

# La conception d'emballages sûrs est à portée de main

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- ▶ UMR 1145 Ingénierie Procédés Aliments  
Equipe Interactions Matériaux et Milieux au Contact  
UMT SafeMat « Matériaux Sûrs »  
AgroParisTech site de Massy



# Anatomie d'une crise

## Les solutions (1..7)

## Conclusions

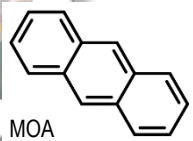
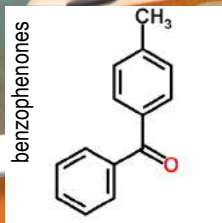
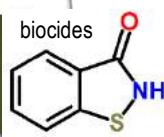
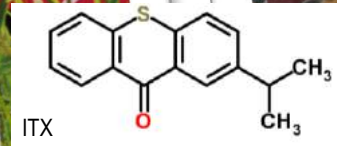
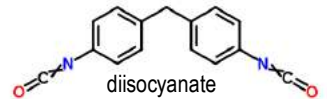
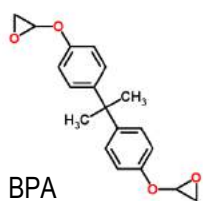
CONTENT



INRA  
SCIENCE & IMPACT

UMT  
SAFEMAT  
MATÉRIEL AU CONTRAINT  
DES ALIMENTES







Is it safe?  
How to assess it?  
How to grant it?



PENDANT PLUS

TOUTES LES SUBSTANCES AN

OUVRAGE soumis au Bureau  
Manufactures, revêtu de son  
sur l'invitation de S. Exc.

PAR APPERT

Propriétaire à Massy, Dépar  
ancien Confiseur et Distillat  
la Maison ducale de Christi

## LA CONSERVE ALIMENTAIRE

Bulletin mensuel de Vulgarisation Théorique et Pratique de Fabrication

PARAISANT LE 15 DE CHAQUE MOIS

Rédigé par un groupe de Fabricants-Industriels et de Chefs d'Emplois de cette Industrie



L'enseignement sera tout à la fois théorique et pratique.

Dans la voie pratique, le Comité de Direction se propose, non pas d'organiser une usine de fabrication de conserves et de produits alimentaires divers, destinée à concurrencer l'industrie libre, mais de créer des laboratoires d'essais et d'enseignement que dirigera un praticien qualifié et où chaque fabricant pourra venir se documenter et concourir aux progrès de la science alimentaire.

Les essais théoriques seront dirigés par un

Le règlement de 1908: « ...aucune substance alimentaire ne doit contenir de produit nuisible, produits chimiques... »

Nicolas APPERT  
(1750-1841)

**École Nationale  
D'INDUSTRIE ALIMENTAIRE**  
Nicolas Appert

COMITÉ DE DIRECTION  
Bourse du Commerce  
— Paris —

L'idée de la création de cette école dont nous avons été les plus fervents propagandistes vient d'être mise définitivement au point par un groupe de praticiens, de chimistes et d'agronomes distingués qui vont en assurer le fonctionnement.

l'enseignement à la question des machines, appareils et ustensiles employés par l'industrie alimentaire. Un ingénieur diplômé, M. RAYMOND MONOT, des usines de Diétrich, est chargé d'organiser cette partie du programme.

M. MORÉAL DE BRÉVANS, le distingué sous-directeur du laboratoire municipal, a bien voulu se charger de l'enseignement si important de la chimie appliquée à l'alimentation.

Enfin M. ED. JACQUET, ingénieur-agronome, administrateur de l'école, occupera la chaire de professeur d'« Alimentation Commerciale ».

Ajoutons que notre bulletin transformé en revue bi-mensuelle à laquelle collaboreront désormais les personnalités ci-dessus, devient le Bulletin Officiel de l'École.

En un mot et suivant l'exemple d'autres pays, une Université nouvelle et bien moderne vient de naître en France, celle de l'Industrie Alimentaire. Cette industrie quitte ainsi, définitivement, le domaine empirique pour rentrer dans celui des sciences exactes, où elle avait

sa place déjà marquée par les exigences et le progrès sans cesse grandissants de la vie contemporaine.

Pour le Comité de Direction :  
Aug. CORTHAY.

## Causerie Professionnelle par Nicolas APPERT

### Méflons-nous des Conservés Étrangères

Nous donnons ci-dessous la traduction d'un extrait du passage que M. Hamel consacre à la législation et l'inspection des conserves alimentaires au Canada, dans le traité qu'il publie en ce moment. (Modern practice of canning meats):

« Comparés avec les règlements qui ré-

« Nous comprenons bien que les chimistes du Ministère sont là pour condamner tout produit alimentaire où l'analyse révélerait la présence d'un produit chimique dangereux, mais pour ceux qui sont au courant des discussions en cours entre les hygiénistes les plus distingués du monde entier au sujet de la plus ou moins grande nocivité de tel ou tel antiseptique, la satisfaction est maigre.

« Je répète que le fabricant de conserves en boîtes n'a pas besoin d'antiseptiques pour assurer la conservation indéfinie de ses produits. La stérilisation lui suffit.

« Pourquoi donc ne pas faire comprendre au monde entier que les mots « CANADA APPROVED » de l'étiquette signifient absence entière de substances nuisibles, aussi bien dans les conserves que dans les viandes fraîches.

« Que si quelques antiseptiques sont considérés comme inoffensifs par le Ministère de l'Agriculture, pourquoi ne pas faire connaître de ce

Pour protéger les fabricants Canadiens contre la concurrence des États-Unis, il était nécessaire de créer une législation, au moins sur le papier.

« Je ne parle pas ici de l'inspection des viandes fraîches qui est soumise à un groupe de savants et de vétérinaires de valeur.

« Mais l'acheteur éclairé de conserves alimentaires quelles qu'elles soient, viandes, poissons, fruits ou légumes est loin d'avoir obtenu la même sécurité.

« Le règlement en date de 1908 qui régit l'inspection des conserves alimentaires nous dit : Aucune substance alimentaire ne doit contenir de produit nuisible, produits chimiques, colorants ou antiseptiques, et plus loin on nous dit : Il sera fourni aux Inspecteurs par les soins du Ministère de l'Agriculture les noms des antiseptiques et colorants inoffensifs dont l'emploi est permis. L'addition de tout autre empêchera le produit de recevoir l'étiquette constatant l'inspection.

en considération la qualité de la soudure employée, pas plus que celle de l'acide, et il semble que sur ce point les japonais sont bien en avance sur nous lorsqu'ils donnent les commandes pour leur armée.

« Pour en finir, il semble que des instructions plus complètes auraient été pour le plus grand intérêt du fabricant lui-même, en donnant au public consommateur une garantie parfaite de sécurité. La consommation en aurait été accrue en regagnant la confiance des consommateurs qui sont peu confiants dans les conserves, généralement sans raisons, d'ailleurs. »

G. T. HAMEL, ingénieur.

L'auteur faisant une œuvre purement technique et non de polémique est évidemment très modéré. Mais pour qui lit entre les lignes et pour nous qui savons combien sont rares parmi le personnel de l'inspection les gens compétents, toutes les places étant prises par les politiciens, nous ne nous sentons pas rassurés.

## Italian police seize contaminated Nestle baby milk

22 Nov 2005 16:45:09 GMT

Source: Reuters



(Adds Tetra Pak comment in paragraph 11)

By Massimiliano Di Giorgio and Isabel Strassheim

ROME/ZURICH, Nov 22 (Reuters) - Italian police seized around 30 million litres of baby milk produced by Swiss food giant Nestle <NESN.VX> on Tuesday after tests showed it was contaminated with traces of ink used in the packaging.

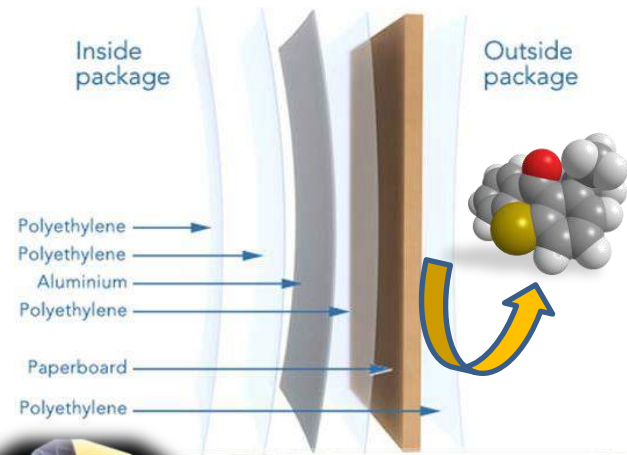
Nestle said the chemical substance was not harmful, but announced it was recalling the infant food in four European countries, including Italy, because of the problem, which related to Tetra Pak cartons.

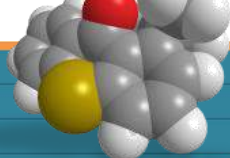
Italian Agriculture Minister Gianni Alemanno demanded tests to see if babies given the contaminated milk over a prolonged period faced health risks.

"It is incredible that such defenceless beings as babies should face such serious risks in a product as widely used as milk," Alemanno said in a statement.

Italian officials said they had already seized about 2 million litres of Nestle baby milk earlier this month after finding traces of isopropylthioxanthone (ITX), an ink component used in the offset printing process of the Tetra Pak cartons.

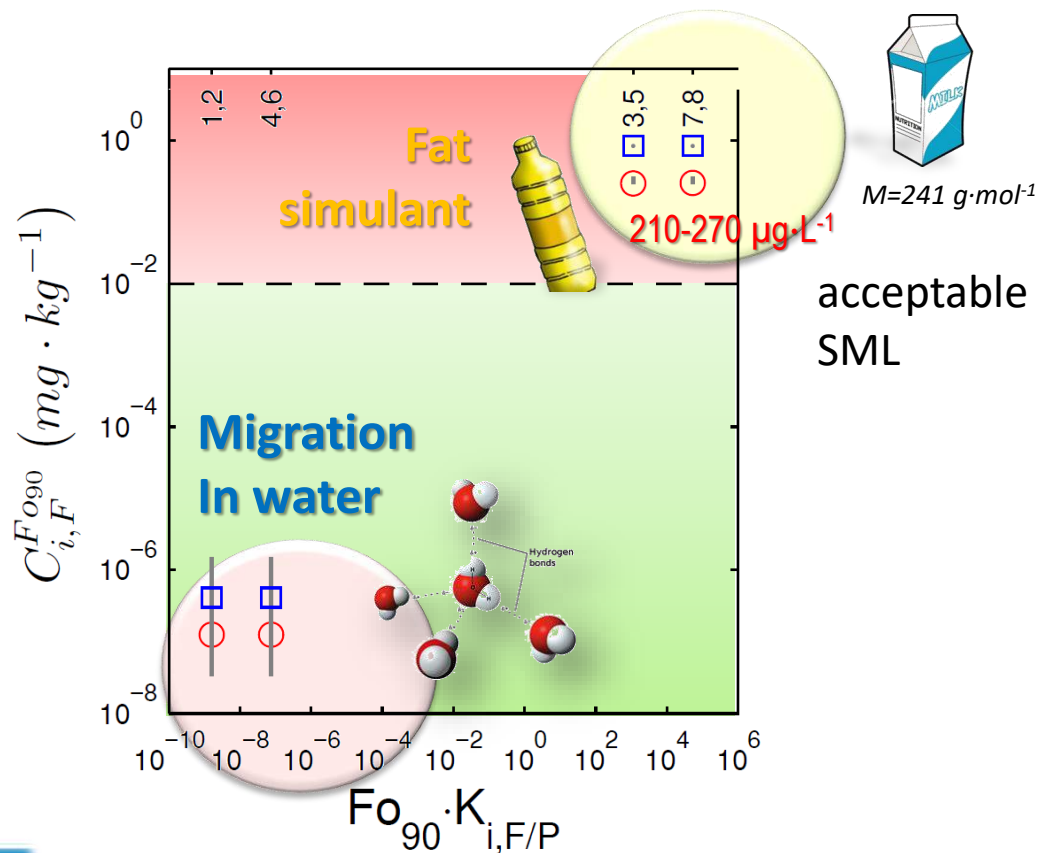
"It is incredible that such defenseless beings as babies should face such serious risks in a product as widely used as milk"





|                                                 | Migrant                                                         | 2-ITX                                                                 |
|-------------------------------------------------|-----------------------------------------------------------------|-----------------------------------------------------------------------|
|                                                 | Homologous migrant†                                             | not available                                                         |
|                                                 | Polymer                                                         | LDPE††                                                                |
| PARAMETER                                       | notation (unit)                                                 |                                                                       |
| Thickness                                       | $l_p$ (μm)                                                      | 50                                                                    |
| Volume dilution ratio                           | $L_{F/P}$ (-)                                                   | 360                                                                   |
| Biot mass number                                | $Bi$ (-)                                                        | $10^3$                                                                |
| Contact Time                                    | $t$ (days)                                                      | 90                                                                    |
| Temperature                                     | (°C)                                                            | 4                                                                     |
| Likely initial concentration <sup>a</sup>       | $\bar{C}_{i,P}^0$ <sup>a</sup> (mg·kg <sup>-1</sup> )           | $100 \pm 10$                                                          |
| Conservative initial concentration <sup>b</sup> | $(C_{i,P}^0)^+$ <sup>b</sup> (mg·kg <sup>-1</sup> )             | 300                                                                   |
| Likely diffusion coefficient <sup>c</sup>       | $\bar{D}_{i,P}$ <sup>c</sup> (m <sup>2</sup> ·s <sup>-1</sup> ) | $8.4 \cdot 10^{-16}$<br>[ $7.6 \cdot 10^{-16}$ $9.2 \cdot 10^{-16}$ ] |
| Conservative diffusion coefficient <sup>d</sup> | $D_{i,P}^+$ <sup>d</sup> (m <sup>2</sup> ·s <sup>-1</sup> )     | $3.9 \cdot 10^{-14}$                                                  |
| Likely partition coefficient <sup>e</sup>       | $\bar{K}_{i,F/P}$ (-)                                           | $1.4 \cdot 10^{-9}$<br>[ $3.7 \cdot 10^{-10}$ $5.1 \cdot 10^{-9}$ ]   |
| Conservative partition coefficient              | $K_{i,F/P}^+$ (-)                                               | $10^3$                                                                |

Food Additives and Contaminants, 2009, 26(12), 1556-1573.

