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

Anna Kärrman

MTM Research Centre
Örebro University, Sweden
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

\[ \text{HF} + \text{electricity} \rightarrow \]

Perfluorooctanesulfonyl fluoride (POSF)

\[ \text{N-Alkylperfluorooctane sulfonamide} \] (FOSA)

\[ \text{N-Alkylperfluoroctane sulfonamidoethanol} \] (FOSE)

- 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 exclusively*

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
PFOS on the Stockholm Convention

Acceptable purpose:
- Photo-imaging
- Photo-resist and anti-reflective coatings for semiconductors
- 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

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Formula</th>
<th>Name</th>
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</thead>
<tbody>
<tr>
<td>L-PFOS</td>
<td>(\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{SO}_3^-)</td>
<td>(n)-perfluoro-octanesulfonate</td>
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<td>1-PFOS</td>
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Chromatographic separation

**Acquity C$_{18}$ 50*2.1 mm, 1.7µm**

$H_2O$:MeOH:2mM NH$_4$Ac

4: MRM of 6 Channels ES-
498.95 > 98.7 (PFOS99)
1.83e5

499>99

3.90 4.00 4.10 4.20

**Acquity C$_{18}$ 100*2.1 mm, 1.7µm**

$H_2O$:MeOH:AcN:2mM NH$_4$Ac

2: MRM of 11 Channels ES-
498.95 > 79.7 (PFOS80)
3.44e3

499>80

Waters Acquity UPLC-Quattro Premier XE
MS - negative electrospray

PFOS Full scan MS1 cone voltage 65 V

Molecular ion weight $m/z$ 499
Product ion scan PFOS

![Diagram of PFOS molecule with product ions]

- [SO₃⁻]
- [FSO₃⁻]
- "0"-serie [M-CF₃(CF₂)ₓ⁻]  64 eV
- "9"-serie [M- SO₃(CF₂)ₓ⁻]  32 eV

**Waters Quattro Premier XE**
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

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Quantification using linear response

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overestimate

underestimate
Response factors – PFOA isomers

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Challenges in the identification of isomers

PFHxS

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

Challenges in the identification of isomers

**PFOS**

PFOS (2.8 ng/g) in Salmon liver

Salmon liver RADAR Spectra

Simultaneously MRM and Full scan

Isotopic interference on Pre-cursor mass

XIC 499 m/z

PFOS
499>80
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

PFOA:
- 150 ng/mL

PFOS:
- 30 ng/mL

413 > 369

499 > 80
PFOS isomers in Swedish blood

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

- 3.3 ng/mL
- 3.5 ng/mL
PFOS isomer pattern in human blood from different countries

PFOA isomers in Swedish blood

Males, n=31

- Low 0.5-2.8 ng/mL
- Medium 1.3-4.6 ng/mL
- High 2.1-8.4 ng/mL
- Ski wax technician 99 ng/mL
Isomer distribution in the environment
Isomer profiles in the environment around a AFFF point source
Soil chromatograms

PFOS

3,5- and 4,4-PFOS

1-PFOS

PFOA

5-PFOA

499>99

499>80

413>169

413>219

413>369
PFOS isomers in soil

PFOS isomers in soil

% of total concentration (ng/g d.w.)

63%  84%

PFOS conc.
….water, sediment, biota

- Seepage water: 59.6%, n=3
- Sediment: 78.5%, n=3
- Crab: 79.7%, n=1
- Fish liver: 88.4%, n=4
PFOA isomers

……not detected in sediment and biota
PFOS isomers in marine mammals

PFOS isomers in mink from Sweden

Rotander A, Kärrman A, et al., Not published
Useful tool for source elucidation?
Useful tool for source elucidation?

Pitfalls:

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

![Diagram showing data in soil, water, and biota]
Useful tool for source elucidation?

Opportunities:

• 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?

![Graph showing data points and bars representing different concentrations of PFOS]
Thanks for your attention