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Outdoor jackets as a source of PFASs in the environment

Erfassung der Expositionspfade von per- und polyfluorierten Chemikalien (PFC) durch den Gebrauch PFC-haltiger Produkte – Abschätzung des Risikos für Mensch und Umwelt (FKZ: 3711 63 418)

REACH in der Praxis

UBA, Berlin, 25 September 2013

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Questions asked and answers sought

Where produced ?

How many produced ?

How many imported into EU / Germany ?

Recyling possible/performed ?

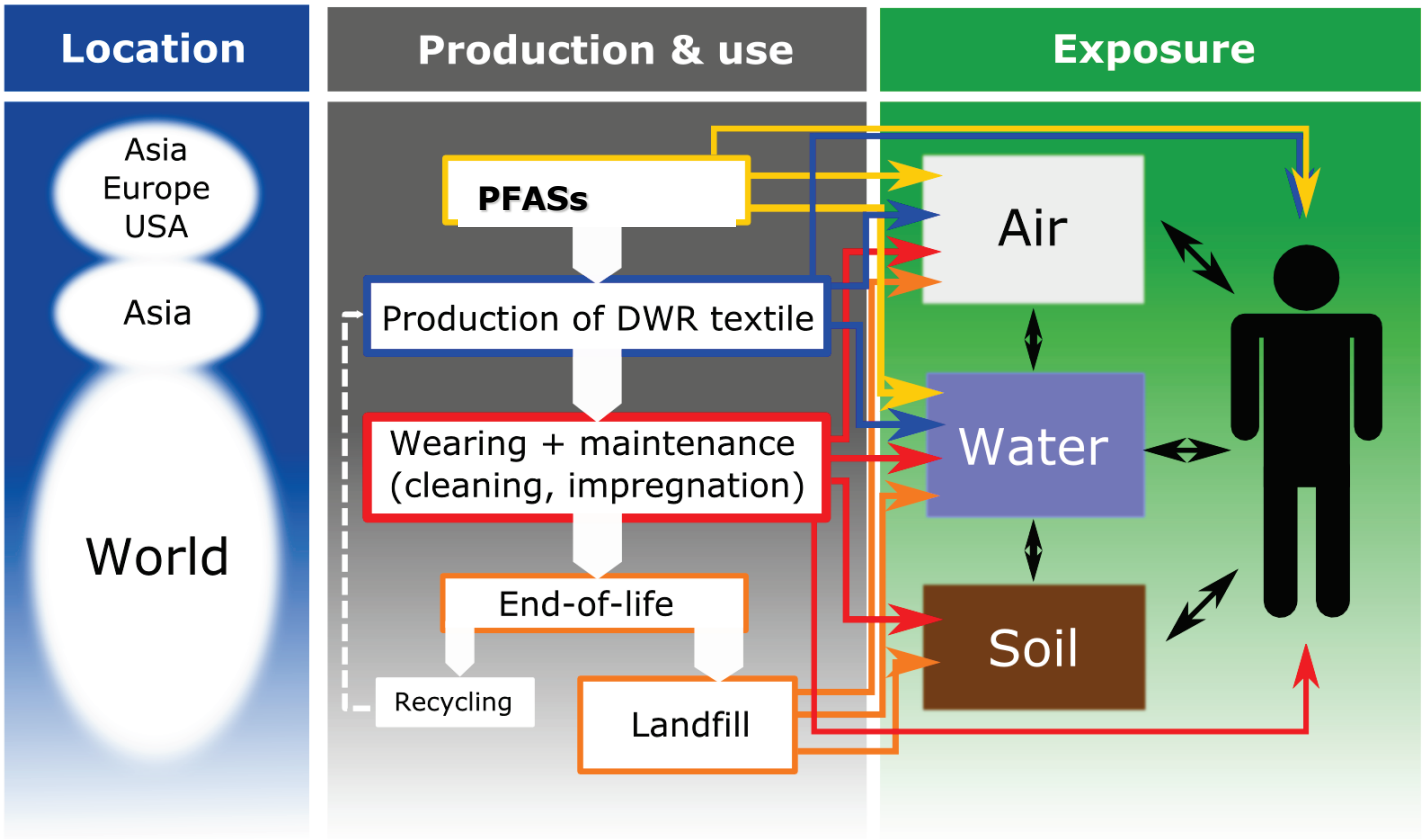
Per and polyfluoroalkyl substances (PFASs) present in which concentrations ?

(validation of analytical methods and comparison to literature data!)

Environmental Exposure ?