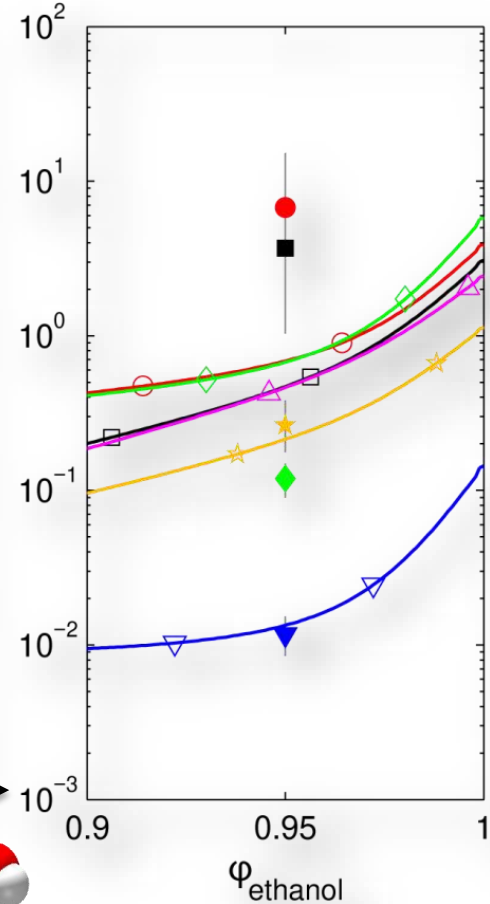
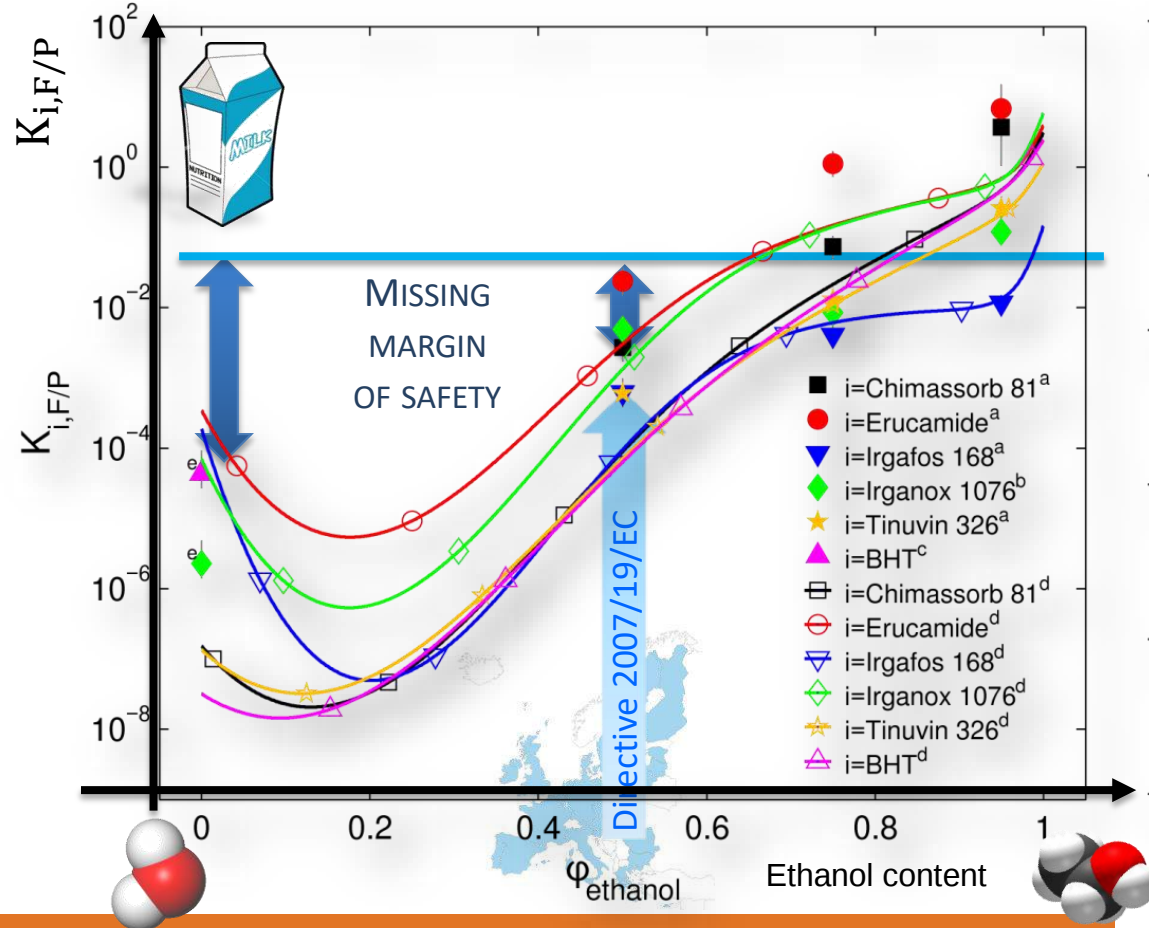


|    | Date of case | Last change | Reference | Country |
|----|--------------|-------------|-----------|---------|
| 6. | 08/09/2005   |             | 2005.631  | ITALY   |

**RASFF Portal**

food contact materials

migration of isopropyl thioxanthone (250  $\mu\text{g/L}$ ) from packaging of milk for babies from Spain



# SOLUTION 1

**Modeling**

solution 3

solution 4

solution 5

solution 6

solution 7

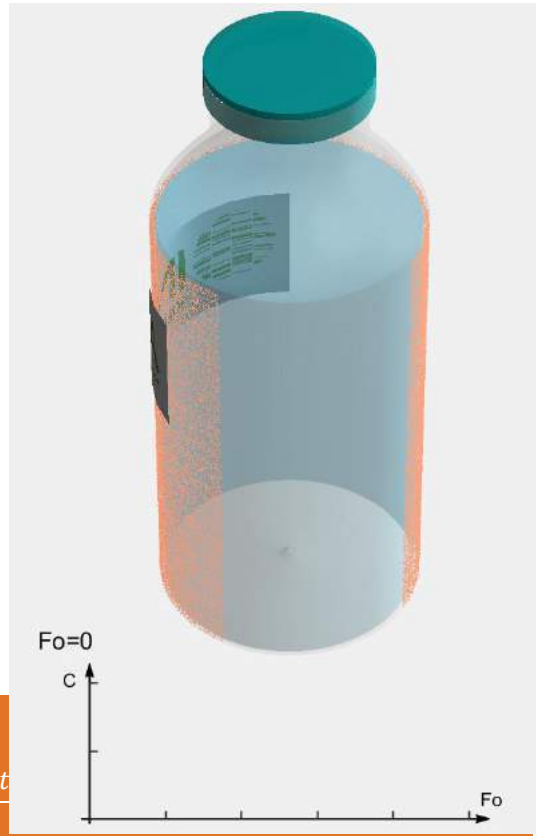
## Conclusions

# MIGRATION: SOME TYPICAL CASES

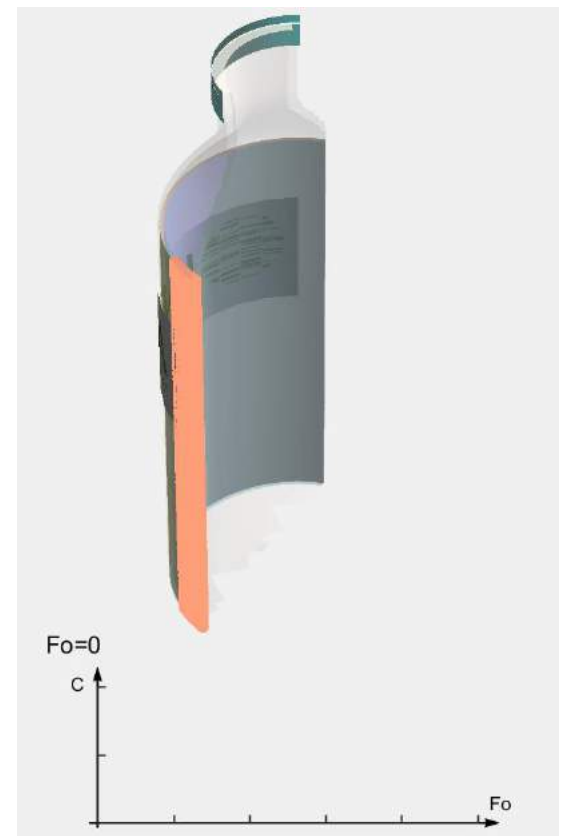
monolayer



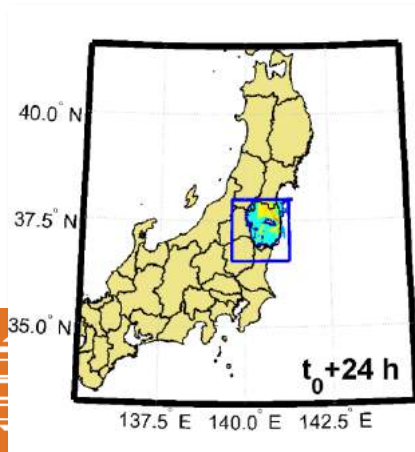
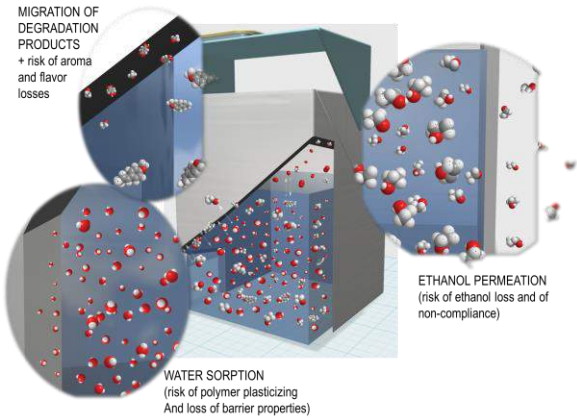
with barrier to diffusion



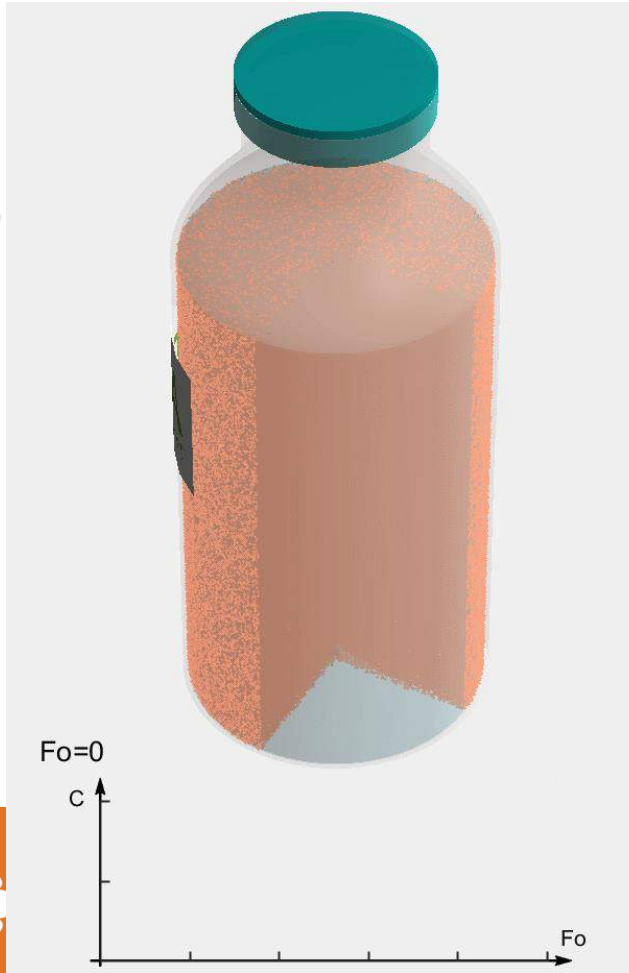
multilayer



$$Fo = \frac{D_P t}{l_P^2}$$

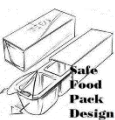


## alcoholic beverages



## radionuclides





## FMECA « milk for infants stored in a brick »

| Formulation | Design | Process | Informations | Mechanisms |
|-------------|--------|---------|--------------|------------|
|-------------|--------|---------|--------------|------------|

**Formulation**

- monomers (plastics, adhesives)
- catalysts
- antioxidants
- lubricants
- biocides (cardboard, ink)
- mineral oil (cardboard)
- solvents
- photoinitiators
- other residus (NIAS)

**Highly concentrated**

- antioxidants, lubricants, biocides
- mineral oils, photoinitiators
- monomers, catalysts, solvents
- other residues

**design**

**two components:**

- brick body (4 materials, 5 layers)
- cap (two materials incl. the sealing system)

**six materials**

- LDPE, PP (cap)
- aluminum foil
- cardboard (origin)
- « ink »

**Barri**

- Mat
- rese
- weig
- Mat
- rese
- mol
- cont

**Process**

- production, storage, assembly of materials
- assembly and storage of components
- printing (printing technology, curing/drying,...)
- storage of empty packaging
- aseptic packaging filling (temperature, pretreatment,...)
- storage and retailing of the bricks filled with milk

**Informations**

- identity & assembly
- formula (substar or not)
- test con the risk
- conditio packagi consum

**My Information**

My user: **demouser** (change user)  
My project: **common** (change project)  
My database: **common2013a.sfp3.database.xml**  
My Application: **Diffusion\_1DFV2n** (change application)

INRA/SFP3 - 2013-04-18 22:03:53

**Archived simulations or templates**

acetaldehyde\_PET3  
Import properties from a previous result file in the current form  
(geometry) (formulation) (contact conditions) (transport prop.) (all)  
Import a concentration profile  
(Concentration profile)  
Clear all properties in the current form  
(form reset)  
Search migrants/data: Migrants (H,B,ML,...) Transport Properties  
named/UPAC Acetaldehyde

**Contact conditions**

L\_P 100 mF m<sup>2</sup> import  
V\_F cm<sup>3</sup> import  
A\_F cm<sup>2</sup> import  
rho\_F 1 kg m<sup>-3</sup> or g cm<sup>-3</sup> import  
rho\_F 1 kg m<sup>-3</sup> or g cm<sup>-3</sup> import

**Layer selector**

Layer 1  
L\_P 300 μm import  
rho\_P 1 kg m<sup>-3</sup> or g cm<sup>-3</sup> import  
K\_F/P 0.1 import T  
D\_P 1e-015 m<sup>2</sup> s<sup>-1</sup> import T  
Conc. 50 ppm import

