

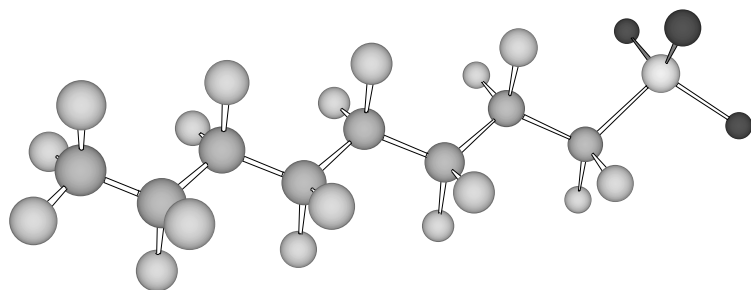
Perfluorinated organic compounds in the European environment– Achievements of the PERFORCE project

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Overview

- **Introduction**
 - **Perfluorinated organic compounds (PFCs)**
 - **Target analytes**
- **The PERFORCE project**
- **Analysis of PFCs**
 - **PFCs in water**
 - **PFCs in sediment**
 - **Other matrices**
- **Transport and bioaccumulation**
- **Conclusions**



Introduction

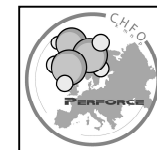
- **Perfluorinated organic compounds (PFCs)**
 - **Produced and applied for more than 50 years!**
 - **Development of LC-MS made environmental trace analysis possible**
- **”new/emerging environmental pollutants”**

Properties

- **non inflammable, surface active**
 - **wetting and leveling**
- e.g., Fire fighting foams,**
Coatings, Electronics, Herbicides, Metal
Finishing, Oil wells, Polymerisation

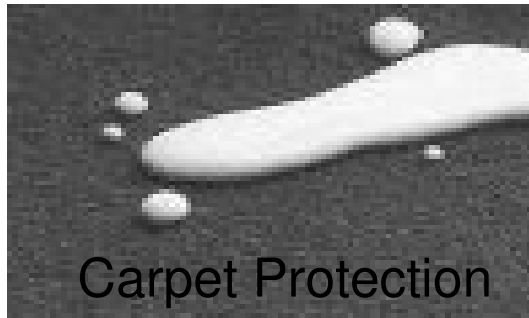


www.wfrfire.com



Introduction

- **Perfluorinated organic compounds (PFCs)**
Properties
 - both hydrophobic and oleophobic
 - **Surface treatment: Carpets, clothing, leather and paper products etc.**



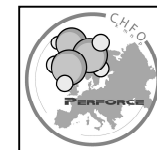
Excerpt of 3M commercial



www.swisspack.ch

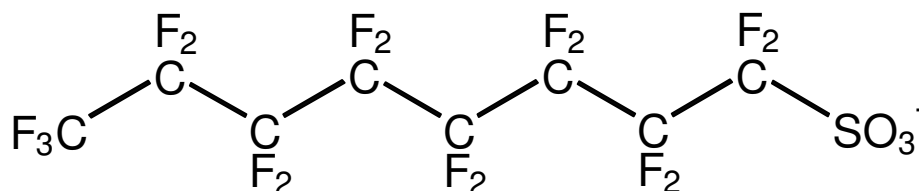


- **Fluoropolymer production**
- **Speciality chemicals**

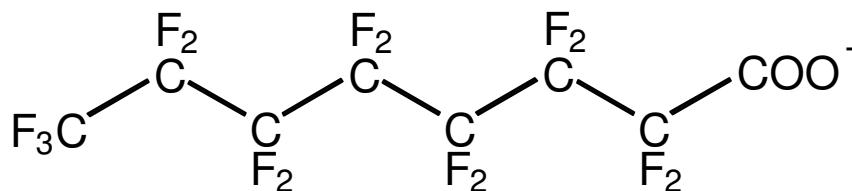


Target analytes

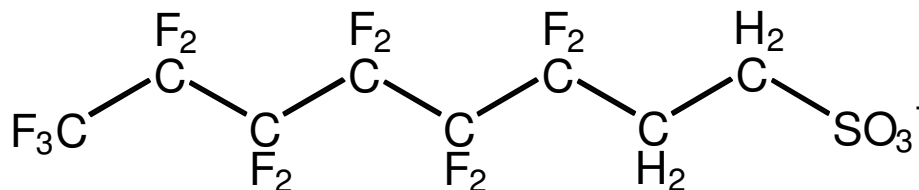
PFOS



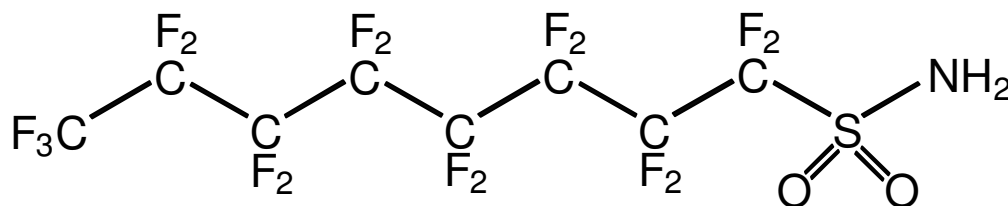
PFOA



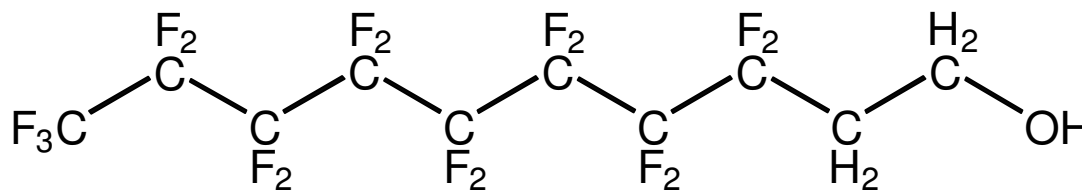
6:2 FTS



PFOSA



8:2 FTOH



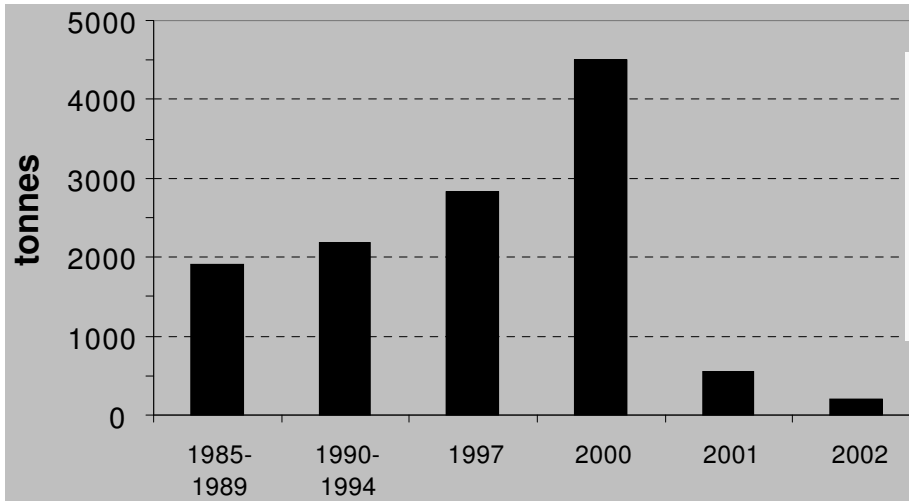
Abbreviations:

