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

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flavourings | additives | contact materials
exposure task

European Commission

SEVENTH FRAMEWORK PROGRAMME

Project partners of WP4.2

- **Fraunhofer IVV, Freising, Germany (coordination)**
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- **FABES GmbH, Munich, Germany**
  Dr. Peter Mercea, Dr Otto Piringer
- **EU DG Research, Joint research Centre, IHCP, Ispra, Italy)**
  Dr. Catherine Simoneau & co-workers,
- **The Food and Environment Research Agency FERA, York, UK**
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- **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

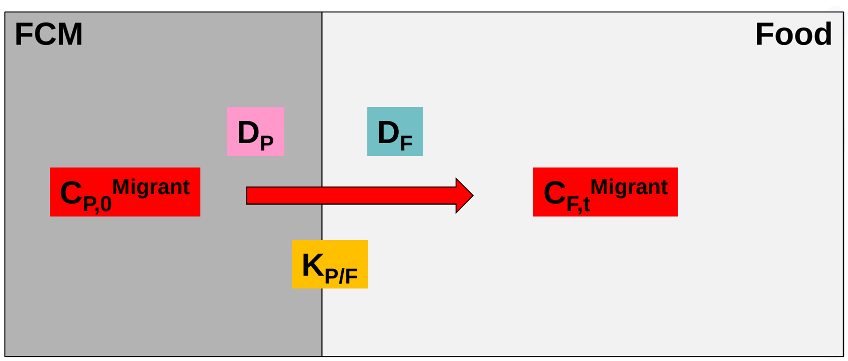
Overall objective of WP4.2

EXPOSURE$_{\text{from Food Packaging}}$ =

MIGRATION (Conc. in Food) x Food Consumption

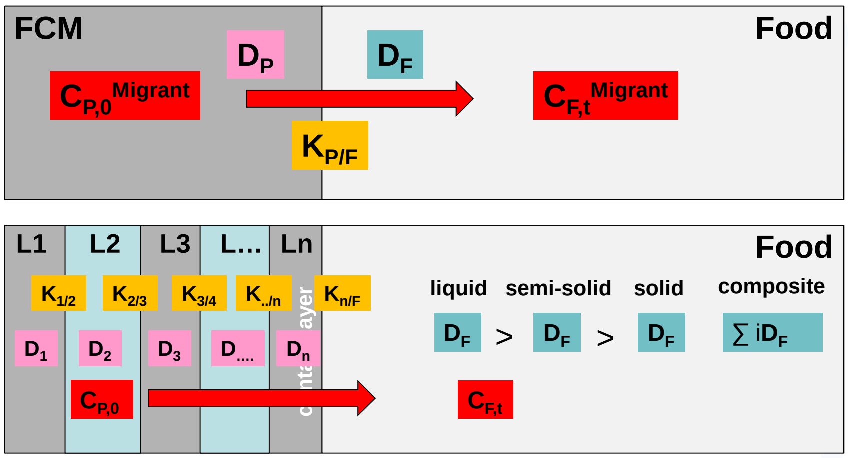
To establish a verified modelling tool for mono and multi-layer packaging materials for migration into foods under actual conditions of use in order <u>to deliver reliable concentration estimates for use in consumer exposure modelling</u>

A very ambitious undertaking …….

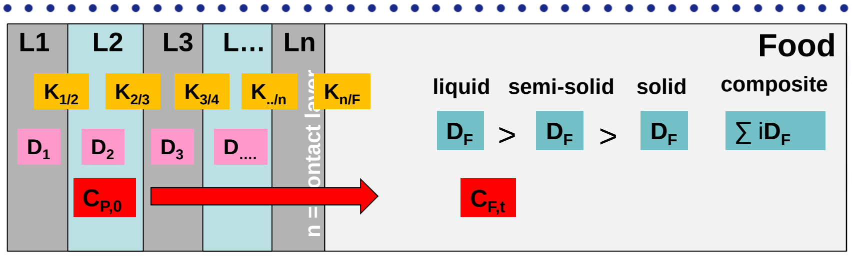


$$C_{F,t}^{Migrant} = f\,(C_{P,0}^{Migrant}, D_P, D_F, K_{P/F}, t, \text{packaging structure})$$

A very ambitious undertaking …….