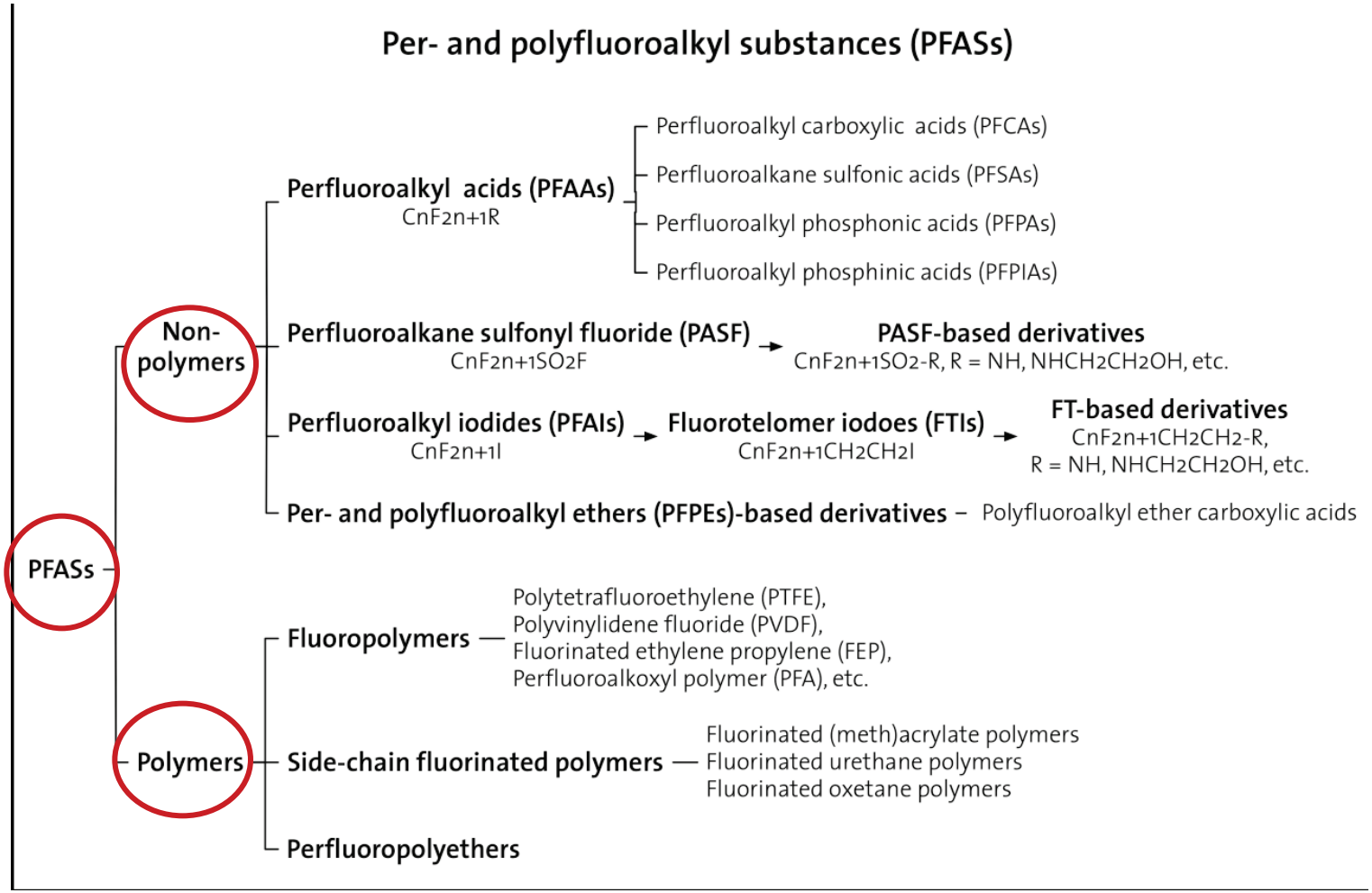
Human Exposure ?

DWR textiles



PFAS Definition

- **Polymeric and Non-Polymeric PFASs [1)]**

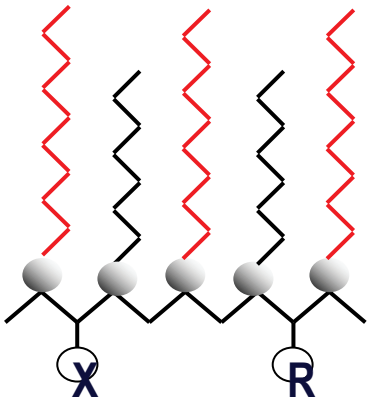


[1)] Buck, R. C.; Franklin, J.; Berger, U.; Conder, J. M.; Cousins, I. T.; De Voogt, P.; Jensen, A. A.; Kannan, K.; Mabury, S. A.; van Leeuwen, S. P. J. Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins. Integr Environ Assess Manag **2011**, 7, 513–541

Scientific information from literature research

Water-repellent and dirt-repellent textiles may consist of woven materials of PTFE, polyester, polyamide, etc., which are impregnated with a dispersion polymer with ”telomer tails”.

Much evidence indicates that these carbon chain tails can be released from polymers and/or that the impregnating agent contains uncombined residual telomers.



Ref.: Perfluorinated substances and their uses in Sweden, KEMI Report 7/06 ISSN: 0284-1185, Stockholm, 2006, Swedish Chemicals Agency.

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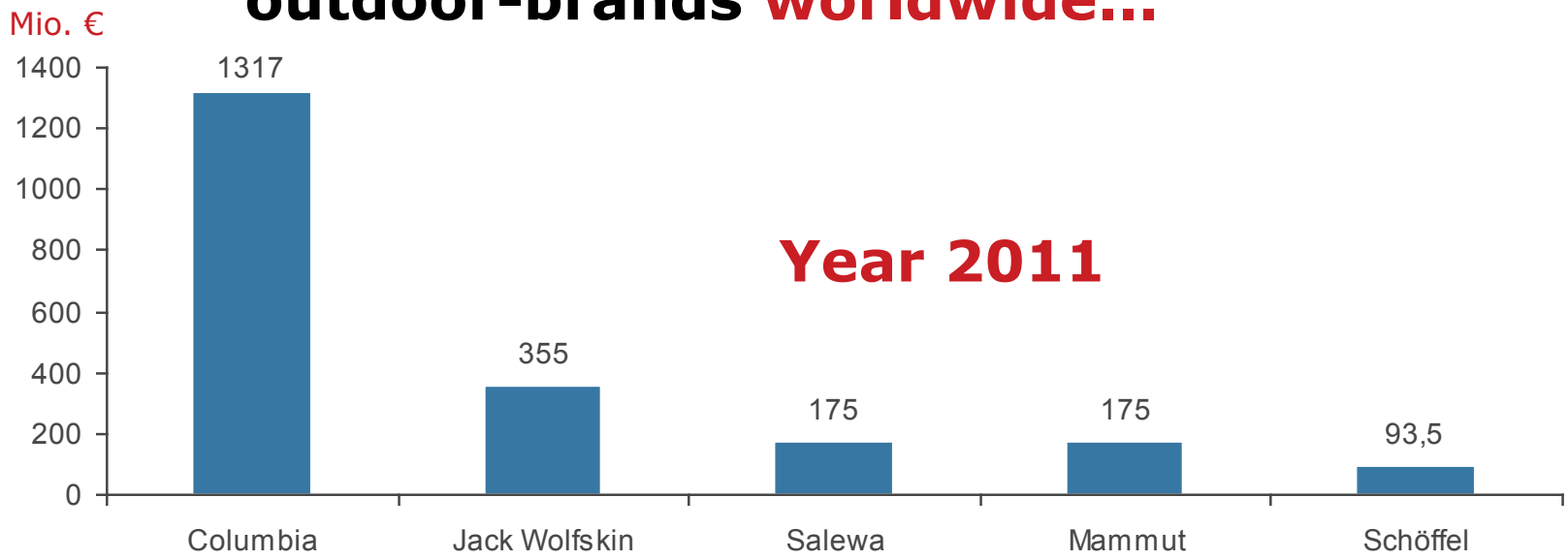
We know the turnover of the leading outdoor-brands worldwide…



