Migration of Perfluorochemicals From Food Contact Materials

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Why are we interested in perfluoro chemical migration?

- Perfluoro chemicals found in human serum (Olsen et al. 1999). Occupational exposure.
- May 2000, 3M Company announce phase out of perfluorooctyl chemistry.
- Elderly in Seattle WA are found to have perfluoro chemicals in their serum (Olsen et al. 2003).
Why are we interested in perfluorochemical migration?

- PFOA is biopersistent / bioaccumulative
- **Half-life** in human serum may be 4.4 years (Butenhoff et al. 2004).
- Potential concerns for carcinogenesis; developmental/reproductive and immunotoxic.
- Many fluorochemicals regulated for food-contact contain PFOA as an impurity and/or have chemical moieties similar to PFOA.
2-perfluorooctylethanol or (8:2 telomer alcohol) has been shown to biodegrade to PFOA

Perfluorooctanoic acid = PFOA

Structures of perfluorochemicals found in human serum

- Perfluorooctanesulfonate = PFOS

- Perfluorooctanoic acid = PFOA
Typical Commercial Products Potentially Made with Fluorochemicals
Food package types that contain fluorochemicals

Polymers
- cookware
- tubing
- gaskets

Paper
- microwave popcorn
- muffin bags
- french fry bags
- pizza liners
- sandwich wrappers
- burger/pizza boxes
Historical Regulation in the USA

• 1962  PTFE for cookware
• 1984  perfluorochemical elastomers
• 1958  paper coatings (prior-sanctioned)
• 1962  1st paper coatings (petition)
Where are perfluorochemicals for paper regulated?

• In US approximately 15 materials are regulated

• BfR also has a number of perfluorochemicals regulated
Types of perfluorochemicals added to food contact paper

- **Perfluoro telomer type**
  - $C_6$, $C_8$, $C_{10}$, $C_{12}$, $C_{14}$ based

- **Polymeric type**
Typical structures of perfluoro telomer based paper coatings

m/z = 889

m/z = 1021

m/z 1202
Analysis of PTFE Cookware for PFOA
## Summary of PFOA analysis of some polymers

<table>
<thead>
<tr>
<th>Material</th>
<th>Conc. PFOA µg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTFE Cookware</td>
<td>4-75</td>
</tr>
<tr>
<td>Dental Floss</td>
<td>3</td>
</tr>
<tr>
<td>Dental Tape</td>
<td>4</td>
</tr>
<tr>
<td>PTFE Sealant Tape</td>
<td>1800</td>
</tr>
<tr>
<td>FEP Tubing</td>
<td>ND</td>
</tr>
</tbody>
</table>
Does PFOA migrate from PTFE during cooking?

- Use PTFE sealant film for migration test.
- PTFE film has $C_{p0} = 1.8 \, \text{mg/kg}$
- Test for migration at $100^\circ\text{C}$ and $175^\circ\text{C}$ into water and oil.
Typical LCMS analysis for PFOA migrating from PTFE into Miglyol at 100 °C
Migration of PFOA from PTFE sealant film after 2hrs at cooking temperatures

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Medium</th>
<th>$M_t$ (PFOA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100°C</td>
<td>Water</td>
<td>150 ng/dm² (1.6 ± 0.4 µg/kg)</td>
</tr>
<tr>
<td></td>
<td>Miglyol</td>
<td>120 ng/dm² (1.3 ± 0.07 µg/kg)</td>
</tr>
<tr>
<td>175°C</td>
<td>Miglyol</td>
<td>710 ng/dm² (7.7 ± 0.1 µg/kg)</td>
</tr>
</tbody>
</table>
Fractional PFOA Migration from PTFE

- Fractional Migration oil at 175°C  \( M_t/M_\infty = 17\% \)

- Fractional Migration water at 100°C  \( M_t/M_\infty = 4\% \)
Simulated Loss of PFOA from Cookware based on Fractional Migration, Potential Values

$C_P_0 = 75 \text{ ng/g}$
Simulated Loss of PFOA from Cookware based on Fractional Migration, Potential Values

Sinclair et al., Environ. Sci. Tech. 2007 at 179° - 233°C
Does PTFE Degrade to PFOA at High Temperature?

- FDA, No detectable increase in PFOA in PTFE
- Sinclair et al., Environ. Sci. Tech. 2007, No PFOA
Fluorochemicals for Food Contact Paper
Fluorochemical Paper coatings

- Fluorochemical paper concentrations can be up to 0.5% or 5000 mg/kg.

- Temperature range for paper applications: -5°C – 200+ °C.

- Most perfluoro telomer based paper treatments have molecular weights >1000 but the molecular size is similar to much smaller molecules.
Migration of chemicals with MW > 1000?