- PF..: perfluoro...
- FT..: fluorotelomer...
- ...S: ...sulfonate
- ...A: ...acid/carboxylate
- ...SA: ...sulfonamide
- ...SE: sulfonamidoethanol
- ..OH: ..alcohol
- ..X.:

- B** butyl (C4)
- Hx** hexyl (C6)
- O** octyl (C8)
- N** nonyl (C9)
- D** decyl (C10)
- a.s.o.**

PFC Production Trends

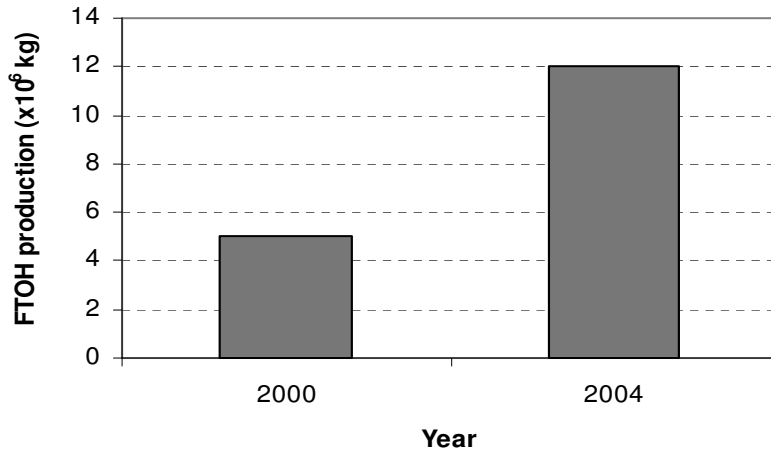
(taken from C.Butt, SETAC E 2006)



Production of perfluorooctane sulfonyl fluoride (PFOSF)

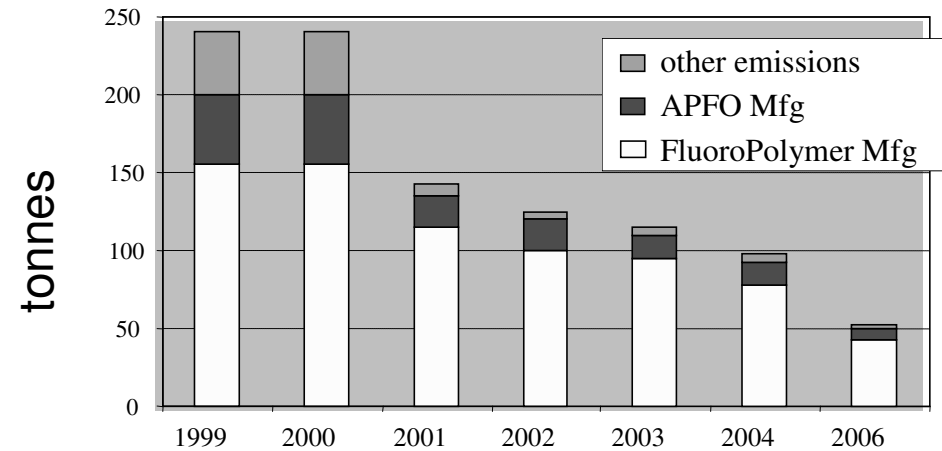
DT = ~11 yrs (Smithwick *et al.* 2006)

- similar to observed increase of PFOS in polar bears



FTOH Production (2000-2004)

(US EPA docket AR226-1914)



PFOA emissions

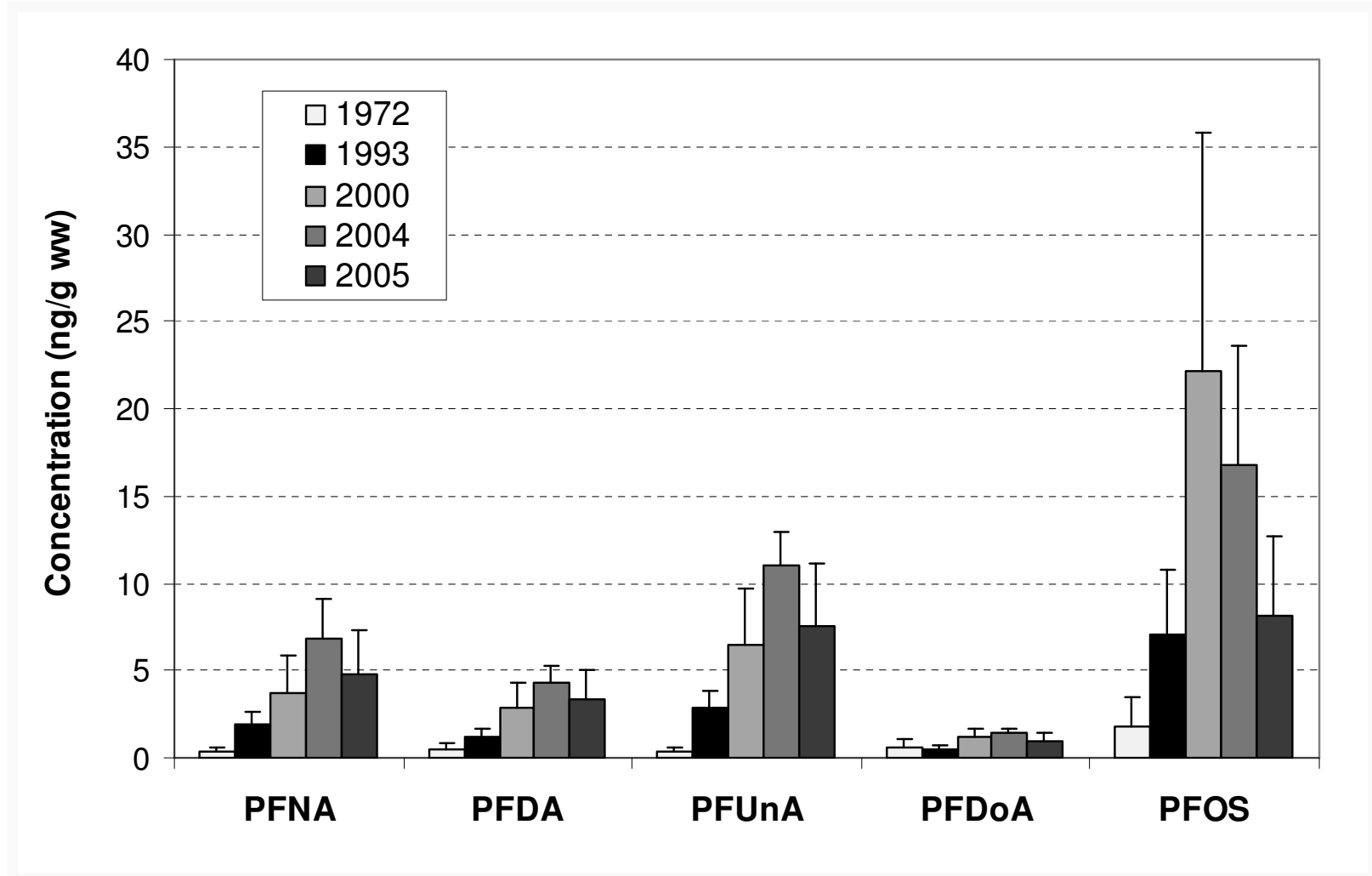
historical trend of PFOA emissions from all sources from 1999-2006 (Prevedouros *et al.* 2006)

- trends for other PFCAs?



