Development of a probabilistic model to establish concentrations of migrants from packaging materials in foods

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(on behalf of all Partners from WP4.2)

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Project partners of WP4.2

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• FABES GmbH, Munich, Germany
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  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
Overall objective of WP4.2

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\textsubscript{from Food Packaging} = MIGRATION (Conc. in Food) x Food Consumption

A very ambitious undertaking .......

\[ C_{F,t}^{\text{Migrant}} = f (C_{P,0}^{\text{Migrant}}, D_p, D_F, K_{P/F}, t, \text{packaging structure}) \]
A very ambitious undertaking ........

FCM

C \_P,0 \_Migrant

D \_P

D \_F

C \_F,1 \_Migrant

K \_P/F

L1 L2 L3 L... Ln

K \_1/2 K \_2/3 K \_3/4 K \_n/F

D \_1 D \_2 D \_3 D ... D \_n

C \_P,0

liquid semi-solid solid composite

D \_F > D \_F > D \_F \sum iD \_F

C \_F,1

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)
A resolvable challenge?

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- Several thousands of food items
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- A few thousands of migrants with variation in $C_{p,0}$
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- 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 item numbers to a manageable size?

Five tasks to achieve objective of WP4.2

1. Extensive kinetic FCS migration studies both from tailor-made and representative industrial packaging materials in contact with foods to derive not overly conservative but best-fit migration modelling parameters of diffusion coefficients both for contact materials and foods as well as partition constants between them.
2. From (1): New classification of foods/food groups based on solubility properties of foods for FCS with clustering to reduce the immense number of food items to an overseeable size
3. Study into partitioning of packaging migrants within multi layers / multi-materials to establish reference parameters for migration modelling
4. Migration modelling for multi-layer/multi-material packaging in contact with foods, including set-off and paper/board.
5. Probabilistic modelling of concentration of FCS in packed foods and link to exposure modelling in WP8
(1) Extensive kinetic migration studies

Examples: Migration from LDPE film – oil versus soft cheese

- Styrene - Olive oil
- Styrene - Soft cheese
- ATBC - Olive oil
- ATBC - Soft cheese
(1) Extensive kinetic migration studies

Examples: Migration ATBC from LDPE film – foods versus foods

- ATBC – Soft cheese
- Sausage (Landjäger)
- Margarine
- Tuna

(1) Extensive kinetic migration studies

- Approx. 730 kinetic migration experiments (~ 9 time points) measured
  - From: LDPE, PA, Paper&Board
  - Into: 41 different foods (FACET standard or model foods),
    ethanol-water mixtures, Tenax® (MPPO adsorbent)
  - Using: 18 model migrants
  - At: 5°C < T < 100°C

- From these experiments physico-chemical parameters were derived
  - Diffusion coefficients in Foods $D_F$ in support of a general concept to estimate $D_F$ for any migrant in any food => Task (4)
  - Partition constants $K_{PF}$ as a basis for the new classification of foods => Task (2)
  - Supplementary $D_{FCM}$ data in support of the migration model => Task (4)
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(2) New classification of foods .........

STEP 1:

Calibration of the system
- Migration of model migrants from LDPE in ethanol-water mixtures
- Published data

=> Plot: \( \log K_{PF} / \log P_{OW} \)
(2) New classification of foods .......

PROCEDURE to express all foods as ethanol-water equivalents:

*NOTE: The FACET standard (model) foods were selected such that they are representative of the 18 FACET_Tier1 food groups*

1. Based on the log $K_{P/F}$ - log $P_{O/W}$ plot evaluation all 41 FACET standard (model) foods were assigned to ethanol-water mixtures
2. All FACET WP4_Tier3 foods were allocated to the most appropriate standard (model) foods and thus to their ethanol-water equivalents.
(2) New classification of foods ……