A resolvable challenge?



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)

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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 Ko/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

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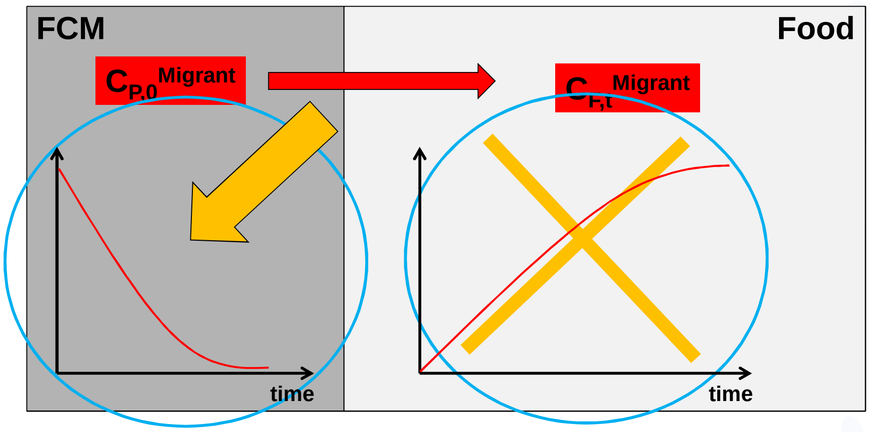
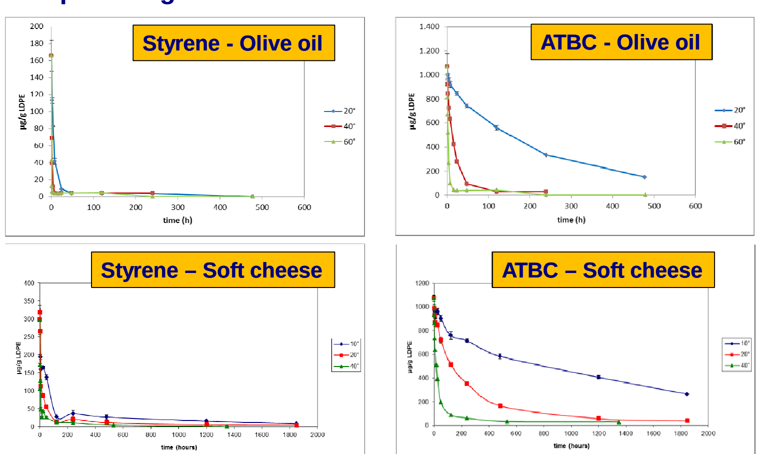
(1) Extensive kinetic migration studies



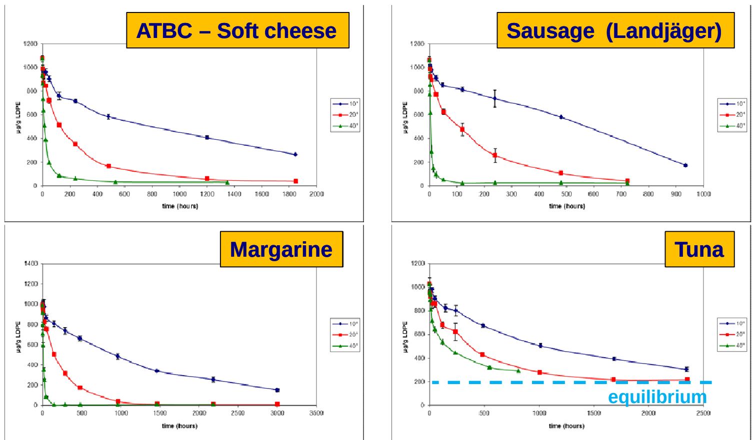
(1) Extensive kinetic migration studies

Examples: Migration from LDPE film – oil versus soft cheese



(1) Extensive kinetic migration studies

Examples: Migration ATBC from LDPE film – foods versus foods



(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 $K_{P/F}$ 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 ………

