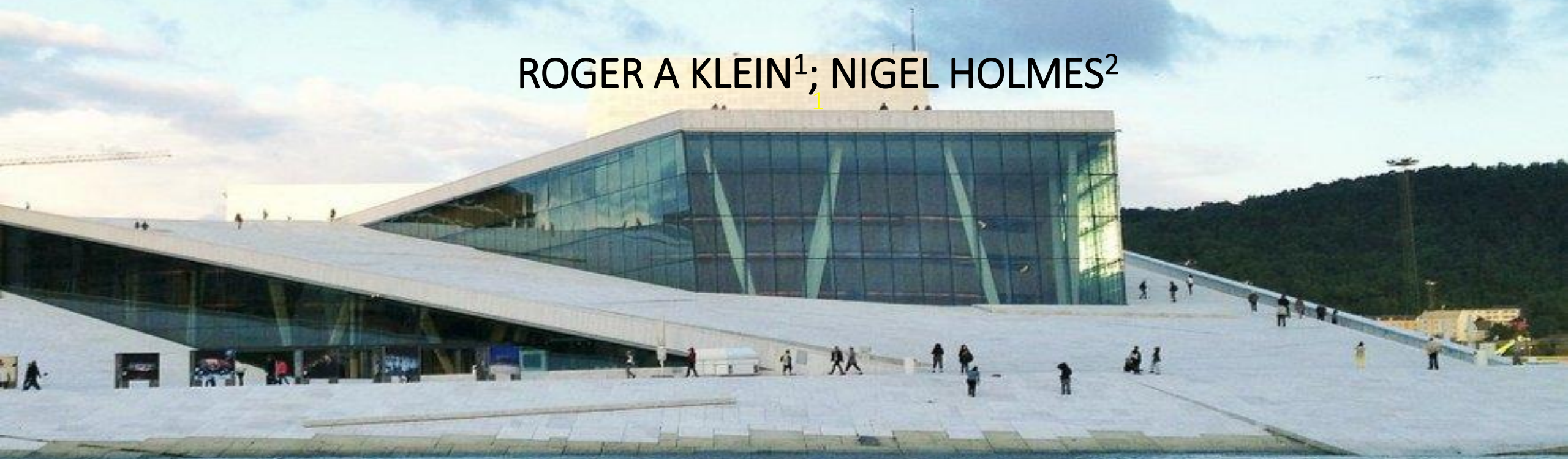


# Fluorochemicals - What is the Fuss All About?

ROGER A KLEIN<sup>1</sup>; NIGEL HOLMES<sup>2</sup>



Cambridge, UK, and Christian Regenhard Center for Emergency Response Studies (RaCERS), John Jay College of Criminal Justice, City University New York (CUNY), New York NY 20019 USA

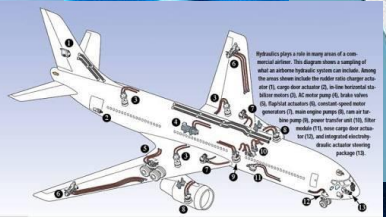
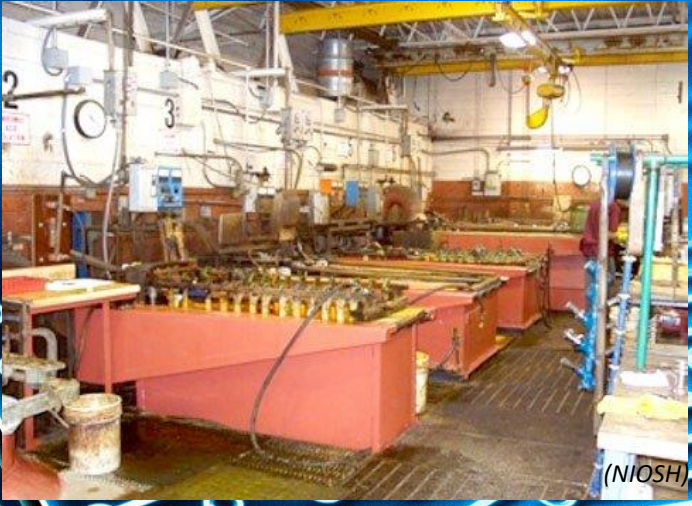
<sup>2</sup>Dept. of Environment & Heritage Protection, Queensland Government  
Brisbane 4000 QLD Australia

<rogeraklein@yahoo.co.uk> ; <nigel.holmes@ehp.qld.gov.au>





# Wide Range of End-User Products





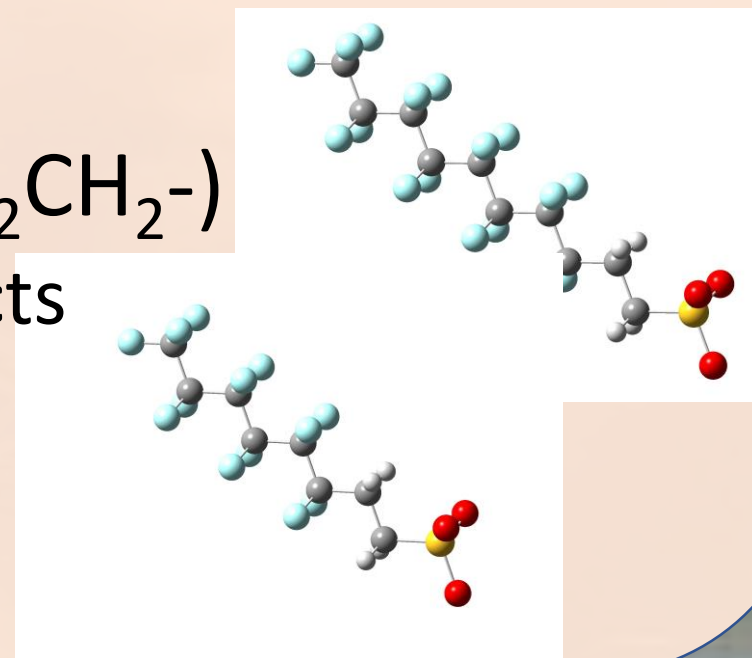
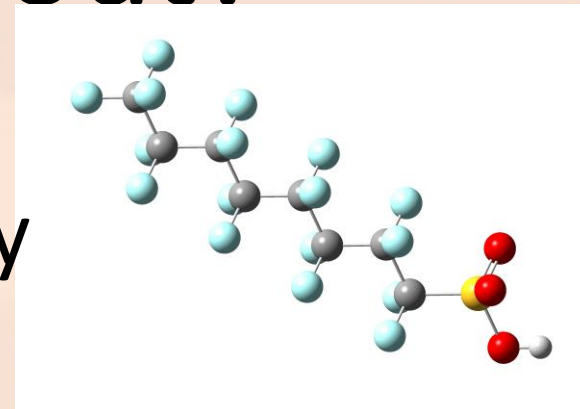
# What is the Fuss All About?

- Waste Streams of Concern
- Firewater runoff containing fluorochemicals
  - Current operations
  - Legacy incident and training sites – airports and airbases
  - Accidental discharge
  - Old foam stocks
- Landfill leachates
  - Textiles and fabrics
- Waste water treatment plant (WWTP)
  - Biosolids – contaminated with short and long chains including PFOA
    - Then used for agricultural soil improvement and in domestic compost products
  - Effluent – failure to capture short chains
- Manufacturing



# What is the Fuss All About?

- PFOS-base products ( $C_8F_{17}SO_3H$ )
  - Now legacy in most countries but may occur in waste streams or washouts
  - Odd and even chain-length, branched chain isomers (ie PFHxS, PFDS)
- Fluorotelomer products ( $C_nF_{(2n+1)}CH_2CH_2-$ )
  - Widely used in many consumer products
  - Even chain-length ( $n=4,6,8,\dots$ )
  - Degrade to PFCAs as end-point



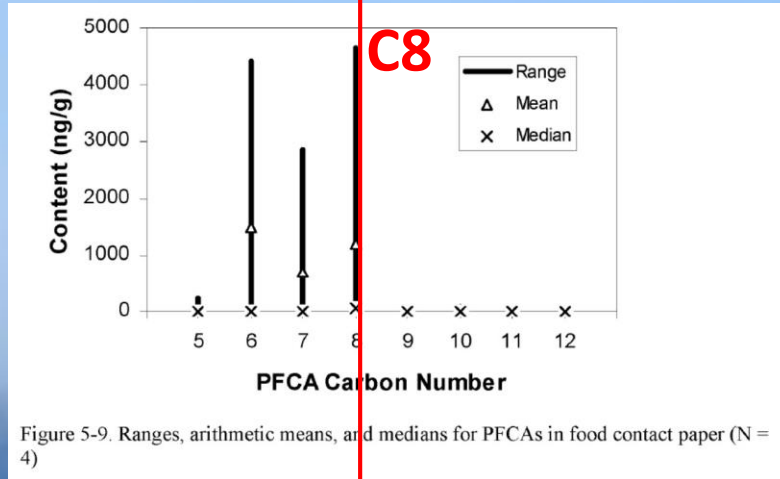


# What is the Fuss All About?

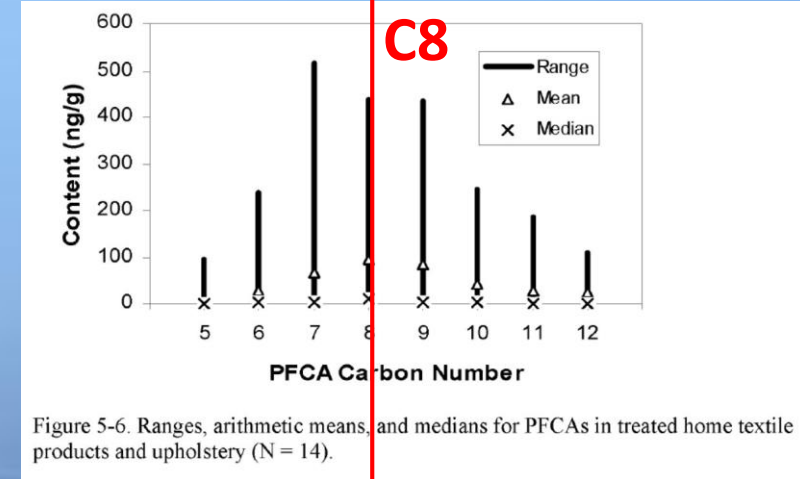
- Indirect Human Exposure
  - Drinking water
  - Food, agriculture, fisheries
- Direct Human Exposure
  - Domestic products
  - Impregnated clothing
  - Respirable air
- Long-term Environmental Contamination
  - Extreme environmental persistence
  - Long-range transport
- Scientific Uncertainty
  - Unknown toxicity and bio-accumulation profiles for end-point degradation products
  - All extremely environmentally persistent
  - Long human half lives
  - Probable links versus proven cause-and-effect
- Legal and Financial Liability
  - Reputational and brand image damage

