Structural isomers of perfluorinated alkyl acids, useful tool for source elucidation?

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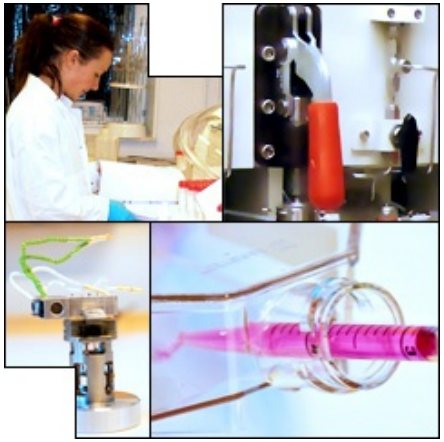


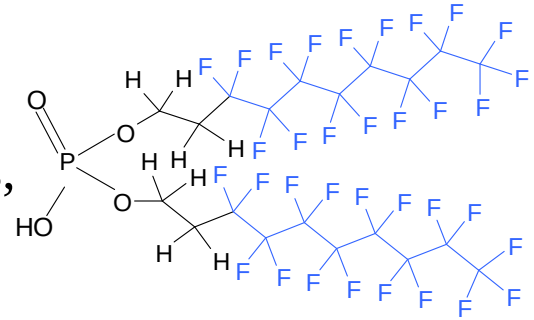
MAN TECHNOLOGY ENVIRONMENT RESEARCH CENTRE

Outline

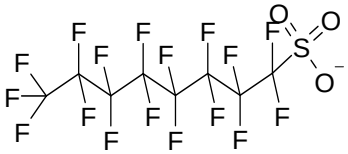
- Structural isomers of perfluorinated alkyl acids
  - Sources
  - Analysis and implication on quantification
- Ocurrence in human blood
- Distribution in the environment
  - Case study after AFFF contamination
- Useful tool for source elucidation?

Introduction – Perfluorinated alkyl acids

- Polyfluorinated compounds
  - Telomer alcohols, Polyfluorinated phosphoric acids, acrylates, olefins...



- Perfluorinated compounds
  - PFOA, PFOS, ...



Synthesis - Electrochemical fluorination

ECF results in mixtures branched/linear isomers (30/70)

Electro-Chemical Fluorination Cells
Octanesulfonyl fluoride

⇓ HF + electricity

Perfluorooctanesulfonyl fluoride)
(POSF)

⇒ Sulfonates
Quarternary Ammonium
Salts
Amines
Amphoterics

PFOS

⇓ alkylamine

N-Alkylperfluorooctane sulfonamide
(FOSA)

⇒ Amides
Oxazolidinones
Alkoxylates
Silanes
Carboxylates

PFOA

⇓ ethylene carbonate

N-Alkylperfluorooctane
sulfonamidoethanol
(FOSE)

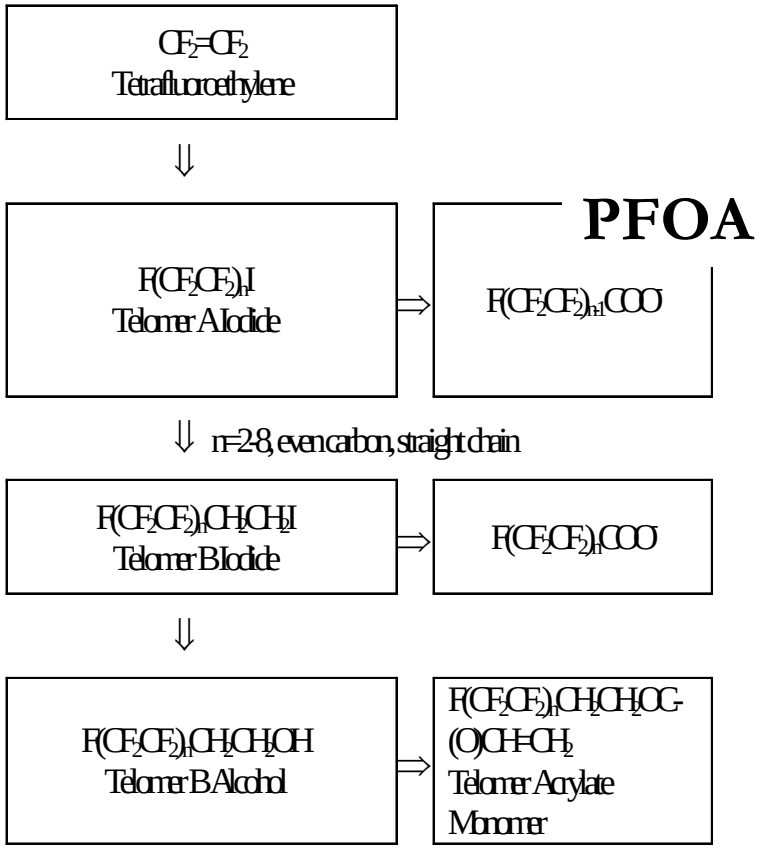
⇒ Adipates
Phosphate Esters
Fatty Acid Esthers
Alcohols
Urethanes
Copolymers
Acrylates

- Impregnation of leather, fabric
- Treatment of paper, e.g. food contact paper
- Fire-fighting foam
- Metal plating
- Photoindustry

References : 3M och DuPont

Synthesis - Telomerization

Telomerization gives the linear structure exclusivly*



Polymers och elastomers - the major fluoropolymer being PTFE

- Cooking utensils
- High temperature app.
  - Engines, oils, heat exchangers

Fire-fighting foam

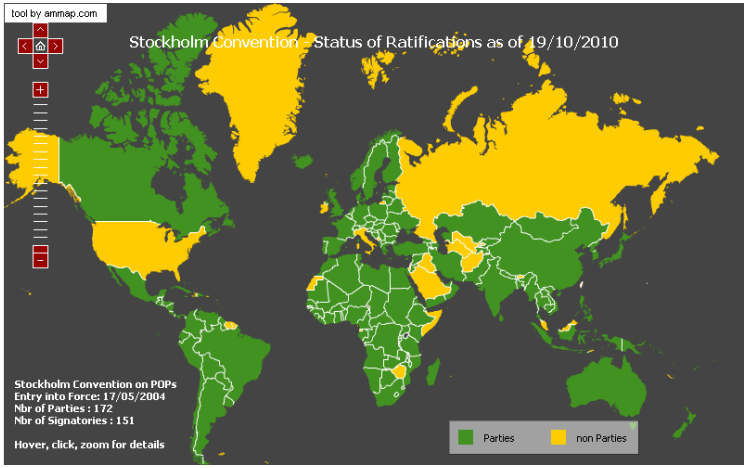
- 6:2 FluoroTelomerSulfonate

References : 3M och DuPont

* with exception of isopropyl geometry

UNEP

PFOS on the Stockholm Convention



Acceptable purpose:

- Photo-imaging
- Photo-resist and anti-reflective coatings for semi-conductors
- Etching agent for compound semiconductors and ceramic filters
- Aviation hydraulic fluids
- Metal plating (hard metal plating)
  - only in closed-loop systems
- Certain medical devices (such as ethylene tetrafluoroethylene copolymer (ETFE) layers and radio-opaque ETFE production, in-vitro diagnostic medical devices, and CCD colour filters)
- Fire-fighting foam
- Insect baits for control of leaf-cutting ants from *Atta spp.* and *Acromyrmex spp.*

Specific exemption:

- Photo masks in the semiconductor and liquid crystal display (LCD) industries
- Metal plating (hard metal plating)
- Metal plating (decorative plating)
- Electric and electronic parts for some colour printers and colour copy machines
- Insecticides for control of red imported fire ants and termites
- Chemically driven oil production
- Carpets
- Leather and apparel
- Textiles and upholstery
- Paper and packaging
- Coatings and coating additives
- Rubber and plastics

Structural isomers of PFOS identified in technical mixtures

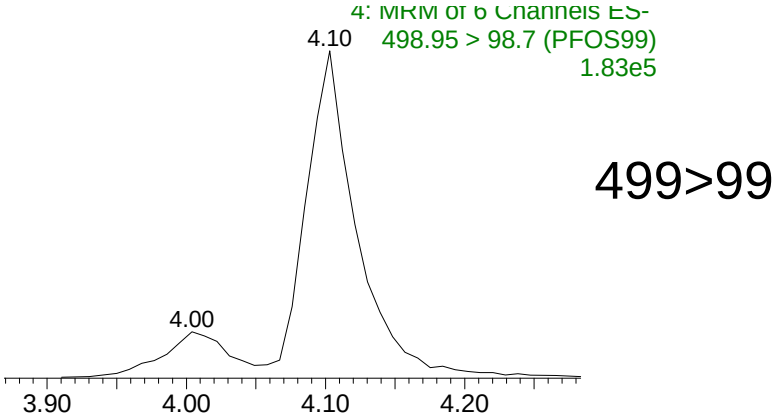
Abbreviation	Formula	Name
L-PFOS	$CF_3CF_2CF_2CF_2CF_2CF_2CF_2CF_2SO_3^-$	*n*-perfluoro-octanesulfonate
1-PFOS	$CF_3CF_2CF_2CF_2CF_2CF_2CF(\mathbf{CF_3})SO_3^-$	perfluoro-1-methyl-heptanesulfonate
2-PFOS	$CF_3CF_2CF_2CF_2CF_2CF(\mathbf{CF_3})CF_2SO_3^-$	perfluoro-2-methyl-heptanesulfonate
3-PFOS	$CF_3CF_2CF_2CF_2CF(\mathbf{CF_3})CF_2CF_2SO_3^-$	perfluoro-3-methyl-heptanesulfonate
4-PFOS	$CF_3CF_2CF_2CF(\mathbf{CF_3})CF_2CF_2CF_2SO_3^-$	perfluoro-4-methyl-heptanesulfonate
5-PFOS	$CF_3CF_2CF(\mathbf{CF_3})CF_2CF_2CF_2CF_2SO_3^-$	perfluoro-5-methyl-heptanesulfonate
6-PFOS	$CF_3CF(\mathbf{CF_3})CF_2CF_2CF_2CF_2CF_2SO_3^-$	perfluoro-6-methyl-heptanesulfonate
4,4-PFOS	$CF_3CF(\mathbf{CF_3})_2CF_2CF_2CF_2CF_2SO_3^-$	perfluoro-4,4-dimethyl-hexanesulfonate
3,5-PFOS	$CF_3CF(\mathbf{CF_3})CF_2CF(\mathbf{CF_3})CF_2CF_2SO_3^-$	perfluoro-3,5-dimethyl-hexanesulfonate
4,5-PFOS	$CF_3CF(\mathbf{CF_3})CF(\mathbf{CF_3})CF_2CF_2CF_2SO_3^-$	perfluoro-4,5-dimethyl-hexanesulfonate
5,5-PFOS	$CF_3C(\mathbf{CF_3})_2CF_2CF_2CF_2CF_2SO_3^-$	perfluoro-5,5-dimethyl-hexanesulfonate

