Danish Survey (2010-2011) of PFAS migration from food packaging paper and board to food simulants and food

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Technical University of Denmark

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Thanks to colleagues in project

• Colleagues at DTU-Food
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• Students
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  Linda Bengtström (Ph.D.)

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  DTU-Food
  Food and Veterinary Admin.
  CeHoS
Outline

• Background: PFAS in food paper and board
• Design of the Survey on PFAS in paper and board
• PFAS quantification by UHPLC-ESI-MS/MS
• Results – migration and survey
• Conclusions
• Outlook
PFAS prevent uptake of grease/water from food - *fluorinated chains* repel water and oils/fats

**Applied (sized/coated)**
- Internally: Into the pulp, for flexible paper
- Externally: On the surface, for board in printing

**Attachment to paper**
- Deposited or bound to paper, e.g. via ester bonds

**Migration from paper**
- Direct contact with the food at high temperatures
- Single use packaging => repeated exposure
PFAS in industrial blends and paper migrates

More than 100 substances

Complex mixtures
- mono, di, tri-PAPs
- S-diPAPs
- SN-diPAPs
- Per-/poly-fluoropolyethers (PFPEs)
- Fluoroacrylates
- PFOS derivatives e.g. N-MeFOSE, N-EtFOSE

Fluorinated polyethers \( F(CF_2)y(CH_2CH_2O)xCH_2CH_2OH \)
Structures of per and poly-fluorinated alkyl surfactants (PFAS)

A surfactant has a polar head and hydrophobic tail

**Per-fluorochain:** only CF₂
**Poly-fluorinated chain:** CF₂ and CH₂

<table>
<thead>
<tr>
<th>Structure</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{F} {\text{CF}_2}_x \text{OH})</td>
<td>PFCA</td>
</tr>
<tr>
<td>(\text{F} {\text{CF}_2}_x \text{SO}_2\text{OH})</td>
<td>PFSA</td>
</tr>
<tr>
<td>(\text{F} {\text{CF}_2}_x \text{S} \text{NH}_2)</td>
<td>PFSAA</td>
</tr>
<tr>
<td>(\text{F} {\text{CF}_2}_x \text{OH})</td>
<td>FTOH</td>
</tr>
<tr>
<td>(\text{F} {\text{CF}_2}_x \text{PO}_2\text{OH})</td>
<td>monoPAPS</td>
</tr>
<tr>
<td>(\text{F} {\text{CF}_2}_x \text{PO}_2\text{OH})</td>
<td>diPAPS</td>
</tr>
<tr>
<td>(\text{F} {\text{CF}_2}_x \text{S} \text{PO}_2\text{OH})</td>
<td>S-diPAPS</td>
</tr>
<tr>
<td>(\text{F} {\text{CF}_2}_x \text{S} \text{PO}_2\text{OH})</td>
<td>Fluoroacrylate</td>
</tr>
</tbody>
</table>
Degradation of PFAS

Poly-fluorinated degrade to per-fluorinated substances

mono, di-PAPS
mono, di-polyfluorinated alkyl phosphate esters

heat, water
biodegradation

FTOH
fluorotelomer alcohols

oxidation
biodegradation

PFCA
perfluoro alkyl carboxylates
(e.g. PFOA)
Health concerns of PFAS

• **Toxicity of PFAS**
  - persistent (PFOS listed as POPs on Stockholm Conv.)
  - highly bioaccumulative: 4-9 years half lives
  - likely human carcinogens of PFOA
  - immunosuppressants
  - metabolic disrupters: cholesterol, obesity?
  - endocrine disrupting effect of PFCA, FTOH and PAPs

• **Few toxicity data on PFAS**
  PFOA TDI: 1.5 ug/kg bw/day
  PFOS TDI: 0.15 ug/kg bw/day

• **Degradation products of perPFAS are found everywhere**
  - in the environment and in animals
  - human blood (>95% of US citizens, levels 2-30 000 ng/mL)
  - in water, dust, materials, food and food packaging

• **Sources of are not accounted for**
  - 30-70% of fluorocarbons in human blood are “unknown”
Background for the Survey

- **US FDA 2005**, **2008**: PFAS in popcorn bags and in popcorn and oil
- Visit to U. of Toronto 2006: 3 of 10 samples had PFAS by $^{19}$F NMR

