DWR based on SFPs as effect of aging and washing of the fabrics. : Effect of washing, : Effect of weathering, : Compounds present in DWR of fabrics.

In conclusion, PFAS based DWRs are not stable and the stressors applied during the use phase contribute to the emission over time. The effects of aging, washing and tumble drying on the concentrations of residual or unreacted PFASs in fabrics coated with DWR based on SFPs, are not just depending on the type of formulation, and on the PFASs present in the textiles, but also on the type of fabric. The PA fabrics and PES fabrics in our study which were coated with the same DWR emulsions contained different concentrations of PFASs. Volatile PFASs, were found in higher concentrations in the PA fabrics than in the PES fabrics. Longer-chain PFAAs are not

detected before and after aging on the FC-6 coated fabrics, but are present on the FC-8 coated fabrics. Aging of the FC-6 coated, as well as of the FC-8 coated fabrics resulted in an increase in PFAA concentrations. The effect of aging on the volatile PFASs was depending on the type of fabric. An increase was observed on the PES fabrics, while no effect or a decrease was observed on the PA fabrics. Tumble drying on its own did not cause an observable effect, but washing either in combination with tumble drying or without tumble drying caused a decrease of the extractable PFAA concentrations. The PFAAs which are leached of, short-chain PFAAs for the FC-6 fabrics and short and longer-chain PFAAs for the FC-8 coated fabrics, do end up in the sewage system. Via the sewage water treatment plant the PFAAs finally end up in the surface water. The effect of washing on the volatile PFASs is depending on the type of PFAS, the type of DWR, and the type of FC chemistry of the DWR coating. In general volatile PFASs are emitted from the textiles, and the concentrations in the textiles decrease. However, washing can also cause the release of the unextractable fraction of volatile PFASs or the hydrolyses of FTOH precursors resulting in higher detected compounds in the fabric. This effect becomes stronger by a combination of aging and washing. The volatile PFASs which are detected on the fabrics after aging and washing can emit to the outdoor environment by evaporation when wearing the clothes, or to the indoor environment when the clothes are hanging in the closet or on the coat rack. This increases the concentrations of PFASs in indoor environments and the exposure risk for consumers. Since the results in this study showed that aging and washing can increase the concentrations of PFAA congeners substantially in fabrics with SFP treatments it can be concluded that a substance by substances regulation of PFAAs is not sufficient. The transformation of PFAA precursor associated with production impurities and/or the degradation of SFPs results in a complex mixture of different PFAAs and other PFASs. Their occurrence is dependent on materials combinations as well as the conditions of weathering and washing which makes the predictions of exact concentrations impossible. The authors therefore would strongly support the new proposal for a broad restriction under REACH covering all PFASs as a group[51].

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References

1. Holmquist, H.; Schellenberger, S.; van der Veen, I.; Peters, G. M.; Leonards, P. E. G.; Cousins, I. T., Properties, performance and associated hazards of state-of-the-art durable water repellent (DWR) chemistry for textile finishing. *Environment International* 2016, 91, 251-264.
2. Schellenberger, S.; Gillgard, P.; Stare, A.; Hanning, A.; Levenstam, O.; Roos, S.; Cousins, I. T., Facing the rain after the phase out: Performance evaluation of alternative fluorinated and non-fluorinated durable water repellents for outdoor fabrics. *Chemosphere* 2018, 193, 675-684.
3. Buck, R. C.; Franklin, J.; Berger, U.; Conder, J. M.; Cousins, I. T.; de Voogt, P.; Jensen, A. A.; Kannan, K.; Mabury, S. A.; van Leeuwen, S. P. J., Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. *Integrated Environmental Assessment and Management* 2011, 7, 513-541.
4. Dinglasan, M. J. A.; Ye, Y.; Edwards, E. A.; Mabury, S. A., Fluorotelomer alcohol biodegradation yields poly- and perfluorinated acids. *Environmental Science & Technology* 2004, 38, 2857-2864.
5. Wang, N.; Szostek, B.; Buck, R. C.; Folsom, P. W.; Sulecki, L. M.; Gannon, J. T., 8-2 Fluorotelomer alcohol aerobic soil biodegradation: Pathways, metabolites, and metabolite yields. *Chemosphere* 2009, 75, 1089-1096.
6. Liu, J.; Lee, L. S.; Nies, L. F.; Nakatsu, C. H.; Turco, R. F., Biotransformation of 8:2 fluorotelomer alcohol in soil and by soil bacteria isolates. *Environmental Science & Technology* 2007, 41, 8024-8030.
7. Li, F.; Su, Q.; Zhou, Z.; Liao, X.; Zou, J.; Yuan, B.; Sun, W., Anaerobic biodegradation of 8:2 fluorotelomer alcohol in anaerobic activated sludge: Metabolic products and pathways. *Chemosphere* 2018, 200, 124-132.
8. Russell, M. H.; Himmelstein, M. W.; Buck, R. C., Inhalation and oral toxicokinetics of 6:2 FTOH and its metabolites in mammals. *Chemosphere* 2015, 120, 328-335.
9. Ellis, D. A.; Martin, J. W.; De Silva, A. O.; Mabury, S. A.; Hurley, M. D.; Sulbaek Andersen, M. P.; Wallington, T. J., Degradation of fluorotelomer alcohols: A likely atmospheric source of perfluorinated carboxylic acids. *Environmental Science & Technology* 2004, 38, 3316-3321.
10. Wallington, T. J.; Hurley, M. D.; Xia, J.; Wuebbles, D. J.; Sillman, S.; Ito, A.; Penner, J. E.; Ellis, D. A.; Martin, J.; Mabury, S. A.; Nielsen, O. J.; Sulbaek Andersen, M. P., Formation of $C_7F_{15}COOH$ (PFOA) and other perfluorocarboxylic acids during the atmospheric oxidation of 8:2 fluorotelomer alcohol. *Environmental Science & Technology* 2006, 40, 924-930.
11. Wang, N.; Szostek, B.; Buck, R. C.; Folsom, P. W.; Sulecki, L. M.; Capka, V.; Berti, W. R.; Gannon, J. T., Fluorotelomer alcohol biodegradation- direct evidence that perfluorinated carbon chains breakdown. *Environmental Science & Technology* 2005, 39, 7516-7528.
12. Kim, M. H.; Wang, N.; Chu, K. H., 6:2 Fluorotelomer alcohol (6:2 FTOH) biodegradation by multiple microbial species under different physiological conditions. *Applied Microbiology and Biotechnology* 2014, 98, 1831-1840.
13. Abraham, K.; Mielke, H.; Fromme, H.; Völkel, W.; Menzel, J.; Peiser, M.; Zepp, F.; Willich, S. N.; Weikert, C., Internal exposure to perfluoroalkyl substances (PFASs) and biological markers in 101 healthy 1-year-old children: associations between

levels of perfluorooctanoic acid (PFOA) and vaccine response. *Archives of Toxicology* 2020, 94, 2131-2147.
14. Schümann, M.; Lilienthal, H.; Hölzer, J., Human biomonitoring (HBM)-II values for perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) - Description, derivation and discussion. *Regulatory Toxicology and Pharmacology* 2021, 121, 104868.
15. UNEP, United Nations Environment Programme, Technical paper on the identification and assessment of alternatives to the use of perfluorooctane sulfonic acid in open applications. UNEP/POPS/POPRC.8/INF/17, Geneva, 2012; p 48.
http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC8/MeetingDocuments/tabid/2801/Default.aspx.
16. Lassen, C.; Jensen, A. A.; Warming, M., Alter*Environment International* 2015, 75, 172-179.
18. SUPFES, Substitution in Practice of Prioritized Fluorinated Chemicals to Eliminate Diffuse Sources. Formas 2012-11652-24486-65. https://www.ri.se/en/what-we-do/projects/supfes (22-05-2021).
19. Glüge, J.; Scheringer, M.; Cousins, I. T.; DeWitt, J. C.; Goldenman, G.; Herzke, D.; Lohmann, R.; Ng, C. A.; Trier, X.; Wang, Z., An overview of the uses of per- and polyfluoroalkyl substances (PFAS). *Environmental Science: Processes & Impacts* 2020, 22, 2345-2373.
20. Van der Veen, I.; Hanning, A.; Stare, A.; Leonards, P. E. G.; de Boer, J.; Weiss, J. M., The effect of weathering on per- and polyfluoroalkyl substances (PFASs) from durable water repellent (DWR) clothing. *Chemosphere* 2020, 249, 126100.
21. Guo, Z.; Liu, X.; Krebs, K. A.; Roache, N. F., Perfluorocarboxylic acid content in 116 articles of commerce, EPA/600/R-09/033, US-EPA (Environmental Protection Agency), March 2009, p 51. http://www.oecd.org/env/48125746.pdf.
22. Santen, M.; Kallee, U., Chemistry for any weather – Greenpeace tests outdoor clothes for perfluorinated toxins, Greenpeace, Hamburg, 2012, p 44. http://www.greenpeace.org/romania/Global/romania/detox/Chemistry%20for%20any%20weather.pdf.
23. Brigden, K.; Hetherington, S.; Wang, M.; Santillo, D.; Johnston, P., Hazardous chemicals in branded luxury textile products on sale during 2013, Technical Report 01/2014, Greenpeace Research Laboratories, Exeter, UK, February 2014; p 32.
https://www.greenpeace.to/greenpeace/wp-content/uploads/2014/02/Technical-Report-01-2014.pdf.
24. Kallee, U.; Santen, M., Chemistry for any weather – Part II, Executive summary – Outdoor report 2013, 12/2013, Greenpeace, Hamberg, 2013, p 11. http://m.greenpeace.org/italy/Global/italy/report/2013/toxics/ExecSummary_Greenpeace%20Outdoor%20Report%202013_1.pdf.
25. Schulze, P.-E.; Norin, H., Fluorerade miljögifter i allvädersklader, svenska naturskyddsförening, 2006, p 26.
https://cdn.naturskyddsforeningen.se/uploads/2021/05/11102858/fluorerade_miljogifter_i_allvadersklader.pdf.