http://de.statista.com/statistik/daten/studie/225982/umfrage/Umsatz-der-führenden-Outdoor-Marken

In Europe more than 100 brands contribute to a turnover in 2011 of more than 10 billion €…

European Outdoor Group (EOG); press release July 2012

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From these approx. 10 billion € , the market share of apparel is 52 % …

European Outdoor Group (EOG); press release July 2012

…and of DWR textiles about 22 %…

Press release DPA; ISPO; 29.01.2013

The sales by country are 24 % for Germany in 2011…

European Outdoor Group (EOG); press release July 2012

Thus we can estimate a turnover of approx. 550 Mio. € for DWR textiles in Germany in 2011…

However, we do NOT know the turnover and share of those DWR jackets which are produced by companies being not member of the EOG. These are most likely the jackets in the price range between 10 and 100 €.

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What we know regarding the trade of jackets for Germany

anoraks including windbreaker made of cotton, chemical fibers and garment	Export		Import		Surplus Import
	pieces (Mio)	weight (Mio kg)	pieces (Mio)	weight (Mio kg)	pieces (Mio)
men	10.157	8.449	32.495	28.662	22.338
women	29.408	18.369	82.971	55.769	53.564
Sum Year 2009	**39.565**	**26.818**	**115.466**	**84.431**	**75.902**
men	12.634	10.539	35.506	29.632	22.872
women	33.805	21.095	83.845	53.910	50.040
Sum Year 2010	**46.439**	**31.634**	**119.351**	**83.543**	**72.912**
men	12.421	9.986	41.975	33.565	29.554
women	33.934	20.157	92.160	57.547	58.226
Sum Year 2011	**46.355**	**30.144**	**134.135**	**91.113**	**87.780**

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What we do **NOT** know regarding the trade of jackets for Germany ….and the EU

Are these „outdoor" jackets ?

Are these jackets resistent against water and dirt (durable water resistent = DWR jackets) ?

Are these treated with polymeric PFASs ?

Is the membrane made of polymeric PFASs ?

Assumtions for estimations of non-polymeric PFASs content in DWR

Own investigations (*Eschauzier et. al, PFAS workshop 2012)* as well as personal communication with producers show, that polymeric PFAS contain approx. 0.1 % non-polymeric PFAS (mainly FTOH!).

Two different polymeric PFAS quantified upon non-polymeric PFAS impurities gave the following results:

Sample 1: mainly 6:2-FTOH

Sample 2: mainly 8:2-FTOH and 10:2-FTOH

Assumptions for estimations of PFASs content in DWR

We postulate, that the ratio of the residual FTOHs in individual polymeric PFASs is similar to the pattern covalently bound in the polymer.

Remark: polymeric PFASs level varies dependent on membrane material and water and grease repellency to be reached

Questions asked and answers sought

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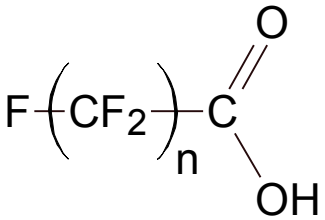
Investigations performed upon the occurrence of non-polymeric PFASs in DWR jackets

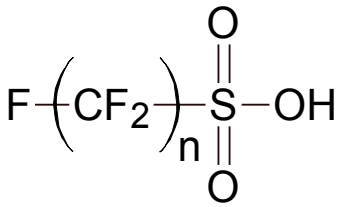
- 16 different DWR jackets were purchased end 2011/beginning 2012.
- Jackets were selected depending on sales no., (e.g. Media Control), membrane type , price etc.
- Jackets should have been produced in Europe and Asian countries, however production mainly done in China & SE Asia!
- Textiles were analyzed upon selected PFASs.

Analyzed compounds

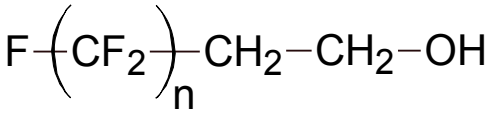
PFCAs (n = 4-14)



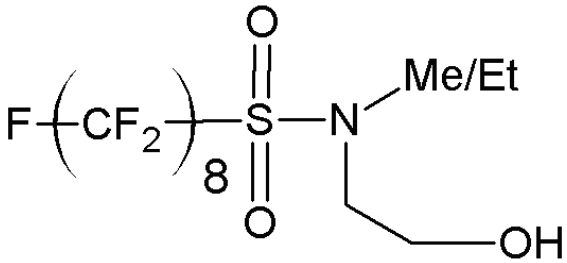
PFSAs (n = 4, 6-8, 10)



Fluorotelomer alcohols (n = 6, 8, 10)