F versus H

MW = 1121

MW = 510
MW = 1121  
Molecular Area = 558Å²  
Molecular Volume = 609Å³

MW = 510  
Molecular Area = 541Å²  
Molecular Volume = 530Å³

C_{71}H_{141}  
MW = 997  
Molecular Volume = 1225Å³
Is PFOA in Perfluorochemical Paper Coatings and treated Paper Products?
## Concentration of PFOA in Perfluoro Paper Coatings and Paper Products

<table>
<thead>
<tr>
<th>Material</th>
<th>$C_{p0}$</th>
<th>PFOA (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfluoro paper coating (not applied)</td>
<td></td>
<td>88 - 160</td>
</tr>
<tr>
<td>Popcorn bags</td>
<td></td>
<td>0.3</td>
</tr>
<tr>
<td>Muffin bag</td>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td>Sub Sandwich wrapper</td>
<td></td>
<td>0.5 – 1.2</td>
</tr>
<tr>
<td>Hash brown potato bag</td>
<td></td>
<td>0.9</td>
</tr>
</tbody>
</table>
Migration of PFOA from microwave popcorn bags?

Temperature of oil from microwave susceptor heating

Time (min)

Temperature °C

0 0.5 1 1.5 2 2.5 3 3.5

0 50 100 150 200 250
Migration of PFOA from microwave popcorn bags?

None detected into oil

Test for perfluorochemical migration from commercially produced paper
Typical structures of Perfluoro telomer based paper coatings
Test conditions for perfluorochemical migration

- Food simulating liquids/foods at 100 °C
- Single-sided contact with paper
- Contact time 15 minutes
- LCMS analysis for perfluorochemical
Typical structures of Perfluoro telomer based paper coatings
Migration results for incidental contact, Coating A
Migration results for incidental contact, Coating B

- Water
- Vinegar
- 10% EtOH
- 20% EtOH
- 25% EtOH
- 30% EtOH
- Butter
- Oil
Migration results for incidental contact, Coating $\mathcal{C}$, paper produce in 1987

![Bar chart showing relative migration in mg/kg for various substances: Water, Vinegar, 10% EtOH, 25% EtOH, Butter, Oil. The x-axis represents different substances, and the y-axis represents relative migration in mg/kg. Butter shows the highest migration value.](image)
Potential Problem for Exposure Estimates?

Water and oil are not the extremes!
Typical Migration Results From a Polymer

Migration of Irganox 1076 from PP at 135°C
Migration into Emulsions

- **Butter = water-in-oil Emulsion (20% / 80%)**

- **Non-ionic surfactant** (polyoxyethylene sorbitan / oil / water)

- **Ionic surfactant** (lecithin / oil / water)
Migration from paper, 40°C 1 day

- Butter
- Chocolate spread
- Emulsion -nonionic
- Emulsion -ionic
- Oil
- Oil + ionic (soy)
- Oil + nonionic

Migration µg/cm²

- 0
- 0.2
- 0.4
- 0.6
- 0.8
- 1.0
- 1.2
Migration of Fluorochemical is Kinetic to food at 40°C
Do Perfluoro telomer Paper Coatings Migrate Under Actual Conditions of Use?
Migration from microwave susceptor into oil
## Results for migration of fluorotelomer from popcorn bags

<table>
<thead>
<tr>
<th>Concentration in Popcorn Oil before Heating</th>
<th>Concentration in Miglyol after 2 min. microwave heating</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4 mg/kg</td>
<td>2.1 mg/kg</td>
</tr>
<tr>
<td>4 μg/ dm²</td>
<td>7 μg/ dm²</td>
</tr>
</tbody>
</table>
LCMS analysis of Popcorn for the Migration of Fluorotelomer from Popcorn bag

m/z = 921 --  
m/z = 1021 --  
m/z = 1121 --
### Migration of perfluorotelomer into microwave popcorn

<table>
<thead>
<tr>
<th>Brand</th>
<th>mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.2</td>
</tr>
<tr>
<td>B</td>
<td>0.8</td>
</tr>
<tr>
<td>C</td>
<td>3.8</td>
</tr>
<tr>
<td>D</td>
<td>1.2</td>
</tr>
<tr>
<td>E</td>
<td>2.1</td>
</tr>
</tbody>
</table>
Conclusions of Migration Tests

• The food simulants **water** and **oil** are not the extremes for these fluorochemicals.

• The soy emulsifier (lecithin, 0.05%) can change oil into a potent solvent for migration.

• Fluorotelomers do **migrate** to food in the **mg/kg** (ppm) range.
Migration to oil = none

Migration to oil + emulsifier = huge