**Help**

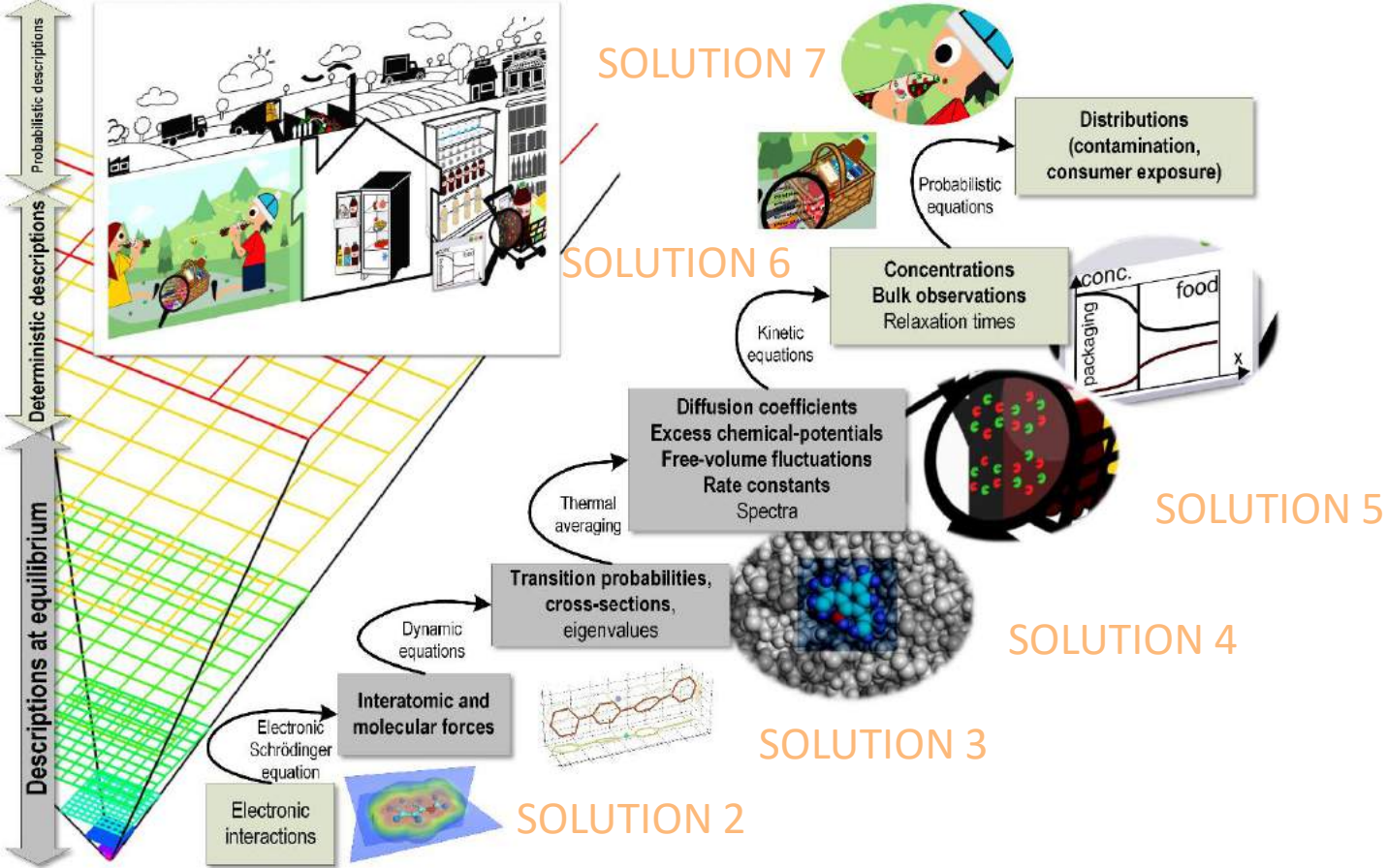
**Acetaldehyde**  
Name: Acetaldehyde (Acetic aldehyde/Ethanal/Ethyl aldehyde/CH3CHO/Acetaldehyd/Aldéhyde acétique/Aldéhyde acéte/WC-C2602,...)  
CAS: 75-07-0  
REF: 10060  
InChIKey: HXWJQKUNTFH-WHFPODA-N  
Formula: C2H4O  
M: 44.053 g/mol  
SMIL: 6 ppm  
EFSA: Group TDI = 0.1 mg/kg b.w. (calculated as acetaldehyde (including 10060 and 23020))  
Toxicity profiles similar to methaldehyde. A 2-year oral rat study and a 3-generation oral rat study including teratogenicity with methanethaldehyde. The reports on nasal carcinogenicity after inhalation were considered without relevance for effects from oral intake of smaller doses, (adopted at 113rd SCF meeting) (17-18 September 1998).  
http://europa.eu.int/comm/food/fs/sc/scf/out16\_en.html  
FIH Regulation: + sensitive / or

Acceptable threshold or specific migration limit: 6 ppm

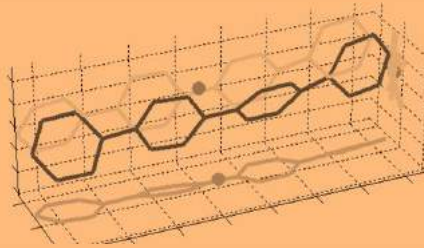
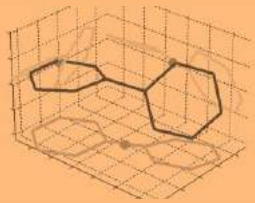
SFP3: a framework to deploy migration simulation and decision tools  
SAFE FOOD PACKAGING PORTAL ©INRA/Olivier Vitrac

**Step 1**

**Step 4**



*Food Research International 2017, 88, Part A, 91-104.*



# SOLUTION 2

**additives with low  
diffusion coefficients**

solution 3

solution 4

solution 5

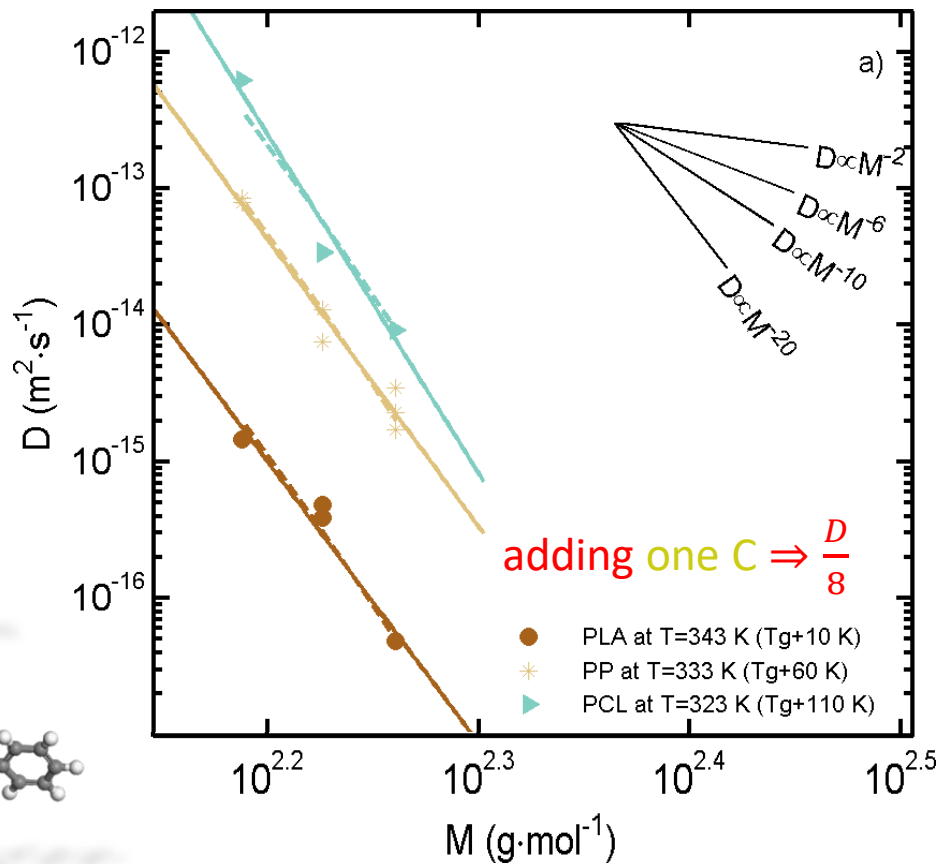
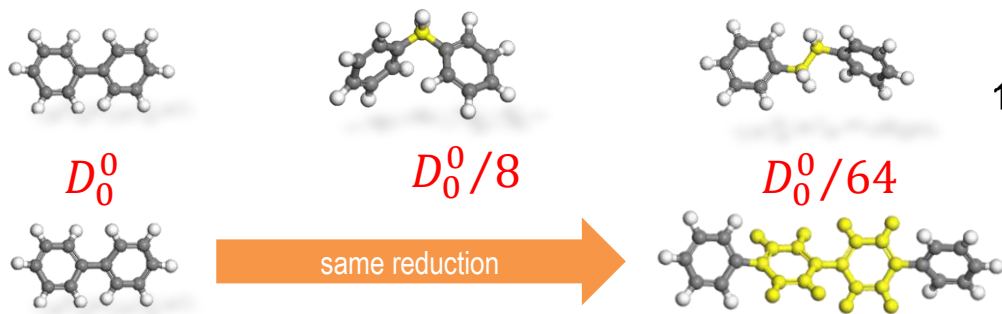
solution 6

solution 7

Conclusions



$$D(M, T, T_g) = D_0 \exp\left(-\frac{E_a^{blob}}{RT}\right) \times \exp\left(-\frac{E^{*(M)} - E_{blob}^*}{RT}\right) \left(\frac{M}{M_{blob}}\right)^{-\alpha(T, T_g)}$$



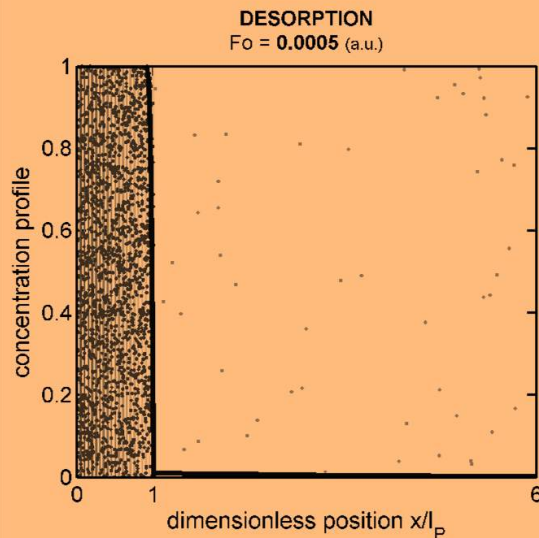
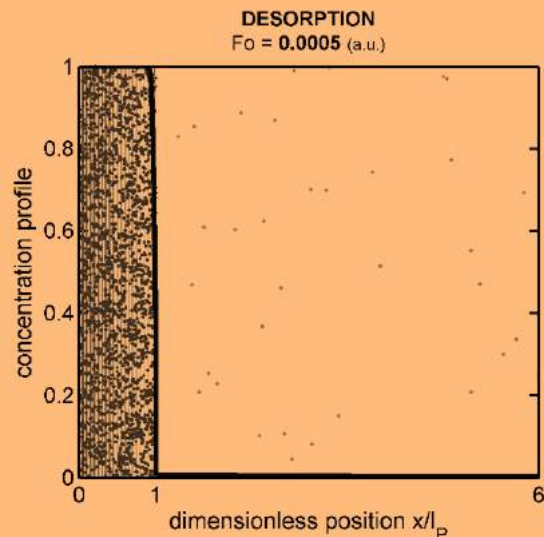
$K_{i,P}/F=$

50

50 times for chemical affinity for P

1/50

50 times for chemical affinity for F



# SOLUTION 3

**Solubility barrier  
for apolar or low  
polar substances**

solution 4

solution 5

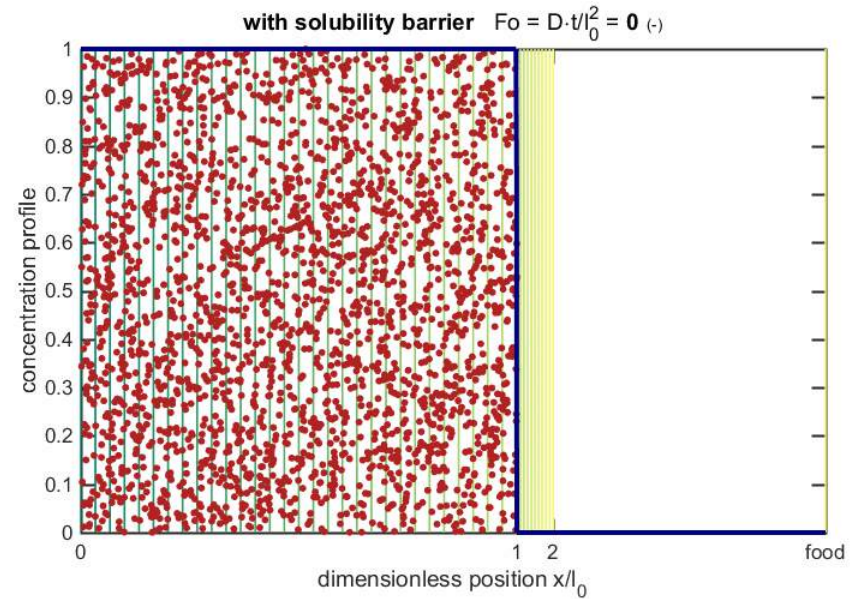
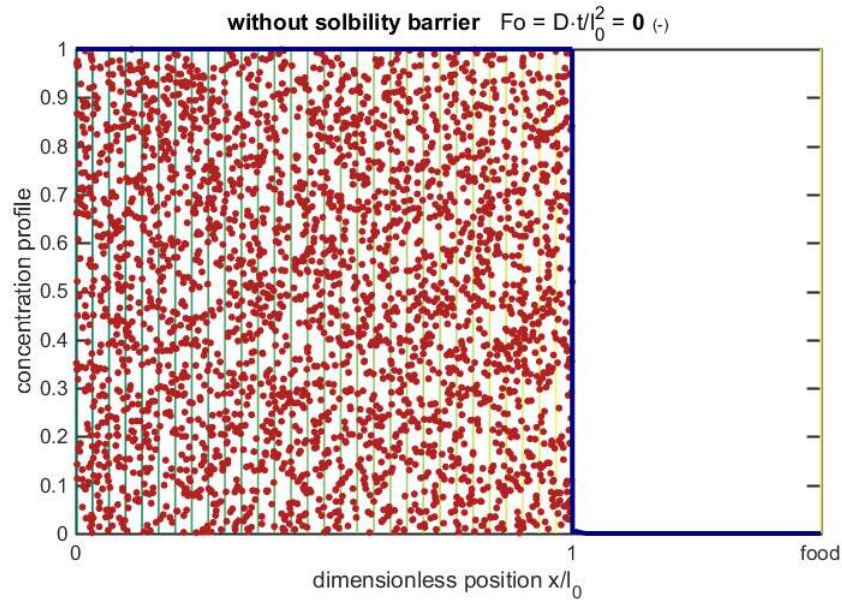
solution 6