26. KEMI, Swedish Chemicals Agency, Perfluorinated substances and their uses in Sweden, ISSN: 0284-1185, Swedish Chemicals Agency, ISSN: 0284-1185, 7/06, Stockholm, November 2006, p 60. http://www.kemi.se/Documents/Publikationer/Trycksaker/Rapporter/Report7_06.pdf.
27. Gremmel, C.; Frömel, T.; Knepper, T. P., Systematic determination of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in outdoor jackets. *Chemosphere* 2016, 160, 173-180.
28. Vestergren, R.; Herzke, D.; Wang, T.; Cousins, I. T., Are imported consumer products an important diffuse source of PFASs to the Norwegian environment? *Environmental Pollution* 2015, 198, 223-230.
29. Herzke, D.; Olsson, E.; Posner, S., Perfluoroalkyl and polyfluoroalkyl substances (PFASs) in consumer products in Norway – A pilot study. *Chemosphere* 2012, 88, 980-987.
30. Robel, A. E.; Marshall, K.; Dickinson, M.; Lunderberg, D.; Butt, C.; Peaslee, G.; Stapleton, H. M.; Field, J. A., Closing the mass balance on fluorine on papers and textiles. *Environmental Science & Technology* 2017, 51, 9022-9032.
31. Van der Veen, I.; Weiss, J. M.; Hanning, A.; de Boer, J.; Leonards, P. E. G., Development and validation of a method for the quantification of extractable perfluoroalkyl acids (PFAAs) and perfluorooctane sulfonamide (FOSA) in textiles. *Talanta* 2016, 147, 8-15.
32. Langberg, H. A.; Arp, H. P. H.; Breedveld, G. D.; Slinde, G. A.; Høiseter, Å.; Grønning, H. M.; Jartun, M.; Rundberget, T.; Jenssen, B. M.; Hale, S. E., Paper product production identified as the main source of per- and polyfluoroalkyl substances (PFAS) in a Norwegian lake: Source and historic emission tracking. *Environmental Pollution* 2021, 273, 116259.
33. Chen, J.; Tang, L.; Chen, W.-Q.; Peaslee, G. F.; Jiang, D., Flows, stock, and emissions of poly- and perfluoroalkyl substances in California carpet in 2000–2030 under different scenarios. *Environmental Science & Technology* 2020, 54, 6908-6918.
34. Schroeder, T.; Bond, D.; Foley, J., PFAS soil and groundwater contamination via industrial airborne emission and land deposition in sw Vermont and eastern New York State, USA. *Environmental Science: Processes & Impacts* 2021, 23, 291-301.
35. Lin, Y.; Jiang, J.-J.; Rodenburg, L. A.; Cai, M.; Wu, Z.; Ke, H.; Chitsaz, M., Perfluoroalkyl substances in sediments from the Bering Sea to the western Arctic: Source and pathway analysis. *Environment International* 2020, 139, 105699.
36. Zhang, B.; He, Y.; Huang, Y.; Hong, D.; Yao, Y.; Wang, L.; Sun, W.; Yang, B.; Huang, X.; Song, S.; Bai, X.; Guo, Y.; Zhang, T.; Sun, H., Novel and legacy poly- and perfluoroalkyl substances (PFASs) in indoor dust from urban, industrial, and e-waste dismantling areas: The emergence of PFAS alternatives in China. *Environmental Pollution* 2020, 263, 114461.
37. Yong, Z. Y.; Kim, K. Y.; Oh, J.-E., The occurrence and distributions of per- and polyfluoroalkyl substances (PFAS) in groundwater after a PFAS leakage incident in 2018. *Environmental Pollution* 2021, 268, 115395.
38. D'Ambro, E. L.; Pye, H. O. T.; Bash, J. O.; Bowyer, J.; Allen, C.; Efstathiou, C.; Gilliam, R. C.; Reynolds, L.; Talgo, K.; Murphy, B. N., Characterizing the air emissions, transport, and deposition of per- and polyfluoroalkyl substances from a

fluoropolymer manufacturing facility. *Environmental Science & Technology* 2021, 55, 862-870.
39. Qu, Y.; Huang, J.; Willand, W.; Weber, R., Occurrence, removal and emission of per- and polyfluorinated alkyl substances (PFASs) from chrome plating industry: A case study in southeast China. *Emerging Contaminants* 2020, 6, 376-384.
40. International Organization for Standardization, EN-ISO 6330: 2012, Textiles - Domestic washing and drying procedures for textile testing. 2012.
41. International Organization for Standardization, EN-ISO 4992: 2013, Steel castings — Ultrasonic testing. 2013.
42. Bonas, G.; Zervou, M.; Papaeoannou, T.; Lees, M., "SoftCRM": a new software for the Certification of Reference Materials. *Accreditation and Quality Assurance* 2003, 8, 101-107.
43. Deopura, B. L.; Padaki, N. V., Chapter 5 - Synthetic textile fibres: Polyamide, polyester and aramid fibres. In *Textiles and Fashion*, Sinclair, R., Ed. Woodhead Publishing, 2015, pp 97-114.
44. Li, L.; Liu, J.; Hu, J.; Wania, F., Degradation of fluorotelomer-based polymers contributes to the global occurrence of fluorotelomer alcohol and perfluoroalkyl carboxylates: A combined dynamic substance flow and environmental fate modeling analysis. *Environmental Science & Technology* 2017, 51, 4461-4470.
45. Washington, J. W.; Jenkins, T. M., Abiotic Hydrolysis of Fluorotelomer-Based Polymers as a source of perfluorocarboxylates at the global scale. *Environmental Science & Technology* 2015, 49, 14129-14135.
46. Washington, J. W.; Jenkins, T. M.; Rankin, K.; Naile, J. E., Decades-scale degradation of commercial, side-Chain, fluorotelomer-based polymers in soils and water. *Environmental Science & Technology* 2015, 49, 915-923.
47. Butt, C. M.; Young, C. J.; Mabury, S. A.; Hurley, M. D.; Wallington, T. J., Atmospheric chemistry of 4:2 fluorotelomer acrylate [$C_4F_9CH_2CH_2OC(O)CH$ץCH_2]: Kinetics, mechanisms, and products of chlorine-atom- and OH-radical-initiated oxidation. *The Journal of Physical Chemistry A* 2009, 113, 3155-3161.
48. Schellenberger, S.; Jönsson, C.; Mellin, P.; Levenstam, O. A.; Liagkouridis, I.; Ribbenstedt, A.; Hanning, A.-C.; Schultes, L.; Plassmann, M. M.; Persson, C.; Cousins, I. T.; Benskin, J. P., Release of side-chain fluorinated polymer-containing microplastic fibers from functional textiles during washing and first estimates of perfluoroalkyl acid emissions. *Environmental Science & Technology* 2019, 53, 14329-14338.
49. Salopek Čubrić, I.; Čubrić, G.; Potočić Matković, V. M., Behavior of polymer materials exposed to aging in the swimming pool: focus on properties that assure comfort and durability. *Polymers* 2021, 13, 2414.
50. Arrieta, C.; Dong, Y.; Lan, A.; Vu-Khanh, T., Outdoor weathering of polyamide and polyester ropes used in fall arrest equipment. *Journal of Applied Polymer Science* 2013, 130, 3058-3065.
51. REACH, 2nd Stakeholder consultation on a restriction for PFAS. National Institute for Public Health and the Environment (RIVM); Bundesanstalt fur Arbeitsschutz und Arbeitsmedizin (baua); Swedisch Chemical Agency (KEMI); Norwegian Environment Agency; Ministry of Environment and Food of Denmark: https://link.webropolsurveys.com/Participation/Public/c4d58b80-5227-4f31-b656-92bc0669e41e?displayId=Ger2322406 (14 September 2021).

Supporting Information

S5-1. General compound, sample and technical information

The data in the Tables S5-1.1 and S5-1.2 show the general information of the compounds (Table S5-1.1 PFAAs, Table S5-1.2 volatile PFASs) assessed and analysed in this study. In Table S5-1.3 information on the fabrics and the DWR formulation is given, and in Table S5-1.4 the technical specifications and settings of the aging, washing and tumble drying methods are given.

Table S5-1.1 Full names, CAS numbers, acronyms, and chemical formula of PFAAs assessed and analysed in this study and their isotope-labeled ISs.

Compounds	CAS No.	Abbreviation	Formula
Perfluorobutanoic acid	375-22-4	PFBA	C_3F_7COOH
Perfluoropentanoic acid	2706-90-3	PFPeA	C_4F_9COOH
Perfluorohexanoic acid	307-24-4	PFHxA	$C_5F_{11}COOH$
Perfluoroheptanoic acid	375-85-9	PFHpA	$C_6F_{13}COOH$
Perfluorooctanoic acid	335-67-1	PFOA	$C_7F_{15}COOH$
Perfluorononanoic acid	375-95-1	PFNA	$C_8F_{17}COOH$
Perfluorodecanoic acid	335-76-2	PFDA	$C_9F_{19}COOH$
Perfluoroundecanoic acid	2058-94-8	PFUnDA	$C_{10}F_{21}COOH$
Perfluorododecanoic acid	307-55-1	PFDoDA	$C_{11}F_{23}COOH$
Perfluorotridecanoic acid	72629-94-8	PFTrDA	$C_{12}F_{25}COOH$
Perfluorotetradecanoic acid	376-06-7	PFTeDA	$C_{13}F_{27}COOH$
Perfluorobutane sulfonate anion	45187-15-3	PFBS	$C_4F_9SO_3^-$
Perfluorohexane sulfonate anion	108427-53-8	PFHxS	$C_6F_{13}SO_3^-$
Perfluoroheptane sulfonate anion	375-92-8	PFHpS	$C_7F_{15}SO_3^-$
Perfluorooctane sulfonate anion	45298-90-6	PFOS	$C_8F_{17}SO_3^-$
Isotope-Labeled PFAAs			
Perfluoro-n-[1,2,3,4-$^{13}C_4$]butanoic acid	na	$^{13}C_4$-PFBA	
Perfluoro-n-[1,2,3,4,5-$^{13}C_5$]pentanoic acid	na	$^{13}C_5$-PFPeA	
Perfluoro-n-[1,2-$^{13}C_2$]hexanoic acid	na	$^{13}C_2$-PFHxA	
Perfluoro-n-[1,2,3,4-$^{13}C_4$]heptanoic acid	na	$^{13}C_4$-PFHpA	
Perfluoro-n-[1,2,3,4-$^{13}C_4$]octanoic acid	na	$^{13}C_4$-PFOA	
Perfluoro-n-[1,2,3,4,5-$^{13}C_5$]nonanoic acid	na	$^{13}C_5$-PFNA	
Perfluoro-n-[1,2-$^{13}C_2$]decanoic acid	na	$^{13}C_2$-PFDA	
Perfluoro-n-[1,2-$^{13}C_2$]undecanoic acid	na	$^{13}C_2$-PFUnDA	
Perfluoro-n-[1,2-$^{13}C_2$]dodecanoic acid	na	$^{13}C_2$-PFDoDA	
Perfluoro-1-hexane[$^{18}O_2$]sulfonate anion	na	$^{18}O_2$-PFHxS	
Perfluoro-1-[1,2,3,4-$^{13}C_4$]octane sulfonate anion	na	$^{13}C_4$-PFOS	

na = not available

Table S5-1.2 Full names, CAS numbers, acronyms, and chemical formula of volatile PFASs assesses and analysed in this study and their isotope-labeled ISs.

