



DETOX

**Chemistry for Any Weather
Per- and Polyfluorinated
Chemicals**

in Textile Products

Manfred Santen

Performance Days Munich, April 2015

www.greenpeace.de

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Greenpeace Identity, Values and Goals

Our purpose

Greenpeace is an independent global campaigning organization that acts to change attitudes and behaviour, to protect and conserve the environment and to promote peace by:

- Investigating, exposing and confronting environmental abuse
- Challenging the political and economic power of those who can effect change
- Driving environmentally responsible and socially just solutions that offer hope for this and future generations
- Inspiring people to take responsibility for the planet



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Detox Challenges

- **Global water crisis**
- **Few hazardous chemicals regulated vs thousands used**
- **Lack of good regulation and enforcement in the global south**
- **Demand for more transparency rapidly increasing but no tools yet in place**
- **Brands take advantage of this situation: opacity and double standards**



Rio Santiago, Mexico

1090 chemicals have been found in the Rio Santiago,
12 are regulated...



Citarum river, Indonesia: This most polluted river in the world receives discharges from thousands of factories including textile, millions of people live in its basin which also provides water for Jakarta.



**Manila, Philippines: Unidentified discharge, with unidentified chemicals...
Local communities do not know which chemicals they are exposed to and
who is releasing them**

Why textiles...?

involves intensive use of chemicals and water

uses many hazardous chemicals for preparations of the dyes and pigments

causes substantial pollution of waterways globally

example of global industry in which respecting the law does not prevent from polluting waterways with hazardous chemicals and selling products containing hazardous chemicals

Detox Goal for 2020

**Bring about a 50%
reduction in the use of
hazardous chemicals,
from across sectors of
industry**



Detox Our Fashion Demands

Zero discharge of all hazardous chemicals by 2020 (Meaning their total elimination of ALL haz chemicals from across the entire supply chain and product life-cycle)

Transparency commitment with discharge data uploaded of suppliers (building on the public's "Right to Know" what is in our rivers and in our products)

Short term elimination of the worst chemicals e.g. Total elimination of Alkylphenols and Perfluorinated Chemicals

Collaboration with suppliers, NOT contract cancellation

Deto水



<http://www.youtube.com/watch?v=uZuccisukaU>

The story so far...

The Detox campaign was launched in July 2011 and, following 3 years of people powered campaigning almost 30 global fashion and textile companies have made landmark commitments to bringing about transformational change within the industry.

Nike, Adidas, Puma, H&M, M&S, C&A, Li-Ning, Zara, Mango, Esprit, Levi's, Uniqlo, Benetton, Victoria's Secret, G-Star Raw, Valentino, Coop, Canepa, Burberry and Primark, Lidl, Tchibo, Miroglio Group.



... And what about the OUTDOOR SECTOR?