enantiomers

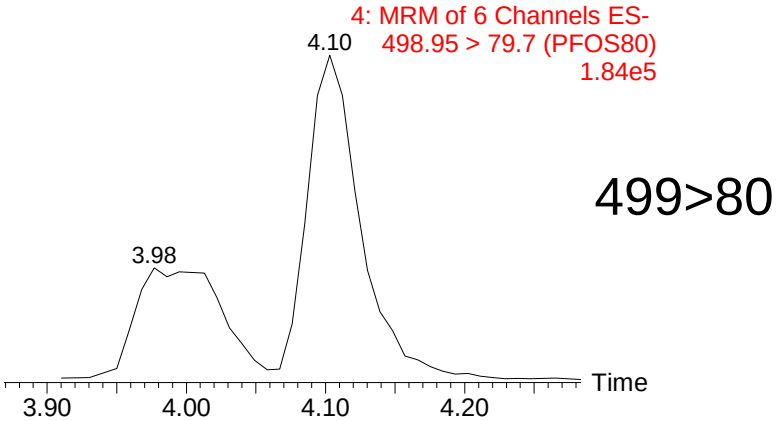
Chromatographic separation

Acquity C_{18} 50*2.1 mm, 1.7µm

H_20:MeOH:2mM NH_4Ac



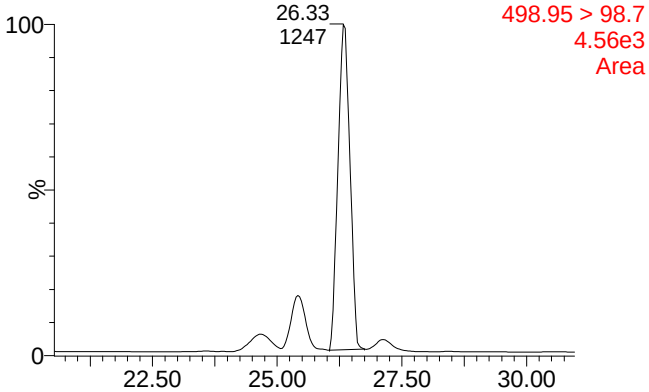
499>99

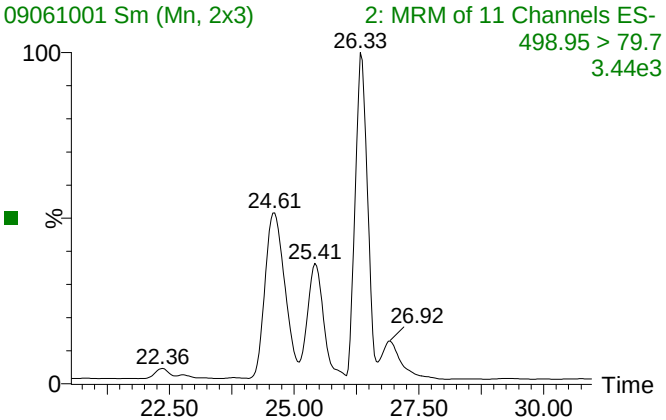


499>80

Acquity C_{18} 100*2.1 mm, 1.7µm

H_20:MeOH:AcN:2mM NH_4Ac

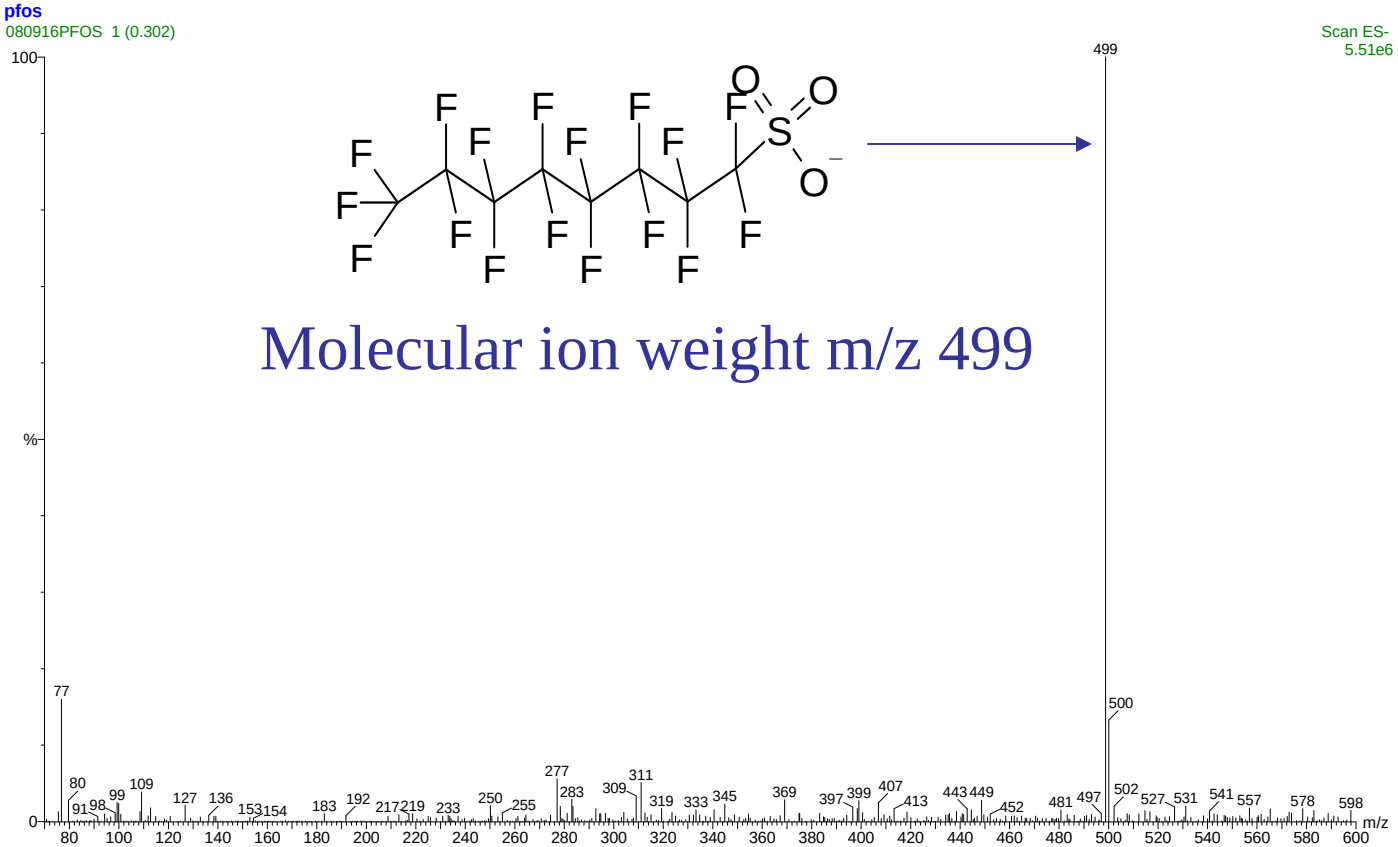




Waters Acquity UPLC-Quattro Premier XE

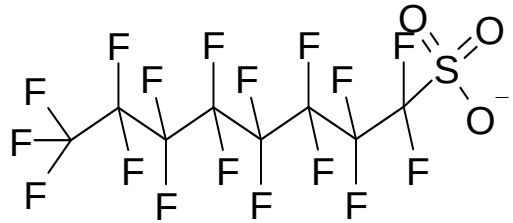
MS - negative electrospray

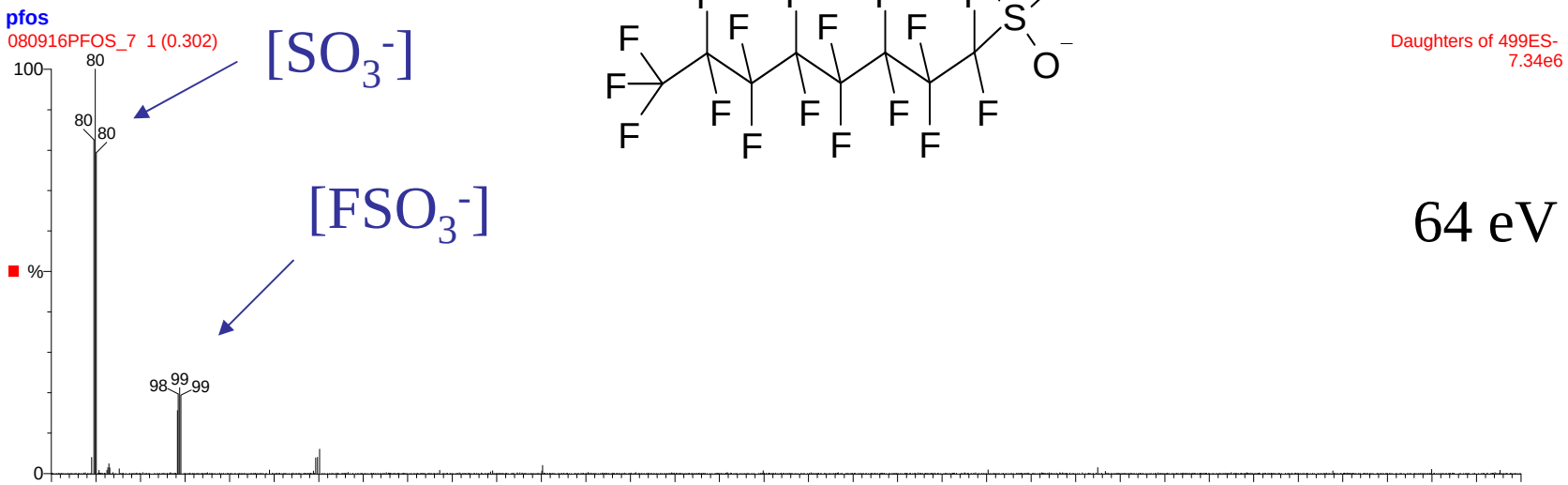
PFOS Full scan MS1 cone voltage 65 V

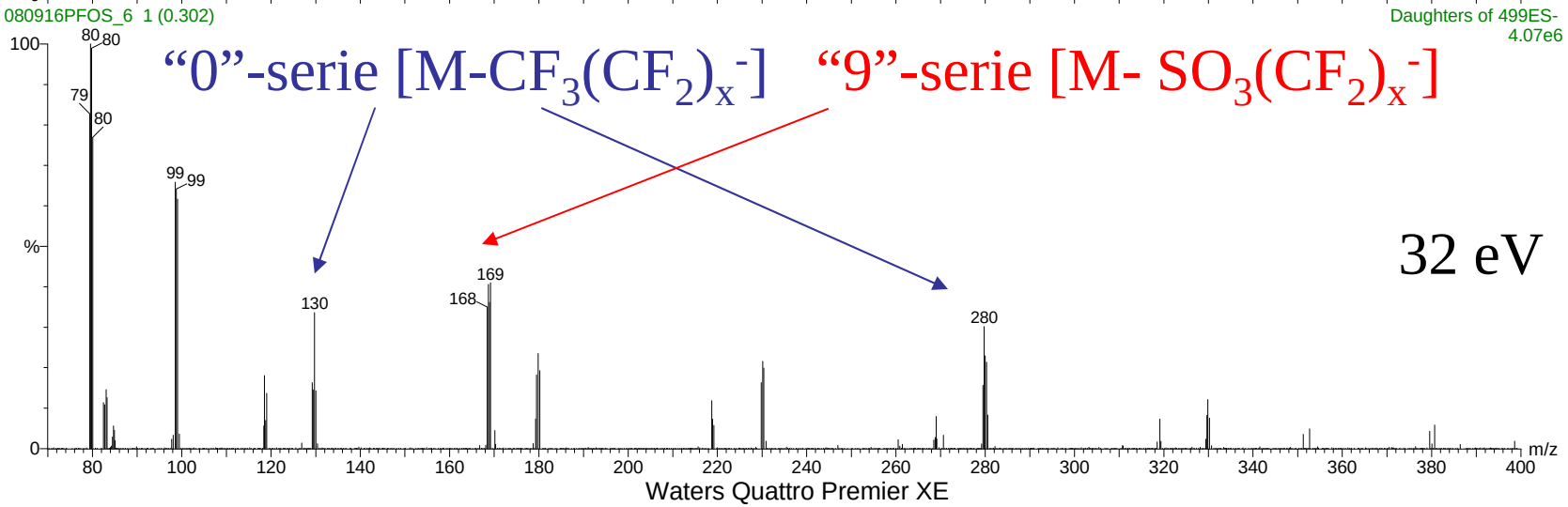


Waters Quattro Premier XE

Product ion scan PFOS

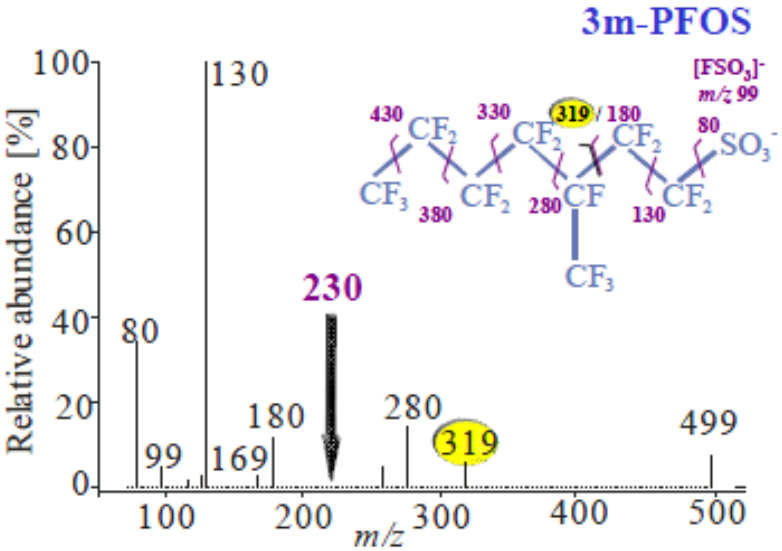






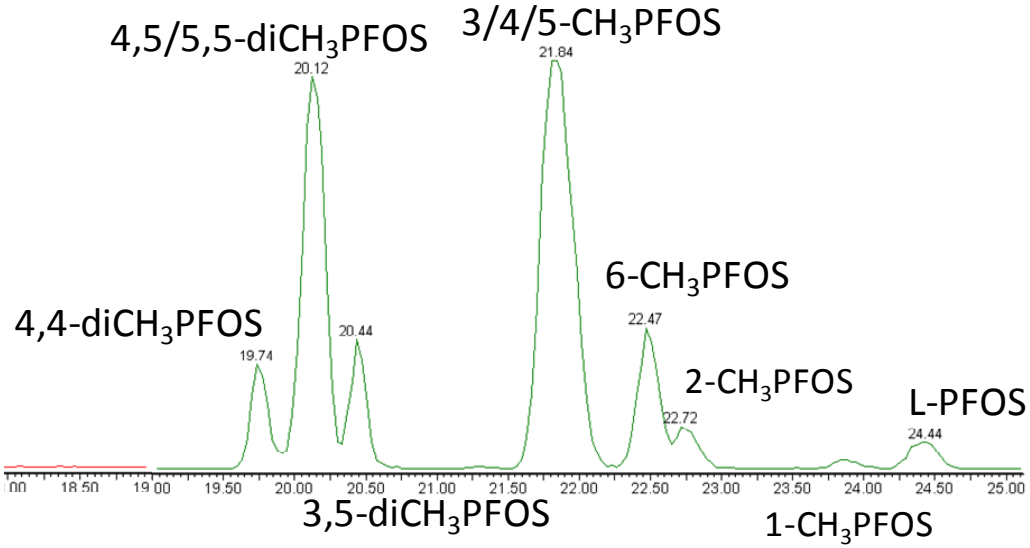
Branching affects CID

- Most published methods use m/z 99 for quantification
  - some isomers do not produce the m/z 99 ion
- Missing fragments can be used for mass spectrometric separation