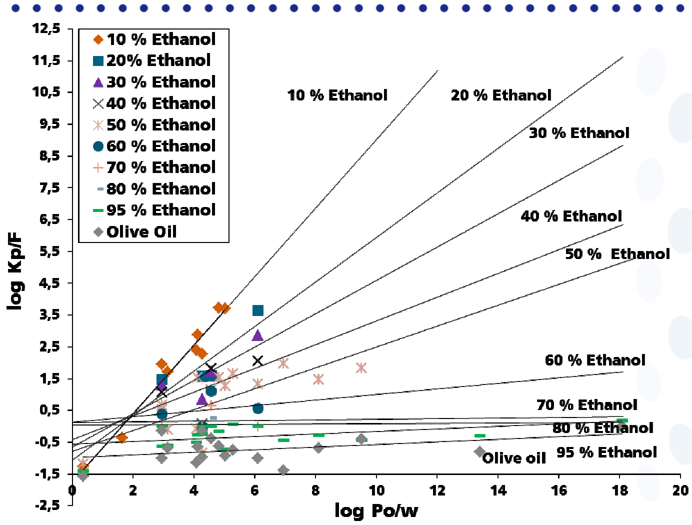
STEP 1:

Calibration of the system

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

- Published data

=> Plot:
log $K_{P/F}$ / log $P_{O/W}$



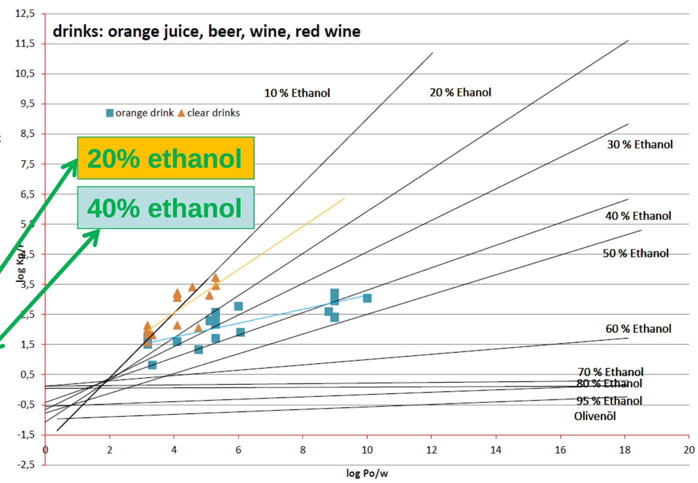
(2) New classification of foods ………

STEP 2:

Population of the system with food data

- $K_{P/F}$ data from Task (1)

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



(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

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

(2) New classification of foods ……

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

WP4_tier3	WP4_tier3 Name	Simulant according to PIM	Ethanol equivalency [% ethanol]	Equivalent to FACET WP4-2 model food
P.12.2.6	Instant soup	MPPO	55	instant soup
P.12.2.7	Hot vended soup		50% 40 50% 25	50% orange juice 50% apple sauce
P.12.3.1	Herbs & spices	MPPO	35	wheat flour
P.12.3.2	Salt	MPPO	10	none
P.12.4.1	Yeast	MPPO	60	ground nuts
P.13.1.1	Infant milk formula	MPPO	50	milk powder
P.13.1.2	Dried baby food	MPPO	55	instant soup
P.18.3.3	Hot pizza		20% 60 20% 25 60% 50	20% cheese, 20% tomato sauce, 60% of b-toast
P.18.4.1	Instant noodles	MPPO	35	noodles
P.18.4.2	Canned/preserved pasta	MPPO	40 % 40 60% 25	40 % cheese sauce, 60% tomato sauce

Five tasks to achieve objective of WP4.2

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(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

*) Principle published in Piringer&Baner (ed): Plastic Packaging – Interactions with Food and Pharmaceuticals(ed.), Wiley-VCH 2008, §4.3.4, pp. 109.