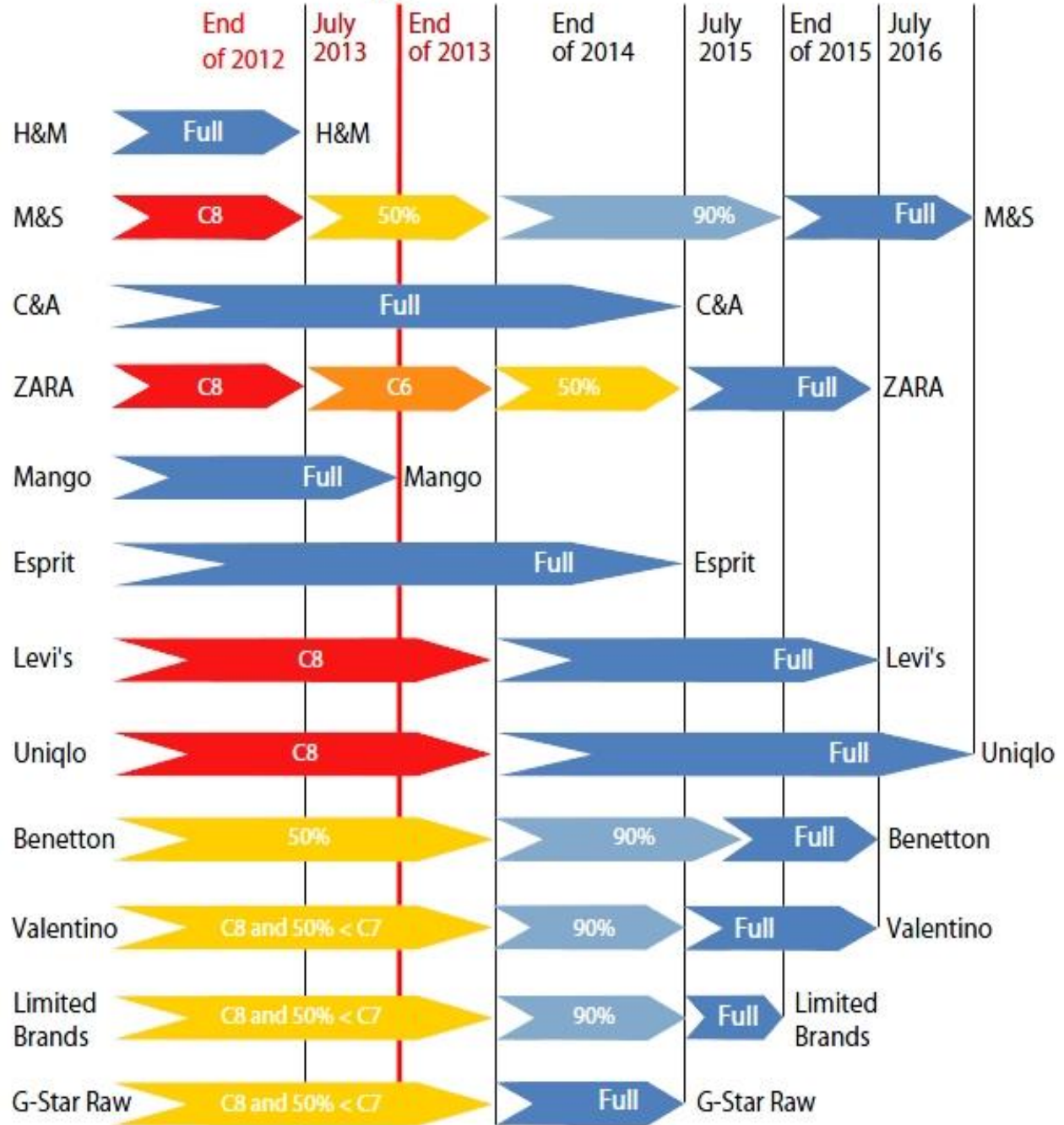
Detox: 11 priority substance groups as a starting point:

1. alkyphenoles
2. per- and polyfluorinated chemicals PFC
3. phtnates
4. brominated and chlorinated flame retardends
5. azo dyes
6. organotin compounds
7. chlorobenzenes
8. chlorinated solvents
9. chlorophenoles
10. Short chain chlorinated paraffines
11. Heavy metals: cadmium, lead, mercury, chromium (VI)

PFC-exit dates of detox brands

June 2014:
Adidas
 announces to
 be 99% PFC-
 free by end of
 2017

October 2014:
Puma will be
 100% PFC-free
 by end of 2017



Chemistry for any weather

Greenpeace tests outdoor clothes for perfluorinated toxins

FACE

Chemistry for Any Weather – Part II

Report 2013

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A Red Card for sportswear brands

Hazardous chemicals found in World Cup merchandise

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Chemistry for Any Weather - PFCs:

Why are per- and polyfluorinated chemicals a problem?

