MASS TRANSPORT IN, THROUGH, FROM FOOD PACKAGING

PERMEATION, MIGRATION, DIFFUSION, SORPTION, REGULATION, RISK ASSESSMENT/MANAGEMENT

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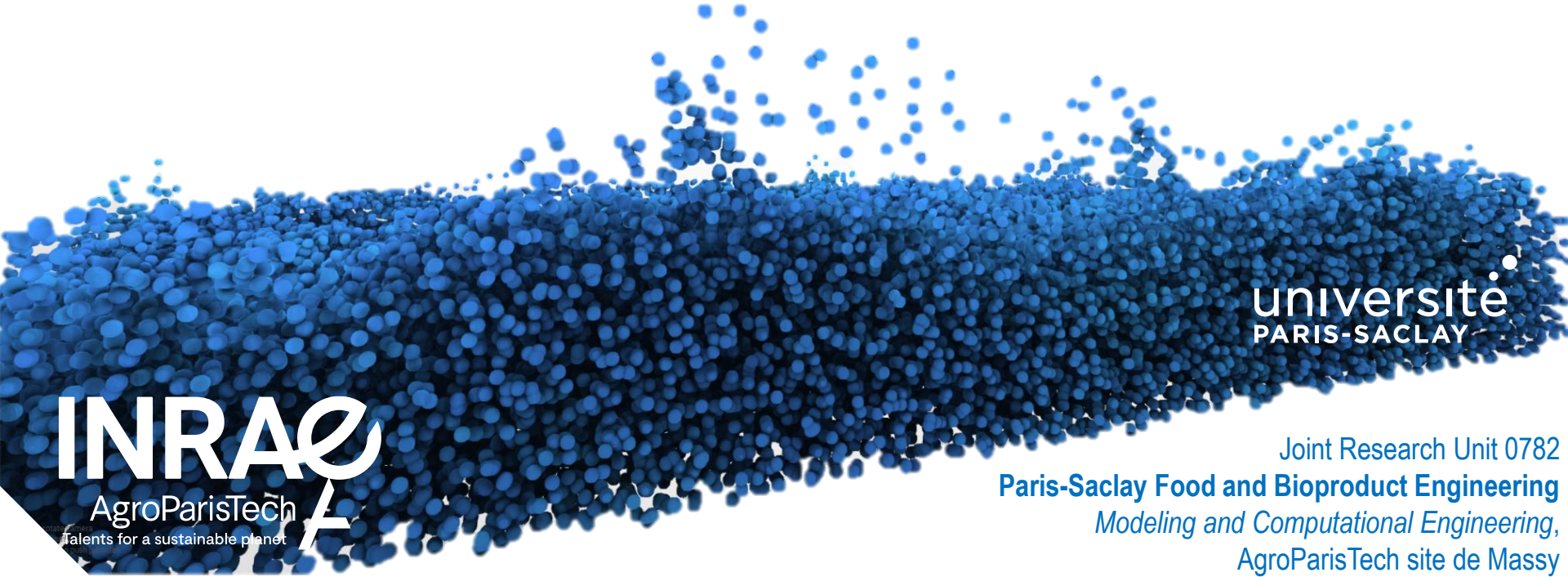

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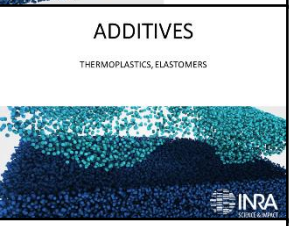
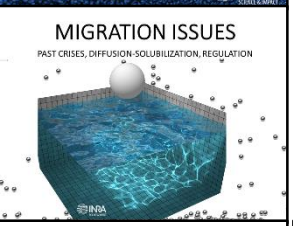
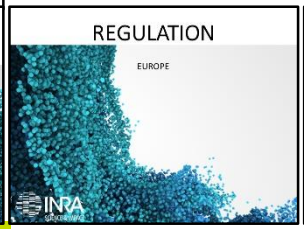
Talents for a sustainable planet

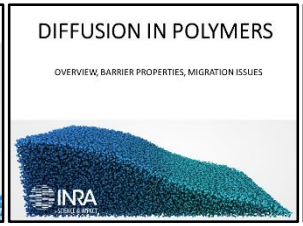
université PARIS-SACLAY

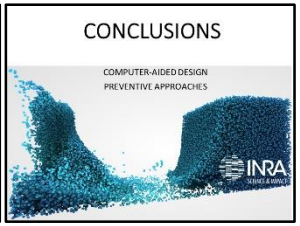
Joint Research Unit 0782
Paris-Saclay Food and Bioproduct Engineering
Modeling and Computational Engineering,
AgroParisTech site de Massy









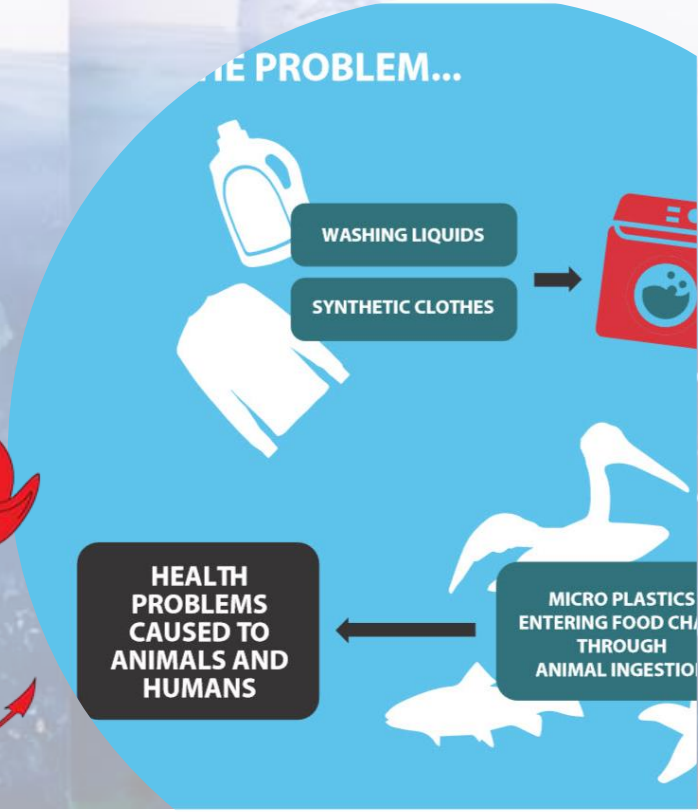


CONTENT

- FOOD PACKAGING OVERVIEW
- PERMEATION & BARRIER MATERIALS
- MIGRATION ISSUES
- TOXICITY
- REGULATION
- DIFFUSION IN POLYMERS
- CONCLUSIONS


drying
salting
1950
1980
1990
2000
Ultra
High
Temperature
Milk
Milk
Film Overwrap
CO₂ Gas Retards Spoilage Bacteria,
Extends Product Freshness
Meat Tray
Gas Modifier in
Anti-Microbial
CO₂ Slows the Respiration Rate
and Ethylene Binding,
Extending Product Freshness
Film Overwrap
Sliced Tomato Tray
Gas Modifier
Highly Absorbent Pad
Wicks and Retains Juice
The Food Production Chain

Bulky, useless, hazardous packaging



European Commission

Impact assessments

Impact assessments examine whether there is a need for EU action and analyse possible impacts of available solutions. These are carried out during the preparatio phase, before the Commission finalises a proposal for a new law. They provide evidence to inform and support the decision-making process.

PAGE CONTENTS

The need for impact assessments

Impact assessments are carried out on initiatives expected to have significant economic, social or environmental impacts. These can be:

- legislative proposals
- non-legislative initiatives (e.g. financial programmes, recommendations for the negotiations of international agreements)
- implementing and delegated acts

INRA SCIENCE & IMPACT


Emballages plastiques : 1964 à nos jours

EUROPEAN
GREEN
DEAL

TOMORROW EVERYTHING SHOULD BE REUSABLE,
REFILLABLE, RECYCLABLE

TURNING GREEN

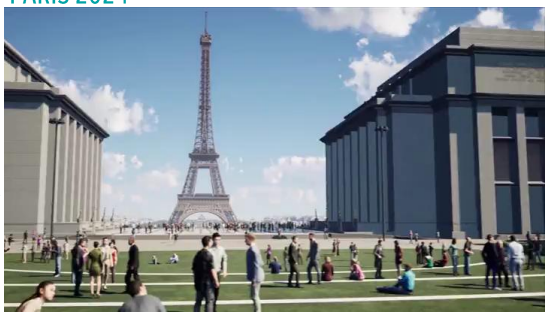
We are sleeping on a volcano... A wind of revolution blows; the storm is on the horizon.

Alexis de Tocqueville (1848, just prior revolutions in Europe).

TURNING GREEN

TOMORROW EVERYTHING SHOULD BE REUSABLE, REFILLABLE, RECYCLABLE

PARIS 2024



PARIS 2050

ANTI-WASTE LAW for a circular economy (France)

2020

Disposable cutlery, straws and swizzle sticks banned in 2021

free plastic toys banned in 2021

Plastic confetti banned in 2021

No cups, plates or cotton swabs allowed

2021

Prohibition of the mention biodegradabl

Expanded PS containers are not

Recycling bins in supermarkets

2022

Mandatory water fountains

Plastic tea bags banned by 2022

Banning packaging around fruit and vegetables in 2022

Cardboard and packaging to be sorted

Promote bulk to reduce packaging

2023

Inform on endocrine disruptors

Mixed deposit for reuse and recycling

5% packaging reusable

2024

100% of packaging recycled by January 1, 2025

A polluter-pays system for hygiene textiles from 2024

Five-year ecodesign plans

Disposable dishes in fast-food restaurants prohibited

Environmental and societal labelling

2025

2026

Ban plastic containers for heating food for infants and young children.