# PFCAs in Articles of Commerce

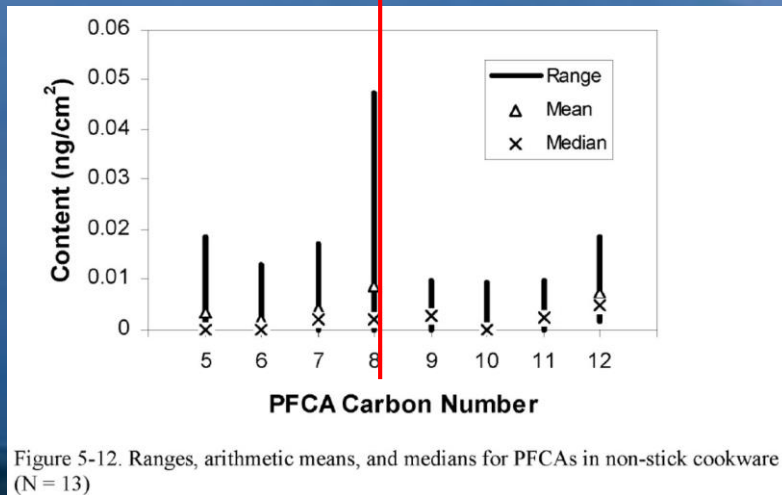
Food contact paper



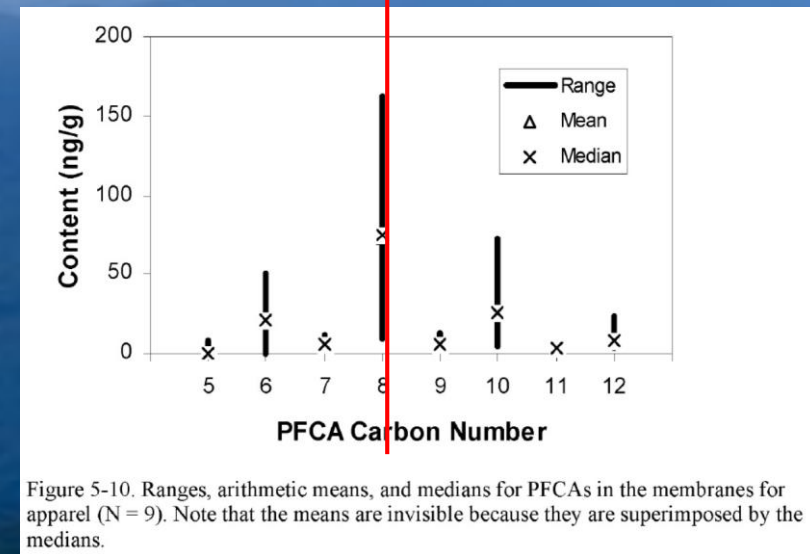
Home textiles



Cookware



Apparel



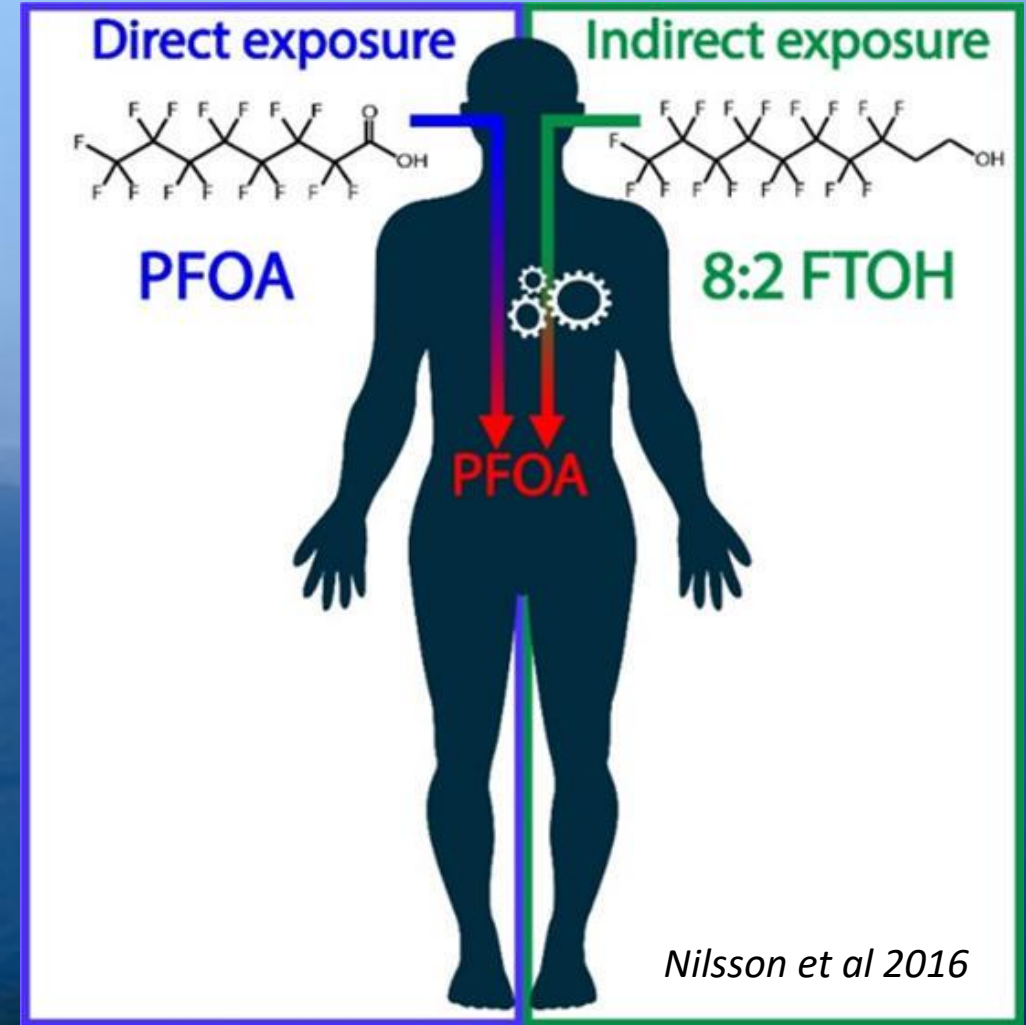
data from Guo et al (2009)



# Non-industrial products – uncontrolled use

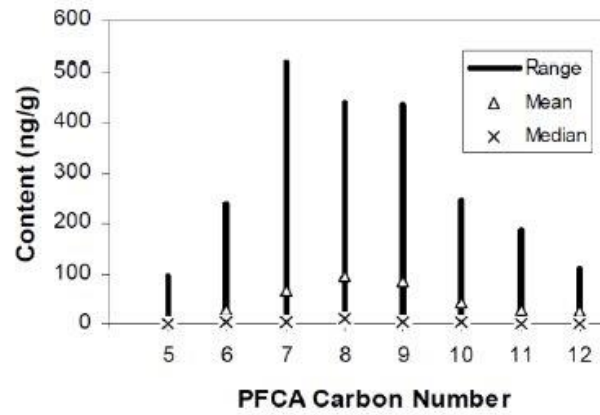
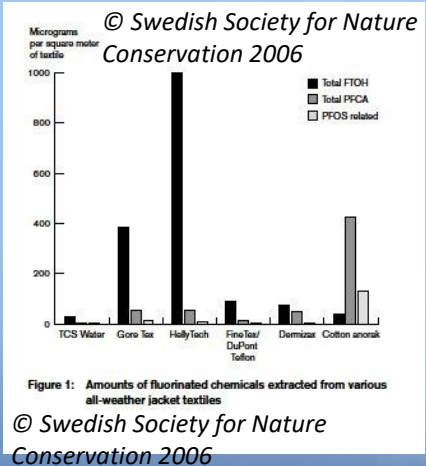