- usage or byproducts in the production of fluoropolymers for water and stain repellents (DWR)
- -> emission directly from production sites
- -> residues in textiles – releases during storage, use, end of life
- **no future for C8-PFC:**
- PFOS is already phased out from textile production
- PFOA will be phased out now

Industry promotes FTOH (Fluorotelomers) and shorter chain PFC as alternative

FTOH (fluorotelomer alcohols)

textiles:

- Key raw materials in the production of fluorinated polymers (DWR – durable water repellent finish)

Environment:

- **Highly persistent and volatile**, detected in the atmosphere
- Indoor air concentrations **much higher** than outdoor air (especially high in outdoor gear stores)
- Precursors for some PFAS i.e. PFOA, degrade to PFCA by atmospheric / metabolic oxidation
- Metabolic intermediates can be much more toxic than PFCA (fresh water organisms)

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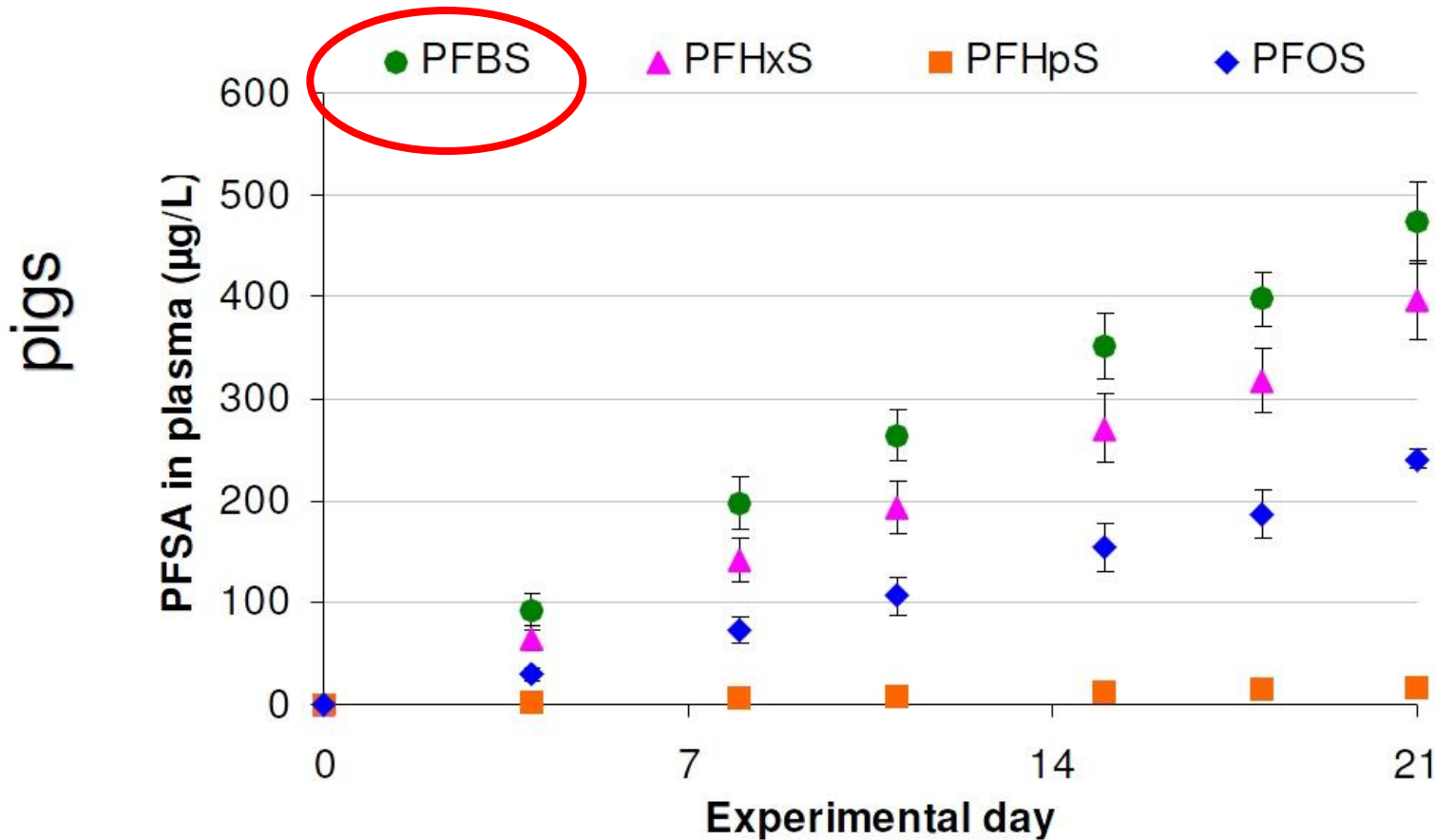
Short chain PFC: C4 & C6 carboxylates / sulfonates