solution 7

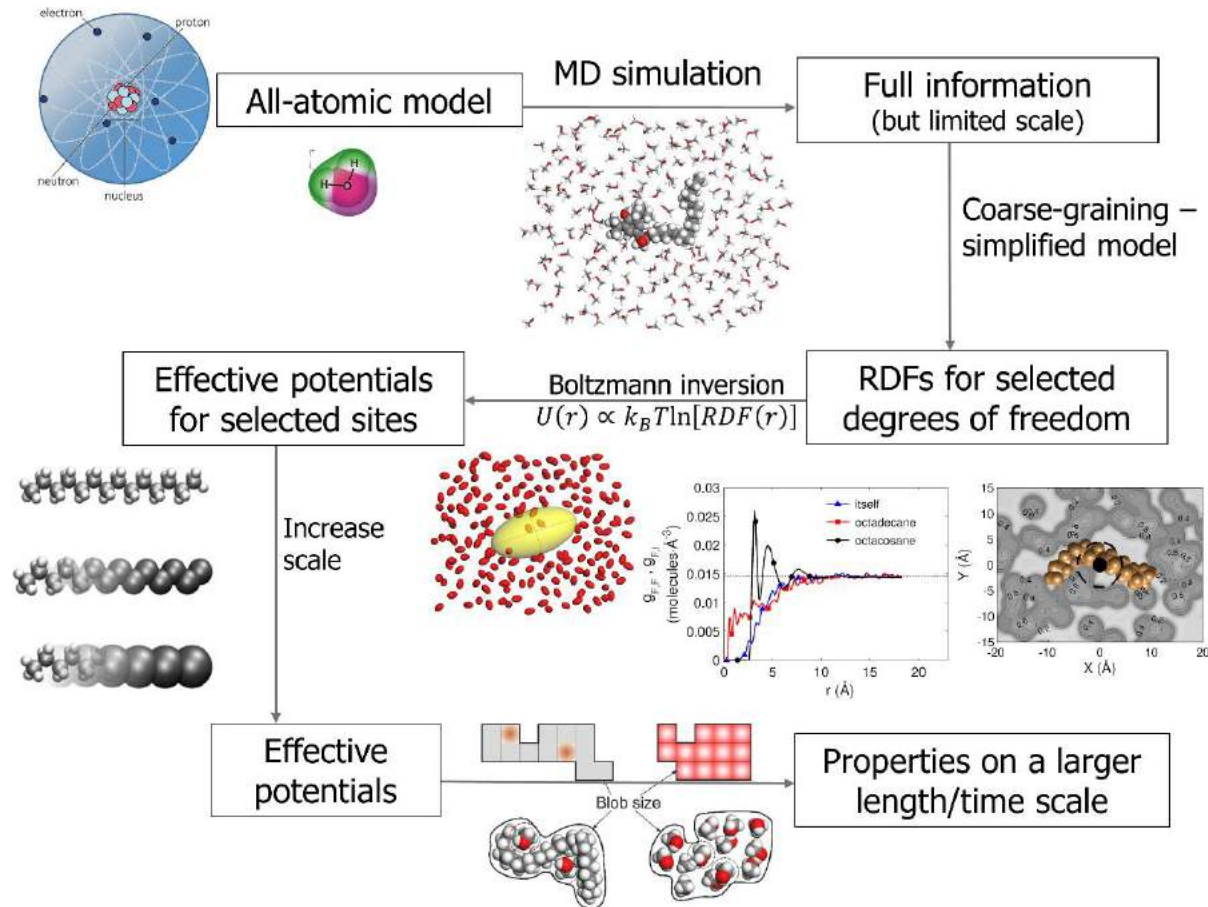
Conclusions

# THE CONCEPT OF SOLUBILITY BARRIER

## CHANGING THE CHEMICAL AFFINITY CLOSE TO THE SURFACE



**Excess mixing  
enthalpy:**  
atomistic scale



**Excess mixing  
Entropy:** coarse  
grained repre-  
sentations

*Food Research International* **2017**, *88*, 91-104.

*Journal of Polymer Science Part B: Polymer Physics* **2014**, *52*, 1252-1258.

*Journal of Chemical Reactor Engineering* **2010**, *8*.

*Industrial & Engineering Chemistry Research* **2010**, *49*, 7263-7280 ; **2009**, *48*, 5285-5301.

PE

EVA33

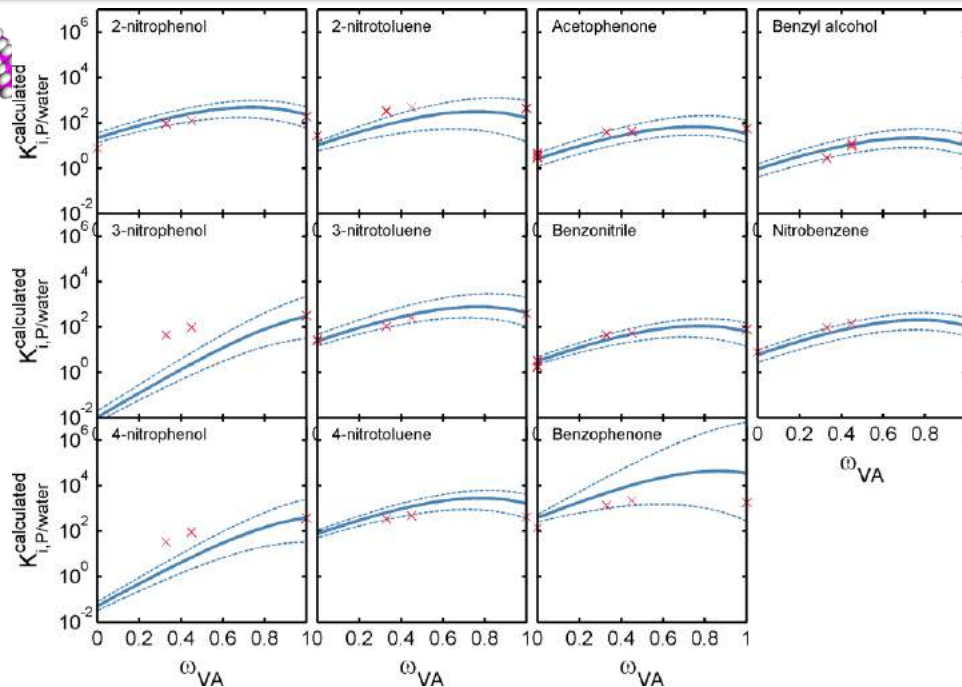
EVA45

PVAc

ACETYLATION RATE FROM 0 TO 100%

APOLAR

POLARITY++



**INRA**  
SCIENCE & IMPACT

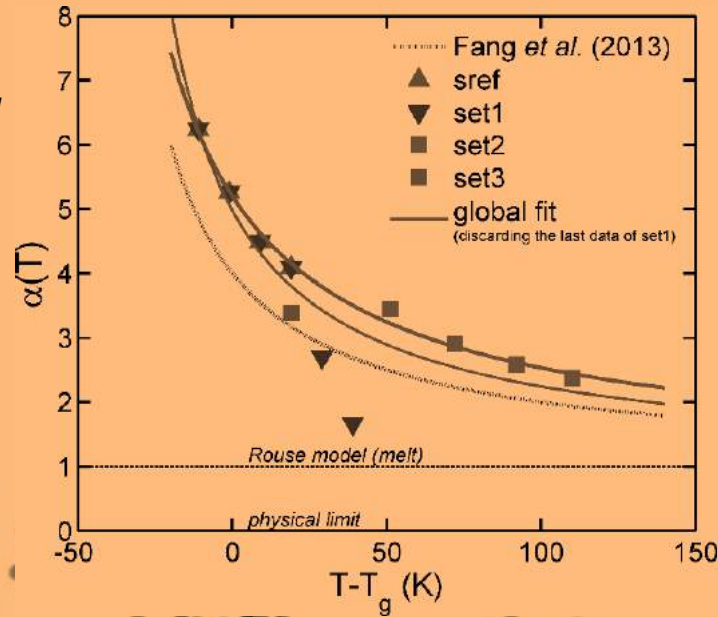
Industrial & Engineering Chemistry Research **2017, 56, 774–787.**



CARREFOURS  
DE L'INNOVATION AGRONOMIQUE

$$D_1 = \bar{D}_0 \exp\left(-\frac{E^*}{RT}\right) \exp\left(-\frac{\xi}{0.24} \alpha_{probe}^{(T, T_g)}\right)$$

$$\alpha(T, T_g) = \begin{cases} 1 + \frac{K_\alpha}{T - T_g + K_\beta} & \text{for } T \geq T_g \\ 1 + \frac{K_\alpha}{\frac{\alpha_2^g}{\alpha_{c2}}(T - T_g) + K_\beta} & \text{for } T < T_g \end{cases}$$



# SOLUTION 4

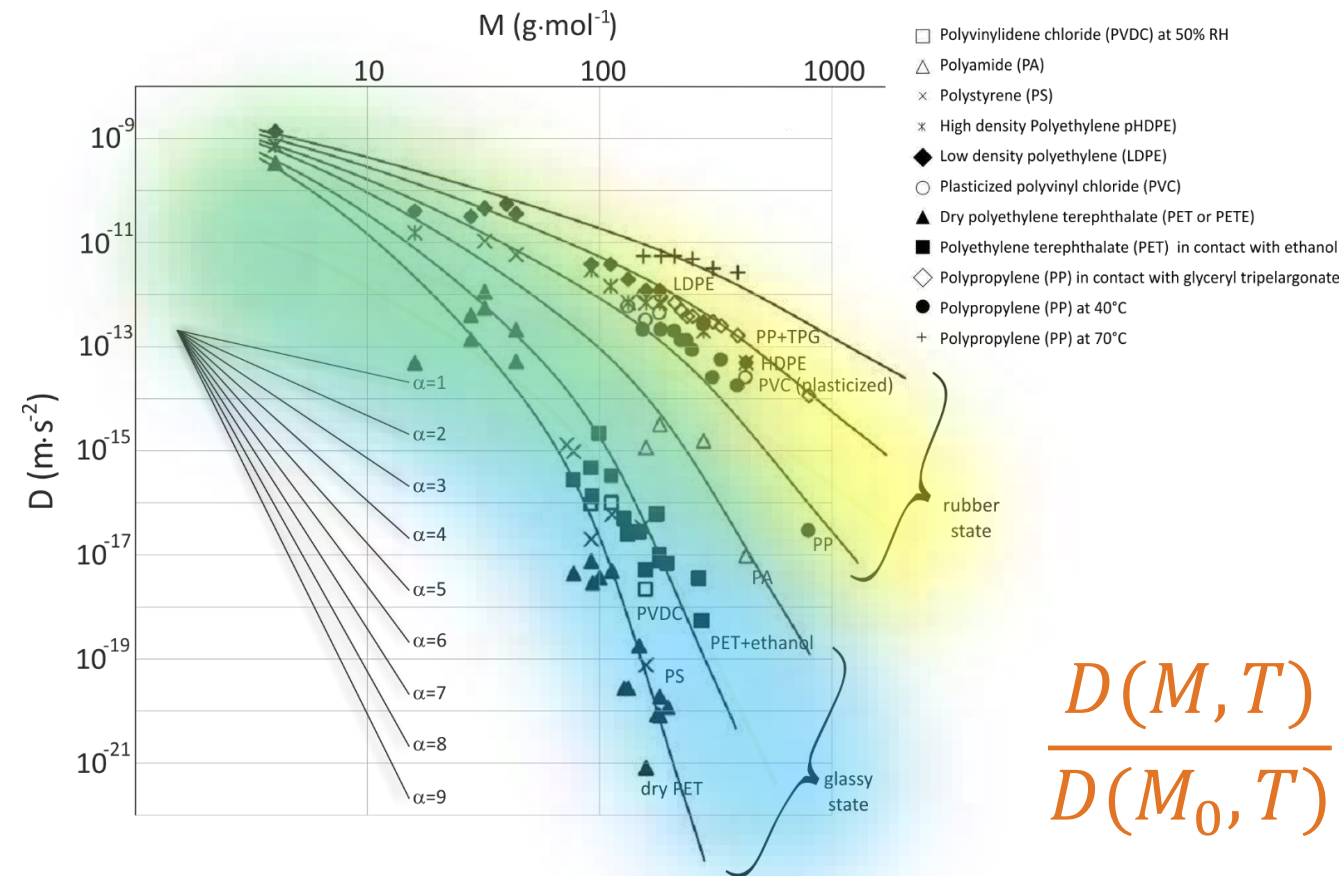
Diffusion barrier with  
materials with high  $T_g$   
polar substances