Direct human exposure  
by aerosol – liver toxicity

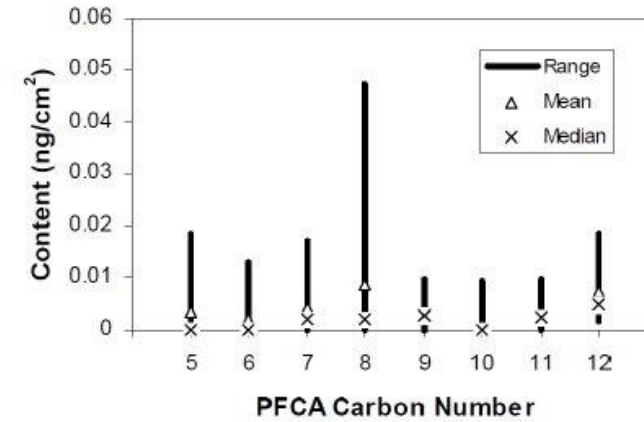




# Domestic products – in the home

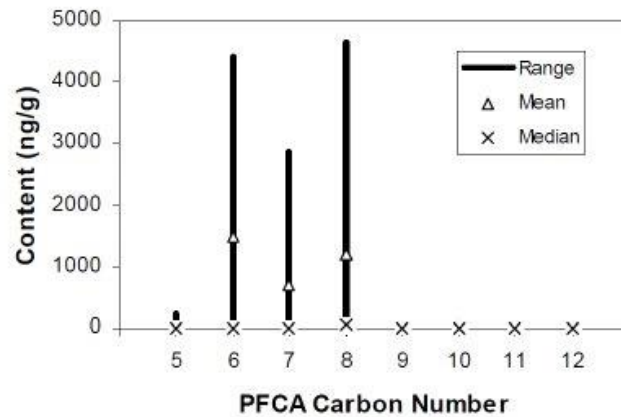


Treated Home Textiles

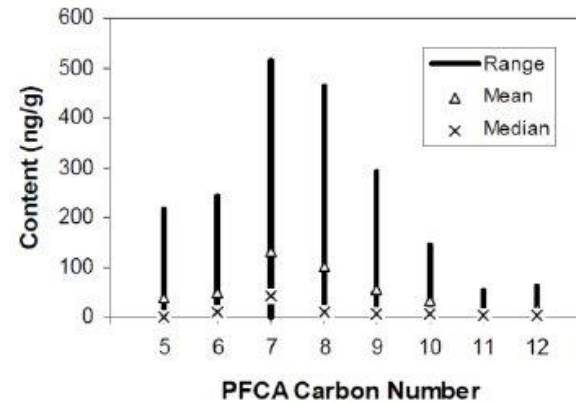


Non-stick cookware

data from Guo et al (2009) USEPA



Food contact paper

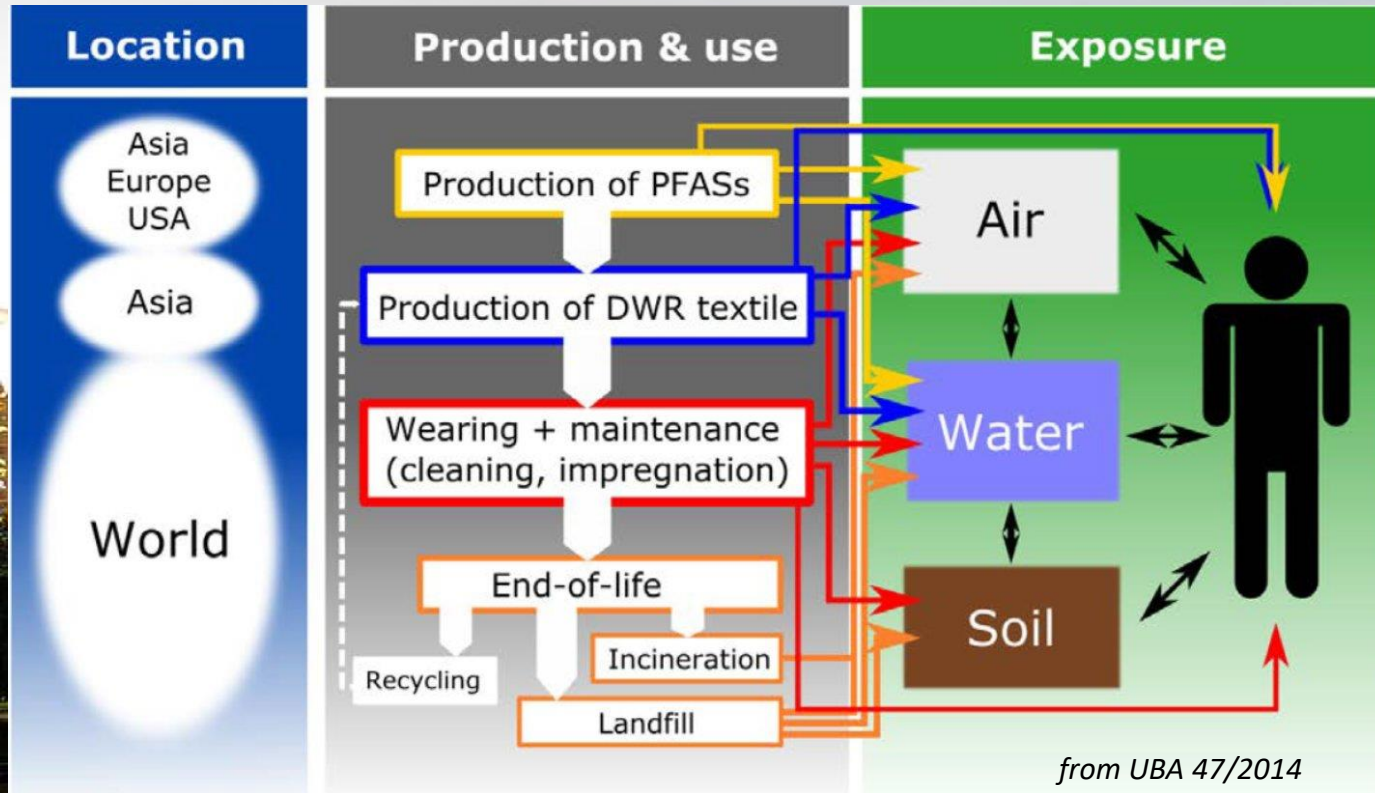


Pre-Treated Carpet

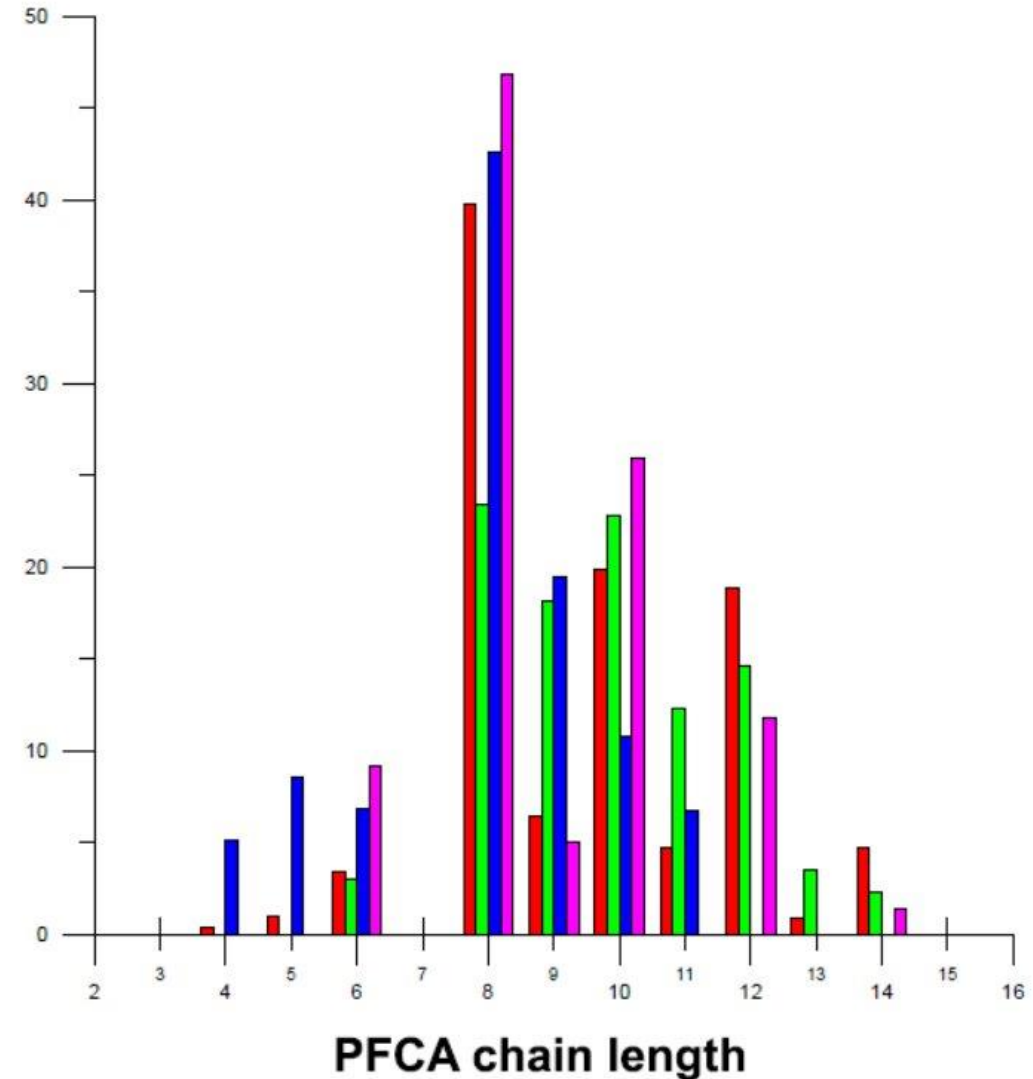




# Human Exposure to PFAS



PFCA wt% extracted



Impregnated All-weather Outdoor Clothing





# Based on C6 chemistry.....? Really?

*data from Joensson et al SWEREA (2015)*

## Main PFASs detected in textile samples

- |   |   |   |
|---|---|---|
| ➤ PFBA <ul style="list-style-type: none"><li>• 47% of samples</li><li>• 0.02-28 <math>\mu\text{g}/\text{m}^2</math><br/>(median 0.17 <math>\mu\text{g}/\text{m}^2</math>)</li></ul>   | ➤ PFBS <ul style="list-style-type: none"><li>• 18% of samples</li><li>• 0.02-42 <math>\mu\text{g}/\text{m}^2</math><br/>(median 0.69 <math>\mu\text{g}/\text{m}^2</math>)</li></ul>     | ➤ 8:2 FTOH* <ul style="list-style-type: none"><li>• 92% of samples</li><li>• 1.5-380 <math>\mu\text{g}/\text{m}^2</math> (median 17 <math>\mu\text{g}/\text{m}^2</math>)</li></ul>    |
| ➤ PFHxA <ul style="list-style-type: none"><li>• 76% of samples</li><li>• 0.03-6.4 <math>\mu\text{g}/\text{m}^2</math><br/>(median 0.21 <math>\mu\text{g}/\text{m}^2</math>)</li></ul> | ➤ L-PFOS <ul style="list-style-type: none"><li>• 18% of samples</li><li>• 0.02-3.2 <math>\mu\text{g}/\text{m}^2</math><br/>(median 0.09 <math>\mu\text{g}/\text{m}^2</math>)</li></ul>  | ➤ 10:2 FTOH* <ul style="list-style-type: none"><li>• 90% of samples</li><li>• 0.06-130 <math>\mu\text{g}/\text{m}^2</math> (median 4.1 <math>\mu\text{g}/\text{m}^2</math>)</li></ul> |
| ➤ PFOA <ul style="list-style-type: none"><li>• 96% of samples</li><li>• 0.01-5.1 <math>\mu\text{g}/\text{m}^2</math><br/>(median 0.25 <math>\mu\text{g}/\text{m}^2</math>)</li></ul>  | ➤ 6:2 FTOH* <ul style="list-style-type: none"><li>• 88% of samples</li><li>• 0.43-360 <math>\mu\text{g}/\text{m}^2</math><br/>(median 24 <math>\mu\text{g}/\text{m}^2</math>)</li></ul> | ➤ 8:2 FTAC* <ul style="list-style-type: none"><li>• 46% of samples</li><li>• 0.29-280 <math>\mu\text{g}/\text{m}^2</math> (median 2.6 <math>\mu\text{g}/\text{m}^2</math>)</li></ul>  |