- **persistent**
detectable in: house dust, drinking water
snow, glacier ice, rain water, rivers, lakes
animal organs (penguins, turtle, polar bear)
breast milk, blood
- **mobile**
transportation into remote areas (Tierra del Fuegos)
bind poorly with sediment and soil particles
= increased infiltration to ground water
= not managable (cannot be filtered out)
= increasing use – increasing exposure

C4 in pigs (plasma):

steady increase 19

concentrations increase with decreasing chain length (PFBS>PFHxS>PFOS)

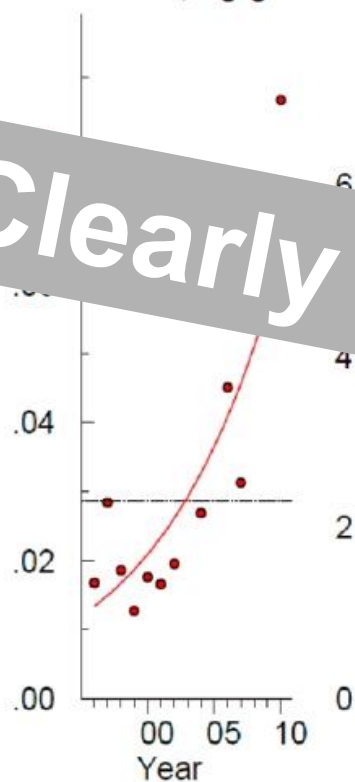


Lit: Numata, J.; Kowalczyk, J.; Adolphs, J.; Ehlers, Schafft, H.; Fürst, P.; Müller-Graf, C.; Lahrsen-Wiederholt, M.; Greiner, M. (2014) Toxicokinetics of Seven Perfluoroalkyl Sulfonic and Carboxylic Acids in Pigs Fed a Contaminated Diet. J. Agric. Food Chem. In Print. doi: 10.1021/jf405827u

C4 in Swedish Blood Samples

- significant increase of PFBS in blood from young women

PFBS, ng/g ww.



Temporal trend of PFBS
41%

Clearly not "green chemistry"

Temporal trend of PFBS in pooled blood serum samples from primiparous nursing women (N = 413), living in Sweden 1996–2010 (Environ. Sci. Technol. 2012, 46, 9071–9079).



Helsingør Statement: Scientists warn to use short chain PFC as an alternative

"We recommend that known and safe chemicals are used, or that new alternatives are developed which are not toxic, persistent and do not accumulate in humans or the environment. Fluorochemicals should only be used where they are truly essential, and not in common consumer products"

Handling Editor: J. de Boer

Keywords:

PFOA
PFOS
PBT chemicals
Fluorinated surfactants
Fluorinated polymers

to be persistent, bioaccumulative and toxic, they are being replaced by a wide range of fluorinated alternatives. We summarize key concerns about the potential impacts of fluorinated alternatives on human health and the environment in order to provide concise information for different stakeholders and the public. These concerns include, amongst others, the likelihood of fluorinated alternatives or their transformation products becoming ubiquitously present in the global environment; the need for more information on uses, properties and effects of fluorinated alternatives; the formation of persistent terminal transformation products including PFCAs and PFSA; increasing environmental and human exposure and potential of adverse effects as a consequence of the high ultimate persistence and increasing usage of fluorinated alternatives; the high societal costs that would be caused if the uses, environmental fate, and adverse effects of fluorinated alternatives had to be investigated by publicly funded research; and the lack of consideration of non-persistent alternatives to long-chain PFASs.

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DO WITHOUT
400
FLUORINATED
PREVENT
300
INTO THE E
200
No. 1395

Greenpeace – request to the German Environmental Agency (Umweltbundesamt) according to Environmental Information Law (Umwelt-Informations-Gesetz UIG) :

Publicly available draft of common EU action plan regarding REACH-substances assessments contains several per- and polyfluorinated Chemicals (PFC), among them
2 short chain PFC (6 perfluorinated C-atoms)

QUESTION: Why did UBA refer to which criteria assess these substances?

