université PARIS-SACLAY

UMT SAFEMAT MATÉRIAUX AU CONTACT DES ALIMENTS

INRAe

AgroParisTech INSTITUT DES SCIENCES ET INDUSTRIES DU VIVANT ET DE L'ENVIRONNEMENT PARIS INSTITUTE OF TECHNOLOGY FOR LIFE, FOOD AND ENVIRONMENTAL SCIENCES

FOOD Risk

Nîmes Jan 30-31, 2020

The fate of food packaging substances: cross-contaminations, migrations, etc. a main challenge for the 21st century

Olivier Vitrac, olivier.vitrac@agroparistech.fr

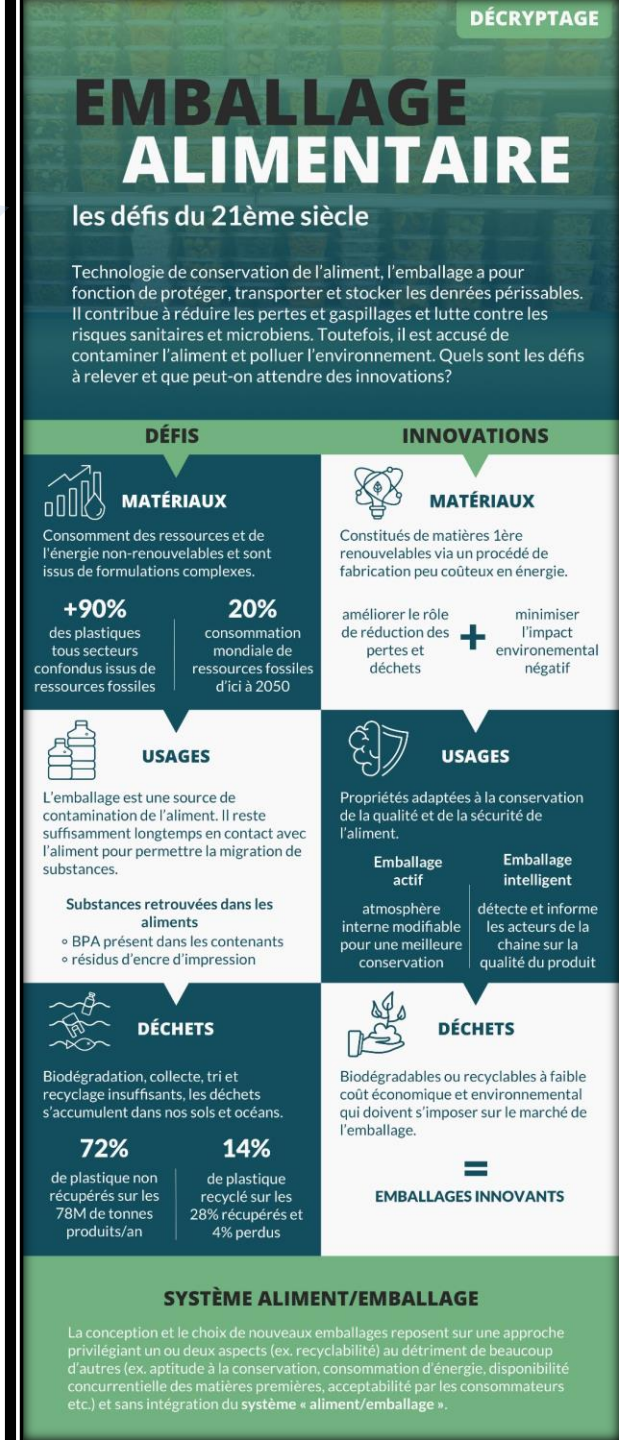
University of Paris-Saclay, INRAe, AgroParisTech

UMR 0782 SayFood "*Food Processing and Engineering of Paris-Saclay*"

UMT SafeMat "*Safe Food Contact Materials*" between AgroParisTech/INRAe and LNE

1 rue des Olympiades, 91300 Massy, France

LNE LABORATOIRE NATIONAL DE MÉTROLOGIE ET D'ESSAIS

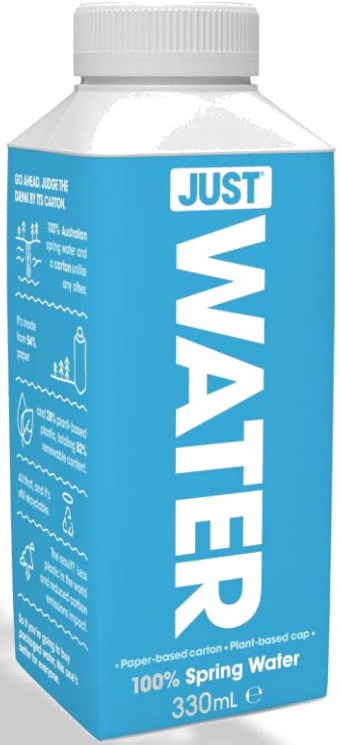


1964

La malbouffe et les additifs, progrès ou danger pour le futur ?

Archive INA

https://www.youtube.com/watch?v=aZcNza1xHSk


JUST
WATER
• Paper-based carton • Plant-based cap •
100% Spring Water
330mL


JUST
WATER
100% Spring Water
500mL
JUST
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Infused
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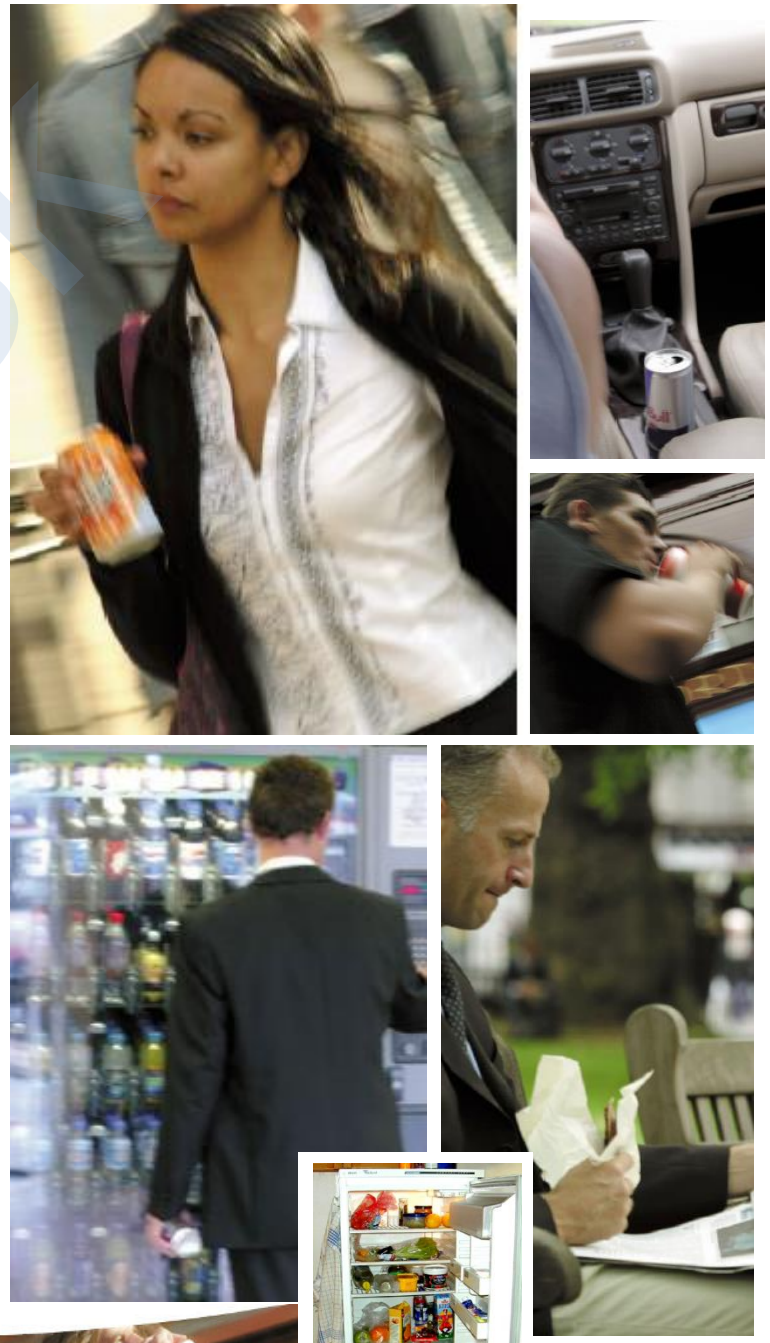


https://fitness.agroparistech.fr/fitness/external/IHEST

INRAE

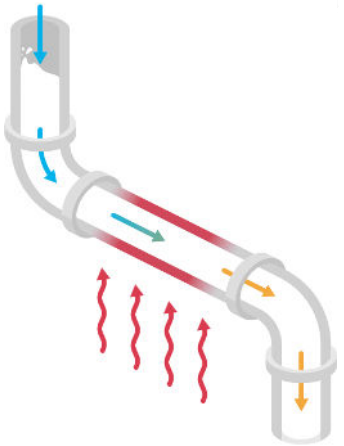
- Turn into constructive controversy

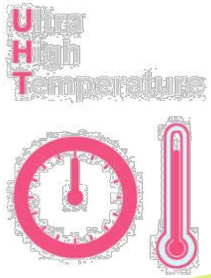
"Truth in science can be defined as the working hypothesis best suited to open the way to the next better one." — Konrad Lorenz, Austria

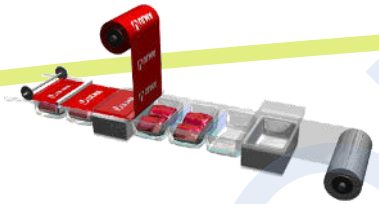
1950

1980

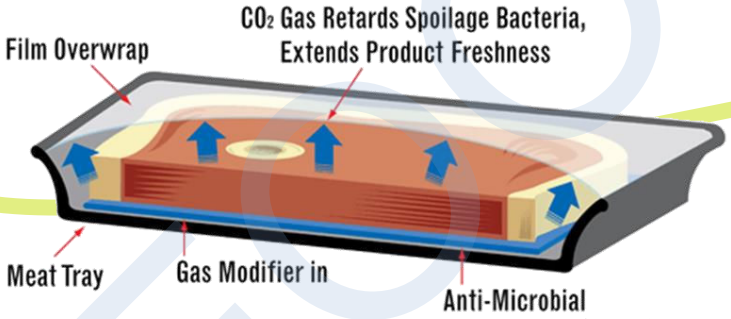
1990

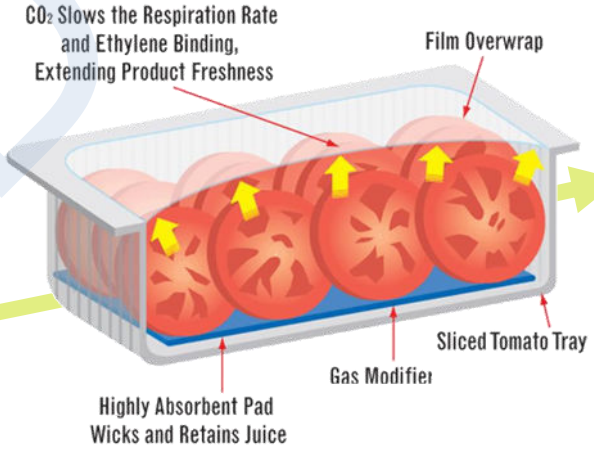


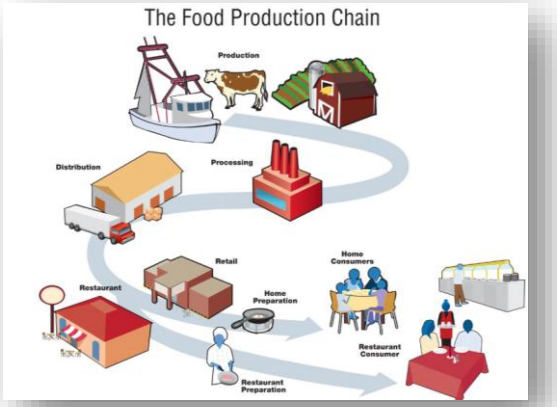




2000







Protective, active, intelligent, useful packaging

> 60% of ingested Chemicals are coming from Packaging (exposome)

Compliance (contaminations) of 70% of plastics tested by Modeling

Contaminations from non-plastic Materials not considered

CIRCULAR ECONOMY vs SAFETY

Food Packaging Forum

Workshop "Predicting the safety of food contact articles" - New science and digital opportunities
4 October 2018, Zurich, Switzerland
https://www.foodpackagingforum.org/events/predicting-the-safety-of-food-contact-articles-new-science-and-digital-opportunities

« Ce grand homme à mon avis mérite d'être préféré à tous les autres… il a établi une doctrine fondée sur des raisons physiques et palpables sans se servir des énigmes inintelligibles qui font tourner la tête plutôt que d'instruire »

François-Marie-Pompée Colonna – Abrégé de la doctrine de Paracelse et de ses Archidoxes - Paris, 1724.

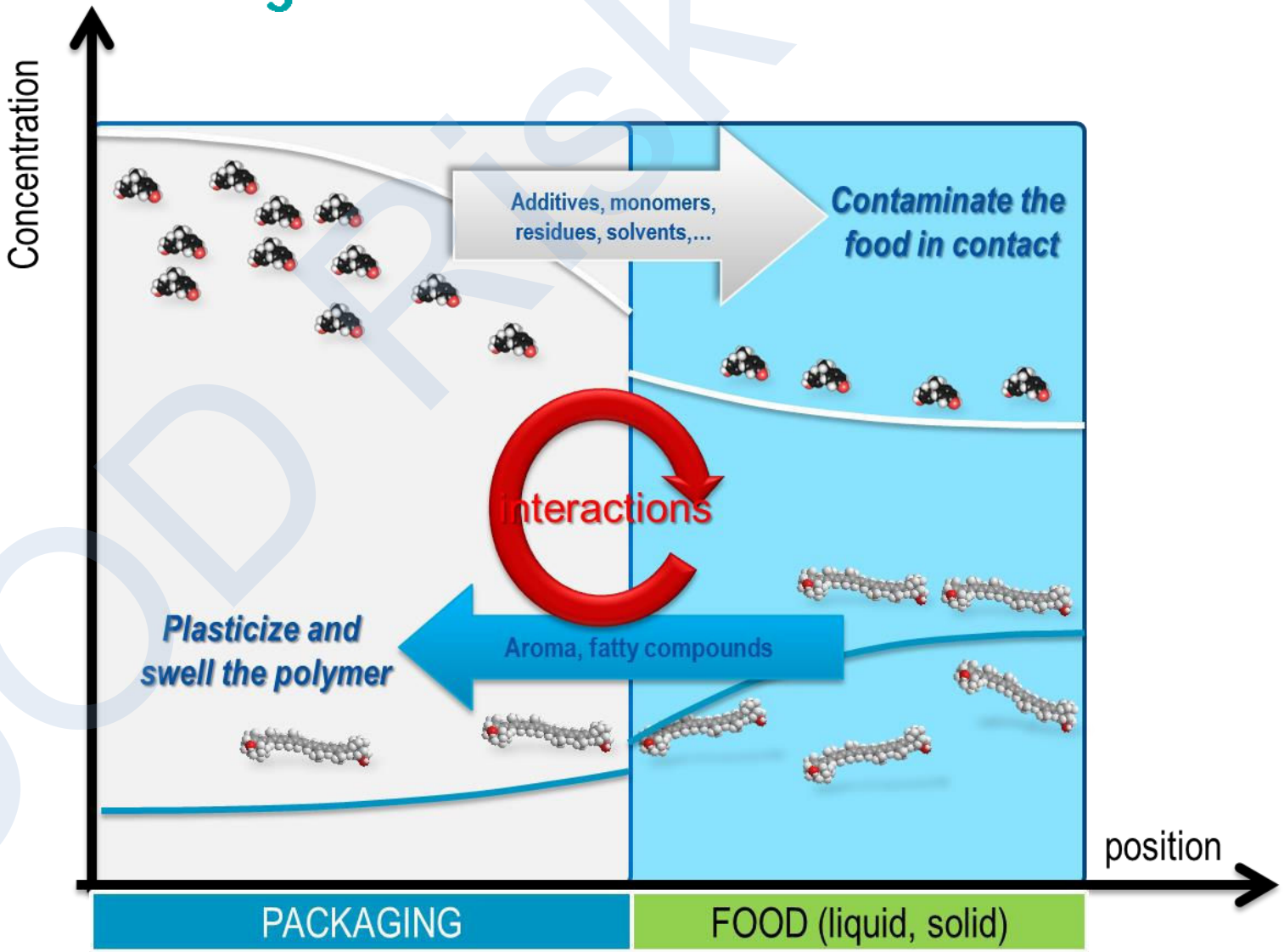
Contamination with contact

= migration

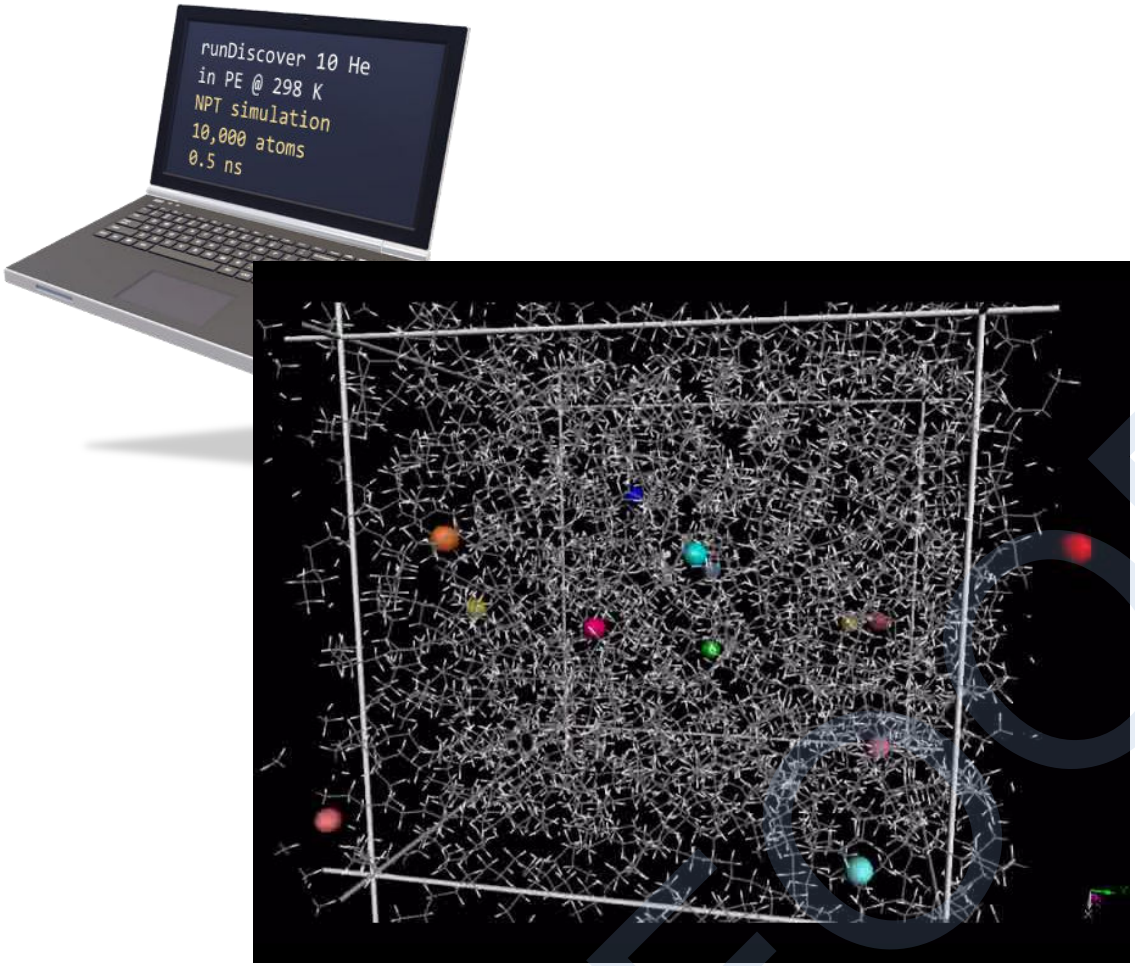
old routes = new issues

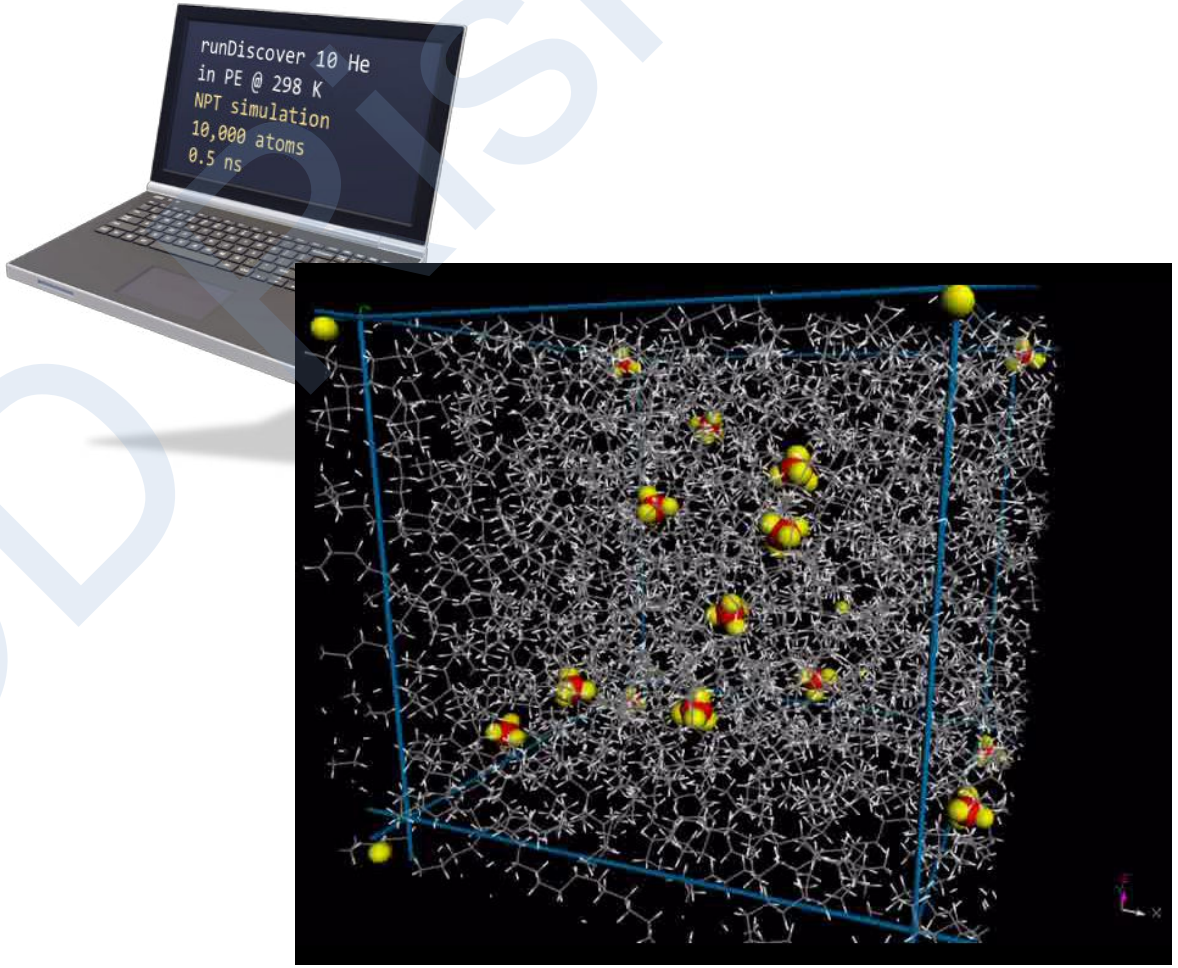
The conventional description of migration

Observational evidences



The kinetics of migration depends on the diffusivity of the sustance



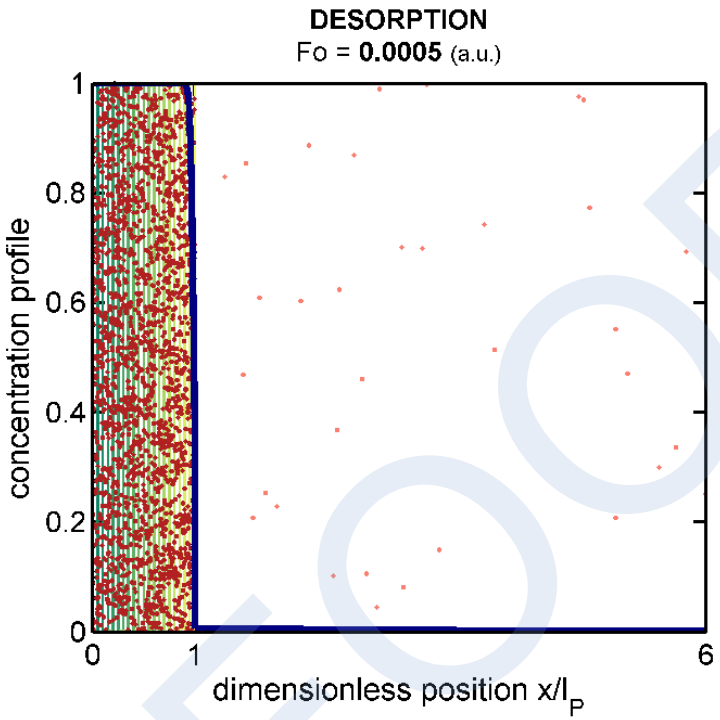


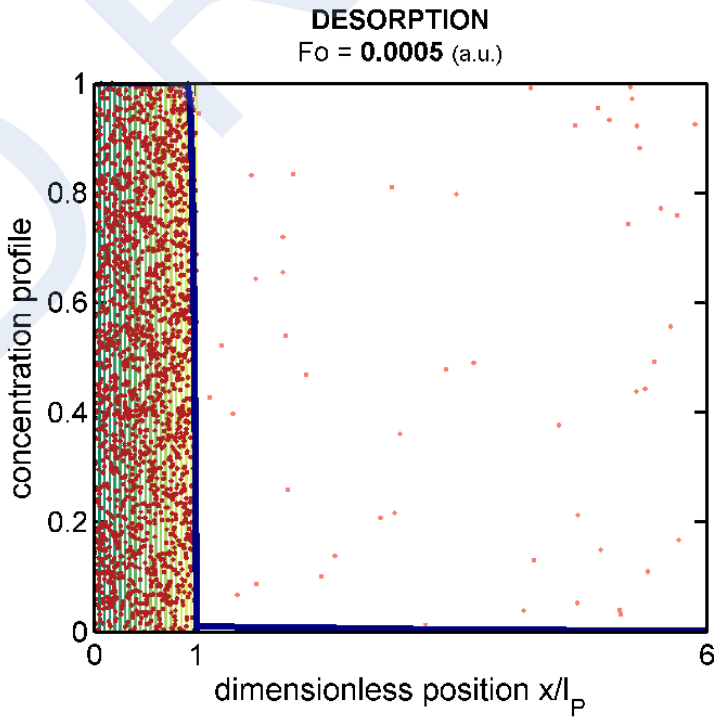
$$D \approx \frac{1}{6}\frac{\partial}{\partial t}\left\langle \left(\boldsymbol{x}_{CM}(t) - \boldsymbol{x}_{CM}(0)\right)^2 \right\rangle$$

The conventional description of migration

The level of contamination depends essentially on the fatty character of the food in contact

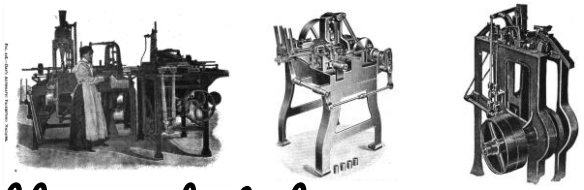
	50 × more chemical affinity for P	50 × more chemical affinity for F
$K_{i,F/P}$=	1/50	50





$$K_{i,F/P} = \frac{C_{i,F}^{eq}}{C_{i,P}^{eq}} = \frac{1}{1 - crystallinity} \frac{\gamma_{i,P_{amorphous}}^{v}}{\gamma_{i,F}^{v}}$$

Food inertia: a long history



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

L'ART DE CONSERVER,

PENDANT PLUSIEURS ANNÉES,

TOUTES LES SUBSTANCES ANIMALES ET VÉGÉTALES;

OUVRAGE soumis au Bureau consultatif des Arts et Manufactures, revêtu de son approbation, et publié sur l'invitation de S. Exc. le Ministre de l'intérieur.