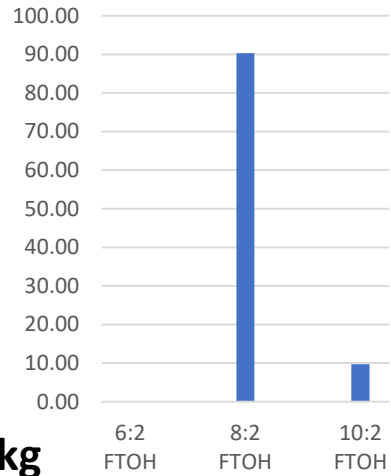
*Ionic PFASs and neutral PFASs are detected in textiles of outdoor clothing at quantifiable concentrations. Neutral PFASs are present at higher concentrations than ionic PFASs.*



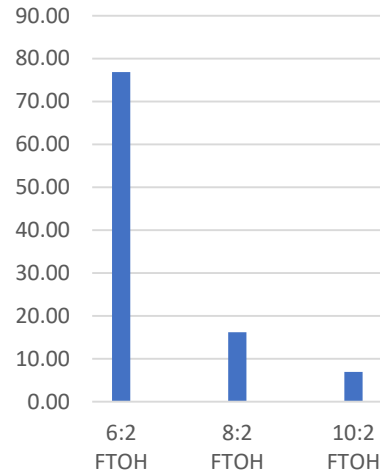
# Extractable PFCs in DWR Jackets

data from UBA (47/2014)