Langlois et al. Fluoros 2005

Response factors - PFOS



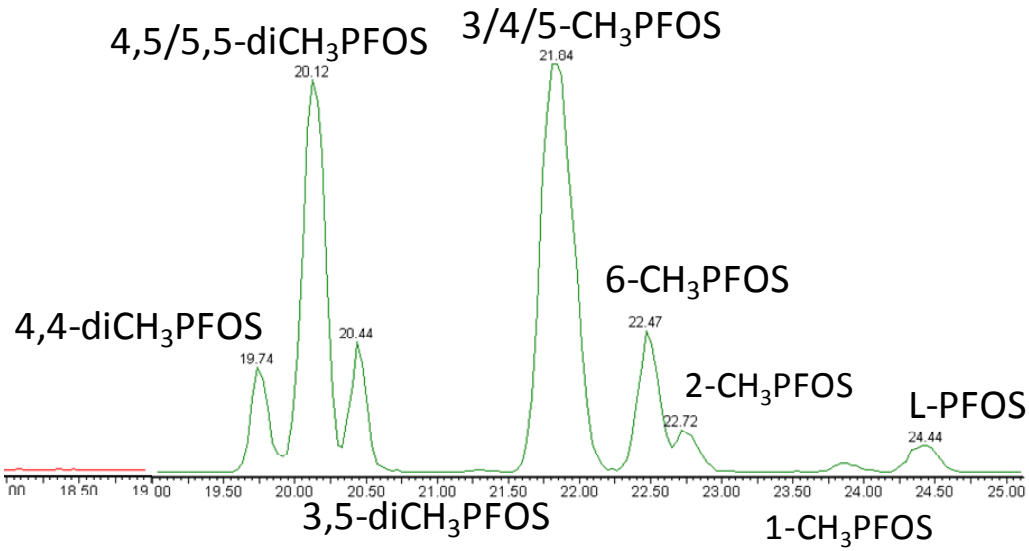
	4,4	5,5	4,5	3,5	5	4	3	6	2	1	Linear
499>80	0.75	2.03	1.43	1.58	1.95	1.72	1.08	1.11	0.52	-	1
499>99	-	0.15	-	0.12	0.37	0.28	0.35	0.80	0.71	0.35	1
499>130	3.1	27	1.3	27	14	5.7	16	4	0.64	-	1

Berger U., Kaiser MA., Kärrman A., Barber, JL., van Leeuwen, SPJ. 2011. Recent developments in trace analysis of poly- and perfluoroalkyl substances. Analytical and Bioanalytical Chemistry 400(6) 1625-1635

Quantification using linear response

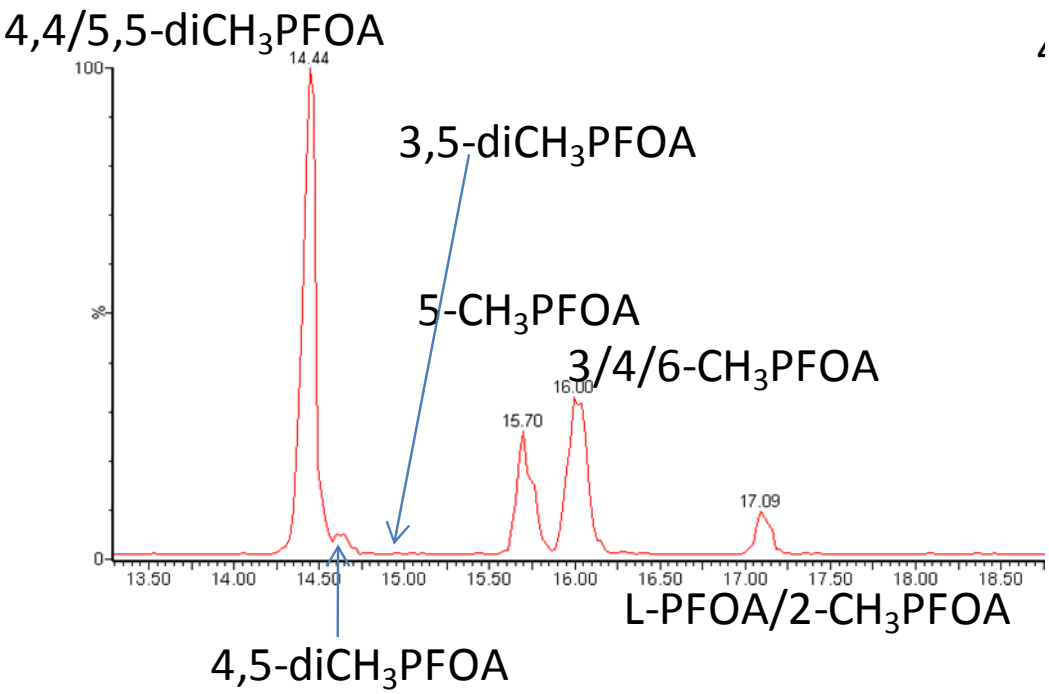
overestimate

underestimate



	4,4	5,5	4,5	3,5	5	4	3	6	2	1	Linear
499>80	0.75	2.03	1.43	1.58	1.95	1.72	1.08	1.11	0.52	-	1
499>99	-	0.15	-	0.12	0.37	0.28	0.35	0.80	0.71	0.35	1
499>130	3.1	27	1.3	27	14	5.7	16	4	0.64	-	1

Response factors – PFOA isomers

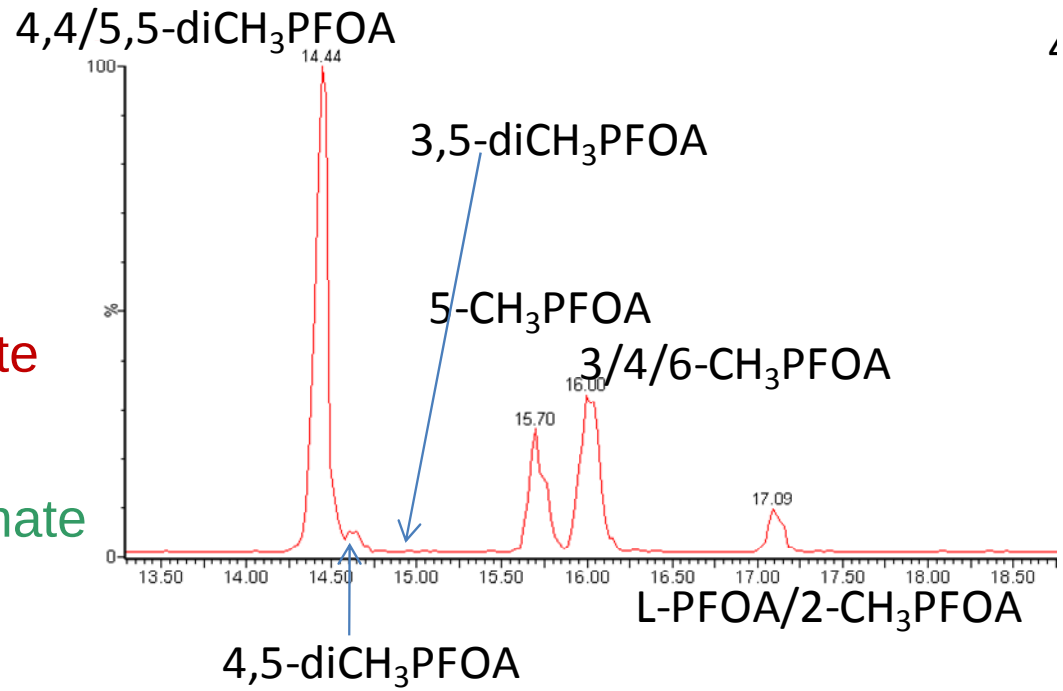


	4,4	5,5	4,5	3,5	5	3	4	6	2	Linear
413>369	<0.01	-	0.11	-	0.17	0.03	0.26	0.59	0.01	1
413>219	-	43	-	-	11	-	0.22	1	-	1
413>169	0.01	-	0.66	0.12	0.16	0.02	-	3.12	0.03	1

Quantification using linear response

overestimate

underestimate

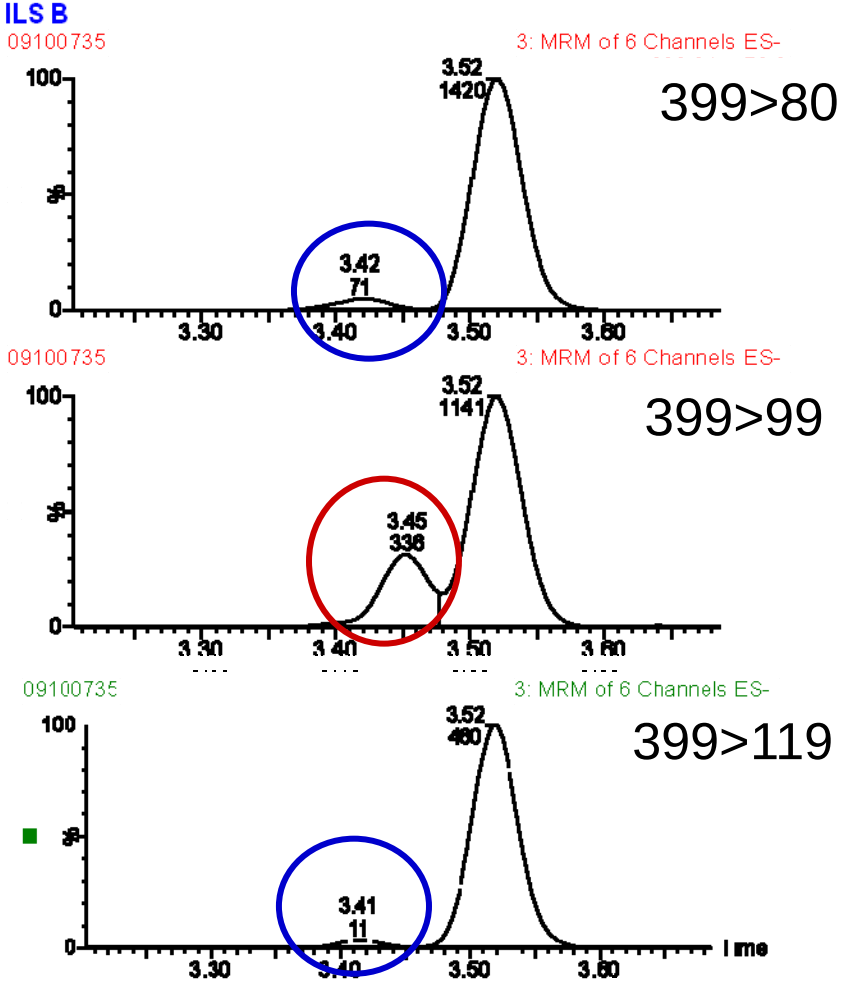


	4,4	5,5	4,5	3,5	5	3	4	6	2	Linear
413>369	<0.01	-	0.11	-	0.17	0.03	0.26	0.59	0.01	1
413>219	-	43	-	-	11	-	0.22	1	-	1
413>169	0.01	-	0.66	0.12	0.16	0.02	-	3.12	0.03	1