Resolute Bay Ringed Seals

(taken from C.Butt, SETAC E 2006)





The PERFORCE project

Funded by the European Union (NEST-508967)

2004-2006; budget ~ 800 k€

Consortium

University of Amsterdam (coordinator)



University of Antwerp



Norwegian Institute for Air Research



Netherlands Institute for Fisheries Research



Stockholm University



Du Pont de Nemours (Belgium) BVBA





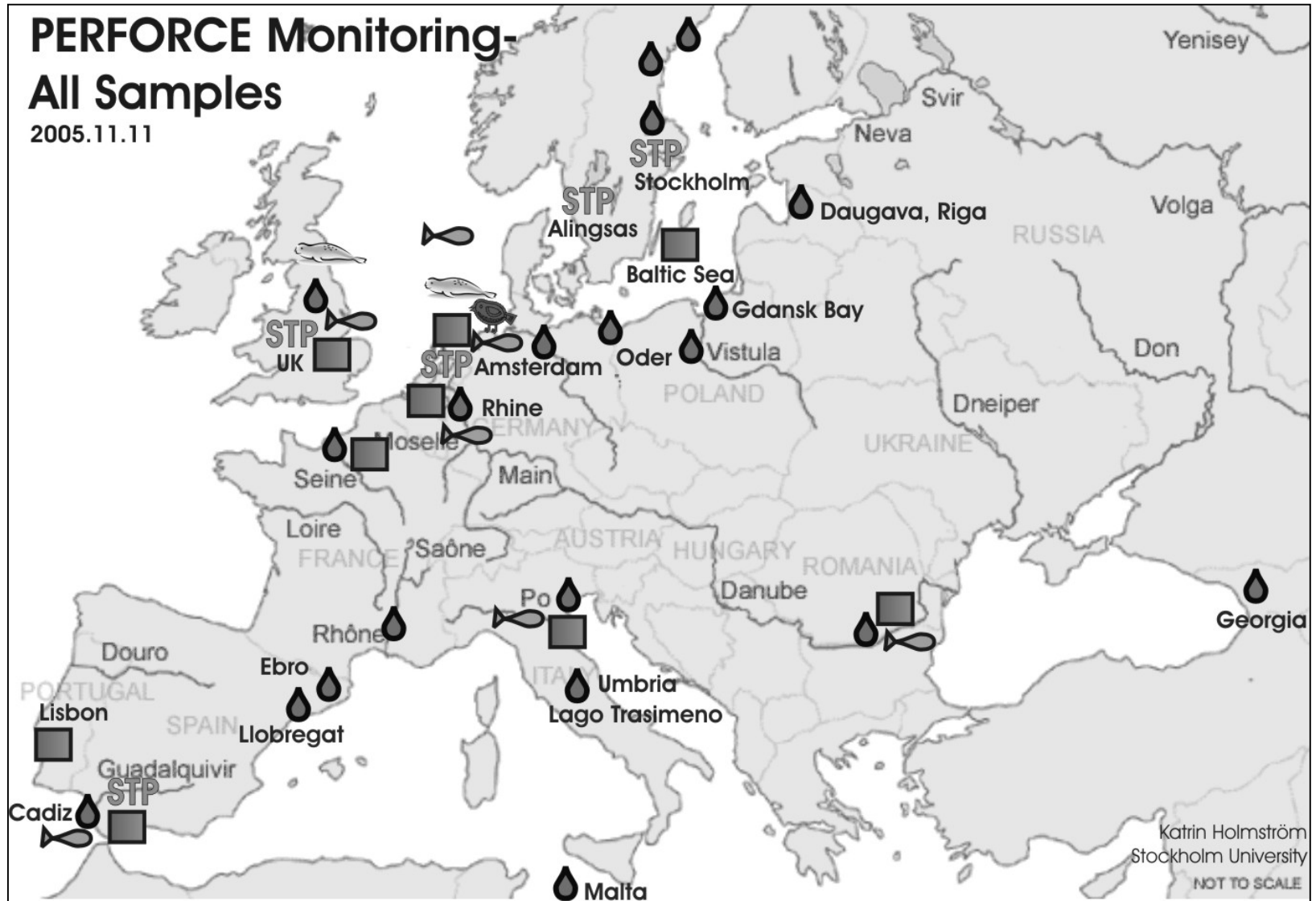
The PERFORCE project

Objectives

- **Physico-chemical parameters**
 - **Evaluation of sources and routes in Europe**
 - **New chemical and biological techniques**
 - **Quality assurance, interlaboratory studies**
 - **European monitoring**
- **Exposure assessment in Europe**