PAR APPERT,

Propriétaire à Massy, Département de Seine et Oise, ancien Confiseur et Distillateur, élève de la bouche de la Maison ducale de Christian IV.

« J'ai pensé que votre découverte méritait » un témoignage particulier de la bienveillance » du Gouvernement ».

Lettre de S. Exc. le Ministre de l'intérieur.

A PARIS,

CHEZ PATRIS ET Cie IMPRIMEURS-LIBRAIRES, QUAI NAPOLÉON, AU COIN DE LA RUE DE LA COLOMBE, N° 4.

1810.

8me ANNÉE. — N° 19 JUILLET 1910

LA CONSERVE ALIMENTAIRE

Bulletin mensuel de Vulgarisation Théorique et Pratique de Fabrication

PARAISSANT LE 15 DE CHAQUE MOIS

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

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 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 technologue éminent, M. CROLBOIS, chef de laboratoire à l'Institut Pasteur.

Une très large place sera réservée, dans 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'Ecole.

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

290 LA CONSERVE ALIMENTAIRE

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

Méfions-nous des Conserves 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 régissent l'inspection des conserves alimentaires aux Etats-Unis et en Europe, ceux du Canada sont encore à l'état embryonnaire.

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

« Je ne parle pas ici de l'inspection des viandes fraiches 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.*

« 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 susbstances nuisibles, aussi bien dans les conserves que dans les viandes fraiches.

« Que si quelques antiseptiques sont considérés comme inoffensifs par le Ministère de l'Agriculture, pourquoi ne pas faire connaître au public comme aux fabricants le nom de ce qui est permis et de ce qui est prohibé?

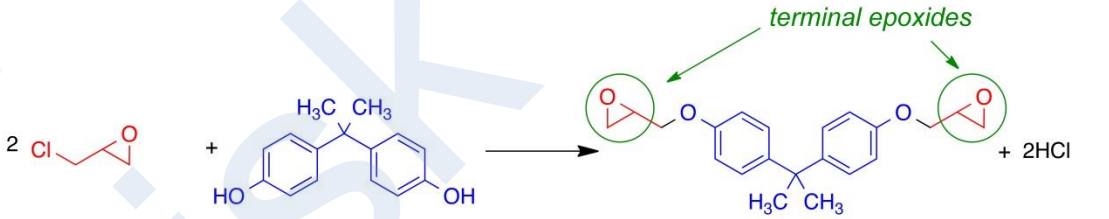
« Le règlement de 1908 ne prend nullement en considération la qualité de la soudure employée, pas plus que celle de l'acide, et il semble que sur ce point les japonais sont bien en avance sur nous lorsqu'ils donnent les commandes pour leur armée.

« 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 rassu-

Google Trends / Bisphenol A: (Worldwide)



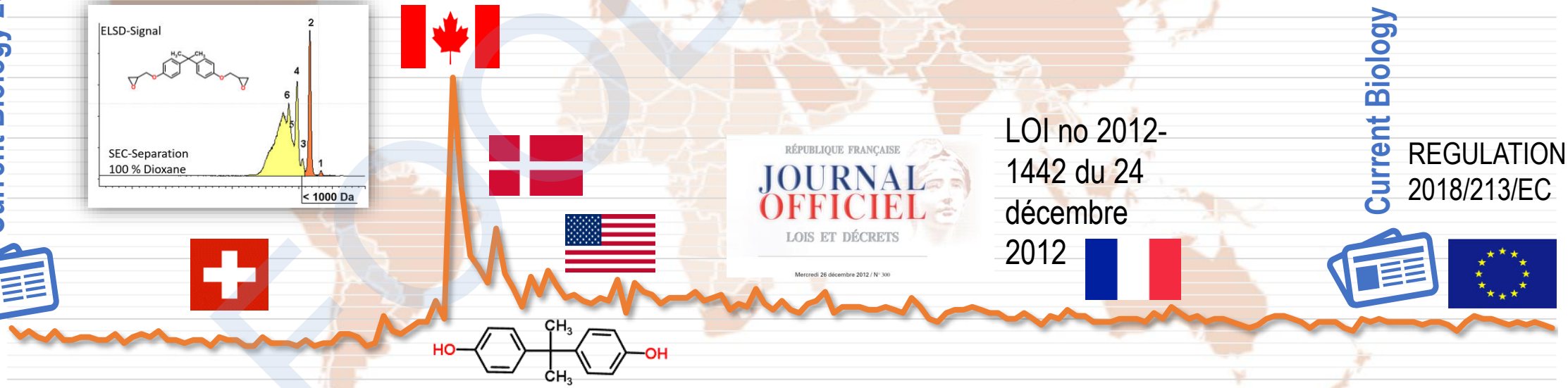
epichlorohydrin | bisphenol A | bisphenol A diglycidylether | hydrogen chloride

#	M +1	Substances (originated from the resin)
1	359	BADGE·H_2O
2	341	BADGE
3	643	BADGE(n=1)·H_2O
4	569	Cyclo-DiBADGE
5	625	BADGE(n=1)
6	927	BADGE(n=2)·H_20
7	491	BADGE·tBuPh*
8	909	BADGE(n=2)
9	775	BADGE(n=1)·tBuPh
10	641	BADGE·2tBuPh
11	477	BADGE·H2O·BuEtOH**
12	403	BADGE·EG*** (+)
13	459	BADGE·BuEtOH
14	509	BADGE·H2O·tBuPh
15	577	BADGE·2BuEtOH
16	687	BADGE(n=1)·EG (+)
18	743	BADGE(n=1)·BuEtOH
19	609	BADGE·BuEtOH·tBuPh
20	971	BADGE(n=2)·EG (+)

* tBuPh tert.-Butylphenol (chain stopper)
** BuEtOH Butoxyethanol
*** EG Ethyleneglycol
(+) Further confirmations are necessary

Current Biology 2003, 13, 546

Current Biology 2018, 28,1



LOI no 2012-1442 du 24 décembre 2012

REGULATION 2018/213/EC

CANCO: Ensuring the safety of consumers: can **coatings** for direct food contact. Project QLAM-2001-00066.

INRA SCIENCE & IMPACT

Current Biology, Vol. 13, 546–553, April 1, 2003, ©2003 Elsevier Science Ltd. All rights reserved. DOI 10.1016/S0960-9822(03)00189-1

Bisphenol A Exposure Causes Meiotic Aneuploidy in the Female Mouse

Patricia A. Hunt,[1,*] Kara E. Koehler,[1]
Martha Susiarjo,[1] Craig A. Hodges,[1]
Arlene Ilagan,[1] Robert C. Voigt,[2,5] Sally Thomas,[3]
Brian F. Thomas,[4] and Terry J. Hassold[1]
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Case Western Reserve University
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[3]Thoren Caging Systems
Hazleton, Pennsylvania 18201
[4]RTI International
Research Triangle Park, North Carolina 27709-2194

Summary

Background: There is increasing concern that exposure to man-made substances that mimic endogenous hormones may adversely affect mammalian reproduction. Although a variety of reproductive complications have been ascribed to compounds with androgenic or estrogenic properties, little attention has been directed at the potential consequences of such exposures to the genetic quality of the gamete.
Results: A sudden, spontaneous increase in meiotic disturbances, including aneuploidy, in studies of oocytes from control female mice in our laboratory coincided with the accidental exposu
environmental source of bisphe
estrogenic compound widely us
polycarbonate plastics and epo
damaged caging material as the
as we were able to recapitulate
ties by intentionally damaging c
In subsequent studies of female
daily oral doses of BPA to direc
that low levels of BPA disrupt female meiosis. Our results demonstrated that the meiotic effects were dose dependent and could be induced by environmentally relevant doses of BPA.
Conclusions: Both the initial inadvertent exposure and subsequent experimental studies suggest that BPA is a potent meiotic aneugen. Specifically, in the female mouse, short-term, low-dose exposure during the final stages of oocyte growth is sufficient to elicit detectable meiotic effects. These results provide the first unequivocal link between mammalian meiotic aneuploidy and an accidental environmental exposure and suggest that the oocyte and its meiotic spindle will provide a sensitive assay system for the study of reproductive toxins.

Introduction

An estimated 10%–25% of fertilized human oocytes are aneuploid; thus, numerical chromosome abnormalities are the leading cause of miscarriage, congenital defects, and mental retardation [1]. Because almost all such aneuploidy derives from meiotic errors, considerable effort has been directed at identifying factors that increase meiotic nondisjunction. A number of potential risk factors, including irradiation (e.g., [2, 3]), smoking or drinking (e.g., [4, 5]), oral contraceptives and fertility drugs (e.g., [4, 6]), and environmental pollutants/pesticides (e.g., [7]), have been suggested. However, significant effects have been small and difficult to verify or disputed, making positive associations hard to establish. In part, this may reflect difficulties in detection. For example, the extraordinary effect of maternal age on aneuploidy may obscure less obvious associations. Further, previous studies may have focused on the "wrong" population; that is, most utilized liveborns, although virtually all aneuploidy terminates in miscarriage. Thus, the contribution of environmental insults to meiotic chromosome errors remains unknown.

We recently experienced an inadvertent environmental exposure in our mouse colony to 2,2-(4,4-dihydroxydiphenol)propane, or bisphenol A. Bisphenol A (BPA) is the monomer that is polymerized to manufacture polycarbonate plastic products and resins, such as those used to line cans containing food and beverages and those found in dental sealents. The exposure was accompanied by highly significant increases in meiotic
abnormalities, including nondisjunction;
l A was implicated as a potent disruptor
e ability to experimentally recreate the
allowed us to verify our initial observations
ose-response studies.

A Sudden Increase in Meiotic Abnormalities Is Correlated with Damage to Caging Materials

We recently reported meiotic studies of mouse mutants with defects in the alignment of the chromosomes on the first meiotic (MI) spindle [8]. This meiotic abnormality, which we have termed congression failure (Figure 1), is of particular relevance to humans because it is an age-related feature of human oocytes and has been postulated to be causally related to the well-known increase in aneuploidy associated with advancing maternal age [9].

In the course of meiotic studies of mouse oocytes conducted in 1998, we observed a sudden and dramatic change in congression failure levels. The first wave of follicles that initiate growth in the sexually immature ovary provides access to a large cohort of oocytes, and, typically, only 1%–2% of oocytes from control females exhibit congression failure at metaphase I [8]. However, in experiments conducted in August 1998, congression failure levels suddenly spiked, and approximately 40% of control oocytes exhibited this phenotype or more severe aberrations (Figures 1 and 2).

At the same time that these studies were being conducted, we were also using the animal facility to house

*Correspondence: pah13@po.cwru.edu
[5]Present address: Lab Products, 742 Sussex Avenue, P.O. Box 639, Seaford, Delaware 19973.

2003

Current Biology
Report

CellPress

Replacement Bisphenols Adversely Affect Mouse Gametogenesis with Consequences for Subsequent Generations

Tegan S. Horan,[1] Hannah Pulcastro,[1] Crystal Lawson,[1] Roy Gerona,[2] Spencer Martin,[2] Mary C. Gieske,[1] Caroline V. Sartain,[1] and Patricia A. Hunt[1,3,*]
[1]School of Molecular Biosciences, Center for Reproductive Biology, Washington State University, Pullman, WA, USA
[2]School of Medicine, University of California, San Francisco, CA, USA
[3]Lead Contact
*Correspondence: pathunt@wsu.edu
https://doi.org/10.1016/j.cub.2018.06.070

SUMMARY

20 years ago, accidental bisphenol A (BPA) exposure caused a sudden increase in chromosomally abnormal eggs from our control mice [1]. Subsequent rodent studies demonstrated developmental effects of exposure with repercussions on adult health and fertility (e.g., [2–9]; reviewed in [10–17]). Studies in monkeys, humans, fish, and worms suggest BPA effects extend across species (e.g., [18–30]; reviewed in [31–33]). Widespread use has resulted in ubiquitous envir
and human BPA exposure.
sulted in "BPA-free" produc
turally similar bisphenols t
environmental and huma
[34–41]). We report here stu
changes mirroring our pre
and implicating exposure t
replacement) from damaged polysulfone cages. Like with BPA [1, 2, 5], our data show that exposure

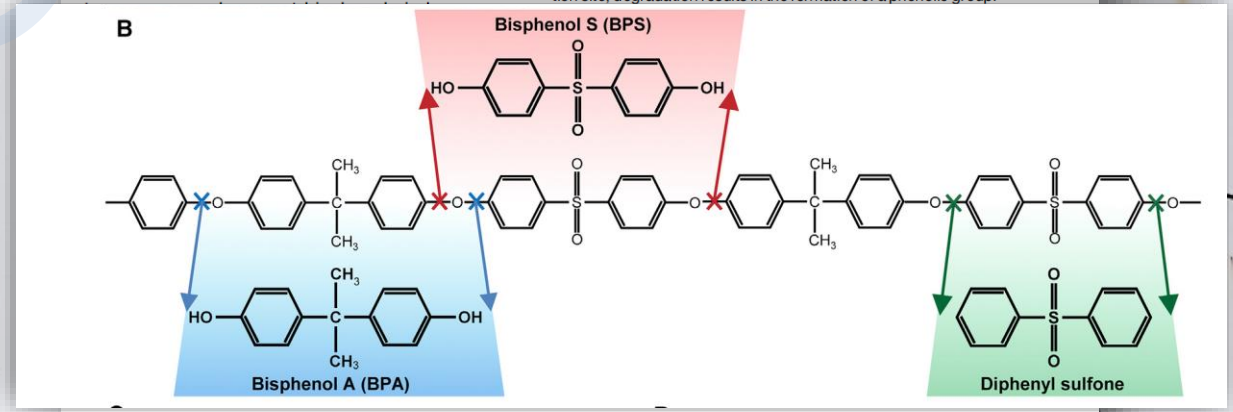
Results and Discussion

In the course of meiotic studies in male and female mice, we observed variation in meiotic recombination (measured by the number of MLH1 foci in pachytene stage meiocytes), with levels in some controls reaching values characteristic of BPA-exposed animals [2, 5]. Although the change in pooled data was subtle, variation among litters was striking (Figure 1). Given our previous experience with BPA leaching from polycarbonate cages and water bottles [1], damaged materials were an obvious suspect. When white residue was evident on the surface of some polysulfone cages in our facility (Figure 2A), we suspected that exposure to chemicals leaching from the damaged polymer was eliciting
ts.

ted Contaminant

is comprised of BPA and diphenyl sulfone (Fig-
, we suspected that these were the contaminants
iquid chromatography-tandem mass spectrometry
analysis of a methanol extraction of damaged ca-
r, demonstrated the presence of both BPA and
2C–2F). Because polymeric aromatic ethers, like
eric counterparts, cannot undergo nucleophilic substitution to generate an unsubstituted aromatic ring at the reaction site, degradation results in the formation of a phenolic group.

2018




BADGE,BPA
diisocyanate
biocides
ITX
benzophenones
MOA
AgroParisTech
TUNA
OPEN
INRA
MILK
SAFEMAT
MATERIAUX AU CONTACT DES ALIMENTS

Food and Feed borne crises throughout the food chain

Nestlé
Good Food, Good Life

Bovine Spongiform Encephalopathy
B S E

Sudan red

Dioxins

Chloramphenicol
CAP

Mycotoxins

destroy consumer's confidence in food

But what about food packaging

Nestlé
Good Food, Good Life

Nonylphenol
NP

?

Semicarbazide/SEM

[redacted]

Organic solvents/
residues

Bisphenol A diglycidyl ether
(BADGE)

Italian police seize contaminated Nestle baby milk

22 Nov 2005 16:45:09 GMT
Source: Reuters

PREVIOUS | NEXT

Forest Ranger officials check a package of baby milk made by Swiss food group Nestle in a supermarket in Italy November 22, 2005. Italian police seized around 30 million litres of baby milk produced by Nestle on Tuesday after tests showed traces of ink, and the company said it was recalling the infant food in four European countries.
REUTERS/HO

(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.

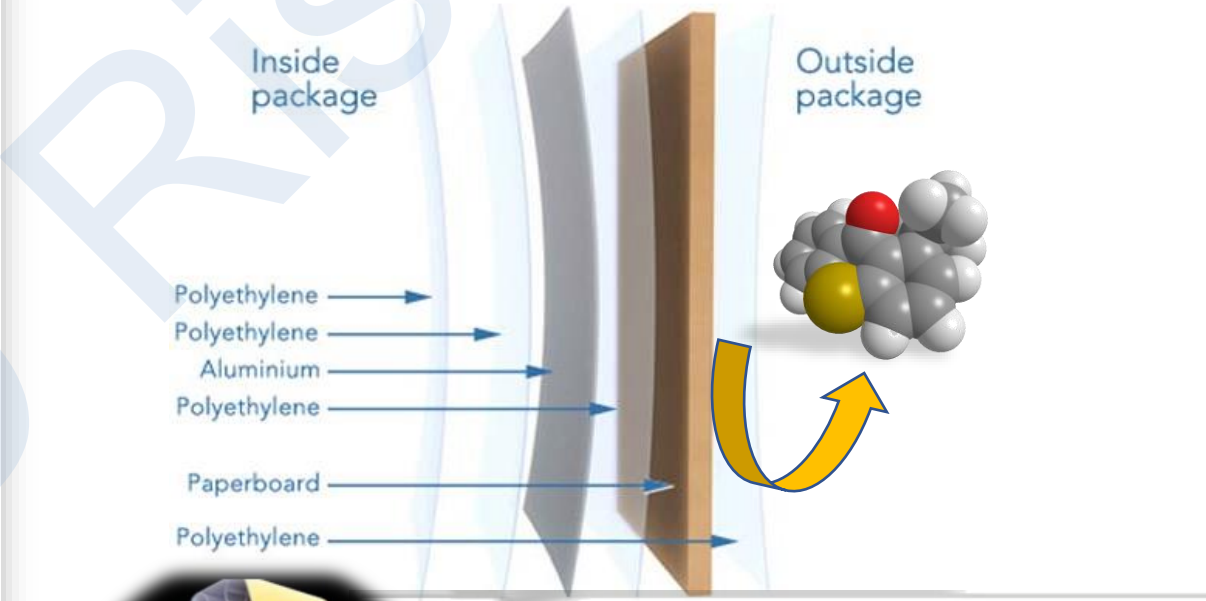
Nestle said the chemical substance was not harmful, but announced it was recalling the infant food in four European countries, including Italy, because of the problem, which related to Tetra Pak cartons.

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

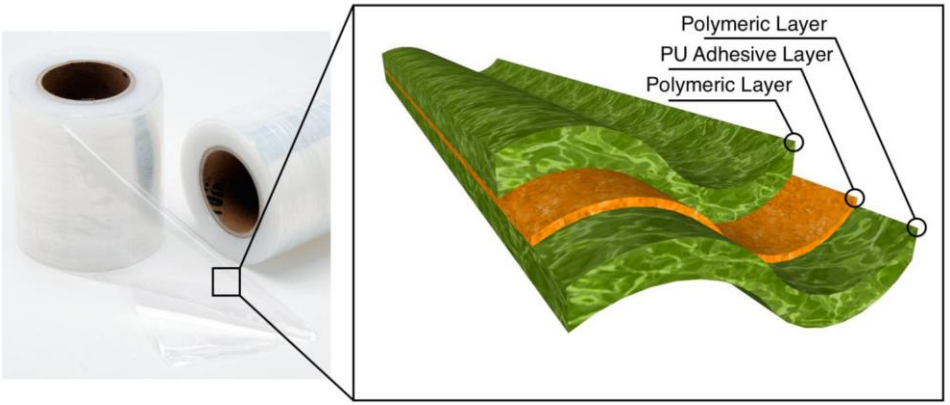
"It is incredible that such defenceless beings as babies should face such serious risks in a product as widely used as milk," Alemanno said in a statement.