solution 5

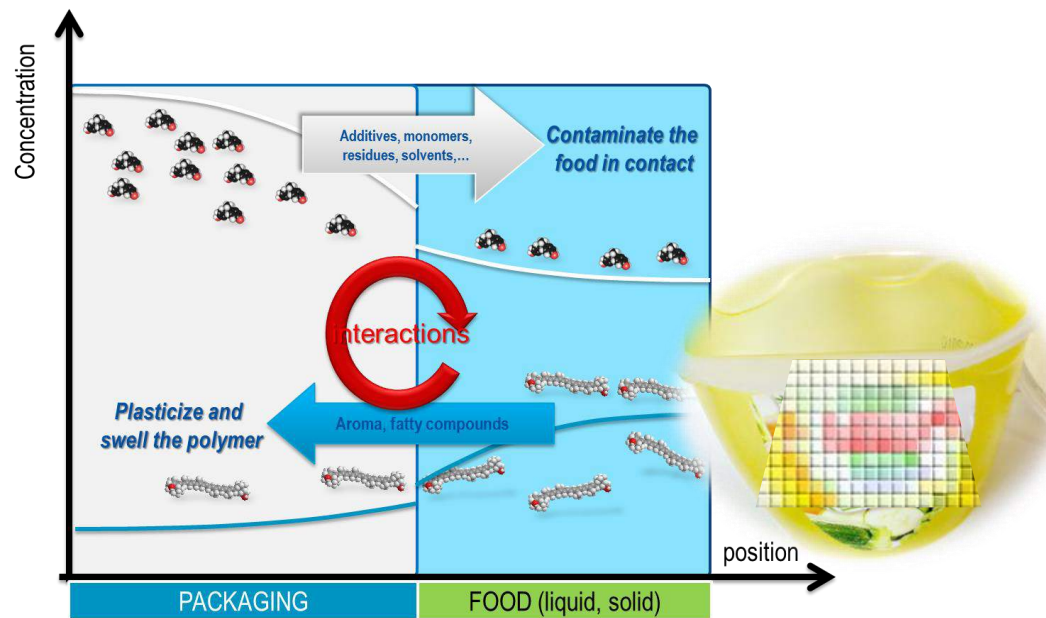
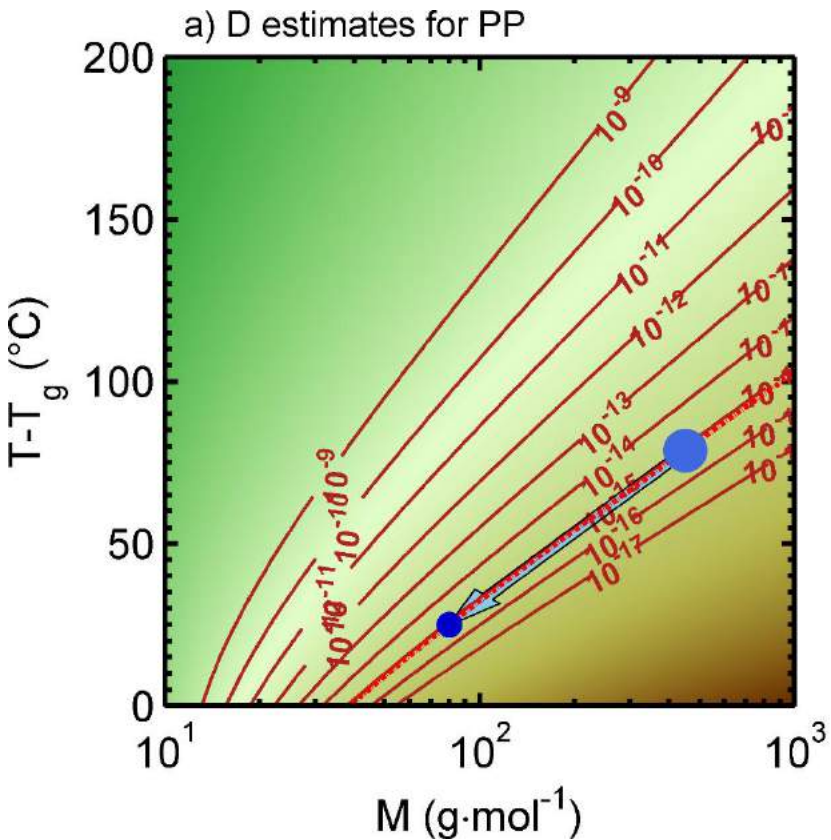
solution 6

solution 7

Conclusions



$$\frac{D(M, T)}{D(M_0, T)} \propto \left( \frac{M}{M_0} \right)^{-\alpha(T, T_g)}$$



## SOURCES DE CONTAMINATION DES ALIMENTS PAR LES HUILES MINÉRALES



# SOLUTION 5

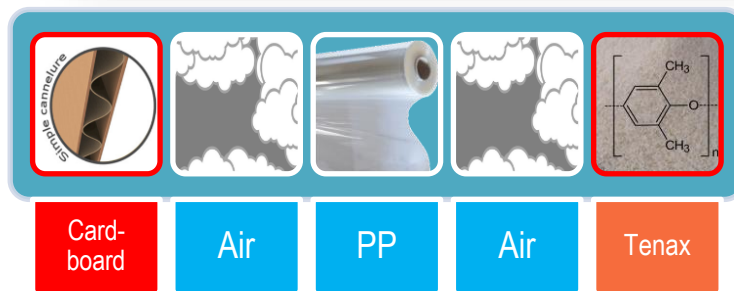
Adding a gas phase  
to slowdown migration

solution 5

solution 6

solution 7

Conclusions



## SURROGATES (I)

Decane (C10)

Tetradecane (C14)

Hexadecane (C16)

Octadecane (C18)

Eicosane (C20)

Tetracosane (C24)

Octacosane (C28)

Dibutyl phthalate (DBP)

Bis(2-ethylhexyl) phthalate (DEHP)

Benzylbutyl phthalate (BBP)

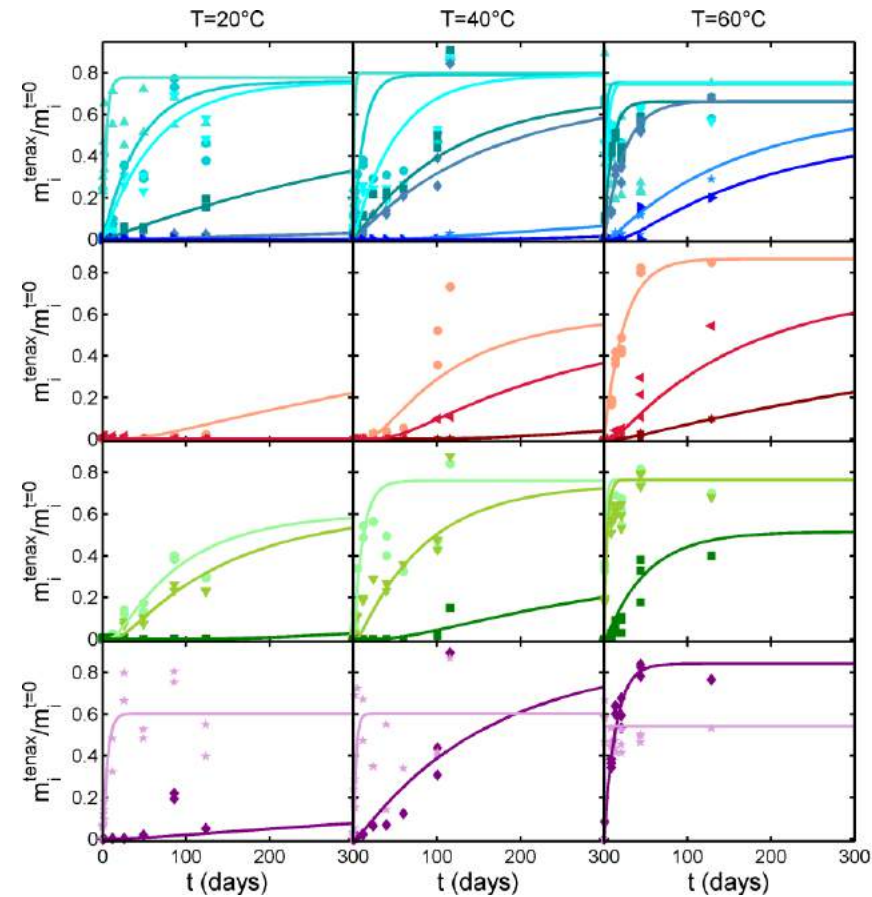
Benzophenone

4-methyl benzophenone (MBP4)

Isopropyl-9H-thioxanthen-9-one

Anthracene

Naphthalene

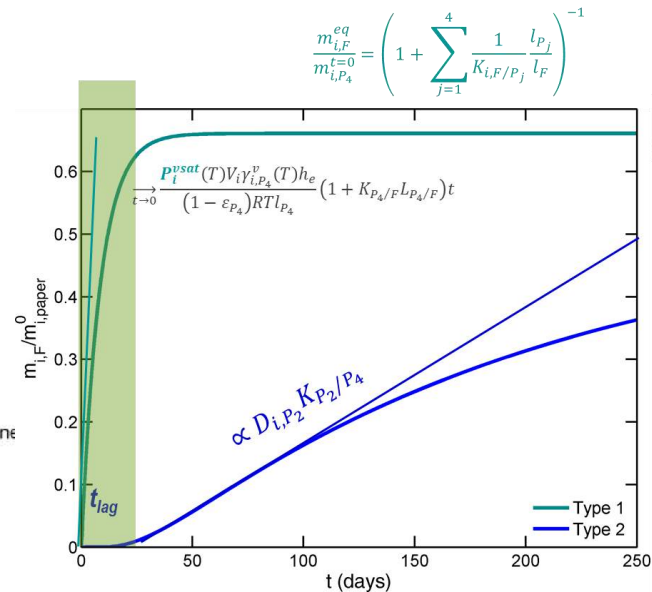


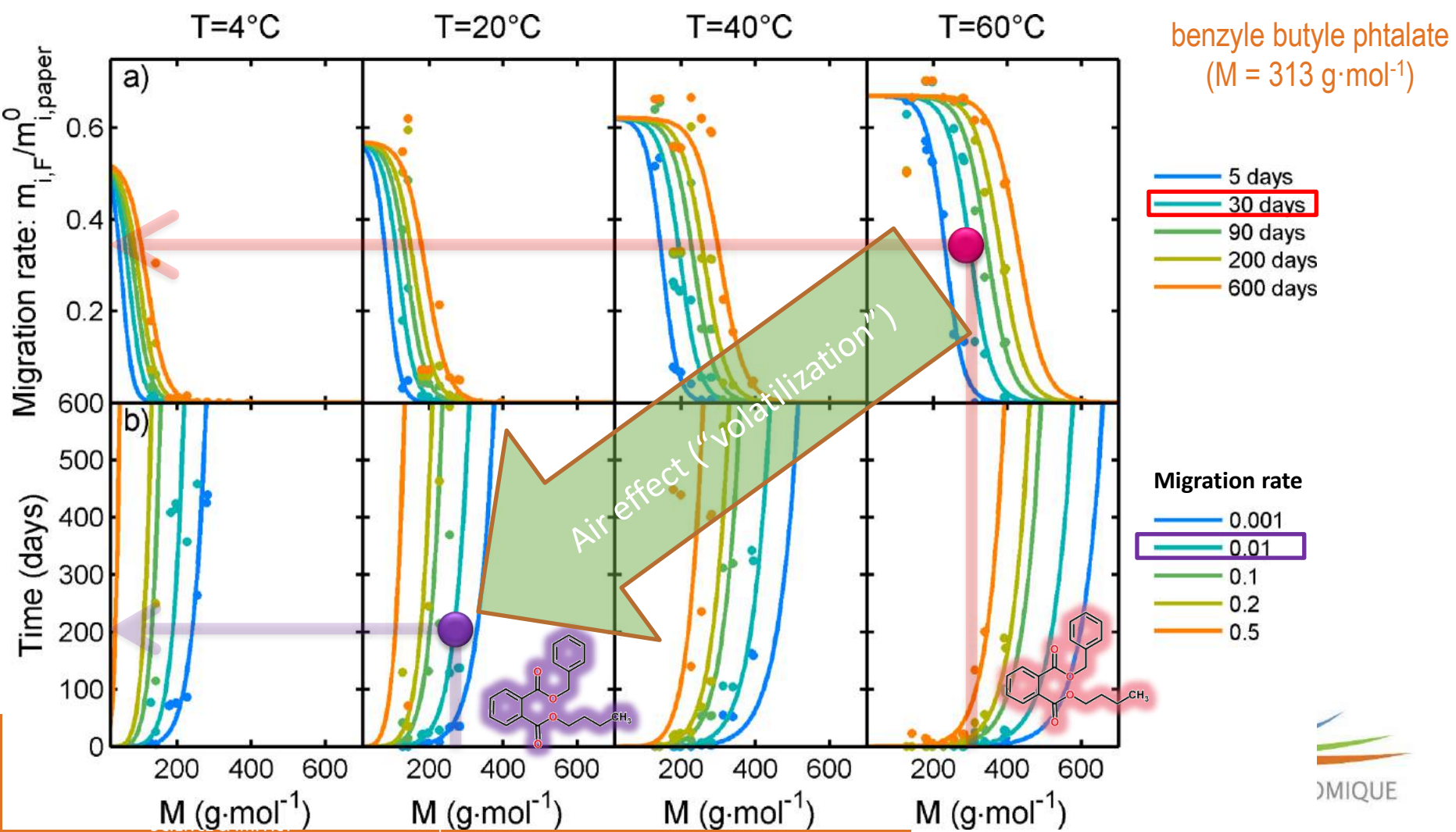
▲ C10  
 ● C14  
 ▼ C16  
 ■ C18  
 ◆ C20  
 ★ C24  
 ▲ C28

● DBP  
 ◆ DEHP  
 ▼ BBP

● Benzophenone  
 ▼ MBP4  
 ■ ITX

◆ Anthracene  
 ★ Naphthalene

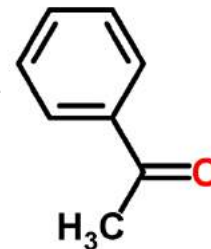




## >> FMECAKairP acetophenone

LOAD\_CHEMSPIDER extraction of ChemSpiderID=7132 ('acetophenone') completed in 10.26 s  
LOAD\_CHEMISPIDER: updated cache  
7132.mat 21-sept.-2015 21:37:19 77.6 kBytes C:\Data\Olivier\INRA\Codes\MS\cache.ChemSpider  
CHEMSPIDER reuses cached data for 'acetophenone' (date=21-sept.-2015 21:37:19)

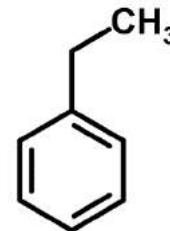
ans =  
9.1995e-06



## >> FMECAKairP ethylbenzene

LOAD\_CHEMSPIDER extraction of ChemSpiderID=7219 ('ethylbenzene') completed in 11.9 s  
LOAD\_CHEMISPIDER: updated cache  
7219.mat 21-sept.-2015 21:42:34 107.1 kBytes C:\Data\Olivier\INRA\Codes\MS\cache.ChemSpider  
CHEMSPIDER reuses cached data for 'ethylbenzene' (date=21-sept.-2015 21:42:34)