10% reusable packaging

2027

2040

0% of packaging are recycled since zero waste

100% reusable packaging

ero disposable plastic

TURNING GREEN

TOMORROW EVERYTHING SHOULD BE
REUSABLE, REFILLABLE, RECYCLABLE

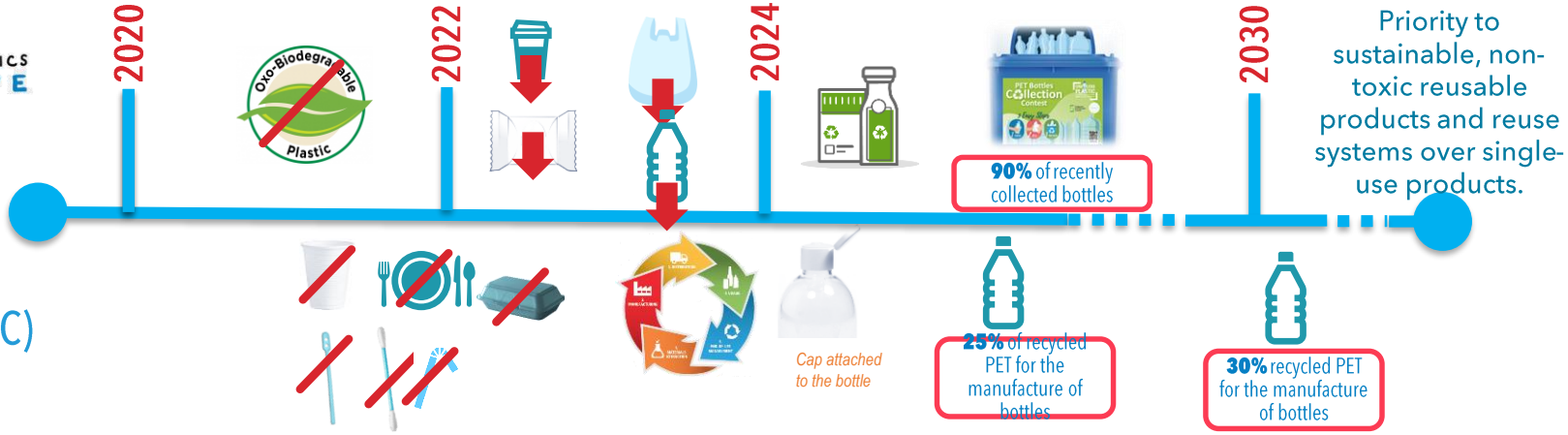
17 PARTNERSHIPS FOR THE GOALS

SUSTAINABLE DEVELOPMENT GOALS

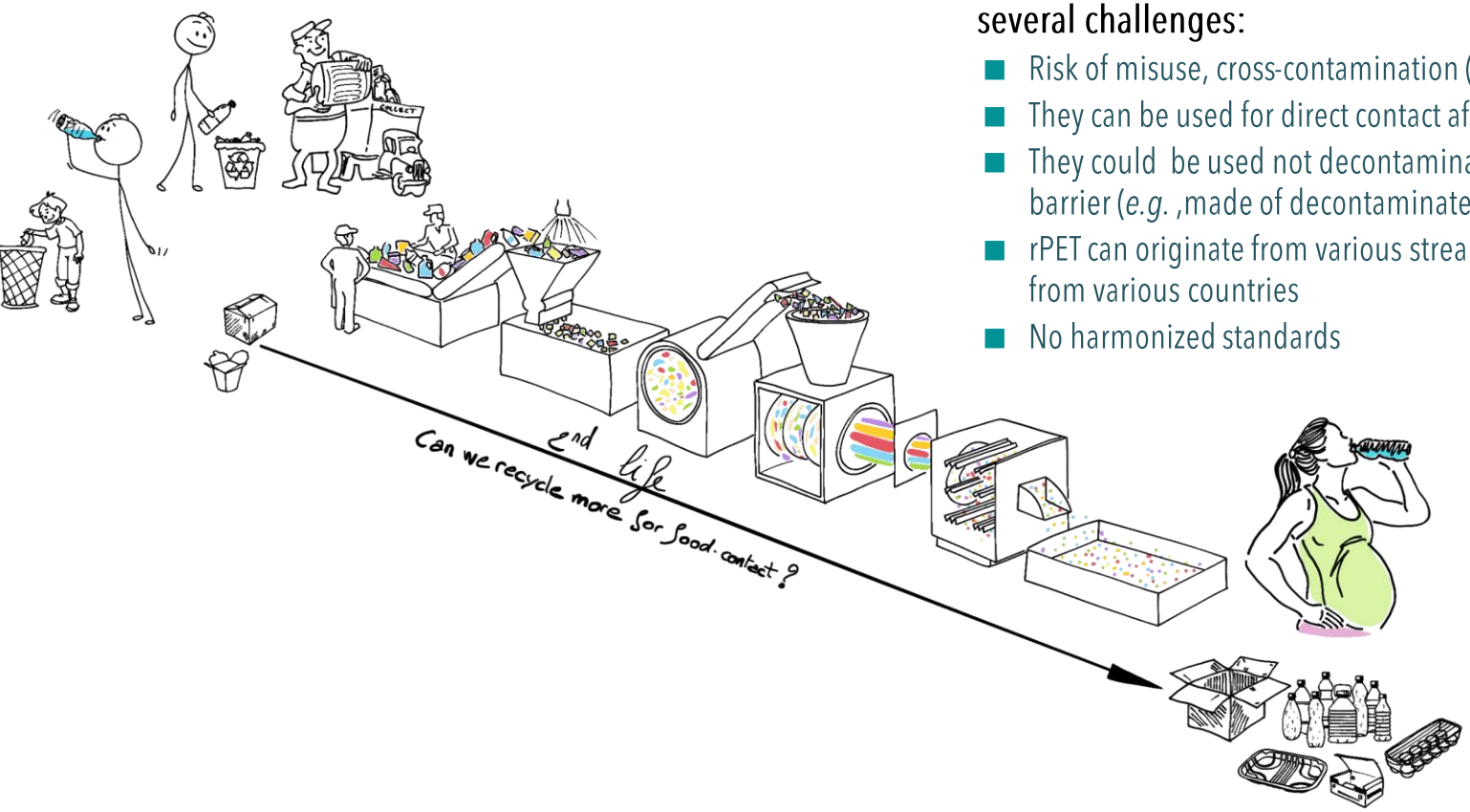
Food Packaging impacts 12 of 17 goals

SINGLE-USE PLASTICS DIRECTIVE

(2019/904/EC)



The challenge of recycling plastics for food contact.



All plastics including biosourced and biodegradable materials will need to be recyclable for the same use (food contact for food packaging).

Only PET is currently recycled at global scale, but with several challenges:

- Risk of misuse, cross-contamination (ex. from carboard)
- They can be used for direct contact after decontamination
- They could be used not decontaminated behind a functional barrier (*e.g.* ,made of decontaminated rPET)
- rPET can originate from various streams (food contact or not) and from various countries
- No harmonized standards

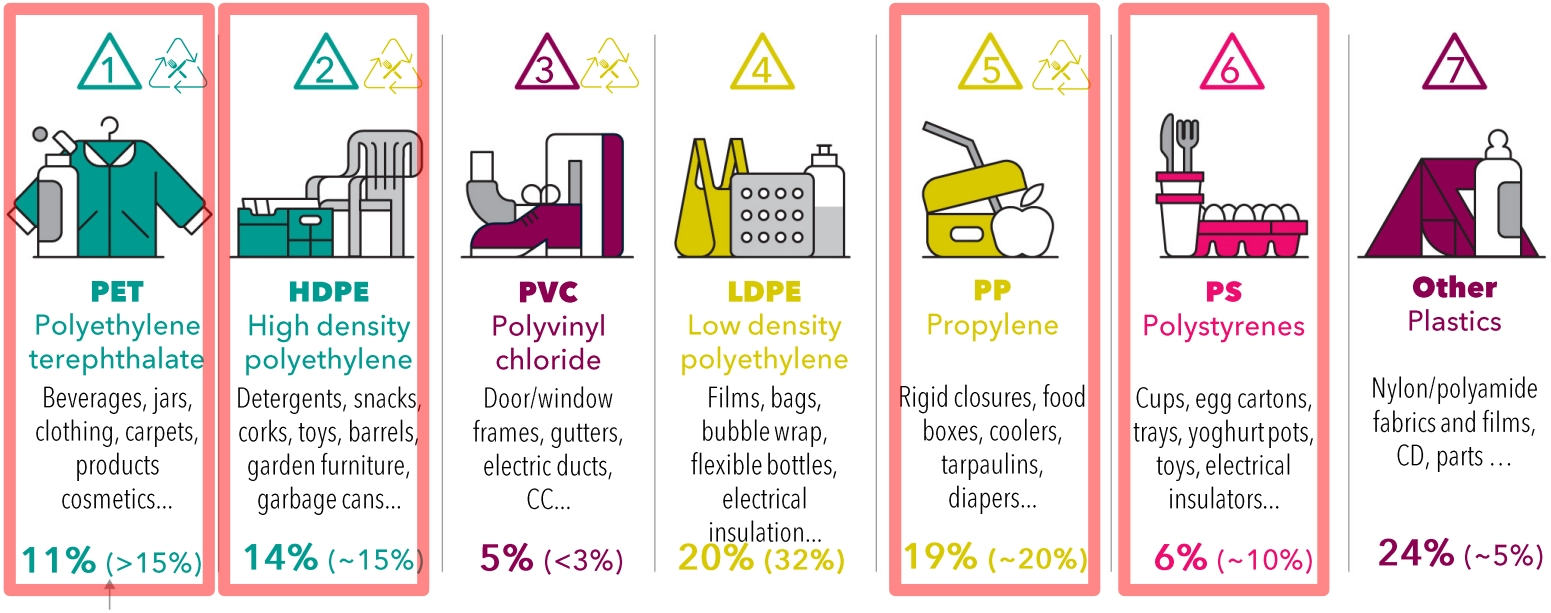
Recycling more plastics beyond PET

% plastic wastes in 2015
(% food packaging wastes, Plastics Europe 2016)

Globally, 18% of plastics are recycled, compared to almost zero in 1980. Plastic bottles are one of the most widely recycled products (including now to make new bottles). Other plastics are either discarded or recycled for lesser quality uses.

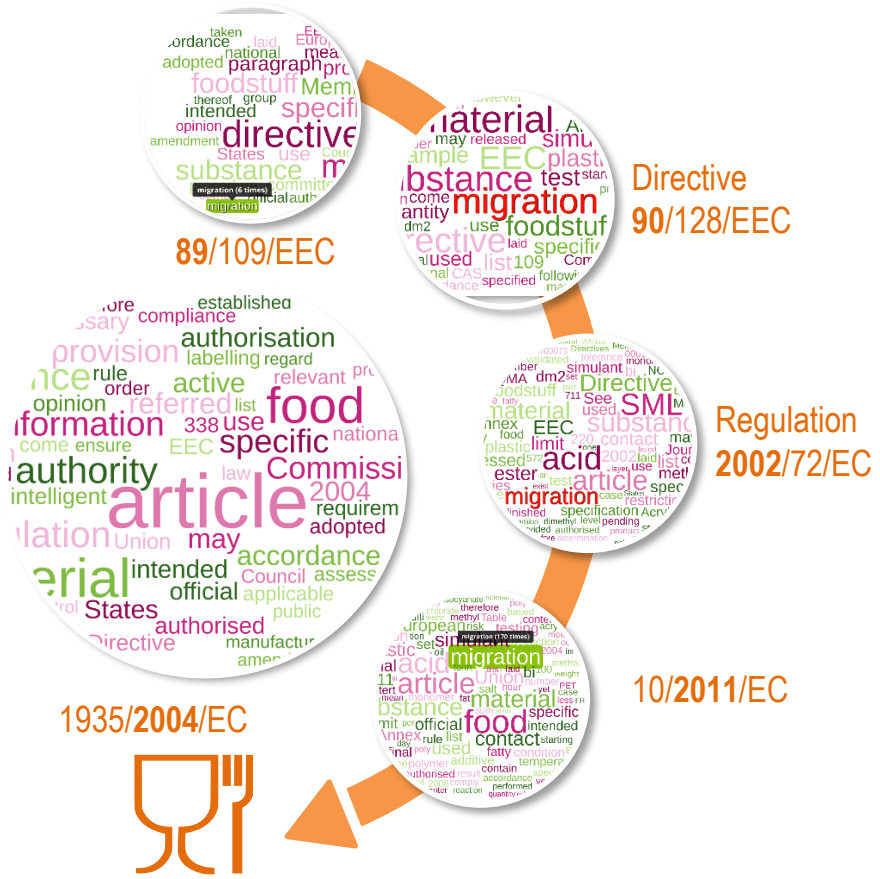
Recycling difficulties - any purpose
(variable according to regions/countries