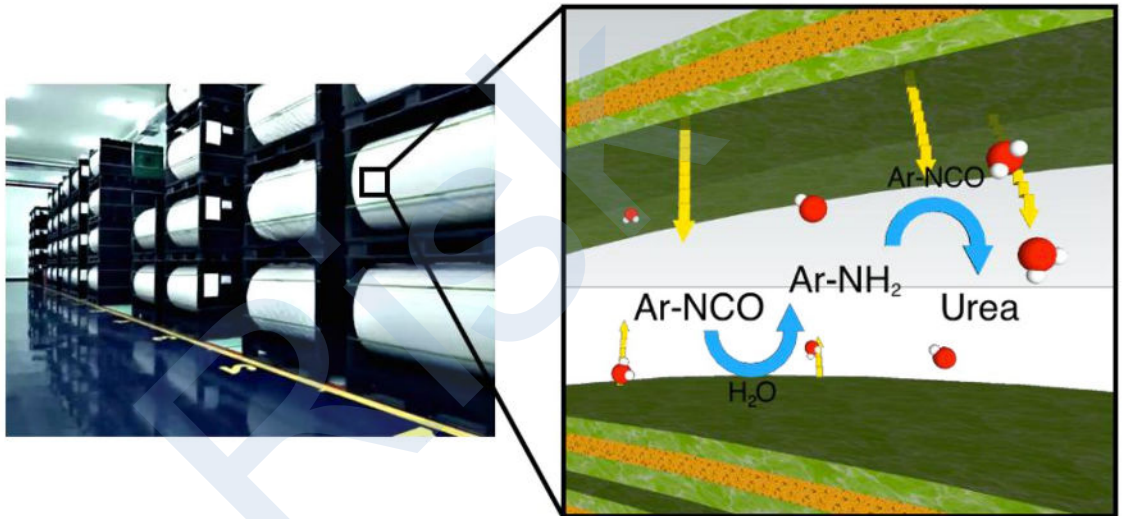
Italian officials said they had already seized about 2 million litres of Nestle baby milk earlier this month after finding traces of isopropylthioxanthone (ITX), an ink

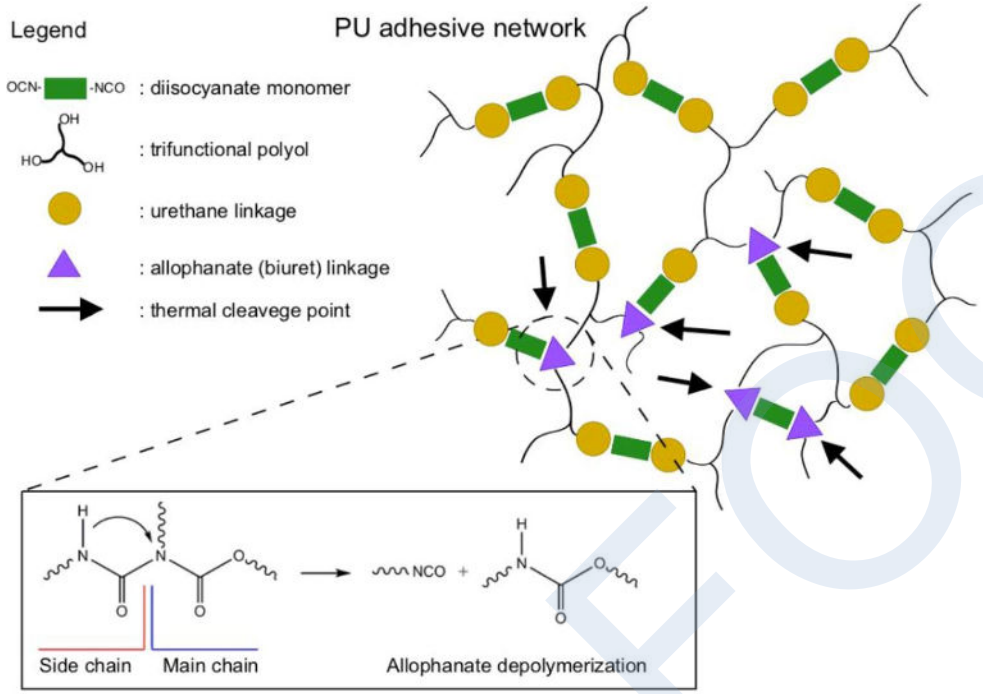
"It is incredible that such defenseless beings as babies should face such serious risks in a product as widely used as milk"

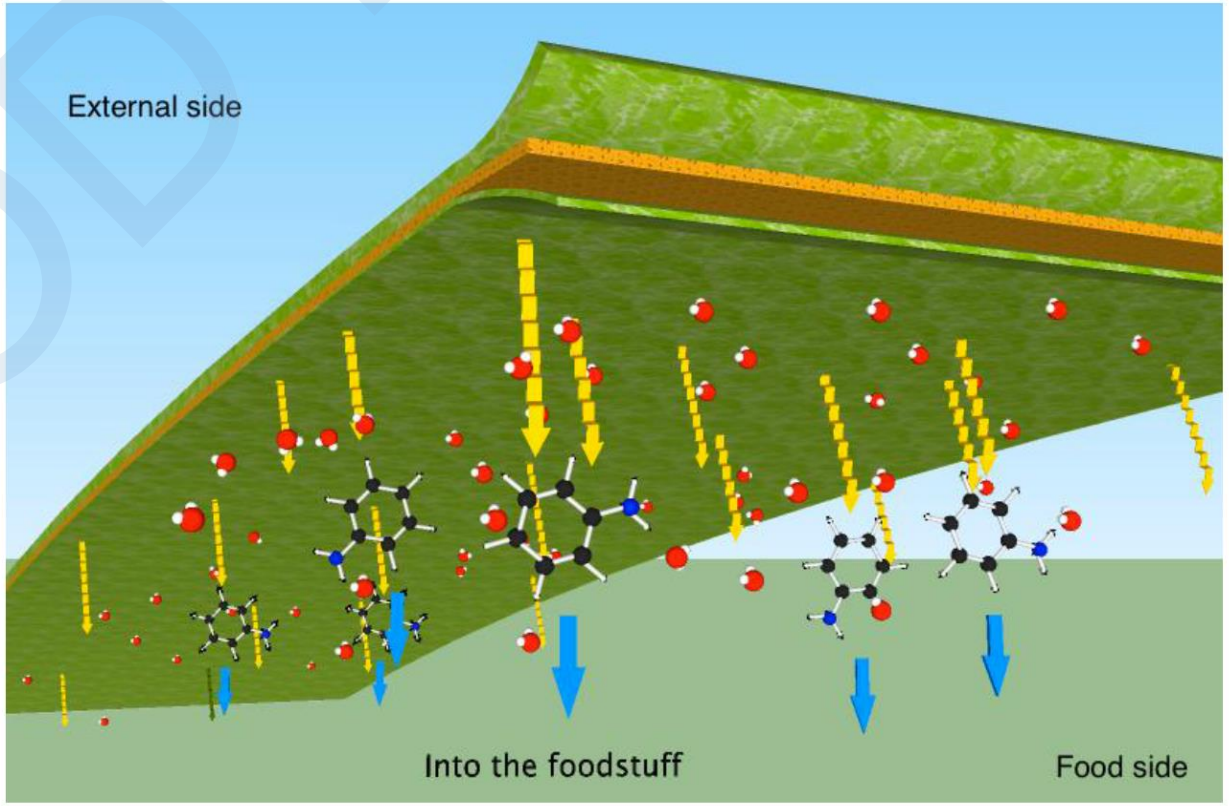


REUTERS FOUNDATION AlertNet


Polymeric Layer
PU Adhesive Layer
Polymeric Layer


Ar-NCO
Ar-NH2
Urea
Ar-NCO
H2O


Legend
PU adhesive network
OCN- -NCO : diisocyanate monomer
: trifunctional polyol
: urethane linkage
: allophanate (biuret) linkage
: thermal cleavege point
NCO
Side chain
Main chain
Allophanate depolymerization


External side
Into the foodstuff
Food side

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https://ec.europa.eu/food/safety/chemical_safety/food_contact_materials_en

FOOD

European Commission

European Commission > Food Safety > Food > Chemical safety > Food Contact Materials

HEALTH | FOOD | ANIMALS | PLANTS | AMR

CHEMICAL SAFETY

- Contaminants
- Residues of Veterinary Medicines
- Hormones in Meat
- Pesticide Residues
- Food Contact Materials
  - Legislation
  - Authorisations
  - Non-harmonised
  - Consultation

ALL TOPICS

Food Contact Materials

Food comes into contact with many materials and articles during its production, processing, storage, preparation and serving, before its eventual consumption. Such materials and articles are called **Food Contact Materials (FCMs)**. Food contact materials are either intended to be brought into contact with food, are already in contact with food, or can reasonably be brought into contact with food or transfer their constituents to the food under normal or foreseeable use. **This includes direct or indirect contact.** Examples include:

- containers for transporting food
- machinery to process food
- packaging materials
- kitchenware and tableware

The term **does not cover fixed public or private water supply equipment**.

FCMs should be sufficiently inert so that their constituents neither adversely affect consumer health nor influence the quality of the food. To ensure the safety of FCMs, and to facilitate the free movement of goods, EU law provides for binding rules that business operators must comply with.

The EU Rules on food contact materials can be of general scope, i.e. apply to all FCMs or apply to specific materials only. EU law may be complemented with Member States national legislation if specific EU rules do not exist.

The safety of FCM is evaluated by the **European Food Safety Authority** (EFSA). At EFSA's website you can search for opinions on substances to be used in food contact materials.

The safety of Food Contact Materials is tested by the business operators placing them on the market, and by the competent authorities of the Member States during official controls. Scientific knowledge and technical competence on testing methods is being maintained by the **European Reference Laboratory for Food Contact Materials (EURL-FCM).** Its website provides guidelines and other resources concerning the testing of food contact materials.

Principles for EU legislation

Union legislation on food contact materials at EU level aims to:

- Protect consumers' health
- Ensure the effective functioning of the internal market

Contacts

- SANTE-fcm@ec.europa.eu
- National authorities
- European professional organisations
- European Reference Laboratory on Food Contact Materials (EURL-FCM)
- European Food Safety Authority

Training

For government officials engaged in food and feed safety inspection of selected countries training on food contact materials is provided free of charge under BTSF. Also refer to the European Training Platform for Safer Food.

Share

RELATED LINKS

- Food Contact Materials Database
- Multi-language versions of brochures and guidance

RELATED DOCUMENTS

- EU guidelines on conditions and procedures for the import of polyamide and melamine kitchenware originating in or consigned from China and Hong Kong
- EU Guidance to the Commission Regulation (EC) No 450/2009 on active and intelligent materials and articles intended to come into contact with food

QUICK LINKS

- Rapid Alert for Food and Feed (RASFF)
- Health and food audits and analysis
- European Food Safety Authority (EFSA)
- Better Training for Safer Food (BTSF)
- E-News
- Events
- Videos

Legislation

I. General legislation

The framework Regulation

Regulation (EC) No 1935/2004 provides a harmonised legal EU framework. It sets out the general principles of safety and inertness for all Food Contact Materials (FCMs).

The principles set out in Regulation (EC) No 1935/2004 require that materials do not:

- Release their constituents into food at levels harmful to human health
- Change food composition, taste and odour in an unacceptable way

Moreover, the framework provides:

- for special rules on active and intelligent materials (they are by their design not inert)
- powers to enact additional EU measures for specific materials (e.g. for plastics)
- the procedure to per
  FCMs involving the E
- rules on labelling inc
  bottle, or a soup s
  information, please r
  contact materials.
- for compliance docun

Regulation on Good Manu

Regulation (EC) No 2023/2
so that the specifications fo

- premises fit for purpo
- documented quality
  premises, and
- selection of suitable s
  the safety and inertn

Good manufacturing rules a
materials, although the pro

II. EU legislation

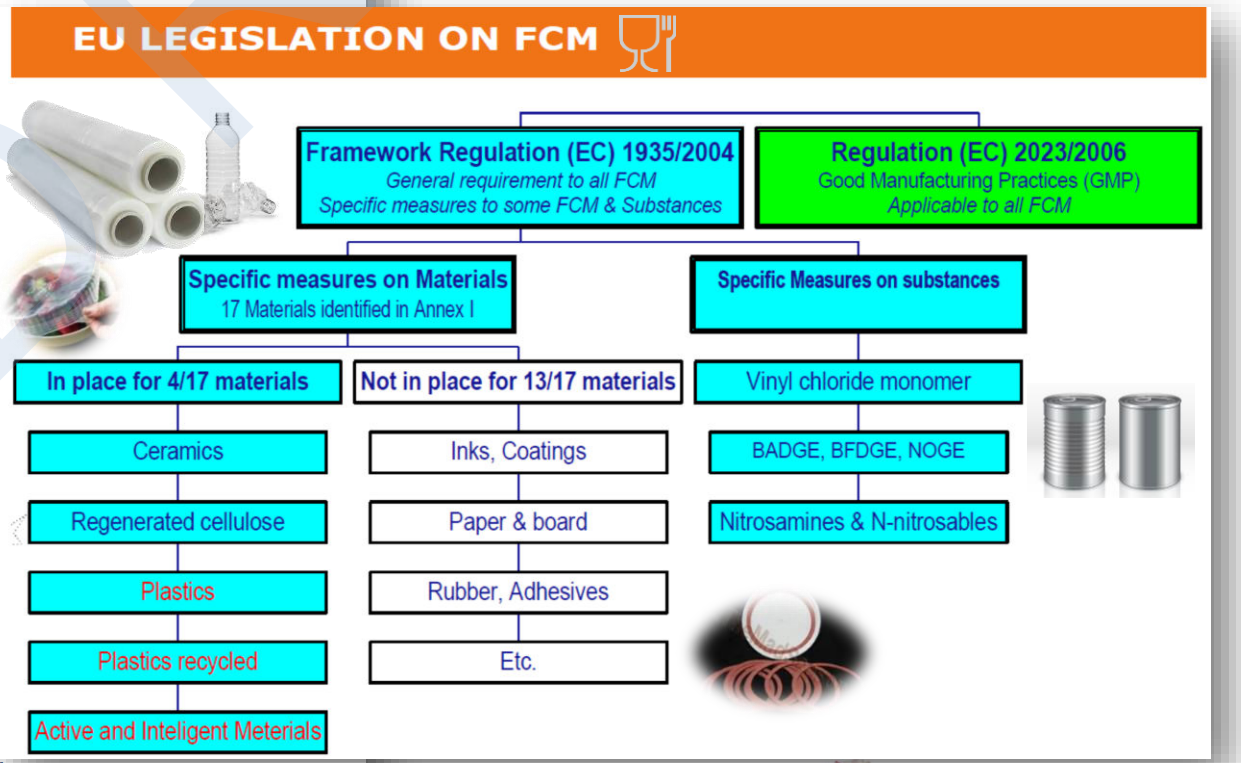
In addition to the general
cellulose film, plastics (in
materials — are covered by
starting substances used to

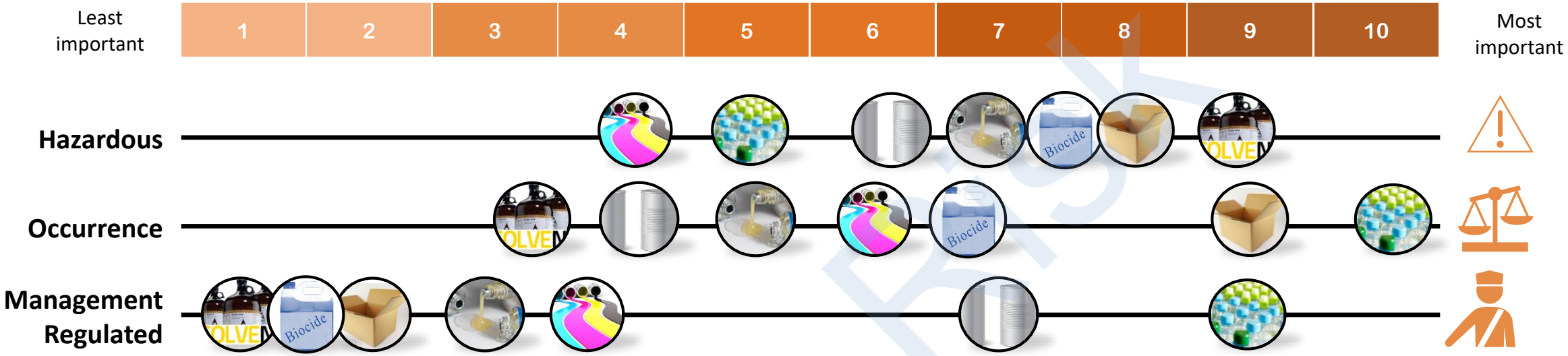
- Plastic Materials
- Active and Intelligent M
- Recycled Plastic Materi
- Ceramics
- Regenerated Cellulose

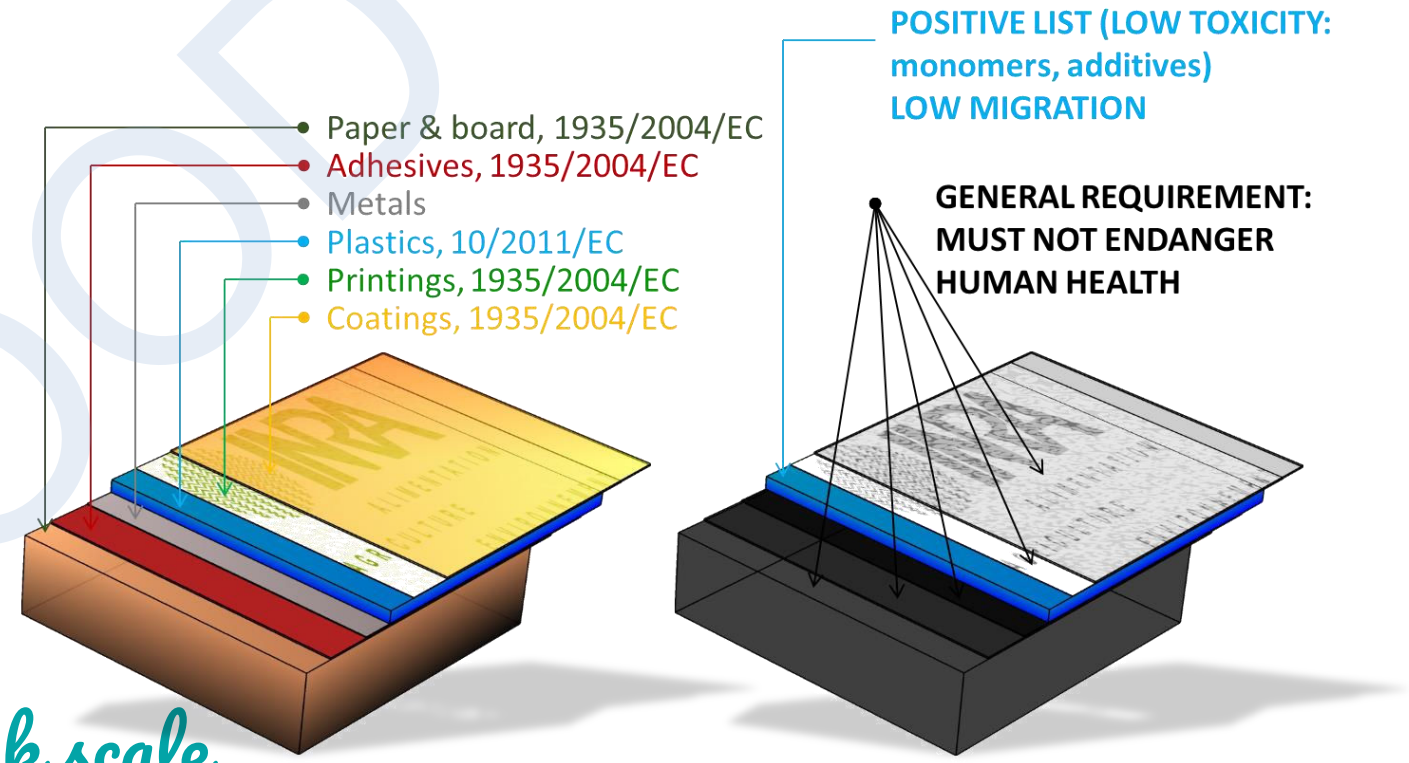
III. Other Legislation

Legislation on Specific Substances

- Regulation 1895/2005/EC - restricting use of certain epoxy derivatives in materials and articles intended to come into contact with food
- Directive 93/11/EEC - release of N-nitrosamines and N-nitrosatable substances from rubber teats and soothers



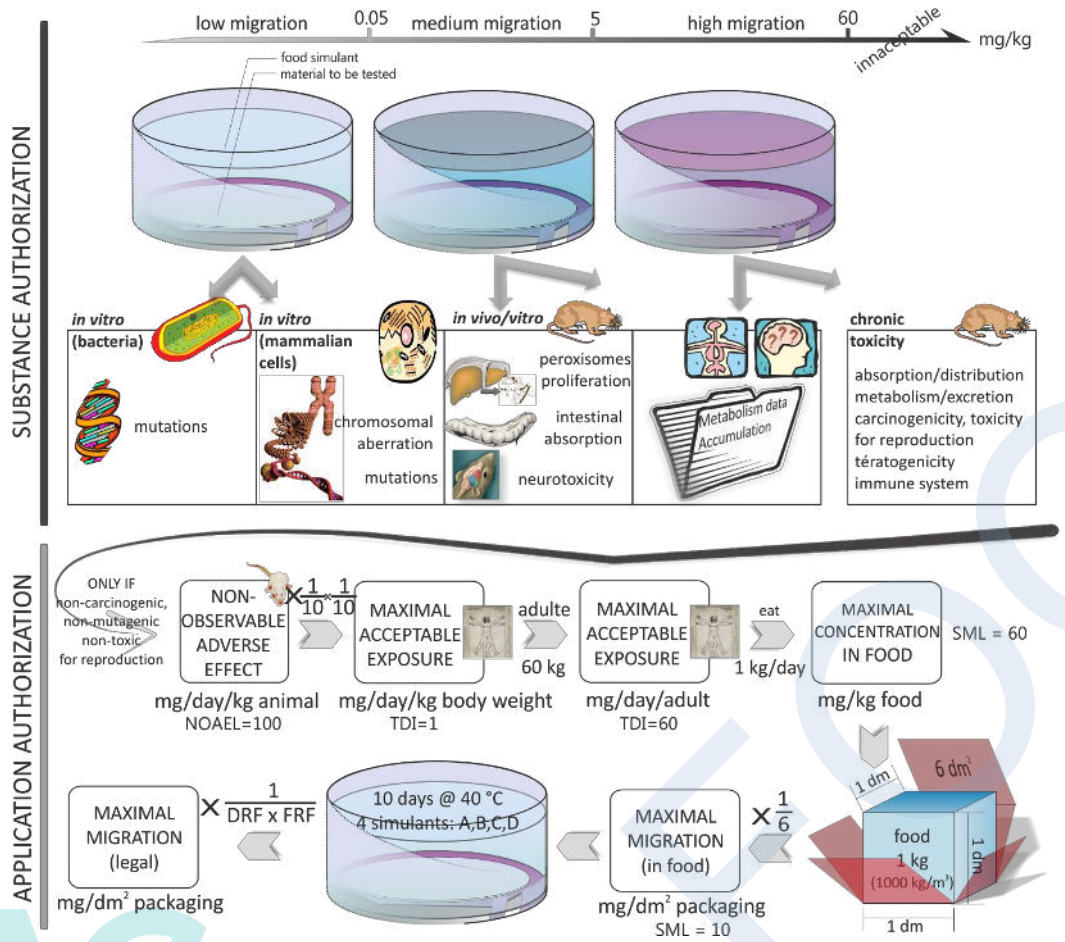




Contradictions and risk scale

SPECIFIC RULES FOR PLASTICS

EU regulation 10/2011/EC

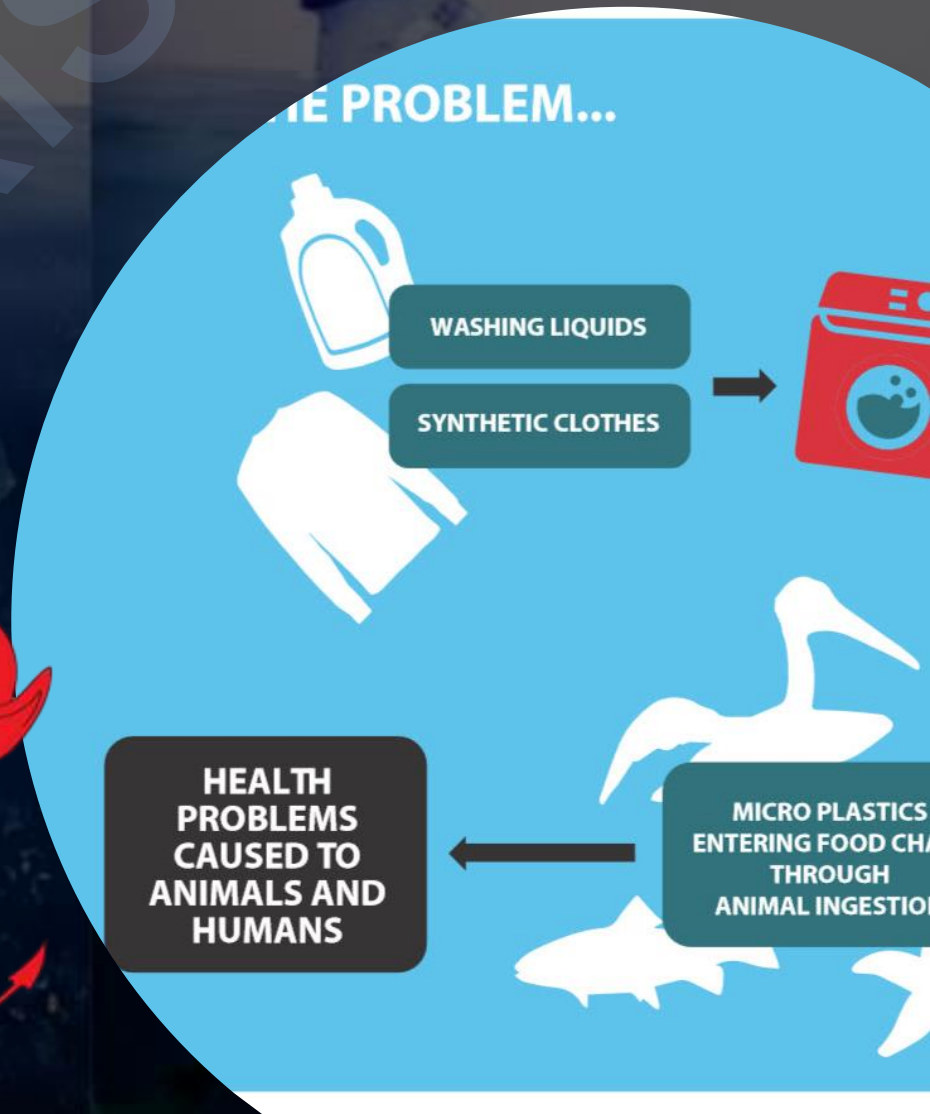


https://www.plasticseurope.org/application/files/2615/2933/0926/The_Role_of_Food_Packaging_2018.pdf

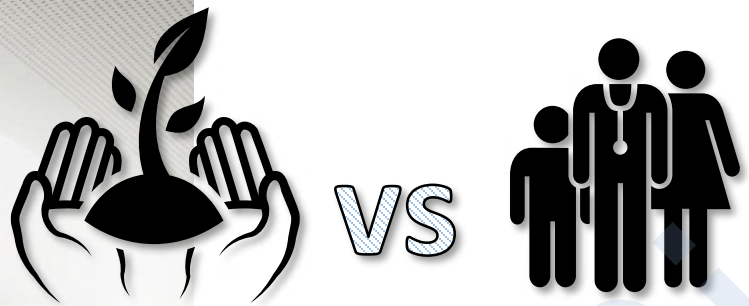
New contaminants

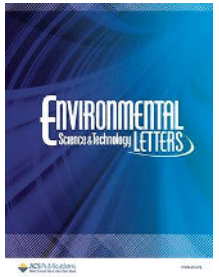
=Non Intentionally Added Substances

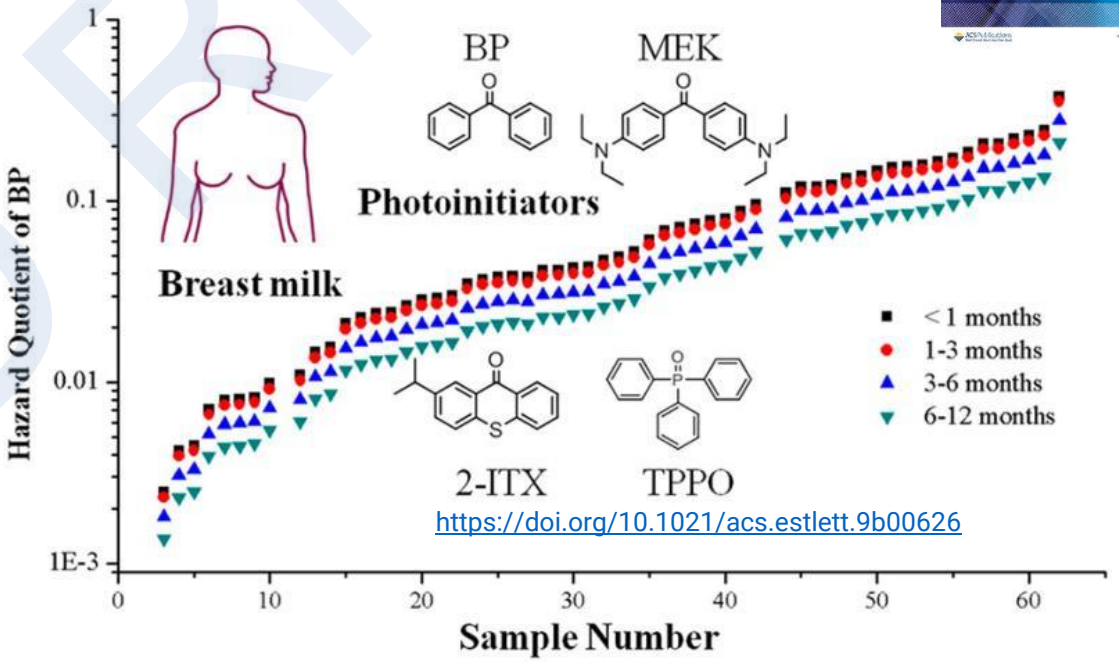
Packaging have been used for long before thinking about the consequences



Bulky, unnecessary, hazardous packaging



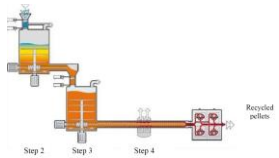




https://doi.org/10.1021/acs.estlett.9b00626

EFSA has issued upward of 140 positive scientific opinions on the safety of processes to recycle plastics for use in food contact material.