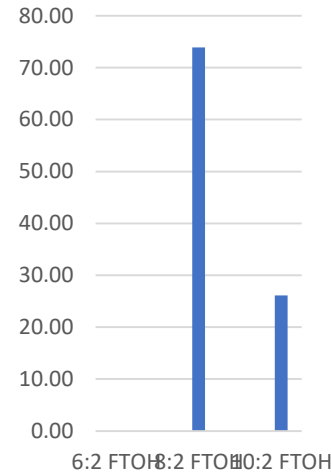
**J6% FTOHs**



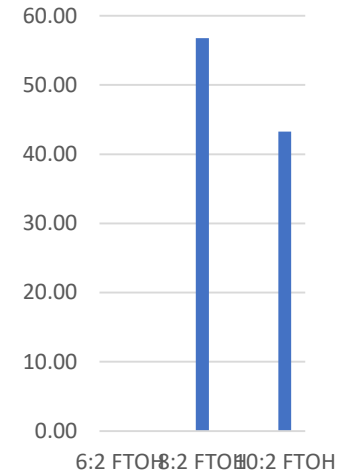
**J7%**



**J14%**

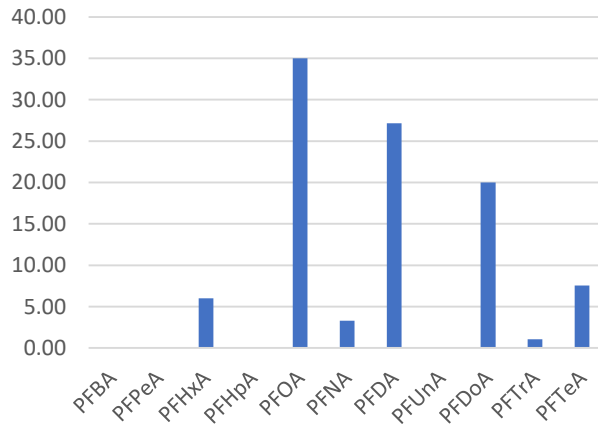


**J15%**

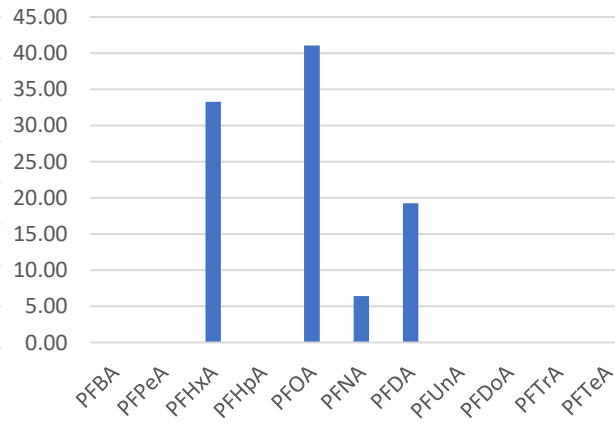


µg/kg

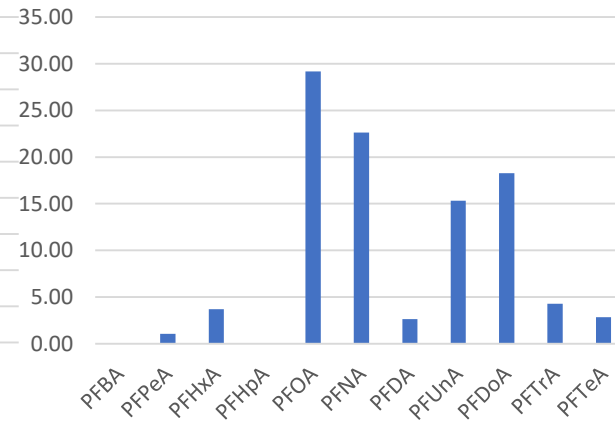
**J6% PFCAs**



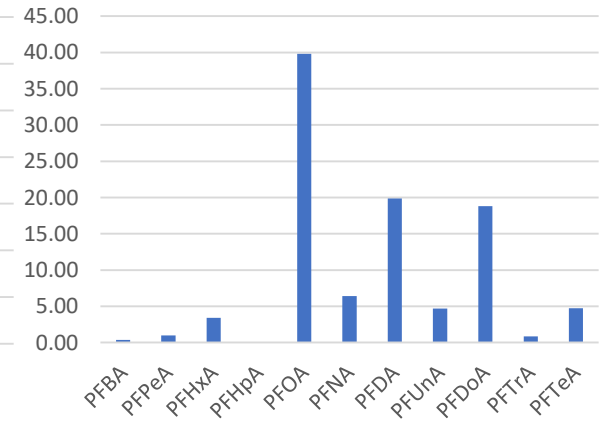
**J7%**



**J14%**



**J15%**

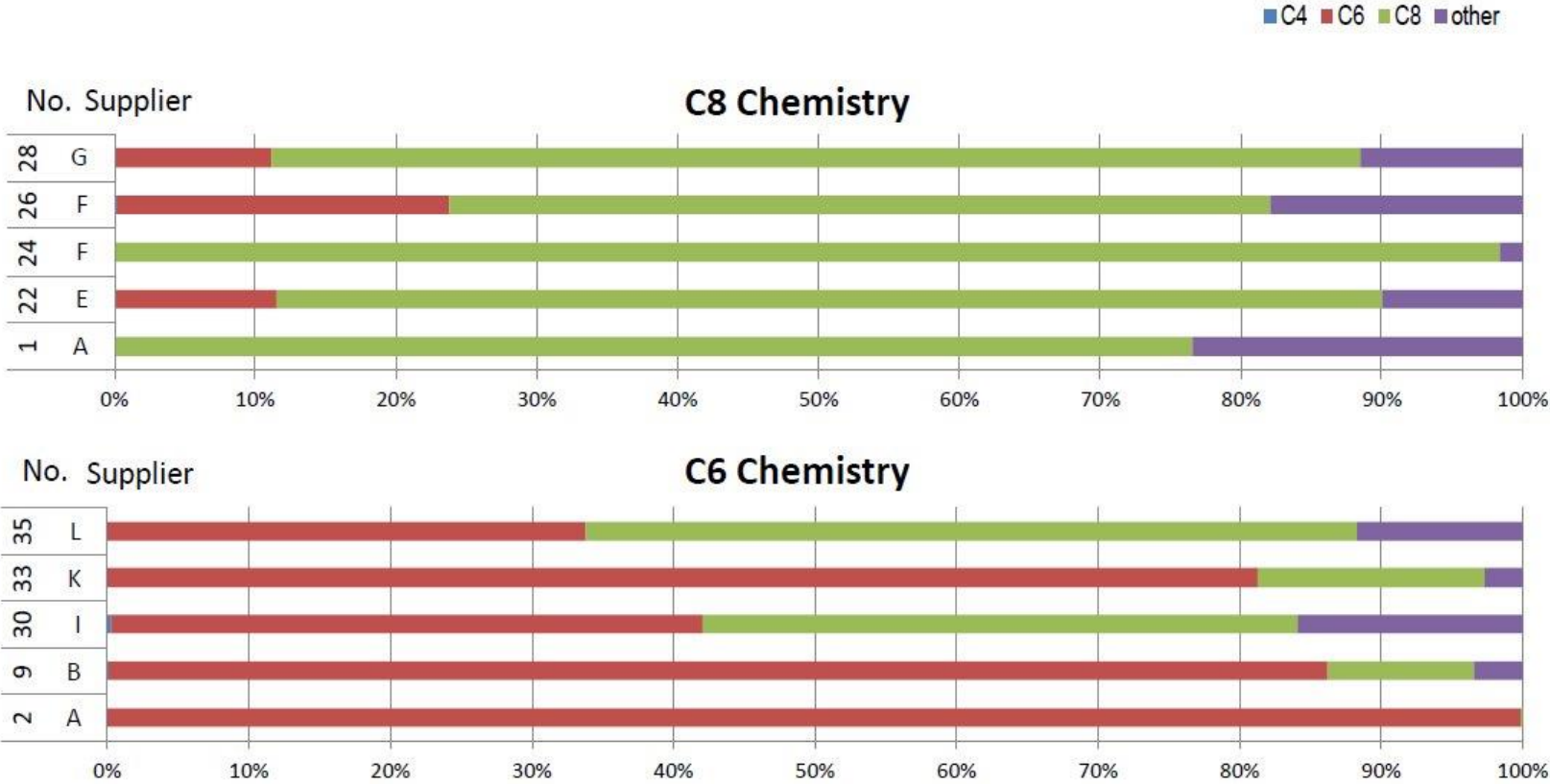




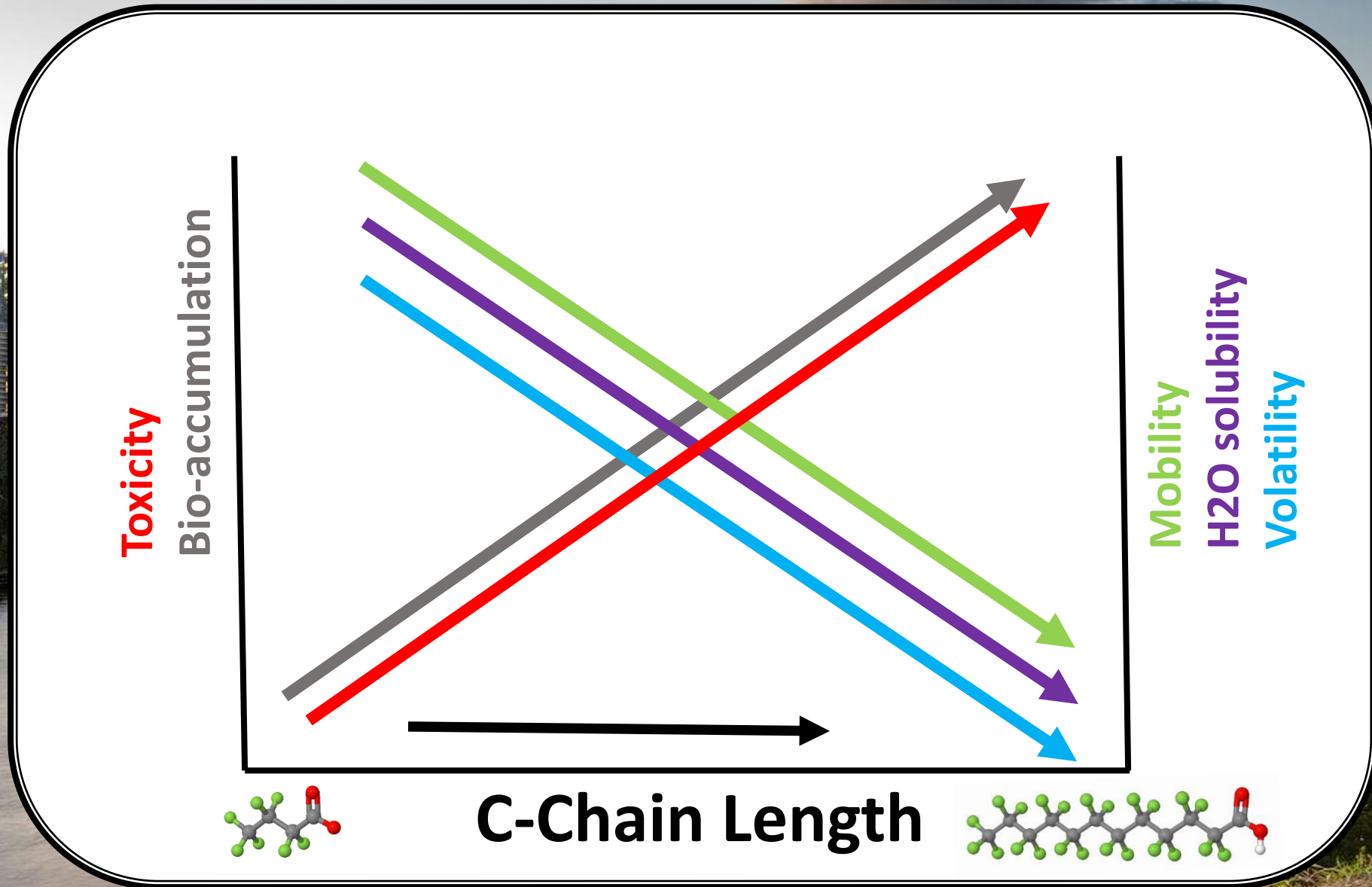
# Based on C6 chemistry.....? Really?

data from Joensson et al SWEREA (2015)