- **PhD 2007-2011**: PFAS in paper and board for food packaging
- EU Commission recommendation to national authorities March 2010: Measure PFOA, 8:2 FTOH, 8:2 mono and diPAPs in food
- EU PerFOOD project: focus on PFCA, FTOH
- Danish Veterinary and Food Authority 2010: **Survey PFAS in packaging**

- Results of PhD 2011, 4, 5:
  - **74 samples** from retail shops in Denmark (54), Sweden (6), Canada (15)
  - 57% samples contained PAPs; 16% ‘unknown’ PFAS by $^{19}$F NMR
  - 510 µg g$^{-1}$ paper (0.08 – 9100 µg g$^{-1}$ paper)

  => Media attention in fall 2011 in DK
  => Risk of migration?

1 Begley et al. 2005: Perfluorochemicals: potential sources of and migration from food packaging. Food Addit Contam 22(10):1023–1031, 9
Legislation for PFAS in Europe

• EU Framework Regulation 1935/2004, Article 3:  
  *substances may not migrate in amounts harmful to human health*

• No specific EU legislation on paper and board  
  => no specific migration limits  
  => no technical legislation on testing

• Other legislation/guidance:  
  German BfR, US FDA  
  Council of Europe (9 PFAS): Use plastic testing conditions for paper and board

• Action limits made for survey – for further toxicological evaluation  
  PFCA, FTOH, PAPs: 90 ug PFOA eq./kg food (as non-detection compounds)  
  PFSA and derivatives: 9 ug PFOS eq./kg food (as Cramer III compounds)
Design of Survey on PFAS in paper and board

- Originally designed as enforcement campaign => ‘suspect’ samples
- changed to a survey because no specific EU limits for PAPs
- 83 samples analysed:
  65 by food inspectors (without food)
  18 by the DTU-Food (with food)
- Sampled 2010-2011 in Denmark

<table>
<thead>
<tr>
<th>No. of samples</th>
<th>Type of packaging</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Bread (paper bags)</td>
</tr>
<tr>
<td>18</td>
<td>Flour, oats and cereals (paper bags)</td>
</tr>
<tr>
<td>4</td>
<td>Bread and cake mixtures (board boxes)</td>
</tr>
<tr>
<td>10</td>
<td>Cakes, biscuits and tartelettes</td>
</tr>
<tr>
<td>4</td>
<td>Microwave popcorn (paper bags)</td>
</tr>
<tr>
<td>4</td>
<td>Dairy products (board)</td>
</tr>
<tr>
<td>3</td>
<td>Chocolate (board)</td>
</tr>
<tr>
<td>3</td>
<td>Coffee (paper bags)</td>
</tr>
<tr>
<td>3</td>
<td>Tea (paper bags)</td>
</tr>
<tr>
<td>3</td>
<td>Baking paper</td>
</tr>
<tr>
<td>5</td>
<td>Muffin- and baking (paper cups)</td>
</tr>
<tr>
<td>8</td>
<td>Sandwich and lunch packaging (paper sheets)</td>
</tr>
<tr>
<td>8</td>
<td>Take away food (board and paper)</td>
</tr>
<tr>
<td>4</td>
<td>Board packaging (various)</td>
</tr>
</tbody>
</table>
Design of Survey:
Choice of migration test conditions

• **Screening tests**
  - 50% ethanol, 3 subsamples, 3 days, 60 °C
  - semi-quantitative SIR-method

• Screening samples above action limits => new **migration tests**
  - migration times according to use
  - 3 single sub-samples,
  - verification by MRM-method

• Fatty, emulsified foods:
  - 50% ethanol,
  - times and temperatures according to use

Dry foods and high T:
  Is Tenax suitable for PFAS?