ONLY recycled PET is authorized in EU.



500 M€ have been invested in plants capable of converting recycled plastic materials into materials suitable for packaging and food contact applications

In 2014, more than 50% of the recycled PET in Europe was used in food contact applications.

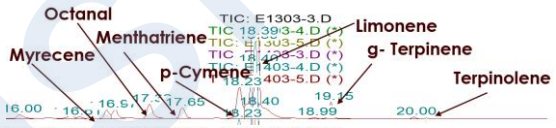
The lack of harmonisation amongst Member States generates legal uncertainty and unnecessary burden for the industry using recycled materials.

It also sets up obstacles for the Circular Economy

Recycling plastics for food contact

REGULATION 282/2008/EC

Misuse issues (post-use contaminations) of Polyethylene terephthalate **(PET)** can be easily handled : glassy polymer, it is mainly contaminated by small contaminants which can be removed by a devolatilization step above T_g

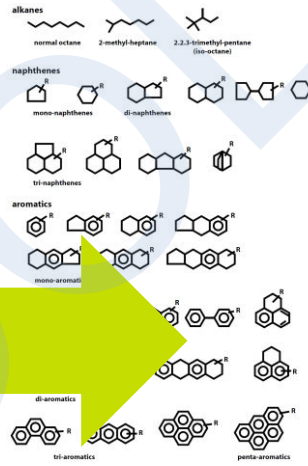


1. Filling and use of HDPE milk bottles
2. Recollection
3. Sorting

Foodgrade HDPE milk bottles

Recycling

Polyolefins are rubber polymers which can be easily contaminated by high molecular weight contaminants after use.



Paper and board contains large amount of residues from printing inks: aromatic (carcinogenic) and aliphatic **mineral oils** can be transferred without contact and lead to cross-contamination between materials

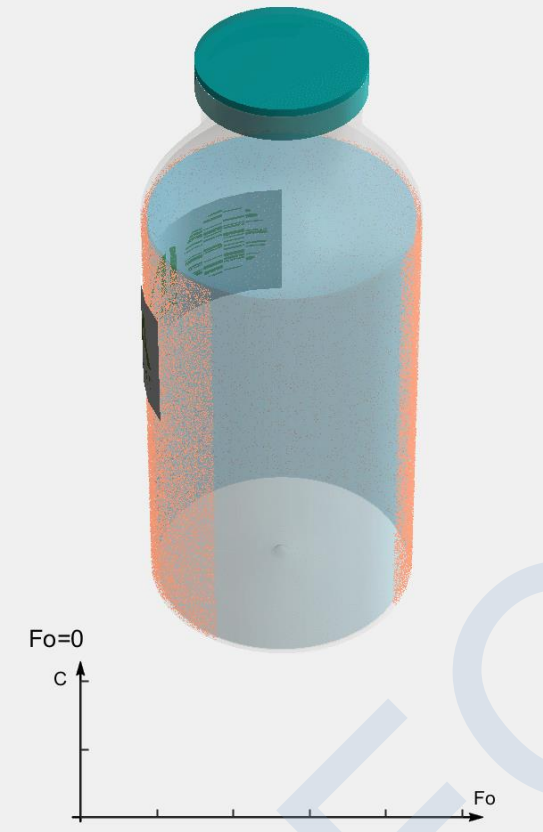
*J. of Chromatography A. 2013;**1293:107-19.***

Recycling of PET vs other materials

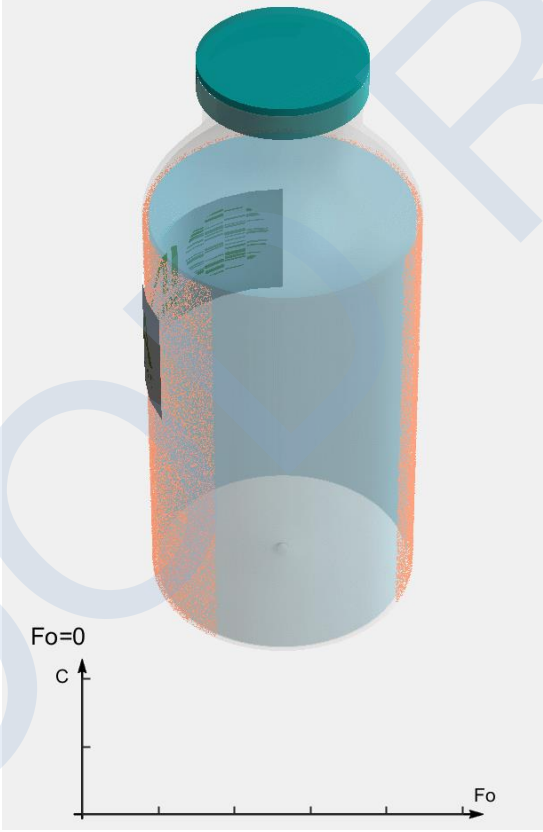
Recycled PET for food contact is authorized (282/2008/EC)
Recycled polyolefins are authorized only in Germany
Recycled paper and boards is source of recurring crises in EU.

How to used recycled recycled materials

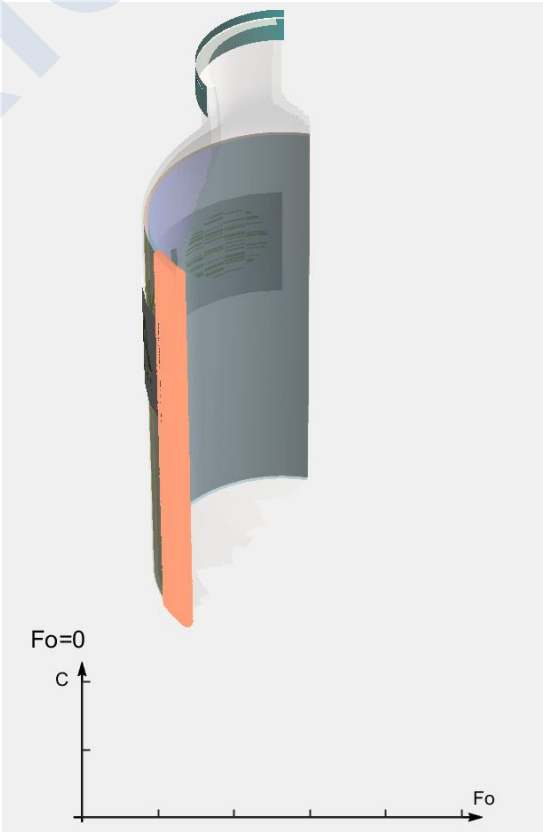
Within monolayer materials
Rule of TTC (Total Threshold of Concern)



Behind a functional barrier
rule of 10 ppb for non-carcinogenic, non-mutagenic, non-reprotoxic

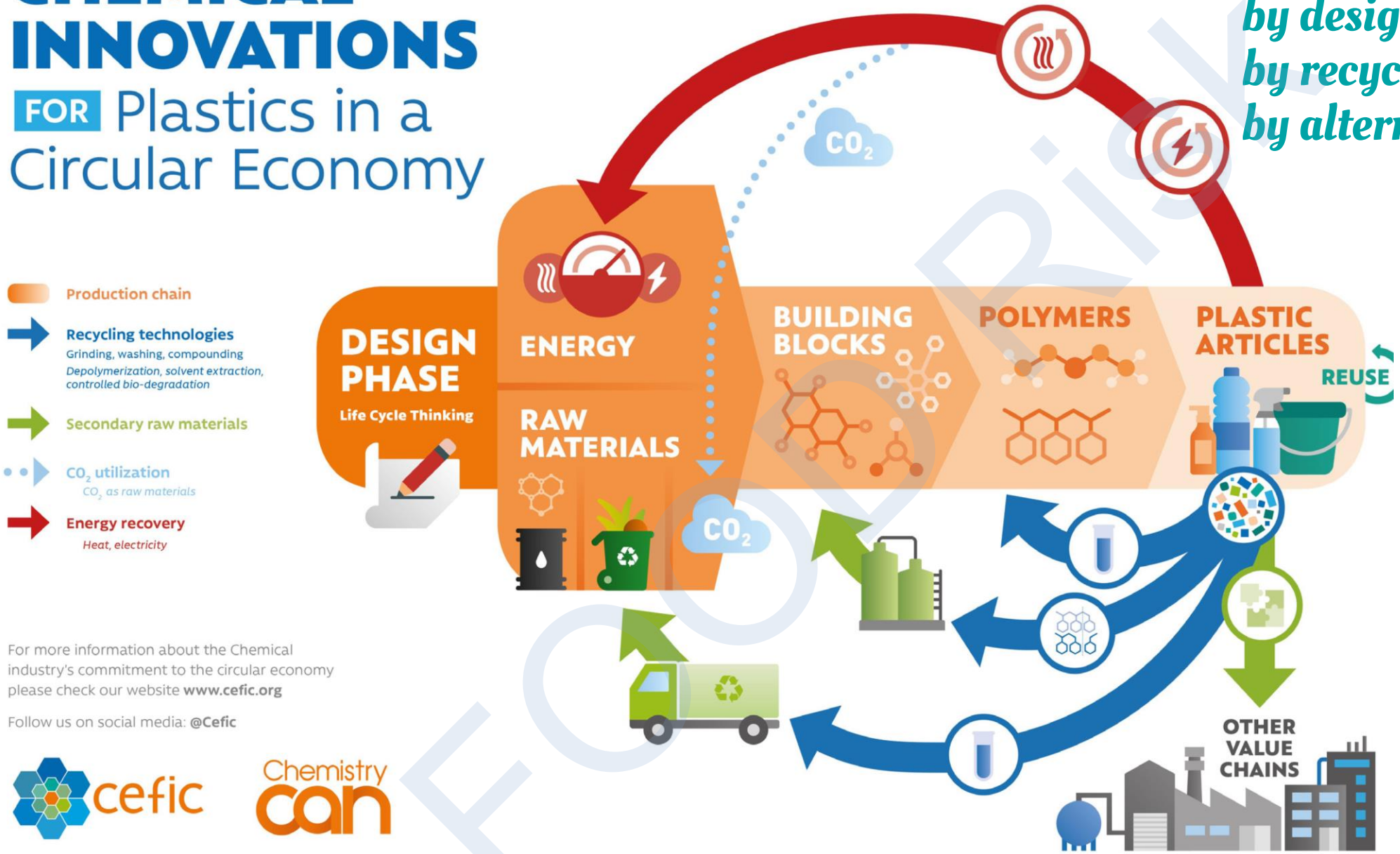


Within multilayer and/or multimaterial
No-clear guidance, specific rules case-by-case



CHEMICAL INNOVATIONS FOR Plastics in a Circular Economy

> *Circularity*
> *by design*
> *by recycling*
> *by alternative feedstocks*



For more information about the Chemical industry's commitment to the circular economy please check our website **www.cefic.org**

Follow us on social media: **@Cefic**

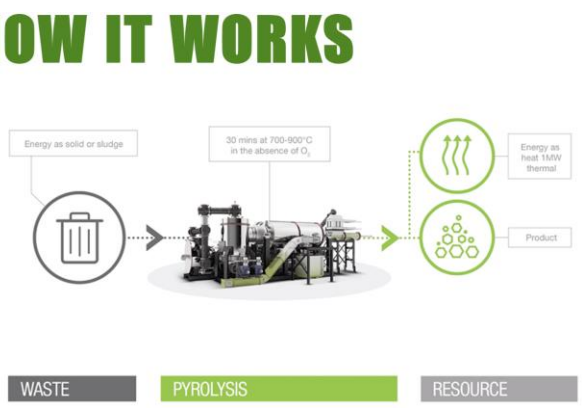
cefic

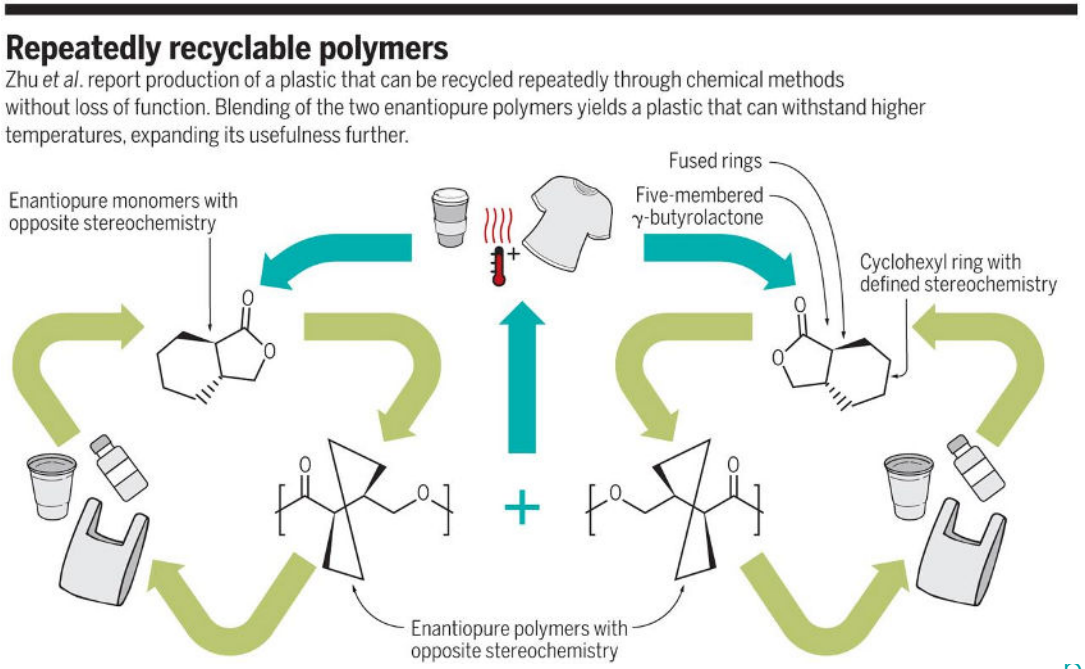
Chemistry can

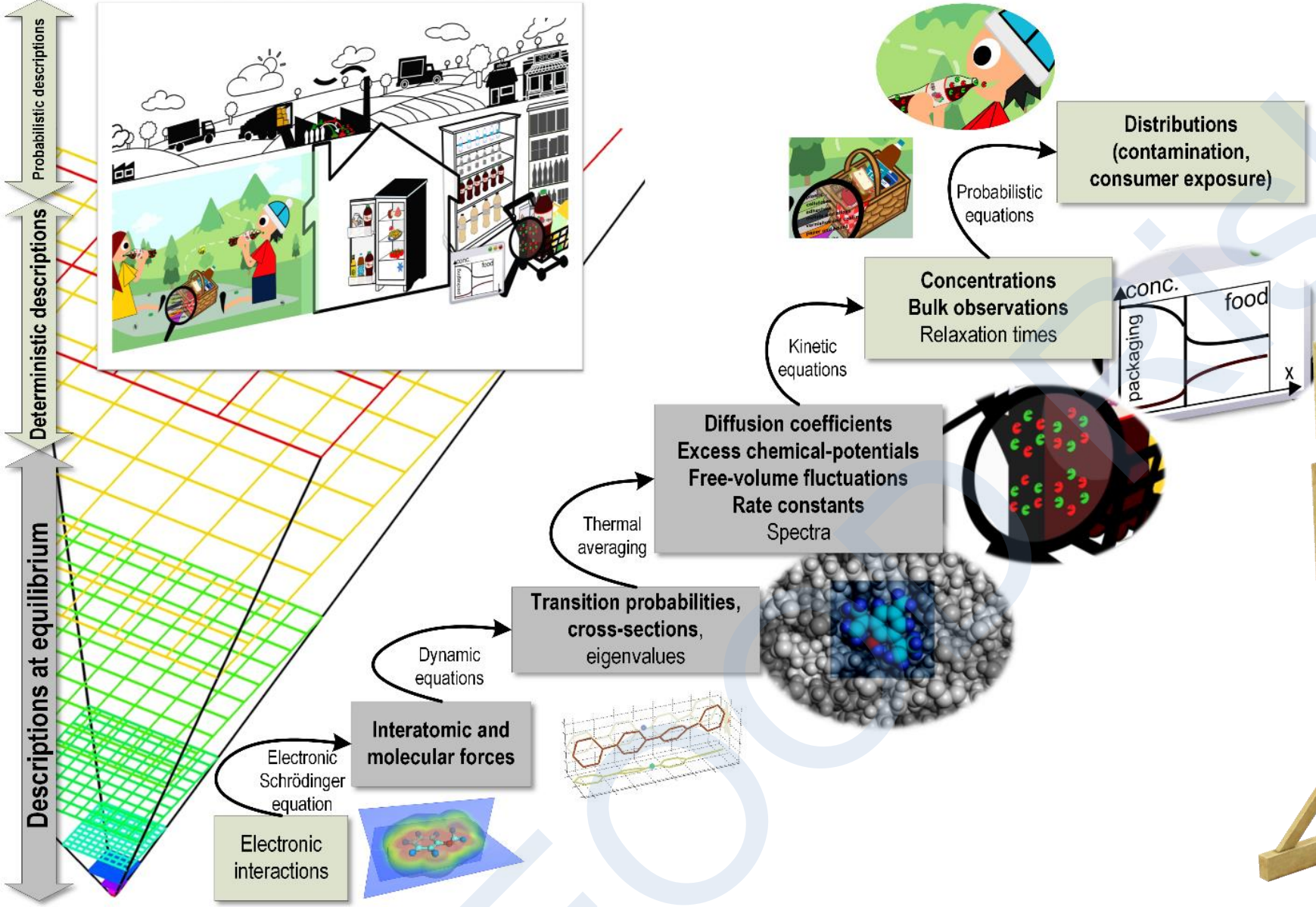
Source: Cefic

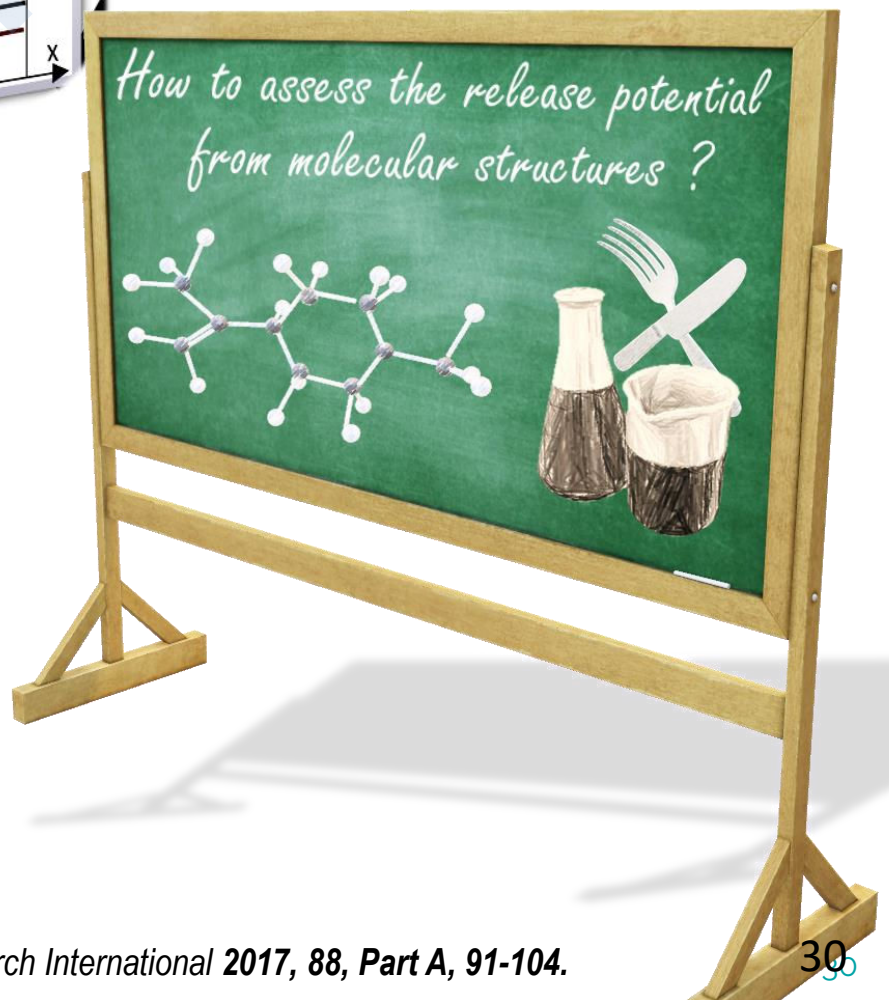
Current researches

- MATERIAL DESIGN
  - Longer lifetime
  - Decrease material usage
  - Improve sorting, separation, recyclability
  - Trigger biodegradability
- ARTICLE DESIGN
  - Design for dismantling
  - Decrease material usage
  - Digital design for reuse
  - Digital development of biobased
- RECYCLING
  - Mechanical
  - Chemical
  - Thermal and thermomechanical
  - Multimaterial, multilayer
- FEEDSTOCKS
  - Plastic waste based
  - Food waste based
  - CO/CO_2 based





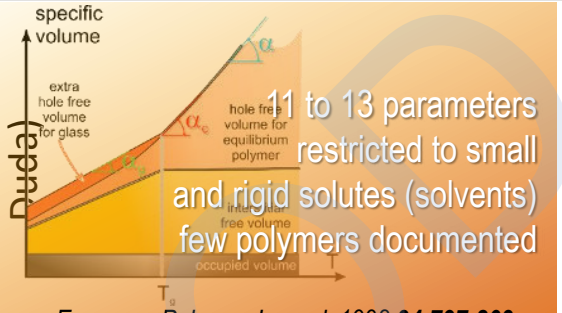
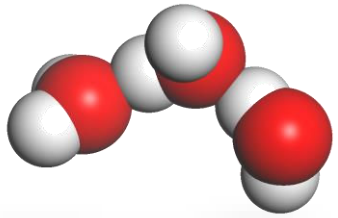
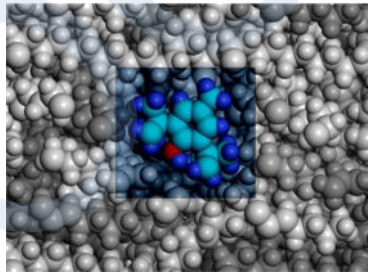
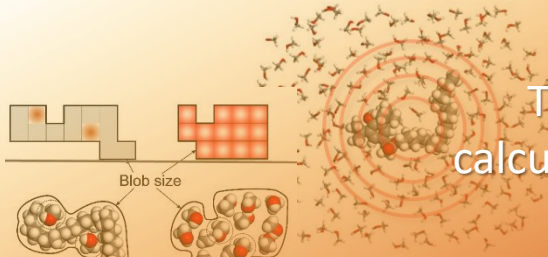


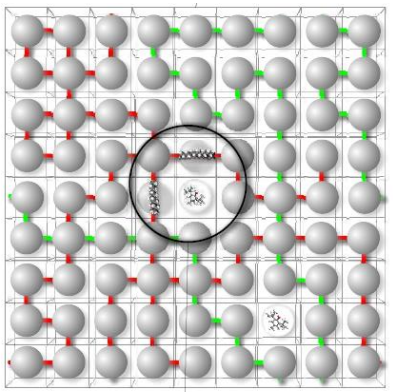


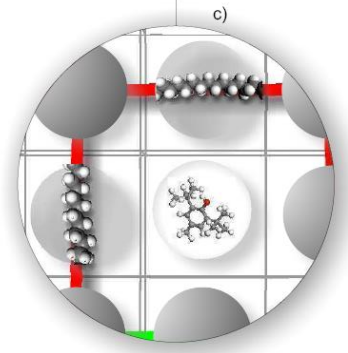
Food Research International ***2017, 88, Part A, 91-104.***