The PERFORCE project



19 June 2006

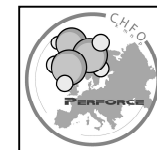
Norman workshop Stresa Italy



Workpackage 1

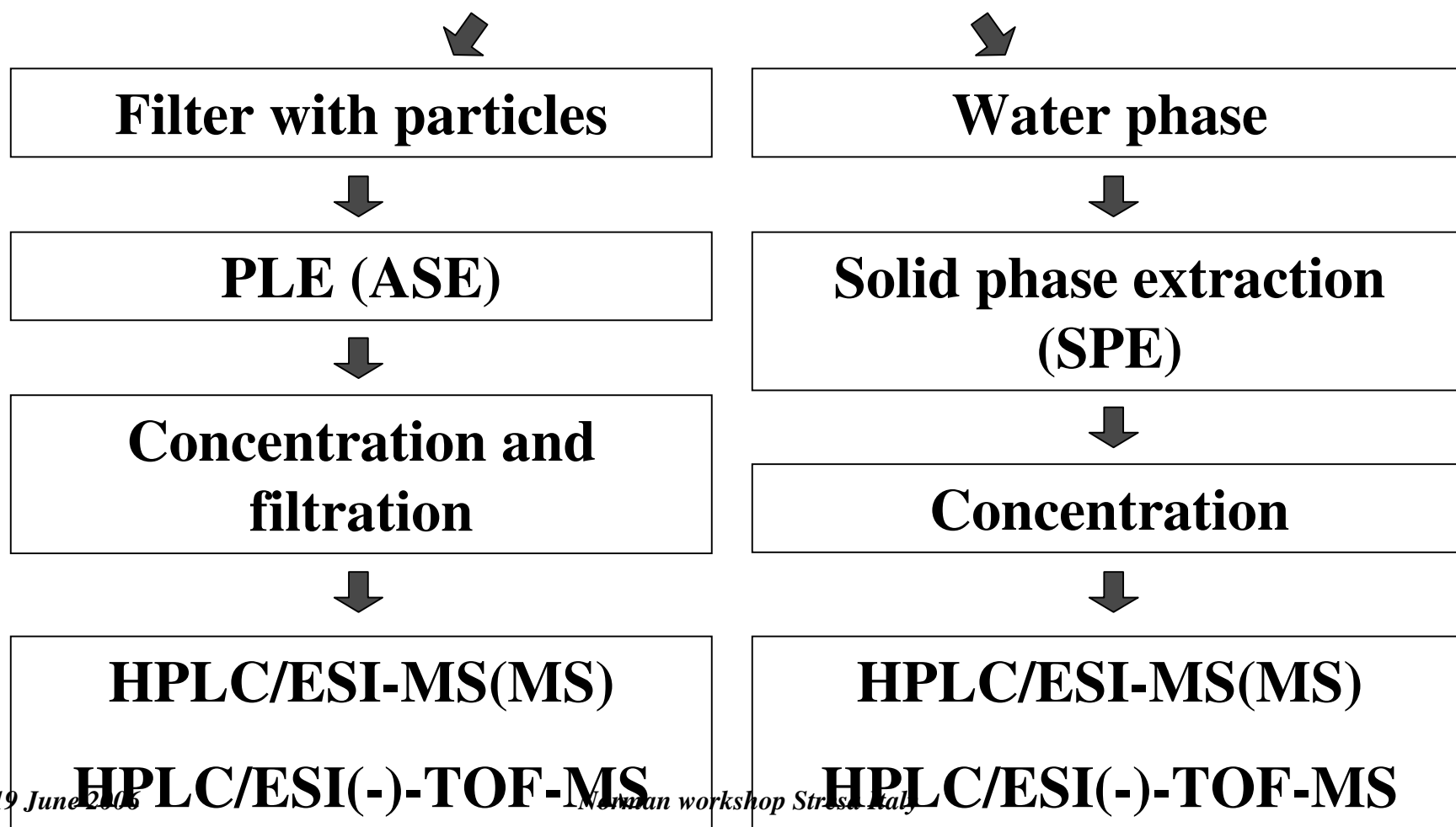
Analytical method development

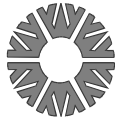
- **Analytical challenges**
 - **Most target PFCs are ionic (not volatile) and**
 - **do not possess a chromophore group**
 - **require LC-MS for trace analysis**
 - **Pure and well characterised standards lacking**
 - **Blank problems: e.g. PTFE contains PFOA**
 - **Most PFCs are poorly soluble in water or hexane**
 - **Several PFCs are surface active**
 - **Matrix effects in MS ionisation**



PFCs in water samples

Filtration of 500 mL water sample





Particle/water phase distribution

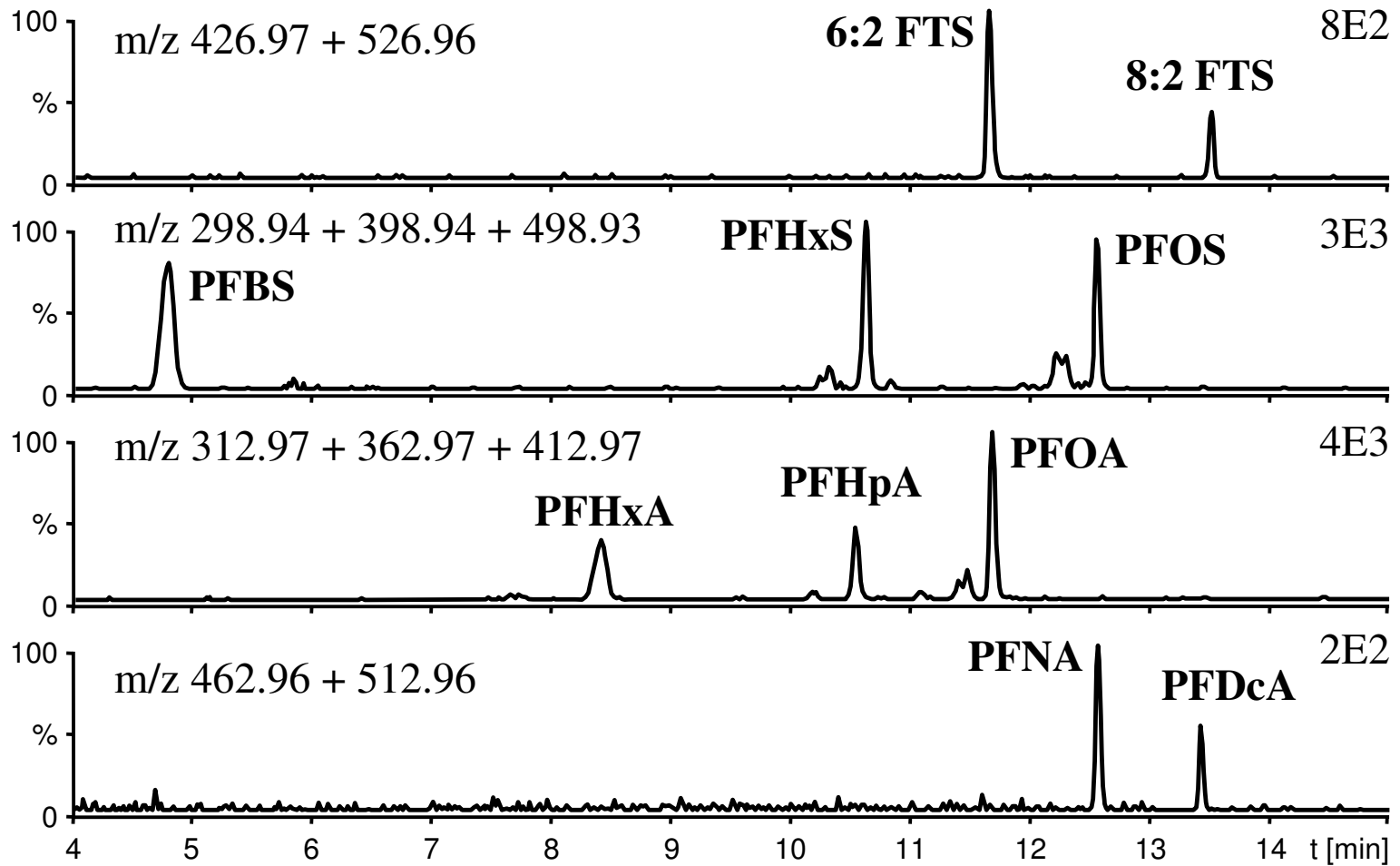
	6:2 FTS	PFOSA	PFBS	PFHxS	PFOS	PFDCS
Dissolved in water [%]	98	13	98	95	79	29
Bound to particles [%]	2	87	2	5	21	71
	PFHxA	PFHpA	PFOA	PFNA	PFDCa	PFDoA
Dissolved in water [%]	97	98	90	70	61	22
Bound to particles [%]	3	2	10	30	39	78

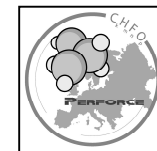




Sample chromatogram

Landfill effluent (water phase)