Challenges in the identification of isomers

PFHxS

PFHxS in human serum

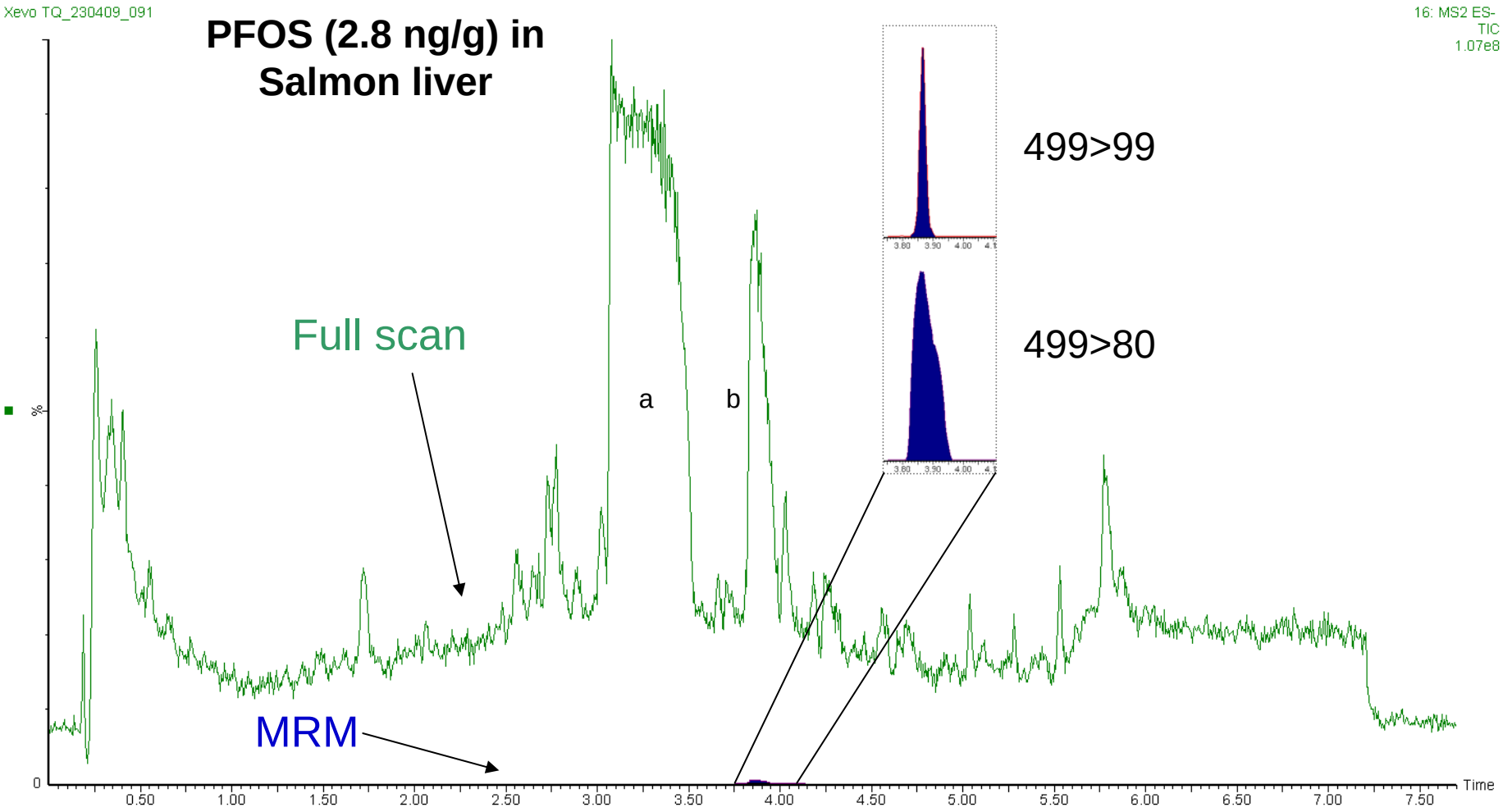


- Pregnandiol sulfonate isomers
- 399>119 is ”clean”
- 399>80 better than 399>99
- Chromatographic separation possible but can be difficult with ”ordinary” C18

Chan et. al 2009. Rapid communications in mass spectrometry, 23 :405-1410.

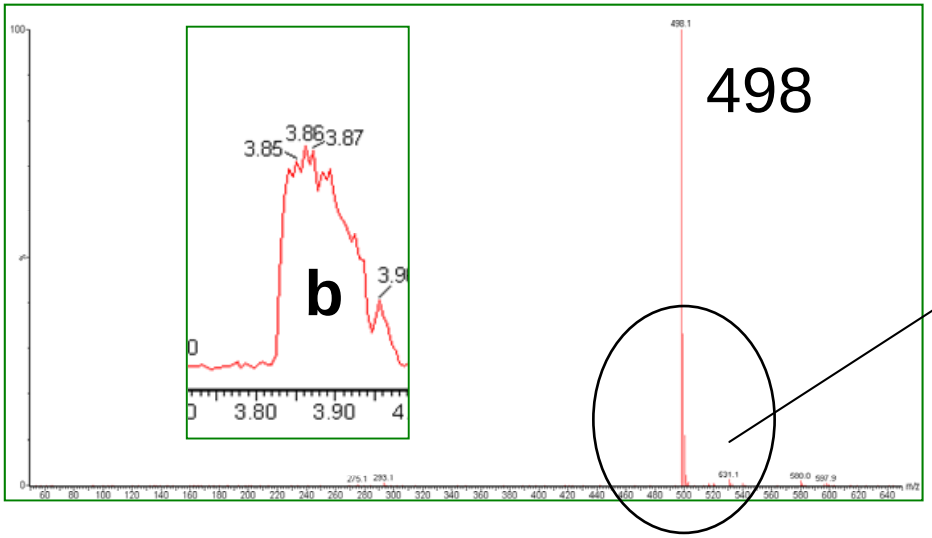
Challenges in the identification of isomers

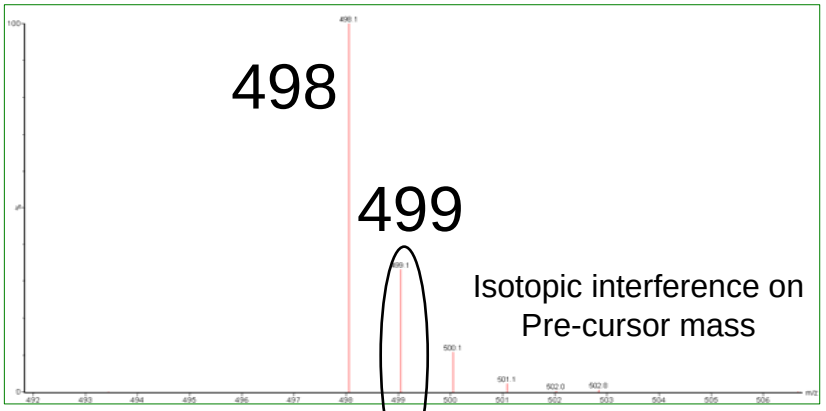
PFOS

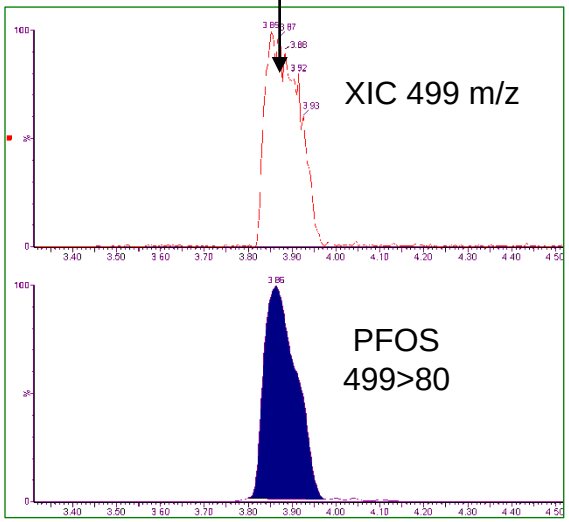


Silcock, P.J., Kärrman, A., Worrall, K., van Bavel, B. 2009. Organohalogen Compounds 71, 1210-1215

Salmon liver RADAR Spectra





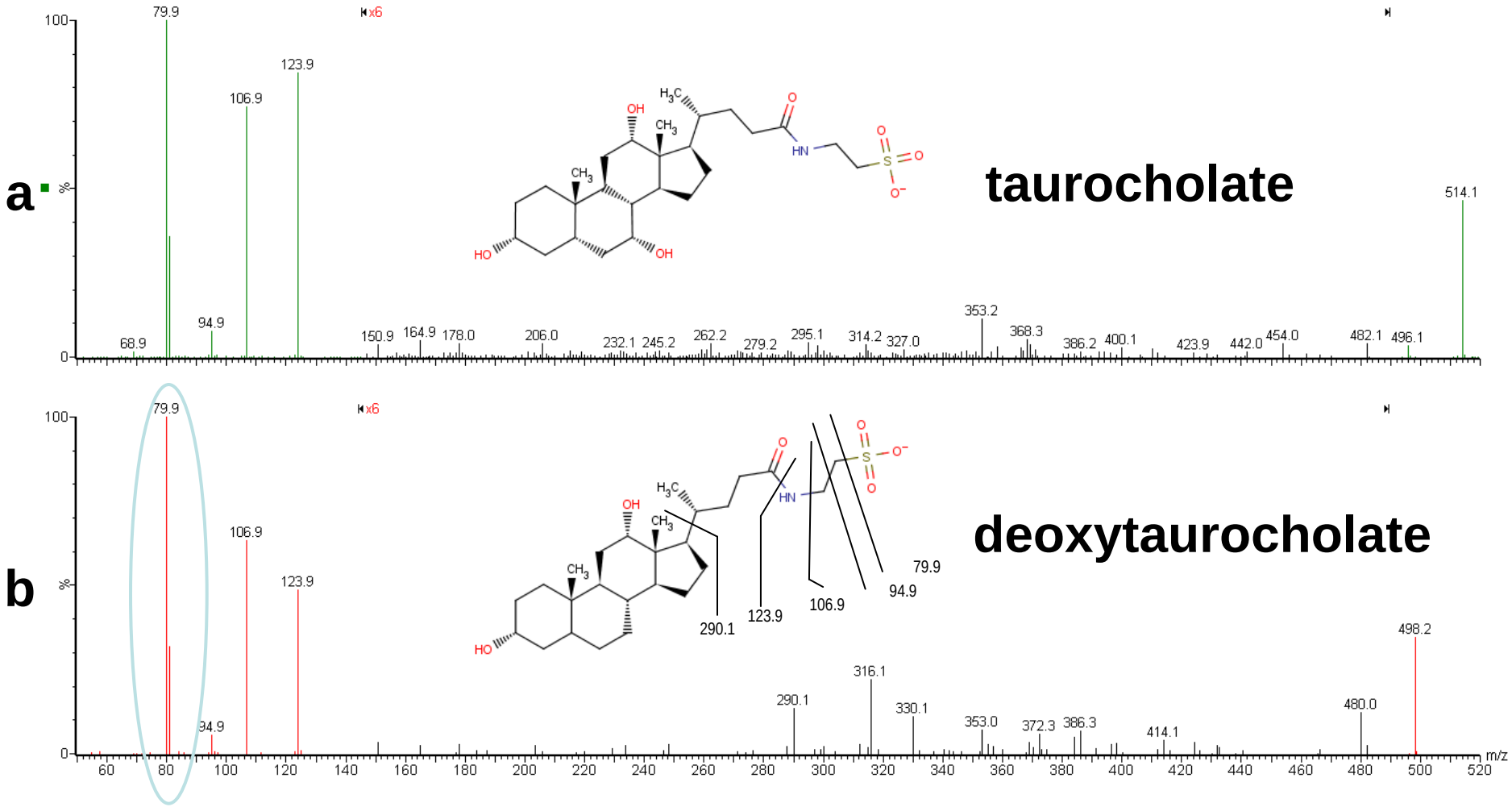


RADAR

=

Simultaneously MRM and Full scan

Product ion experiments



In accordance with Benskin et. al 2007. Analytical chemistry, 79 :6455-6464

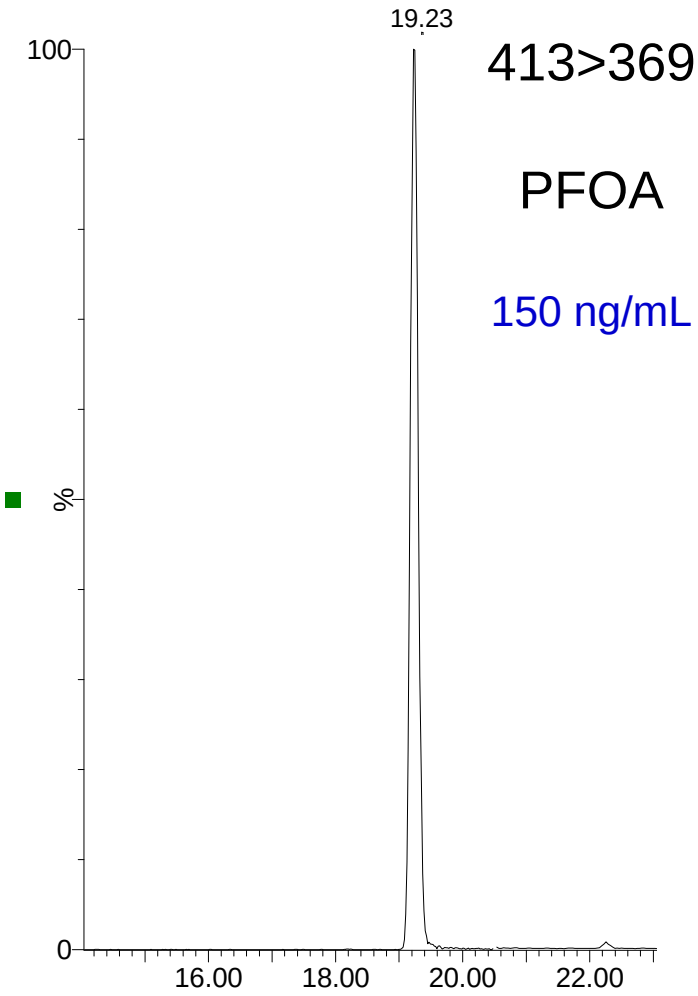
Occurrence of isomers in human blood

ECF: ~70% linear isomer

Telomerization: 100% linear isomer

Preferential accumulation of the linear structure is expected, based on lab studies on rodents