**FACET tier3 food groups - PIM simulants - ethanol-water equivalents**

<table>
<thead>
<tr>
<th>WP4_tier3</th>
<th>WP4_tier3 Name</th>
<th>Simulant according to PIM</th>
<th>Ethanol equivalency [% ethanol]</th>
<th>Equivalent to FACET WP4-2 model food</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.01.1.1</td>
<td>Liquid milk</td>
<td>E50</td>
<td>60</td>
<td>UHT milk</td>
</tr>
<tr>
<td>P.01.1.2</td>
<td>Flavoured milk drinks</td>
<td>E50</td>
<td>60</td>
<td>UHT milk</td>
</tr>
<tr>
<td>P.01.1.3</td>
<td>Drinking yoghurt</td>
<td>E50</td>
<td>50</td>
<td>Yoghurt</td>
</tr>
<tr>
<td>P.01.1.4</td>
<td>Sour milk drinks</td>
<td>E50</td>
<td>60</td>
<td>UHT milk</td>
</tr>
<tr>
<td>P.01.1.5</td>
<td>Soy beverages</td>
<td></td>
<td>60</td>
<td>UHT milk</td>
</tr>
<tr>
<td>P.01.1.6</td>
<td>Condensed/ evap milk</td>
<td>E50</td>
<td>60</td>
<td>condensed milk</td>
</tr>
<tr>
<td>P.01.1.7</td>
<td>Powdered milk</td>
<td>MPPO</td>
<td>50</td>
<td>milk powder</td>
</tr>
<tr>
<td>P.01.1.8</td>
<td>Cream</td>
<td>E50</td>
<td>95</td>
<td>cream</td>
</tr>
<tr>
<td>P.01.2.1</td>
<td>Processed cheese</td>
<td>E50</td>
<td>50</td>
<td>soft cheese</td>
</tr>
<tr>
<td>P.01.2.2</td>
<td>Unprocessed cheese</td>
<td>X/3</td>
<td>60</td>
<td>Gouda</td>
</tr>
<tr>
<td>P.02.1.1</td>
<td>Butter</td>
<td>X/2</td>
<td>95</td>
<td>margarine</td>
</tr>
<tr>
<td>P.02.1.2</td>
<td>Cooking margarine</td>
<td>X/2</td>
<td>95</td>
<td>margarine</td>
</tr>
<tr>
<td>P.02.1.3</td>
<td>Spreadable oils &amp; fats</td>
<td>X/2</td>
<td>95</td>
<td>margarine</td>
</tr>
</tbody>
</table>

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<th>WP4_tier3</th>
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<th>Equivalent to FACET WP4-2 model food</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.12.2.6</td>
<td>Instant soup</td>
<td>MPPO</td>
<td>55</td>
<td>instant soup</td>
</tr>
<tr>
<td>P.12.2.7</td>
<td>Hot vended soup</td>
<td></td>
<td>50% 40</td>
<td>50% orange juice</td>
</tr>
<tr>
<td>P.12.3.1</td>
<td>Herbs &amp; spices</td>
<td>MPPO</td>
<td>35</td>
<td>wheat flour</td>
</tr>
<tr>
<td>P.12.3.2</td>
<td>Salt</td>
<td>MPPO</td>
<td>10</td>
<td>none</td>
</tr>
<tr>
<td>P.12.4.1</td>
<td>Yeast</td>
<td>MPPO</td>
<td>60</td>
<td>ground nuts</td>
</tr>
<tr>
<td>P.13.1.1</td>
<td>Infant milk formula</td>
<td>MPPO</td>
<td>50</td>
<td>milk powder</td>
</tr>
<tr>
<td>P.13.1.2</td>
<td>Dried baby food</td>
<td>MPPO</td>
<td>55</td>
<td>instant soup</td>
</tr>
<tr>
<td>P.18.3.3</td>
<td>Hot pizza</td>
<td></td>
<td>20% 60</td>
<td>20% cheese, 20% tomato sauce, 60% of b-toast</td>
</tr>
<tr>
<td>P.18.4.1</td>
<td>Instant noodles</td>
<td>MPPO</td>
<td>35</td>
<td>noodles</td>
</tr>
<tr>
<td>P.18.4.2</td>
<td>Canned/preserved pasta</td>
<td>MPPO</td>
<td>40 % 40 60% 25</td>
<td>40 % cheese sauce, 60% tomato sauce</td>
</tr>
</tbody>
</table>
Five tasks to achieve objective of WP4.2

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(4) Migration modelling for multi-layer/multi-material packaging in contact with foods, including set-off and paper/board.