PFCs in water: qualitative results

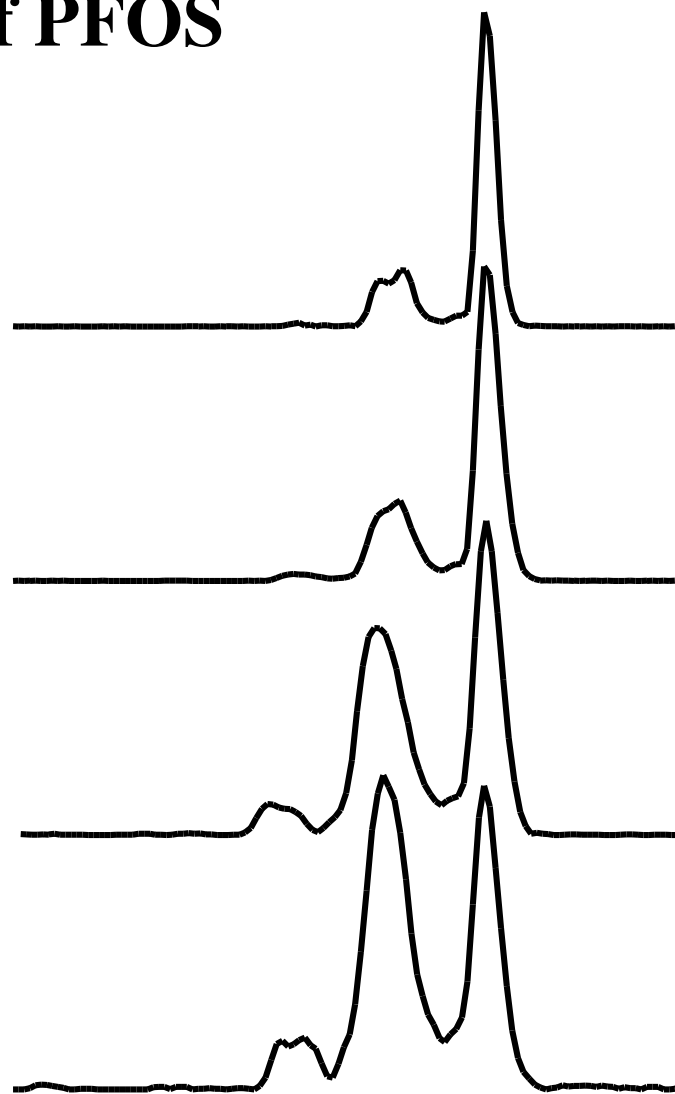
Isomers of PFOS

Reference standard

Sea water

**Landfill effluent
(water phase)**

**Landfill effluent
(particle phase)**

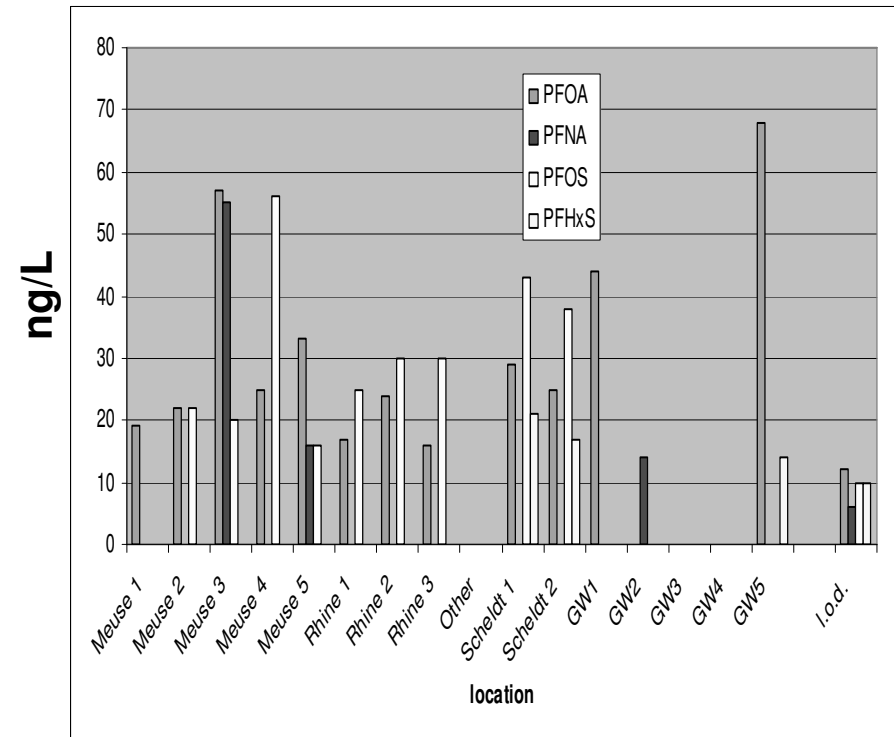
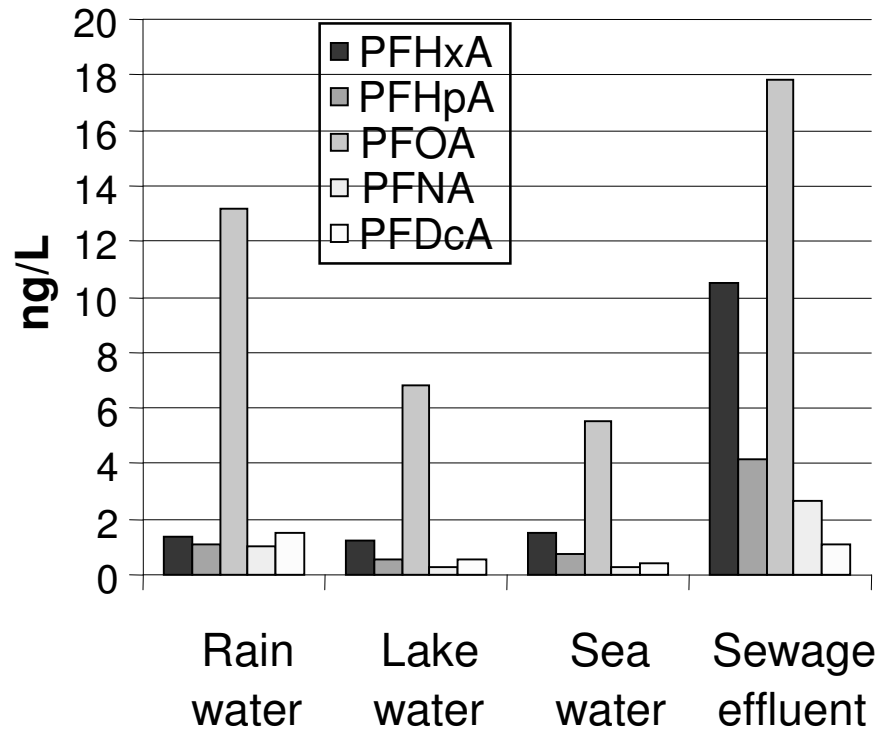




PFCs in water: quantitative results



Nordic samples; Dutch samples (sum of particle and water phases)
 Carboxylates (mean values); PFCA and PFS



PFCs in sediment samples

C.R. Powley et al. (2005)
Anal. Chem. 77, 6353-6358

Freeze-drying and
homogenisation of sample

↓ NaOH treatment

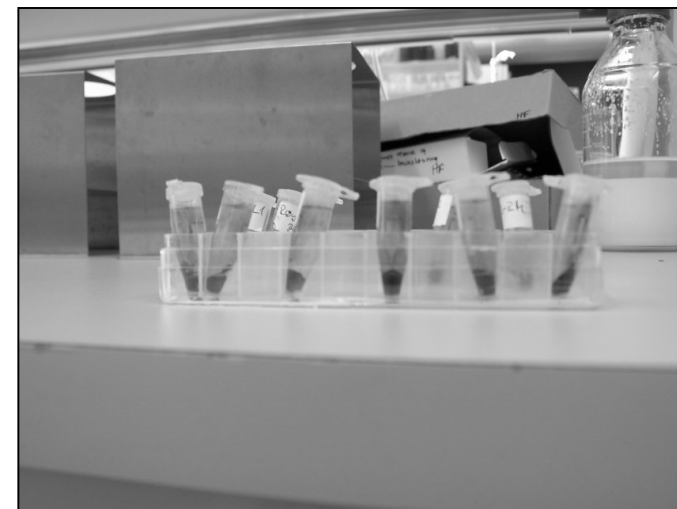
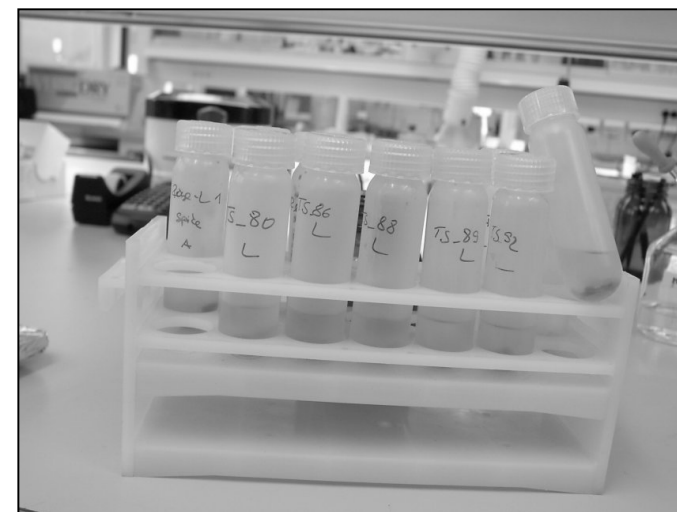
Extraction with methanol

