Classification of foodstuffs based on their solubility properties for potential migrants from food contact materials (in support of exposure estimation)

Roland Franz
Fraunhofer IVV, Freising, Germany

http://www.ivv.fraunhofer.de

ILSI Europe 5th International Symposium on Food Packaging
Scientific Developments supporting Safety and Innovation
14–16 November 2012, Berlin, Germany
This work was done as a key element of WP 4.2 of the FACET project.
Great appreciation to my co-authors and all FACET WP4.2 partners

- Fraunhofer IVV, Freising, Germany (coordination WP 4.2)
  **Annika Seiler**, Chinawat Tongchat

- FABES GmbH, Munich, Germany
  **Dr. Peter Mercea**, Dr Otto Piringer

- EC, Joint Research Centre, IHCP, Ispra, Italy
  **Aurelie Bach**, Dr. Catherine Simoneau,

- The Food and Environment Research Agency FERA, York, UK
  **Dr. Malcolm Driffield**, Dr. Laurence Castle

- University Santiago de Compostela, Spain
  **Prof. Perfecto Paseiro-Losada** & co-workers

- National Institute INCDTIM, Cluj-Napoca, Romania
  Dr. Valer Tosa

- FACET Industry Group
  Dr. Peter Oldring, Dr. Ralf Eisert, Dr. Jean-Jaques Azens
Motivation for and objective of FACET WP4.2

Expected difficulties to overcome

Some experimental kinetic migration results

Foodstuffs expressed by ethanol-in-water equivalents

How is the new classification of foods used for exposure estimation

Conclusions
Overall objective of WP 4.2:
To establish a verified modelling tool for mono and multi-layer packaging materials for migration into foods under actual conditions of use in order to deliver reliable concentration estimates for use in consumer exposure modelling.

EXPOSURE$^{\text{from Food Packaging}}$ = MIGRATION$^{(\text{Conc. in Food})} \times \text{Food Consumption}$
Determinants of migration - Monolayer

\[ C_{F,t}^{\text{Migrant}} = f (C_{P,0}^{\text{Migrant}}, D_P, D_F, K_{P/F}, t, \text{packaging structure}) \]

Fraunhofer IVV
Determinants of migration - multi-layer - complexity of foods

\[ C_{F,t} = f \left( C_{P,0}, nD_P, iD_F, nK_{L/L} (L/F), t, \text{complex pack. structure} \right) \]
Enormous complexity of food packaging scenarios

We have to do with:

- **Several thousands of food items**
- A few hundreds of materials in layers of FCM
- **A few thousands of migrants with variation in $C_{P,0}$**
- Up to 5 layers in one FCM, in many cases more (up to 10)
- Structural variability: $d$ (L), Food volume, FCM contact area
- Wide range of FCM-Food contact conditions ($t$, $T$)

Solution only via clustering and read-across:

- **Foodstuffs**: common physico-chemical similarities such as solubility properties for migrants (fat content) and diffusion resistance for migrants (viscosity, texture)
- **FCM materials**: common polarity characteristics, similar diffusion behaviour for migrants
- **Migrants**: Molecular weight and polarity ($\log K_{o/w}$)

Reduction of food item numbers to a manageable size?
Experimental setup and test systems

Test materials: LDPE, PA, Paper&Board
Migrants: 18 model migrants
Foods: 41 different foods (FACET standard or model foods)
Food simulants: various ethanol-water mixtures, Tenax® (MPPO adsorbent)
Conditions: ~ 9 time points until equilibrium at 5°C < T < 100°C
Experimental results – examples of kinetic migration profiles

Migration from LDPE film – olive oil versus soft cheese

**Experimental results**

- **Styrene - Olive oil**
  - $K_{P/F} = 0.7$
  - Temperature: 20°C, 40°C, 60°C

- **ATBC - Olive oil**
  - $K_{P/F} = 0.7$
  - Temperature: 20°C, 40°C, 60°C

- **Styrene - Soft cheese**
  - $K_{P/F} = 2.0$
  - Temperature: 10°C, 20°C, 40°C

- **ATBC - Soft cheese**
  - $K_{P/F} = 1.7$
  - Temperature: 10°C, 20°C, 40°C
Experimental results – examples of kinetic migration profiles