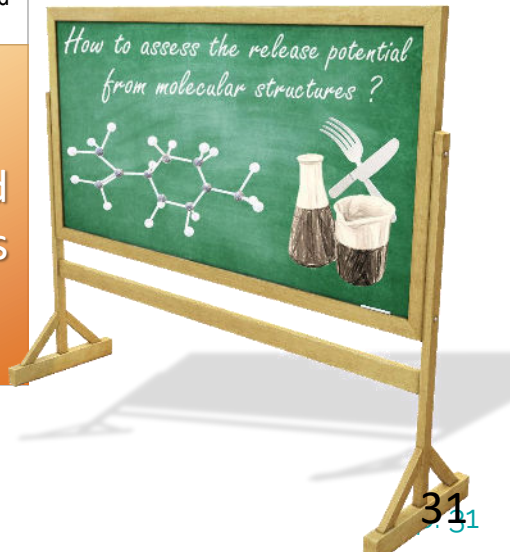
coarse

detailed

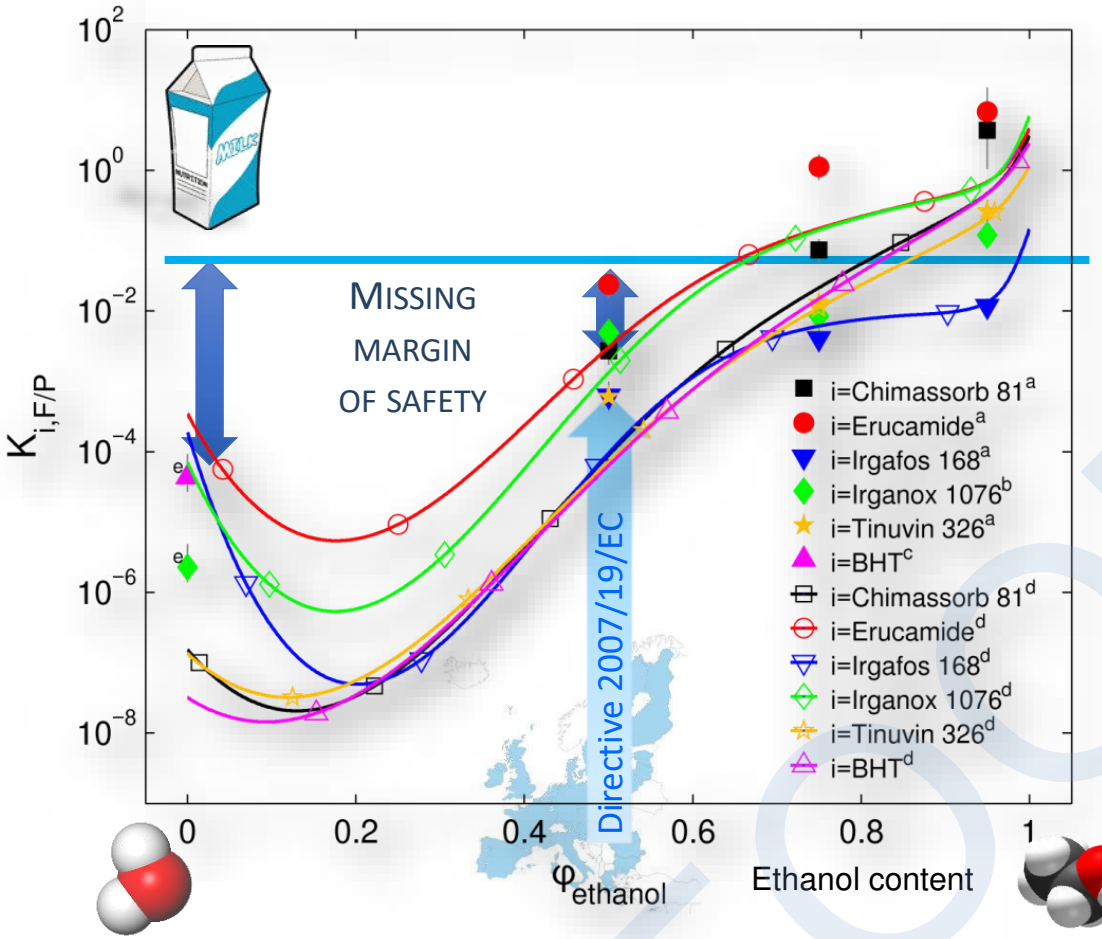
	TRANSPORT diffusion coefficients D and their activation E_a	THERMODYNAMICS chemical affinity (Flory-type isotherms)
Worst-case approaches (arbitrary)	For compliance testing (Piringer's equation) *Food Additives and Contaminants. 2005;**22:73-90.***	$K_{F/P} = 1 \; or \; 10^{-3}$ JRC Scientific and Technical Reports EUR 27529 EN. Ispra (Italy): European Commission; 2015.
Group contribution methods (fitting)	Decision tree *Journal of Applied Polymer Science. 2006;**101:2167-86.***	UNIQUAC, UNIFAC, Flory—Huggins Prausnitz, Lichtenthaler & de Azevedo. Molecular Thermodynamics of Fluid-Phase Equilibria: Pearson Education; 1998.
Theory from first principles (statistical physics)	Free-volume theory (Vrentas-Duda)  *European Polymer Journal. 1998;**34:797-803.***	Self-association theory  Kontogeorgis & Folas. Thermodynamic Models for Industrial Applications: From Classical and Advanced Mixing Rules to Association Theories: Wiley; 2009.
Full atomistic simulation or coarse-grained (no assumptions)	for $D \geq 10^{-14} m^2 . s^{-1}$  *Journal of Chemical Physics. 2010;**132:194902.***	 *Industrial & Engineering Chemistry Research. 2010;**49:7263-80.***

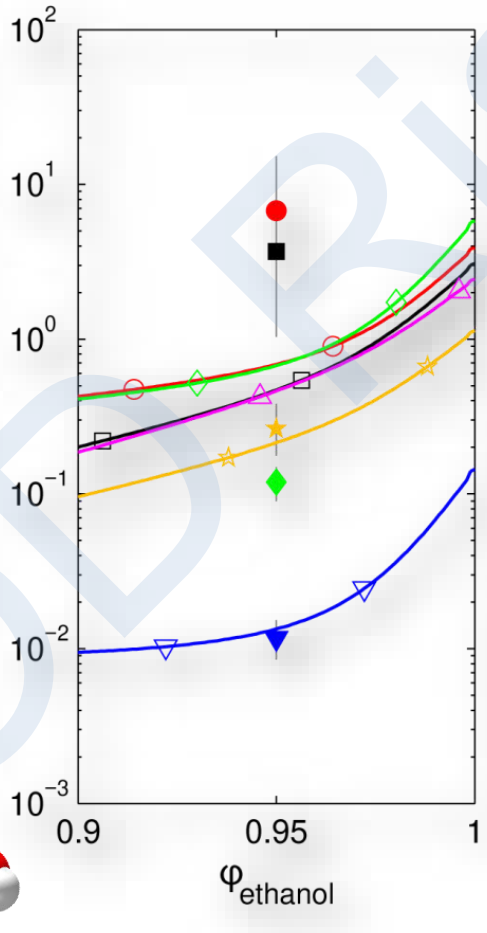


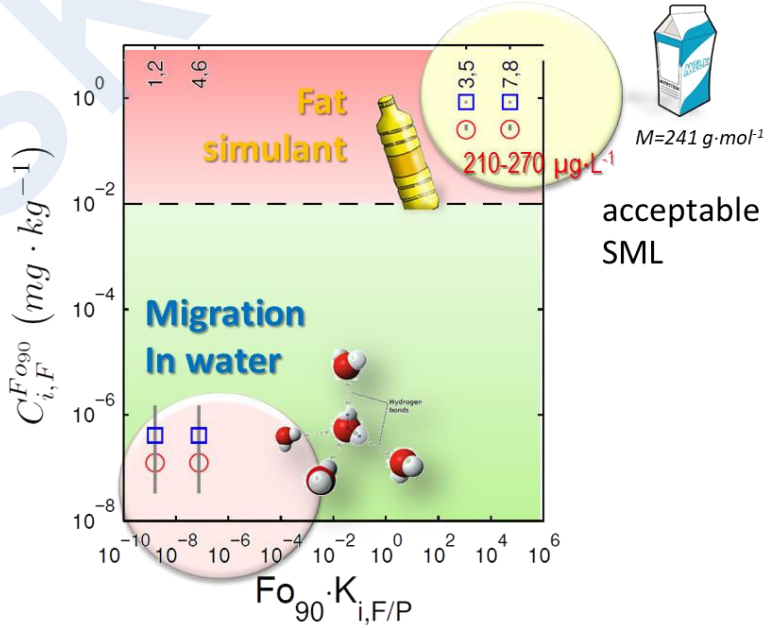




Molecular modeling challenged the choice of food simulants



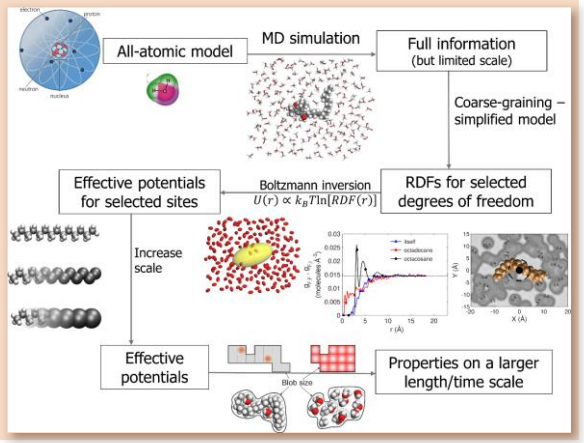


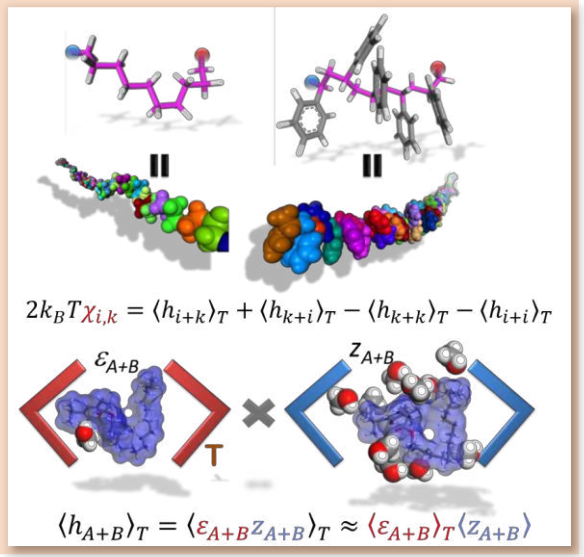


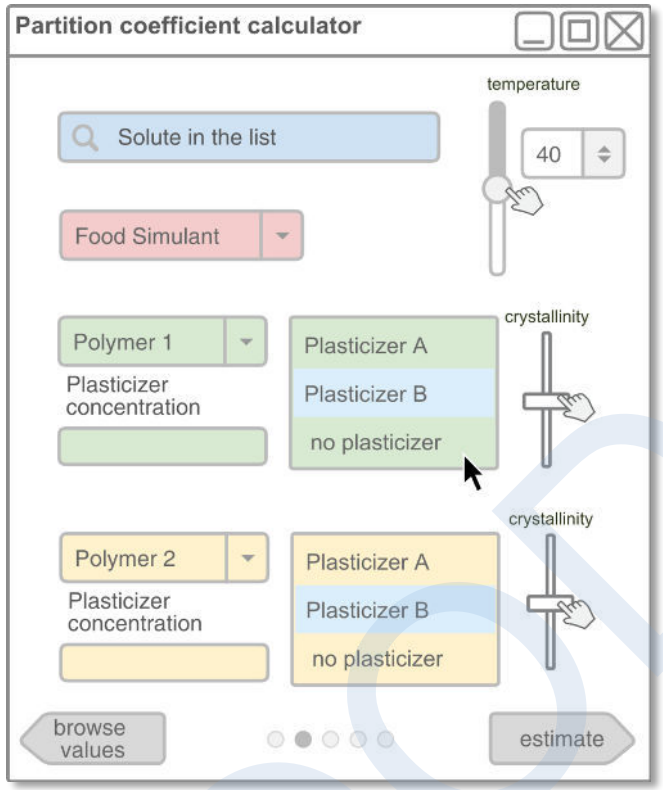
Ind. Eng. Chem. Res. 2010, 49(16), 7763-7780.
Food Additives and Contaminants, 2009, 26(12), 1556-1573.

	Date of case	Last change	Reference	Country	
6.	08/09/2005		2005.631	ITALY	food contact materials
RASFF Portal					migration of isopropyl thioxanthone (250 µg/l) from packaging of milk for babies from Spain

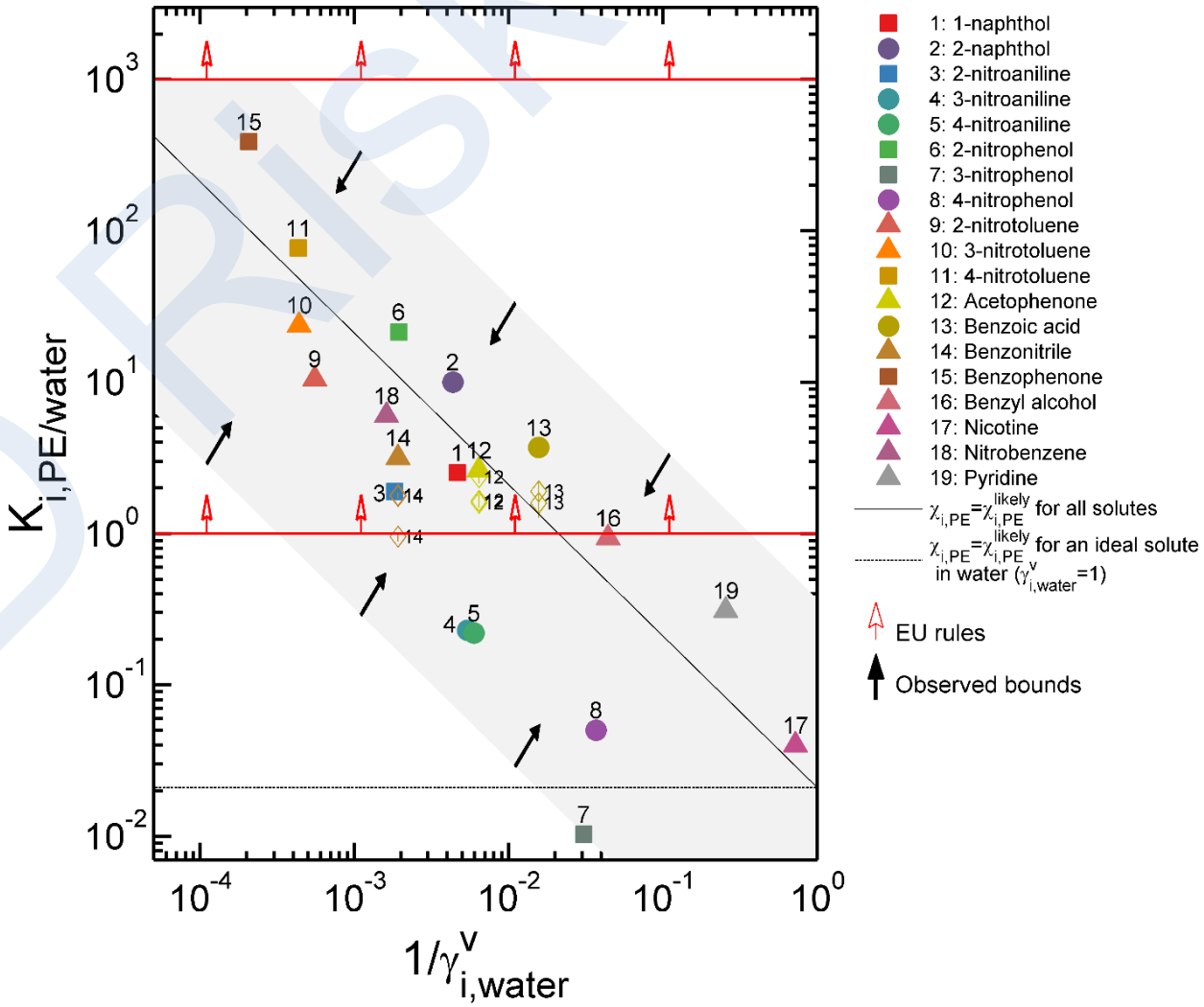
Prediction of partition coefficients (NIAS, water)







Industrial & Engineering Chemistry Research 2009, 48 (11), 5285 5301.
International Journal of Chemical Reactor Engineering 2010, 8.
Industrial & Engineering Chemistry Research 2010, 49 (16), 7263 7280.
Industrial & Engineering Chemistry Research 2017, 56 (3), 774 787.



$$\{\mu_{i,k}^{excess}\}_{k=P,F} = \ln\gamma_{i,k}^{v} = \left(1-\frac{1}{r_k}\right)\phi_k + \chi_{i,k}\phi_k^2$$

$$2k_B T\chi_{i,k} = \langle h_{i+k}\rangle_T + \langle h_{k+i}\rangle_T - \langle h_{k+k}\rangle_T - \langle h_{i+i}\rangle_T$$

$$K_{i,P/F}^{semi-crystalline} \approx \frac{1-crystallinity}{\phi_{i,F}^{sat}\exp(1+\chi_{i,P})}$$

Contamination without contact

Cross-contamination=Main of NIAS and new (old) routes of contamination

old routes = new issues

Hazard Analysis *vs* Risk assessment

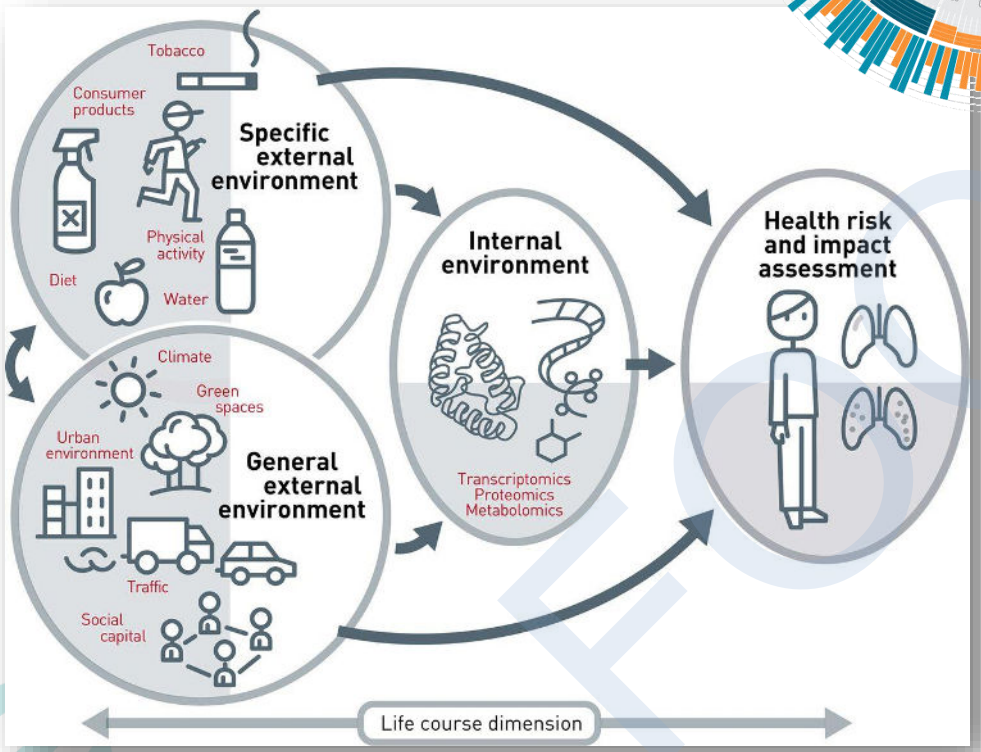
Hazard – health

Risk – occurrence

The cascade of risk assessment and management

Chronic exposure

Human exposome



			Risk Tradeoff
		Risk balancing	Conflicts *cognitive, evaluative, normative*
	Scientific risk assessment	Conflict: *evaluative*	
Routine	Conflict: *cognitive*	Targets: BfR, anses, ISTITUTO SUPERIORE DI SANITÀ, FOOD STANDARDS AGENCY, efsa European Food Safety Authority	Targets:DG SANCO, industry stakeholders 
Target: *industry*	Target: *professional associations*		
Discourse: *internal*	Discourse: *cognitive*	Discourse: *reflective*	Discourse: *participatory*
Outcome: *simple*	**Outcome: *complex***	**Outcome: *uncertain***	**Outcome: *ambiguous***

OUTGASSING DATA

NASA and ESA maintain lists of materials with low-outgassing properties suitable for use in spacecraft, as outgass products can condense onto optical elements, thermal radiators, or solar cells and obscure them. Materials not normally considered absorbent can release enough light weight molecules to interfere with industrial or scientific vacuum processes. Moisture, sealants, lubricants, and adhesives are the most common sources, but even metals and glasses can release gases from cracks or impurities.

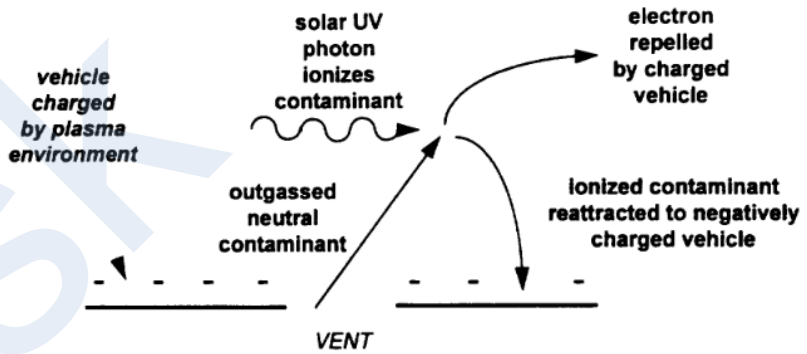
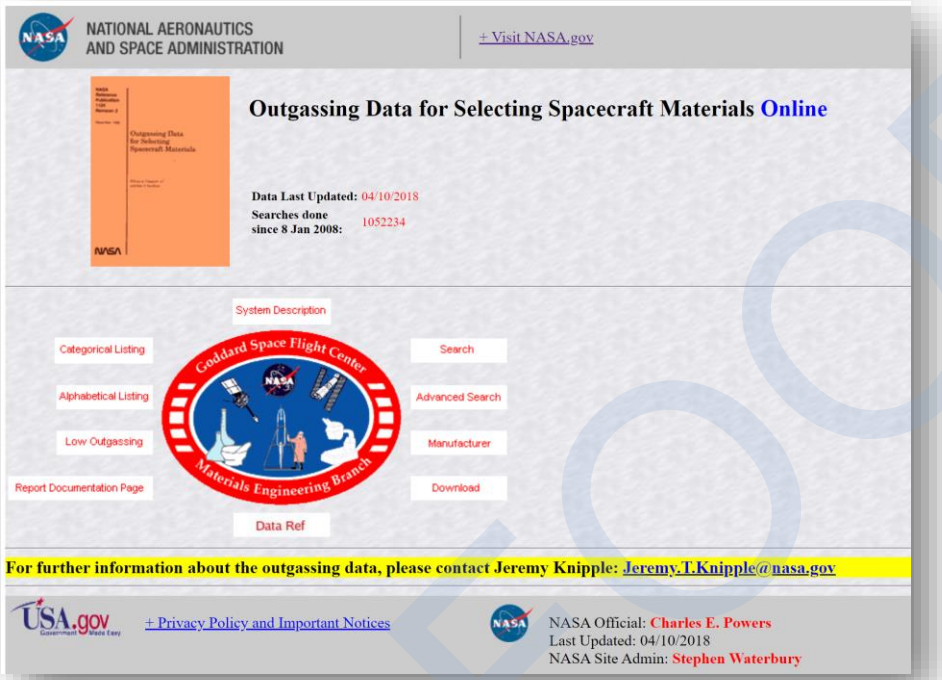
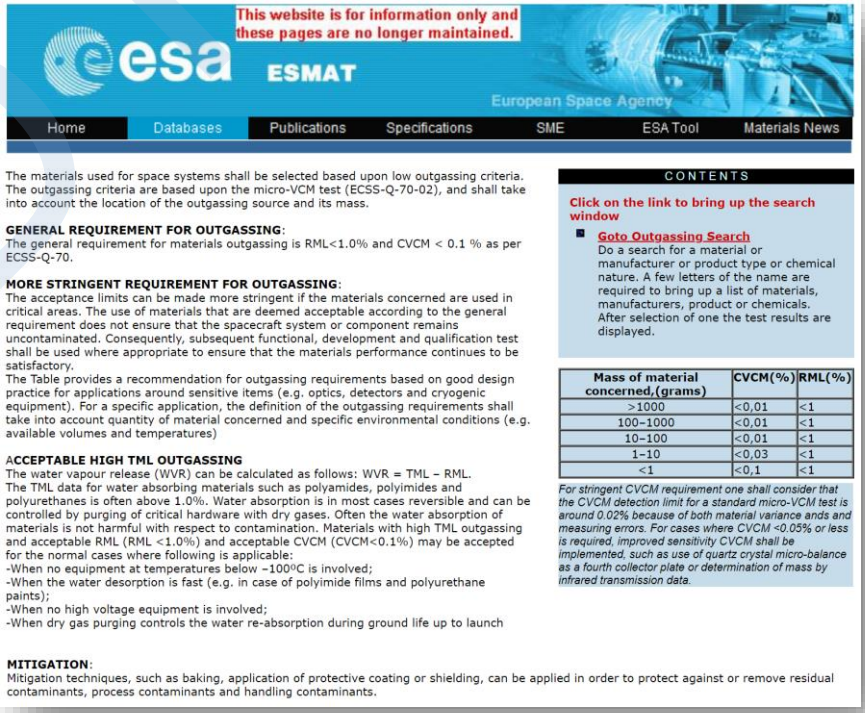


Figure 2-14. Electrostatic reattraction of ionized contaminants.