↓ Centrifugation
(Concentration)

Clean up with ENVI-Carb

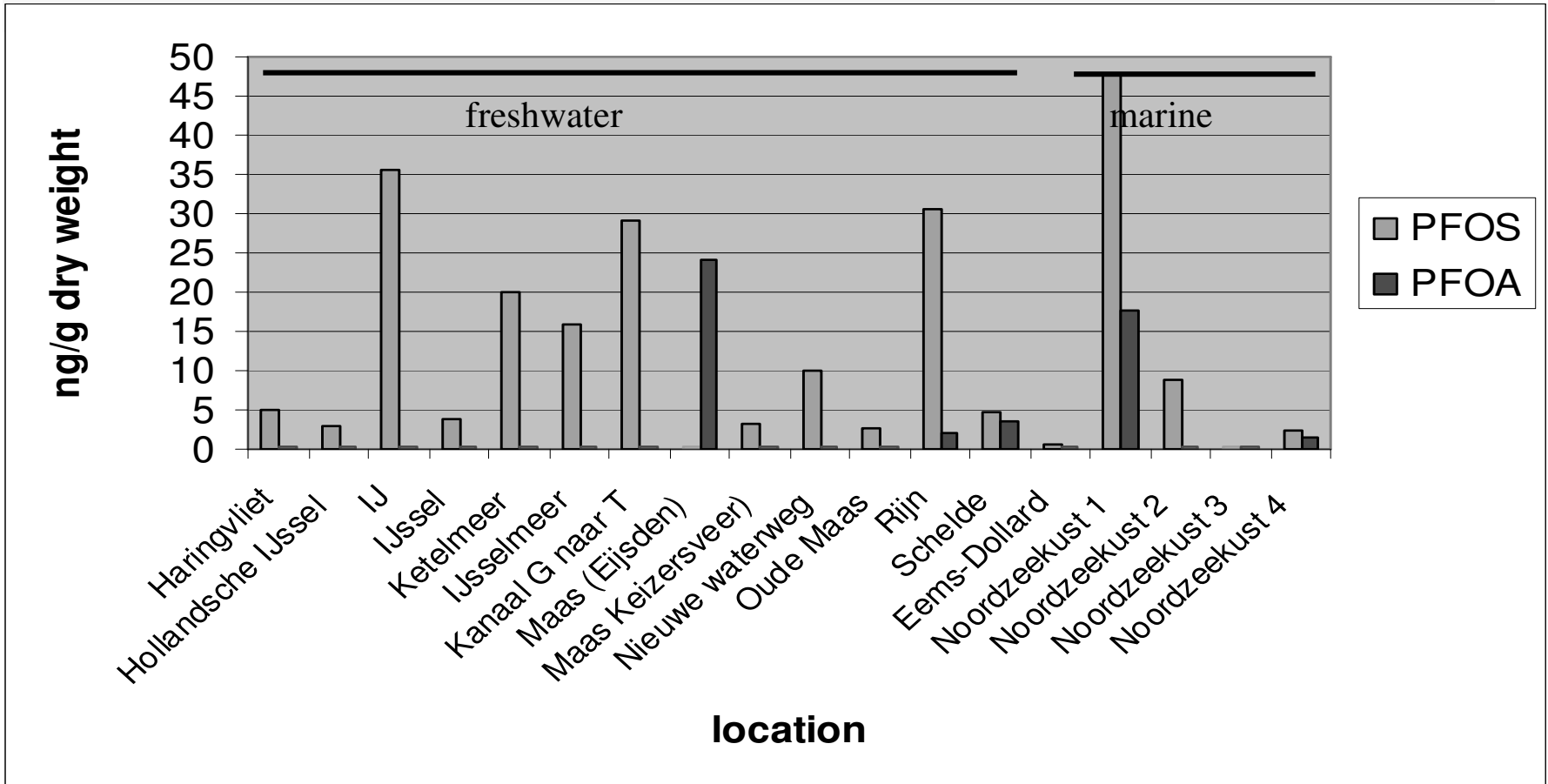
↓ Centrifugation

HPLC/MS





Monitoring the Environment



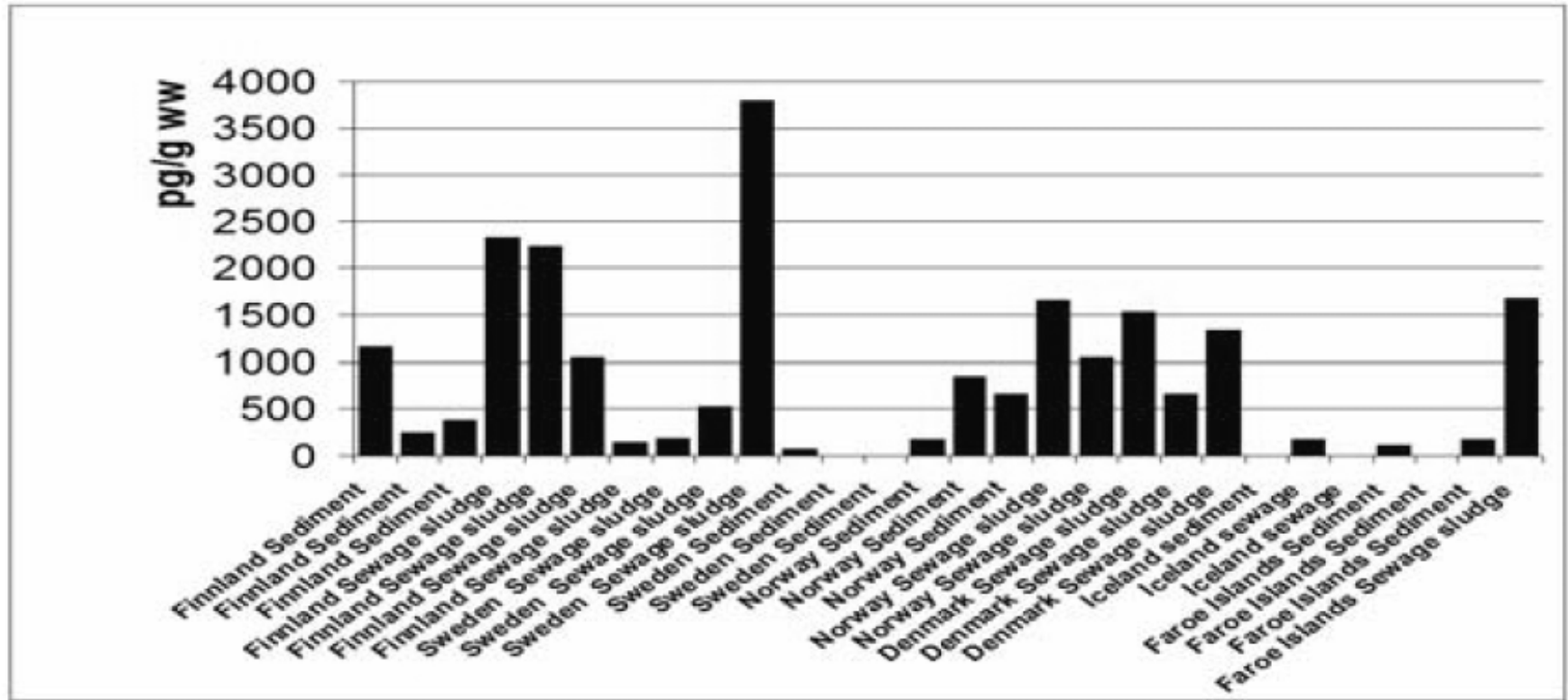
PFOS and PFOA in suspended matter from fresh waters and marine waters in the Netherlands (De Voogt et al. , 2004)