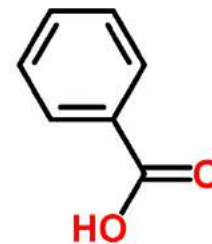
ans =  
2.2485e-04



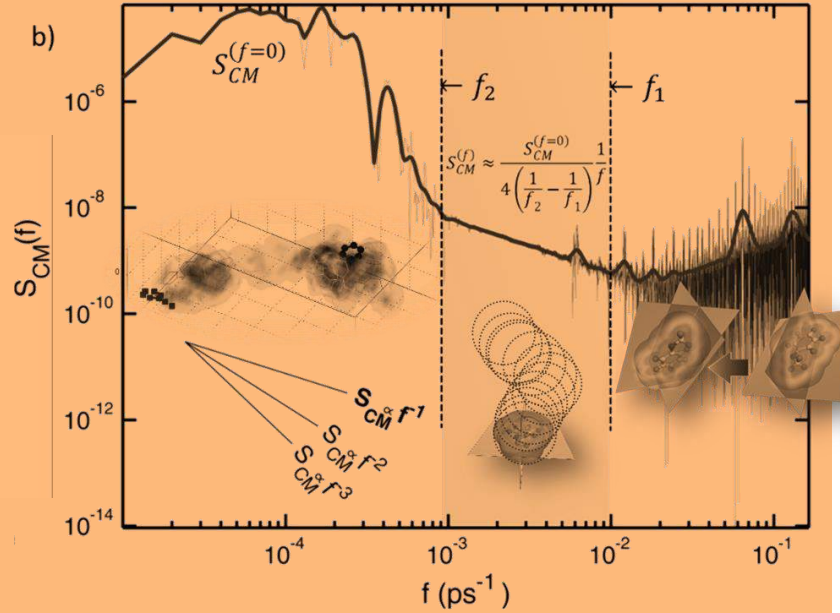
## >> FMECAKairP 'benzoic acid'

LOAD\_CHEMSPIDER extraction of ChemSpiderID=238 ('benzoic acid') completed in 5.746 s  
LOAD\_CHEMISPIDER: updated cache  
238.mat 21-sept.-2015 21:45:01 41.2 kBytes C:\Data\Olivier\INRA\Codes\MS\cache.ChemSpider  
CHEMSPIDER reuses cached data for 'benzoic acid' (date=21-sept.-2015 21:45:01)

ans =  
1.3674e-08



Spectral density of  $\frac{1}{\pi} \frac{\partial}{\partial t} \langle \|x_{CM}(t) - x_{CM}(0)\|^2 \rangle$ , denoted  $S_{CM}(f)$

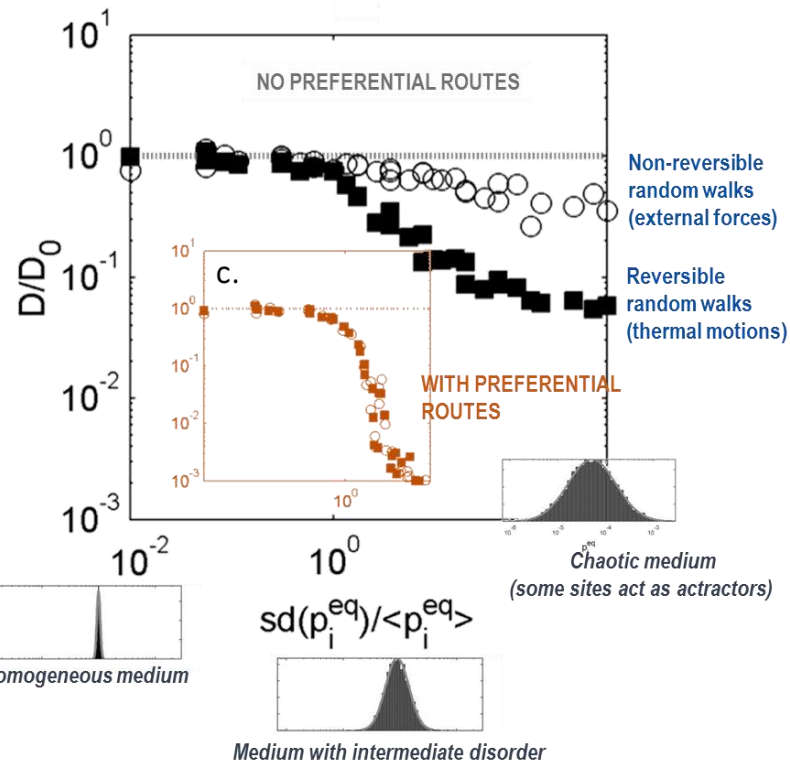
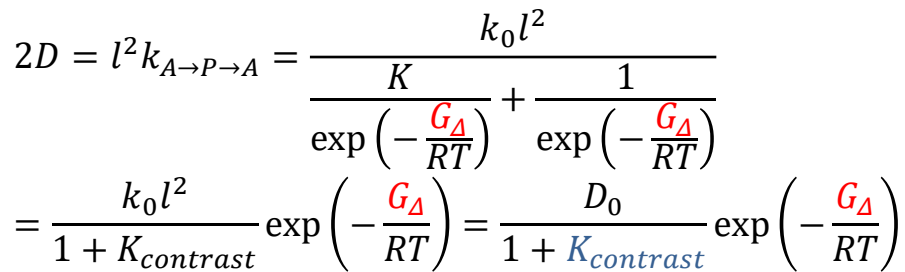


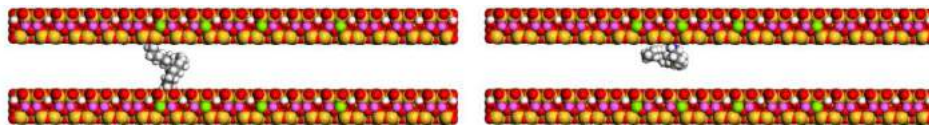
# SOLUTION 6

Trapping migrants

solution 7

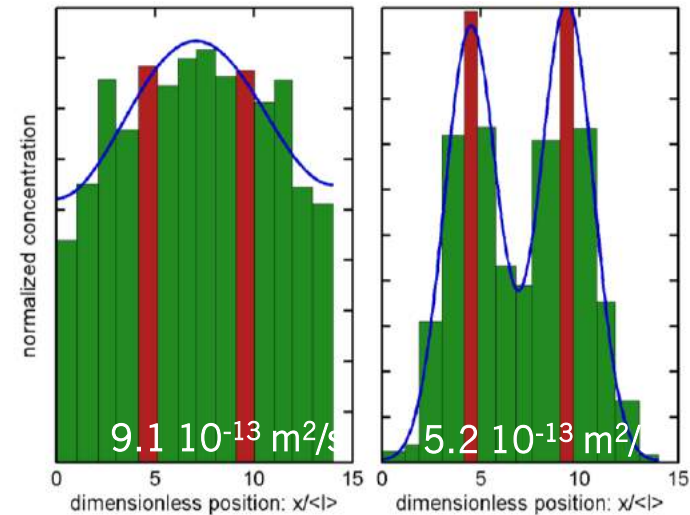
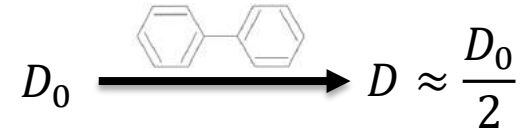
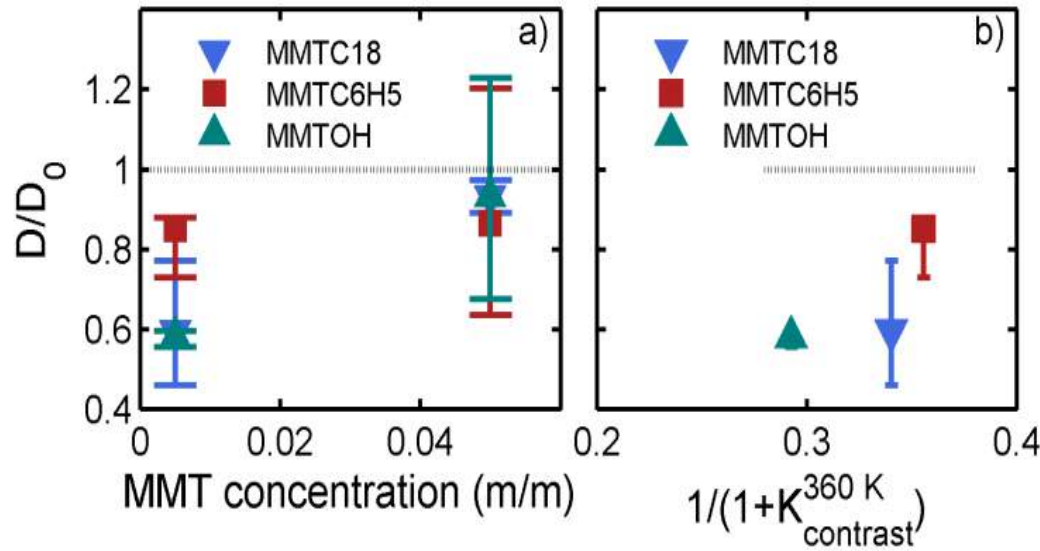
Conclusions





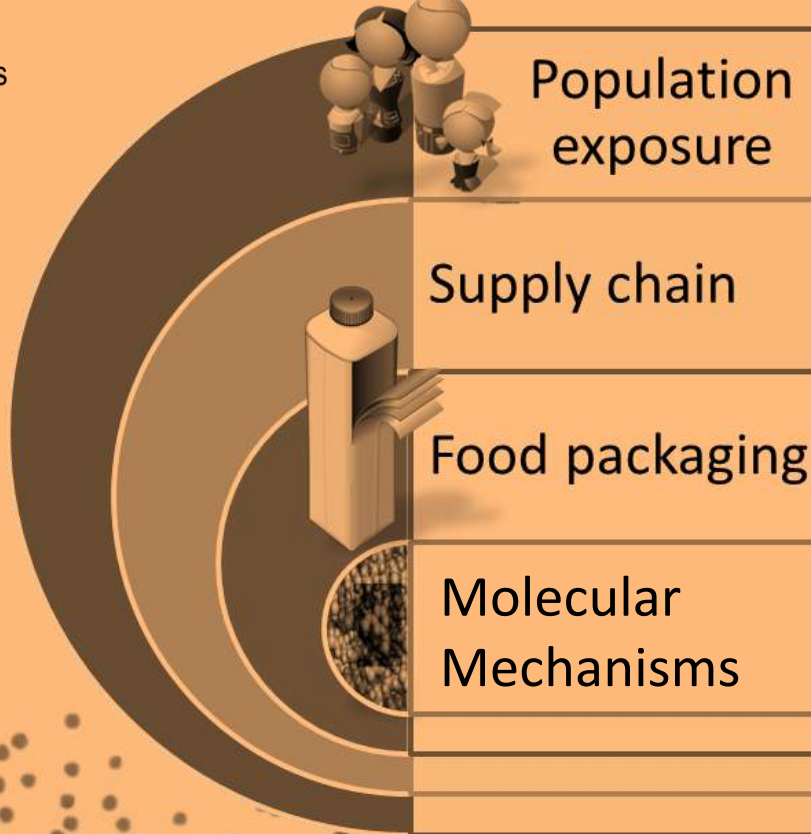
stack of 14 films assembled as  
[0 0 0 0 1 0 0 0 0 1 0 0 0 0]

- 1 = source, 0 = virgin
- film thickness: 40  $\mu\text{m}$
- contact time: 20 min



Defect and Diffusion Forum 2011, Diffusion in Materials - DIMAT 2011, 269-274.

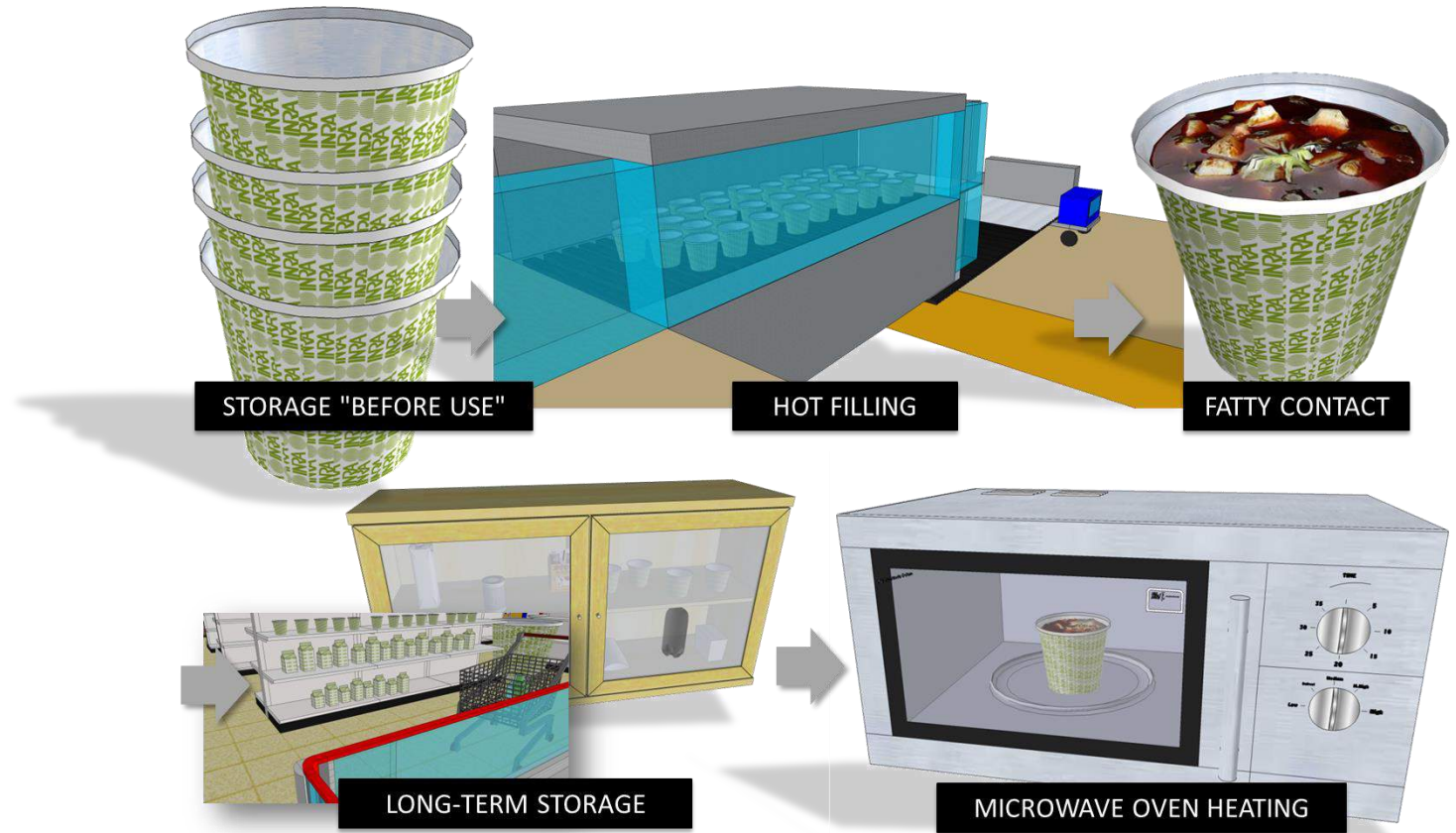
- ❖ List of components and functions
- ❖ Failure = migration mode tree
- ❖ **Severity** =  $f(C_F)$ 
  - Dimensionless scale
  - Normalized by toxicological data
  - Substance and material independent
  - Linear to  $C_F$  for acceptable  $C_F$  values and non-linear beyond
- ❖ **Criticality ranking**
  - by component
  - by substance
  - by process or storage step
  - Comparative designs
- ❖ Ensuring **detectability** via calculations and simulation