## Patterns of PFASs in textile samples



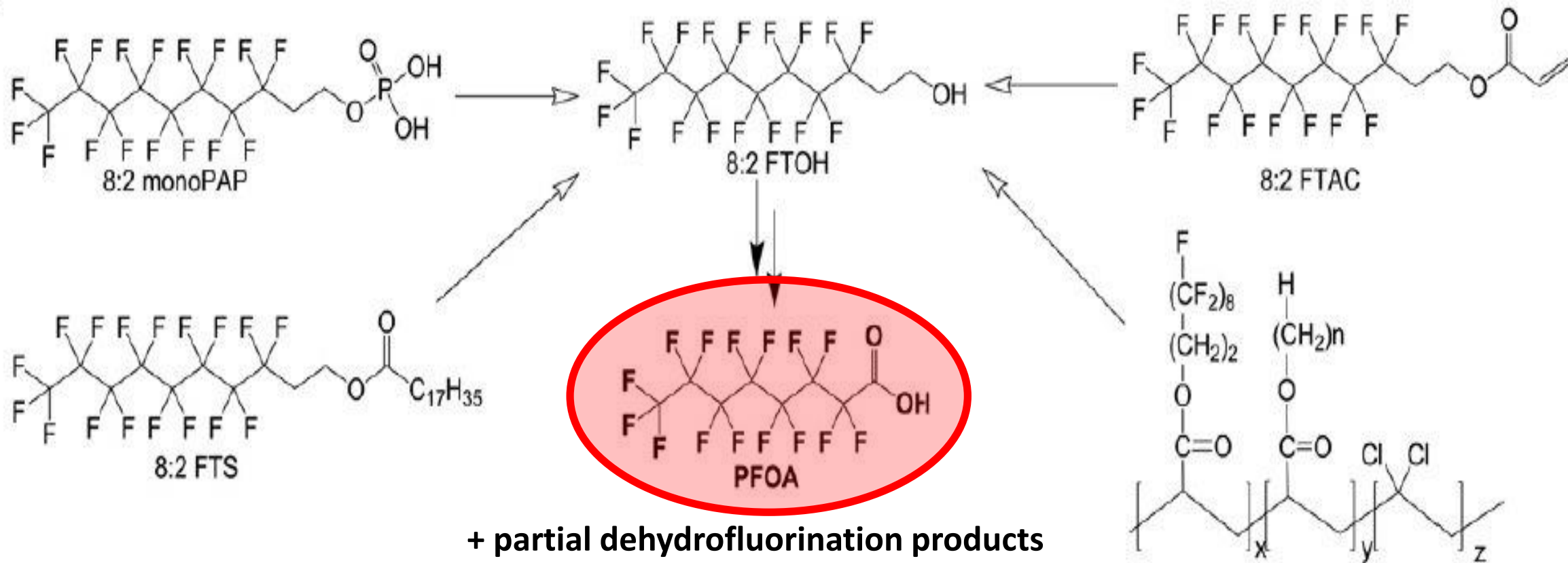
# Risk Considerations





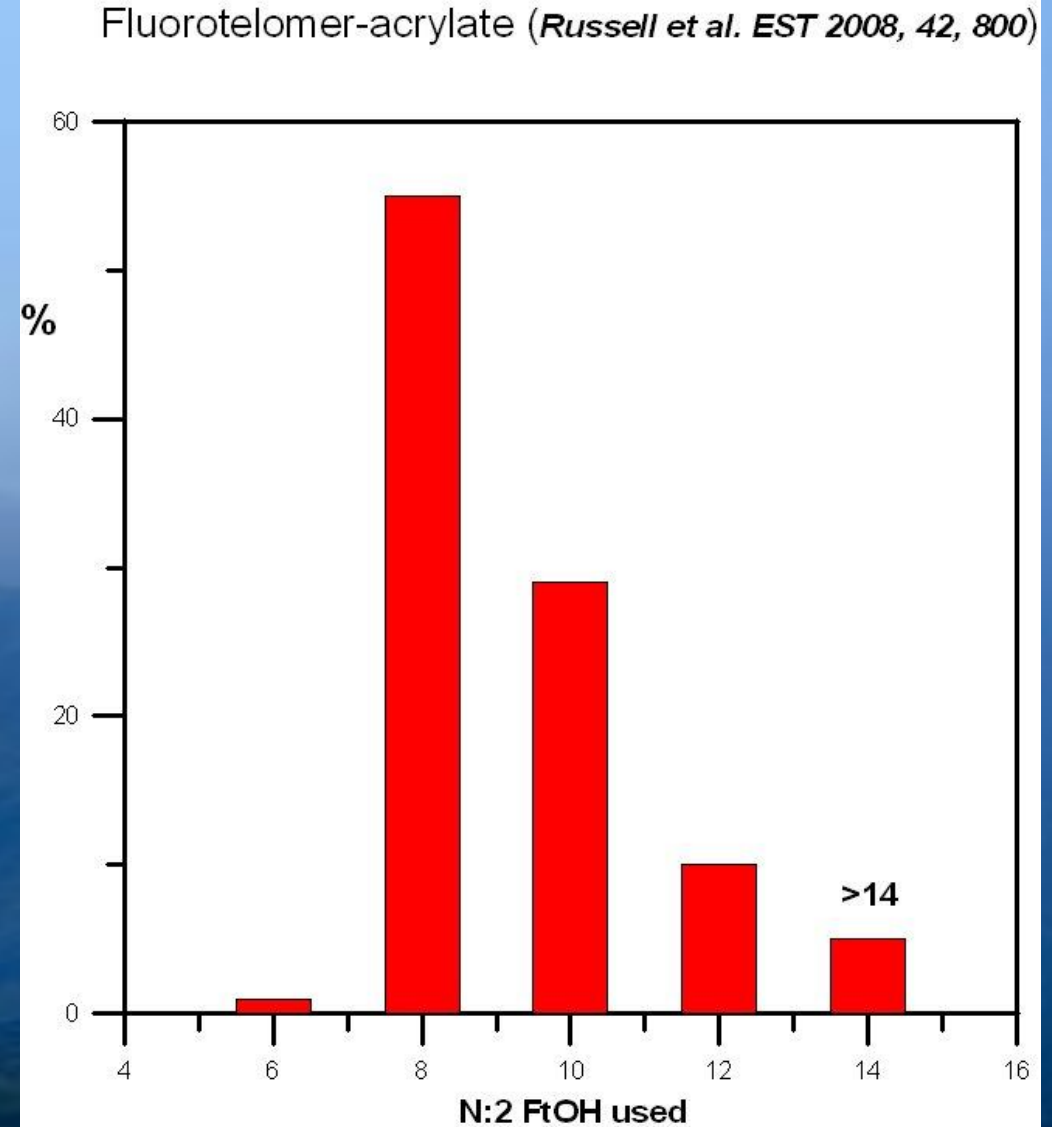
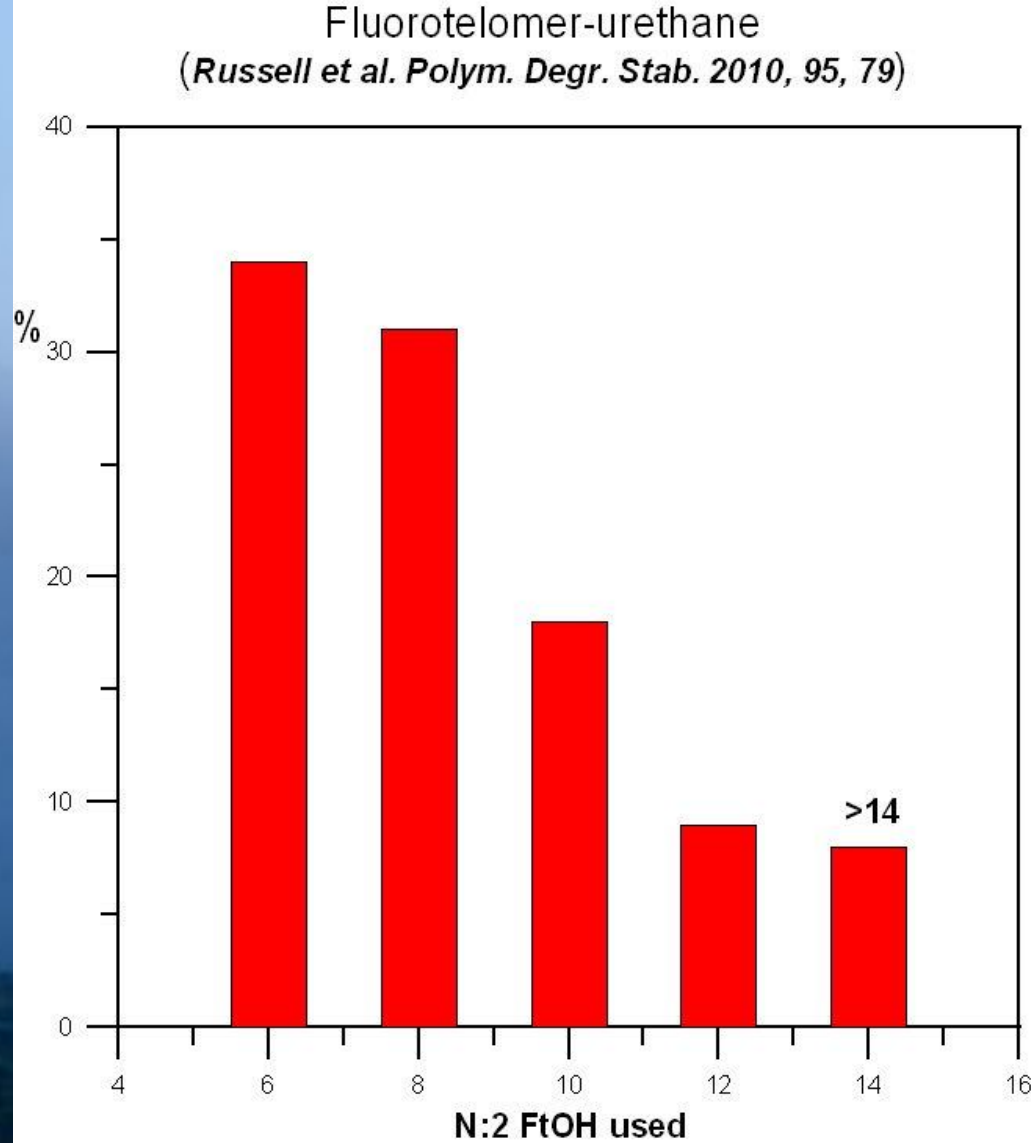
# 8:2 Fluorotelomer derivatives → PFOA

A



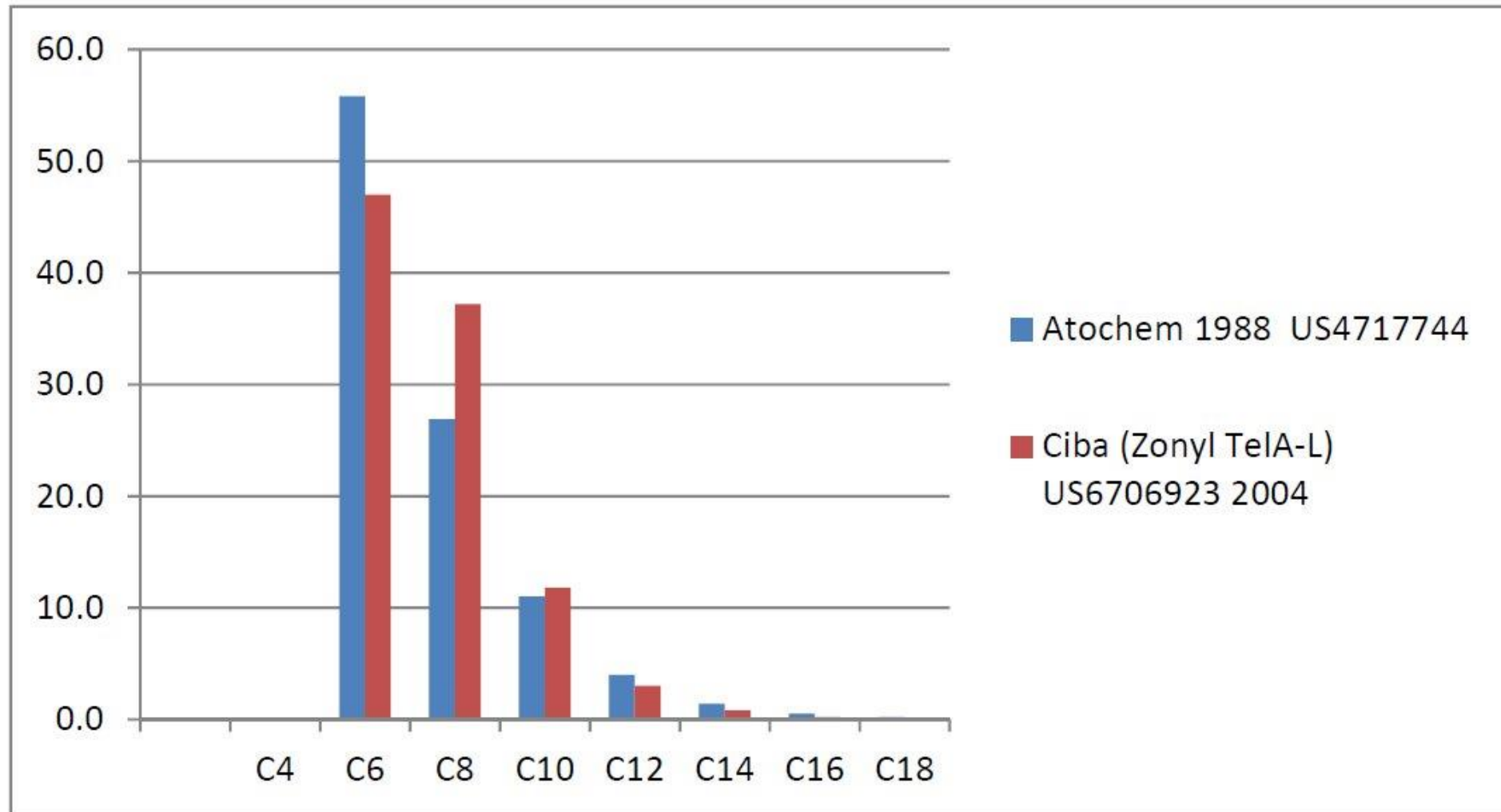
and other N:2 FT derivatives to N-PFCAs plus other products