Compounds	CAS No.	Abbreviation	Formula
4:2-Fluorotelomer alcohol	2043-47-2	4:2 FTOH	$C_4F_9CH_2CH_2OH$
6:2-Fluorotelomer alcohol	647-42-7	6:2 FTOH	$C_6F_{13}CH_2CH_2OH$
8:2-Fluorotelomer alcohol	678-39-7	8:2 FTOH	$C_8F_{17}CH_2CH_2OH$
10:2-Fluorotelomer alcohol	865-86-1	10:2 FTOH	$C_{10}F_{21}CH_2CH_2OH$
6:2 Fluorotelomer acrylate	17527-29-6	6:2 FTAC	$C_6F_{13}CH_2CH_2OC(O)CH=CH_2$
8:2 Fluorotelomer acrylate	27905-45-9	8:2 FTAC	$C_8F_{17}CH_2CH_2OC(O)CH=CH_2$
10:2 Fluorotelomer acrylate	17741-60-5	10:2 FTAC	$C_{10}F_{21}CH_2CH_2OC(O)CH=CH_2$
6:2 Fluorotelomer methacrylate	2144-53-8	6:2 FTMAC	$C_6F_{13}CH_2CH_2OC(O)C(CH_3)=CH_2$
8:2 Fluorotelomer methacrylate	1996-88-9	8:2 FTMAC	$C_8F_{17}CH_2CH_2OC(O)C(CH_3)=CH_2$
10:2 Fluorotelomer methacrylate	2144-54-9	10:2 FTMAC	$C_{10}F_{21}CH_2CH_2OC(O)C(CH_3)=CH_2$
Isotope-Labeled volatile PFASs			
6:2 Fluorotelomer alcohol-D2	na	D_2-6:2 FTOH	
6:2 Fluorotelomer acrylate-D3	na	D_3-6:2 FTAC	
6:2 Fluorotelomer methacrylate-D5	na	D_5-6:2 FTMAC	

na = not available

Table S5-1.3 Fabrics and DWRs formulations (subtracted from Table S2 of Schellenberger et al.[1]

Fabric	Supplier	Chemistry	Specifiactions	
PA	FOV AB Borås, Sweden	Polyamide	115 +/- 5 g/m2; black dyed, plain polyamide fabric with a square pattern ripstop design; ready for finishing; Threads per cm warp; weft= 60 +/- 1; 33 +/- 1	
PES	FOV AB Borås, Sweden	Polyester	120 +/- 5 g/m2; black dyed, plain polyester fabric; ready for finishing; Threads per cm warp; weft= 60 +/- 2; 38 +/- 1	
DWR-Type	**Supplier**	**Chemistry**	**Formulation**	**Curing conditions**
FC-8	NDA*	C8 based L-SFP	1: 80 g/L C8-based polymer	1. Drying: 120°C; 3 min (wait for 10 min)
				2. Curing: 175°C; 35 sec
FC-6	NDA	C6 based s-SFP	1: 80 g/L C6-based polymer	1. Drying: 120°C; 3 min (wait for 10 min)
			2: 10g/L Cross linker	2. Curing: 175°C; 35 sec
FC-4	not stated	C4 based s-SFP	1: C4-based polymer	1. Drying: 120°C; 3 min
			2: HC-based Extender	2. Curing: 160°C; 5 min

NDA = Non-disclosure agreement; SFP= side-chain fluorinated polymers

Table S5-1.4 Conditions of ATLAS weather-o-meter Cr 3000 for a weathering experiment (total duration 300 h).

Method:	A1 (ISO4892-2)
Exposure cycles:	102 min dry, 18 min water spray
Broadband (300-400 nm):	60 ± 2 W/m2
Narrowband (340 nm):	0.51 ± 0.02 W/m2nm
Black standard temperature* (˚C):	65 ± 3˚C
Chamber temperature :	38 ± 3˚C
Humidity:	50 ± 10 %

* Reference temperature on a black metal plate in the ATLAS weather-o-meter Cr 300

S5-2. Homogeneity of PFASs in fabrics coated with DWR formulations

For a general assessment of the distribution of PFAS concentrations in fabrics coated with DWR emulsions by the method described by Schellenberger et al.[1], a homogeneity test is performed on the FC-4 coated PES fabrics (see Table S5-1.3).

For this, 20 samples were analysed out of one piece of FC-4 coated PES fabric (40x35 cm), and 10 samples out of another piece (40x35 cm) of FC-4 coated PES fabric. Out of all the relevant PFAAs, only PFBA was present in quantifiable concentrations in this coated material. Results of the concentration and distribution of PFBA in the fabrics are given in Table S5-2.1 and are shown on the corresponding spots of the fabric in Figure S5-2.1. The mean concentration determined in the FC-4 coated PES fabrics was 23 µg/kg PFBA. The calculated relative standard deviation (RSD) of twenty analyses of samples originating from the first piece of fabric was 13%. The RSD of ten analyses of the second piece of fabric was 11%. The overall RSD of all 30 measurements was 14%. Although those RSDs are slightly higher than the RSDs (4-13%) of the repeatability determination of the analyses method as previously reported by Van der Veen et al.[2], the fabrics are homogeneous for PFBA on the 99% confidence level as determined with the soft CRM software[3].

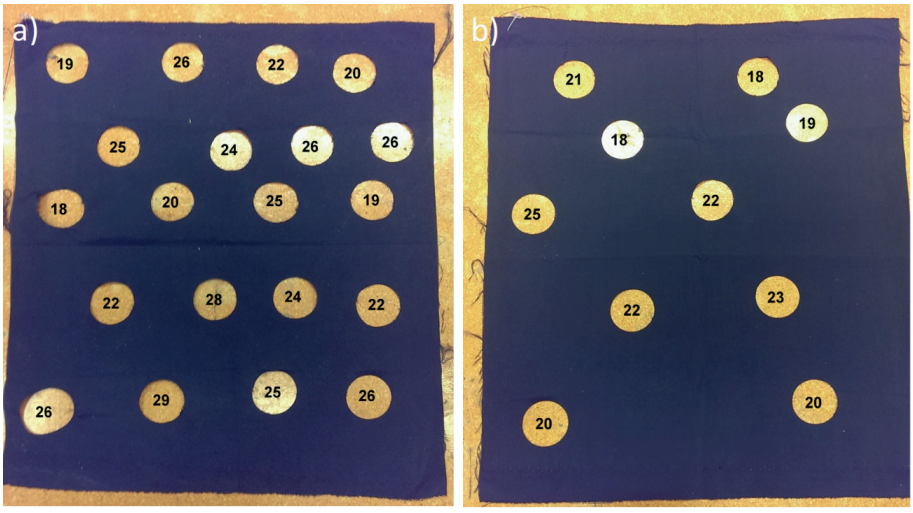

Figure S5-2.1 PFBA concentrations (µg/kg) determined in Fabric FC-4 PES represented on the spots the samples were taken from; a) Fabric 1; b) Fabric 2.

Table S5-2.1 Results of the homogeneity test of PFASs in FC-4 coated PES fabrics.

FC-4 PES	Sample no.	PFBA (µg/kg)
Fabric 1	1	19
	2	26
	3	22
	4	20
	5	25
	6	24
	7	26
	8	26
	9	18
	10	20
	11	25
	12	19
	13	22
	14	28
	15	24
	16	22
	17	26
	18	29
	19	25
	20	26
	Mean	**24**
	Stdev	**3.2**
	RSD	**13%**
Fabric 2	1	21
	2	18
	3	18
	4	19
	5	25
	6	22
	7	22
	8	23
	9	20
	10	20
	Mean	**21**
	Stdev	**2.3**
	RSD	**11%**
All samples	**Mean**	**23**
	Stdev	**3.2**
	RSD	**14%**

There was not enough material of the four types of repellent fabrics of interest in our study (FC-6 and FC-8 coated PA and PES fabrics) to perform all required experiments plus an extensive homogeneity test as has been performed on the FC-4 PES fabric. Instead the homogeneity of PFASs on those four types of repellent fabrics was assessed by cutting seven pieces (approximately 5*5 cm) out of each fabric for the analyses of PFAAs (n= 5, no. 1- 5), and volatile PFASs (n=2, no. 6 and 7). The numbers of the samples are corresponding with the position on the fabric from where the samples were taken, as can be seen in the schematic overview of a piece of fabric in Figure S5-2.2. PFAS concentrations determined in the samples are shown in Figures S5-2.3 (FC-6 PA), S5-2.4 (FC-6 PES), S5-2.5 (FC-8 PA), and S5-2.6 (FC-8 PES), and are given in Table S5-3.1.

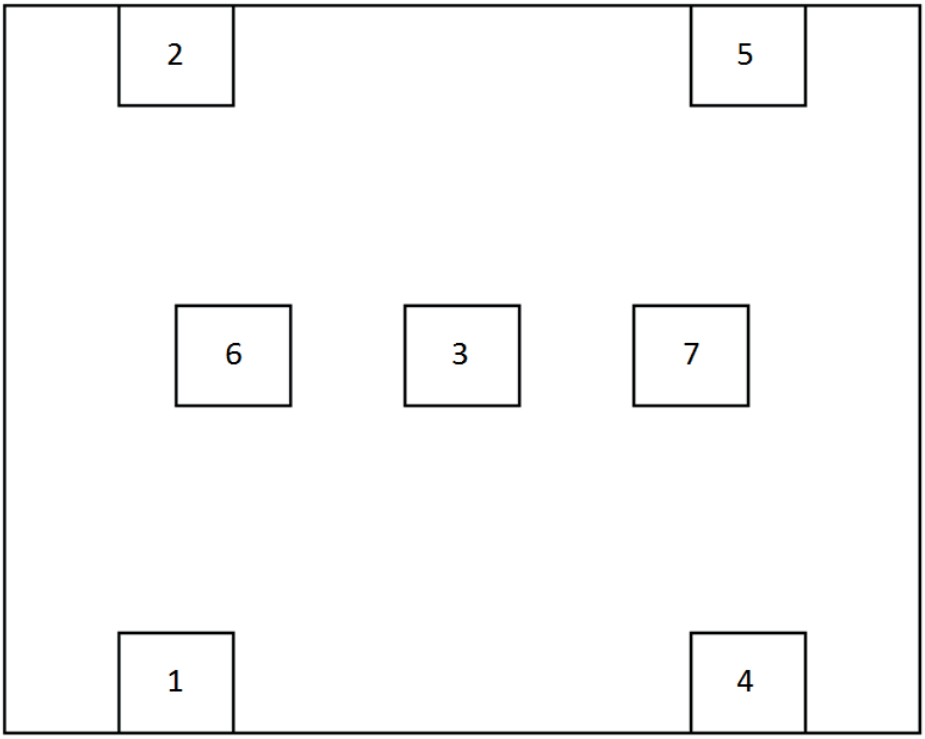

Figure S5-2.2 Schematic overview of repellent fabric, representing the positions of which the samples are taken from for homogeneity testing of PFAAs (No. 1-5) and volatile PFASs (No. 6 and 7).

Fabric FC-6 PA

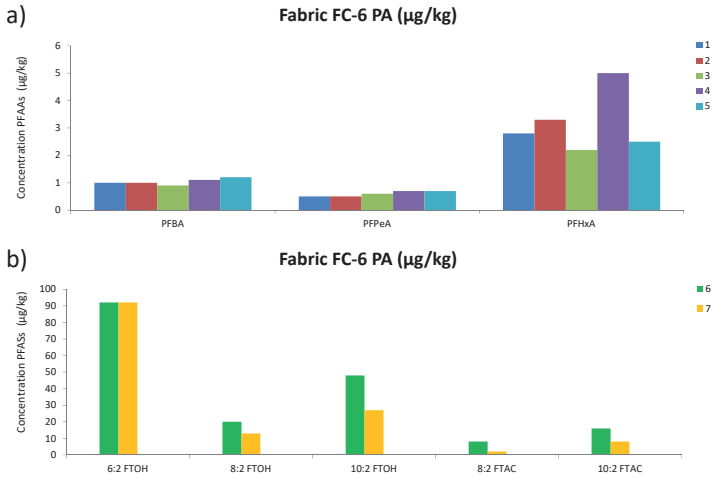

Figure S5-2.3 PFAS concentrations (µg/kg) of Fabric FC-6 PA. The numbers 1-7 correspond with the positions of the samples on the fabric (see Figure S5-2.2); a) PFAAs (1-5); b)Volatile PFASs (6 and 7).

In Figure S5-2.3 the PFAS concentrations (a: PFAAs, b: volatile PFASs) detected in samples of the FC-6 coated PA fabric are shown. In Fabric FC-6 PA three PFAAs (PFBA, PFPeA, and PFHxA) could be quantified, and five volatile PFASs (6:2 FTOH, 8:2 FTOH, 10:2 FTOH, 8:2 FTAC and 10:2 FTAC). For PFAAs, the RSDs over five samples were 11% for PFBA, 17% for PFPeA, and 35% for PFHxA with a difference of a factor 2.3 between the highest and the lowest concentration quantified for PFHxA. RSDs of the volatile PFASs in the two samples were 0% (6:2 FTOH) , 30% (8:2 FTOH), 40% (10:2 FTOH), 83% (8:2 FTAC) and 46% (10:2 FTAC). Except for 6:2 FTOH those RSDs are higher than those previously determined for the repeatabilities (0-28%, mean 7.7%) of the used analyses method [4]. The high inhomogeneity of the FC-6 coated PA fabric for those compounds has been taken into account with the evaluation of the results obtained within the aging and washing studies.