△ easy △ dificult
△ feasible △ Very difficult



Recycled for food contact (PET)

Could be recycled for food contact (polyolefins: PP, HDPE, LDPE)



Food Additives and Contaminants, January 2005; 22(1): 73–90

Taylor & Francis
Taylor & Francis Group

Evaluation of migration models that might be used in support of regulations for food-contact plastics

T. BEGLEY[1], L. CASTLE[2], A. FEIGENBAUM[3], R. FRANZ[4], K. HINRICHS[5], T. LICKLY[6], P. MERCEA[7], M. MILANA[8], A. O'BRIEN[9], S. REBRE[10], R. RIJK[11], & O. PIRINGER[7]

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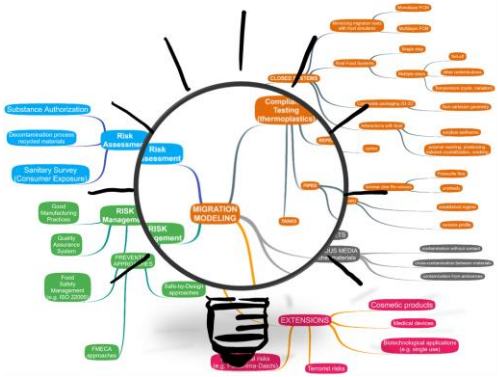
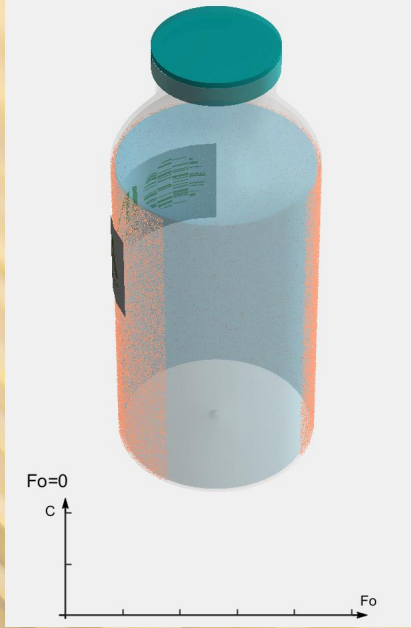


Contribution of INRA



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

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

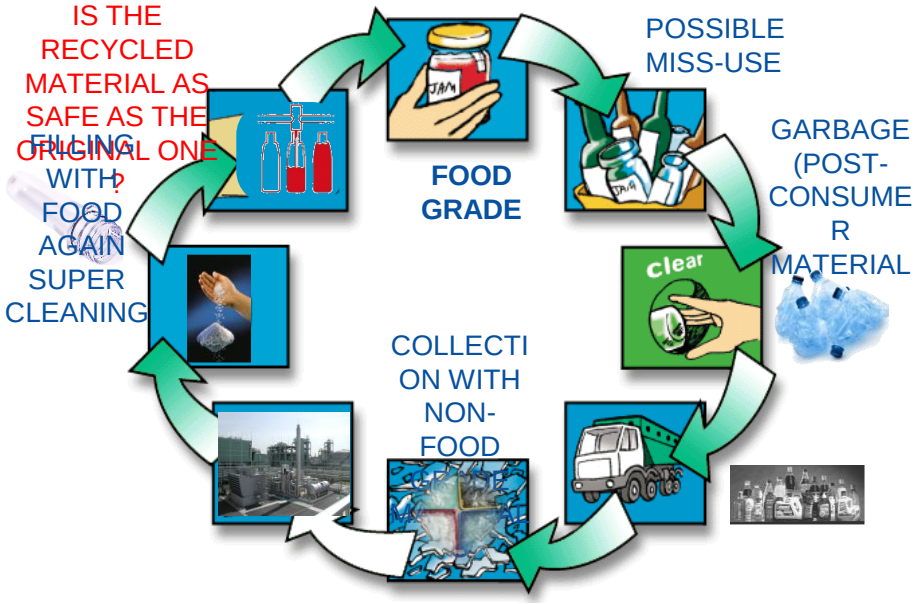
Contaminations from non-plastic Materials not considered

CIRCULAR ECONOMY vs SAFETY

Food Packaging Forum

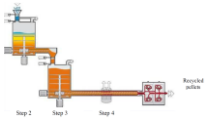
Workshop "Predicting the safety of food contact articles" - New science and digital opportunities
4 October 2018, Zurich, Switzerland
https://www.foodpackagingforum.org/events/predicting-the-safety-of-food-contact-articles-new-science-and-digital-opportunities

INRA SCIENCE & IMPACT



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.



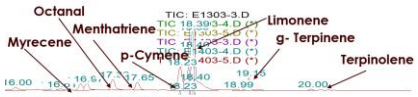
500 M€ have been invested in plants capable of converting recycled plastic materials into materials suitable for packaging and food contact applications

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

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_a

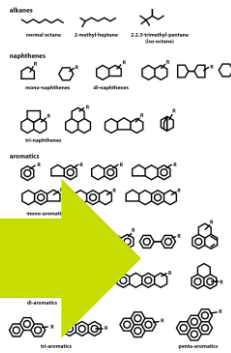


1. Filling and use of HDPE milk bottles
2. Recollection
3. Sorting

Foodgrade HDPE milk bottles

Recycling

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



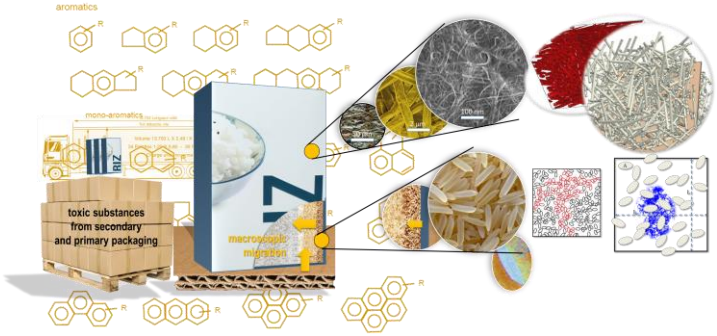
Paper and board contains large amount of residues from printing inks: aromatic (carcinogenic) and aliphatic **mineral oils** can be transferred without contact and lead to cross-contamination between materials

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

Is the substitution of plastics by recyled paper & board a safer solution?

Recycled P&B are a very important source of mineral oils, which can contaminate food without contact and across a plastic layer.

- Germany recommends not to use recycled P&B in microwave oven.
- France requires an evaluation of the risk of contamination from secondary and ternary packaging.
- Detection limit ~10 mg/kg (Koster et al., 2020)

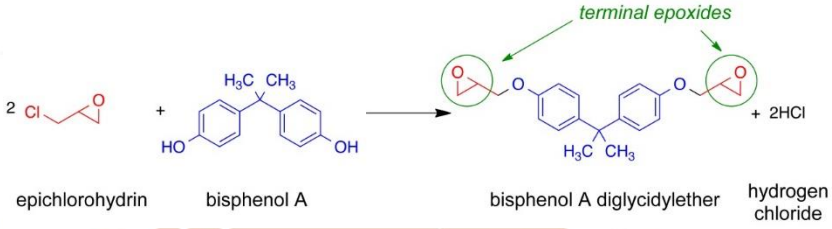


Food type	Maximum level of contamination by mineral oils	Origin
Chocolate and chocolate products	>100 mg·kg^{-1}	Cardboard
Baby milk	10-80 mg·kg^{-1}	Cardboard
Cereal Products	30 mg·kg^{-1}	Cardboard and printing inks
Pasta	10 mg·kg^{-1}	cardboard box
Edible oil	100-1000 mg·kg^{-1}	Containers

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

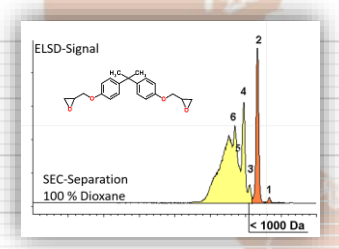
INRA SCIENCE & IMPACT

Google Trends / Bisphenol A: (Worldwide)



#	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_2O
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



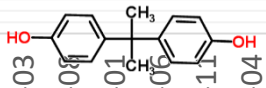
Current Biology 2003, 13, 546

Current Biology 2018, 28,1

RÉPUBLIQUE FRANÇAISE
JOURNAL OFFICIEL
LOIS ET DÉCRETS

LOI no 2012-1442 du 24 décembre 2012

REGULATION 2018/213/EC



2004-01 2004-06 2004-11 2005-04 2005-09 2006-02 2006-07 2006-12 2007-05 2007-10 2008-03 2008-08 2009-01 2009-06 2009-11 2010-04 2010-09 2011-02 2011-07 2011-12 2012-05 2012-10 2013-03 2013-08 2014-01 2014-06 2014-11 2015-04 2015-09 2016-02 2016-07 2016-12 2017-05 2017-10 2018-03 2018-08

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

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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 exposure of our animals to an environmental source of bisphenol A (BPA). BPA is a potent estrogenic compound widely used in the manufacture of polycarbonate plastics and epoxy resins. Subsequent studies of damaged caging material as the source of the exposure, as well as we were able to recapitulate the meiotic disturbances by intentionally damaging cages and water bottles. In subsequent studies of female mice, we found that daily oral doses of BPA to directly test the hypothesis 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 chromosome abnormalities, including nondisjunction; bisphenol A was implicated as a potent disruptor [illegible] ability to experimentally recreate the [illegible] allowed us to verify our initial observations [illegible] dose-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

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Current Biology
Report

Replacement Bisphenols Adversely Affect Mouse Gametogenesis with Consequences for Subsequent Generations

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[3]Lead Contact
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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 environmental contamination and human BPA exposure. Consumer concern has resulted in "BPA-free" products produ[illegible] naturally similar bisphenols that are [illegible] environmental and human cont[illegible] [34–41]). We report here studies init[illegible] changes mirroring our previous B[illegible] and implicating exposure to BPS (a replacement) from damaged polysulfone cages. Like with BPA [1, 2, 5], our data show that exposure to common replacement bisphenols induces germline effects in both sexes that may affect multiple generations. These findings add to growing evidence of the biological risks posed by this class of chemicals. Rapid production of structural variants of BPA and other EDCs circumvents efforts to eliminate dangerous chemicals, exacerbates the regulatory burden of safety assessment, and increases environmental contamination. Our experience suggests that these environmental contaminants pose a risk not only to reproductive health but also to the integrity of the research environment. EDCs, like endogenous hormones, can affect diverse processes. The sensitivity of the germline allows us to detect effects that, although not immediately apparent in other systems, may induce variability that undermines experimental reproducibility and impedes scientific advancement.