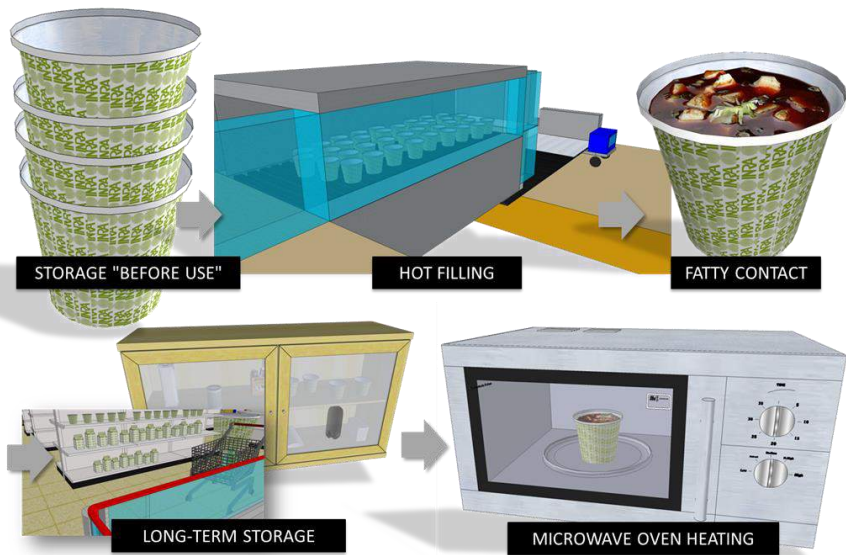


# SOLUTION 7

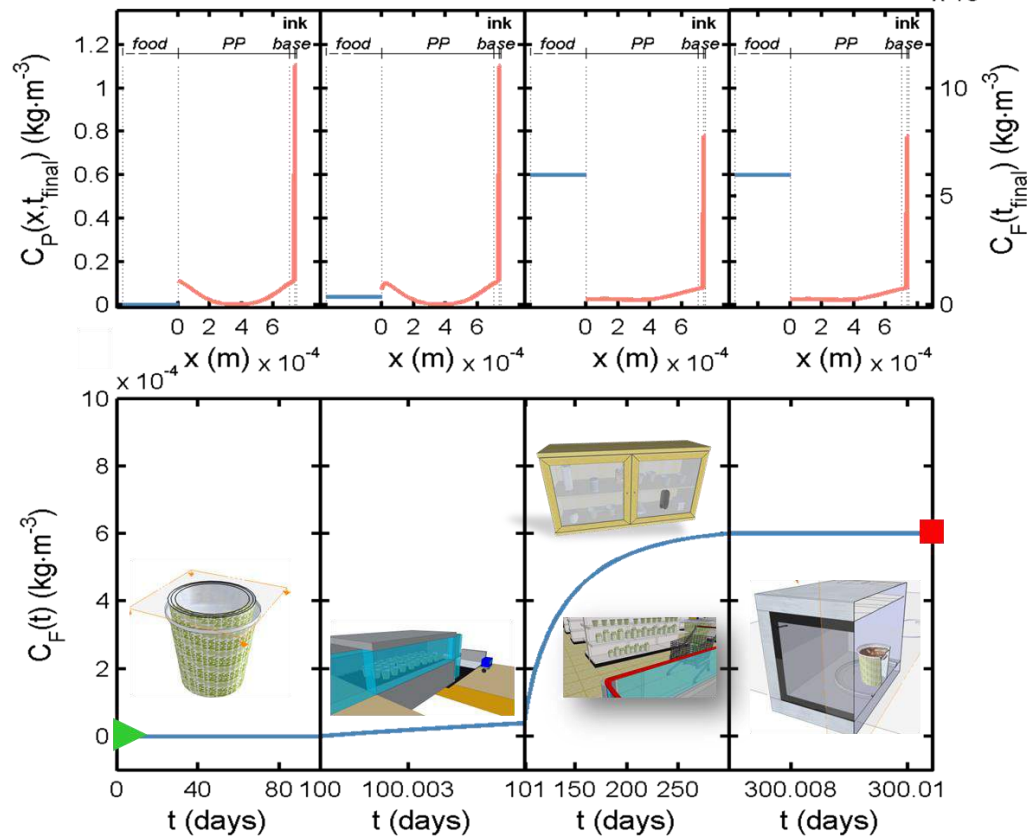
Identification,  
avoidance,  
correction  
of critical steps  
components,  
substances, etc.  
Conclusions

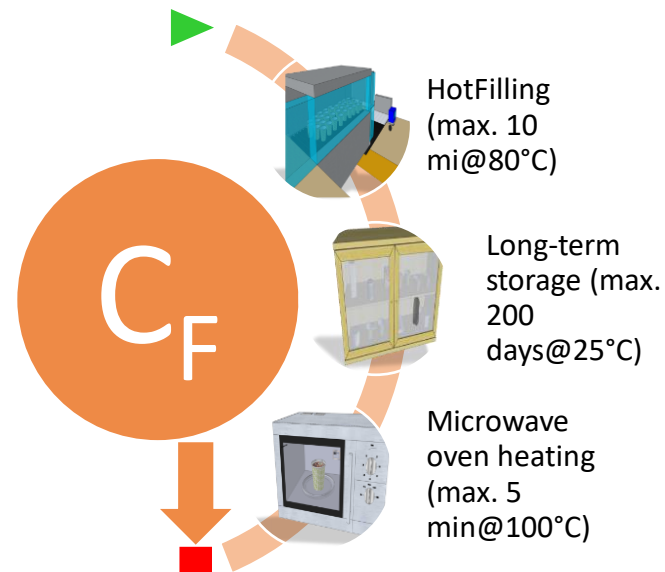
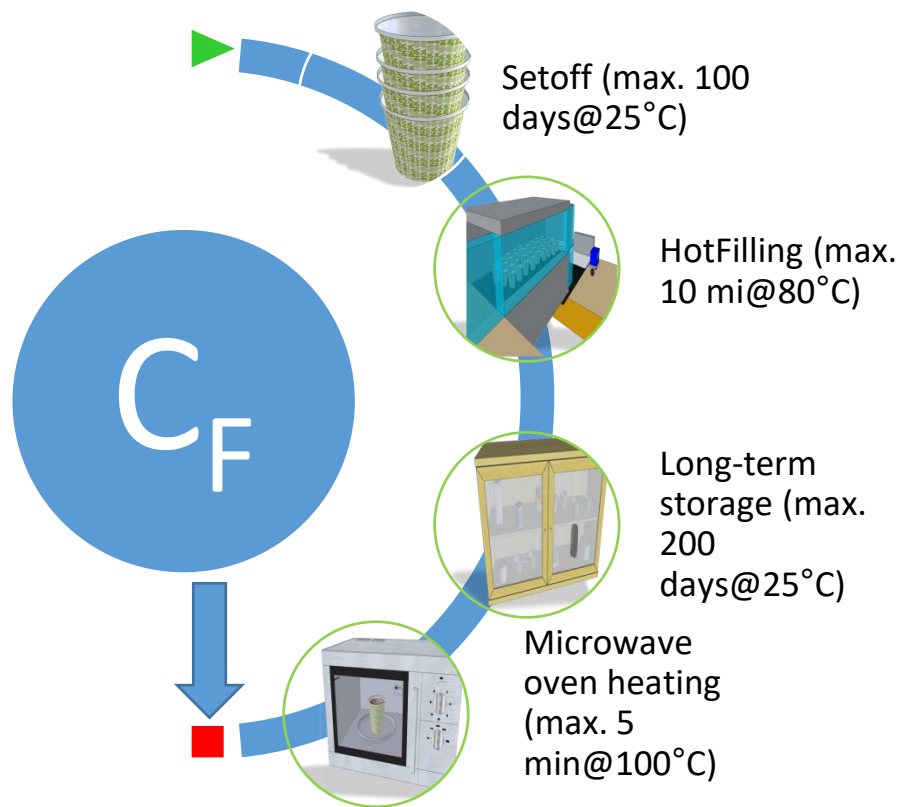
Risk of  
contamination  
by a photoinitiator  
in UV-curing  
printing ink



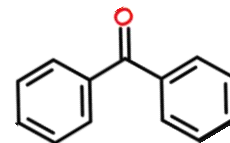
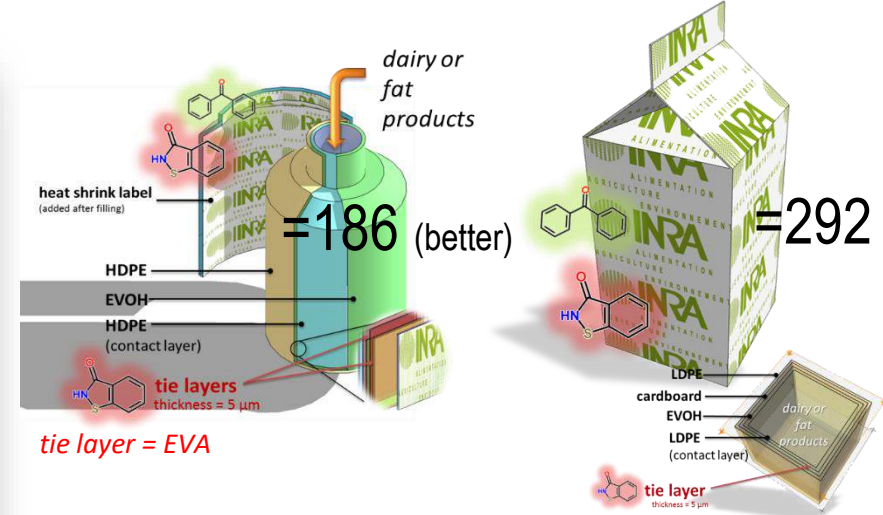
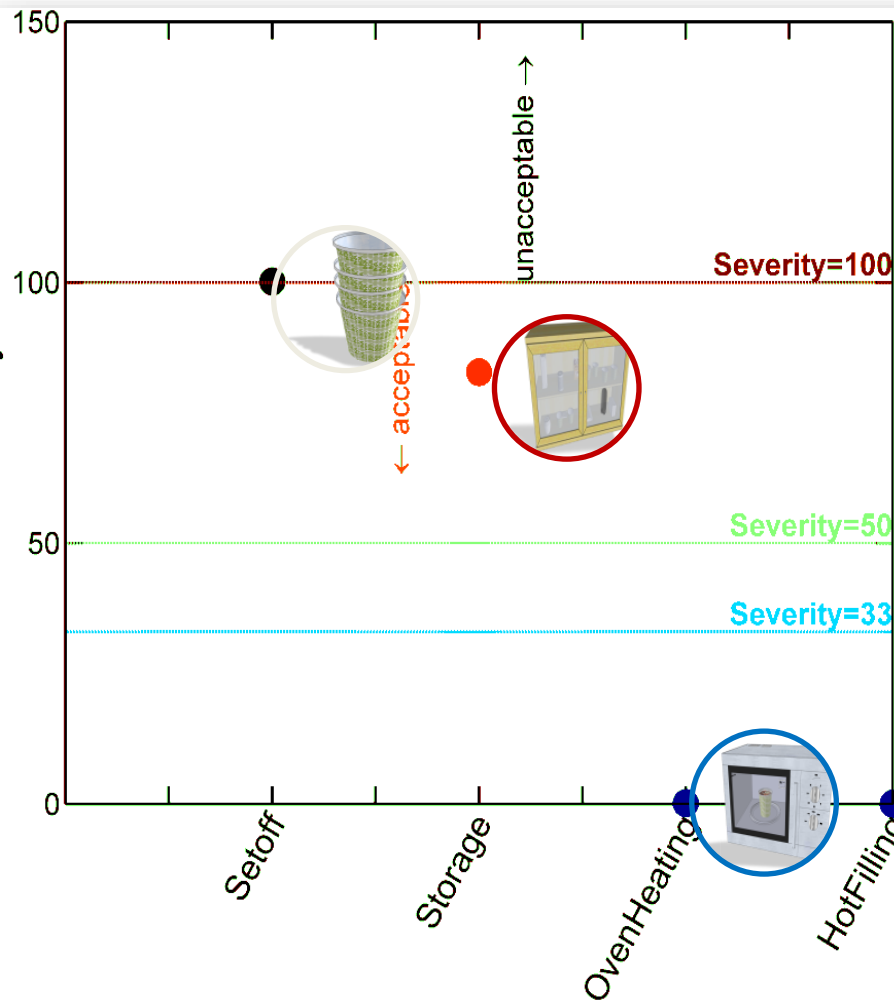