Fabric FC-6 PES

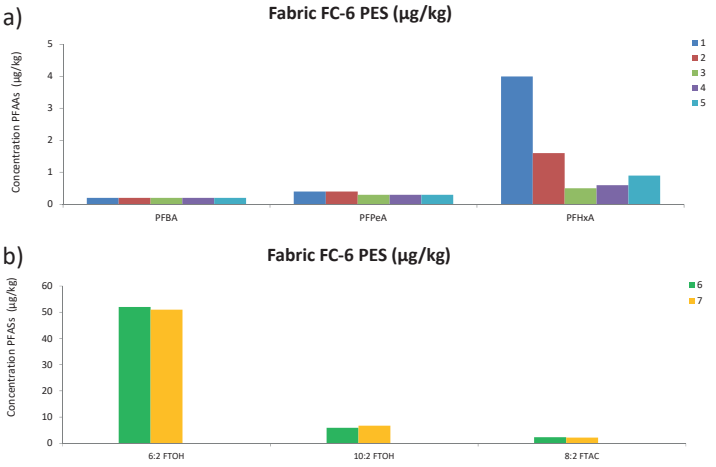

Figure S5-2.4 PFAS concentrations (µg/kg) of Fabric FC-6 PES. The numbers 1-7 correspond with the positions of the samples on the fabric (see Figure S5-2.2); a) PFAAs (1-5); b)Volatile PFASs (6 and 7).

In Figure S5-2.4 the PFAS concentrations detected in seven pieces (approximately 5*5 cm) of Fabric FC-6 PES are shown. In Fabric FC-6 PES three PFAAs (PFBA, PFPeA, and PFHxA) could be quantified, and three volatile PFASs (6:2 FTOH, 10:2 FTOH and 8:2 FTAC). The RSDs over 5 samples were 0% for PFBA and 16% for PFPeA. For PFHxA the RSD was 95% with a difference of a factor 8 between the highest and the lowest concentration quantified. The RSD for the volatile PFASs are 1.4% (6:2 FTOH) , 8.8% (10:2 FTOH), and 6.1% (8:2 FTAC), which is lower than the RSD of the repeatability (0-28%, mean 7.7%) of the analyses method[4].

Fabric FC-8 PA

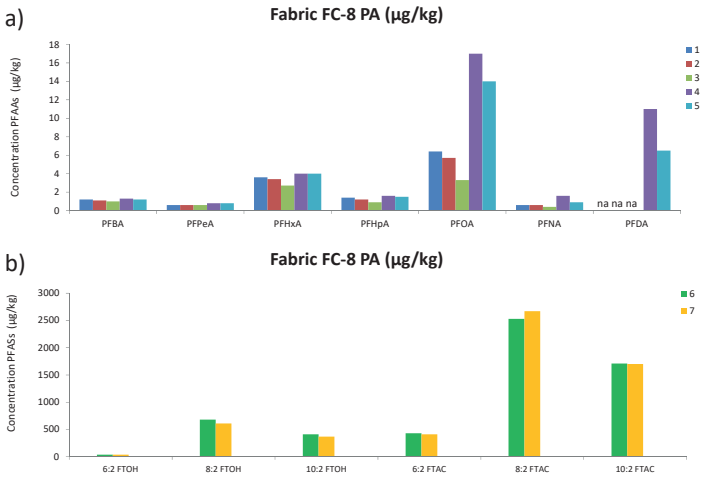

Figure S5-2.5 PFAS concentrations (µg/kg) of Fabric FC-8 PA. The numbers 1-7 correspond with the positions of the samples on the fabric (see Figure S5-2.2); a) PFAAs (1-5); b)Volatile PFASs (6 and 7). (na = not available due to a low recovery of the labeled internal standard).

In Figure S5-2.5 the PFAS concentrations detected in samples of the FC-8 coated PA fabric are shown. Fabric FC-8 PA contained seven quantifiable PFAAs (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, and PFDA), and six volatile PFASs (6:2 FTOH, 8:2 FTOH, 10:2 FTOH, 6:2 FTAC, 8:2 FTAC and 10:2 FTAC). PFDA could only be quantified in two of the samples (No 4, and 5), because the recovery of the labeled internal standard of PFDA ($^{13}C_2$-PFDA) in samples No 1,2 and 3 was too low to calculate an accurate concentration of PFDA. The relative standard deviations (RSDs) for PFBA, PFPeA, PFHxA, and PFHpA over five samples were all between 10 and 20%, which is higher than previously reported for the repeatability of the analyses method (0.1-8.7%) by Van der Veen et al.[2].

For PFOA a difference of a factor 5 has been quantified between the highest and the lowest concentration (RSD: 63%), and for PFNA a factor of 3.7 (RSD 57%). The high RSDs for those compounds in the analyses of Fabric FC-8 PA have been taken into account with the evaluation of the results obtained within the aging and washing studies.

For the volatile PFASs the RSDs over two samples were 0.0% (6:2 FTOH) - 7.7% (8:2 FTOH), which is lower than the repeatabilities determined for the method as reported in Van der Veen et al.[4].

Fabric FC-8 PES

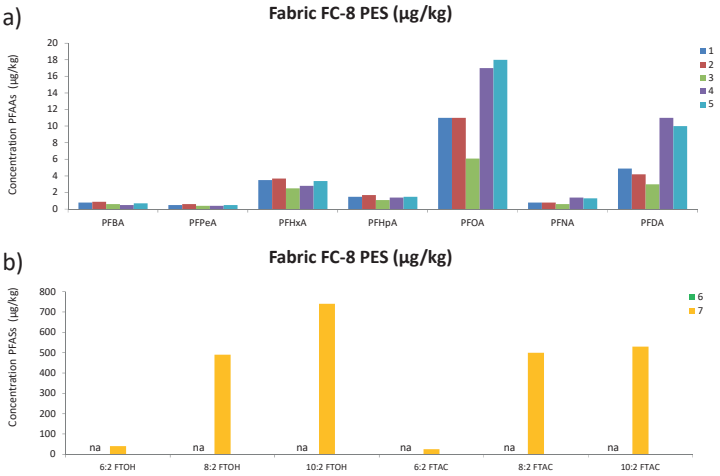

Figure S5-2.6 PFAS concentrations (µg/kg) of Fabric FC-8 PES. The numbers 1-7 correspond with the positions of the samples on the fabric (see Figure S5-2.2); a) PFAAs (1-5); b)Volatile PFASs (6 and 7). (na= not available).

In Figure S5-2.6 the PFAS concentrations of samples of Fabric FC-8 PES are shown. Fabric FC-8 PES contained seven quantifiable PFAAs (PFBA, PFPeA, PFHxa, PFHpA, PFOA, PFNA and PFDA), and six quantifiable volatile PFASs (6:2 FTOH, 8:2 FTOH, 10:2 FTOH, 6:2 FTAC, 8:2 FTAC and 10:2 FTAC). The RSDs of the PFAAs over five samples were 15-23% for PFBA, PFPeA, PFHxA, and PFHpA. For PFOA (RSD: 39%), PFNA (RSD: 36%), and PFDA (55%) the RSDs were higher with a difference of a factor 3.0, 2.3 and 3.7 respectively between the highest and the lowest concentration. Results showed that higher concentrations of those PFASs could be detected on the right side of the fabric. The RSDs determined here have been taken into account with the evaluation of the results obtained within the aging and washing studies. Since sample No. 6 was lost during analyses of the sample, the homogeneity of volatile PFASs on Fabric FC-8 PES could not be determined.

Conclusion

The homogeneity of PFASs in the four coated fabrics differ per compound, and per fabric. The RSDs of this limited homogeneity tests were taken into account with the evaluation of the results obtained within the aging and washing studies.

S5-3. PFAS Concentrations

PFAS concentrations are quantified in four DWR coated fabrics before and after weathering, washing and tumble drying experiments. In Table S5-3.1 the PFAS concentrations in the original coated fabrics, and after the different experiments are given.

Table S5-3.1 PFAS concentrations quantified in DWR coated fabrics, before and after aging, washing and tumble drying experiments (µgkg).

			ionic PFAS														
	Sample description	Sample No	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	PFBS	PFHxS	PFHpS	Tot-PFOS
FC-6 PA	original	1	1.0	0.5	2.8	<0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		2	1.0	0.5	3.3	<0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		3	0.9	0.6	2.2	<0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		4	1.1	0.7	5.0	<0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		5	1.2	0.7	2.5	<0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		average	1.0	0.6	3.2	<0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	aged	8	3.7	8.8	34	7.6	<0.4	<0.3	<0.1	<0.4	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	aged + 5x washed and tumble dryed	10	<2.0	3.9	26	6.1	<0.2	<0.2	<0.1	<0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	aged + 10x washed and tumble dryed	12	<1.9	2.5	20	4.2	<0.2	<0.2	<0.1	<0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	aged + 5x washed, not tumble dryed	14	1.5	3.1	20	6.3	<0.3	<0.3	<0.3	<0.3	<0.1	<0.1	<0.1	<0.1	<1.7	<0.1	<0.2
	not aged, 5x washed and tumble dryed	16	0.5	0.6	3.3	<0.5	<0.3	<0.3	<0.3	<0.3	<0.1	<0.1	<0.1	<0.1	<1.3	<0.1	<0.1
	not aged, not washed, 5x tumble dryed	18	1.4	<0.2	17	<0.6	<0.3	<0.3	<0.3	<0.3	<0.1	<0.1	<0.1	<0.1	<1.5	<0.1	<0.1
FC-6 PES	original	20	0.2	0.4	4.0	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		21	0.2	0.4	1.6	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		22	0.2	0.3	0.5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		23	0.2	0.3	0.6	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		24	0.2	0.3	0.9	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
		average	0.2	0.34	1.5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	aged	27	<3.1	<0.4	2.6	1.5	<0.4	<0.3	<0.1	<0.3	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	aged + 5x washed and tumble dryed	29	<2.0	2.6	10	2.3	<0.2	<0.2	<0.1	<0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	aged + 10x washed and tumble dryed	31	<1.7	2.2	7.9	1.9	<0.2	<0.2	<0.1	<0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
FC-8 PA	original	33	1.2	0.6	3.6	1.4	6.4	0.6	na	na	na	na	na	<0.3	<0.2	<0.2	<0.6
		34	1.1	0.6	3.4	1.2	5.7	0.6	na	na	na	na	na	<0.3	<0.2	<0.2	<0.6
		35	1.0	0.6	2.7	0.9	3.3	0.4	na	na	na	na	na	<0.3	<0.2	<0.2	<0.6
		36	1.3	0.8	4.0	1.6	17	1.6	11	na	na	na	na	<0.3	<0.2	<0.2	<0.6
		37	1.2	0.8	4.0	1.5	14	0.9	6.5	na	na	na	na	<0.3	<0.2	<0.2	<0.6
		average	1.2	0.7	3.5	1.3	9.3	0.8	8.8	na	na	na	na	<0.3	<0.2	<0.2	<0.6
	aged	40	3.8	4.6	12	11	29	12	11	4.0	5.8	<0.3	<0.1	<0.1	<0.1	<0.1	<0.1
	aged + 5x washed and tumble dryed	42	<2.0	1.6	5.7	5.1	15	4.3	5.1	1.1	2.1	0.2	0.3	<0.1	<0.1	<0.1	<0.1
	aged + 10x washed and tumble dryed	44	<2.0	<0.8	4.1	3.5	12	3.1	4.4	0.9	1.7	0.3	0.6	<0.1	<0.1	<0.1	<0.1
FC-8 PES	original	46	0.8	0.5	3.5	1.5	11	0.8	4.9	<1.8	<7.0	<0.4	<1.8	<0.1	<0.1	<0.1	<0.4
		47	0.9	0.6	3.7	1.7	11	0.8	4.2	<1.7	<7.0	<0.4	<1.6	<0.1	<0.1	<0.1	<0.4
		48	0.6	0.4	2.5	1.1	6.1	0.6	3.0	<1.3	<7.0	<0.3	<1.1	<0.1	<0.1	<0.1	<0.4
		49	0.5	0.4	2.8	1.4	17	1.4	11	<1.3	<7.0	<0.3	<1.3	<0.1	<0.1	<0.1	<0.4
		50	0.7	0.5	3.4	1.5	18	1.3	10	<1.3	<7.0	<0.3	<1.5	<0.1	<0.1	<0.1	<0.4
		average	0.7	0.5	3.2	1.4	13	1.0	6.6	<1.8	<7.0	<0.4	<1.8	<0.1	<0.1	<0.1	<0.4
	aged	53	<3.5	<0.5	<0.6	1.1	5.0	4.4	9.4	20	36	5.1	1.1	0.8	<0.1	<0.1	<0.1
	aged + 5x washed and tumble dryed	55	<1.9	<0.5	1.2	2.0	4.5	2.6	3.5	1.5	2.8	1.0	1.2	<0.1	<0.1	<0.1	<0.1
	aged + 10x washed and tumble dryed	57	<2.0	<0.4	0.8	1.4	3.6	1.6	3.3	0.9	2.5	0.5	0.8	<0.1	<0.1	<0.1	<0.1