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 meiotic effects.

Unexpected Contaminant

[illegible]s comprised of BPA and diphenyl sulfone (Fig[illegible], we suspected that these were the contaminants [illegible]quid chromatography-tandem mass spectrometry [illegible] analysis of a methanol extraction of damaged ca[illegible]r, demonstrated the presence of both BPA and [illegible] 2C–2F). Because polymeric aromatic ethers, like [illegible]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. Therefore, damaged polysulfone is, in fact, more likely to generate BPS than diphenyl sulfone is (Figure 2B). Unfortunately, high signal levels in both control and solvent blanks made it impossible to determine if diphenyl sulfone was a significant contaminant.

Replacement bisphenols have rapidly emerged in consumer products, and studies of them are limited. However, plastics containing them can leach estrogenic chemicals [43, 44], and exposure has been reported to induce adverse effects similar to BPA (e.g., [45–52]; reviewed in [53]). Our findings suggest that, although newer polymers like polysulfone are more resistant to chemical damage than polycarbonate is, damage can occur in the course of normal use and may result in the release of contaminants that are not constituent components of the polymer.

Bisphenol Analogs Elicit Meiotic Effects

To eliminate contamination, all caging materials in the facility were replaced, new breeding stocks were purchased, and studies were conducted to confirm that control values in both

Environ Sci Pollut Res (2009) 16:278–286
DOI 10.1007/s11356-009-0107-7

AREA 6 • PERSISTANT ORGANIC POLLUT

Endocrine disruptors in bot
estrogenic burden and migr

Martin Wagner · Jörg Oehlmann

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Abstract

Background, aim, and scope Food consumptio
important route of human exposure to endocrine-dis
chemicals. So far, this has been demonstrated by e
modeling or analytical identification of single substa
foodstuff (e.g., phthalates) and human body fluid
urine and blood). Since the research in this field is foc
few chemicals (and thus missing mixture effects), the
contamination of edibles with xenohormones is
unknown. The aim of this study was to assess the in
estrogenic burden of bottled mineral water as mod
stuff and to characterize the potential sources of th
genic contamination.

Materials, methods, and results In the present st
analyzed commercially available mineral water in an
system with the human estrogen receptor alpha and
estrogenic contamination in 60% of all samples
maximum activity equivalent to 75.2 ng/l of the nat
hormone 17β-estradiol. Furthermore, breeding of th
luskan model *Potamopyrgus antipodarum* in water
made of glass and plastic [polyethylene terepht
(PET)] resulted in an increased reproductive ou
snails cultured in PET bottles. This provides first e
that substances leaching from plastic food pac
materials act as functional estrogens in vivo.

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EDITORIAL

The perils of plastic

A 'round-robin' spam e-mail that is ci
servers worldwide claims that drin
water that has been left in a warm c
breast cancer. Is this warning just an urban
it hold a grain of truth? The FDA, it seems,
the side of caution; earlier this year, the
revised its position on the safety of bisphen
chemical used in the manufacture of plastic
deemed safe for food-contact use, the FI
expressed "some concern" about the potentia
that BPA poses to fetuses, infants and youn

What exactly is BPA and why has its
alarm? First synthesized in 1905, BPA has s
a key component in the production of pla
ing polycarbonate and epoxy resins. Polyc
clear, heat-resistant, shatter-proof materia
that make it ideal for the manufacture of d
particularly those used by young children
Epoxy resins are also used by the food a
industry—they provide the protective co
inside many metal-based cans. Standard
tests supported the safety of BPA and the FI
it for food-contact use in the 1960s. Over
years, however, concern has mounted th
environmental exposure to BPA might dis
functioning of the endocrine system.

The term 'endocrine disruption' was coine
1990s. Endocrine disruptors comprise a div
industrial chemicals that exert numerous de
and functional effects on the endocrine sys
tiple biological pathways. Many of these che
the effects of endogenous hormones, such
BPA and other endocrine-disrupting che
been implicated in obesity, neurological de
ductive dysfunction and cancer. In additio
octanoic acid (PFOA) and perfluorooctan
(PFOS)—common household chemicals fo
stick' and waterproof materials—have re
linked to thyroid disease.

The Endocrine Society has recognized t
problems associated with the widespread
trial chemicals. In June 2009, the society p
findings of a task force commissioned to
the mechanisms of action and potential h
endocrine disruptors (Diamanti-Kandara

cussed (Safe 2000, 2005; Sha
2005) due to the multifactoral
diseases, although evidence fo
to xenohormones and develop
tive disorders strengthens (Sh

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Chemical compounds and toxicological assessments of drinking water stored in polyethylene terephthalate (PET) bottles: A source of controversy reviewed

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ABSTRACT

A declaration of conformity according to European regulation No. 10/2011 is required to ensure the safety of plastic materials in contact with foodstuffs. This regulation established a positive list of substances that are authorized for use in plastic materials. Some compounds are subject to restrictions and/or specifications according to their toxicological data. Despite this, the analysis of PET reveals some non-intentionally added substances (NIAS) produced by authorized initial reactants and additives.

Genotoxic and estrogenic activities in PET-bottled water have been reported. Chemical mixtures in bottled water have been suggested as the source of these toxicological effects. Furthermore, sample preparation techniques, such as solid-phase extraction (SPE), to extract estrogen-like compounds in bottled water are controversial. It has been suggested that inappropriate extraction methods and sample treatment may result in false-negative or positive responses when testing water extracts in bioassays. There is therefore a need to combine chemical analysis with bioassays to carry out hazard assessments.

Formaldehyde, acetaldehyde and antimony are clearly related to migration from PET into water. However, several studies have shown other theoretically unexpected substances in bottled water. The origin of these compounds has not been clearly established (PET container, cap-sealing resins, background contamination, water processing steps, NIAS, recycled PET, etc.).

Here, we surveyed toxicological studies on PET-bottled water and chemical compounds that may be present therein. Our literature review shows that contradictory results for PET-

List of abbreviations: AA, acetaldehyde; APEOs, polyethoxylated nonylphenols; BBP, benzylbutyl phthalate; BHET, bis(hydroxyethyl) terephthalate; BHT, butylated hydroxytoluene; BPA, bisphenol A; DBP, dibutyl phthalate; DiBP, di-iso-butyl phthalate; DEG, diethylene glycol; DEHP, di-2-(ethylhexyl) phthalate; DEHA, bis-2-ethylhexyl adipate; DEP, diethyl phthalate; DMSO, dimethyl sulfoxide; DMT, dimethylterephthalate; DOP, di-n-octyl phthalate; EEC, European economic community; EEQs, estradiol equivalents; GC–MS, gas chromatography–mass spectrometry; HDPE, high density polyethylene; HULYs, human blood lymphocytes; IPA, isophthalic acid; LDH, lactate dehydrogenase; MEG, ethylene glycol; NIAS, non-intentionally added substances; NP, 4-nonylphenol; OP, octylphenol; PA, polyamide; PC, polycarbonate; PhA, phthalic acid; PVC, polyvinylchloride; RPE, relative proliferative effects; Sb_2O_3, antimony trioxide; SEC–HPLC, size exclusion chromatography–high performance liquid chromatography; SML, specific migration limits; SPE, solid-phase extraction; SPME, solid-phase micro-extraction; SODIS, solar water disinfection; TPA, terephthalic acid; TDI, tolerable daily intake; TNPP, tris(nonylphenyl) phosphite; TOC, total organic carbon; YES, yeast estrogen screen.