N-MeFOSE & N-EtFOSE



Sample preparation

- Acidic PFASs:
  - Extraction with acetone/acetonitril (80/20; V/V)
  - Evaporation to dryness at 50°C
  - Reconstitution in H_2O/MeOH (1/1; V/V) and filtration through membrane syringe filter
- Neutral PFASs:
  - Extraction with n-hexane
  - Normal Phase-solid phase extraction (SPE) on silica gel
  - Elution with MeOH
- Instrumental analysis: HPLC-ESI-MS/MS in MRM mode
- **Quality control: use of internal standards, spiking with reference compounds and laboratory blanks**

Non-polymeric PFASs concentrations in „jackets“ [µg/m²]

PFASs	PFBA	PFPeA	PFHxA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTrA	PFTeA	Sum PFCAs
Min	n.d.	n.d.	0.01	0.02	n.d.	< LOQ	n.d.	n.d.	n.d.	n.d.	**0.03**
Max	1.52	4.23	14.7	**171**	27.7	85.3	20.3	80.9	3.07	20.5	**430**
% detected	18.75	62.5	87.5	**100**	93.8	93.8	37.5	43.8	31.3	43.8	

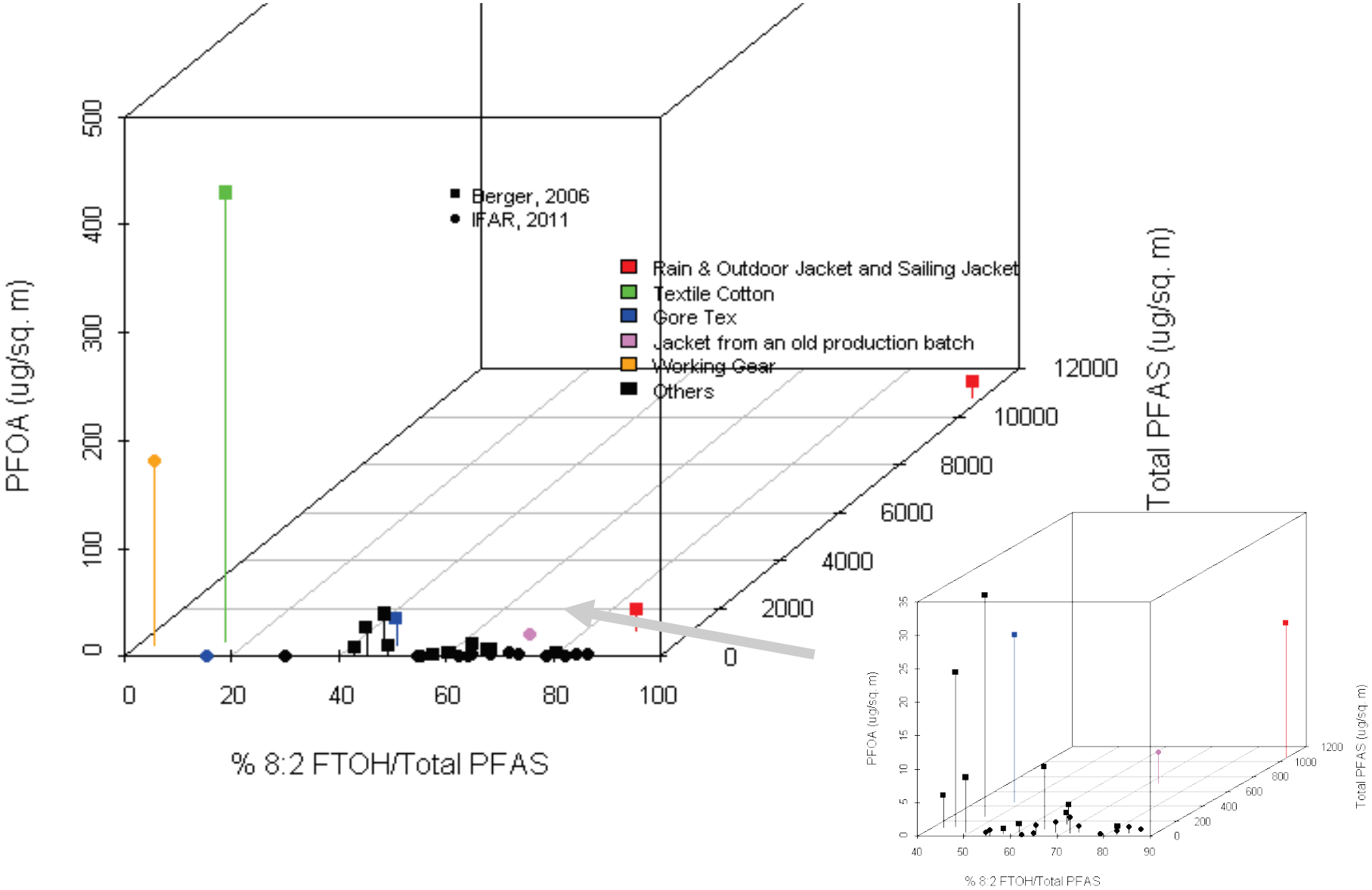
PFASs	6:2-FTOH	8:2-FTOH	10:2-FTOH	Sum FTOHs
Min	n.d.	1.7	1.34	**3.19**
Max	18.6	**516**	182	**698**
% detected	75	**100**	**100**	

PFASs	PFBS	PFHxS	PFHpS	PFOS	PFDS	Sum PFSAs
Min	n.d.	n.d.	n.d.	n.d.	n.d.	**n.d.**
Max	0.51	< LOQ	n.d.	0.54	0.32	**0.86**
% detected	6.3	12.5	0	37.5	18.8	

PFASs	FOSA	N-MeFOSA	N-EtFOSA	N-MeFOSE	N-EtFOSE	Sum FOSA derivatives
Min	n.d.	n.d.	n.d.	n.d.	n.d.	**n.d.**
Max	0.02	n.d.	n.d.	5.02	2.18	**5.02**
% detected	56.3	0	0	75	43.8	