		volatile PFAS									
	Sample description	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	6:2 FTAC	8:2 FTAC	10:2 FTAC	6:2 FTMAC	8:2 FTMAC	10:2 FTMAC
FC-6 PA	original	<2.8	92	20	48	<1.1	8.1	16	<4.5	<1.1	<1.1
		<2.7	92	13	27	<1.1	2.1	8.1	<4.4	<1.1	<1.1
		<2.8	92	17	38	<1.1	5.1	12	<4.5	<1.1	<1.1
	aged	<5.7	87	<2.3	34	<2.2	<4.4	<2.2	<9.4	<2.2	<2.3
	aged + 5x washed and tumble dryed	<3.1	430	<1.2	18	<1.2	<2.3	<1.2	<5.0	<1.2	<1.2
	aged + 10x washed and tumble dryed	<3.3	520	<5.0	17	<1.3	<2.5	<1.3	<5.5	<1.3	<1.3
	aged + 5x washed, not tumble dryed	<7.5	390	<1.7	<1.7	<1.1	<1.1	<1.1	<1.5	<1.5	<1.5
	not aged, 5x washed and tumble dryed	<5.0	150	<1.2	<1.1	<0.7	<0.7	<0.7	<1.0	<1.0	<1.0
	not aged, not washed, 5x tumble dryed	<5.9	85	<1.4	<1.3	<0.9	<0.9	<0.9	<1.2	<1.2	<1.2
FC-6 PES	original	<2.8	52	<1.1	6.0	<1.1	2.4	<1.1	<4.7	<1.1	<1.1
		<2.9	51	<1.1	6.8	<1.1	<2.2	<1.1	<4.7	<1.1	<1.1
		<2.9	52	<1.1	6.4	<1.1	2.4	<1.1	<4.7	<1.1	<1.1
	aged	<5.6	300	<2.2	15	<2.2	<4.2	<2.1	<9.1	<2.2	<2.2
	aged + 5x washed and tumble dryed	<3.4	430	<1.3	<6.3	<1.3	<2.6	<1.3	<5.6	<1.3	<1.4
	aged + 10x washed and tumble dryed	<2.8	460	<1.1	<3.9	<1.1	<2.1	<1.1	<4.6	<1.1	<1.1
FC-8 PA	original	<3.4	38	680	410	430	2540	1710	<5.6	<1.3	<1.4
		<3.5	38	610	370	410	2670	1700	<5.7	<1.4	<1.4
		<3.5	38	650	390	420	2610	1710	<5.7	<1.4	<1.4
	aged	<5.7	10	360	330	<2.2	6.5	<2.2	<9.3	<2.2	<2.3
	aged + 5x washed and tumble dryed	<3.0	30	480	270	<3.0	5.1	<3.0	<3.0	<3.0	<3.0
	aged + 10x washed and tumble dryed	<3.5	13	480	260	<1.4	<2.7	<1.4	<5.8	<1.4	<1.4
FC-8 PES	original	na	na	na	na	na	na	na	na	na	na
		<2.9	41	490	740	26	500	530	<4.8	<1.1	<1.2
		<2.9	41	490	740	26	500	530	<4.8	<1.1	<1.2
	aged	<6.1	50	750	550	<2.4	8.3	<2.3	<10	<2.4	<2.4
	aged + 5x washed and tumble dryed	<3.4	69	510	350	<1.3	9.6	<1.3	<5.6	<1.3	<1.3
	aged + 10x washed and tumble dryed	<3.6	18	420	280	<1.4	<2.7	<1.4	<5.9	<1.4	<1.4

(na= not available due to low IS recovery)

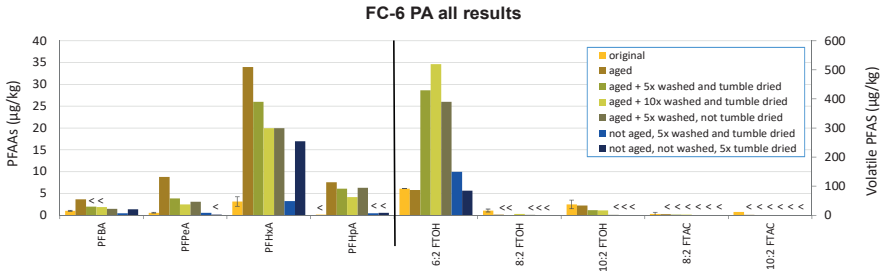

Figure S5-3.1 PFAS concentration (µg/kg) in all analysed FC-6 coated PA samples. <: LOD.

References

1. Schellenberger, S.; Gillgard, P.; Stare, A.; Hanning, A.; Levenstam, O.; Roos, S.; Cousins, I. T., Facing the rain after the phase out: Performance evaluation of alternative fluorinated and non-fluorinated durable water repellents for outdoor fabrics. *Chemosphere* 2018, 193, 675-684.
2. Van der Veen, I.; Weiss, J. M.; Hanning, A.; de Boer, J.; Leonards, P. E. G., Development and validation of a method for the quantification of extractable perfluoroalkyl acids (PFAAs) and perfluorooctane sulfonamide (FOSA) in textiles. *Talanta* 2016, 147, 8-15.
3. Bonas, G.; Zervou, M.; Papaeoannou, T.; Lees, M., "SoftCRM": a new software for the Certification of Reference Materials. *Accreditation and Quality Assurance* 2003, 8, 101-107.
4. Van der Veen, I.; Hanning, A.; Stare, A.; Leonards, P. E. G.; de Boer, J.; Weiss, J. M., The effect of weathering on per- and polyfluoroalkyl substances (PFASs) from durable water repellent (DWR) clothing. *Chemosphere* 2020, 249, 126100.

Chapter

6.

Discussion and Outlook

6.1. Per- and polyfluoroalkyl substance (PFAS) analyses in textiles

The developed method for perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and perfluorooctane sulfonamide (FOSA) in outdoor wear is the first method published that is suitable for the determination of PFASs in textile. It includes two sequential extractions with 5 mL methanol and an extraction time of 30 min, and analysis by high-performance liquid chromatography–tandem mass spectrometry (LC–MS/MS) without further cleaning of the extracts. A method reproducibility of <20% (RSD) and an extraction efficiency of >90% was achieved. Because the limits of detection (LODs) of the developed method were between 0.02 and 0.10 µg/m^2 (equals 0.15 and 3.7 ng/g, respectively), the method was suitable to detect concentrations below the European maximum allowable levels for perfluorooctane sulfonate (PFOS) (1µg/m^2)[1] and perfluorooctanoic acid (PFOA) (0.025 mg/kg)[2] in textile. Analyses were performed on an Agilent 6410 Triple Quad LC-MS/MS (Agilent Technologies, Amstelveen, The Netherlands). Since more sensitive analytical equipment, like e.g. the SCIEX triple Quad™ 6500+ LC-MS/MS system has come to the market after the method was developed and validated, LODs of the developed method would now be approximately 50 fold lower. The influence of matrix on the quantification of perfluoroalkyl acids (PFAAs) with the developed method was studied. All recoveries of the internal standards (ISs) were, besides three exceptions, in the range of 30-130%. Since the same IS recovery pattern was observed for individual PFASs between all replicates of a sample, while those patterns differed between different samples, the lower recoveries of the ISs were most likely not caused by insufficient extraction, but by the matrix causing ion suppression. An additional cleaning step would be needed to reduce the ion suppression.

Although such an additional cleaning step before analysis might reduce ion-suppression, it is highly recommended to use isotope-labeled ISs for each PFAS congener. Unfortunately, to the best of our knowledge, those are still not commercially available for all analysed PFAAs in this thesis. They are still missing for example for perfluorotridecanoic acid (PFTrDA) and perfluoroheptane sulfonic acid (PFHpS). In addition to an extraction method for PFAAs from textiles, described in Chapter 2, also an extraction and analytical method for volatile PFASs from textiles has been developed in this study. This method included two sequential extractions with ethyl acetate, followed by a cleaning step with active carbon and analysis by gas chromatography/electron impact-mass spectrometry (GC/EI-MS) (see Chapter 4).

Analytical methods for ionic and volatile PFASs are currently also available for other matrices than textiles. However, new PFASs like e.g. ammonium 2,3,3,3-tetrafluoro-

2-(heptafluoropropoxy)propanoate (GenX)[3, 4] and ammonium perfluoro-2-[(propoxy) propoxy]-1-propanoate (HFPO-TA)[5], are regularly introduced to the market, or enter the environment through discharges of side products from production processes, like e.g. perfluorobutane sulfonamide (FBSA)[6], N-Methyl perfluorobutane sulfonamide (MeFBSA)[7] and N-Methyl perfluorobutane sulfonamidoacetic acid (MeFBSAA)[8]. Since all these compounds have different properties (e.g. solubility and volatility), there will be a continuous need for extending the available methods, and for more analytical standards, including isotope-labeled analytical standards.

Currently, several thousands of different PFASs exist, and are present in products, in the environment and in the human body. With this high number of PFAS congeners, it is impossible to analyse each individual PFAS congener separately, even in case analytical standards would be available for all PFASs. Because of this, laboratories started to use other methods like the analysis of the total amount of organic fluorine by particle induced γ-ray emission (PIGE) spectroscopy[9], combustion ion chromatography (CIC), and instrumental neutron activation analysis (INAA)[10]. Total organic fluorine analyses have the advantage to measure the total concentration of all per- and polyfluorinated organic compounds present in a sample, including the side-chain fluorinated polymers (SFPs). The obvious disadvantage of performing only total organic fluorine analyses is that all information about individual PFASs is lost. Combination of congener-specific and total fluorine methods is therefore recommended.