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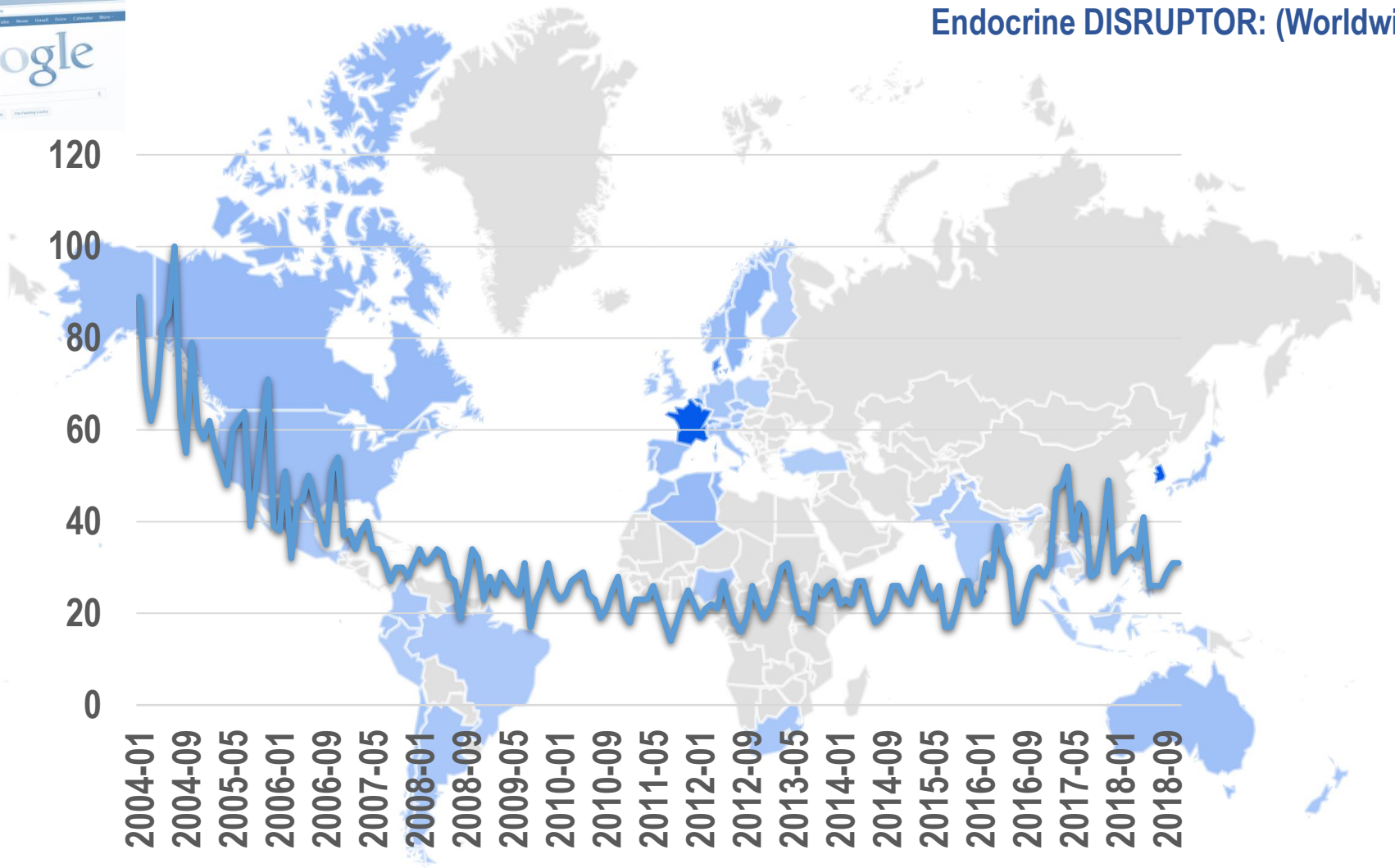
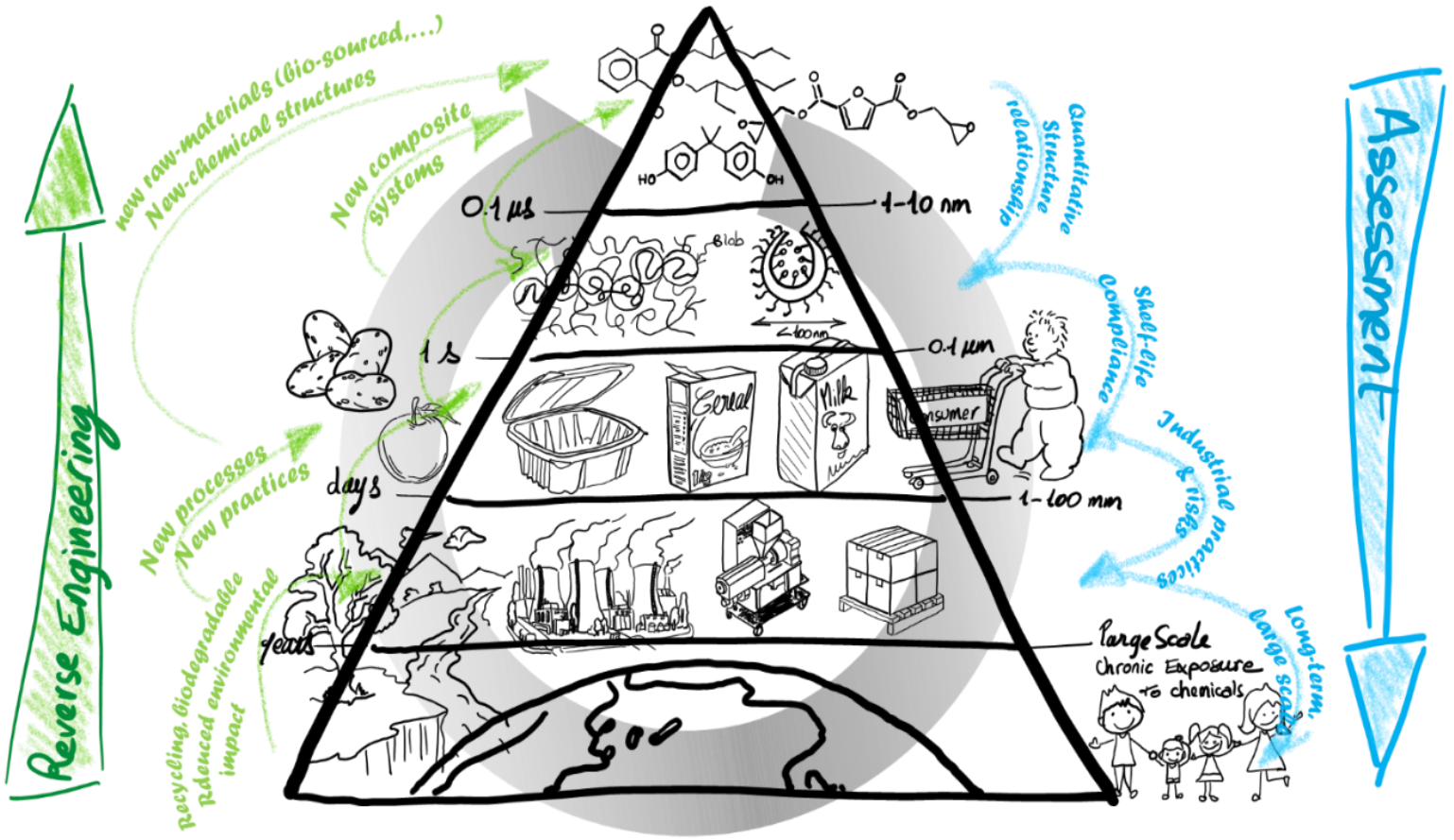
Endocrine DISRUPTOR: (Worldwide)





Role of INRA

Scientific support to global and local solutions and assessments

AgroParisTech

THE SCHOOL OF PACKAGING
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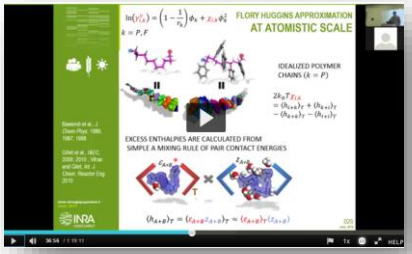

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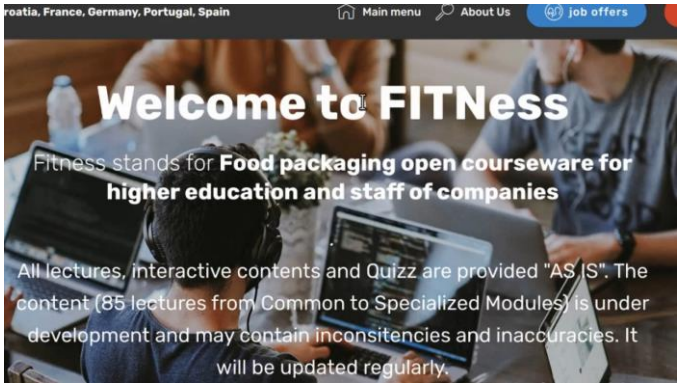

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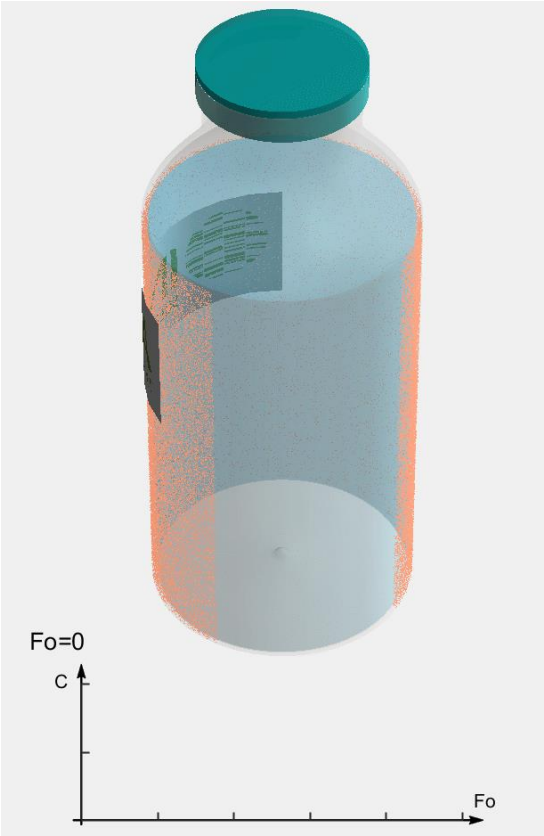
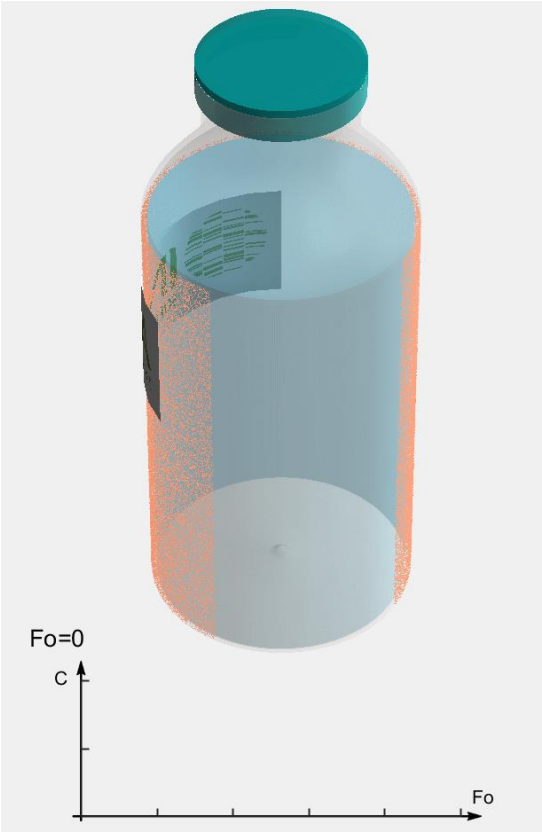
DESORPTION OF PACKAGING CONSTITUENTS (ADDITIVES, MONOMERS AND OLIGOMERS, NIAS…)