	Sum PFASs
Min	**0.03**
Max	**719**

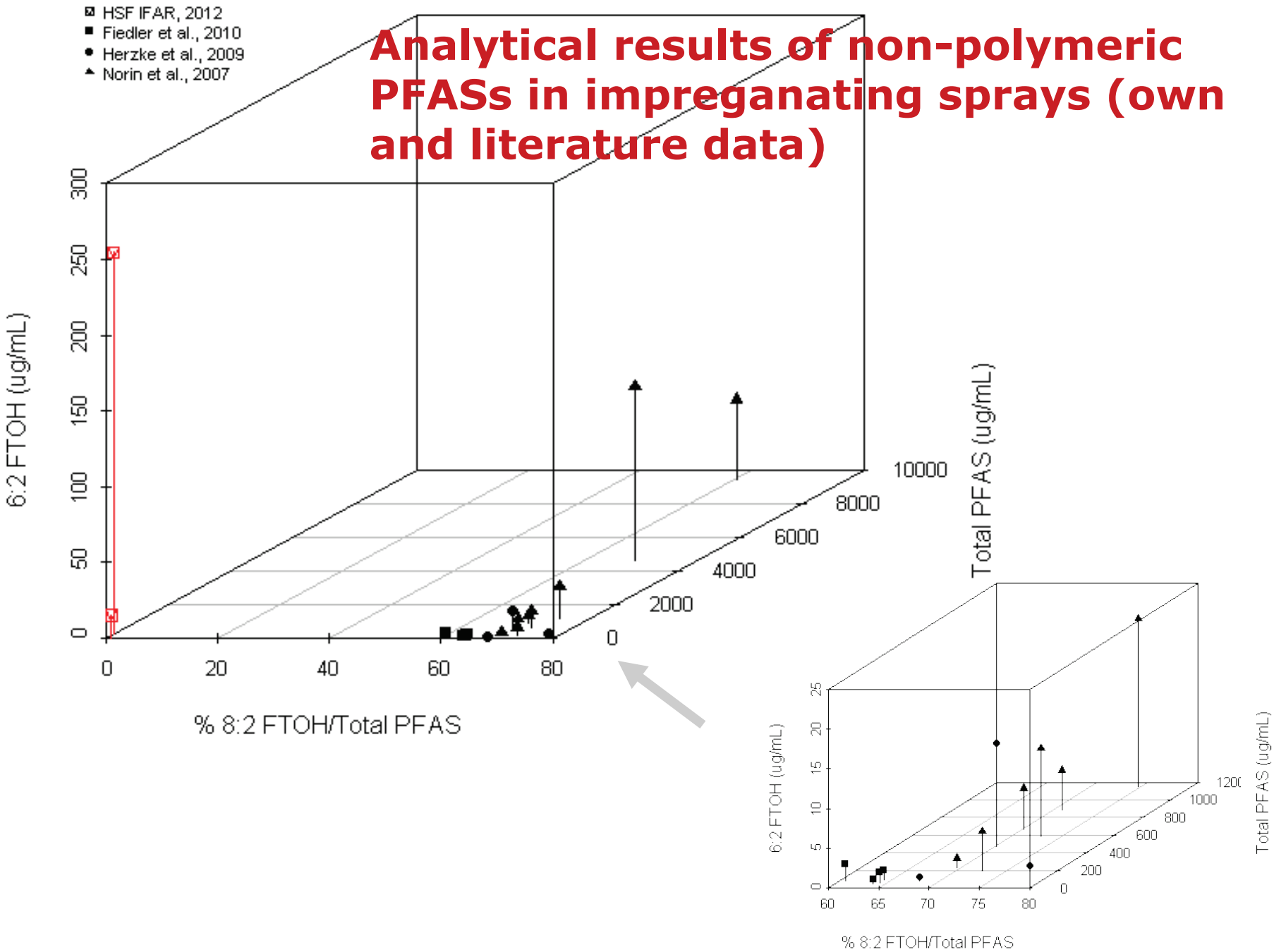
Analytical results of non-polymeric PFASs in „jackets“ (own and literature data)



Impact of so far reported results (Example North Face)

- North Face questions UBA tests; Tuesday, 12 March 2013;
- CALIFORNIA – A major question mark has been raised over the results of textile testing carried out by the German Federal Environment Agency (UBA), which found traces of potentially harmful by-products of fluorine-based (PFC) chemicals on outdoor clothing, after one of the brands concerned – The North Face – carried out new, independent tests of its own, which revealed very different results.
- .. Upon evaluating the results from the UBA test, we were concerned as the results were not indicative of the chemicals used in the manufacturing of our jacket," said The North Face…
- … Regarding the other chemicals detected, findings between 0.007 mg/kg and 0.015 mg/kg of PFOA and 0.005 mg/kg to 0.050 mg/kg of 8:2-FTOH reflect the use of best-in-class fluorochemistry, and does not present any product safety risk….
- However, PFOA by-products of C8-type PFC production do not break down in the environment and are potentially harmful as they accumulate in the bodies or organisms because of their molecular structure are difficult to excrete. As such, the textile industry is now looking to move towards shorter-chain C6 fluorine-based chemistry and other polyurethane-based alternatives that are claimed to be safer – if less effective.

Analytical results of non-polymeric PFASs in impreganating sprays (own and literature data)



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Use of PFASs in textile production

Especially in Norway, Denmark, Sweden and Germany studies regarding the kind and use of PFAS in textile products and impregnation solutions has been performed. However, most of the studies are close to 10 years old and not relevant anymore, since the awareness about the negative features, especially PFOS, PFOA and PFOA-precursor products has led already to a measurable change in this field of application.

With the different measures being planned at present, it can be assumed, that the shift towards PFASs with a perfluorinated chain length of < C7 will be still ongoing.