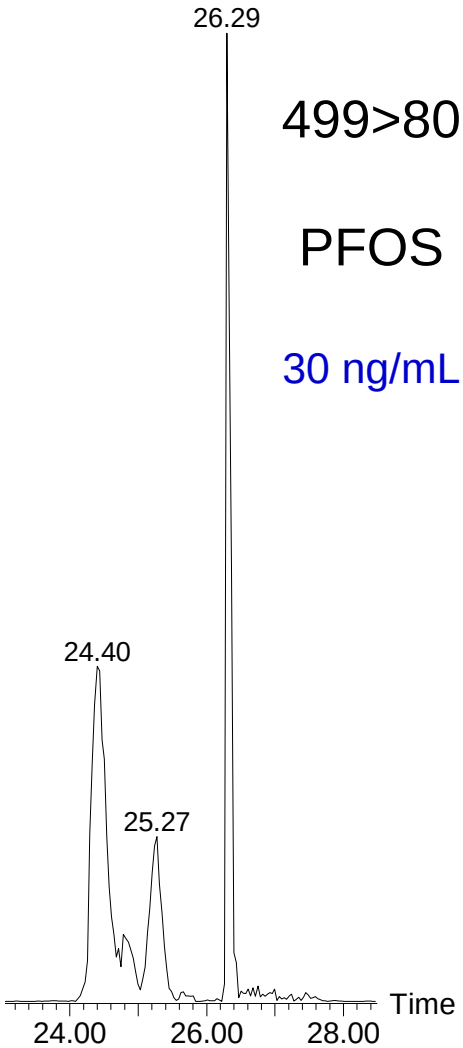
Example of PFOA and PFOS in human blood



413>369

PFOA

150 ng/mL

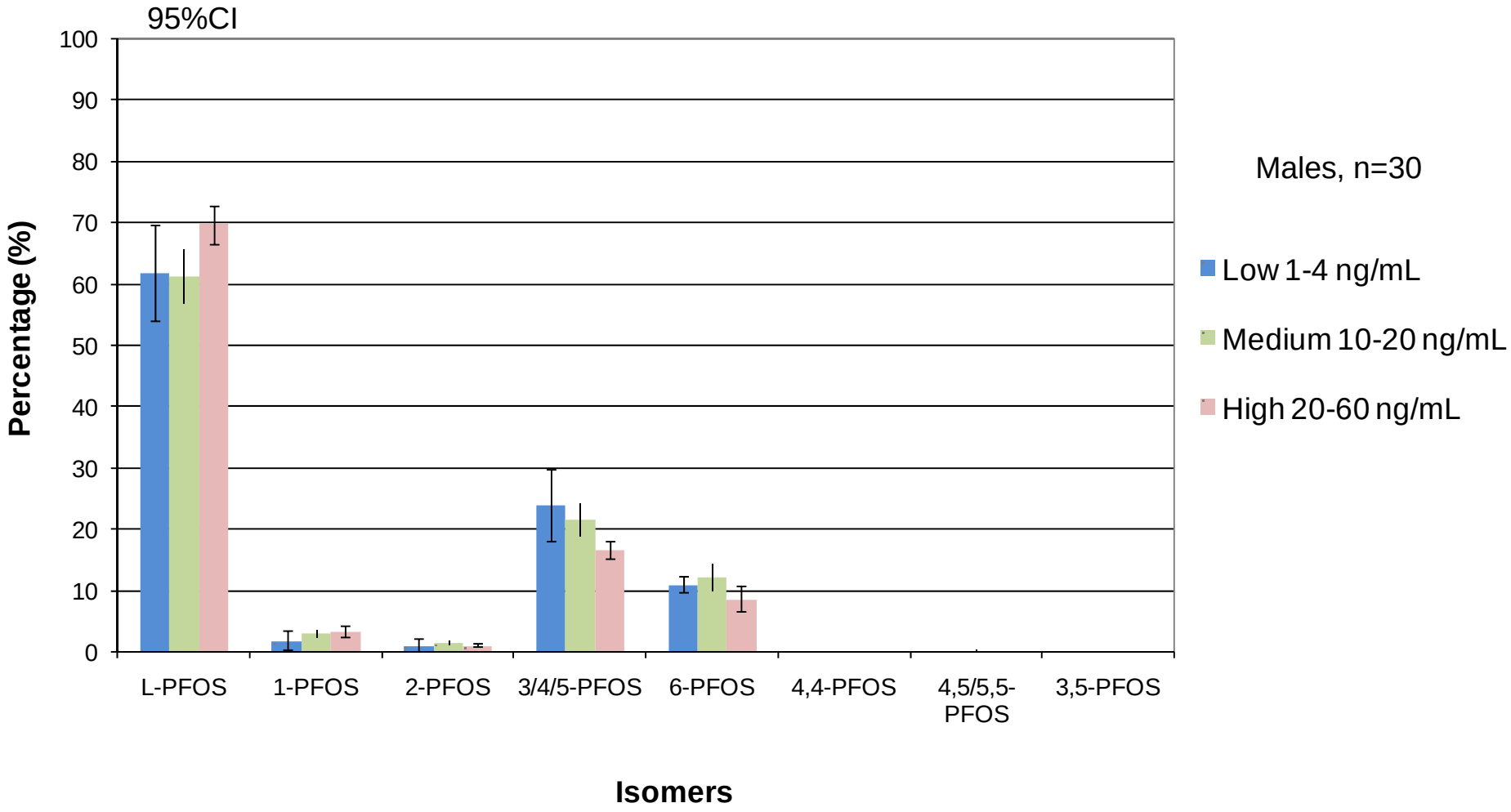


499>80

PFOS

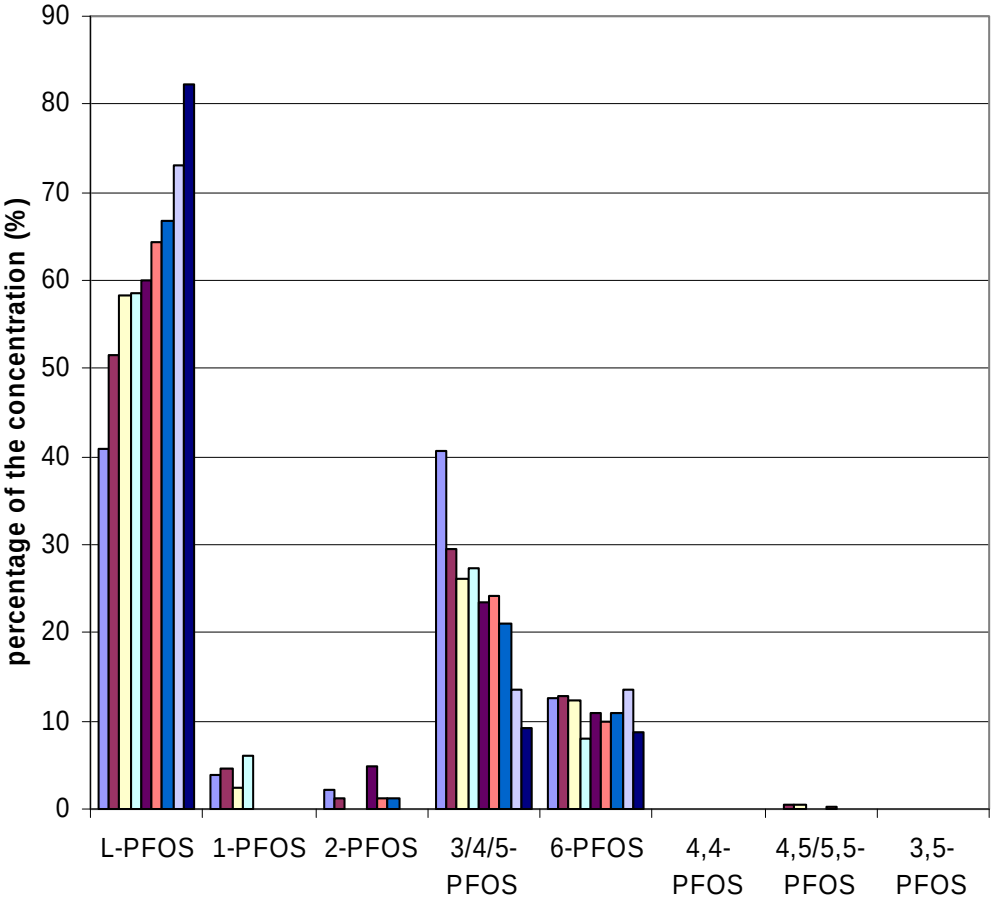
30 ng/mL

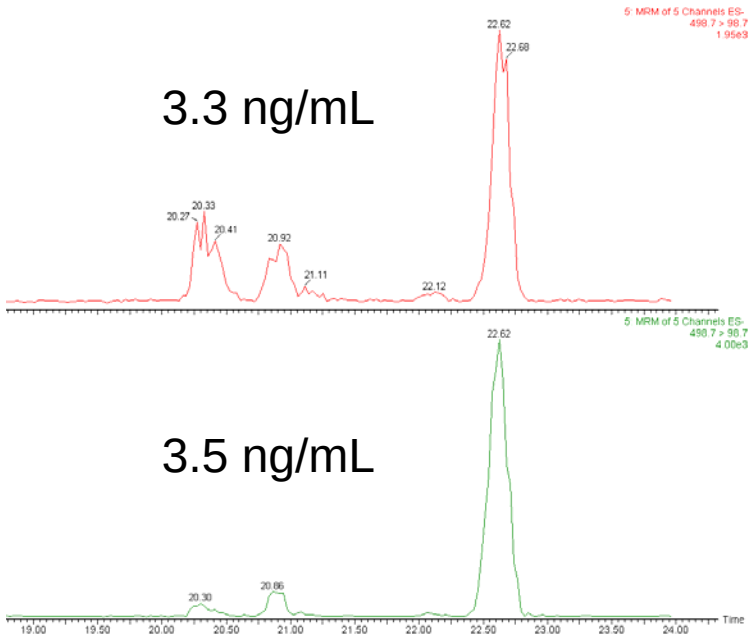
PFOS isomers in Swedish blood



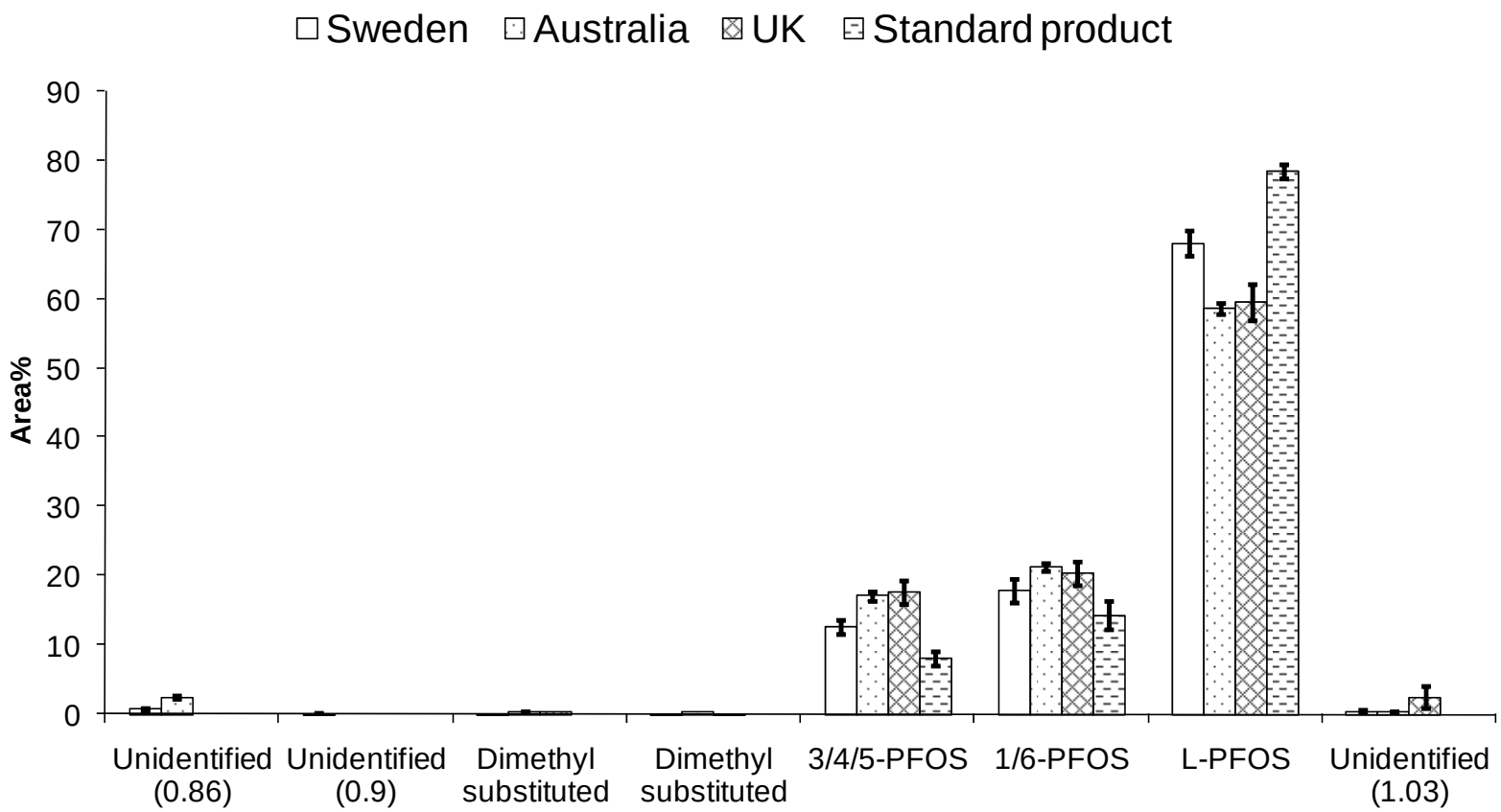
Berger U., Kaiser MA., Kärrman A., Barber, JL., van Leeuwen, SPJ. 2011. Recent developments in trace analysis of poly- and perfluoroalkyl substances. Analytical and Bioanalytical Chemistry 400(6) 1625-1635