SELF-SIMILAR SITUATIONS WHICH OBEY TO THE GENERAL MODEL OF DIFFSION-SOLUBILIZATION

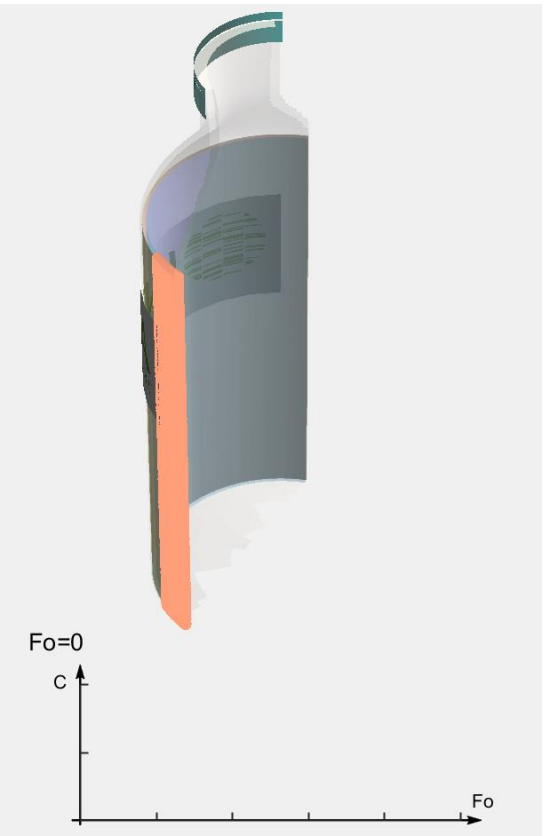
monlayer



with barrier to diffusion

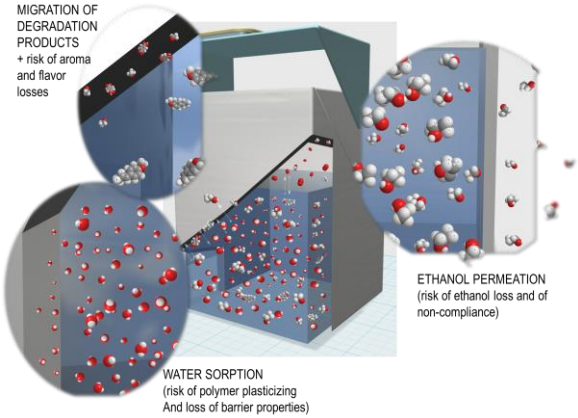


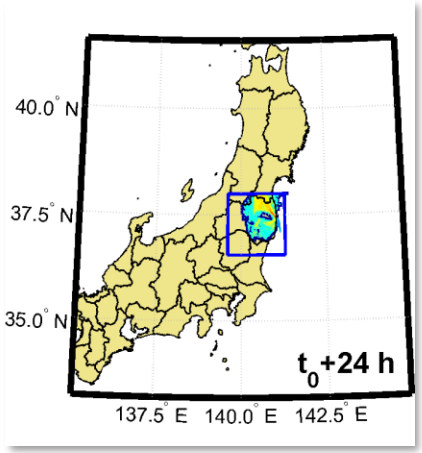
multilayer



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

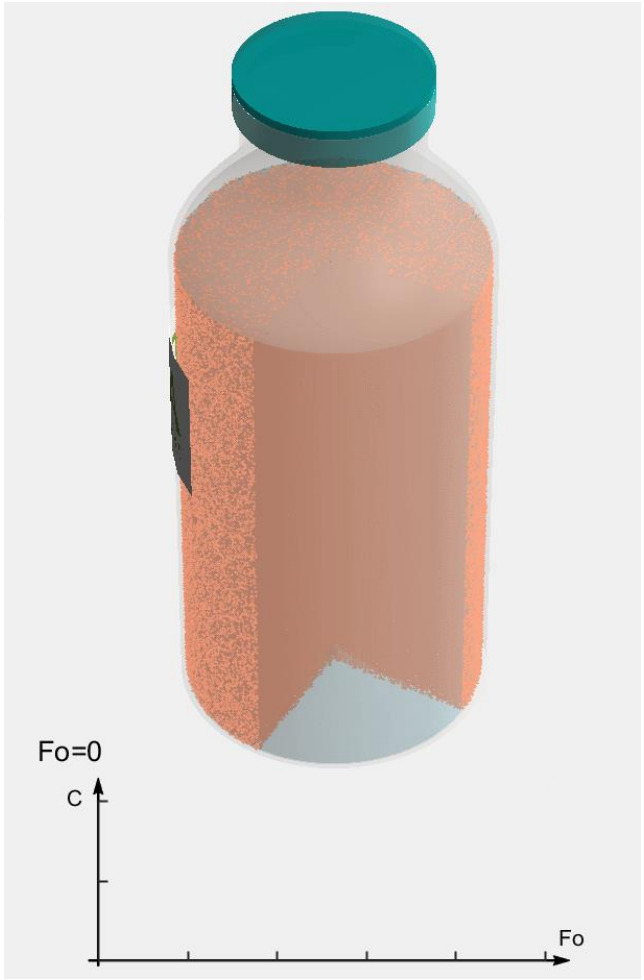
PERMEATION OFFOOD CONTENTS
PERMEATION FROM ENVIRONMENT





Fukushima-Daichi; March 12th, 2011

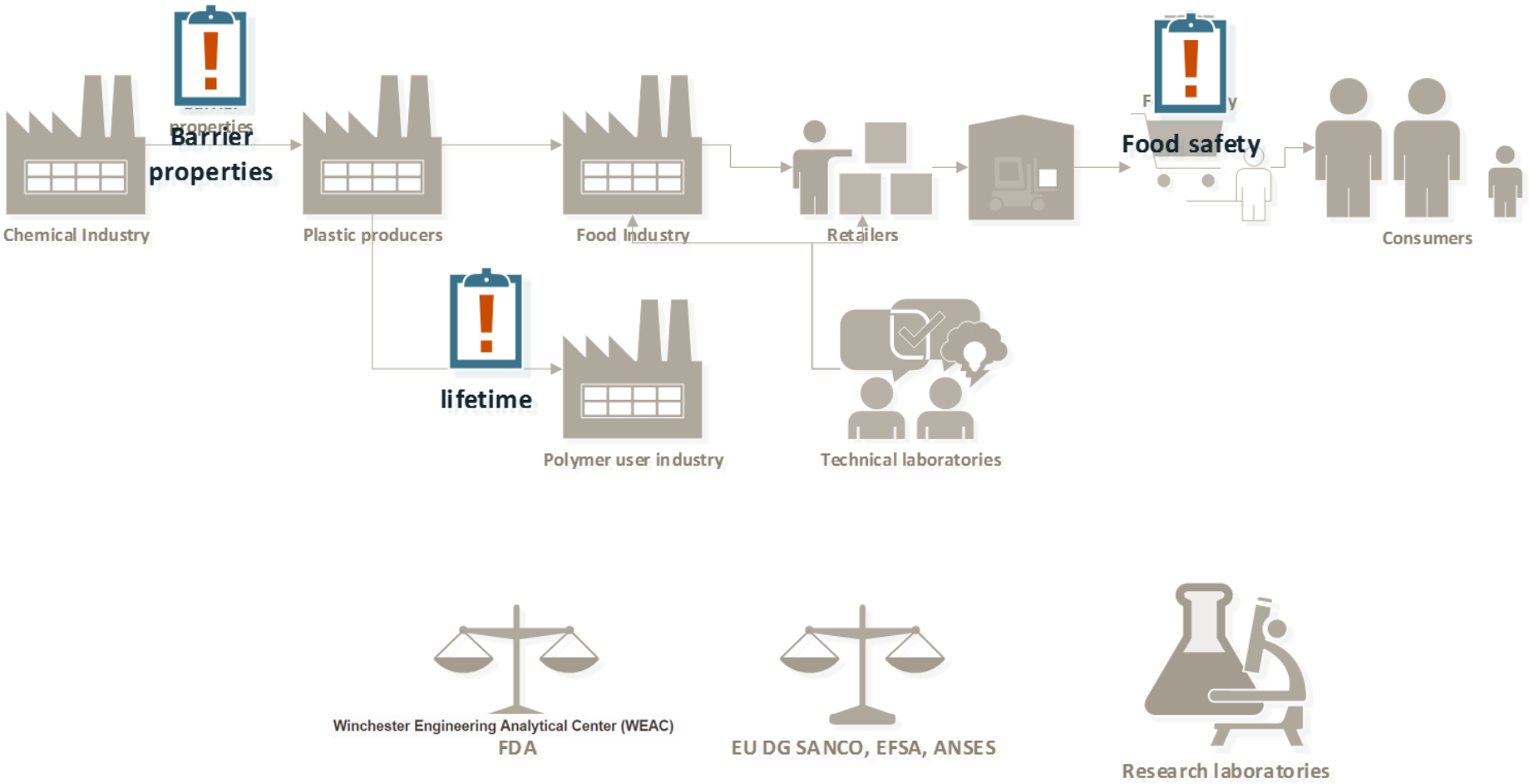
alcoholic beverages



radionuclides

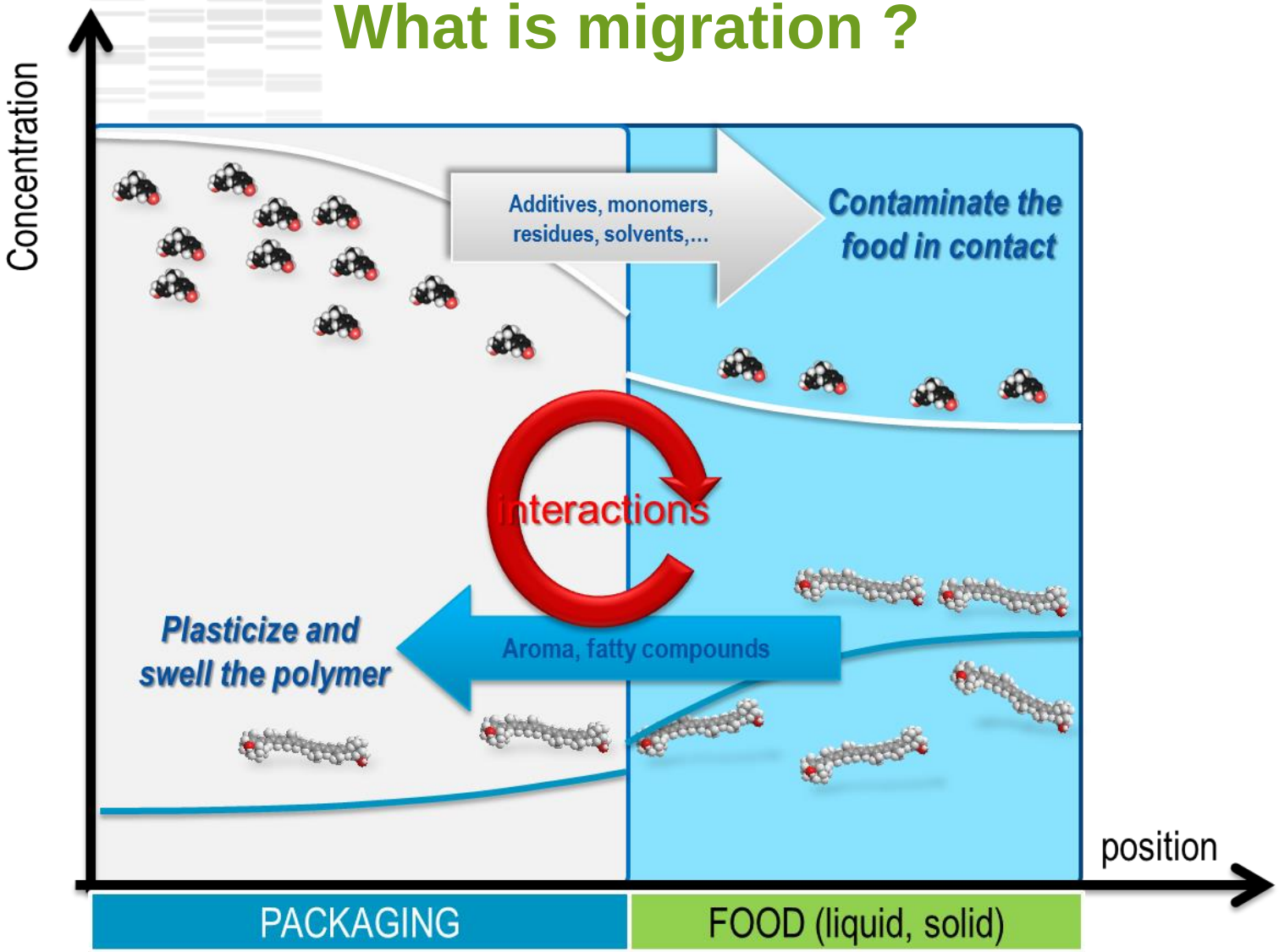
OUR MAIN APPLICATIONS

Overview



REGULATION 10/2011/EC

What is migration ?

