PERFLUORINATED COMPOUNDS LEVELS IN WILD FISH FROM THE CZECH REPUBLIC

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5th meeting on Chemistry & Life 2011, 14 – 16 September 2011
Brno, Czech Republic
Perfluoroalkylated substances (PFAS)

- Emerging contaminants
- Unique physico-chemical properties
  - C – F strong bond
  - High chemical stability
  - Photostability and thermostability
  - Hydrophobicity and oleophobicity – surface active compounds
- Using in various industry and household products
  (Protection of textile, carpet, leather (PTFE-Teflon, Gore-Tex), fire – fighting foam)

Exposition routes: oral, dermal and inhalation

Diverse effects:
- Reproduction cycle disorder
- Human evolution disorder
- Hepatoxicity, spasms, weight decrease, death

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Incidence of PFASs in the environment

Abiotic & biotic compartments

Sediments
(river, sea)

Sewage sludge
(Water waste treatment plants)

Water
(river, sea, tap, rain)

Dust
(home – TV, computer, carpet)

Air
(particles)

Liver

Muscle

Eggs

Kidney

Blood
(serum, plasma, cord)

Breast milk

Animals
(fish, birds, mammals)

Human

PFASs ➔ binding to proteins

X

Other halogentad POPs (e.g. PCB, BFR) ➔ cumulation in lipids

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Legislation and restrictions for PFAS

Perfluorooctane sulfonate (PFOS), pentafluorooctane sulfonamide (PFOA), their structurally related substances.


Adopted on 22 March 2011.

Commission Recommendation of 17 March 2010 on the monitoring of perfluoroalkylated substances in food (with EEA relevance) (2010/161/EU)

The European Commission recommended that further data on PFAS levels in food and in human tissues be determined particularly with respect to monitoring trends in exposure.

Perfluoroalkylated substances (PFAS) are widely used in industrial and consumer applications including non-stick coatings for fabrics and carpets, oil-resistant coatings for paper products approved for food contact, fire-fighting foams, mining and oil well sealants, foam polishes and insecticide formulations. An important subset are the perfluorinated organic surfactants to which perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) belong.

The EFSA recommended that further data on PFAS levels in food and in human tissues be determined particularly with respect to monitoring trends in exposure.

The Stockholm Convention on persistent organic pollutants (POPs) requires contracting parties to undertake monitoring of POPs, their alternatives and candidate POPs and has included PFOS, its salts and perfluorooctanoic acid (PFOA) in Annex B to the Convention among the substances subject to restrictions on production and use.

The Convention on Long-range Transboundary Air Pollution (LRTAP) adopted this recommendation.

1. Member States should monitor during 2010 and 2011 the presence of perfluorooctane sulfonate in food. The monitoring should include a wide variety of foodstuffs reflecting consumer diets including food of animal origin such as fish, meat, eggs, milk and derived products and food of plant origin.

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Experimental part
**Sampling sites**

- 9 localities
- bream, chub, crucian carp, roach, undermouth
- pooled samples – 3 categories: 100 – 300g; 300 – 900g and > 900g
- 60 samples of muscle

**Elbe River:**
- Verdek (1)
- Hradec Kralove (2)
- Obristvi (3)
- Usti nad Labem (4)
- Decin (5)

**Vltava River:**
- Hluboka nad Vltavou (6)
- Podoli (7)
- Sedlec (8)

**Bilina River:**
- Trmice (9)

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## Target analytes

<table>
<thead>
<tr>
<th>#</th>
<th>Analytes</th>
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<tbody>
<tr>
<td>1</td>
<td>C4</td>
<td>PFBA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>C5</td>
<td>PFPeA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>C6</td>
<td>PFHxA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>C7</td>
<td>PFHpA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>C8</td>
<td>PFOA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>C9</td>
<td>PFNA</td>
<td></td>
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<td>7</td>
<td>C10</td>
<td>PFDA</td>
<td></td>
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<tr>
<td>8</td>
<td>C11</td>
<td>PFUdA</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>9</td>
<td>C12</td>
<td>PFDoA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>C13</td>
<td>PFTrDA</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>11</td>
<td>C14</td>
<td>PFTeDA</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>12</td>
<td>C16</td>
<td>PFHxDA</td>
<td></td>
<td></td>
<td></td>
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<td>13</td>
<td>C18</td>
<td>PFODA</td>
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<td>C8</td>
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</tr>
<tr>
<td>21</td>
<td>FOSA</td>
<td>C8</td>
<td>FOSA</td>
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</tbody>
</table>

- **13 perfluorocarboxylic acids (PFCAs)**
- **4 perfluorosulfonic acids (PFSAs)**
- **3 perfluorophosphonic acids (PFAPAs)**
- **1 perfluorosulfonamide (FOSA)**
Analytical method

Fish tissue:

- **2 g sample**
- **Extraction (6 mL methanol)**
- **Clean-up (activated charcoal)**
- **Identification & Quantification**
  - Centrifugation (10000 rpm; 5 min)
  - Filtration (0.2 μm centrifuge filter; 5000 rpm; 2 min)

Total time: 50 min
Instrumental determination

Acquity UPLC (Waters, USA)
AB SCIEX QTRAP® 5500 (AB SCIEX, Canada)