Migration of ATBC from LDPE film – comparison of different foods

10°C, 20°C, 40°C

ATBC – Soft cheese

\[ K_{P/F} = 1.7 \]

Sausage (Landjäger)

\[ K_{P/F} = 0.3 \]

Margarine

\[ K_{P/F} = 0.1 \]

Tuna

\[ K_{P/F} = 12 \]

Equilibrium

Fraunhofer IVV
Experimental results – examples of kinetic migration profiles

Comparison: condensed milk: concentrate versus dilution (1:3)

Conc. cond. milk

20°C
40°C
60°C

K<sub>P/F</sub> = 15

ATBC

20°C
40°C
60°C

K<sub>P/F</sub> = 417

DEHA

Dilut. cond. milk

20°C
40°C
60°C

K<sub>P/F</sub> = 4.7

ATBC

20°C
40°C
60°C

K<sub>P/F</sub> = 22

DEHA

K<sub>P/F</sub> = 4.7

ATBC

K<sub>P/F</sub> = 15

ATBC

K<sub>P/F</sub> = 417

DEHA

K<sub>P/F</sub> = 22

DEHA

Fraunhofer

IVV
Kinetic migration profiles - range of K-values - food types

- Aqueous / non-fatty foods
  - \( K_{P/F} = >> 500 \)
  - \( 500 > K_{P/F} > 20 \)

- Fatty foods
  - \( K_{P/F} = < 20 \)
Foodstuffs expressed by ethanol-in-water equivalents

**STEP 1:**
**Calibration of the system**

- Migration of model migrants from LDPE in ethanol-water mixtures

plus

- Published data

=> Plot: log $K_{P/F}$ / log $P_{O/W}$
STEP 1: Calibration of the system
=> 'World Map' for Foodstuffs

Foods can be localised within ethanol-water areas
Foodstuffs expressed by ethanol-in-water equivalents

**STEP 2:**

**Localisation of foodstuffs in the 'World map'**

- $K_{p/F}$ data from Kinetic migration experiments

Examples
- Clear drinks, (wine, beer)
- Cloudy drinks (orange juice)

![Graph showing the localisation of foodstuffs with different ethanol concentrations. The graph includes data points for orange drinks, clear drinks, and examples of olive oil and orange drink with different ethanol concentrations.]
Foodstuffs expressed by ethanol-in-water equivalents

STEP 2:

Localisation of foodstuffs in the 'World map' - K\text{P/F} data from Kinetic migration experiments

Some dry foods

![Graph showing log K\text{P/F} vs. log Po/w for various foodstuffs at different ethanol concentrations.]

- Butter Toast
- Almonds
- Flour
- milk powder
- rice
- instant soup
- Cake
- Noodles (Pasta)
- DOUGH

Fraunhofer IVV
**Foodstuffs expressed by ethanol-in-water equivalents**

**STEP 2:**

*Localisation of foodstuffs in the 'World map'*

- $K_{P/F}$ data from Kinetic migration experiments

*Cheese & cheese products*

![Graph showing log $K_{P/F}$ vs. log Po/w for different ethanol concentrations and foodstuffs like cheese sauce, cottage cheese, Soft cheese, and Gouda.](image)
Foodstuffs expressed by ethanol-in-water equivalents

**STEP 2:**

**Localisation of foodstuffs in the 'World map'**

- $K_{P/F}$ data from Kinetic migration experiments

Meat products

[Landjäger = fatty sausage]
Foodstuffs expressed by ethanol-in-water equivalents

**STEP 2:**
Localisation of foodstuffs in the ‘World map’

- K<sub>p/F</sub> data from Kinetic migration experiments

Meat with different fat content

- <5% fat => E30
- 5-20% fat => E40
- >20% fat => E50
**STEP 2:**

**Localisation of foodstuffs in the 'World map'**

- $K_{p/F}$ data from Kinetic migration experiments

Some fatty foods

**Foodstuffs expressed by ethanol-in-water equivalents**

![Graph showing the localisation of foodstuffs in a 'World map' with different ethanol concentrations and log $K_{p/F}$ values.](image-url)
### Allocation of ethanol equivalents to FACET_Tier3 food groups