6:2 FtMA: 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl methacrylate (CAS Nr. 2144-53-8)

6:2 FtA: 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl acrylate (CAS Nr. 17527-29-6)

UBA answer via mail from 03.02.2015:

The assessment will be presumably in 2016 according to title VI REACH, published presumably in March with the common action plan

6:2 FtA/6:2 FtMA is an alternative for perfluorooctanoic (PFOA) related substances, **therefore increasing use and production of alternatives is expected.**

In addition **PFHxA is expected to have a high mobility in the environment**, which also needs to be assessed, e.g. in terms of its potential for long-range transport.

Chemistry for any weather

Greenpeace tests outdoor clothes
for perfluorinated toxins

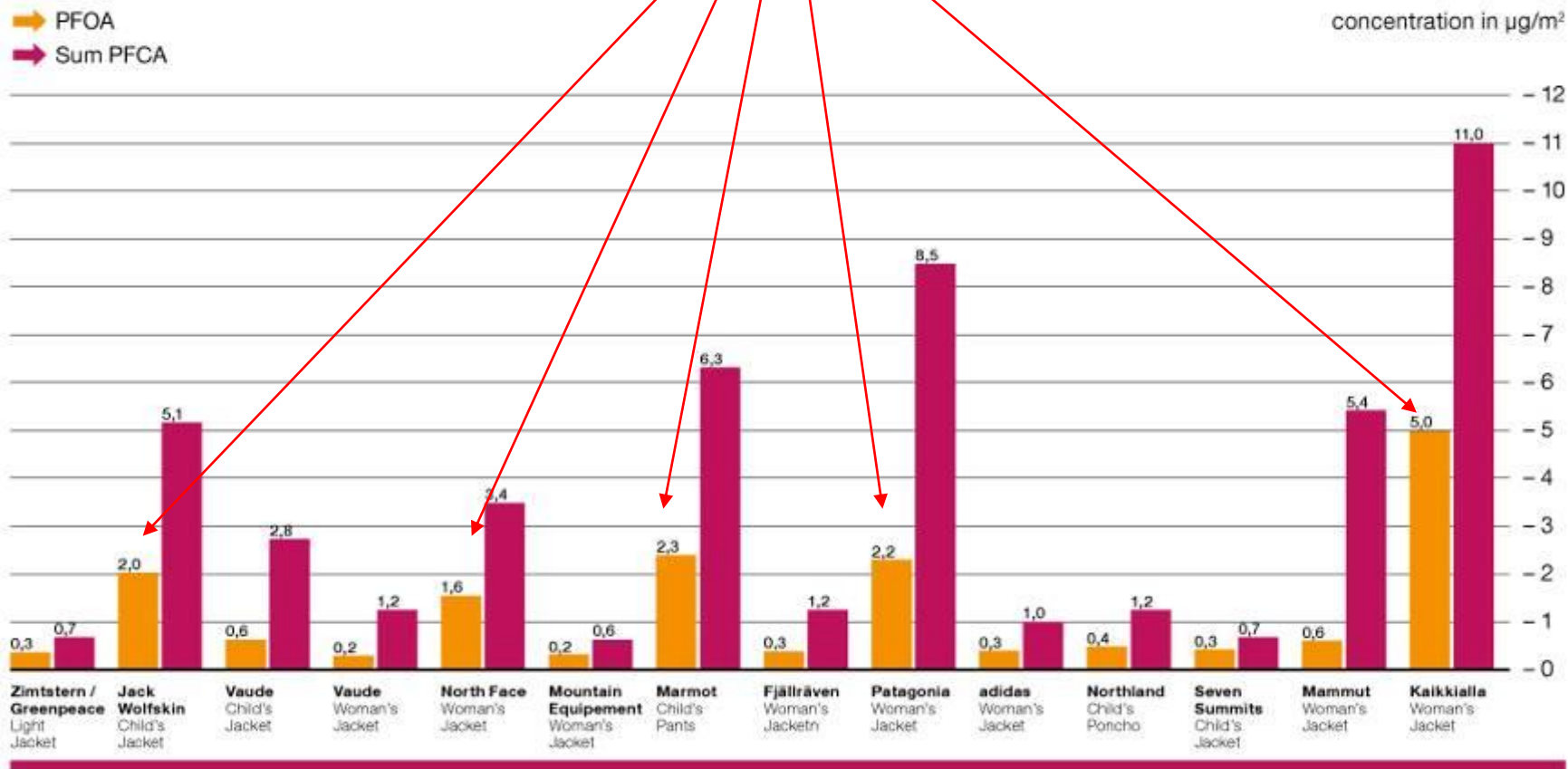
October 2012

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PFOA > 1 $\mu\text{g}/\text{m}^2$ *

Figure 1: Concentrations of perfluorinated carboxylic acids (PFCAs) in 14 samples of outdoor clothing



* PFOS restriction level in textiles is 1 $\mu\text{g}/\text{m}^2$. For other media than textiles, prevention values are usually given for the sum of PFOS and PFOA (Umweltbundesamt, 2011), as the compounds may act synergistic. We applied this concept to the textiles.

Chemistry for Any Weather – Part II

Executive Summary – Outdoor Report 2013

Decem

#DETOX OUT



Adidas
TX GTX Acts j
jacket (GER)



Columbia
Evo Fly Jacket
children's jacket (GER)



Jack Wolfskin
Topaz Jacket Women
jacket (China)



Jack Wolfskin
Nebraska Parka
jacket (GER)



Kaikkialla
Jemina Coat
jacket (GER)



Mammut
Extreme Arctic
gloves (CH)



Mammut
Miva Light Jacket
Women, jacket (CH)



Northland
EXO Pro STR Monie JKT
jacket (A)



Patagonia
W'S Powder Bowl JKT
jacket (US)



Salewa
Kali GTX M JKT
jacket (GER)



Schöffel
Keaton
jacket (GER)



Seven Summit
Monte Viso
jacket (A)



The North Face
Meru Glove
gloves (US)



The North Face
All Terrain II
jacket (GER)



The North Face
W Impervious Jacket
jacket (US)



Vaude
Kids Rain Jacket
children's jacket (GER)