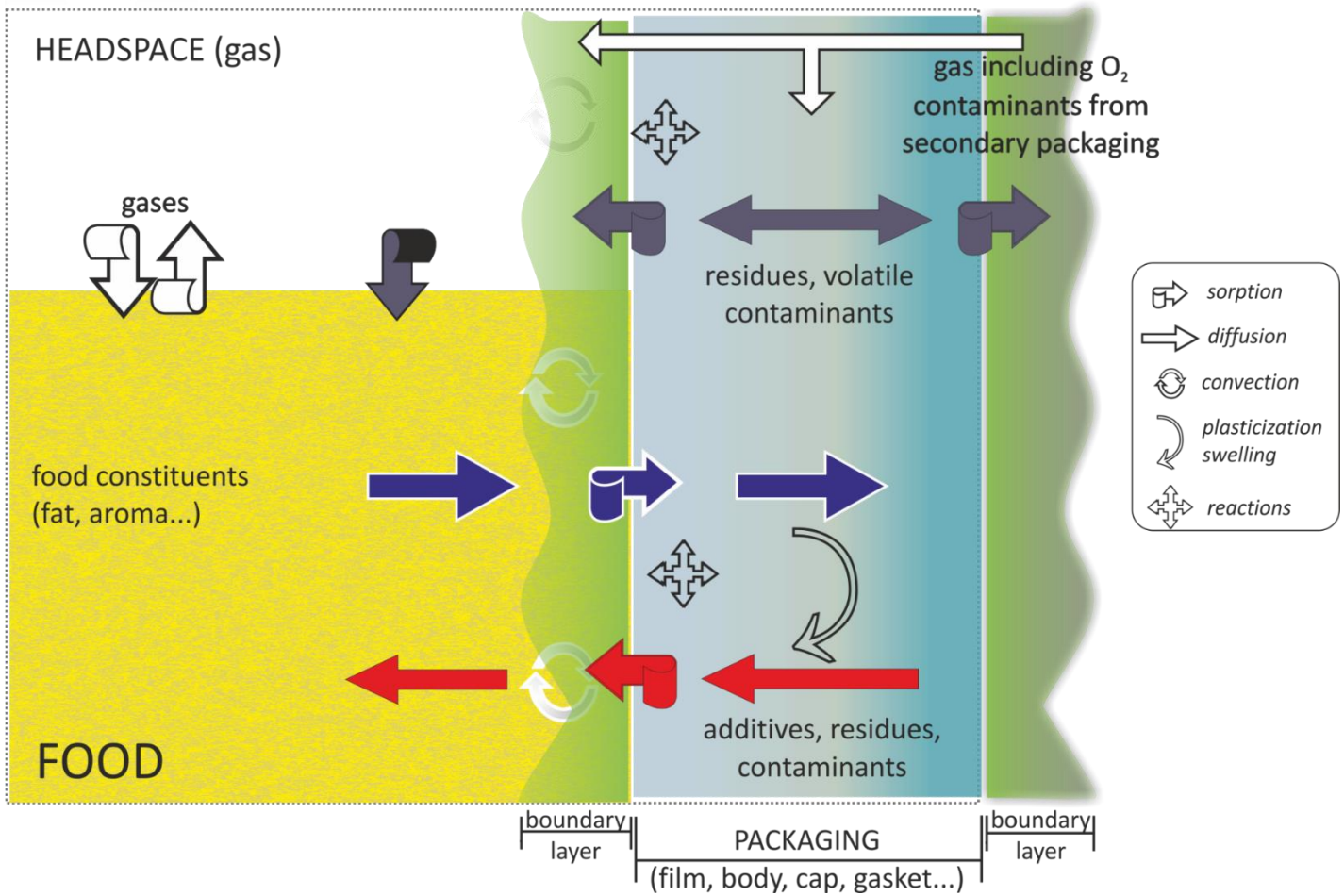


FOOD PACKAGING INTERACTIONS

Example of sterilized product

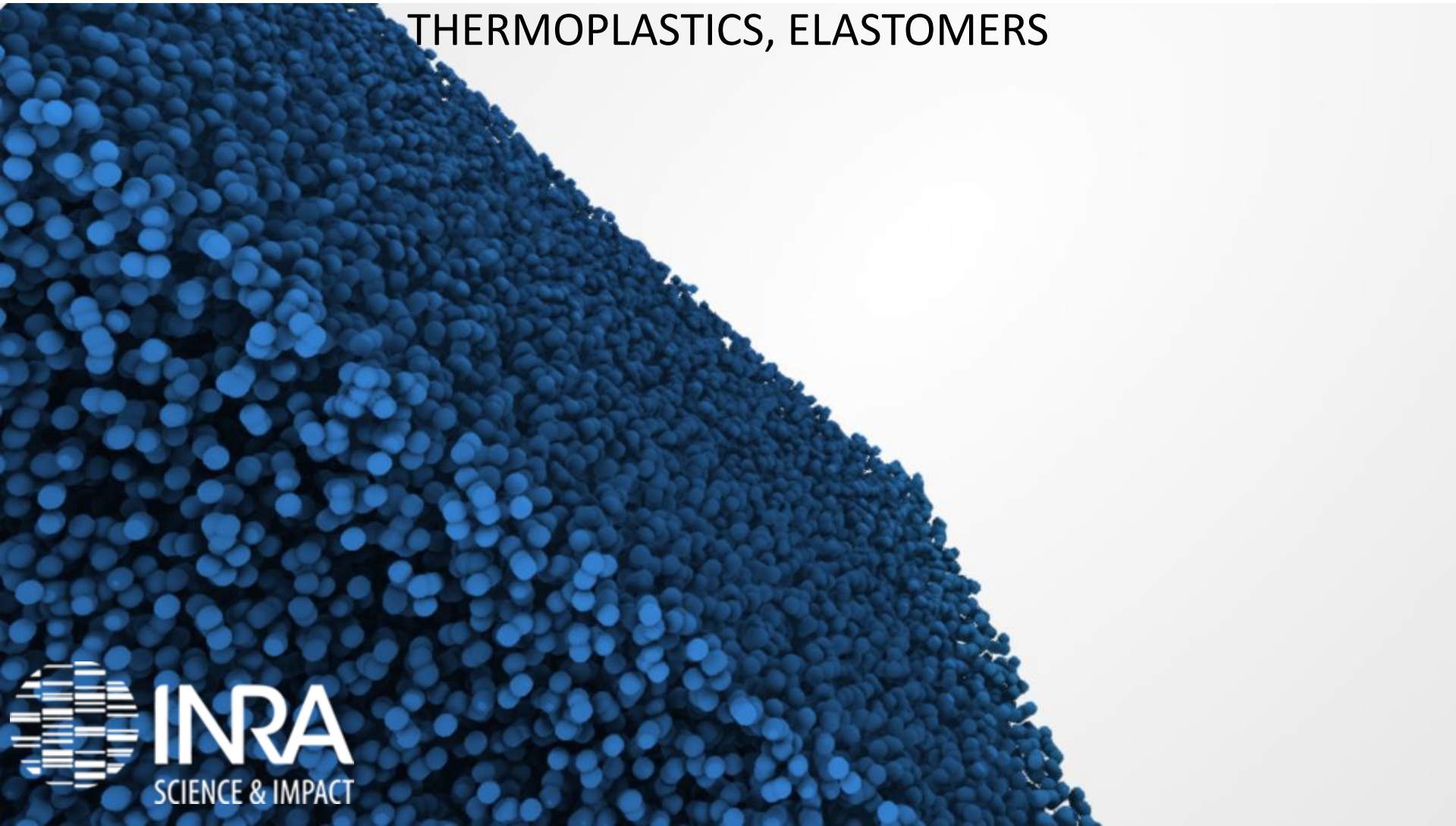
Coupled mass transfer

between the food product and the packaging material



FOOD PACKAGING MATERIALS

THERMOPLASTICS, ELASTOMERS



Classification of polymers

Thermoplastics : A thermoplastic, or thermosoftening plastic, is a polymer that melts, and returns to a solid state upon cooling.

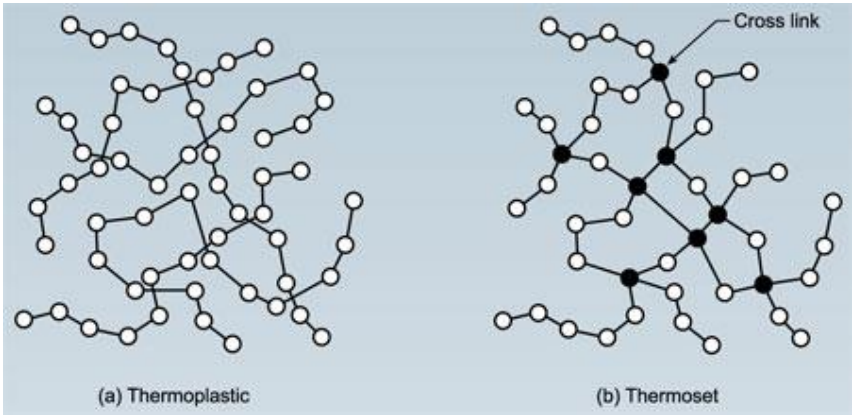
Examples : PE, PP, PS, PVC …

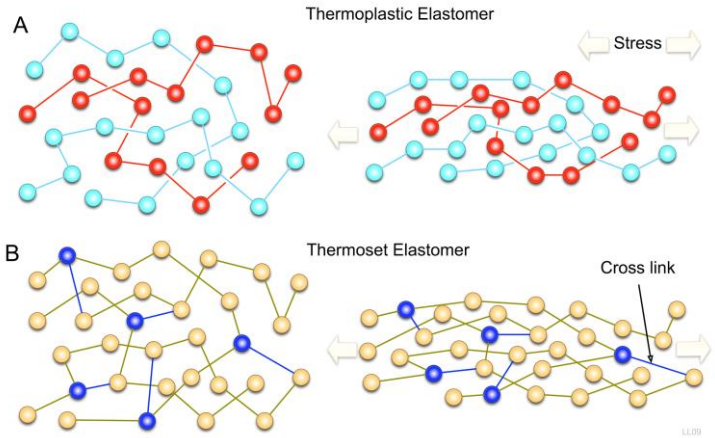
Thermosets : A thermosetting plastic, also known as a thermoset, is polymer material that irreversibly cures. The cure may be induced by heat, generally above 200 °C, through a chemical reaction, or suitable irradiation

Examples : Phenolic, epoxydes …

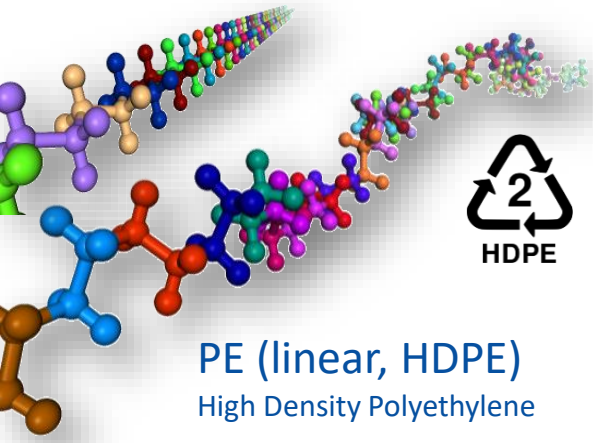
Elastomers : An elastomer is a polymer with viscoelasticity (colloquially "elasticity")