<table>
<thead>
<tr>
<th>FACET Tier 1</th>
<th>FACET_Tier 1 Name</th>
<th>FACET Tier 2</th>
<th>FACET Tier 3</th>
<th>FACET Tier 3 Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.01</td>
<td>Dairy products and analogues</td>
<td>P.01.1 - P.01.2</td>
<td>P.01.1.1 – P.01.1.8 - P.01.2.1 - P.01.2.2</td>
<td>Liquid milk – Cream Processed cheese Unprocessed cheese</td>
</tr>
<tr>
<td>P.02</td>
<td>Fats and oils and fat emulsions</td>
<td>P.02.1 – P.02.2</td>
<td>P.02.1.1 – P.02.2.2</td>
<td>Butter – Vegetable and see oil</td>
</tr>
<tr>
<td>P.03</td>
<td>Fruits, nuts and seeds</td>
<td>P.03.1. – P.03.4</td>
<td>P.03.1.1 – P.03.4.1</td>
<td>Fresh fruit whole or cut – Nut based spreads</td>
</tr>
<tr>
<td>P.17</td>
<td>Desserts (except bakery and fruit desserts)</td>
<td>P.17.1 – P.17.3</td>
<td>P.17.1.1 – P.17.3.1</td>
<td>Spoonable yogurt - Dessert mixes</td>
</tr>
<tr>
<td>P.18</td>
<td>Composite foods</td>
<td>P.18.1 – P.18.5</td>
<td>P.18.1.1 – P.18.5.11</td>
<td>Dressed salads – Hot meals</td>
</tr>
</tbody>
</table>
## Allocation of ethanol equivalents to FACET_tier3_food groups

<table>
<thead>
<tr>
<th>FACET Tier3</th>
<th>FACET Tier 3 Name</th>
<th>PIM Simulant</th>
<th>% Ethanol equivalency</th>
<th>Represented by FACET WP4-2 model food</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.01.1.1</td>
<td>Liquid milk</td>
<td>D1 (E50)</td>
<td>60</td>
<td>UHT milk</td>
</tr>
<tr>
<td>P.01.1.2</td>
<td>Flavoured milk drinks</td>
<td>D1 (E50)</td>
<td>60</td>
<td>UHT milk</td>
</tr>
<tr>
<td>P.01.1.3</td>
<td>Drinking yoghurt</td>
<td>D1 (E50)</td>
<td>50</td>
<td>Yoghurt</td>
</tr>
<tr>
<td>P.01.1.4</td>
<td>Sour milk drinks</td>
<td>D1(E50)</td>
<td>60</td>
<td>UHT milk</td>
</tr>
<tr>
<td>P.01.1.5</td>
<td>Soy beverages</td>
<td>? D1 (E50) ?</td>
<td>60</td>
<td>UHT milk</td>
</tr>
<tr>
<td>P.01.1.6</td>
<td>Condensed/ evap milk</td>
<td>D1 (E50)</td>
<td>60</td>
<td>condensed milk</td>
</tr>
<tr>
<td>P.01.1.7</td>
<td>Powdered milk</td>
<td>E (MPPO)</td>
<td>50</td>
<td>milk powder</td>
</tr>
<tr>
<td>P.01.1.8</td>
<td>Cream</td>
<td>D1 (E50)</td>
<td>95</td>
<td>cream</td>
</tr>
<tr>
<td>P.01.2.1</td>
<td>Processed cheese</td>
<td>D1 (E50)</td>
<td>50</td>
<td>soft cheese</td>
</tr>
<tr>
<td>P.01.2.2</td>
<td>Unprocessed cheese</td>
<td>D2 - X/3</td>
<td>60</td>
<td>Gouda</td>
</tr>
<tr>
<td>P.02.1.1</td>
<td>Butter</td>
<td>D2 - X/2</td>
<td>95</td>
<td>margarine</td>
</tr>
<tr>
<td>P.02.1.2</td>
<td>Cooking margarine</td>
<td>D2 - X/2</td>
<td>95</td>
<td>margarine</td>
</tr>
<tr>
<td>P.02.1.3</td>
<td>Spreadable oils &amp; fats</td>
<td>D2 - X/2</td>
<td>95</td>
<td>margarine</td>
</tr>
</tbody>
</table>
## Allocation of ethanol equivalents to FACET_tier3_ food groups