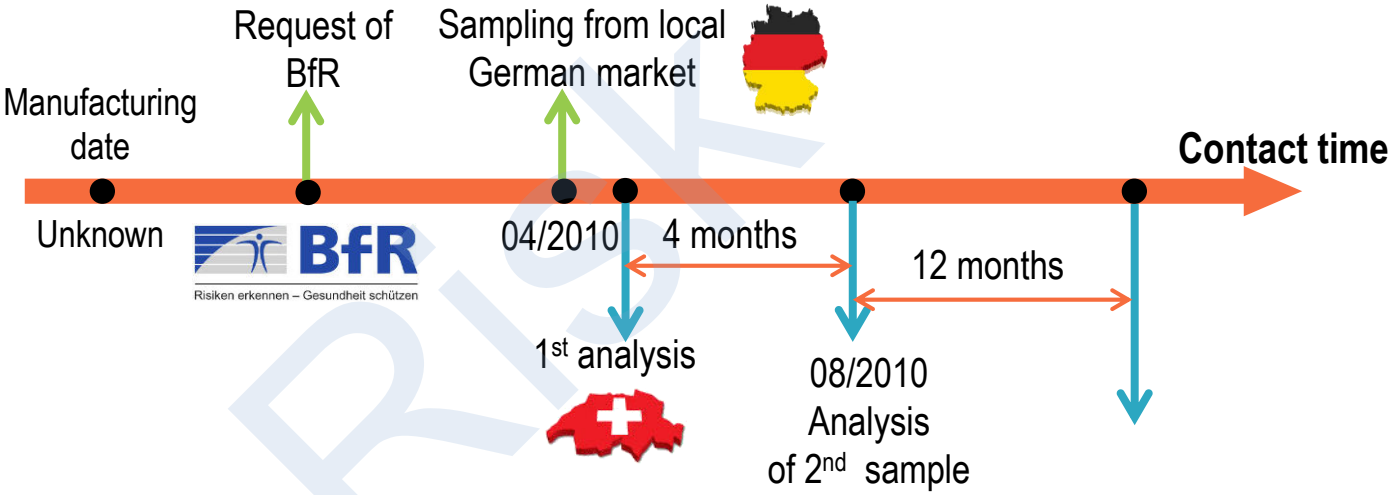
https://outgassing.nasa.gov/

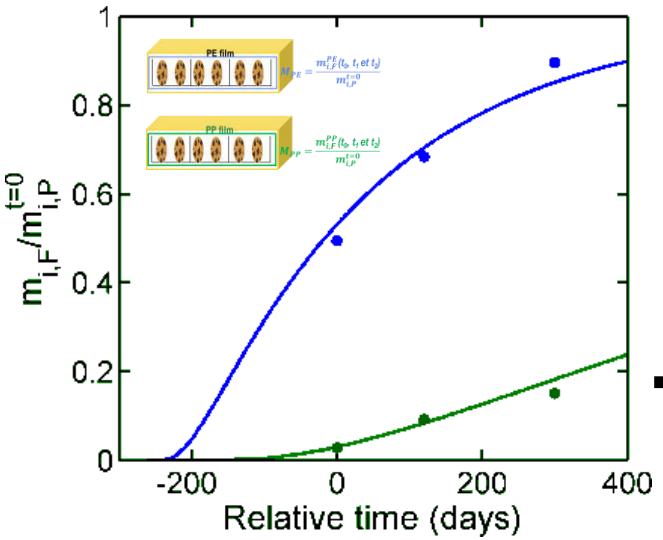


http://esmat.esa.int/services/outgassing_data/outgassing_data.html



119 dry food products
(3 samples/category)
Biedermann et al. (2013)





$$\rightarrow \frac{M_{PE}}{M_{PP}} \propto \frac{D_{i,PE}}{D_{i,PP}}$$

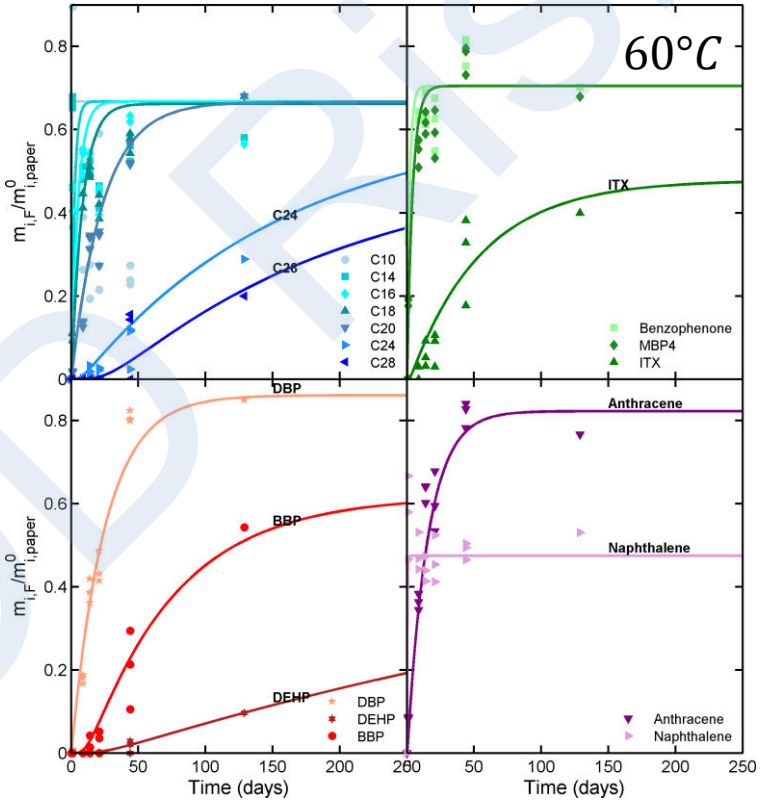
Paper and board = prevalent source of chemical contaminants in food

Mineral Oils, Printing inks, adhesives

CONTAMINATION TROUGH THE GAS PHASE

TENAX packed within a 50 µm thick BOPP bag and exposed to a cardboard material formulated with 15 surrogates

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



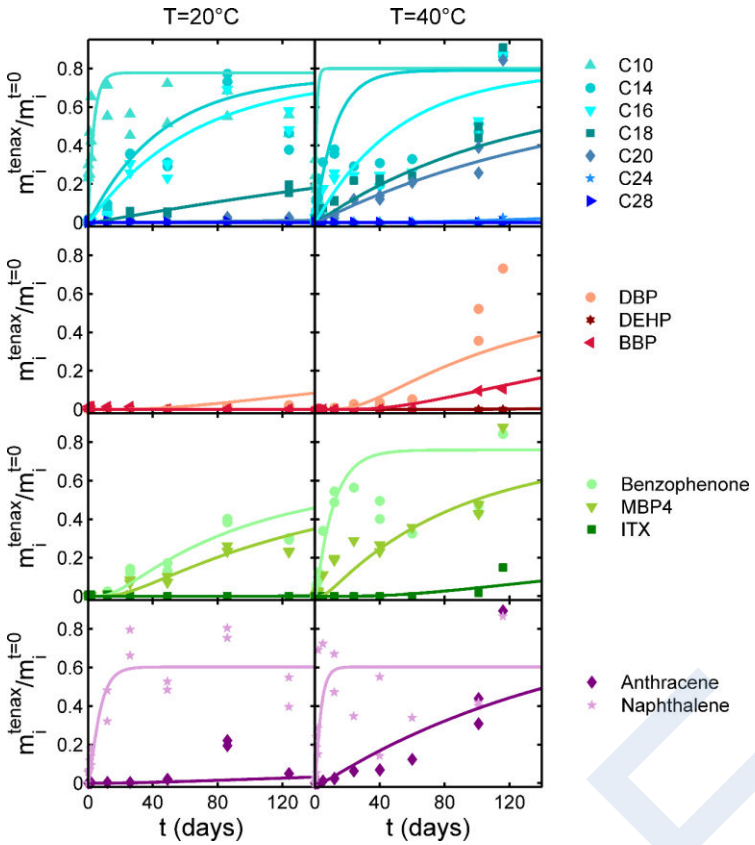
$$\frac{m_{i,F}^{(t)}}{m_{i,P}^{0}} = \frac{V_F}{m_{i,P}^{0}} \int_0^t C_{i,F}^{(t)}\, d\tau$$

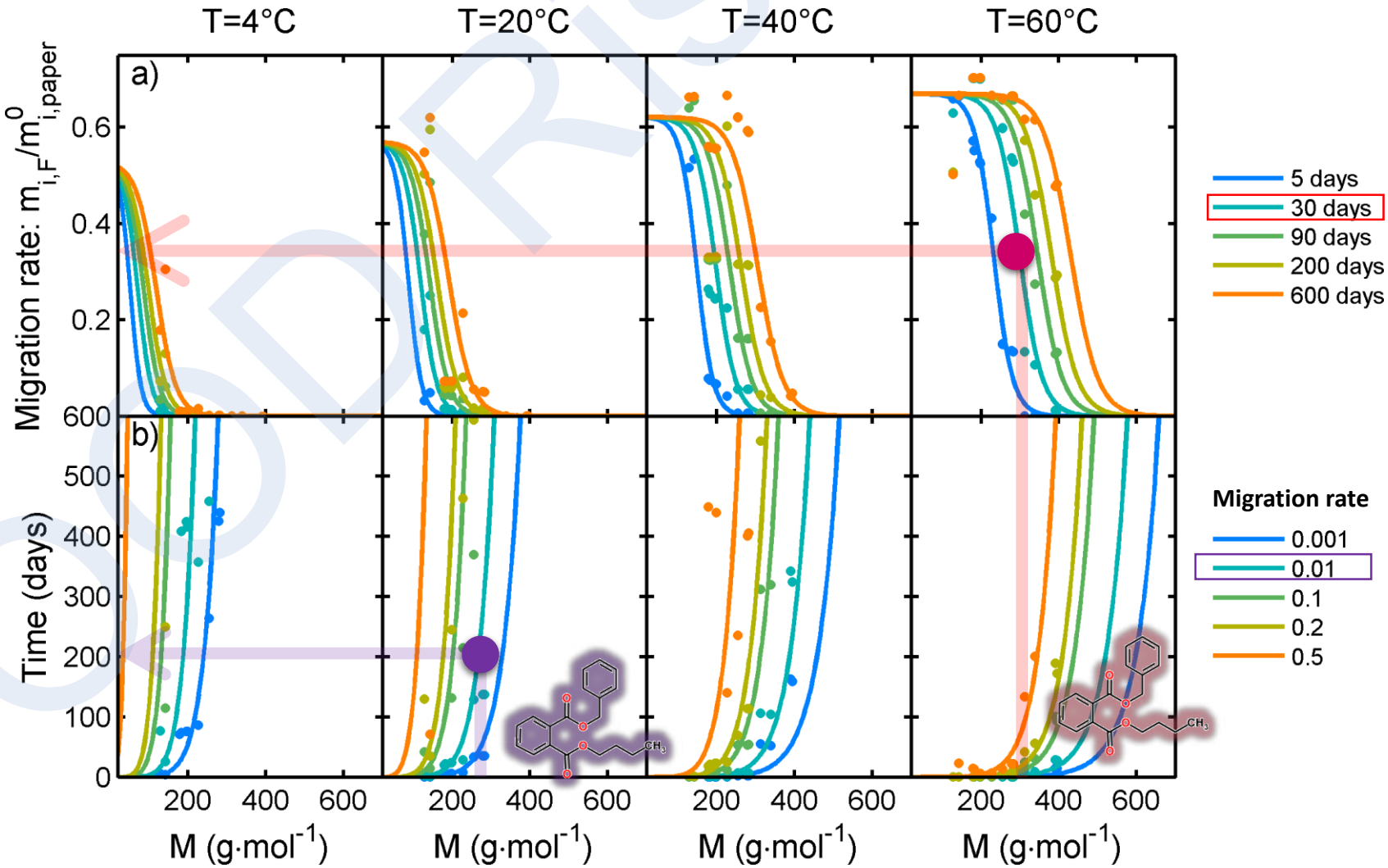
Experimental results at 60°C, *i*=1…15 → **Detailed modeling** with FMECAengine → $\widetilde{C_F}(T,t,i)$ *i* = 1..15 solutes at any temperature → **Simplified modeling** Solute independent → $\widetilde{C_F}(T,t,M)$ simplified at any temperature

Food Additives and Contaminants. 2017;34:1703-20.

CONTAMINATION TROUGH THE GAS PHASE

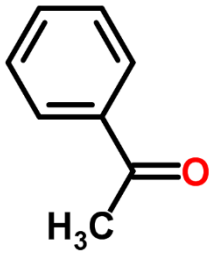
TENAX packed within a 50 µm thick BOPP bag and exposed to a cardboard material formulated with 15 surrogates



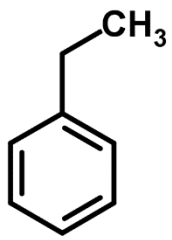


Food Additives and Contaminants. 2017;34:1703-20.

PARTITION COEFFICIENTS WITH AIR




```
>> 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
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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
```
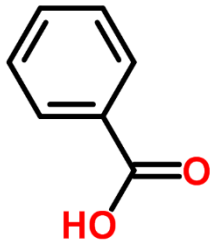
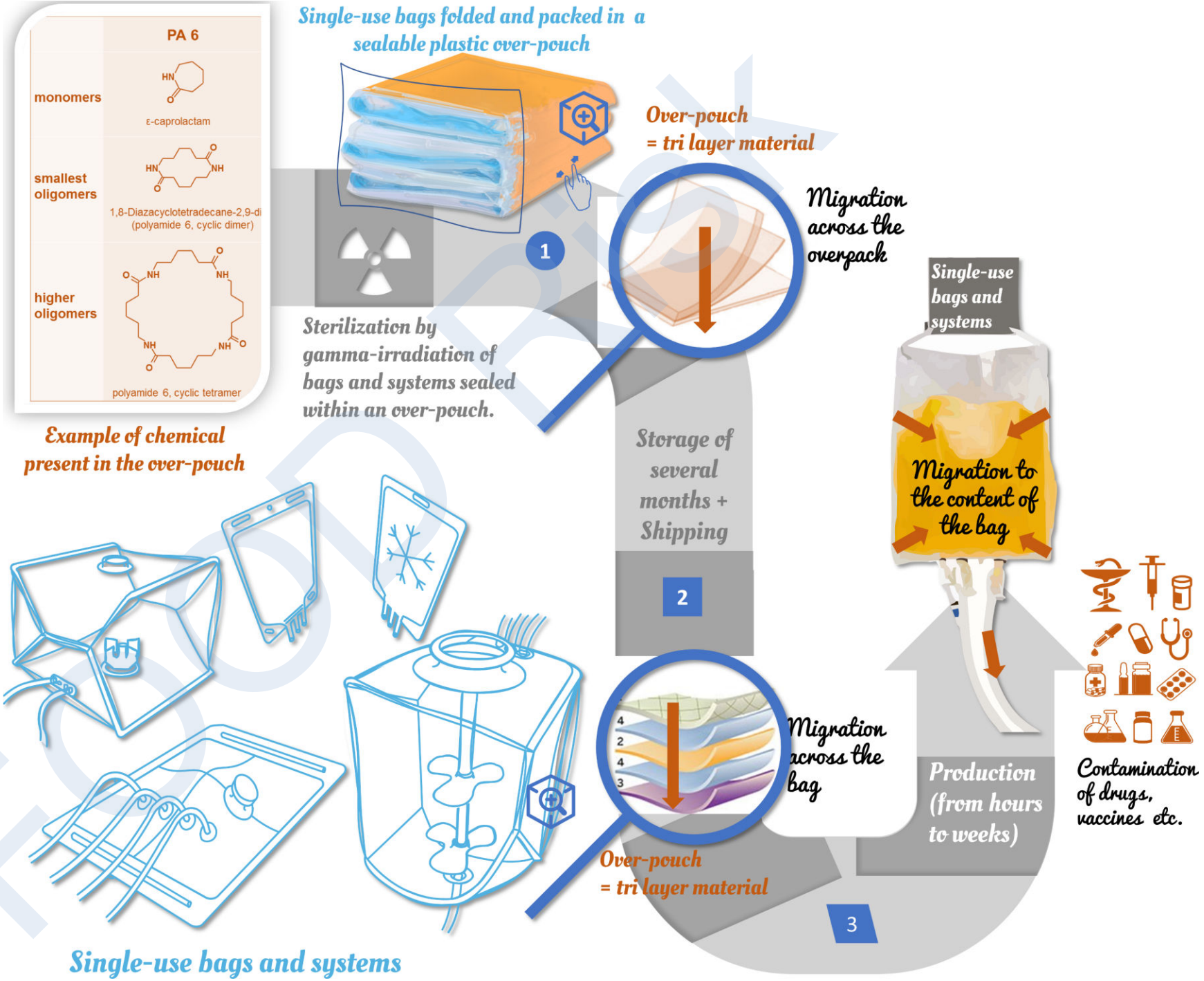




```
>> FMECAKairP 'benzoic acid'
LOAD_CHEMSPIDER    extraction of ChemSpiderID=238 ('benzoic acid') completed in 5.746 s
LOAD_CHEMISPIDER: updated cache
       238.mat21-sept.-2015 21:45:01      41.2 kBytes    C:\Data\Olivier\INRA\Codes\MS\cache.ChemSpider
CHEMSPIDER reuses cached data for 'benzoic acid' (date=21-sept.-2015 21:45:01)
ans =
   1.3674e-08
```

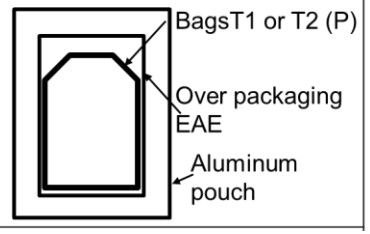
Food Additives and Contaminants 2017, 34 (10), 1703 1720
AIChE Journal 2013, 59, 1183 1212
https://github.com/ovitrac/FMECAengine

Cross-contamination in biotechnological applications



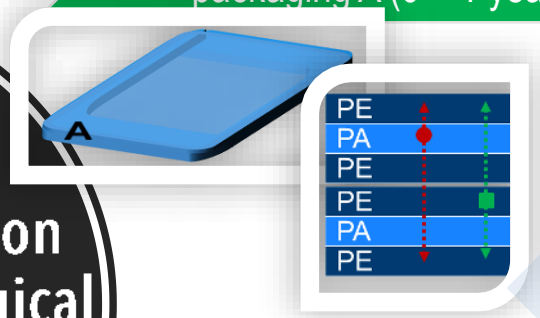
Cross-contamination in biotechnological applications

STEP 1
STUDY
"LOADING"



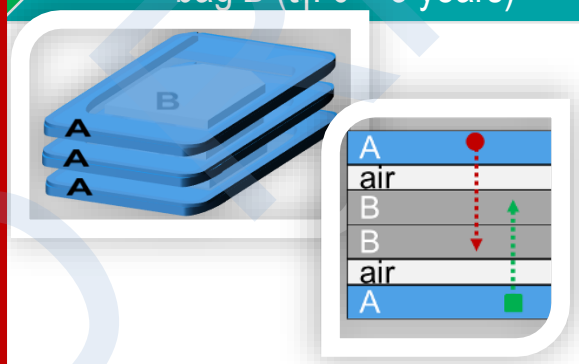
OUR SCOPE

Storage before use of over-packaging A (0 – 1 year)



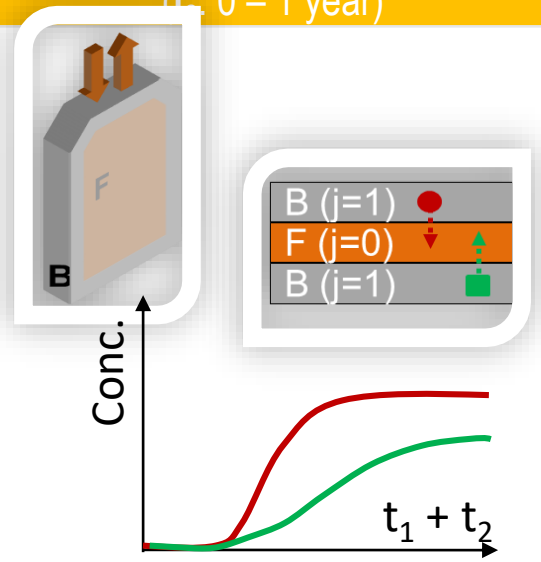
Redistribution of contaminant within the over-packaging

Storage of over-packaging A and bag B (t_1: 0 – 3 years)



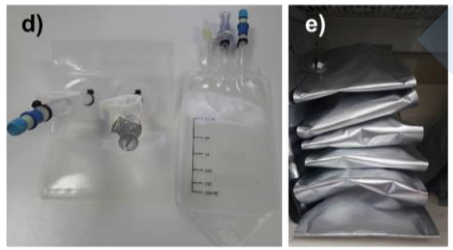
Cross-transfer between over-packaging and bag

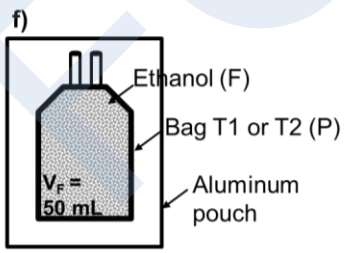
Use of bag B with a liquid F (t_2: 0 – 1 year)



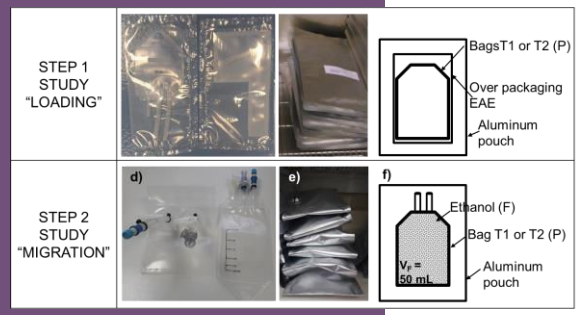
Cross-transfer between bag and liquid in use

STEP 2
STUDY
"MIGRATION"

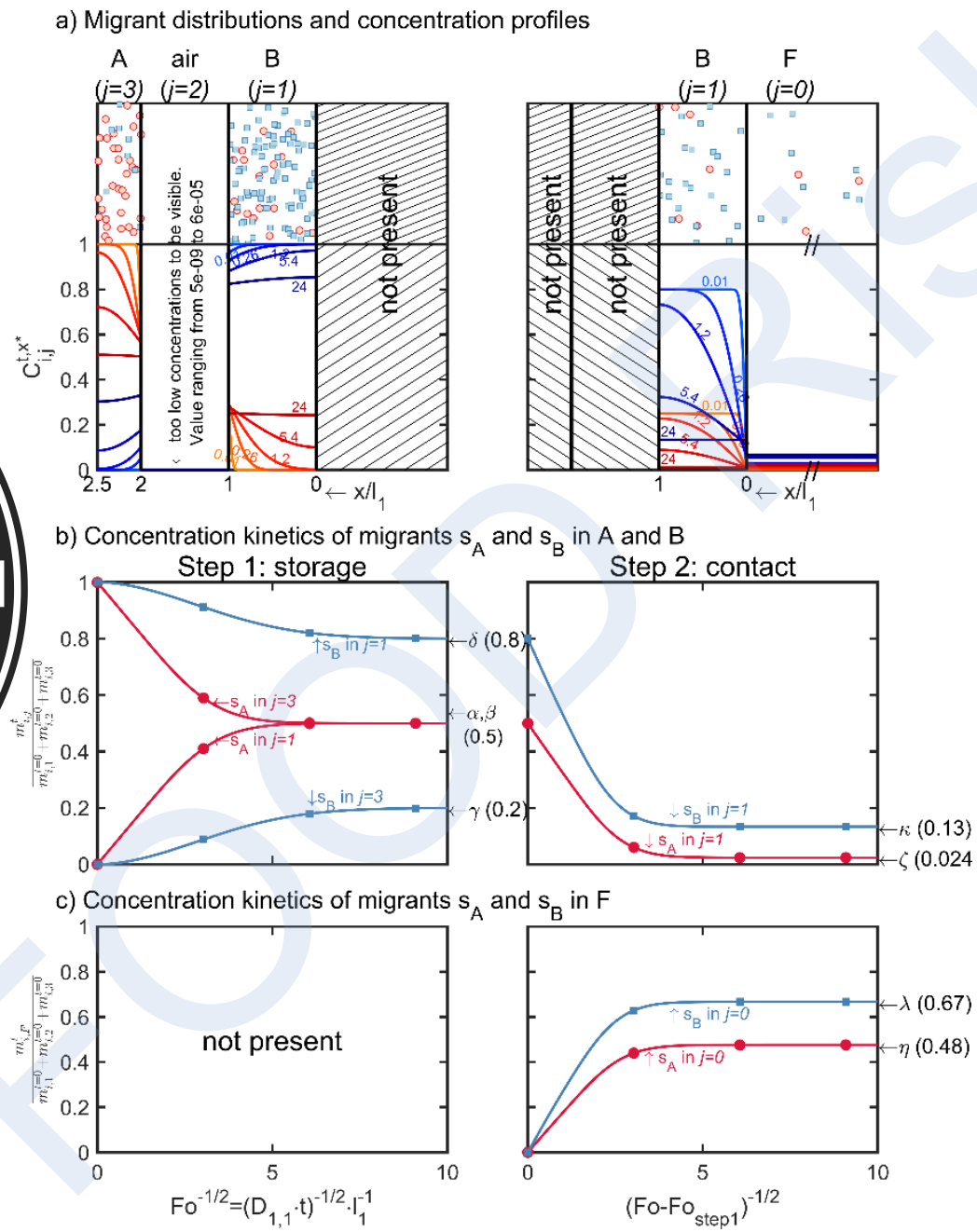


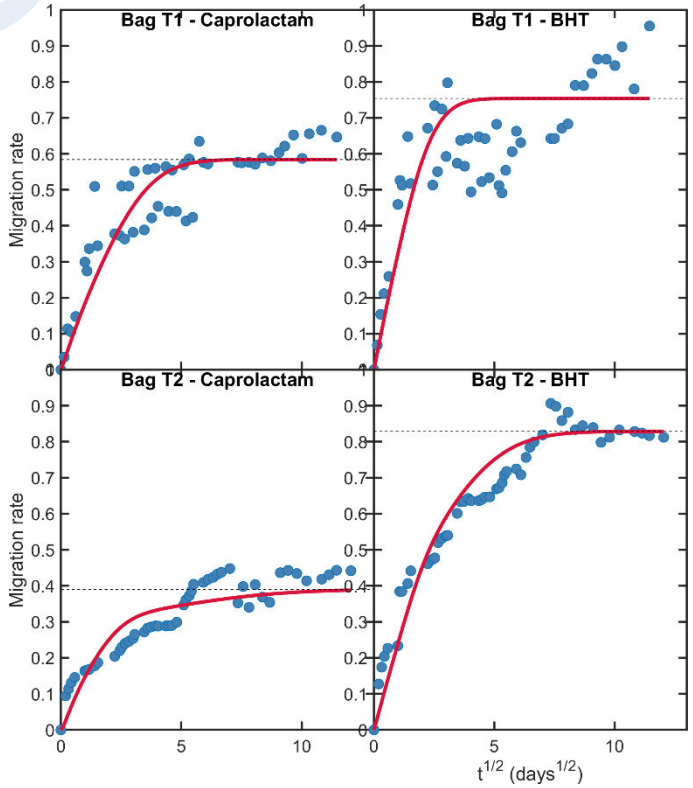


Nguyen P-M, Dorey S, Vitrac O. The Ubiquitous Issue of Cross-Mass Transfer: Applications to Single-Use Systems. *Molecules*. 2019;24:3467.