1: Setoff → 2: HotFilling → 3: Storage → 4: OvenHeating

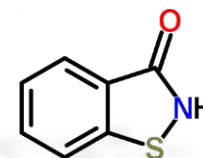




Severity



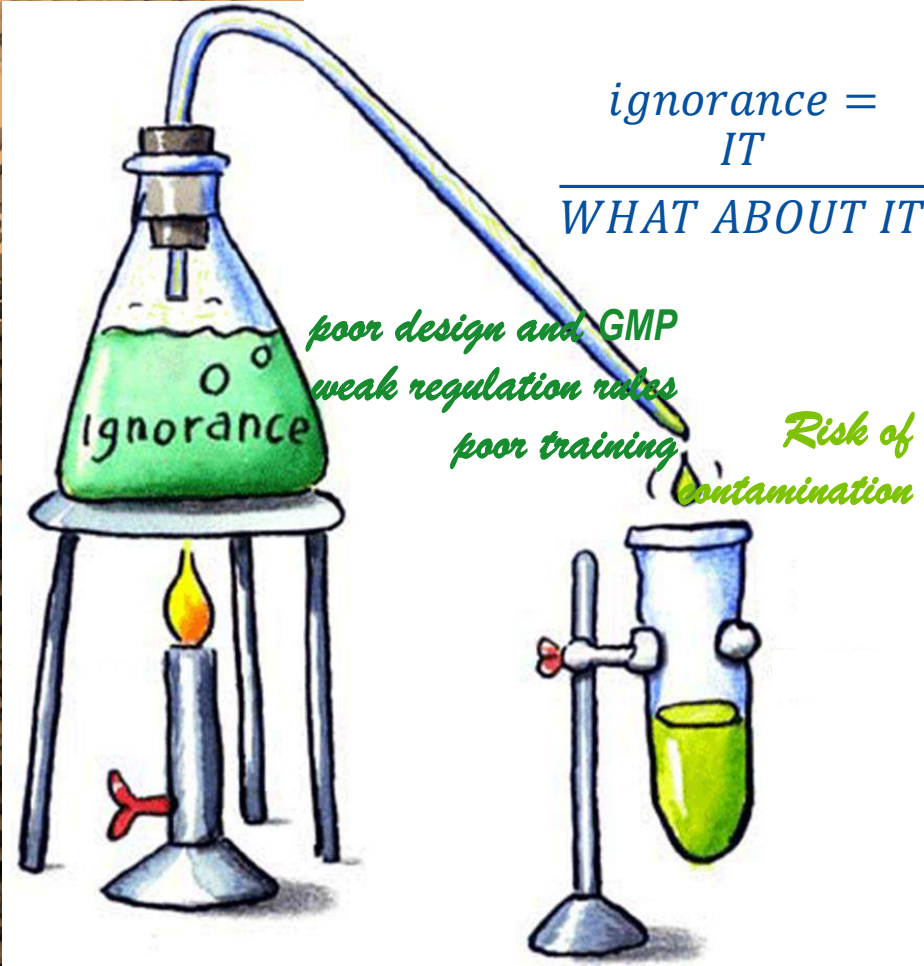
=115  
(almost acceptable)

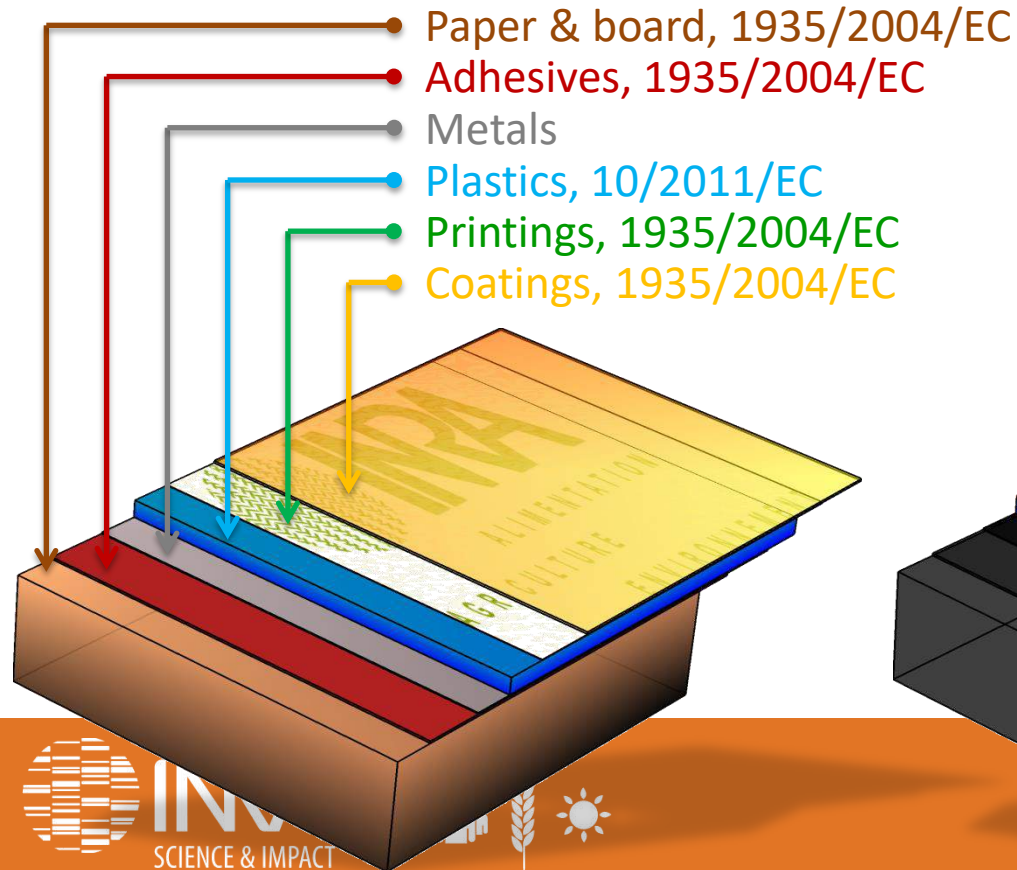


=124

# CONCLUSIONS

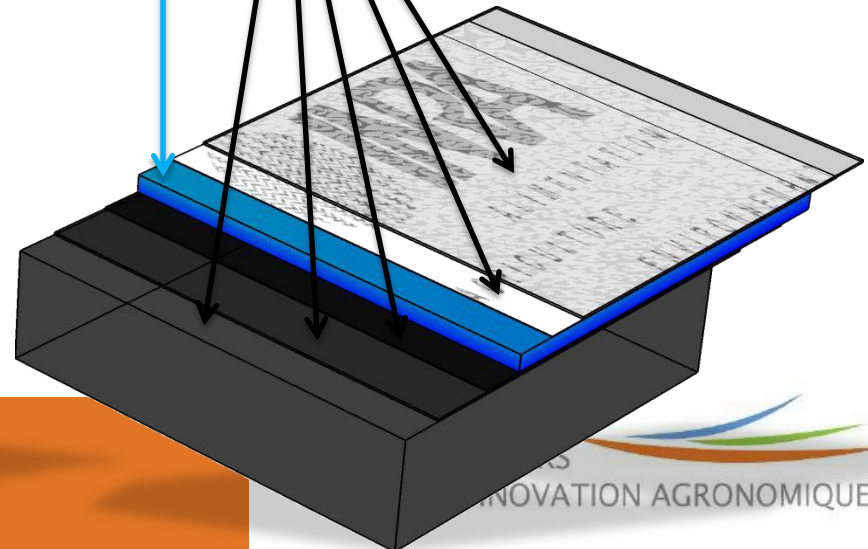
$$\frac{\text{ignorance} = \text{IT}}{\text{WHAT ABOUT IT}}$$





**POSITIVE LIST (LOW TOXICITY:  
monomers, additives)  
LOW MIGRATION**

**GENERAL REQUIREMENT:  
MUST NOT ENDANGER  
HUMAN HEALTH**



**INRAE**  
SCIENCE & IMPACT



**INNOVATION AGRONOMIQUE**

Raw material

Part

Raw material supplier

Part supplier

Component supplier

Final product

Retailer

Consumer

Polymer flakes

additives

Process aids

fibers

plastic film

glue

ink

paper cardboard

body

caps

label

Multilayers materials

bottle

brik

Retailer 1

Retailer 2

Retailer 3

Consumer 1

Consumer 2

Consumer 3

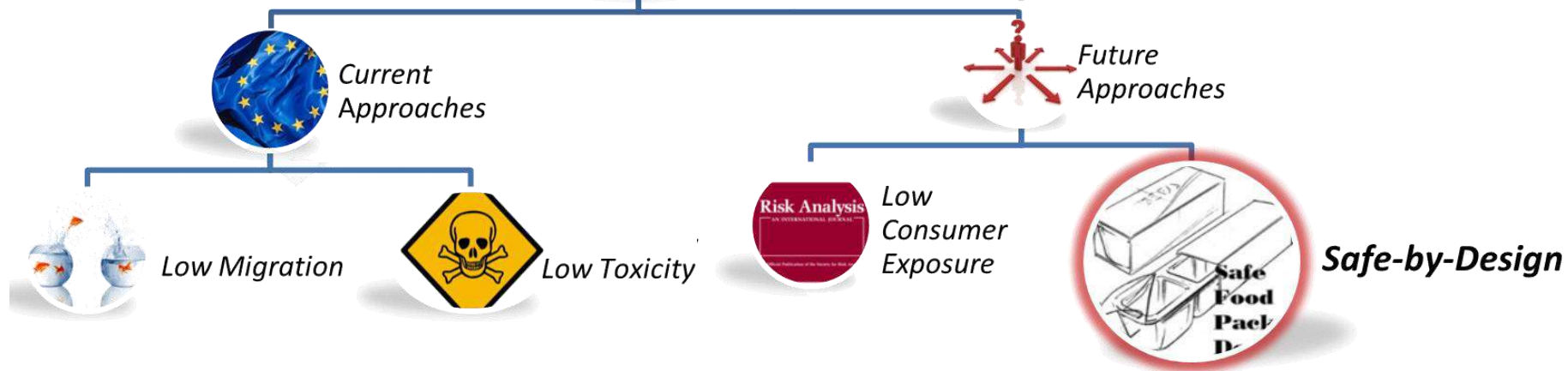
Material flow

Information flow

INNOVATION AGRONOMIQUE



## Safety concepts



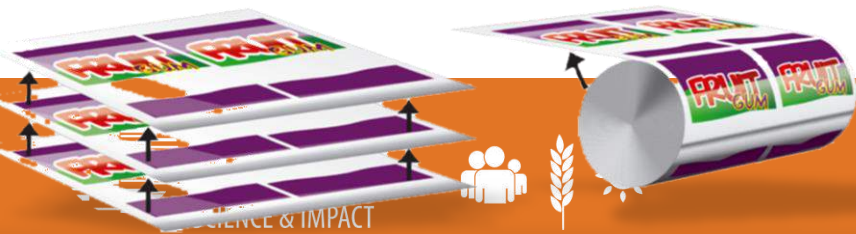
**+VOLUNTARY APPROACHES & LOCAL ORDINANCES**

[Regulation EC 2023/2006](#) - Good Manufacturing Practice for materials and articles intended to come in contact with food

# • PRINTING INKS

(EUPIA guidelines to be revised)

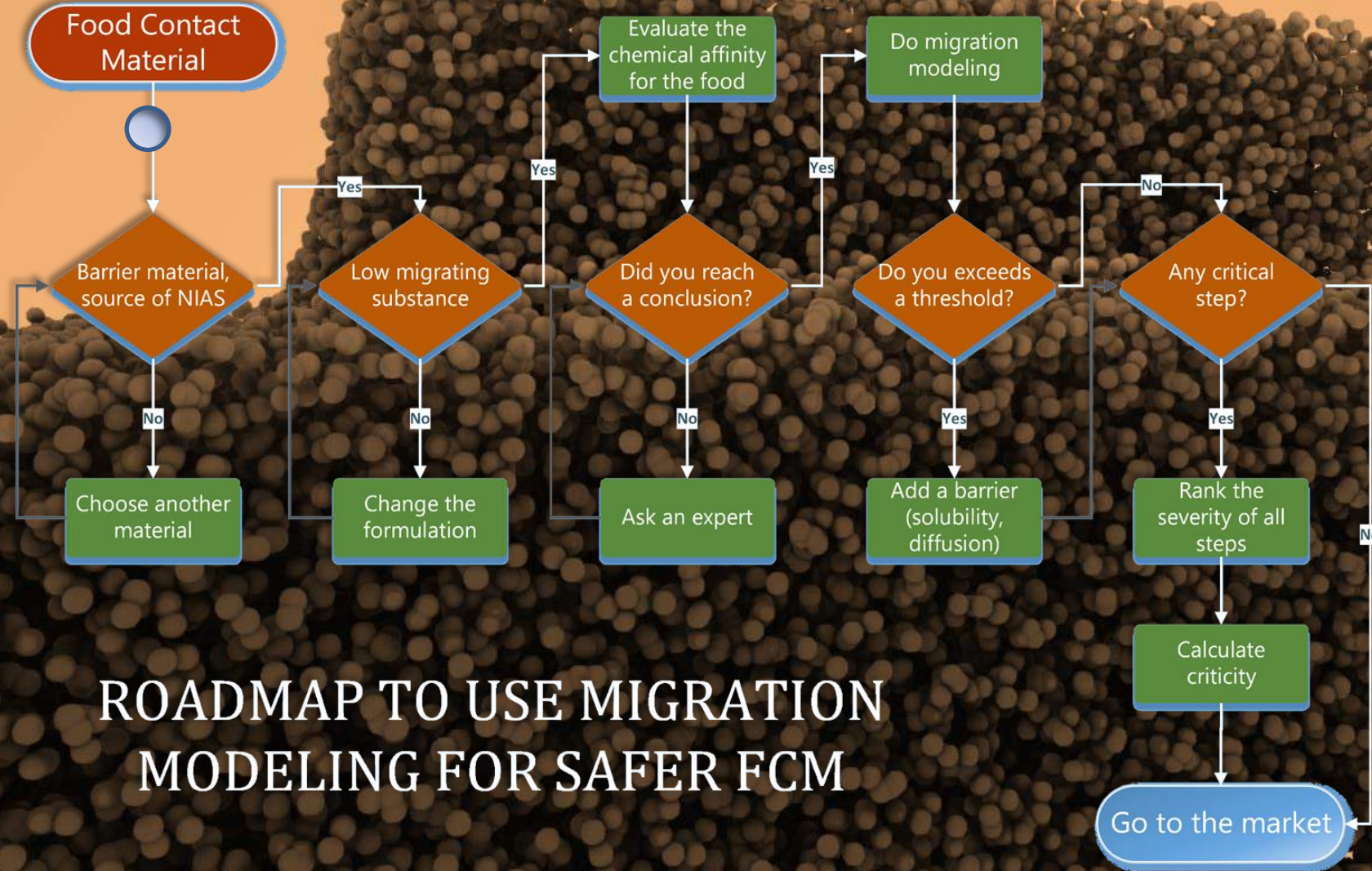
- Exclusion/Negative lists
- Recommended substances
- Purity/traceability requirements
- Migration (less than 10 ppb for non evaluated substances) and risk assessments
- Inks prepared according to GMP
- No-direct contact with food
- No “visible” Set-off in stacks and reels



# • MINERAL OILS

- No recycled paper or paperboard
- No MOSH below C20, migration <2 ppm for C20-C35
- Migration of MOAH (C16-C35) <0.5 ppm
- List of raw materials and production aids
- No holding/reheating above 90°C
- No microwave uses
- With internal bag





# ROADMAP TO USE MIGRATION MODELING FOR SAFER FCM