Another method which is nowadays used by several laboratories is the total oxidizable precursor (TOP) assay[11-13]. With this method all PFAS precursors present in a sample are degraded or transformed into undegradable PFCAs and PFSAs. The PFCAs and PFSAs are analysed before and after the degradation. This method does have some disadvantages like, e.g. the conversion of precursors into PFCA can be incomplete, and other organics which are present in a sample may interfere with the oxidation of the PFAS precursors[14]. With the TOP assay no information is generated on the concentration of each individual PFAS, but it does provide information on the potential risk of a sample, since all PFASs will finally end up in the environment as PFAAs and PFSAs by biotic or abiotic degradation or transformation.

6.2. Fate of PFASs in DWR of clothing

In Chapter 4 it has been demonstrated that weather conditions like sunlight, high temperature, or humidity can have an effect on the congener profile and concentrations of PFASs in DWR-treated outdoor clothing. For some of the PFASs an

increase in concentration was observed after aging. Although in Chapter 4 possible explanations for the occurrence of this increase are given, like degradation of the DWR polymers, non-extractable organic fluorine becoming extractable, or unknown precursors degrading or being transformed into the analysed volatile PFASs, the precise cause of the increase in concentration is still unclear. All results of the research described in this thesis were based on the analysis of single compounds. With the aforementioned techniques like the TOP assay, and total organic fluorine analysis, the balance on PFASs present before and after weathering could be completed. To unravel the details of the processes and transformation routes involved, further research is needed which includes a) the use of TOP assay, which would reveal the amount of precursors present before aging and washing, and the amount of released unextractable PFASs after aging and washing, and b) total F methods, which would reveal the loss of organic fluorine out of the textiles by aging and washing, and c) a combination of TOP assay and total organic fluorine, which would reveal the amount of polymers which are degraded.

In Chapter 5 it is shown that also washing affects the concentration of residual or unreacted PFASs in fabrics coated with DWR based on SFPs. This effect becomes stronger in a combination of aging and washing. Tumble drying did not cause an observable effect. This is a positive result, since most of the manufacturers recommend to tumble dry the outdoor clothing after washing, to regenerate the DWR capacity.

It has been shown that PFAS concentrations in the untreated and treated fabrics are not just depending on the type of DWR formulation used to coat the fabric, but also on the type of fabric (polyamide (PA) or polyester (PES)). Aging could either cause an increase, or a decrease of extractable PFAS concentrations, depending on the type of fabric, and chain length of the PFASs. Washing caused a decrease of PFAA concentrations on the textiles. Volatile PFASs are generally washed off from the textiles. The PFASs which are washed off end up in the sewage system, and via the sewage water treatment plant the PFASs finally end up in surface water as they are only partly removed[15]. Because of the high persistence of PFASs, those compounds will stay in the environment, or end up in the food chain.

These results point to some weaknesses in legislation. Firstly, setting safety standards for only a few individual PFASs is not sufficient to control these harmful substances. Secondly, it has been shown that emission of PFASs from outdoor clothing coated with SFP-based DWR to the environment does take place. To avoid such an emission of PFASs, non-harmful non-fluorinated alternative chemicals are needed in the DWR of outdoor clothing. In the SUPFES project alternative chemicals, which were already

on the market (hydrocarbons, and silicones), were assessed for their performance and their hazard. Results from the technical performance assessment showed inconsistent results for water repellency and durability for the non-fluorinated DWRs. Only some hydrocarbons provided good water repellency and durability. This makes those compounds suitable non-fluorinated alternatives in the DWR for most consumer outdoor clothing[16, 17]. The hydrocarbons have a relatively low hazard[18], and after washing and weathering of fabrics coated with this type of DWR, the water repellence is still maintained[17]. However, with none of the assessed non-fluorinated alternatives (hydrocarbons, and silicones), the oil- and stain repellence, required for certain occupational protective clothing, could be achieved.

6.3. International performance on PFAS analyses

In Chapter 3 of this thesis the results of the fourth round of the United Nations Environment Programme (UNEP) interlaboratory comparison study (ILS) on PFAS analyses show that internationally the analysis of individual PFAS congeners is still a challenge for many laboratories. In this study, in total 1457 z- scores were obtained for PFASs of which 64% were satisfactory. With a coefficient of variation (CV) of 18%, results of PFAS analyses in the human plasma test material of the study looked promising. However, the results of all other matrices (sediment, fish, human milk, human plasma, air extract, and water) did not yet meet the criterion of a maximum uncertainty of ±25%. There were substantial differences in performance and participation between laboratories from different continents. The most important reason for that is the absence of HPLC instrumentation in universities and governmental laboratories in most countries in Africa and South-America, as well as the absence of properly working mass spectrometers.

The gap in the performance of POP analyses in general and the PFAS analysis in particular between developed and developing countries is rather growing than shrinking. In spite of training provided by UNEP, laboratories in developing countries fall short because this type of analysis is not among the priorities in these countries. Lack of instrumentation and experience, difficulties in ordering analytical standards and certified reference materials abroad, and related customs delays, and the absence of proper instrumental service in these countries leads to continuous poor results in ring trials.

There is an increasing number of new PFASs which are being introduced. Besides that, safety standards are being introduced for new PFAS congeners by for example

EFSA, which recently set a new standard for PFASs[19] including perfluorononanoic acid (PFNA). Therefore, there is a continuous need for implementing or adapting methods. However, when laboratories are not even able to submit reliable data on PFASs which are classified as persistent organic pollutants (POPs) and so mandatory to monitor under the Stockholm Convention, it is not realistic to expect those laboratories to perform analyses on other PFAS congeners as well. The TOP assay and the total organic fluorine analyses are also still unknown in developing countries.

6.4. Conclusions

In this study, for the first time, two analytical methods for the analysis of PFASs in textiles haves been developed and validated. The extraction solvents, the number of extractions, and the extraction time were optimized.

Despite that no individual PFAAs and volatile PFASs are used to obtain DWR, this study shows that they are present as impurities and as unreacted products of the production process of the fluorotelomer-based polymers (FTPs). Those PFASs can be released, and emitted to the environment during use, and under certain weather conditions, and also during washing. Results of this study show that aging of DWR can increase the concentrations of extractable PFASs. This increase might be caused by degradation or transformation of other not analysed PFAS congeners, which were present in the textiles before aging. Because of this, legislation and setting safety standards for only some individual PFASs is not enough to protect the consumer. This also emphasizes that replacing one PFAS congener with another PFAS congener is not desirable. The alternative PFASs might also be toxic, and could also degrade or transform into the very persistent PFCAs and PFSAs. The European initiative to ban the use of PFASs as a group[20-22] should, therefore, receive general support.

Regrettable substitution of one PFAS by another should be avoided, although results of the SUPFES project show the challenge to find non-halogenated alternatives with a similar performance to PFASs.

The ILS on the analysis of PFASs described in this thesis shows that developing countries are unable to properly perform such analyses at the moment.

6.5. Future perspectives

Regular international ILSs are needed to ensure a good quality of the analyses of PFASs. A major effort is required to bring developing countries up to date in their performance of the PFAS analysis. This includes improvement of very basic conditions such as instrumental service and fast ordering and custom procedures. In addition, upcoming ILSs should include relevant new PFASs that are found in the environment. More certified reference materials are needed, for materials like outdoor wear. The need for additional analytical PFAS standards and their isotope-labeled analogues remains high.

To complete the mass balance on PFASs before and after treatment of outdoor wear such as weathering, washing and tumble drying, it is recommended to perform TOP assays and total organic fluorine analyses. More research will be needed on the molecular level, to unravel the details of the processes and transformation routes involved in the increase in PFAS concentrations due to weathering.

Considering the environmental- and health impact of PFASs, all applications and use of the entire PFAS group should be banned, including organic fluorine containing replacements, of which not much information is available yet. In contrast with this is the aspect of the need of using PFASs, for example in the DWR of outdoor clothing and uniforms. The SUPFES project has shown that with non-fluorinated alternatives for PFASs in DWR which are available nowadays, water repellence could be reached, but not yet oil, stain and blood repellence. In case the use of PFASs is only a matter of luxury, such as not getting your outdoor clothing dirty so quickly, PFASs could be replaced by non-fluorinated less harmful alternatives, like hydrocarbons. However, there are applications of PFASs in DWR, for which the dirt, oil and stain repellence is required for safety, such as in medical uniforms, and in work wear in the oil industry. For those purposes functional alternatives are required. Until those are available, it may be needed to continue the use of PFASs in those essential applications[23].

PFASs can be harmful to the environment and health. It is highly recommended to prohibit the manufacturing and use of PFASs, except for essential use in case no good alternatives are available yet. However, ultimate efforts should be made in developing proper alternatives, so the use of PFASs in those applications can also soon be phased out.

PFASs are ubiquitous in the environment and humans and due to their high persistence they will not disappear for decades at least. Please let us ensure that we do not pollute the environment any further with these compounds.

References

1. EU, Directive 2006/122/EC of the European Parliament and of the Council of 12 December 2006. *Official Journal of the European Union* 2006, L 372/32, 32-34.
2. EU, COMMISSION DELEGATED REGULATION (EU) 2020/784 of 8 April 2020, amending Annex I to Regulation (EU) 2019/1021 of the European Parliament and of the Council as regards the listing of perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds. *Official Journal of the European Union* 2020, L 188.
3. Wang, Z.; Cousins, I. T.; Scheringer, M.; Hungerbühler, K., Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and their potential precursors. *Environment International* 2013, 60, 242-248.
4. Brandsma, S. H.; Koekkoek, J. C.; van Velzen, M. J. M.; de Boer, J., The PFOA substitute GenX detected in the environment near a fluoropolymer manufacturing plant in the Netherlands. *Chemosphere* 2019, 220, 493-500.
5. Pan, Y.; Zhang, H.; Cui, Q.; Sheng, N.; Yeung, L. W. Y.; Guo, Y.; Sun, Y.; Dai, J., First Report on the Occurrence and Bioaccumulation of Hexafluoropropylene Oxide Trimer Acid: An Emerging Concern. *Environmental Science & Technology* 2017, 51, 9553-9560.
6. Chu, S.; Letcher, R. J.; McGoldrick, D. J.; Backus, S. M., A New Fluorinated Surfactant Contaminant in Biota: Perfluorobutane Sulfonamide in Several Fish Species. *Environmental Science & Technology* 2016, 50, 669-675.
7. Lassen, C.; Brinch, A.; Jensen, A. A., Investigation of sources to PFBS in the environment, M-759|2017, Norwegian environment agency, Kongens Lyngby, Denmark, 15 May 2017. https://www.miljodirektoratet.no/globalassets/publikasjoner/M759/M759.pdf.
8. Newton, S.; McMahen, R.; Stoeckel, J. A.; Chislock, M.; Lindstrom, A.; Strynar, M., Novel Polyfluorinated Compounds Identified Using High Resolution Mass Spectrometry Downstream of Manufacturing Facilities near Decatur, Alabama. *Environmental Science & Technology* 2017, 51, 1544-1552.
9. Robel, A. E.; Marshall, K.; Dickinson, M.; Lunderberg, D.; Butt, C.; Peaslee, G.; Stapleton, H. M.; Field, J. A., Closing the mass balance on fluorine on papers and textiles. *Environmental Science & Technology* 2017, 51, 9022-9032.
10. Schultes, L.; Peaslee, G. F.; Brockman, J. D.; Majumdar, A.; McGuinness, S. R.; Wilkinson, J. T.; Sandblom, O.; Ngwenyama, R. A.; Benskin, J. P., Total Fluorine Measurements in Food Packaging: How Do Current Methods Perform? *Environmental Science & Technology Letters* 2019, 6, 73-78.
11. Janda, J.; Nödler, K.; Scheurer, M.; Happel, O.; Nürenberg, G.; Zwiener, C.; Lange, F. T., Closing the gap – inclusion of ultrashort-chain perfluoroalkyl carboxylic acids in the total oxidizable precursor (TOP) assay protocol. *Environmental Science: Processes & Impacts* 2019, 21, 1926-1935.
12. Zhang, C.; Hopkins, Z. R.; McCord, J.; Strynar, M. J.; Knappe, D. R. U., Fate of per- and polyfluoroalkyl ether acids in the total oxidizable precursor assay and implications for the analysis of impacted water. *Environmental Science & Technology Letters* 2019, 6, 662-668.
13. Al Amin, M.; Sobhani, Z.; Liu, Y.; Dharmaraja, R.; Chadalavada, S.; Naidu, R.; Chalker, J. M.; Fang, C., Recent advances in the analysis of per- and polyfluoroalkyl