Questions asked and answers sought

Where produced ?

PFASs present in which concentrations ?

(Validation of analytical methods and comparison to literature data!)

How many produced ?

How many imported into EU / Germany ?

Environmental Exposure ?

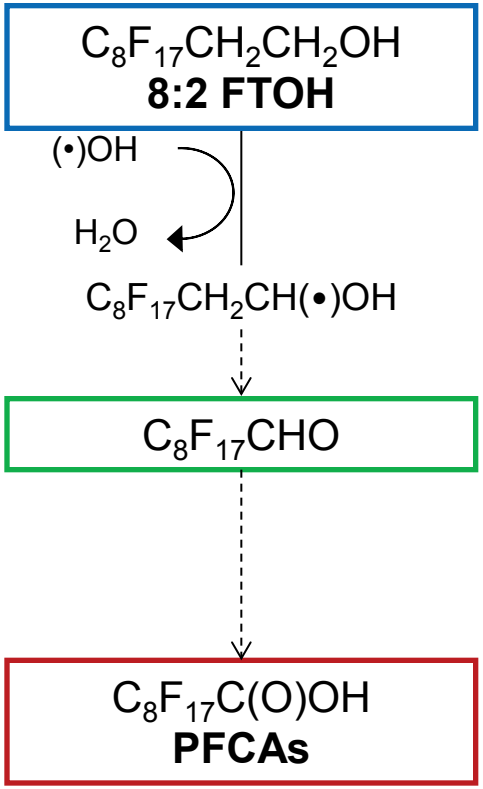
Recyling possible/performed ?

Human Exposure ?

Air emissions

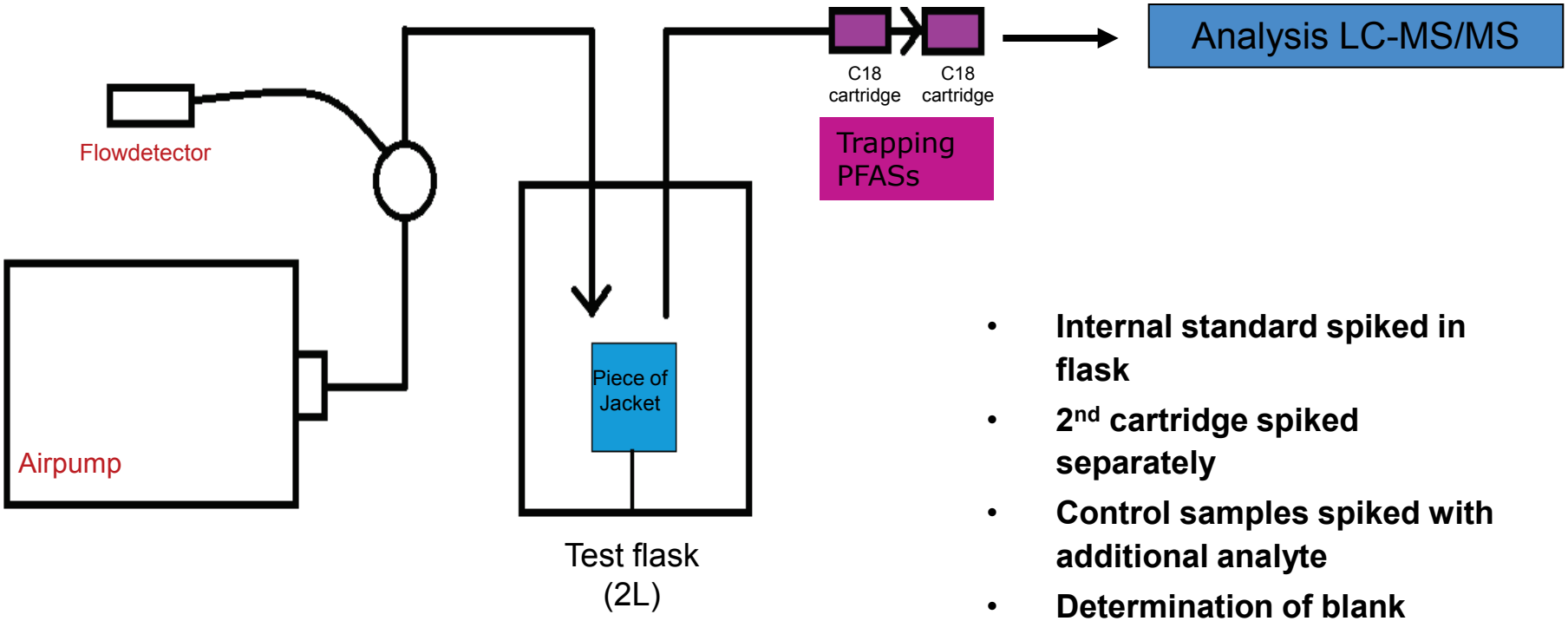
- **Focus on Fluorotelomer Alcohols (6:2 FTOH, 8:2 FTOH and 10:2 FTOH)**
- **Have been measured in indoor & outdoor air**

- Atmospheric oxidation of 8:2 FTOH yields PFOA
- Conversion of 10%



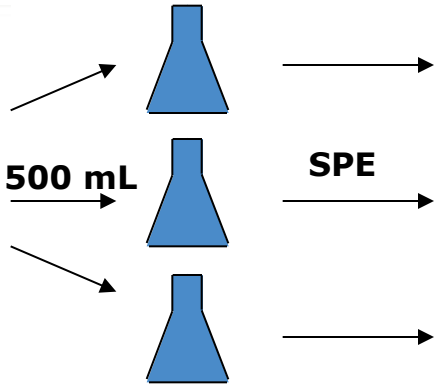
Wallington et al. (2006)