Cross-contamination in biotechnological applications



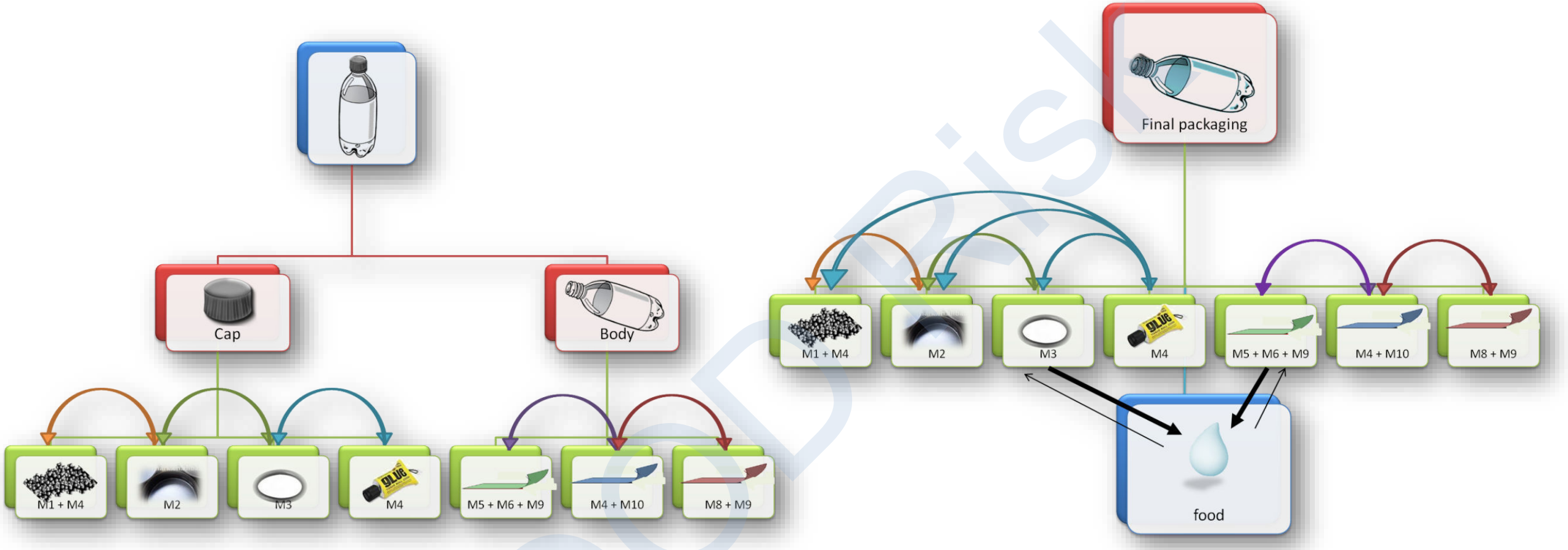


Preventive approaches

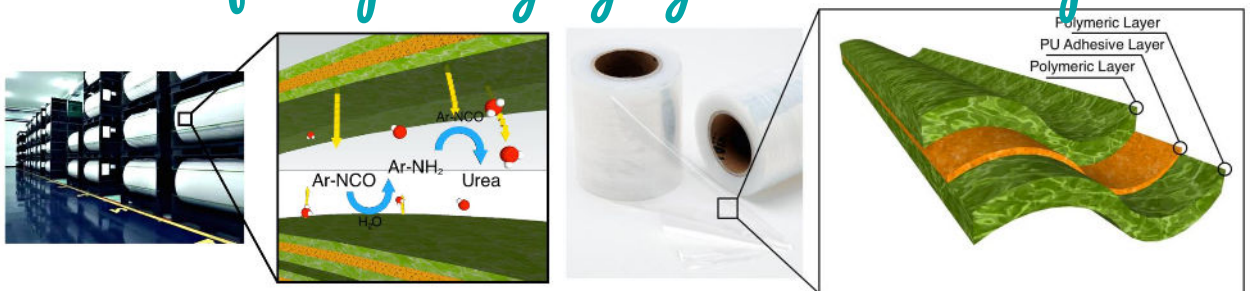
From preventive approaching to integrated engineering

Risk management requires the full cooperation of the supply chain

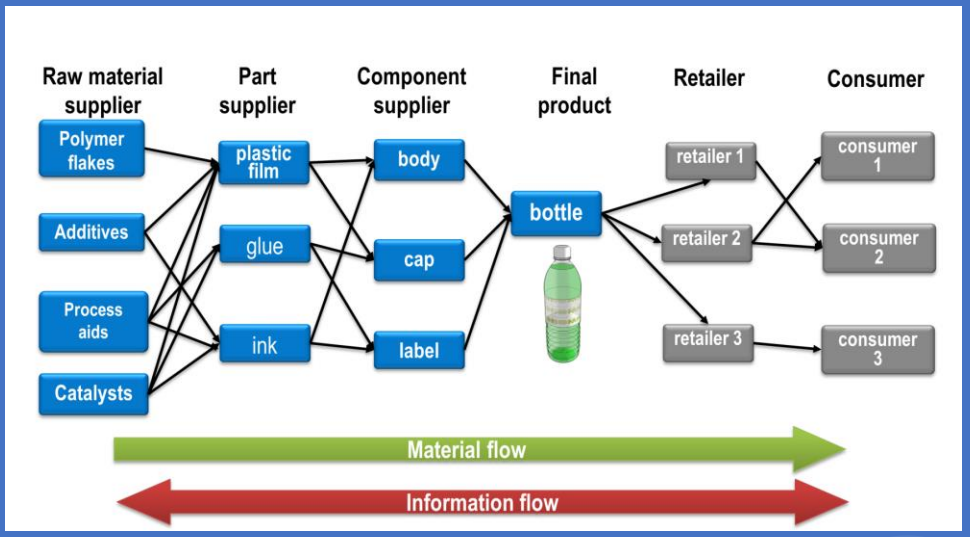
How to establish the responsibility of stakeholders?

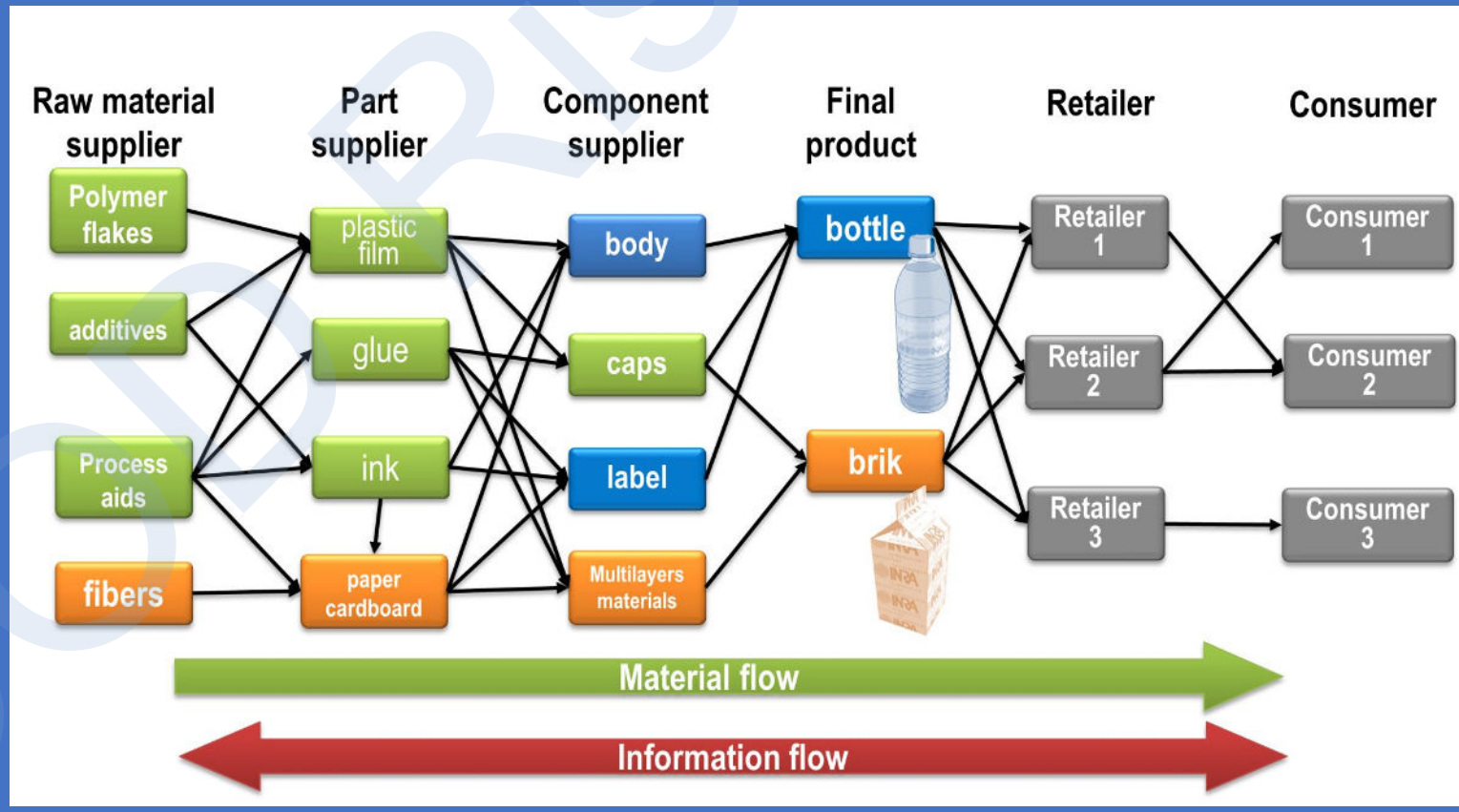


Most of the packaging systems are composite



Developing the cooperation along the supply chain





Safety concepts

Current Approaches

Future Approaches

Low Migration

Low Toxicity

Low Consumer Exposure

Safe-by-Design

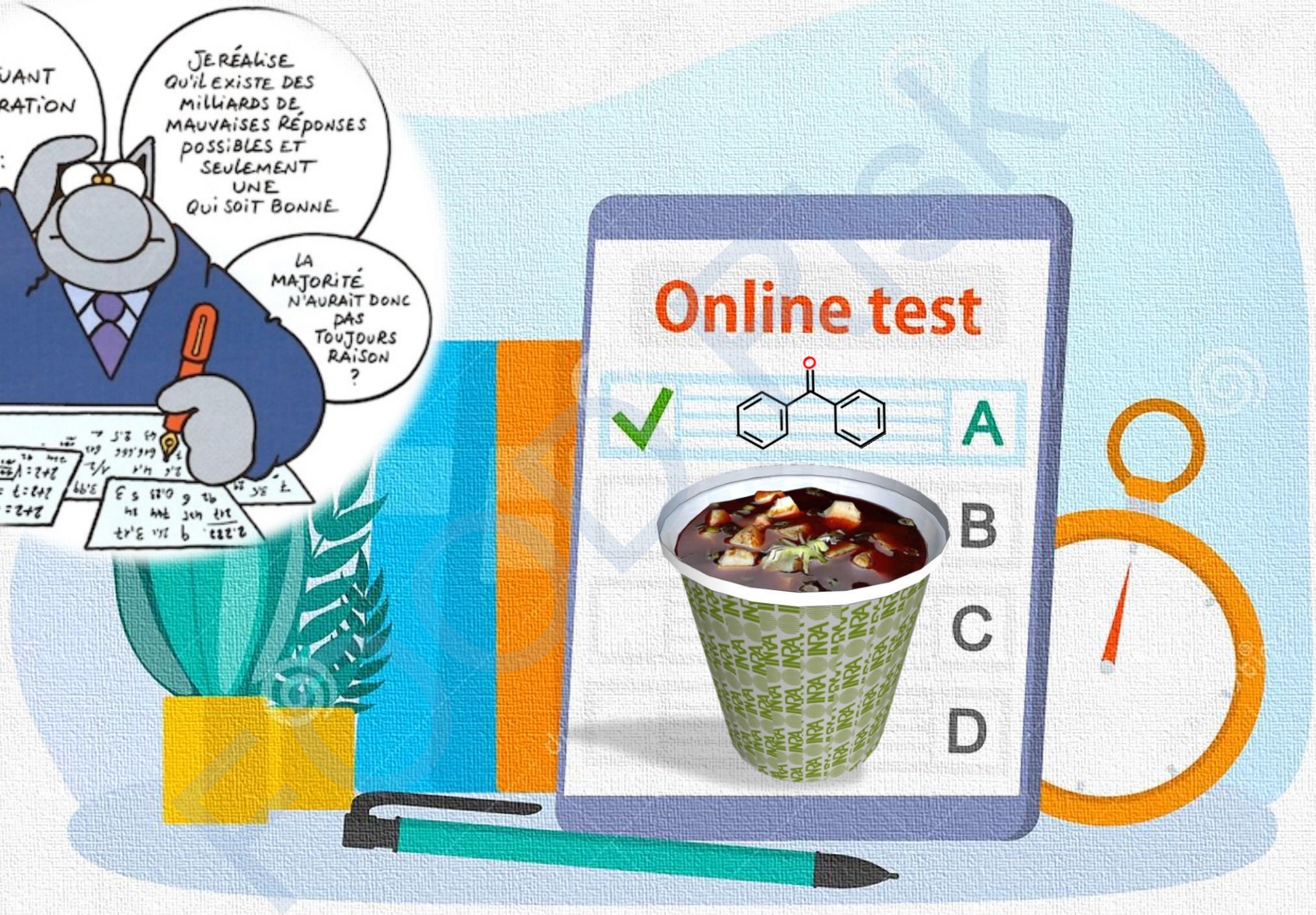
Regulation EC 2023/2006 - Good Manufacturing Practice for materials and articles intended to come in contact with food

+VOLUNTARY APPROACHES & LOCAL ORDINANCES

INRA SCIENCE & IMPACT

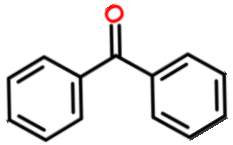
Our recommendations


EN EFFECTUANT UNE OPÉRATION ASSEZ SIMPLE : 2+2
JE RÉALISE QU'IL EXISTE DES MILLIARDS DE MAUVAISES RÉPONSES POSSIBLES ET SEULEMENT UNE QUI SOIT BONNE
LA MAJORITÉ N'AURAIT DONC PAS TOUJOURS RAISON ?

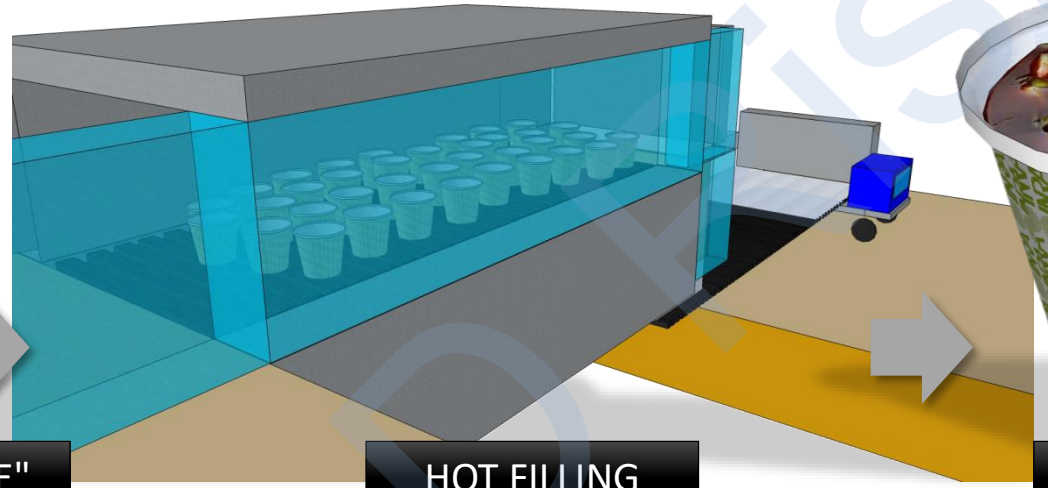

Online test
A
B
C
D

CHAINED STEPS: where is the critical step?

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

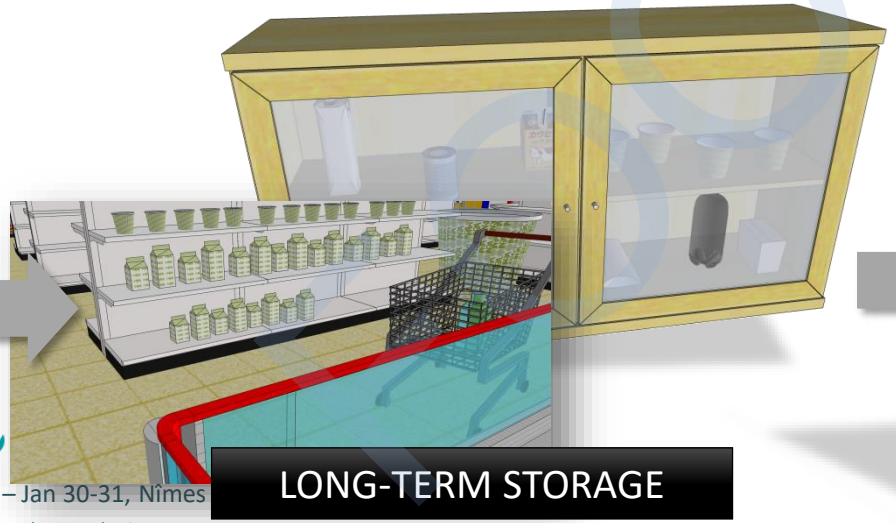


STORAGE "BEFORE USE"