substances (PFAS)—A review. *Environmental Technology & Innovation* 2020, 19, 100879.
14. Winchell, L. J.; Wells, M. J. M.; Ross, J. J.; Fonoll, X.; Norton, J. W.; Kuplicki, S.; Khan, M.; Bell, K. Y., Analyses of per- and polyfluoroalkyl substances (PFAS) through the urban water cycle: Toward achieving an integrated analytical workflow across aqueous, solid, and gaseous matrices in water and wastewater treatment. *Science of The Total Environment* 2021, 774, 145257.
15. Lenka, S. P.; Kah, M.; Padhye, L. P., A review of the occurrence, transformation, and removal of poly- and perfluoroalkyl substances (PFAS) in wastewater treatment plants. *Water Research* 2021, 199, 117187.
16. Schellenberger, S.; Hill, P. J.; Levenstam, O.; Gillgard, P.; Cousins, I. T.; Taylor, M.; Blackburn, R. S., Highly fluorinated chemicals in functional textiles can be replaced by re-evaluating liquid repellency and end-user requirements. *Journal of Cleaner Production* 2019, 217, 134-143.
17. Schellenberger, S.; Gillgard, P.; Stare, A.; Hanning, A.; Levenstam, O.; Roos, S.; Cousins, I. T., Facing the rain after the phase out: Performance evaluation of alternative fluorinated and non-fluorinated durable water repellents for outdoor fabrics. *Chemosphere* 2018, 193, 675-684.
18. Holmquist, H.; Schellenberger, S.; van der Veen, I.; Peters, G. M.; Leonards, P. E. G.; Cousins, I. T., Properties, performance and associated hazards of state-of-the-art durable water repellent (DWR) chemistry for textile finishing. *Environment International* 2016, 91, 251-264.
19. EFSA, EFSA Panel on Contaminants in the Food Chain, Scientific Opinion on the risk to human health related to the presence of perfuoroalkyl substances in food. *EFSA Journal* 2020, 18 (9), 6223.
20. REACH, 2nd Stakeholder consultation on a restriction for PFAS. National Institute for Public Health and the Environment (RIVM); Bundesanstalt fur Arbeitsschutz und Arbeitsmedizin (baua); Swedisch Chemical Agency (KEMI); Norwegian Environment Agency; Ministry of Environment and Food of Denmark: https://link.webropolsurveys.com/Participation/Public/c4d58b80-5227-4f31-b656-92bc0669e41e?displayId=Ger2322406 (14 September 2021).
21. ECHA, REACH restrictions. European Chemical Agency. https://echa.europa.eu/nl/hot-topics/perfluoroalkyl-chemicals-pfas (27-09-2021).
22. EU, Directive 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption. *Official Journal of the European Union* 2020, L 435, 62.
23. Cousins, I. T.; Goldenman, G.; Herzke, D.; Lohmann, R.; Miller, M.; Ng, C. A.; Patton, S.; Scheringer, M.; Trier, X.; Vierke, L.; Wang, Z.; DeWitt, J. C., The concept of essential use for determining when uses of PFASs can be phased out. *Environmental Science: Processes & Impacts* 2019, 21, 1803-1815.

Summary

Summary

Per- and polyfluoroalkyl substances (PFASs) are a class of man-made chemicals, which consist of a fluorinated carbon back bone and a functional group like a carboxylic acid, sulfonic acid, alcohol, etc. Because PFASs have the unique properties of being hydrophobic as well as fat resistant, the compounds are used in a wide range of applications, like non-stick coating in pans, firefighting foams, etc. In outdoor wear side-chain fluorinated polymers (SFPs), which consist of polymers such as polyurethanes or acrylates with PFASs as side-chains, are used to obtain the required water and dirt repellence. In outdoor wear PFASs are present as impurities and as unreacted products of the production process of those SFPs. The study described in this thesis focused on PFASs present in textiles of outdoor wear.

Since no peer-reviewed method was available for the analyses of PFASs in textiles, a method was first developed, optimized and validated for the analyses of perfluoroalkyl carboxylic acids (PFCAs) (C_4-C_{14}), and perfluoroalkane sulfonic acids (PFSAs) (C_4, C_6, C_7, C_8) in textiles. Extraction solvents, extraction duration and number of sequential extractions were optimized. The final method consisted of two sequential liquid-solid extractions (LSE) with 5 mL methanol each, and an extraction duration of 30 min, followed by a concentration step and analysis by high-performance liquid chromatography-tandem mass spectrometry (LC-MS/MS), without further cleaning of the extracts. With the developed method an extraction efficiency of >90% was reached. The overall recoveries of the entire method were > 80%, the repeatabilities were < 9% (n=3), and the reproducibilities were < 20% (n=3). Ion suppression was observed due to matrix effects, but recoveries of the mass labeled internal standards were all > 30%.

Because some of the PFASs are very persistent, bioaccumulative, toxic and very mobile, and hence are ubiquitously present in the environment and in the human body, the use of some PFASs has been restricted, and the regulation of more PFAS compounds is ongoing. The determine whether PFAS concentrations meet the safety standards, there is a need for reliable analytical methods. To avoid that reported concentrations are dependent on the quality of the analysis laboratory, an interlaboratory comparison study (ILS) was organized to assess the overall performance of laboratories worldwide. Participants could report PFAS concentrations in a test solution of the target compounds, and in six matrices (sediment, fish, human milk, human plasma, air extract, and water). In total 53 laboratories registered, of which 39 submitted results for at least one matrix or test solution. The majority of the participating laboratories originated from Western Europe and North-America, and from the Asia-Pacific region. There were no participating laboratories from Africa, and from

Central and Eastern Europe only two participating laboratories submitted results. Only one laboratory from South/Central America reported PFAS concentrations. For the instrumental analysis liquid chromatography (LC) was used by all participants. The preferred detection method used by the majority of the participants was tandem mass spectrometric (MS/MS) detection. 64% of the 1457 assigned z-scores were satisfactory. The mean coefficients of variation (CVs) exceeded the satisfactory limit of 25% for all matrices, except for the human plasma test material (18%). For the test solution the CVs for all PFASs ranged from 7%-24% (mean 14%). For human milk the highest mean CV (61%) was calculated.

The effects of weathering on PFASs from outdoor wear were assessed on thirteen commercial available textile samples with an SFP-based durable water repellent (DWR) coating. The concentrations of perfluoroalkyl acids (PFAAs) and volatile PFASs in the textiles were determined. The described developed and validated method was used for the analysis of PFAAs. Volatile PFASs were extracted from the textiles by LSE with ethyl acetate, and the separation and detection of volatile PFASs was carried out by gas chromatography/electron impact-mass spectrometry (GC/EI-MS). After weathering (exposure to elevated ultra violet (UV) radiation, humidity and temperature) of the thirteen textile samples in an aging device for 300h, the samples were again analysed for their PFAA and volatile PFAS concentrations. Weathering did effect the PFAS concentrations and the PFAS profiles in the DWR coated textiles. An increase of 5-fold to more than 100-fold was observed for the PFAA concentrations in most of the samples, and some PFAAs which were not detected in the textiles before aging were detected in same textiles after weathering. For the volatile PFASs the concentrations increased up to 20-fold. Sinds DWR chemistries are based on SFPs, suggested explanations for the increase in concentrations are hydrolysis of the SFPs or degradation of the DWR polymers. Other possible explanations are the release of the unextractabe fraction, or degradation or transformation of not analysed unknown precursors which were present in the not aged textiles as impurities, into the analyses PFAAs and volatile PFASs.

To determine the fate of PFASs from DWR coated outdoor clothing during use, the effects of aging, washing and tumble drying on extractable PFAS concentrations and profiles in DWR coated textiles were assessed. Two types of fabrics, polyamide (PA) and polyester (PES), which were each coated with perfluorohexane-based short-chain SFPs (FC-6 chemistry) and perfluorooctane-based long-chain SFP (FC-8 chemistry) were aged in an aging device, followed by ten sequential washing and tumble drying cycles. In addition the FC-6 chemistry coated PA fabric was washed and tumble dried without aging.

The concentration of extractable PFAAs increased due to aging as was seen before on the commercial textiles. The effect of aging on the volatile PFASs was dependent of the type of fabric. Extractable PFAA concentrations decreased after washing. Washing in general, caused the volatile PFASs to be partly washed out of the textiles, but washing also appeared to be increasing the volatile PFAS concentration in fabrics. With a combination of aging and washing this effect became stronger. There was no effect of tumble drying on the extractable PFAS concentrations in textiles observed.

Possible degradation and transformation mechanisms and routes, which potentially result in emissions of PFASs to the environment, are described for the increase of extractable PFAS concentrations in fabrics as an effect of aging and washing.

With the study described in this thesis it has been shown that performing a reliable PFAS analysis remains a challenge, especially for laboratories from less developed countries. With the study described in this thesis it has also been shown that PFASs from outdoor wear coated with DWR based on SFPs can be released, and emitted to the environment during use, under certain weather conditions, and also during washing. Since extractable PFAS concentrations increased, it has been shown that legislation and setting safety standards for only some individual PFASs is not enough to protect the environment. Also replacing one PFAS congener with another PFAS congener should be avoided.

Samenvatting

Samenvatting

Per- en polygefluoreerde alkylstoffen (PFASs) vormen een groep synthetische verbindingen die niet van nature voorkomen in het milieu. Deze verbindingen bestaan allemaal uit een keten van gefluoreerde koolstoffen en een functionele groep zoals b.v. een zuurgroep, een sulfonaatgroep of een alcoholgroep. PFASs zijn zowel hydrofoob als vetafstotend. Vanwege deze unieke eigenschappen, worden PFASs in een breed scala aan producten gebruikt, zoals o.a. in de antiaanbaklaag in pannen, blusschuim, enz. In outdoor kleding worden polymeren met gefluoreerde zijketens (SFPs) gebruikt om de kleding water- en vuilafstotend te maken. Deze SFPs bestaan uit polymeren zoals polyurethaan of acrylaten met PFASs als zijketens. In outdoor kleding zijn PFASs aanwezig als verontreinigingen en als niet gereageerde componenten vanuit het SFP productieproces. Het onderzoek dat in dit proefschrift is beschreven, richtte zich op de PFASs die aanwezig waren in textiel van outdoor kleding.