Individual results in the low (1-4 ng/mL) level group



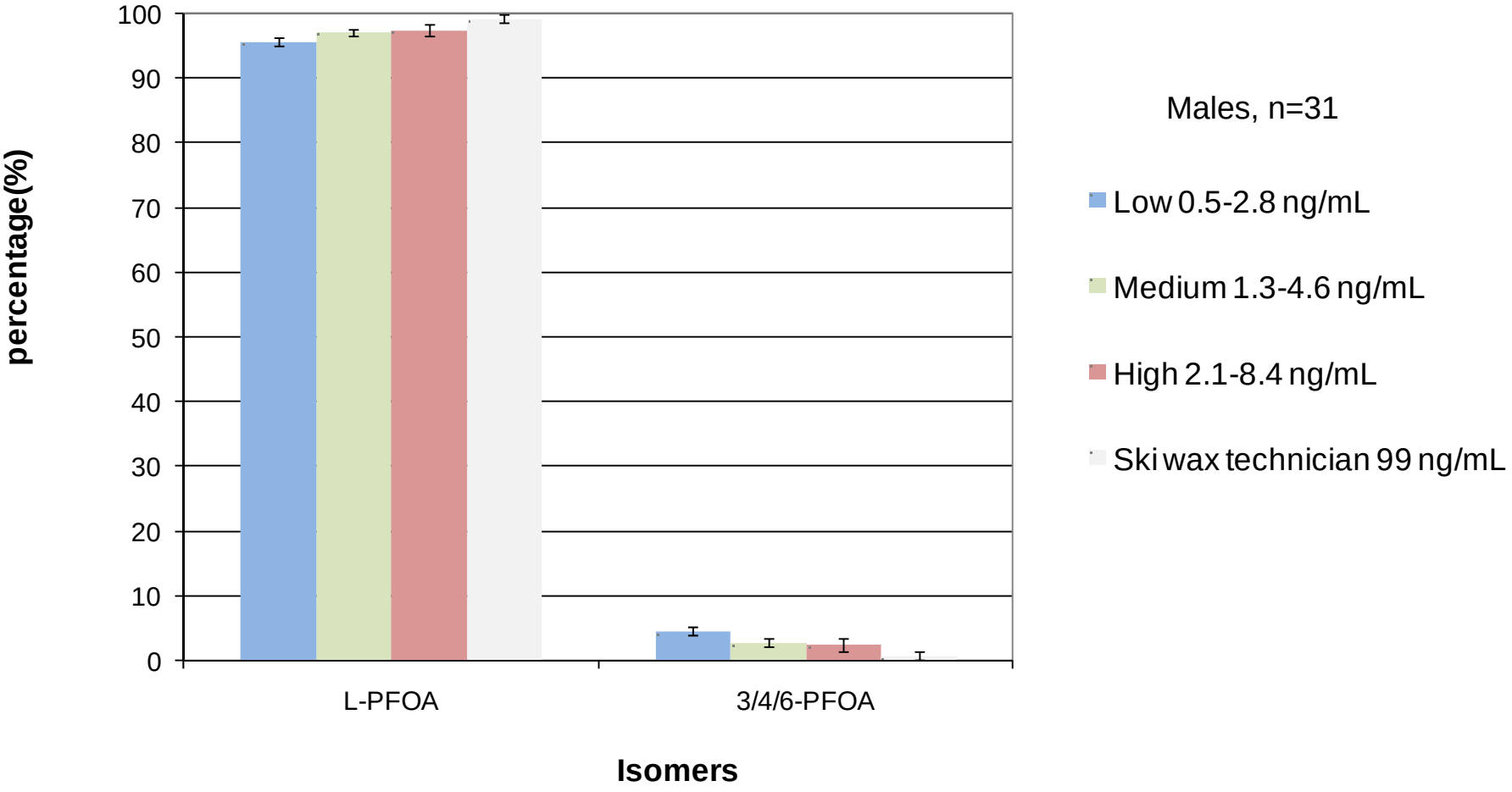


PFOS isomer pattern in human blood from different countries



Kärrman et al. 2007 Environment International, 33 782-788.