Nordic Environment

Kallenborn R, Berger U, Järnberg U, 2004

Nordic Council http://www.sft.no/nyheter/dokumenter/pfas_nmr2004.pdf



SUM PFAS concentration for solid abiotic samples: Sediment and sewage sludge from Nordic countries.

$$SUM\ PFAS = PFOSA + PFHxS + PFOS + PFHxA + PFOA + PFNA.$$





PFCs in sediment: results

- **PFOS is the dominating PFC, followed by PFOA and PFOSA**
- **Typical levels for freshwater¹ and marine^{1,2} sediments < 10 ng/g dry weight**
- **Exception: sedimentation areas; sediments from the North Sea close to oil platforms, impact of fire-fighting foams: PFOS 2-30 ng/g dry weight (unpublished results NILU)**

¹ Nordic Council of Ministers (NMR, 2004): *Perfluorinated Alkylated Substances (PFAS) in the Nordic Environment*, Copenhagen, ISBN 92-893-1051-0, ISSN 0908-6692

² Higgins et al. (2005) *Environ. Sci. Technol.* 39, 3946-3956

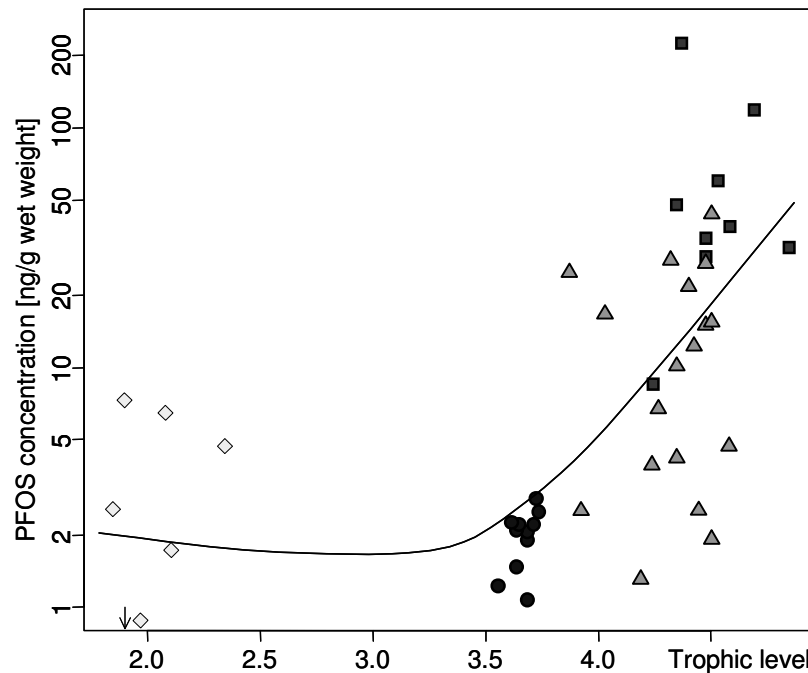




PFCs in biota samples

- **Most frequently used method: ion pair extraction (Hansen)**
- **Active C (Powley) method (similar to sediment) has advantages**

PFOS bioaccumulation in an Arctic marine food web



- ◇ Ice amphipods
- Polar cod
- ▲ Black guillemot
- Glaucous gull

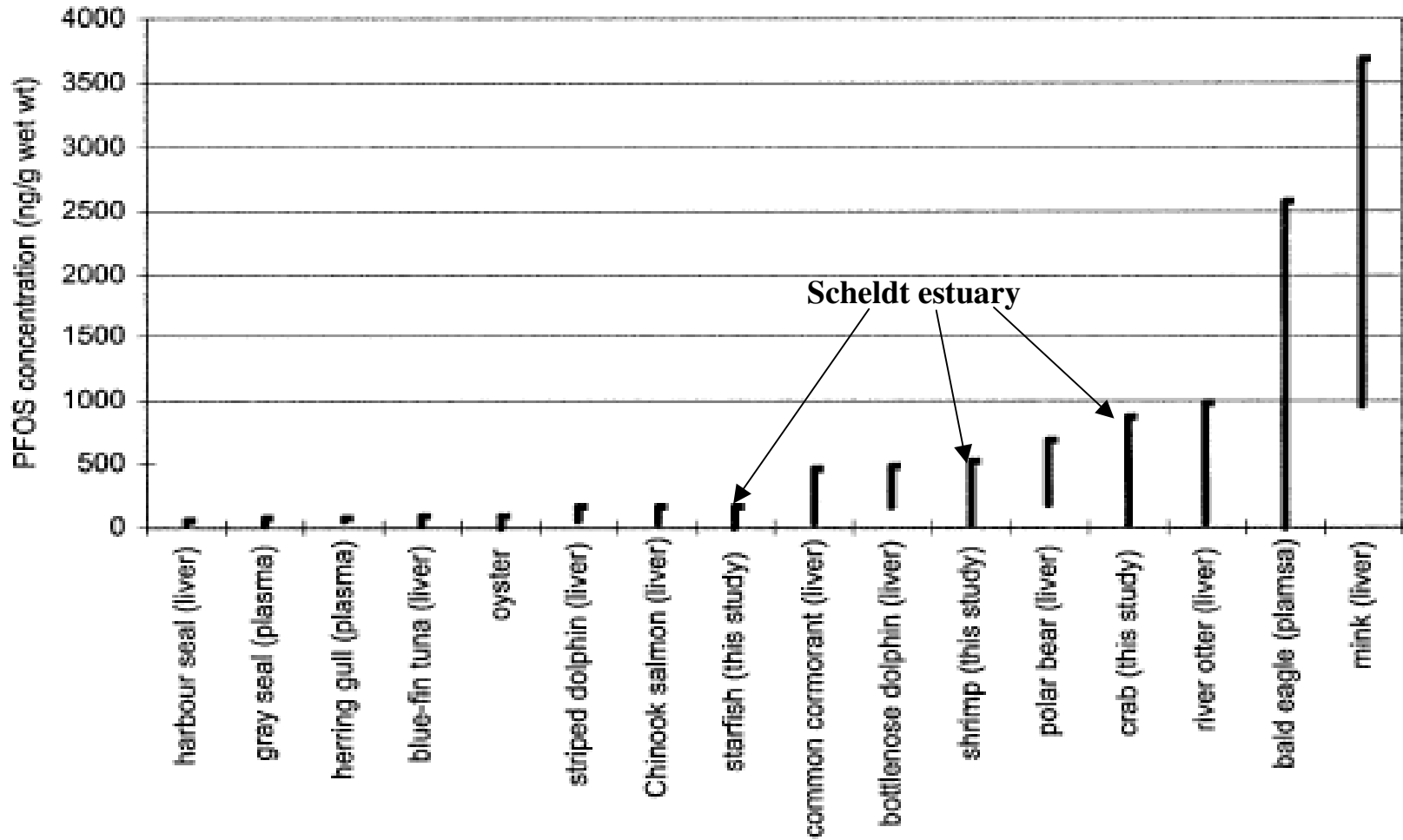
**PFsulfonates \geq C6 and
PFcarboxylates \geq C8
bioaccumulate**