Analytical column: HSS – 100 x 2.1 mm i.d.; 1.8 µm
Injection volume: 5 µL
Mobile phase: 5 mM ammonium acetate : Methanol
Run time: 11.5 min

<table>
<thead>
<tr>
<th>Performance characteristics</th>
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<tbody>
<tr>
<td>LOD (µg/kg)</td>
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<tr>
<td>LOQ (µg/kg)</td>
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<tr>
<td>Recovery (%)</td>
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<tr>
<td>RSD (%)</td>
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<td>Linearity (µg/kg)</td>
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</table>

Matrix matched standard (fish muscle) – 0.3 ng/g

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## Summary of results

<table>
<thead>
<tr>
<th></th>
<th>PFCAs</th>
<th></th>
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<th>PFSAs</th>
<th>FOSA</th>
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<tbody>
<tr>
<td></td>
<td>C5</td>
<td>C8</td>
<td>C9</td>
<td>C10</td>
<td>C11</td>
</tr>
<tr>
<td>Positive samples (%)</td>
<td>36</td>
<td>40</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>C12</td>
<td>C13</td>
<td>C14</td>
<td></td>
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<tr>
<td>Max. concentration (µg/kg)</td>
<td>0.4</td>
<td>0.4</td>
<td>0.6</td>
<td>22</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>7.8</td>
<td>3.7</td>
<td>0.9</td>
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</table>

PFCAs with shorter chain – PFBA (C4), PFHxA (C6), PFHpA (C7) not detected

<table>
<thead>
<tr>
<th></th>
<th>PFSAs</th>
<th>FOSA</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>C6</td>
<td>C8*</td>
</tr>
<tr>
<td>Positive samples (%)</td>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
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</tr>
<tr>
<td>Max. concentration (µg/kg)</td>
<td>0.1</td>
<td>136</td>
</tr>
</tbody>
</table>

PFBS (C4) and perfluorophosphonic acids not detected

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levels of PFASs in fish muscle

- Chub – the most common fish species in the Czech rivers
- Verdek/Elbe River and Trmice/Bilina River – the most polluted sampling sites
- PFASs especially PFOS, the most abundant analyte
- Sum of PFCAs – the highest concentration at Verdek
Contribution of individual PFCAs to Σ PFCAs

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Contribution of PFOS isomers to $\Sigma$ PFOS

**Technical mixture PFOS**

- L-PFOS = 78.8%
- Br-PFOS = 21.2%

**Trmice/Bilina River**

- Chub
- Crucius carp
- Roach
- Nase

<table>
<thead>
<tr>
<th>Location</th>
<th>Br-PFOS</th>
<th>L-PFOS</th>
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</thead>
<tbody>
<tr>
<td>Hluboka n. V.</td>
<td></td>
<td>n/d</td>
</tr>
<tr>
<td>Podoli</td>
<td></td>
<td>n/d</td>
</tr>
<tr>
<td>Praha Sedlec</td>
<td></td>
<td>n/d</td>
</tr>
<tr>
<td>Verdek</td>
<td></td>
<td>n/d</td>
</tr>
<tr>
<td>Hradec Kralove</td>
<td></td>
<td>n/d</td>
</tr>
<tr>
<td>Obristvi</td>
<td></td>
<td>n/d</td>
</tr>
<tr>
<td>Confluence with Bilina</td>
<td></td>
<td>n/d</td>
</tr>
<tr>
<td>Decin</td>
<td></td>
<td>n/d</td>
</tr>
<tr>
<td>Trmice</td>
<td>21.2%</td>
<td>78.8%</td>
</tr>
</tbody>
</table>

Vltava River Elbe River Bilina River

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Follow-up study

- Pooled samples
- Altogether 72 fish muscle samples
- In selected localities also individual samples
- The most common fish species were examined: Bream, Chub, Roach, Perch, Crucian carp, Trout

- Sampling sites – Elbe River, Vltava, Bilina, Lužická Nisa, Morava, Dyje and in pond (Podhradský)
- The sampling localities upstream and downstream from the potential source of PFASs
Results – follow-up survey

- Localities on Bilina River, Lužická Nisa and Morava (distributary) – the most contaminated
- Low levels of PFASs – Dyje River
- No significant differences between localities upstream and downstream from the “source”
Levels of PFASs in fish muscle

- High PFASs levels on the Bilina River confirmed
- The highest concentration of Σ PFASs exceeded 850 μg/kg
- PFOS, the most abundant analyte
- Σ PFCAs – the highest concentration at Bilina River
Contribution of PFCAs in bream muscle

- Comparison of the PFCAs profile in the different localities
- The contribution of individual PFCAs depend on locality / potential source?
- Similar profile in one locality
CONCLUSIONS

- For the first time, the extensive monitoring study was conducted in the Czech Republic.

- PFOS was the most abundant analyte, not only from the group PFSAs.

- The acids with longer carbon chain (C8 >), especially PFNA, PFDA, PFUdA (C11) and PFDoA (C12), represented PFCAs.

- The potential sources of PFCAs in Verdek / Elbe River and PFOS in Trmice / Bílina River, were located.

- The follow-up study confirmed the previous results and the most polluted localities.
Thank for your attention