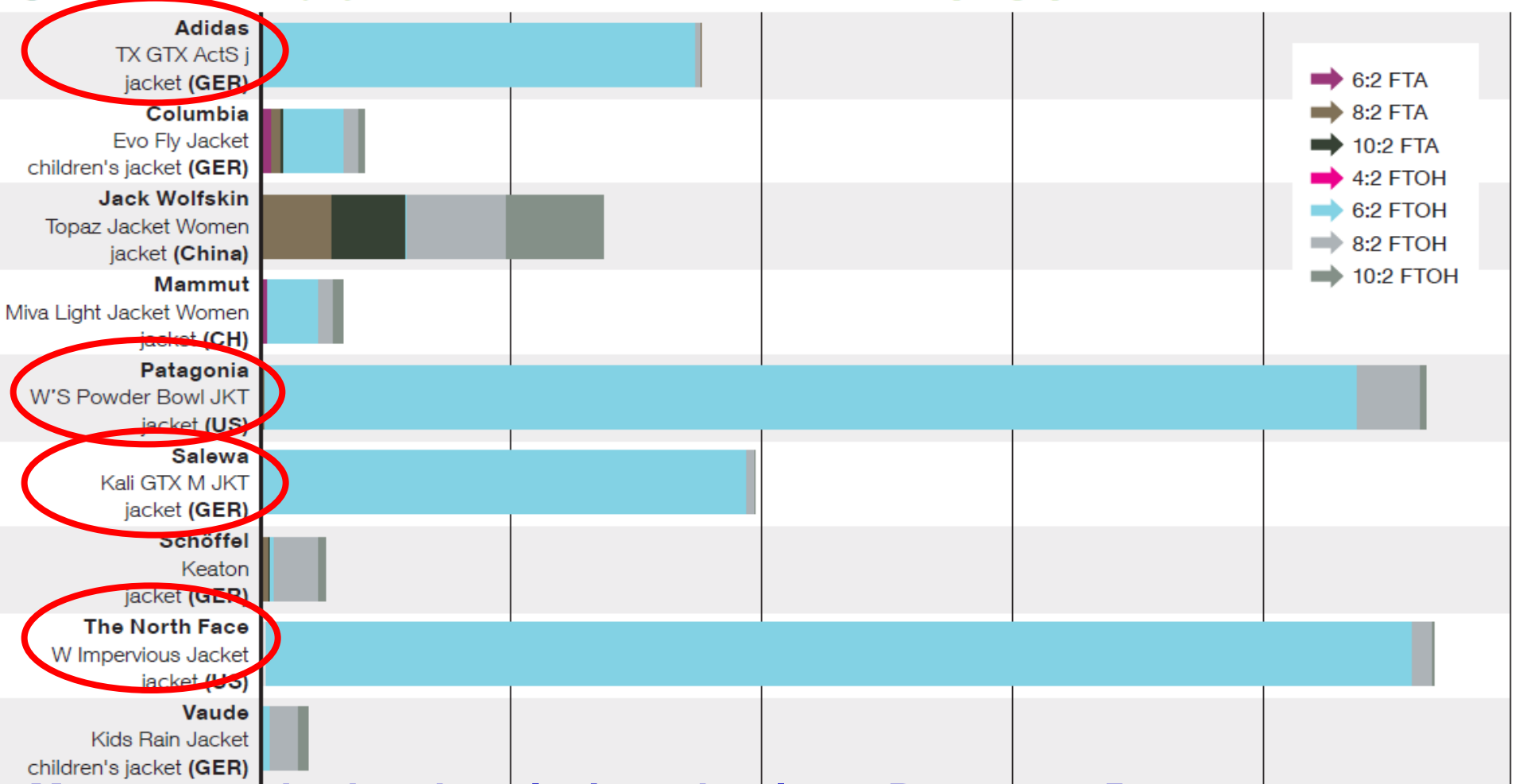
Vaude
Cheilon Stretch Jacket 2
jacket (GER)

New testing in 2013: volatile PFC evaporation from outdoor-jackets

120L stainless steel test
chambers at room temperature



Figure 1 Emissions of polyfluorinated chemicals from Outdoor-Jackets [in ng/d]



More on method and analysis technology: Poster 1095

Emissions of Perfluoroalkyl Compounds (PFASs) from Textiles

Postersession 2, Tuesday 17:20h

Findings test chamber:

- Certain PFCs are released into the air from clothing under ambient conditions
- All 9 tested items released **FTOHs** (fluorotelomer alcohols) and **FTAs** (fluorotelomer acrylates) to surrounding air at room temperature: 540 to 9220 ng/d
- Additional route for FTOHs and FTAs to be released into the environment
- Correlation between C6 (6:2 FTOH) content and C6 emission presumed?
- Jackets Patagonia + The North Face show highest C6 emission – ca. 9µg/d
- Outdoor clothing contributes to PFCs level in indoor air, more research needed to estimate or calculate the contribution