<table>
<thead>
<tr>
<th>FACET Tier 3</th>
<th>FACET Tier 3 Name</th>
<th>PIM Simulant</th>
<th>% Ethanol equivalency</th>
<th>Represented by FACET WP4-2 model food</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.12.2.6</td>
<td>Instant soup</td>
<td>E (MPPO)</td>
<td>55</td>
<td>instant soup</td>
</tr>
<tr>
<td>P.12.2.7</td>
<td>Hot vended soup</td>
<td>? C (E20) ?</td>
<td>50% =&gt; 40</td>
<td>50% orange juice, 50% apple sauce</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>50% =&gt; 25</td>
<td></td>
</tr>
<tr>
<td>P.12.3.1</td>
<td>Herbs &amp; spices</td>
<td>E (MPPO)</td>
<td>35</td>
<td>wheat flour</td>
</tr>
<tr>
<td>P.12.3.2</td>
<td>Salt</td>
<td>E (MPPO)</td>
<td>10</td>
<td>[none]</td>
</tr>
<tr>
<td>P.12.4.1</td>
<td>Yeast</td>
<td>E (MPPO)</td>
<td>60</td>
<td>ground nuts</td>
</tr>
<tr>
<td>P.13.1.1</td>
<td>Infant milk formula</td>
<td>E (MPPO)</td>
<td>50</td>
<td>milk powder</td>
</tr>
<tr>
<td>P.13.1.2</td>
<td>Dried baby food</td>
<td>E (MPPO)</td>
<td>55</td>
<td>instant soup</td>
</tr>
<tr>
<td>P.18.3.3</td>
<td>Hot pizza</td>
<td>? E (MPPO) ?</td>
<td>20% =&gt; 60</td>
<td>20% cheese, 20% tomato sauce, 60% of b-toast</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20% =&gt; 25</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>60% =&gt; 50</td>
<td></td>
</tr>
<tr>
<td>P.18.4.1</td>
<td>Instant noodles</td>
<td>E (MPPO)</td>
<td>35</td>
<td>noodles</td>
</tr>
<tr>
<td>P.18.4.2</td>
<td>Canned/preserved pasta</td>
<td>E (MPPO)</td>
<td>40 % =&gt; 40</td>
<td>40 % cheese sauce, 60% tomato sauce</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>60 % =&gt; 25</td>
<td></td>
</tr>
</tbody>
</table>
How is the new classification of foods used for exposure estimation

K values between food contact polymer and food, $K_{P/F}$, but also between materials of multilayers, $K_{P1/P2}$, are essential for migration and exposure estimation.

(1) $K_{P/F}$ values can be estimated as a function of specific physico-chemical parameters of the MIGRANT, the POLYMER, the ETHANOL conc. (in water) and of T. [This is the so-called ‘Vapour Pressure Index’ method]

=> Migrant specific $K_{p/f}$ values for any food of interest can be calculated via the assigned ethanol-water equivalency

(2) For each of two materials P1 and P2 a $K_{P1/F}$ resp. $K_{P2/F}$ can be calculated and from the ratio of $K_{P1/F}$ / $K_{P2/F}$ a partition constant $K_{P1/P2}$ value for the 2 polymers can be derived. This is also applicable to polymer/cardboard.

=> Migrant specific $K_{P1/P2}$ values for any pair of neighbouring FCM materials of interest can be calculated

Conclusions

- Migrants are soluble in foods according to their solubility properties as determined by the food composition (fat, water, carbohydrates)

- On the other hand, for ethanol-water mixtures, the solubility of migrants is also a function of the ethanol concentration

- => Via \( \log P_{O/W} - \log K_{P/F} \) plots for model migrants generic solubility properties of foods were correlated with those of ethanol-water mixtures

- In this way, ALL foodstuffs can be classified into a reduced number of food categories each represented by a corresponding ethanol-in-water equivalency

- This new classification system (allocation of foods to ethanol equivalents) allows – within the frame of a probabilistic migration model (FACET) - to estimate exposure of migrants from FCM

- Moreover, the established ethanol equivalents for foodstuffs may be usable to refine further the 'Food category specific assignment of food simulants' as listed in Table 2 of Annex III of EU Regulation No.10/2011
Finally with this (old meets new) westside view of my institute

...... and on behalf of all WP4.2 partners:

THANK YOU!

www.ivv.fraunhofer.de