PFOA isomers in Swedish blood



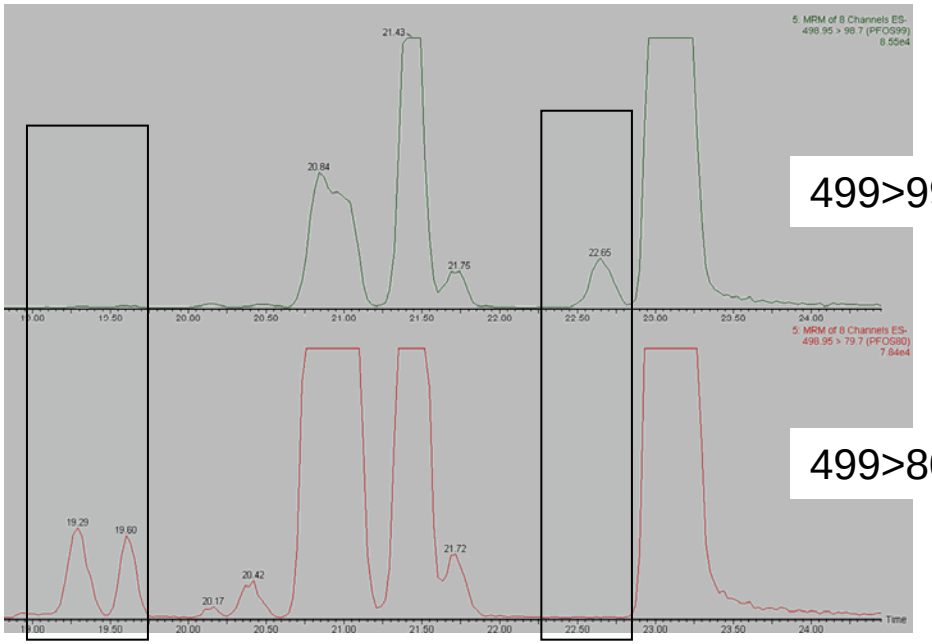
Isomer distribution in the environment

Isomer profiles in the environment around a AFFF point source

Bergen Airport

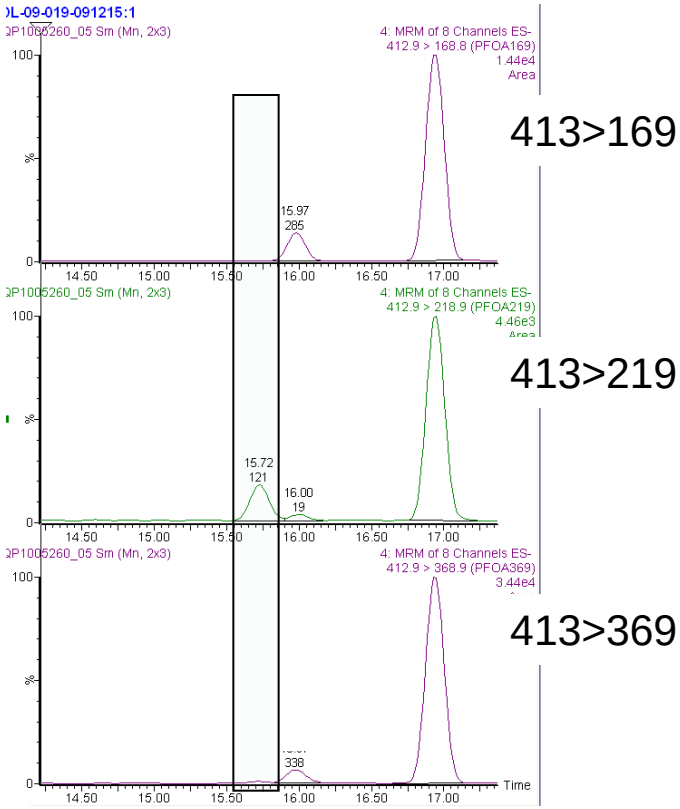
Soil chromatograms

PFOS



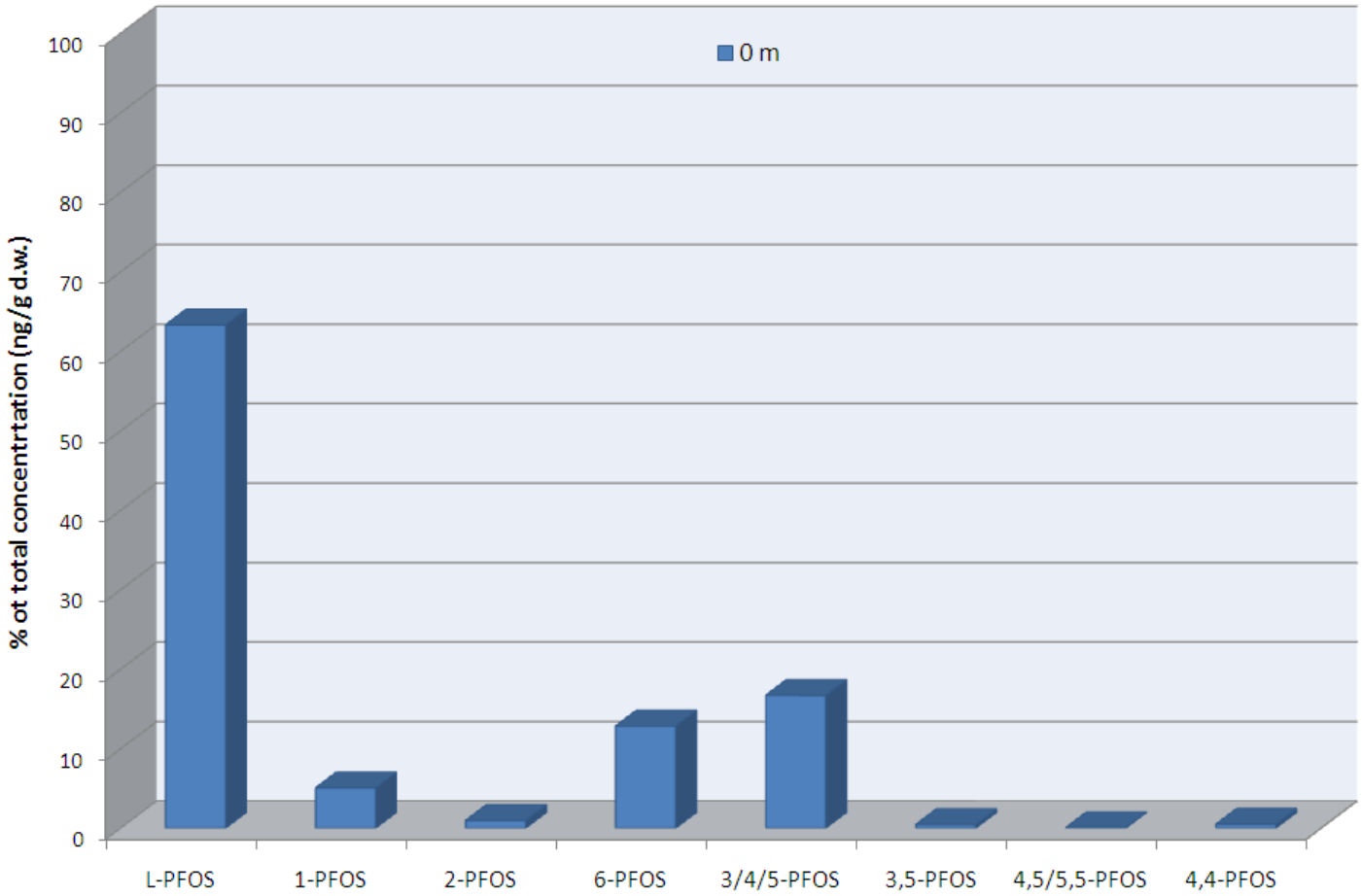
3,5- and 4,4-PFOS **1-PFOS**

PFOA



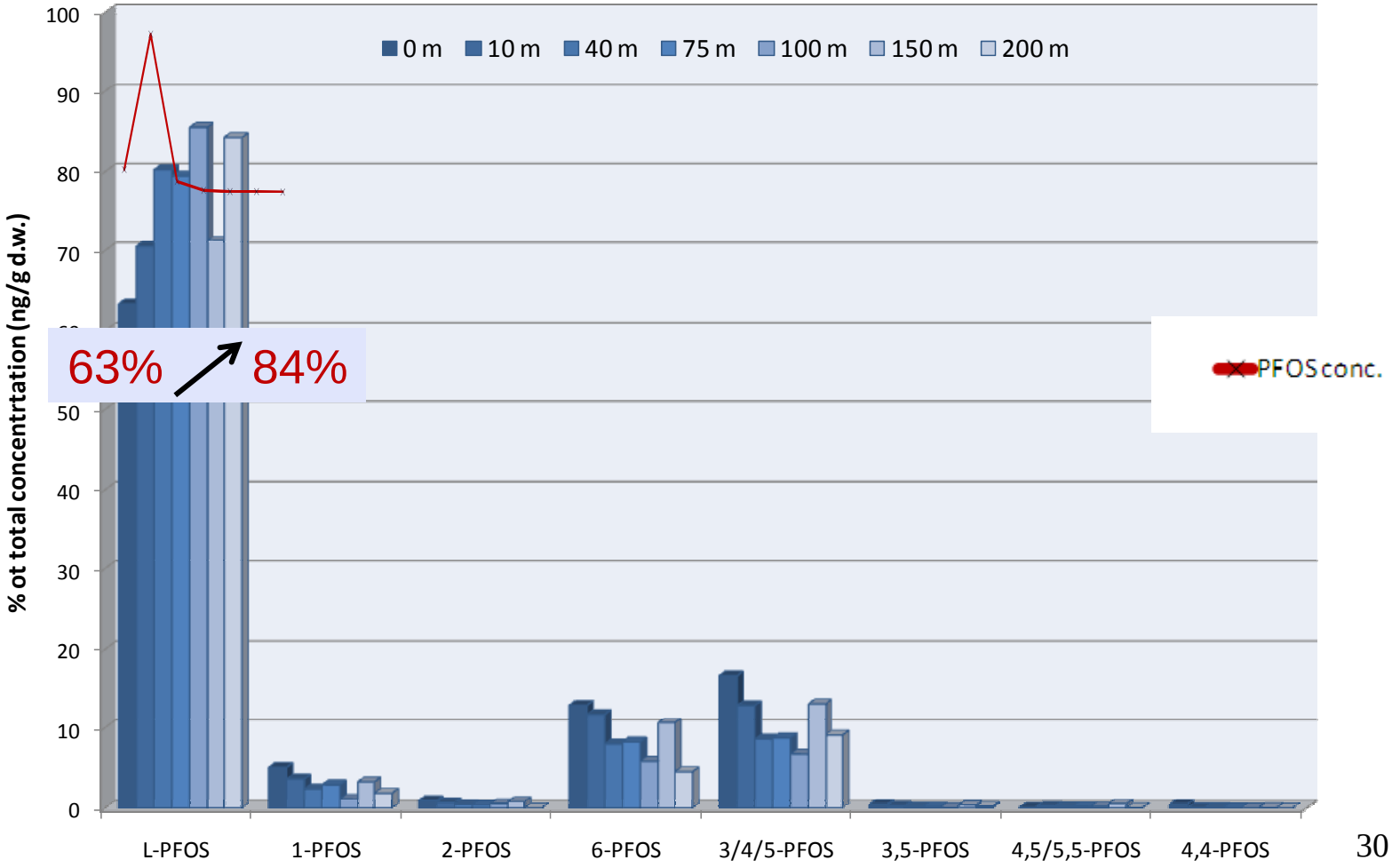
5-PFOA

PFOS isomers in soil

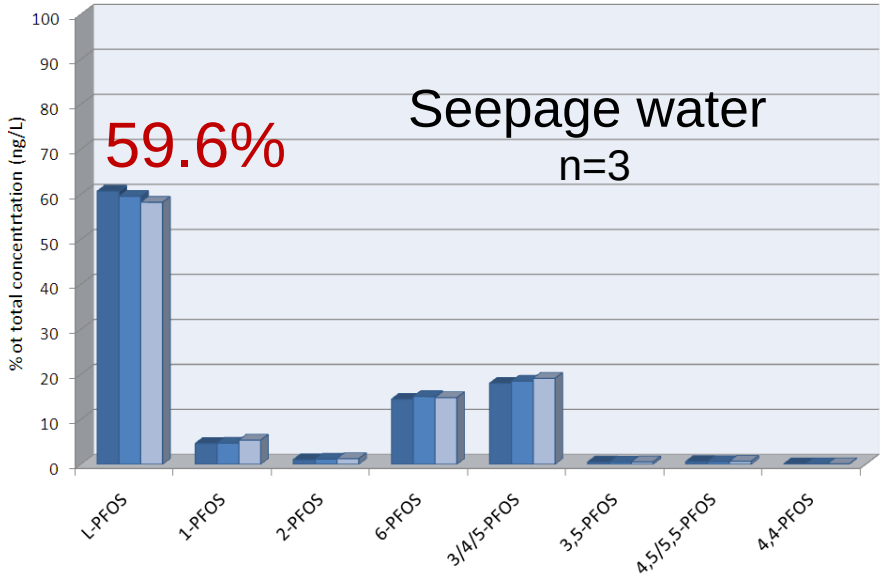


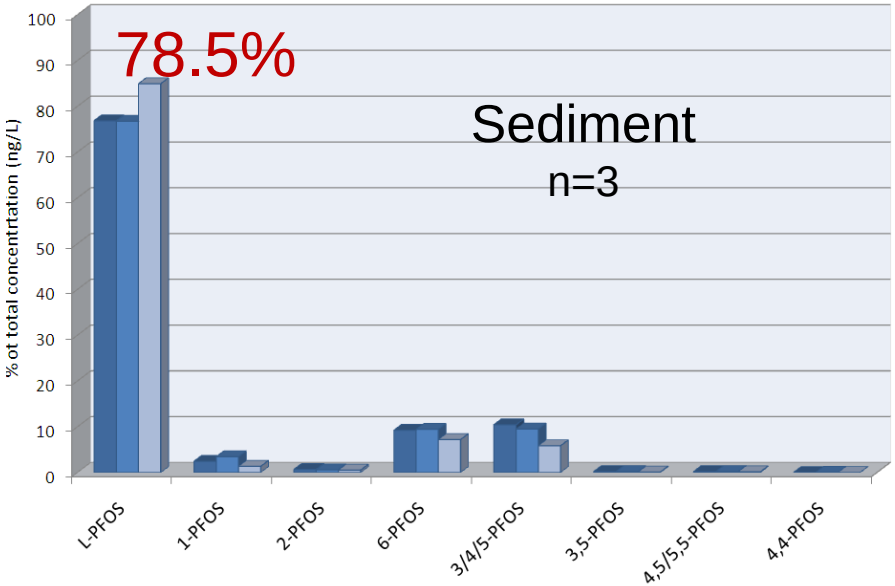
Kärrman, A., Elgh-Dalgren, K., Lafossas, C., Møskeland, T. 2011. ”Environmental distribution of structural isomers of perfluoroalkyl acids after aqueous fire-fighting foam (AFFF) contamination”. Environmental Chemistry 8(4) 372-380