A Red Card for sportswear brands

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Table 2 Results perfluorinated chemicals (PFC) in football boots and gloves

Sample code	KI14002/SWI02	KI14004a/b/NL03/04				KI14007/DE03		KI14008/D 04	KI14026/DE11		
Brand	Adidas	Adidas				Adidas		Adidas	Adidas		
Product	Boots: Predator TRX BE, men	Boots: adizero F50 TRX FG, children (boys)				Boots: Predator Absolode LZ TRX FG J, children (boys)		Boots: Maxx Questra TRX FG J, children (boys)	Boots: nitrocharge 3.0 TRX FG J, children (boys)		
Type of product	Boots	Boots	Boots	Sole	Sole	Boots	Boots	Boots	Boots	Boots	Sole
Concentration	µg/m ²	µg/m ²	µg/m ²	µg/m ²	µg/m ²	µg/m ²	µg/m ²	µg/m ²	µg/m ²	µg/m ²	µg/m ²
PFBS	6,045	1,639	107,553	0,765	<0,879	37,884	12,602	<0,775	<0,930	<0,330	<0,306
PFHxS	<0,757	<0,869	<0,989	<0,651	<0,879	0,639	<0,744	<0,775	<0,930	<0,330	<0,306
PFHpS	<0,757	<0,869	<0,989	<0,651	<0,879	0,639	<0,744	<0,775	<0,930	<0,330	<0,306
PFOS	<0,757	<0,869	<0,989	<0,651	<0,879	0,639	<0,744	<0,775	<0,930	<0,330	<0,306