# Precursor chain-length distribution

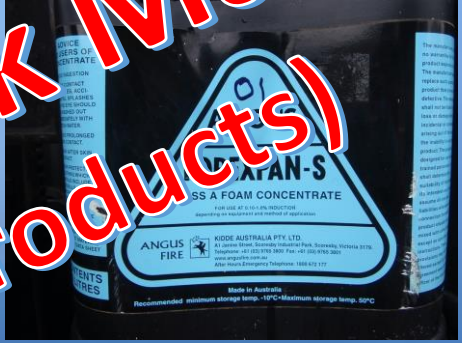




# Firefighting Foam Fluorosurfactants chain-length distribution



# Orphan or Legacy Foam Stocks – Total Organic Fluorine (TOF)



**The Need to Identify “Dark Matter”  
(potential persistent end-products)**

**AFR Class 3**

TOF 1.8-0.4%

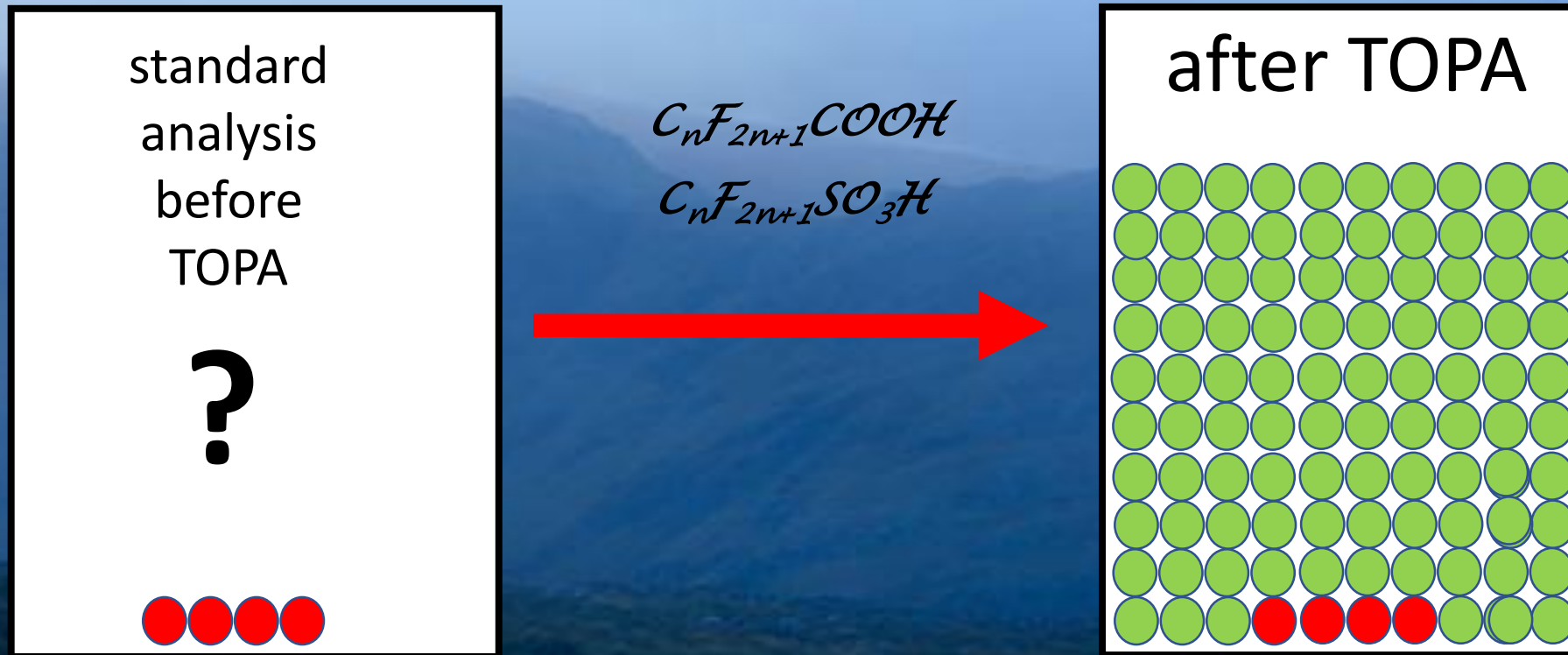
TOF 0.03% (??)

**Class A**

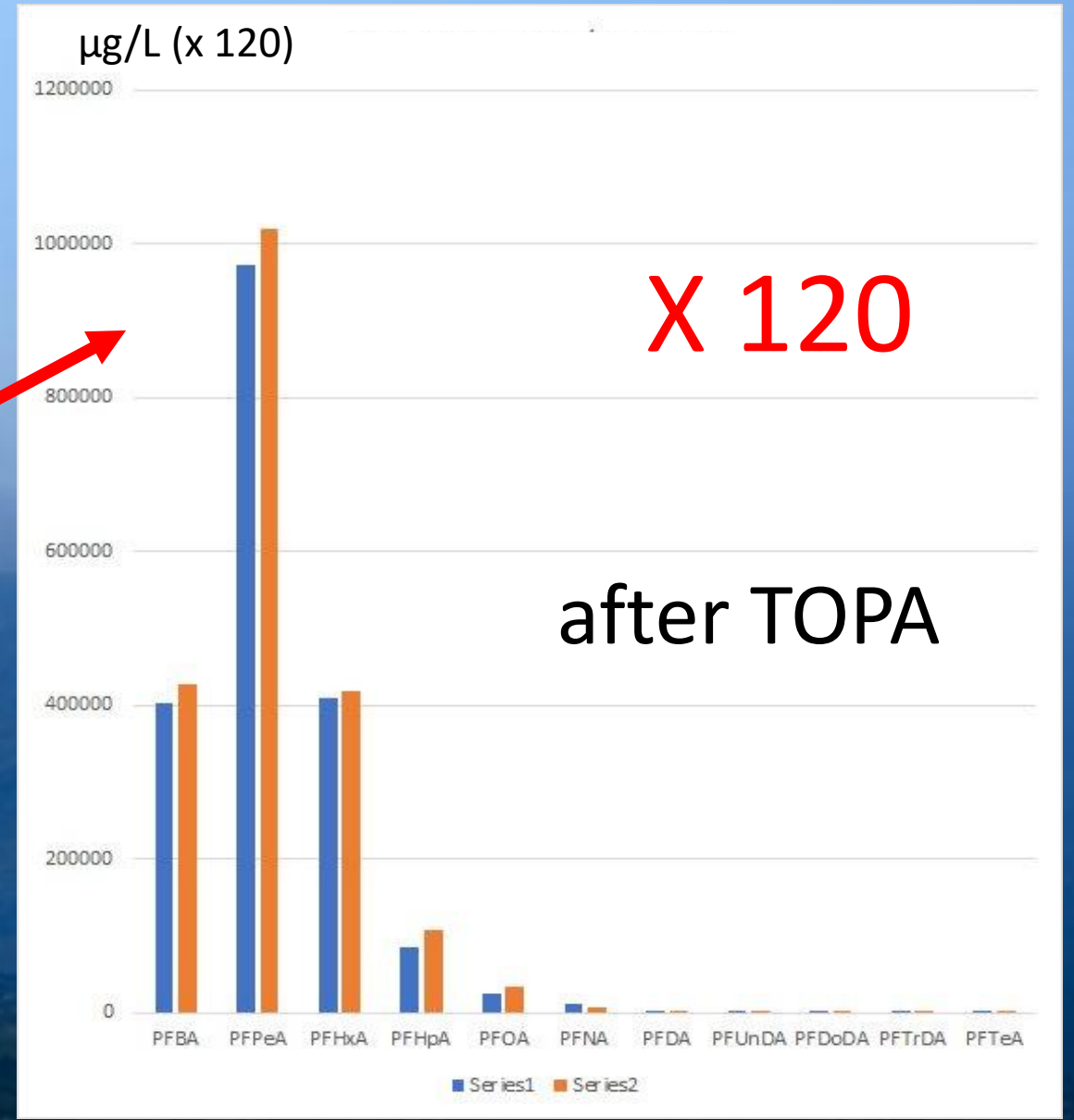
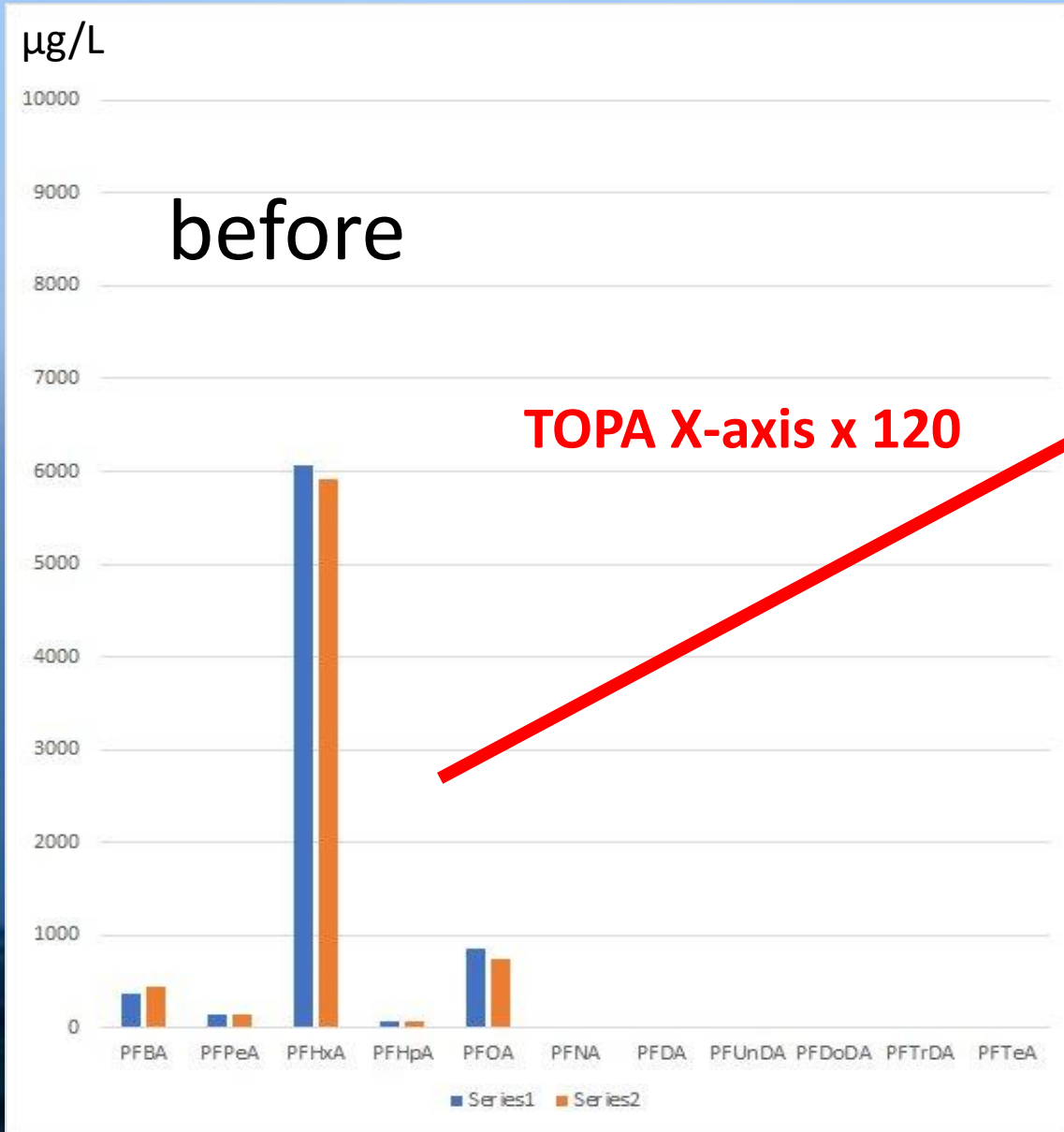