Experimental setup
Air emissions



- **Internal standard spiked in flask**
- **2nd cartridge spiked separately**
- **Control samples spiked with additional analyte**
- **Determination of blank samples**
- **Jackets No. 2, 8. 10 & 14 selected**
- **Analysis of FTOH and FOSE**

Experimental setup
Washing water

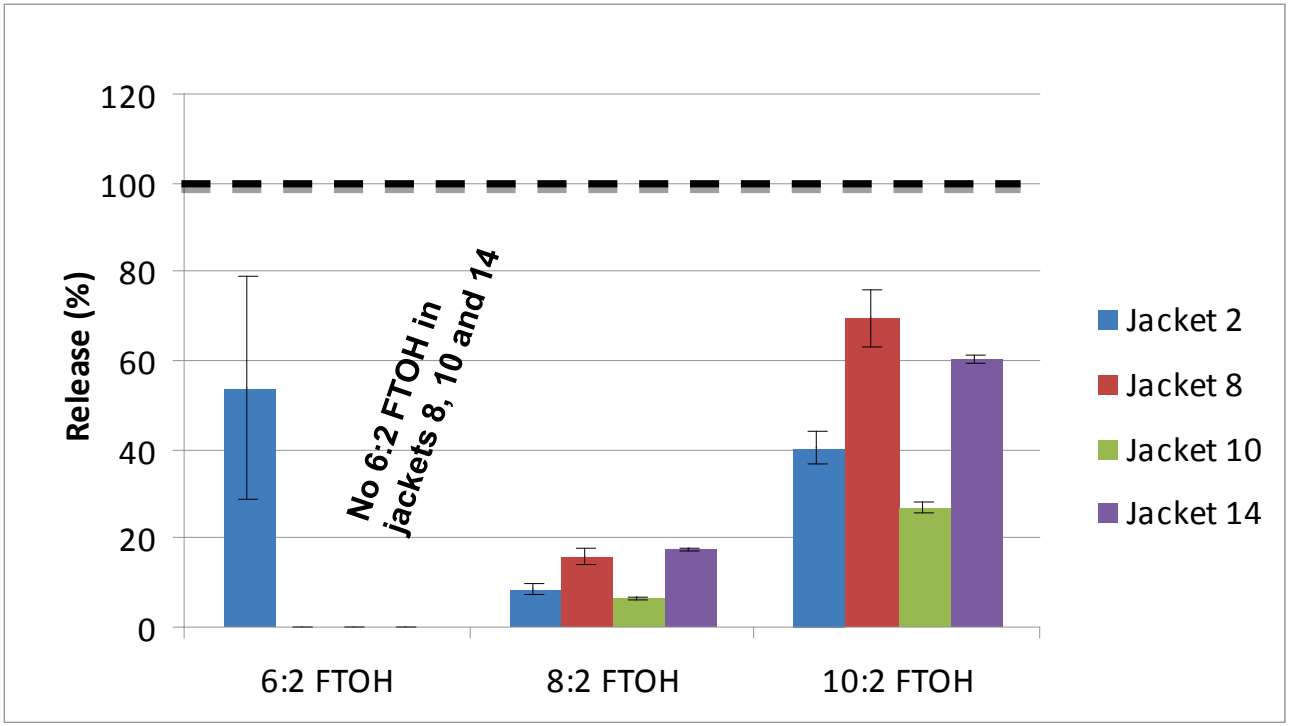


Analysis LC-MS/MS

- Internal standard spiked in sample flask
- Determination of blank samples
- Analysis of PFCAs, PFSAs, FTOHs and FOSEs