• => ... so in the end 5 food analyses were made for packaging
  - with high PFAS levels
  - intended for dry foods and popcos
Quantitative PFAS analysis by UHPLC-MS/MS

Waters Acquity UHPLC–Quattro Ultima ESI− MS/MS MeOH/water with ammonia (pH 9.7)

Screening: SIR method,
Migration: MRM method

49 PFAS incl. isomers
If all PFAS quantified in one run
=> decrease sensitivity
=> Split up in three verification methods:
   1) Even PFCA + PFSA + S-diPAPs
   2) Uneven PFCA + FTOH
   3) Mono- + diPAPs
Matrix effects by NaCl
- internal std's correct for matrix and time effects

• External calibration

• Internal calibration

• also correct for up to 3 days in vials

DTU Food
National Food Institute
Results - screening

- Screening of 83 paper and board:
  45% (37 of 83) had Group 1 PFAS > 90 µg/kg food if all migrate

- Interference from matrix and time consuming => not used further on

- Major groups:
  - diPAPs
  - FTOHs
  - PFCAs
  - two samples w high levels of S-diPAPs

- PFSA hardly present

<table>
<thead>
<tr>
<th>Food</th>
<th>Area (dm²)</th>
<th>Group 1 µg/kg</th>
<th>Food</th>
<th>Area (dm²)</th>
<th>Group 1 µg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wrap</td>
<td>40</td>
<td>130</td>
<td>Melpose</td>
<td>10</td>
<td>380</td>
</tr>
<tr>
<td>Wrap</td>
<td>40</td>
<td>87</td>
<td>Melpose</td>
<td>10</td>
<td>200</td>
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<tr>
<td>Tepose</td>
<td>40</td>
<td>300</td>
<td>Mellemlæg</td>
<td>6</td>
<td>100</td>
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<tr>
<td>Tepose</td>
<td>40</td>
<td>240</td>
<td>Läkerol</td>
<td>40</td>
<td>720</td>
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<tr>
<td>Tepose</td>
<td>40</td>
<td>89</td>
<td>Kage</td>
<td>20</td>
<td>5000</td>
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<tr>
<td>Tartelet</td>
<td>40</td>
<td>1900</td>
<td>Kage</td>
<td>20</td>
<td>590</td>
</tr>
<tr>
<td>Tartelet</td>
<td>40</td>
<td>1200</td>
<td>Kage</td>
<td>20</td>
<td>420</td>
</tr>
<tr>
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<td>15</td>
<td>800</td>
<td>Kage</td>
<td>20</td>
<td>140</td>
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<tr>
<td>Pølsebakke</td>
<td>40</td>
<td>270</td>
<td>Kaffepose</td>
<td>10</td>
<td>230</td>
</tr>
<tr>
<td>Popcorn</td>
<td>100</td>
<td>1200</td>
<td>Kaffe/the</td>
<td>40</td>
<td>310</td>
</tr>
<tr>
<td>Popcorn</td>
<td>100</td>
<td>1100</td>
<td>Kaffe/the</td>
<td>40</td>
<td>250</td>
</tr>
<tr>
<td>Popcorn</td>
<td>100</td>
<td>660</td>
<td>Fastfood</td>
<td>40</td>
<td>210</td>
</tr>
<tr>
<td>Popcorn</td>
<td>100</td>
<td>320</td>
<td>Chokolade</td>
<td>40</td>
<td>390</td>
</tr>
<tr>
<td>Pommesfrit</td>
<td>40</td>
<td>1100</td>
<td>Chokolade</td>
<td>40</td>
<td>120</td>
</tr>
<tr>
<td>Pommesfrit</td>
<td>40</td>
<td>590</td>
<td>Burger</td>
<td>40</td>
<td>790</td>
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<tr>
<td>Müslipose</td>
<td>10</td>
<td>300</td>
<td>Brødpose</td>
<td>10</td>
<td>770</td>
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<tr>
<td>Müslipose</td>
<td>10</td>
<td>160</td>
<td>Brødpose</td>
<td>100</td>
<td>90</td>
</tr>
<tr>
<td>Muffinsform</td>
<td>20</td>
<td>140</td>
<td>Box Small</td>
<td>40</td>
<td>1160</td>
</tr>
<tr>
<td>Muffinsform</td>
<td>20</td>
<td>110</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Results migration and food

MRM analysis of migrates

- 43 samples taken for further analysis
  - 50% ethanol, 60 °C, 2 hrs- 1 day, exact surface area-to volume food

- Only PFAS with authentic standards were quantified
  - 25 had contents > 1 ug/kg
  - 8 had contents > 90 ug/kg

MRM analysis of 5 food samples (SPE clean-up)