(5) Probabilistic modelling of concentration of FCS in packed foods and link to exposure modelling in WP8

(3) Partition constants between materials

- Approx. 50 kinetic partitioning experiments (= migration from a spiked donor material to an ‘empty’ acceptor material) measured
  - Between: LDPE, PA, PET, PP, PVC, Paper, Cardboard materials
  - Using: 18 model migrants
  - At: 20°C < T < 100°C

- Approx. 330 partition constants were derived and used for verification of a procedure for estimation of K-values based on the so-called ‘Vapour Pressure Index’ method (published by Piringer) => Task (4)
Five tasks to achieve objective of WP4.2

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(4) Migration modelling

Principle of the PROCEDURE for the estimation of partition constants for migrants between FCM contact layer and food, $K_{P/F}$

$K_{P/F}$ 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

(4) Migration modelling

Principle of the PROCEDURE for the estimation of partition constants for migrants between two multi-layer materials (polymers, cardboard), $K_{P1/P2}$ or $K_{P1/CB}$

For each of two polymers 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 applicable also to polymer/cardboard systems.

[The data sets derived from the above described material-to-material partitioning experiments were used for refinement of the procedure.]

⇒ Migrant specific $K_{P/F}$ values for any pair of neighbouring FCM materials of interest can be calculated

(5) Probabilistic Migration modelling

Needed: Distributions of realistic diffusion coefficients as well as partition constants for incorporation in the FACET software.

Step 1a: Partners FABES and INCDTIM developed a special software to evaluate in total 5078 data sets (from the project and external published data) to derive modelling parameters for calculation of distributions for diffusion coefficients in 36 standard materials.

Step 1b: Based on physico-chemical considerations, Facet industry group allocated these 36 standard materials to the encoded FACET materials (~ 75 entries for Plastics, ~30 entries for Adhesives, ~40 entries for Inks, ~ 40 entries for Paper&Board)

Step 2: Partners FABES and INCDTIM generated also modelling parameters for calculation of distributions of $K_{P/F}$ and $D_F$ values

⇒ All probabilistic modelling parameters established and corresponding numerical algorithms delivered to CRÈME
Limited Verification – some examples

Migration of Irganox 1076 from HDPE into sunflower oil
10 days@40°C

Distribution established by Partner FABES:
5000 x Monte-Carlo sampling of inputs and stochastic calculation of specific migration

Value range from FACET migration module:
10 iterations only per run

Measured value: 4.4 ppm

Migration of Chimassorb 81 from HDPE into olive oil
1 hour@70°C

Distribution established by Partner FABES:
5000 x Monte-Carlo sampling of inputs and stochastic calculation of specific migration

Value range from FACET migration module:
10 iterations only per run

Measured value: 11.5 ppm

Limited Verification – some examples

Migration of Caprolactam from PA into water
2 hours @ 40°C

Distribution established by Partner FABES:
5000 x Monte-Carlo sampling of inputs and stochastic calculation of specific migration

Measured value: 15.5 ppm

Value range from FACET migration module:
10 iterations only per run


Limited Verification – some examples

Migration of OS351 from PET/adhesive/HDPE multi-layer into cream - 668 hours @ 20°C

Distribution established by Partner FABES:
5000 x Monte-Carlo sampling of inputs and stochastic calculation of specific migration

Measured value: 59 ppm

Value range from FACET migration module:
10 iterations only per run

THANK YOU on behalf of all WP4.2 Partners!

- Fraunhofer IVV, Freising, Germany (coordination)
  Annika Seiler, Chintawat Tongchat, Dr. Roland Franz
- FABES GmbH, Munich, Germany
  Dr. Peter Mecse, Dr Otto Piringer
- EU DG Research, Joint research Centre, IHCP, Ispra, Italy
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