- No detergents used

Results
Air emissions

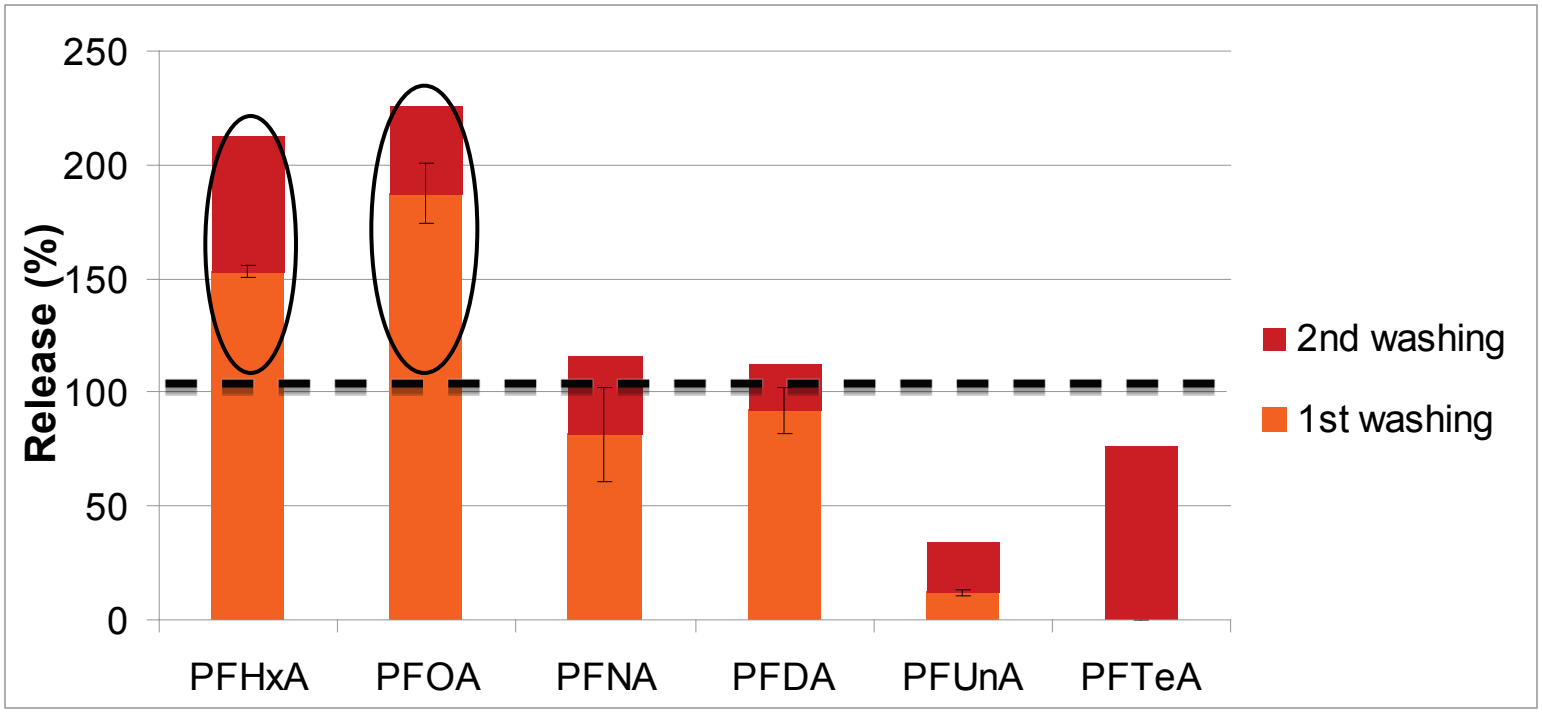


	6:2 FTOH	8:2 FTOH	10:2 FTOH
Jacket 2	**0.71**	**3.46**	**5.69**
Jacket 8	**<LOQ**	**5.83**	**7.95**
Jacket 10	**n.d.**	**4.26**	**2.74**
Jacket 14	**n.d.**	90.6	110

Concentrations in µg/m²

Results

Washing water



	Amount (µg)	Amount (nmol)
8:2 FTOH	29.47	64
PFOA	0.7136	1.7

Total amount in jackets used in the washing machine

→ Transformation of 2.6% of 8:2 FTOH would mean an increase of PFOA with 100%

Environmental exposure
Air emissions

$$E = \frac{\Omega_{jacket} m_{jacket} r SN}{100}$$

Ω_{jacket}=average concentration (kg/jacket)

m_{jacket}=average mass per jacket (kg)

r=release (%)

SN=sales numbers in Germany per year

- 3 scenarios:
  - sales numbers of 22 million [1)]
  - sales numbers of 44 million [2)]
  - sales numbers of 88 million [3)]
- All based on DWR jackets

Compound	Release (%)	Load[1] (kg)	Load[2] (kg)	Load[3] (kg)
6:2 FTOH	**13**	**0.01**	**0.02**	**0.04**
8:2 FTOH	**12**	**0.48**	**0.95**	**1.90**
10:2 FTOH	**50**	**0.60**	**1.20**	**2.40**
8:2 FTOH*	**100**	**3.89**	**7.77**	**15.5**
10:2 FTOH*	**90**	**1.09**	**2.19**	**4.37**

*=worst case scenario

Environmental exposure
Washing water

$$E = \frac{\Omega_{jacket} m_{jacket} rSN}{100}$$

- 3 scenarios:
  - sales numbers of 22 million
  - sales numbers of 44 million
  - sales numbers of 88 million
- All based on DWR jackets

Compound	Release (%)	Load[1] (kg)	Load[2] (kg)	Load[3] (kg)
PFHxA	**216**	**0.01**	**0.03**	**0.05**
PFOA	**235**	**0.07**	**0.13**	**0.27**
PFNA	**131**	**0.03**	**0.05**	**0.10**
PFDA	**119**	**0.04**	**0.08**	**0.17**
PFUnA	**35**	**0.00**	**0.01**	**0.02**
PFTeA	**77**	**0.00**	**0.01**	**0.02**
6:2 FTOH	**-**	**-**	**-**	**-**
8:2 FTOH	**0.7**	**0.03**	**0.05**	**0.10**
10:2 FTOH	**1.0**	**0.01**	**0.02**	**0.05**

Conclusion

- **FTOHs are emitted to the air**

  - releases hypothesized to be in the range of 100% for 8:2 FTOH

- **Environmental load in worst case scenario 15.5 kg for 8:2 FTOH**

  - annual air flux worldwide 100-1,000 tonnes

- **PFCAs are emitted to washing water**

  - average release for PFOA higher than 100%, which could be caused by degradation of precursors

- **Environmental load in worst case scenario 0.27 kg PFOA per year for Germany**

  - contribution to the annual load from German WWTPs approx. 0.5%[a)]
  - contribution to the annual load of a "hypothetic" German river catchment approx. 0.05%[b)]

- **Longer-chain compounds are released to less extend; these may not be present in the used formulations, however they might stem e.g. from other polymeric PFASs used prior in the yarn manufacturing machines, packaging material or just could not be detected in the "matrix" polymeric PFASs.**

calculations based upon:

a) 5×10^{12} L WW per year and an average estimated concentration of 10 ng PFOA/L

b) 4 ng/L PFOA in Rhine at Lobith; 2300 m^3 per s = $72{,}5 \times 10^{12}$ L/year; catchment Rhine: 50 Mio people; 464 kg calculated for 80 Mio people. Industrial emissions have not being separately considered

Outlook

With the given scope of the project including deliverables and milestones – as well as the allocated budget – of course only a limited amount of analyses could be carried out. Anyhow, there are some (scientific) questions, which we propose to tackle in the near future:

- **Continuing analysis of new fabricated DWR jackets, especially from 2013, 2014, 2015….**
- **Investigating further textiles**
- **Determination of the organic bound fluorine parameter AOF**
- **Analysis upon polymers, and studies regarding the formation of transformation products**

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Non-polymeric PFASs analysed so far as the tip of the PFASs iceberg ?

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Acknowledgements

Umwelt Bundes Amt
Für Mensch und Umwelt

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