Perfluoroalkyl substances (PFAS)  
total detected

# The discovery of "Dark Matter"



# Perfluorocarboxylic acids (PFCAs)





# Perfluoroalkyl substances (PFAS)

log<sub>10</sub> µg/L

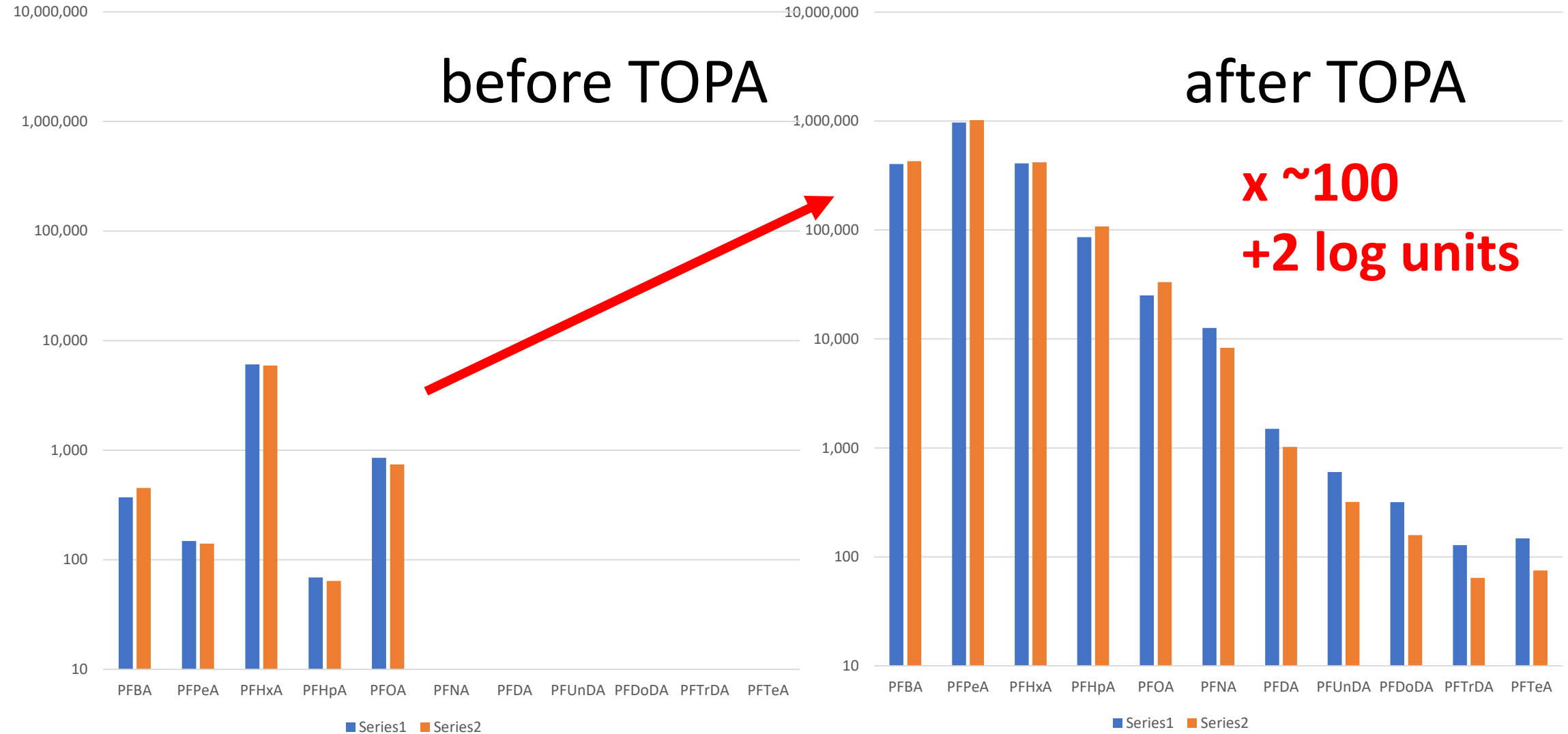
PFCAs before TOPA log-scale

log<sub>10</sub> µg/L

PFCAs TOPA log-scale

before TOPA

after TOPA



**x ~100  
+2 log units**

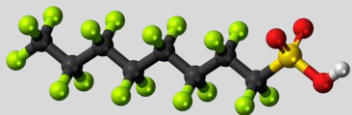
# Scientific Uncertainty

**Cause-and-Effect**  
**or**  
**Probable Link?**

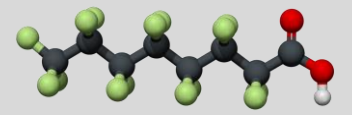


# Scientific Uncertainty

**Different Approaches  
can lead to  
Radically Different  
“Safe Levels”**



PFOS



PFOA

# Scientific Literacy

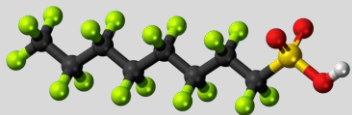
2000-6000  
ng/ml PFOS  
In plasma  
or  
5 ng/ml in  
plasma?

ff

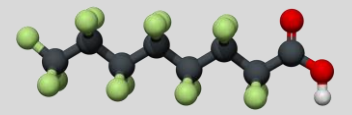
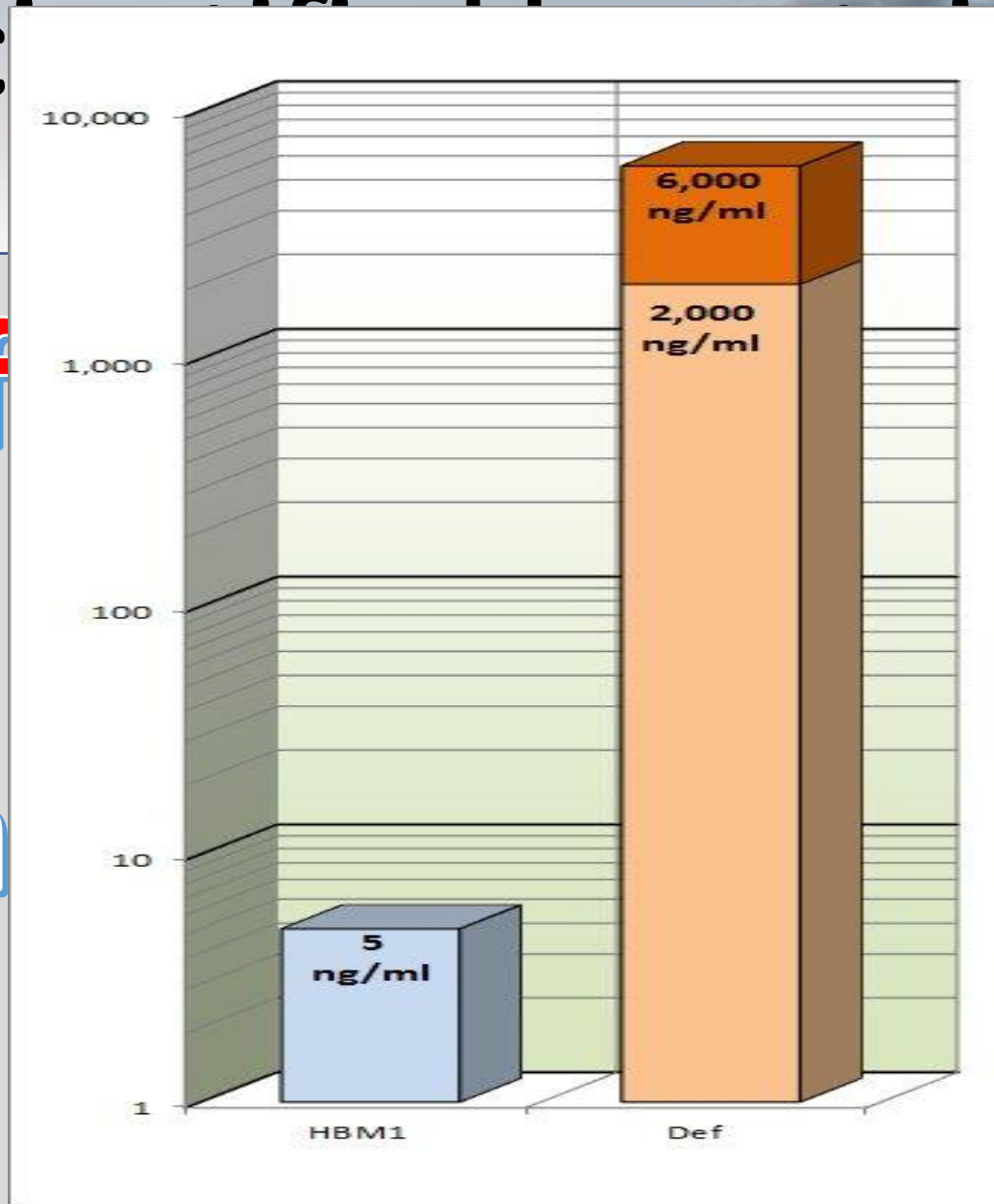
Ra

ches

ent



PFOS



PFOA



# Scientific Uncertainty

**Precautionary Principle  
addresses the  
Scientific Uncertainty**

# Scientific Uncertainty

**More Likely Than Not  
triggers  
Precautionary Principle**



# Holistic Risk Assessment

**Lack of Data == MAXIMUM RISK!**

# Holistic Risk Assessment

**Lack of Data == MAXIMUM RISK!**

**→ A High Index of Suspicion**



# Scientific Uncertainty

**Absence of Evidence  
IS NOT  
Evidence of Absence!**

# Thank You for Your Attention!

- Contact details:
- Nigel Holmes
- Department of Environment & Heritage Protection
- Queensland Government
- [nigel.holmes@ehp.qld.gov.au](mailto:nigel.holmes@ehp.qld.gov.au)
  
- [rogeraklein@yahoo.co.uk](mailto:rogeraklein@yahoo.co.uk)
- Dr. Roger A. Klein
- Cambridge UK