Aangezien er geen peer-reviewed methode beschikbaar was voor de analyse van PFASs in textiel, werd eerst een methode ontwikkeld, geoptimaliseerd en gevalideerd voor de analyse van perfluoralkylcarbonzuren (PFCAs) (C_4-C_{14}) en perfluoralkaansulfonzuren (PFSAs) (C_4, C_6, C_7, C_8) in textiel. Het type oplosmiddel voor de extractie, de extractieduur en het aantal opeenvolgende extracties werden geoptimaliseerd. De uiteindelijke methode bestond uit twee opeenvolgende vloeistof-vaste stof extracties (LSE) met elk 5 ml methanol en een extractieduur van 30 minuten, gevolgd door een concentratiestap en analyse d.m.v. high-performance vloeistofchromatografie-tandem massaspectrometrie (LC-MS/MS), zonder verdere zuivering van de extracten. Met de ontwikkelde methode werd een extractie-efficiëntie van >90% bereikt. De totale recovery's van de gehele methode waren > 80%, de herhaalbaarheid was < 9% (n=3) en de reproduceerbaarheid was < 20% (n=3). Ion suppressie werd waargenomen als gevolg van matrixeffecten, maar de recovery's van de massa-gelabelde interne standaarden waren allemaal > 30%.

Omdat sommige van de PFASs zeer persistent, bioaccumulerend, toxisch en zeer mobiel zijn en daarom alomtegenwoordig zijn in het milieu en in het menselijk lichaam, is het gebruik van sommige PFASs beperkt en wordt momenteel gewerkt aan de regulering van meer PFAS verbindingen. Om te bepalen of PFAS concentraties voldoen aan de normen is er behoefte aan betrouwbare analysemethoden. Om te voorkomen dat gerapporteerde concentraties afhankelijk zijn van de kwaliteit van het analyselaboratorium, werd een interlaboratorium studie (IL) georganiseerd om de algehele prestaties van laboratoria wereldwijd vast te stellen. Deelnemers konden de PFAS concentraties in een testoplossing rapporteren en in zes matrices (sediment,

vis, moedermelk, menselijk plasma, luchtextract en water). In totaal registreerden 53 laboratoria zich voor de IL, waarvan 39 uiteindelijk hun resultaten indienden voor minimaal één matrix of testoplossing. Het merendeel van de deelnemende laboratoria was afkomstig vanuit de Azië-Pacific regio en uit West-Europa en Noord-Amerika. Uit de regio Midden- en Oost-Europa kwamen slechts twee deelnemende laboratoria en uit Zuid en Midden-Amerika deed slechts één laboratorium mee. Geen enkel Afrikaans land deed mee. Alle deelnemers gebruikten vloeistofchromatografie (LC) voor de analyse van de PFASs, waarbij de meest gebruikte detectiemethode tandem-massaspectrometrie (MS/MS) was. 64% van de 1457 toegekende z-scores was voldoende. De gemiddelde variatiecoëfficiënten (CVs) waren voor alle matrices hoger dan de gestelde limiet van 25%, behalve voor het plasma testmateriaal (18%). Voor de testoplossing varieerden de CVs voor alle PFASs van 7%-24% (gemiddeld 14%). Voor moedermelk werd de hoogste gemiddelde CV (61%) berekend.

Vervolgens werd het effect van verwering op PFASs in outdoorkleding onderzocht. In 13 commercieel verkrijgbare stukken textiel met een duurzame waterafstotende (DWR) coating werden de concentraties van perfluoralkylzuren (PFAAs) en vluchtige PFASs bepaald. Voor de analyses van PFAAs werd gebruik gemaakt van de hierboven genoemde ontwikkelde en gevalideerde methode. Vluchtige PFASs werden uit het textiel geëxtraheerd d.m.v. LSE met ethylacetaat. Voor de scheiding en detectie van vluchtige PFASs werd gebruik gemaakt van gaschromatografie/ elektron impact massaspectrometrie (GC/EI-MS). Na verwering (blootstelling aan verhoogde ultraviolette (UV) straling, vochtigheid en temperatuur) van de dertien textielmonsters in een verweringsmachine gedurende 300 uur, overeenkomstig met de levensduur van een jas, werden de monsters opnieuw geanalyseerd op hun PFAA en vluchtige PFAS concentraties. Verwering had effect op zowel de PFAS concentraties als op de PFAS profielen in de DWR-gecoate stukken textiel. In de meeste stukken textiel werd een 5- tot meer dan 100-voudige verhoging waargenomen in PFAA concentratie en sommige PFAAs die niet vóór verwering in het textiel werden gedetecteerd, werden na verwering wel gedetecteerd in hetzelfde stuk textiel. Van de vluchtige PFASs namen de concentraties tot 20 keer toe. Aangezien DWR-chemie gebaseerd is op SFPs, zijn mogelijke verklaringen voor de toename van deze concentraties hydrolyse van de SFPs of afbraak van de DWR-polymeren. Andere mogelijke verklaringen zijn het vrijkomen van de niet-extraheerbare fractie, of degradatie of transformatie van niet geanalyseerde onbekende precursors van PFAAs en vluchtige PFASs, die als onzuiverheden in het niet-verweerde textiel aanwezig waren.

Om het lot van PFASs van DWR-gecoate outdoorkleding tijdens gebruik te bepalen, werden de effecten van verwering, wassen en drogen (in een droogtrommel) op extraheerbare PFAS concentraties en PFAS profielen in DWR-gecoat textiel

onderzocht. Twee typen textiel, polyamide (PA) en polyester (PES), die elk waren gecoat met op perfluorhexaan gebaseerde korte keten SFPs (FC-6-chemie) en op perfluoroctaan gebaseerde lange keten SFPs (FC-8-chemie) werden verweerd in een verweringsmachine, gevolgd door tien opeenvolgende was- en droogcycli. Bovendien werd het met FC-6 chemie gecoate PA-textiel gewassen en in een droogtrommel gedroogd zonder eerdere verwering. De concentratie van extraheerbare PFAAs nam door verwering toe, zoals eerder werd waargenomen bij verwering van het commerciële textiel. Het effect van verwering op de vluchtige PFASs was afhankelijk van het type stof. Extraheerbare PFAA concentraties namen af als gevolg van wassen. Wassen in het algemeen zorgde ervoor dat de vluchtige PFASs gedeeltelijk uit het textiel werden gewassen, maar wassen verhoogde soms ook de vluchtige PFAS concentraties in de stukken textiel. Met een combinatie van verwering en wassen werd dit effect sterker. Het drogen van de stukken textiel in een droogtrommel had geen waarneembaar effect op de extraheerbare PFAS gehalten in textiel. Mogelijke afbraak- en transformatiemechanismen en routes, die kunnen leiden to emissies van PFASs naar het milieu, zijn beschreven voor de toename van extraheerbare PFAS concentraties in DWR gecoate stukken textiel als gevolg van verwering en wassen.

Met de studie beschreven in dit proefschrift is aangetoond dat het uitvoeren van een betrouwbare PFAS analyse vooral voor veel laboratoria uit minder ontwikkelde gebieden een een flinke uitdaging blijft. Verder is aangetoond dat tijdens het wassen en tijdens het gebruik van op basis van SFP DWR gecoate outdoorkleding onder bepaalde weersomstandigheden PFASs kunnen vrijkomen. Deze PFASs komen uiteindelijk in het milieu terecht, waaruit ze door hun hoge persistentie niet of nauwelijks meer verdwijnen. Aangezien de concentraties van individuele extraheerbare PFASs toenamen, is aangetoond dat wetgeving en het stellen van veiligheidsnormen voor slechts enkele individuele PFASs niet voldoende is om het milieu te beschermen. Ook het vervangen van de ene PFAS verbinding door een andere PFAS verbinding moet worden vermeden.

List of publications

List of publications

Fiedler, H.; van der Veen, I.; de Boer, J., Interlaboratory assessments for dioxin-like POPs (2016/2017 and 2018/2019). Chemosphere 2022, 288, 132449.

Fiedler, H.; van der Veen, I.; de Boer, J., Assessment of four rounds of interlaboratory tests within the UNEP-coordinated POPs projects. Chemosphere 2022, 288, 132441.

Van der Veen, I.; Hanning, A.; Stare, A.; Leonards, P. E. G.; de Boer, J.; Weiss, J. M., The effect of weathering on per- and polyfluoroalkyl substances (PFASs) from durable water repellent (DWR) clothing. Chemosphere 2020, 249, 126100.

Fiedler, H.; van der Veen, I.; de Boer, J., Global interlaboratory assessments of perfluoroalkyl substances under the Stockholm Convention on persistent organic pollutants. Trends in Analytical Chemistry 2020, 124, 115459.

Van Mourik, L. M.; van der Veen, I.; Crum, S.; de Boer, J., Developments and interlaboratory study of the analysis of short-chain chlorinated paraffins. Trends in Analytical Chemistry 2018, 102, 32-40.

Holmquist, H.; Schellenberger, S.; van der Veen, I.; Peters, G. M.; Leonards, P. E. G.; Cousins, I. T., Properties, performance and associated hazards of state-of-the-art durable water repellent (DWR) chemistry for textile finishing. Environment International 2016, 91, 251-264.

Van der Veen, I.; Weiss, J. M.; Hanning, A.; de Boer, J.; Leonards, P. E. G., Development and validation of a method for the quantification of extractable perfluoroalkyl acids (PFAAs) and perfluorooctane sulfonamide (FOSA) in textiles. *Talanta* 2016, 147, 8-15.

De Boer, J.; Antelo, A.; van der Veen, I.; Brandsma, S.; Lammertse, N., Tricresyl phosphate and the aerotoxic syndrome of flight crew members – Current gaps in knowledge. *Chemosphere* 2015, 119, S58-S61.

Weiss, J. M.; van der Veen, I.; de Boer, J.; van Leeuwen, S. P. J.; Cofino, W.; Crum, S., Analytical improvements shown over four interlaboratory studies

of perfluoroalkyl substances in environmental and food samples. *Trends in Analytical Chemistry* 2013, 43, 204-216.

Bergman, Å.; Rydén, A.; Law, R. J.; de Boer, J.; Covaci, A.; Alaee, M.; Birnbaum, L.; Petreas, M.; Rose, M.; Sakai, S.; Van den Eede, N.; van der Veen, I., A novel abbreviation standard for organobromine, organochlorine and organophosphorus flame retardants and some characteristics of the chemicals. *Environment International* 2012, 49, 57-82.

Van der Veen, I.; de Boer, J., Phosphorus flame retardants: Properties, production, environmental occurrence, toxicity and analysis. *Chemosphere* 2012, 88, 1119-1153.

Van Leeuwen, S. P. J.; Swart, C. P.; van der Veen, I.; de Boer, J., Significant improvements in the analysis of perfluorinated compounds in water and fish: Results from an interlaboratory method evaluation study. *Journal of Chromatography A* 2009, 1216, 401-409.

Van Leeuwen, S. P. J.; van Velzen, M. J. M.; Swart, C. P.; van der Veen, I.; Traag, W. A.; de Boer, J., Halogenated Contaminants in Farmed Salmon, Trout, Tilapia, Pangasius, and Shrimp. *Environmental Science & Technology* 2009, 43, 4009-4015.

Kotterman, M.; van der Veen, I.; van Hesselingen, J.; Leonards, P.; Osinga, R.; de Boer, J., Preliminary study on the occurrence of brominated organic compounds in Dutch marine organisms. *Biomolecular Engineering* 2003, 20, 425-427.

Submitted:
Van der Veen, I.; Schellenberger, S.; Hanning, A.; Stare, A.; de Boer, J.; Weiss, J. M.; Leonards, P. E. G., The fate of per- and polyfluoroalkyl substances (PFASs) from durable water repellent (DWR) clothing during use. Submitted to *Environmental Science & Technology*.

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