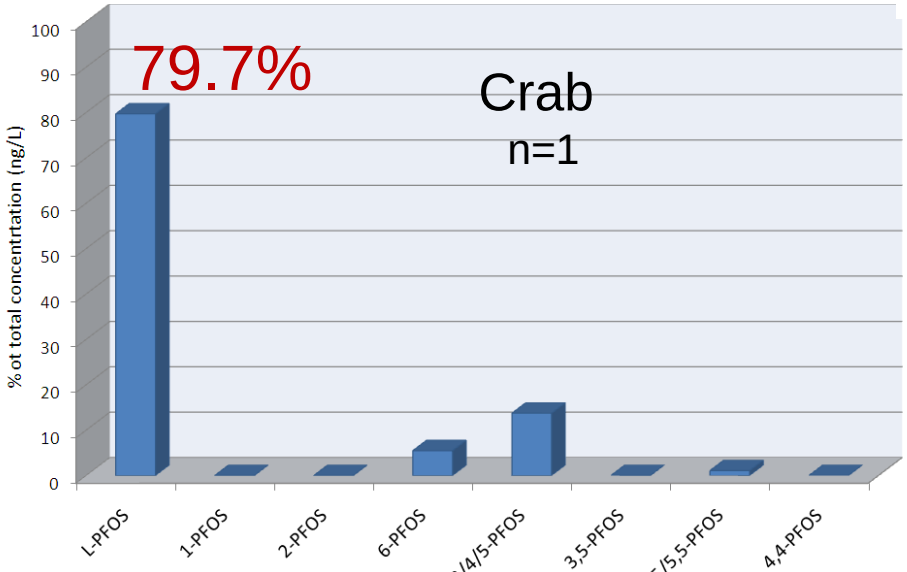
PFOS isomers in soil

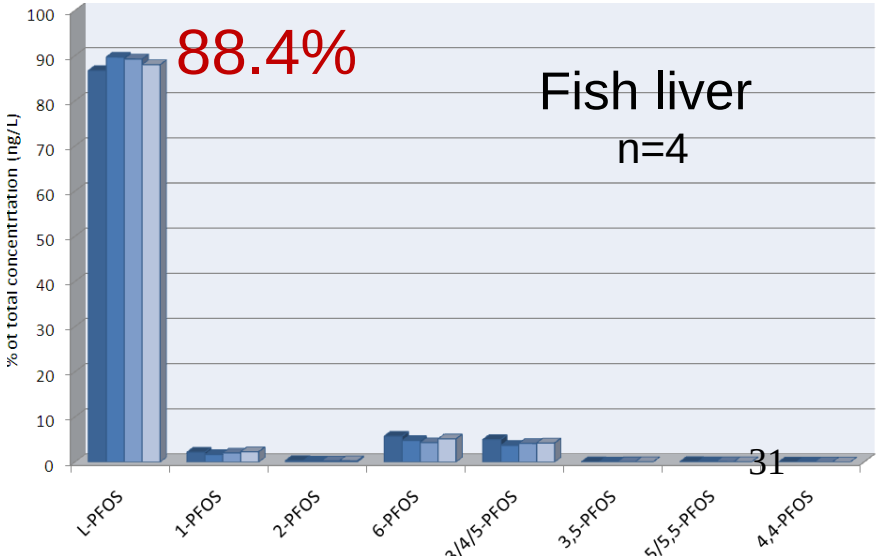


….water, sediment, biota

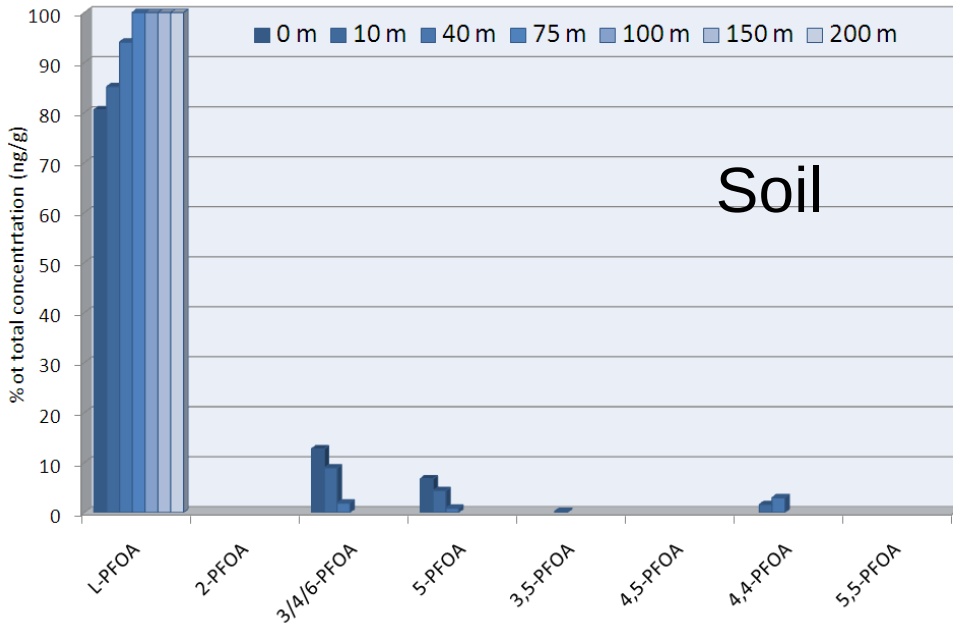


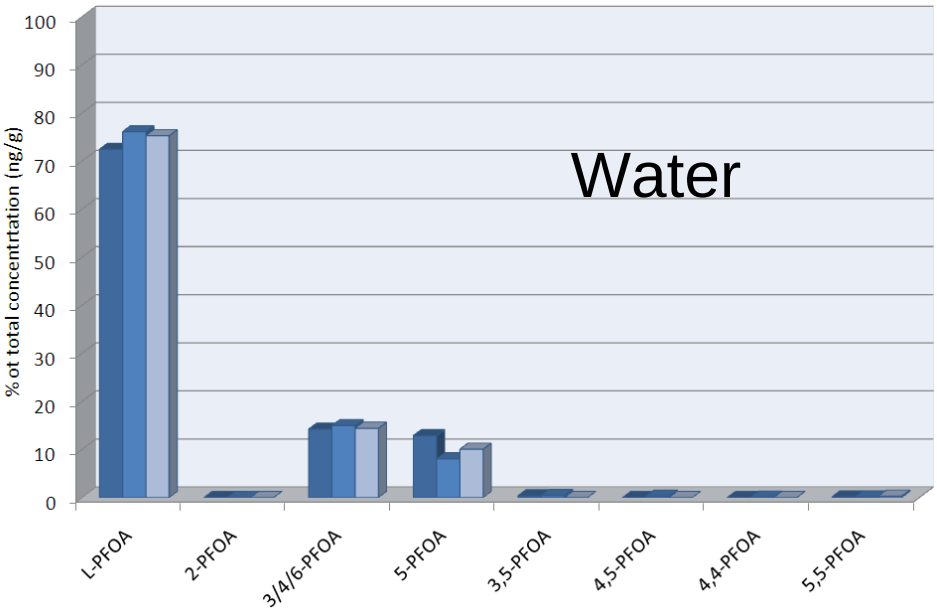






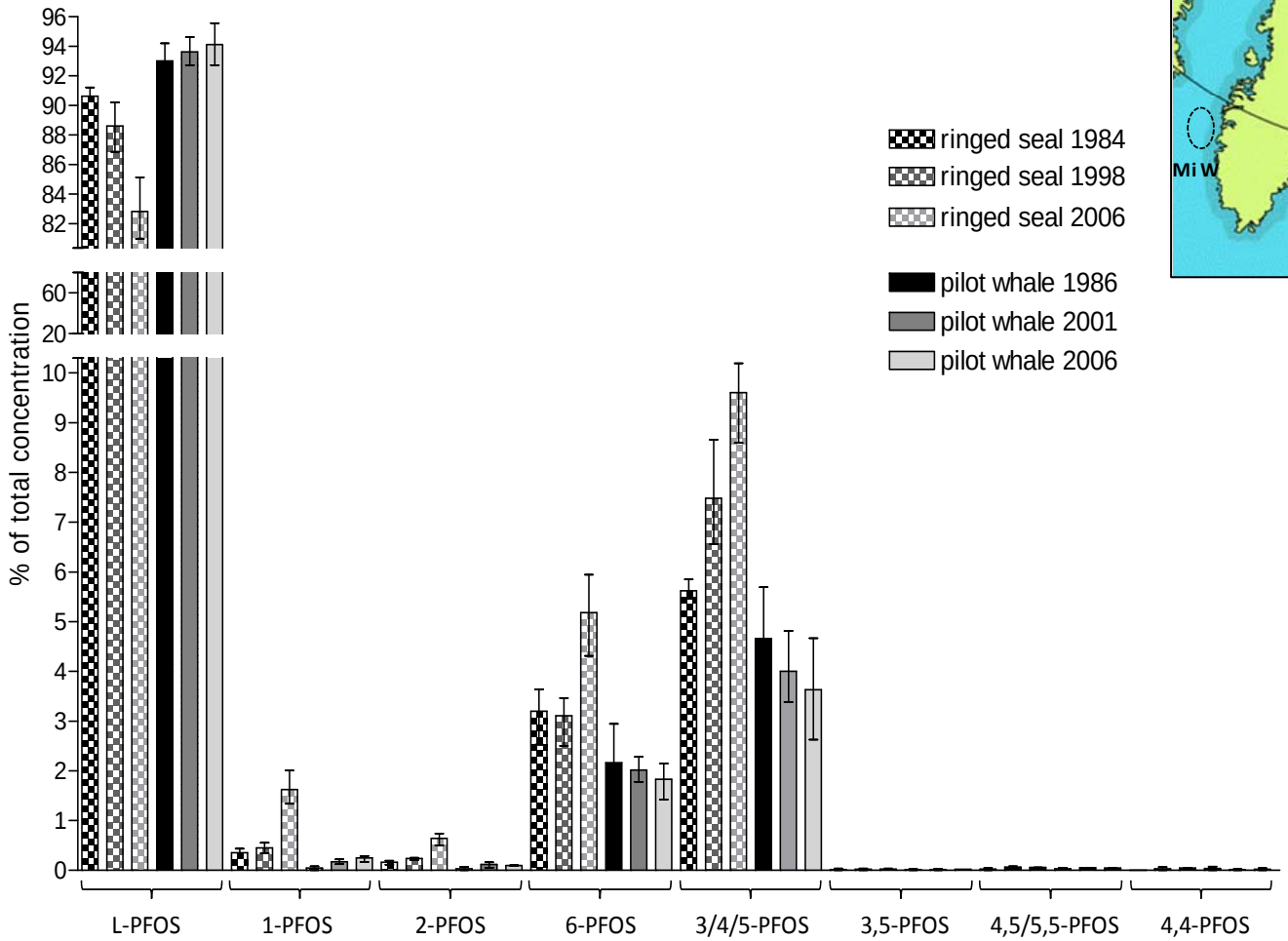
PFOA isomers

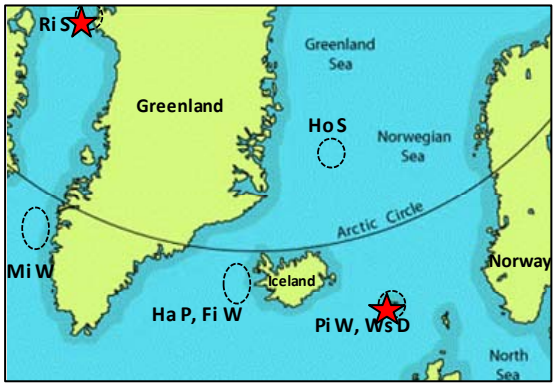




……not detected in sediment and biota

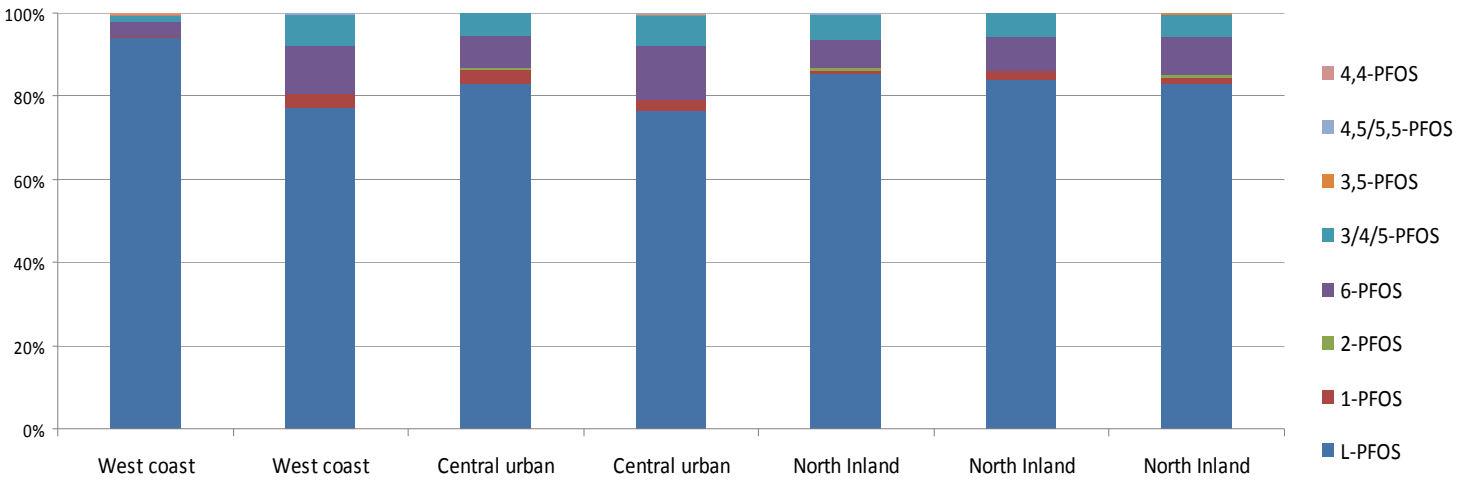
PFOS isomers in marine mammals





Rotander A, Kärrman A, van Bavel B, Polder A, Rigét F, Auðunsson GA, Víkingsson G, Gabrielsen GW, Bloch D, Dam M.
"Increasing levels of long-chain perfluorocarboxylic acids (PFCAs) in Arctic and North Atlantic marine mammals 1984-2009" Chemosphere In Press

PFOS isomers in mink from Sweden



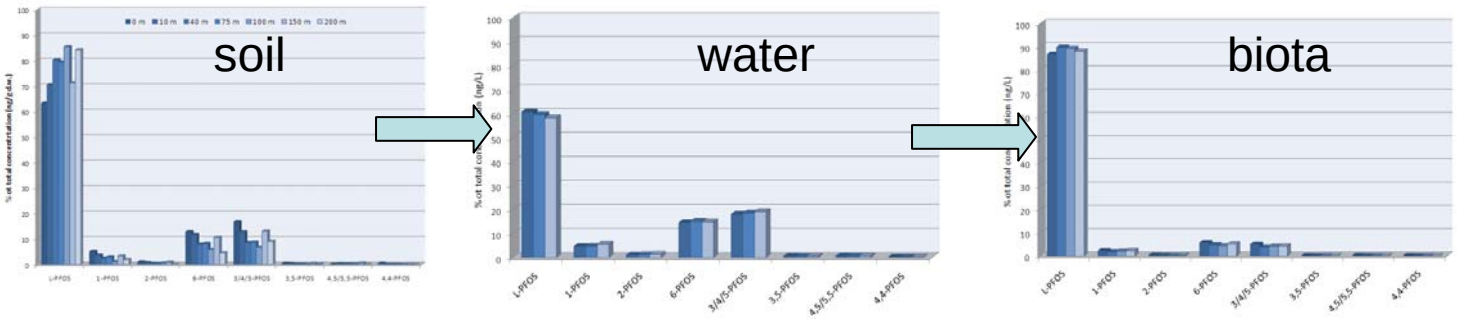
Rotander A, Kärrman A, et al., Not published

Useful tool for source elucidaton?

Useful tool for source elucidation?

Pitfalls:

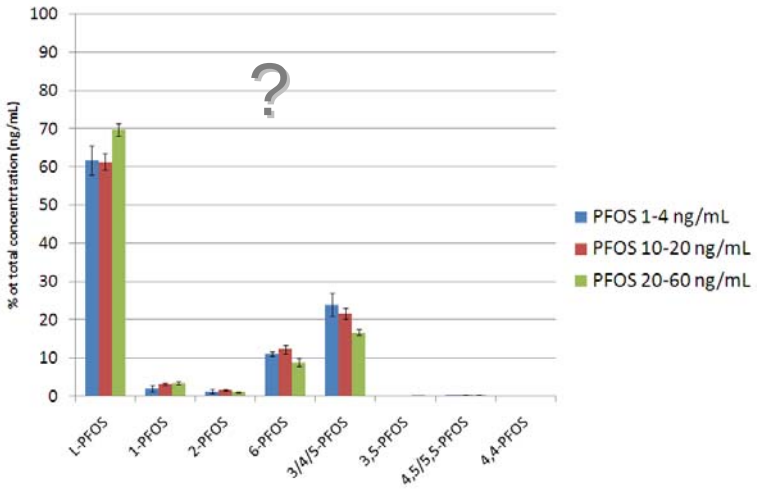
- Biotic and abiotic fractionation of structural isomers
  - Branched isomers more water soluable compared to the linear isomer
  - Different bioaccumulation, linear lower excretion rate



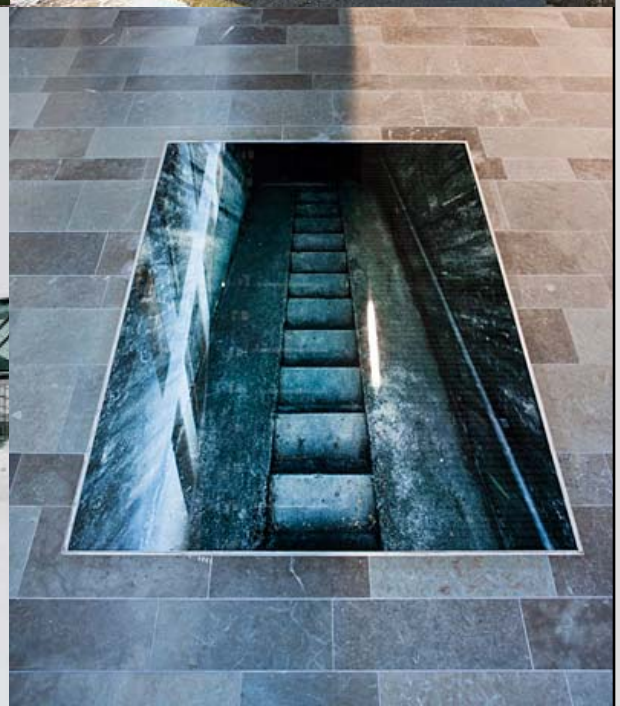
Useful tool for source elucidation?

Oppertunities:

- Tracking exposure sources
  - Differentiate between ”historic” (ECF) and ”current” (telomerization) production
- Human pattern influenced by unknown factor, which can help determine the exposure source
  - Precursor metabolization?



Thanks for your attention



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