- 2 Popcorn – popped in bag: 2.2-18 ug PFOA eq./kg
- 1 Coffee – brewed: < LOD
- 3 Fluor - 10 days in bag: < LOD
- Cake cups – migration: still need to be tested in cake

- High temperatures and water => enhance migration
  (hydrolysis and wetting of paper)
Test of factors influencing PAPs migration into simulants

• 5 - 20 °C: Increasing temperature => decrease migration (behave as non-ionic surfactants?)
• 20 - 35 °C: Increasing temperature => increase migration (increased wetting)

• 0 - 2.5%: Increasing NaCl => increase migration (decreased cmc)
• 2.5 - 5%: Increasing NaCl => decrease migration (more polar solvent)

• 0.5 - 3 hrs: Increasing time => decrease migration (fast release of adsorbed PAPs, but re-adsorption to surfaces?)
• 3 - 6 hrs: Increasing time => increase migration (release of chemisorbed PAPs?)

• Compound depended 6:2 monoPAPs: no effect of time equilibrium reached)
# PAPs migration to butter

## Recoveries

<table>
<thead>
<tr>
<th></th>
<th>6:2 monoPAPs</th>
<th>8:2 monoPAPs</th>
<th>6:2/6:2 diPAPs</th>
<th>8:2/8:2 diPAPs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butter 1</td>
<td>110</td>
<td>98</td>
<td>(218)</td>
<td>115</td>
</tr>
<tr>
<td>Butter 2</td>
<td>98</td>
<td>109</td>
<td>123</td>
<td>112</td>
</tr>
<tr>
<td>Butter 3</td>
<td>110</td>
<td>100</td>
<td>113</td>
<td>111</td>
</tr>
<tr>
<td>Butter 4</td>
<td>102</td>
<td>93</td>
<td>112</td>
<td>104</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>105</strong></td>
<td><strong>100</strong></td>
<td><strong>116</strong></td>
<td><strong>111</strong></td>
</tr>
<tr>
<td><strong>recovery (%)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>RSD (%)</strong></td>
<td>6</td>
<td>7</td>
<td>5</td>
<td>4</td>
</tr>
</tbody>
</table>

**Master thesis by Mette R. von Barner (M.Sc.):** Migration of per- and polyfluoroalkyl substances from paper packaging into food simulants and butter
PAPs migration into butter
contact time: 6 hours

Migration temperature: 5 °C

Migration temperature: 20 °C

Human exposure, but
Temperatures < 20 °C => 50% EtOH overestimates

Master thesis by Mette R. von Barner (M.Sc.): Migration of per- and polyfluoroalkyl substances from paper packaging into food simulants and butter
Conclusions

• PAPs and FTOH-derived **PFAS still used** in ~45% of food paper and board packaging (2010-2011)

• High contents in migrates, migration to popcorn, butter; low migr. to dry foods => **human exposure – what is the exact level?**

• Types of PFAS change rapidly: PFOS-based -> PAPs -> acrylates -> PFPE => **Challenge to develop qualitative and quantitative methods fast enough**
  Lack of authentic and mass labelled standards => semi-quantitative
  => TDI values are lacking => difficult to make risk assessment

• Survey made inspected producers aware of PFAS => **industry show data**

• Plastics migration test conditions do not mimic migration to food well => **Test specific content in paper** (fast) or **test in food** (time consuming)?
  => **Test sum of PFCA precursors** (FTOH, PFCA after forced degradation)?
Analyses of specific substances in complex mixtures: takes time and costly
  => authority response time is long, fewer substances can be measured

Most substances are not monitored for by industry or enforcement
  => Are consumers adequately protected by Framework Regulation, Art. 3?
  => Need for harmonised principles to test for Article 3 substances
  => Harmonised way to deal with semi quantitative data?
     Threshold of Regulatory Concern? Database of TDIs?

More focus on screening by authorities (content in packaging)
  => industry show compliance (quantify)

For PFAS: Alternatives to specific testing:
  => Group sum of PFCA, PFOS precursors, use TDI PFOA, PFOS for risk assessm.
  => Complex mixtures/oils/ethers: Sum all peaks, quantify against one std

Continued need to understand migration and to develop methods
  for surfactants in paper and board: emerging PFAS, in packaging, food, humans