adidas children boots: PFBS: up to 39 µg/m² (=80.000 ng/kg)

Table 2 Results perfluorinated chemicals (PFC) in football boots and gloves

Sample code	KI14010/DE06	KI14015 (1)/ES01 & (2)		KI14001/SWI01		KI14011/DE07		KI14025/DE09		
Brand	Adidas	Adidas		Nike		Nike		Nike		
Product	Gloves: PRED FS JUNIOR, children (boys)	Gloves: PRED JUN IC, unisex		Boots: JR MERCURIAL VICTORY IV FG, children (boys)		Boots: JR MERCURIAL VICTORY IV TF, children (boys)		Boots: JR HYPERVENOM PHELON TF, children (boys)		
Type of product	Gloves	Gloves	Gloves	Boots	Boots	Boots	Boots	Sole	Boots	Boots
Concentration	µg/m ²	µg/m ²	µg/m ²	µg/m ²	µg/m ²	µg/m ²	µg/m ²	µg/m ²	µg/m ²	µg/m ²
PFBS	<0,353	<0,226	<0,165	13,675	10,967	188,571	7,913	<0,695	3,587	15,076
PFHxS	<0,353	<0,226	<0,165	<0,651	<0,576	<0,533	<0,484	<0,695	<0,411	<0,416
PFHpS	<0,353	<0,226	<0,165	<0,651	<0,576	<0,533	<0,484	<0,695	<0,411	<0,416
PFOS	<0,235	<0,151	<0,110	<0,434	<0,384	<0,356	<0,323	<0,464	<0,274	<0,277
PFDS	<0,353	<0,226	<0,165	<0,651	<0,576	<0,533	<0,484	<0,695	<0,411	<0,416
PFBA	<0,353	0,886	0,773	<0,434	<0,384	<0,356	<0,323	<1,391	<0,549	<0,492
PFPA	<0,235	<0,151	<0,110	<0,434	<0,384	<0,356	<0,323	<0,464	<0,274	<0,277
PFHxA	<0,235	0,714	<0,110	<0,434	<0,384	<0,356	<0,323	<0,464	0,618	0,410
PFHpA	<0,235	0,762	<0,110	<0,434	<0,384	<0,356	<0,323	<0,464	<0,274	<0,277
PFOA	<0,235	1,410	1,964	2,489	0,533	<0,356	8,156	<0,464	5,905	0,682
PFNA	<0,235	1,283	<0,110	<0,434	<0,384	<0,356	<0,323	<0,464	<0,274	<0,277
PFDA	<0,235	1,324	0,782	0,913	<0,384	<0,356	0,623	<0,464	2,532	<0,277
PFUnA	<0,235	1,797	<0,110	<0,434	<0,384	<0,356	<0,323	<0,464	<0,274	<0,277
PFDoA	<0,235	<0,151	0,351	<0,434	<0,384	<0,356	1,012	<0,464	1,175	<0,277

PFBS in Nike children boots: up to 189 µg/m² (=200.000 ng/kg)

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JOIN THE DETOX SOLUTION

**Greenpeace calls upon
textile brands**

**to be clean, be transparent,
be proactive & become
Detox Solution LEADER!**

- phase-out ALL PFCs!
- set ambitious short term elimination timelines now – as a starting point (for PFC and other priority hazardous chemicals)!
- to release suppliers' discharge data in China and other countries



<http://www.youtube.com/watch?v=uZucclsuKaU>

**Thank you for
your attention!**

Any Questions?