HOT FILLING

FATTY CONTACT

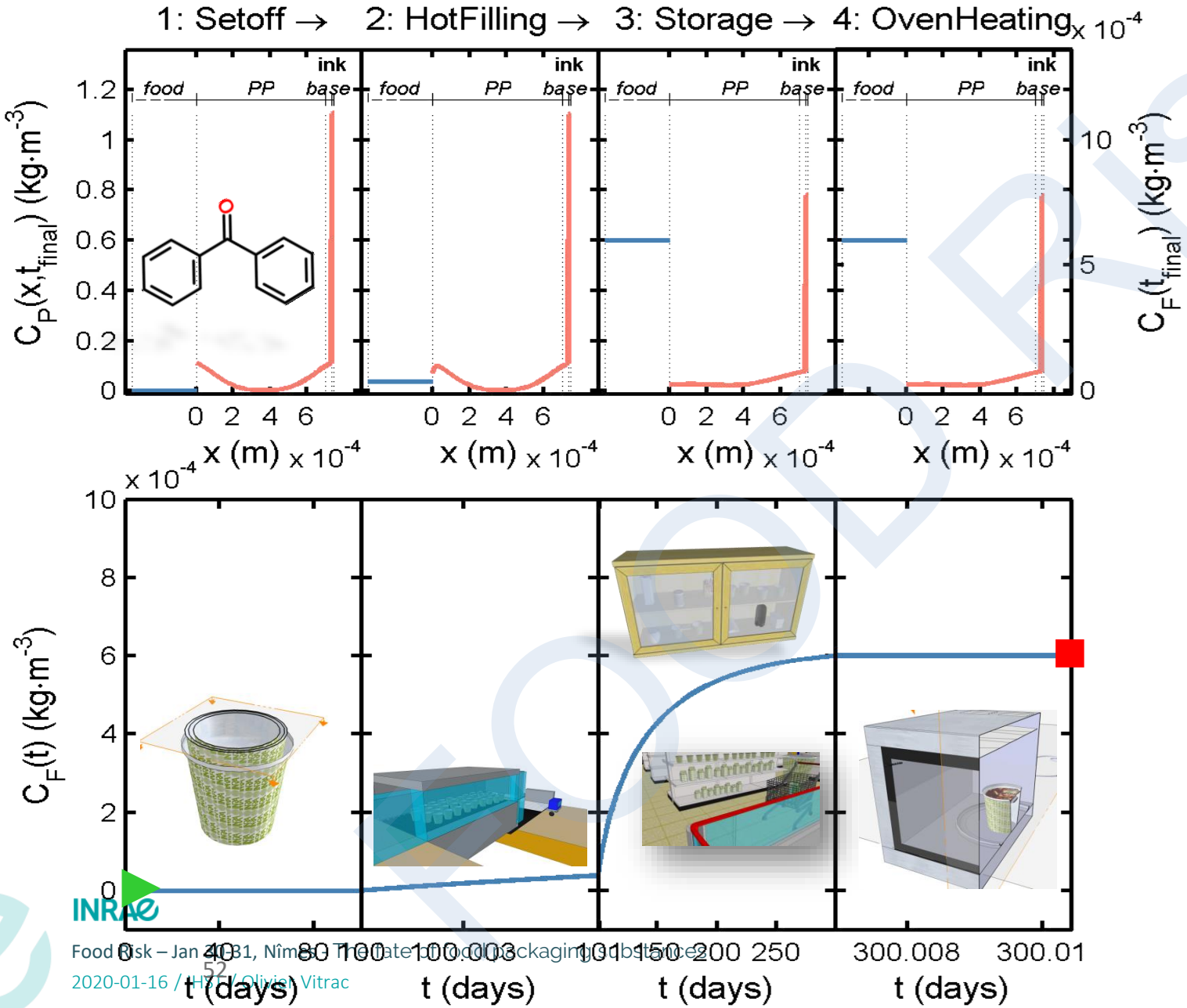


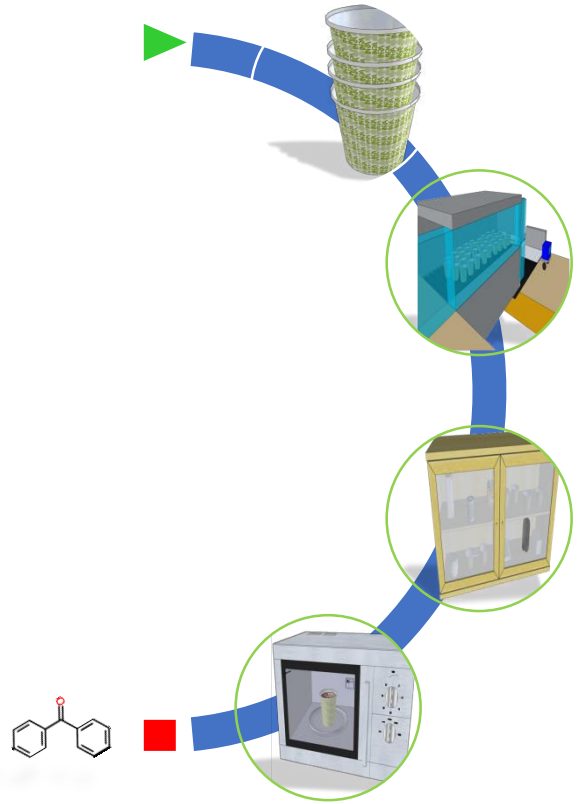
LONG-TERM STORAGE

MICROWAVE OVEN HEATING

CHAINED STEPS

UV-curing printing ink

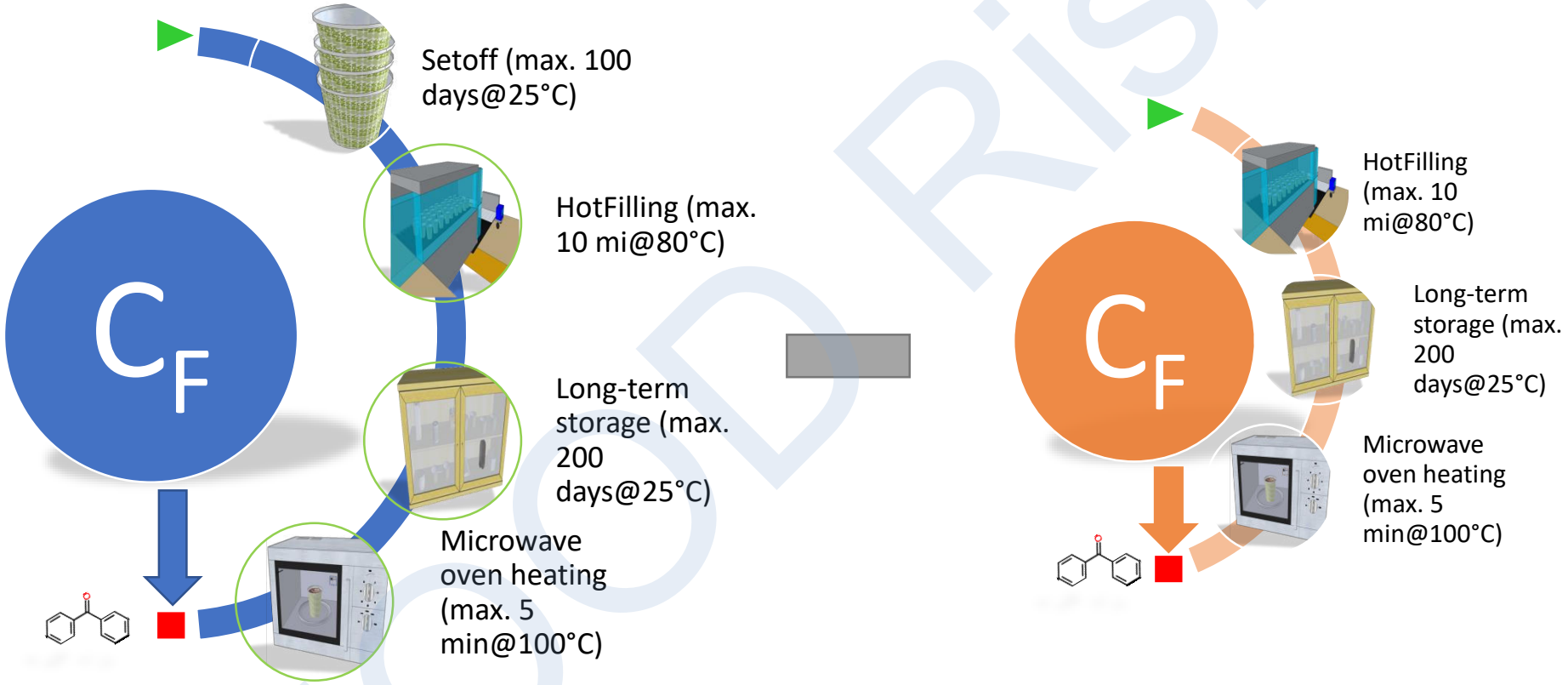




ASSESSING THE SEVERITY OF A SINGLE STEP

CASE OF "SETOFF" STEP

Full methodology described in AIChE J. 2013, 59(4), 1338-1347



comparison with step i alone

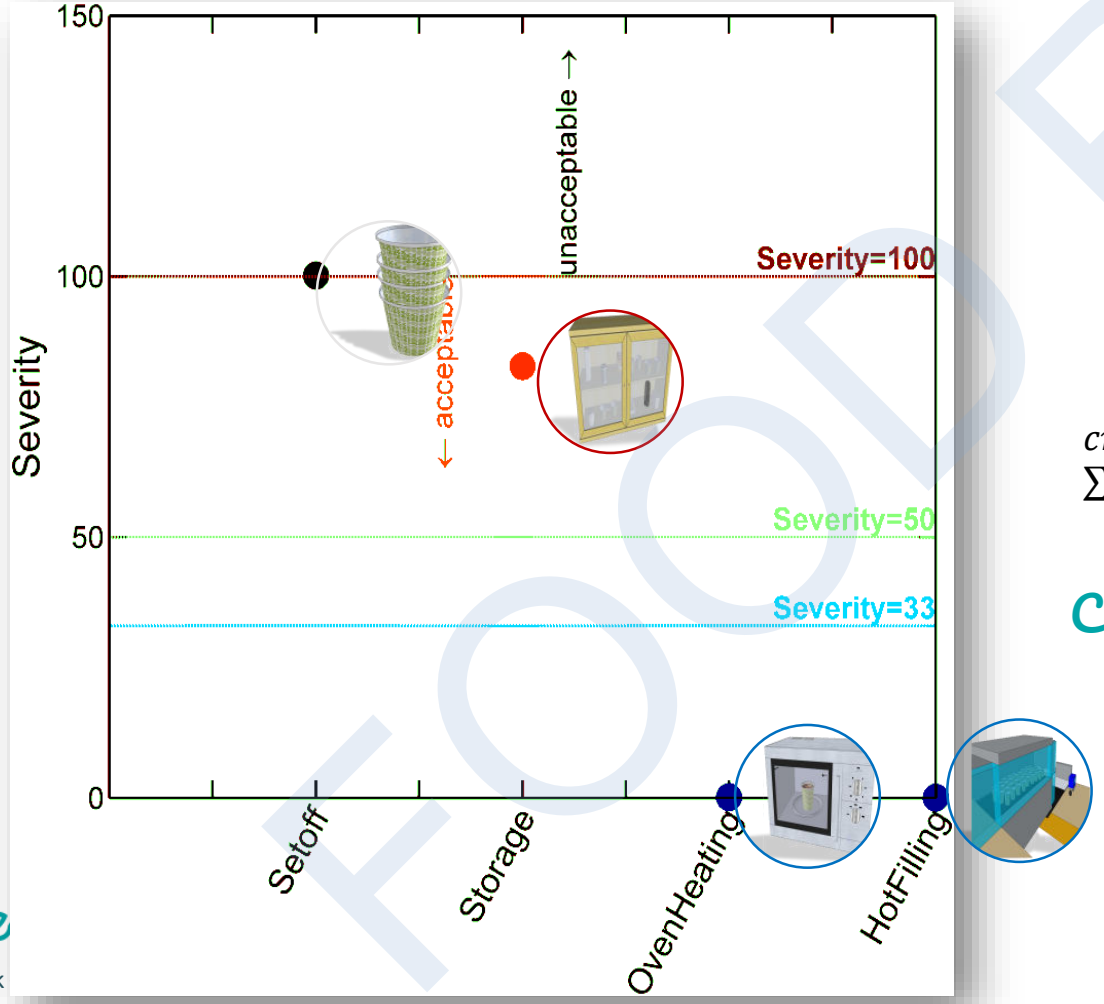
$$\text{Severity}\left(\hat{C}_F(step\,i)\right) = f\left(\max\left(C_{F_M}|_{1\to2\to\cdots\to M} - C_{F_M}|_{1\to2\to\cdots\to M/i}, C_{F_i}|_i\right)\right)$$

comparison with step i removed

COMPARING THE SEVERITY OF SEVERAL STEPS, PACKAGING DESIGNS, SUBSTANCES…

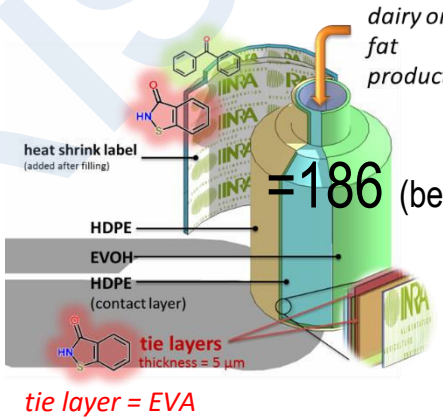
$$severity = 100 \times \frac{C_F}{SML}$$

Critical step (severity scale)

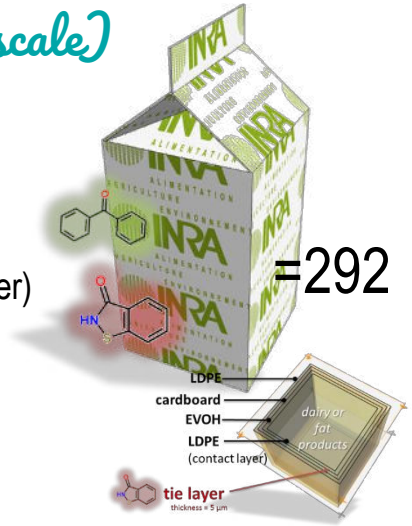


unacceptable when $severity > 100$

Concurrent design (criticality scale)



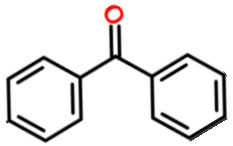
=186 (better)



=292

$$criticality = \sum_{all\ components} \sum_{all\ substances} \sum_{all\ modalities} pr(modality) \times severity$$

Critical substance



=115
(almost acceptable)

=124

Failure Mode Effects and Criticality Analysis

Collaborative research project SafeFoodPack Design

FMECA « milk for infants stored in a brick »					
	Formulation	Design	Process	Informations	Mechanisms
Phase	Formulation	design	Process	Informations	Described mechanisms
Inventaire	• monomers (plastics, adhesives) • catalysts • antioxidants • lubricants • biocides (cardboard, ink) • mineral oil (cardboard) • solvents • photoinitiators • other residus (NIAS)	**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 » • « adhesives »	• 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 • conditions of use or storage by the consumer/end-user: chilled, ambient, oven heating? • Consumption-type (bottle feed with direct contact between the mouth and the neck…)	• identity and nature of **materials** in assemblies • **formulation** of materials (substances specifically regulated or not) • **test conditions** used to evaluate the risk of contamination • **conditions of preparation, packaging filling, storage, consumption** of packaged food • communication of **revisions and modifications** in la formulation, design, process and in the final use	• diffusion across layers • set-off • cross-contamination between materials and with the storage ambience • effects of poor drying and curing on printing inks
Hiérarchisation	**Highly concentrated** • antioxidants, lubricants, biocides • mineral oils, photoinitiators • monomers, catalysts, solvents • other residues	**Barrier material** • aluminum foil **Materials acting as reservoir of low molecular weight contaminants** • ink • adhesive **Materials acting as reservoir of high molecular weight of contaminants** • PP, LDPE • paper and board	**steps associated to long-time contact** • storage of materials • storage of components • storage of finished products **steps associated to high temperatures** • aseptic filling • oven heating **steps which may lead to cross-contamination** • storage • printing • assembling / laminating	• **non-documented** or missing information • **accessible information** • **documented** information, which follow each component and materials • **verifiable and auditable information** • **frequency of update** of information : regular, when a change occur, only when the design is modified,...	• mass transfer, which can be **evaluated rapidly from calculations**: from, trough LDPE, PP layers • mass transfer, which can be tested experimentally in a simple manner : set-off • mass transfer, which require a **depth expertise**: cross-contamination, aging

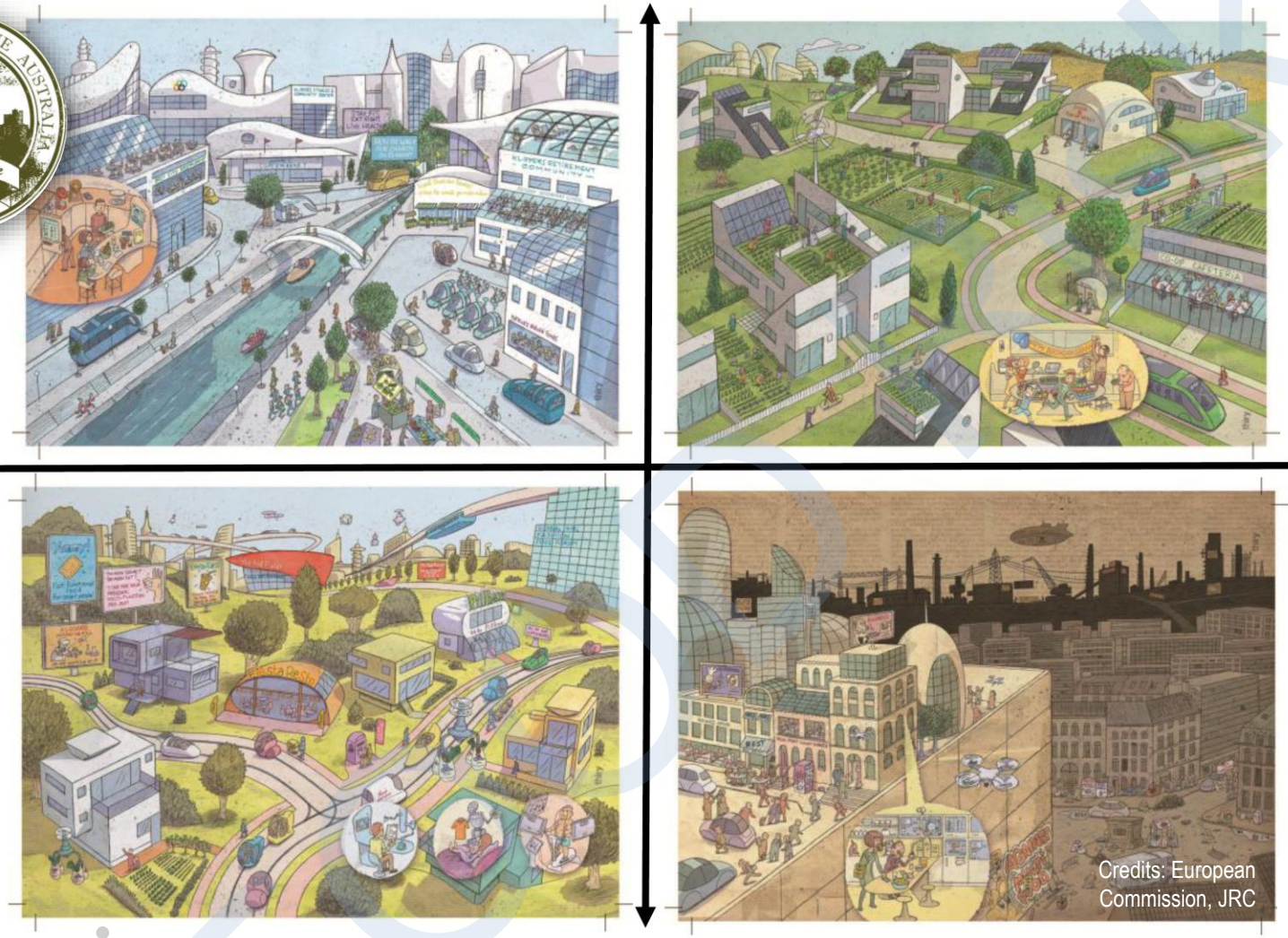
Conclusions & Perspectives

PARIS SMART CITY 2050
Vincent Callebaut Architectures, 2015

Strong community spirit (sustainable, safety and quality)

Low agriculture commodity and food price

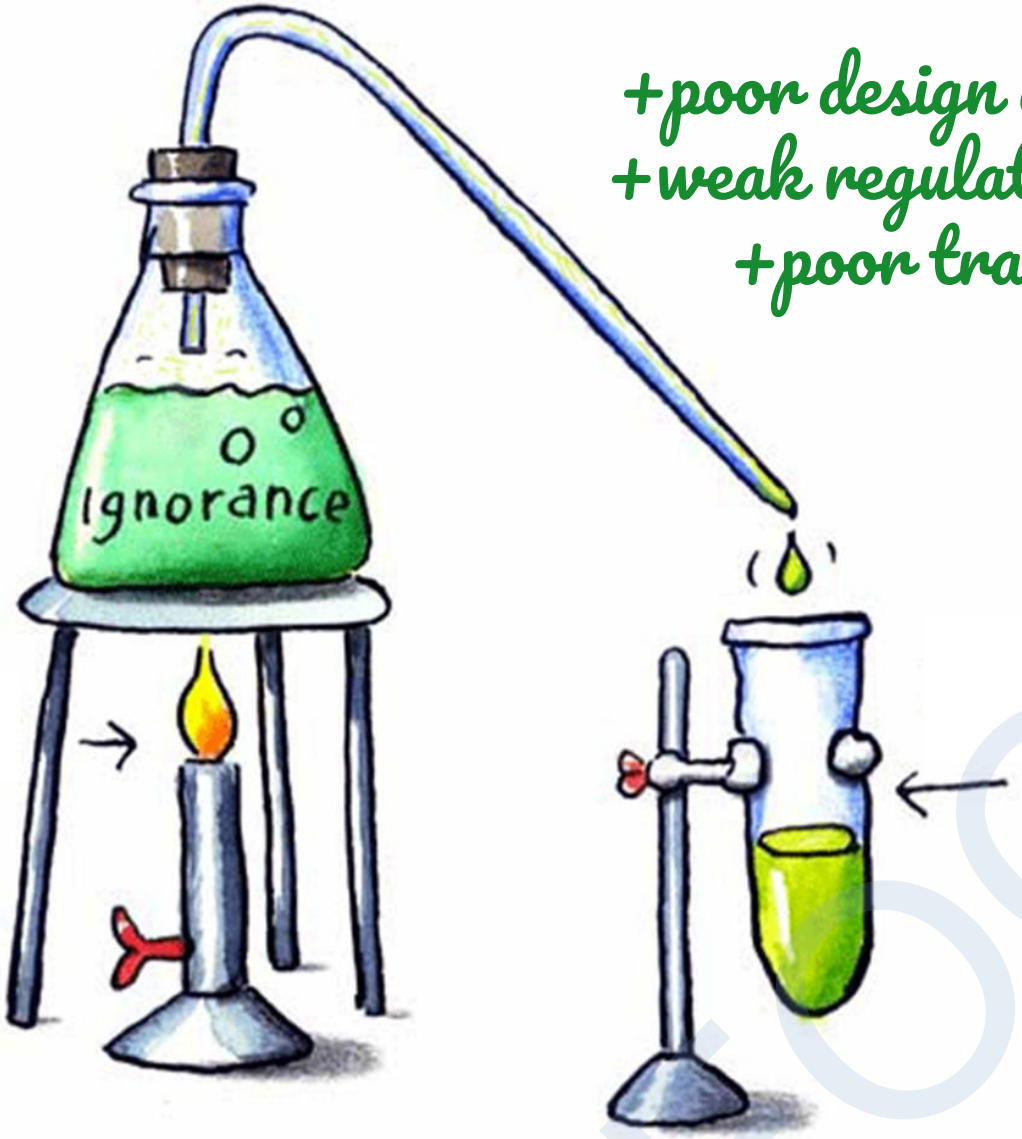
High agriculture commodity and food price



Individualistic society (individual rights and initiatives valued)

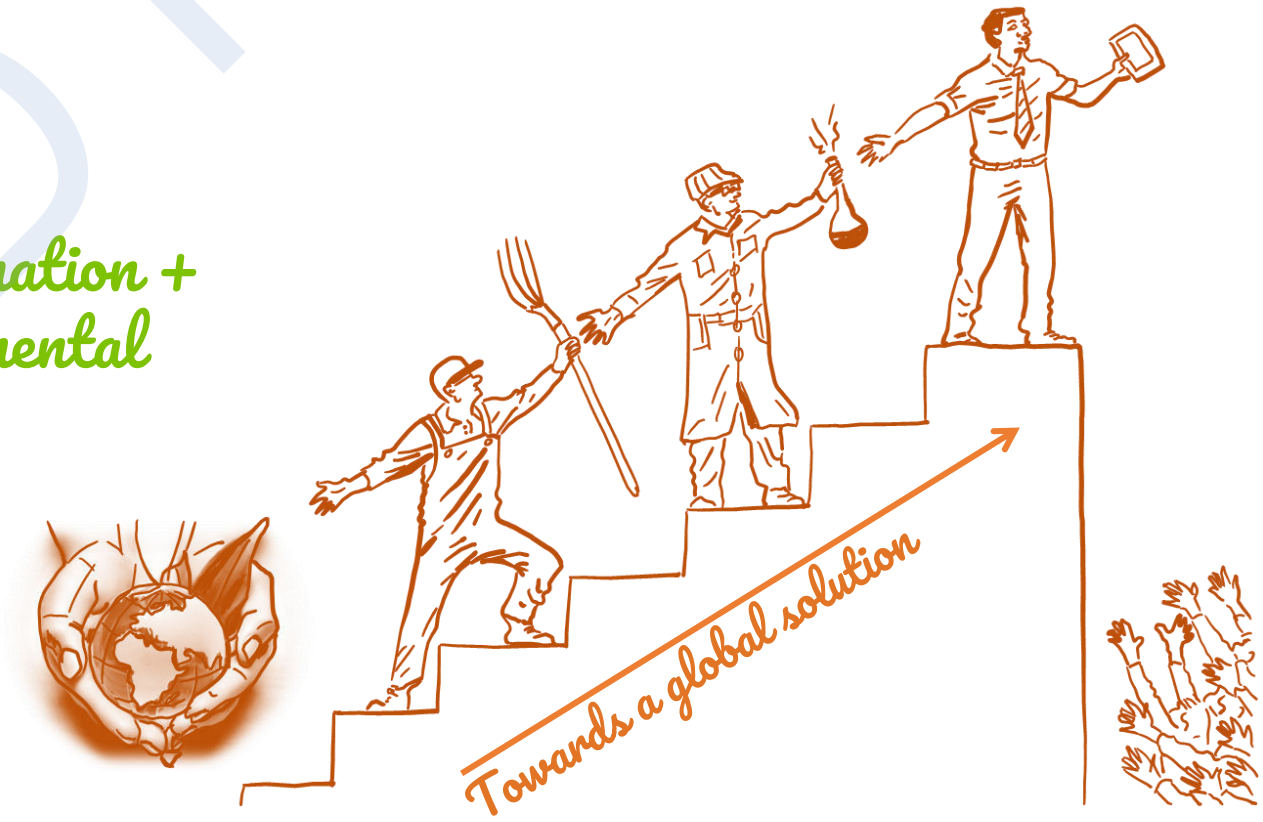
Think BIG with modeling

Let's the food engineer contributes to building the future.



+poor design and GMP
+weak regulation rules
+poor training

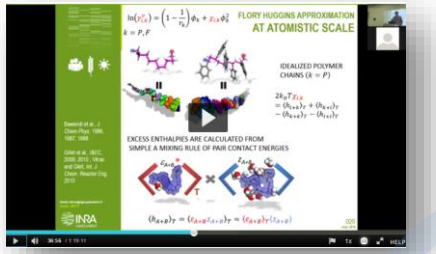
=Risk of Contamination + Environmental impact

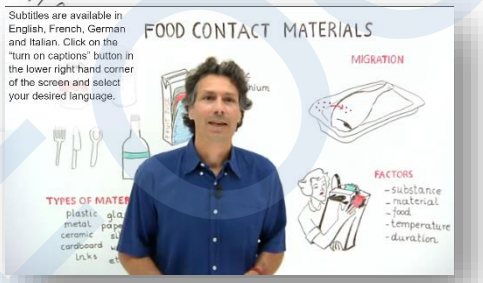


$$ignorance = \frac{IT}{WHAT\ ABOUT\ IT}$$

AgroParisTech

THE SCHOOL OF PACKAGING
MICHIGAN STATE UNIVERSITY





- This lecture: http://modmol.agroparistech.fr/masterEU/

- MY LECTURES AT MSU (MI,USA):
  http://www.fshn.msu.edu/events/event/Vitrac
  diffusion
  https://mediaspace.msu.edu/media/dr.+olivier+vitrac+presentsa+diffusion+coefficients+of+organic+solutes+in+polymersa/1_zz20dgt9
  PARTITIONING
  https://mediaspace.msu.edu/media/Dr.+Olivier+Vitrac+presentsA+An+atomistic+Flory-Huggins+formulation+for+the+tailored+prediction+of+activity+and+partition+coefficients/1_uzi6h91k
  SAFETY MANAGEMENT:
  https://mediaspace.msu.edu/media/WorkshopA+Prediction+of+the+migrationA+beyond+conventional+estimates*/1_won1m7aw

- RISK ASSESSMENT:
  https://www.youtube.com/watch?v=7LMnc4czpuY

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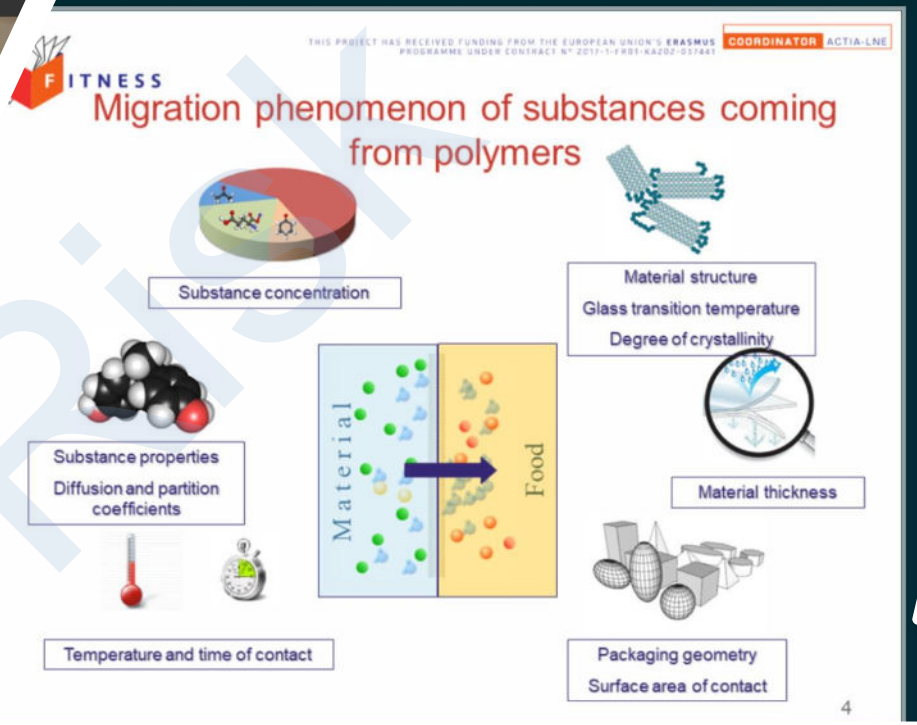
Fitness stands for **Food packaging open courseware for higher education and staff of companies**

All lectures, interactive contents and Quizz are provided "AS IS"
content (85 lectures from Common to Specialized Modules) is
development and may contain inconsitencies and inaccura

SUBSTANCE CONCENTRATION



FITNESS

http://fitness.agroparistech.fr

Co-funded by the Erasmus+ Programme of the European Union

Online lectures

author: undef

part 1/1	references	extra	casestudies	howto	solutions

Session 4. Mass transfer in food packaging - Unit 4.2. Migration modeling in m onomaterial s

4.3 Modelling for multi-materials, multi-steps process

Migration modeling for multi-materials, multi-steps process, reusable materials - SPECIALIZED TRAININ MODULES

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