(4) Migration modelling

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

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

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facet

(5) Probabilistic Migration modelling

Needed: <u>Distributions</u> 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

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SEVENTH FRAMEWORK PROGRAMME

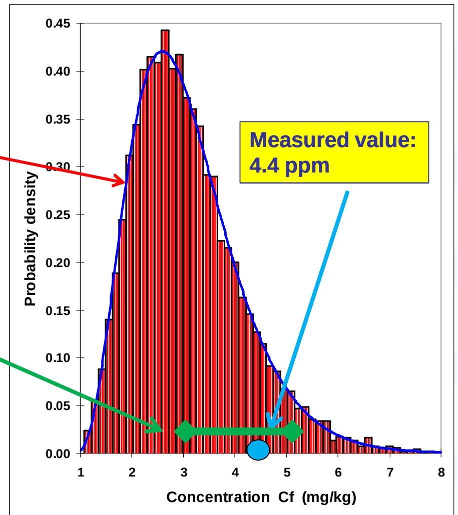
facet

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



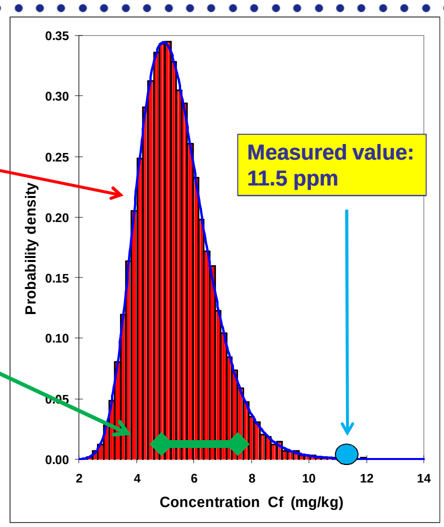
*)Stoffers et al., Food Additiv. Contam. Vol. 21, (12), 2004, pp. 1203–1216

Limited Verification – some examples

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



*)Stoffers et al., Food Additiv. Contam. Vol. 21, (12), 2004, pp. 1203–1216

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

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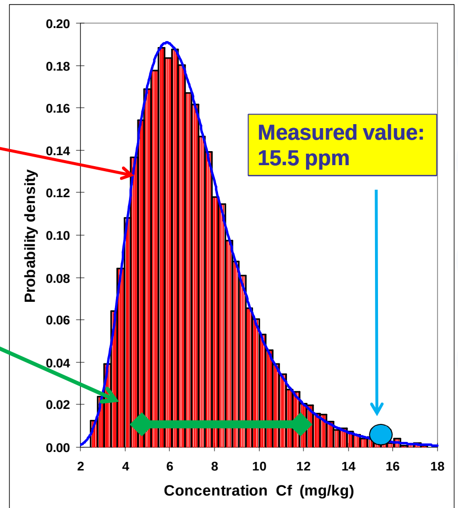

Limited Verification – some examples

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

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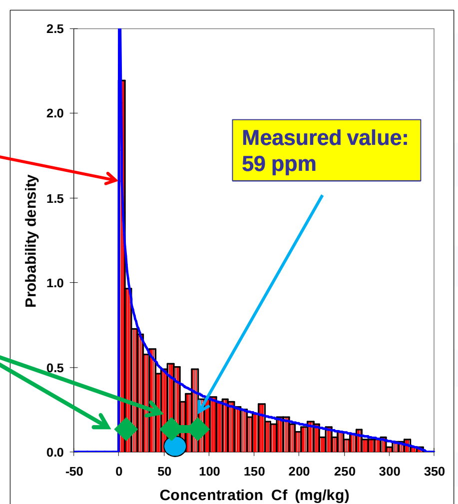

THANK YOU on behalf of all WP4.2 Partners!

- **Fraunhofer IVV, Freising, Germany (coordination)**
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