PFOS:

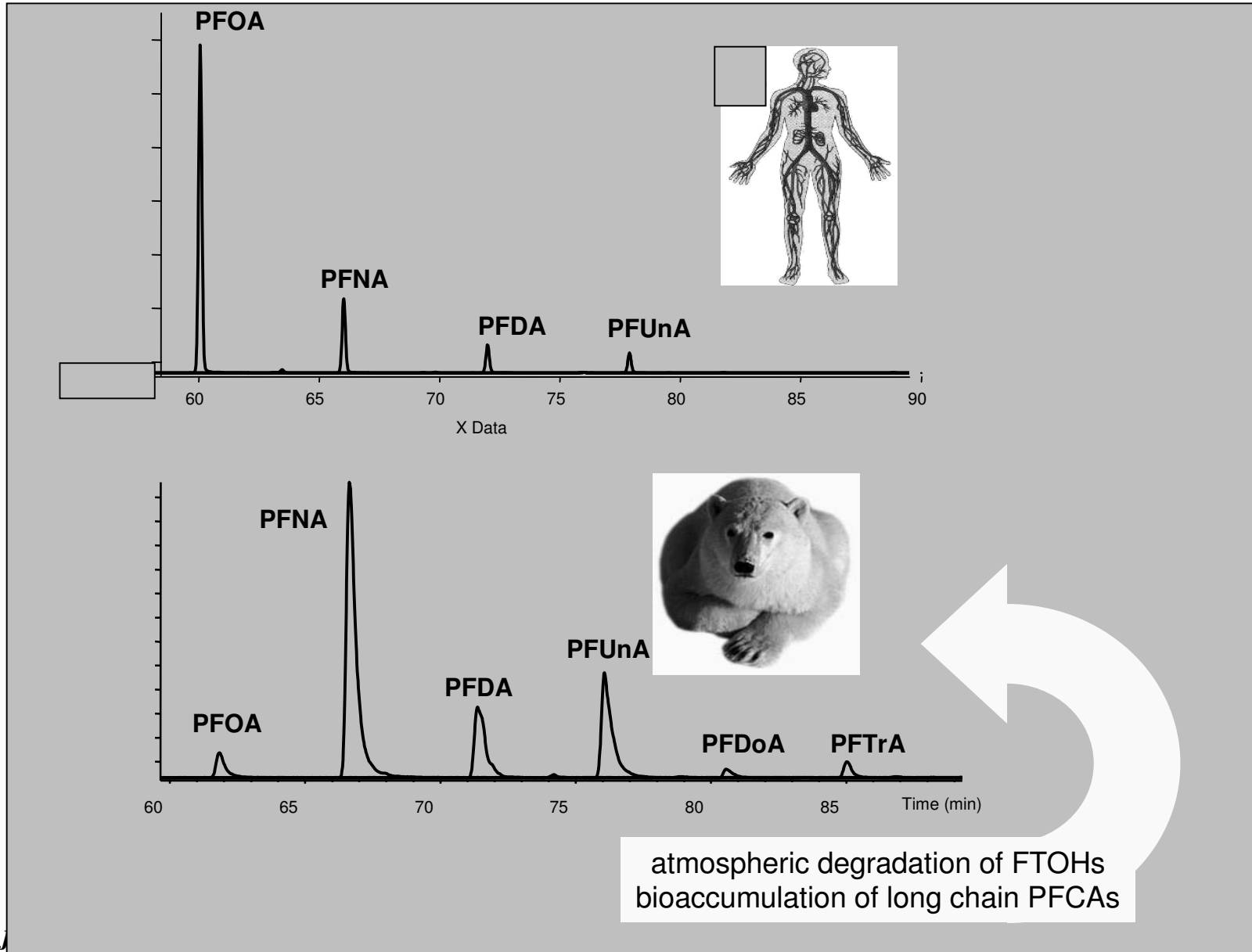
Concentration ranges in aquatic biota ng.g^{-1} ww

Van de Vijver et al. (UA) ETC 2003



PFCA Profile in Humans vs. Arctic biota

(taken from S.Mabury, Univ.Toronto; SETAC E, 2006)



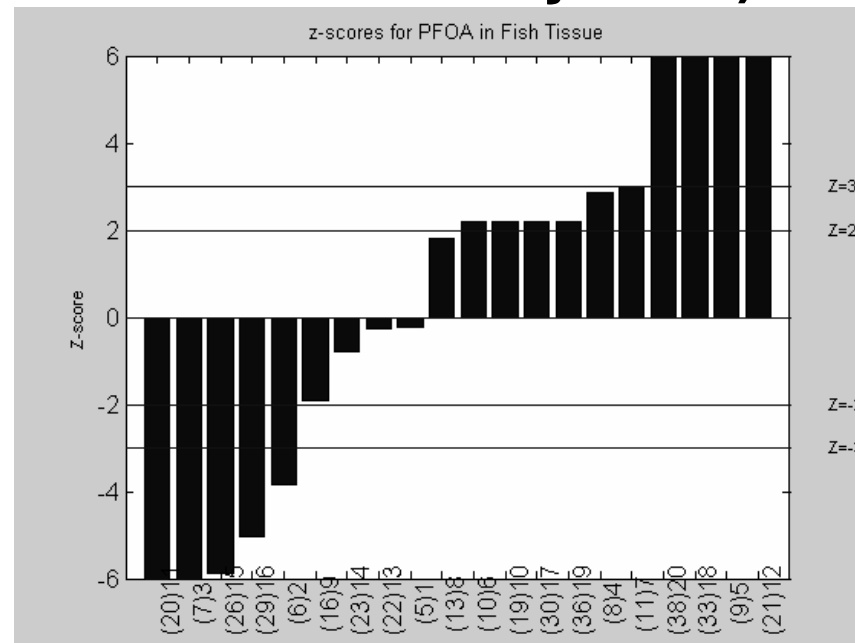


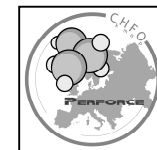
Conclusions (analysis)

- **Analysis of PFCs poses new challenges compared to "classical" POPs**
- **Analytical methods are now available for many different PFCs in all kind of samples**
- **However, uncertainties are still substantial (see first international intercalibration study 2005)**

Satisfactory: 5/20
 Questionable: 6/20
 Unsatisfactory: 9/20

RSD* = 76%
 Van Leeuwen et al. 2005
 RIVO





Conclusions (general)

- **Many data are still lacking to complete an accurate environmental exposure or risk assessment**
- **PFCs are widely distributed in the environment at levels sometimes exceeding PCBs**
- **PFOA and longer alkanoic acids (C₁₀-C₁₄) are found in biota from remote Arctic**
- **PFOS is a PBT chemical and is globally distributed, but concentrations seem to decline since production ban**
- **Oceanic route needs further study**
- **FTOHs can be transformed into PFCAs and FOSAs/FOSEs to PFOS/PFCA**
- **Most PFCs are still in use, political evaluation and action must be taken**



Acknowledgments

Thanks to Urs Berger (ItM Stockholm), many colleagues at IBED and the following institutions for project collaboration or financial support:

European Union (PERFORCE project NEST-508967)

DuPont de Nemours

...and the PERFORCE project team...