Exemples : Silicones, natural rubber …

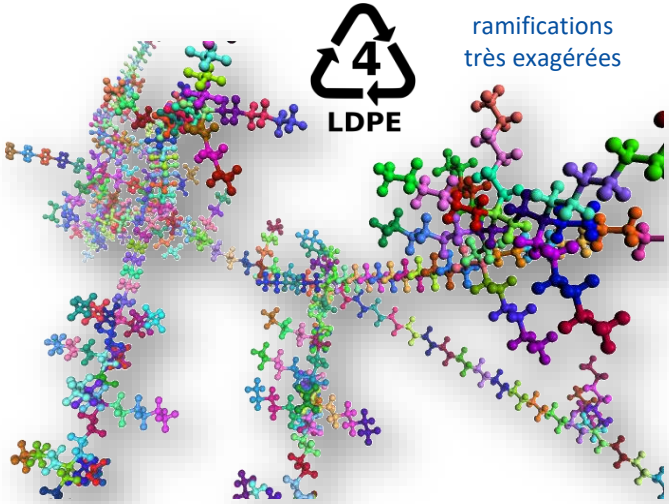




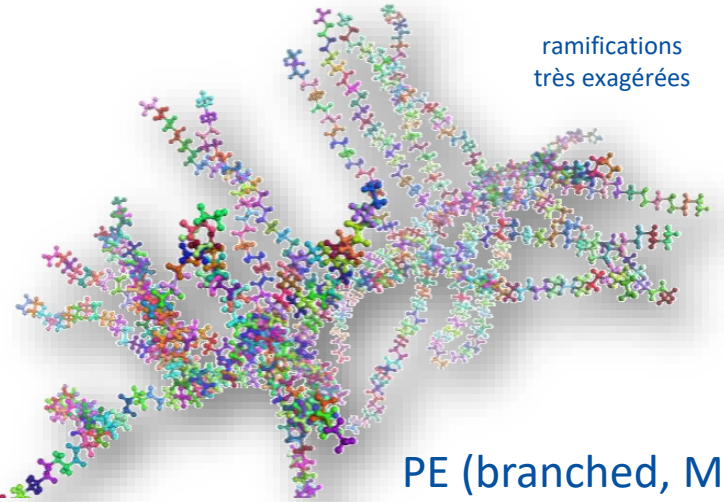
Polyolefins : PE – PP



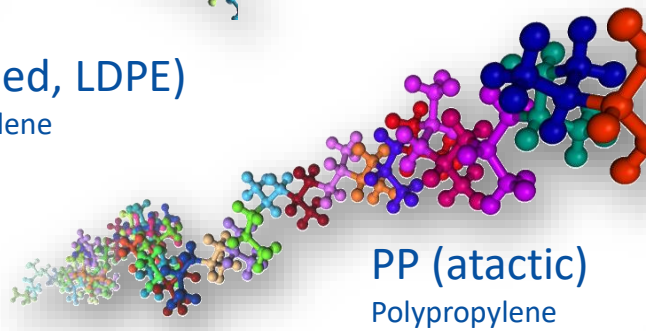
PE (linear, HDPE)
High Density Polyethylene



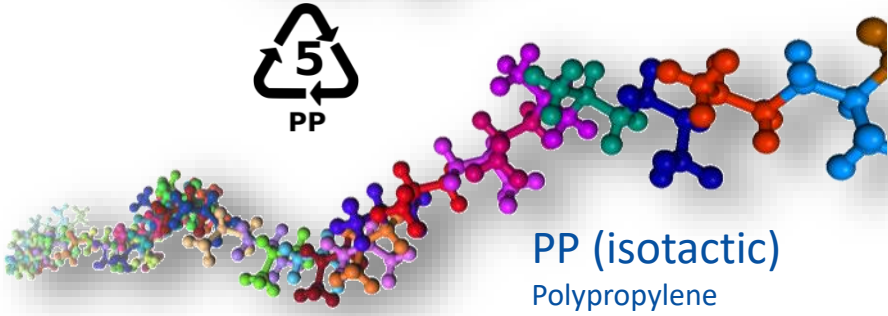
PE (very ramified, LDPE)
Low Density Polyethylene



PE (branched, MDPE)
Medium Density Polyethylene



PP (atactic)
Polypropylene



PP (isotactic)
Polypropylene

POLYOLEFINS

POLYETHYLÈNE

LDPE
(Low density polyethylene)

- Vapour barrier
- Flexibility for seals
- Mouldability • Tearability
- Flexibility • Excellent stretchability • Sterilisation
- Chemical inertness
- Transparency • Tactile effect
- Trays • Boxing
- Screw or clip tops • Nozzles
- Stretchable and retractable films for bundling (multiple-unit packs) and palletting • Bottles
- Stopper seals • Carrier bags
- Small bags • Tubes

HDPE
(High Density Polyethylene)

- Vapour barrier
- Mouldability • Rigidity (for mechanical testing) • Impact resistance • Chemical inertness
- Resistance to stress-cracking
- Sterilisation • Suitable for freezing (-40°C) • Opaqueness
- Large drums
- Screw or clip tops
- Bottles
- Crates and cases • Covers
- Films for postal dispatch
- Flasks • Drums and reusable containers • Pots • Tubes

PP
(Polypropylene)

- Rigidity (Resistance to sterilisation)
- Resistance to cold • Vapour barrier
- Chemical inertness
- Suitable for freezing (-40°C)
- Suitable for micro-waves (+120°C)
- Low density
- Resistant to stress-cracking
- Resistant to folding • Thermal packing • Contact transparency

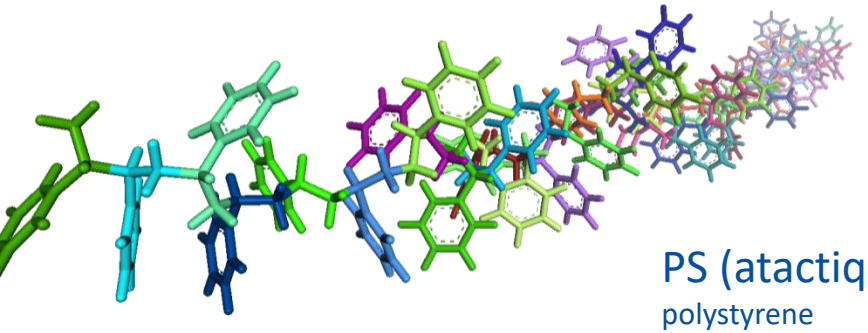
- Clarified PP
- OPP (oriented PP)
- EPP (expanded polypropylene: resistance to repeated impact)

- Alveolate material • Tray containers
- Screw and clip tops
- Reusable crates and cases • Covers
- Thermoforming sheets
- Transparent films and bags
- Bottles
- Reheatable plates • Pots
- Tubs • Tubes

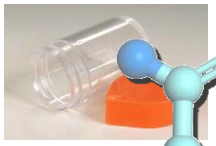
- Flasks
- Films

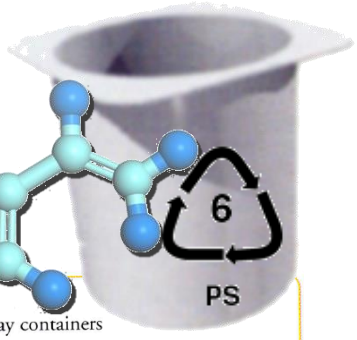
- Reusable wrapping

POLYVINYLS

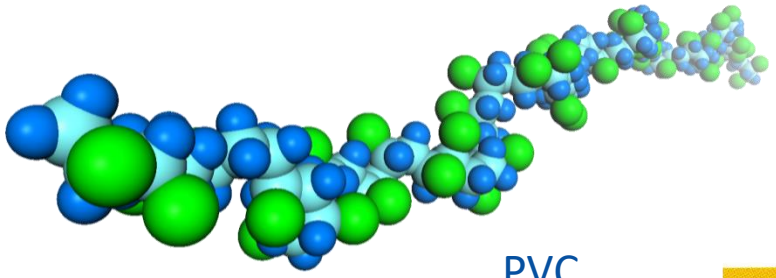


PS (atactique)
polystyrene

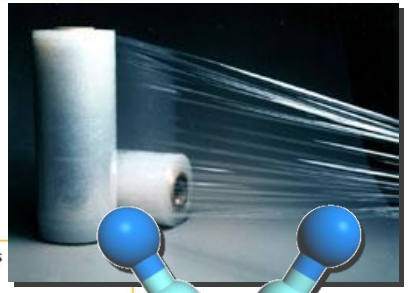


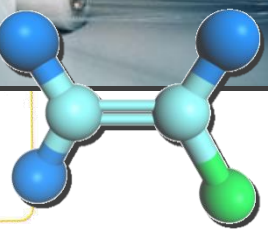


PS (Polystyrene)		
	Compact: ■ Crystal PS: Transparency • Brilliance • Rigidity	• Tray containers (with stretch film)
	■ PS impact: opaque • impact-resistance • Brilliance • Cleavability	• Egg containers • Stoppers • Covers • Thermoforming sheets, pots for dairy products, cups for automatic drink machines
	Direct gassing: • Light • Heat sealable • Warm touch	• Plates/trays

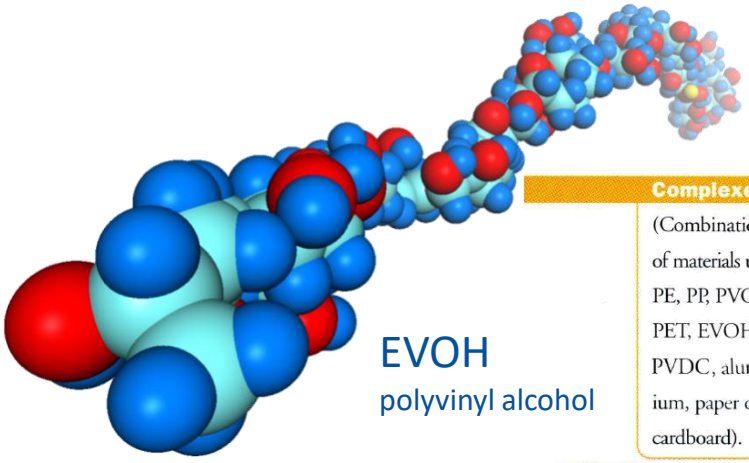


PVC
polyvinyl chloride



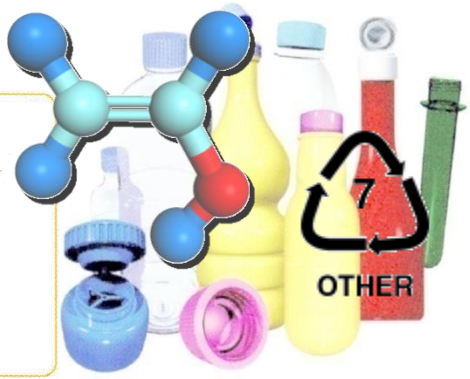


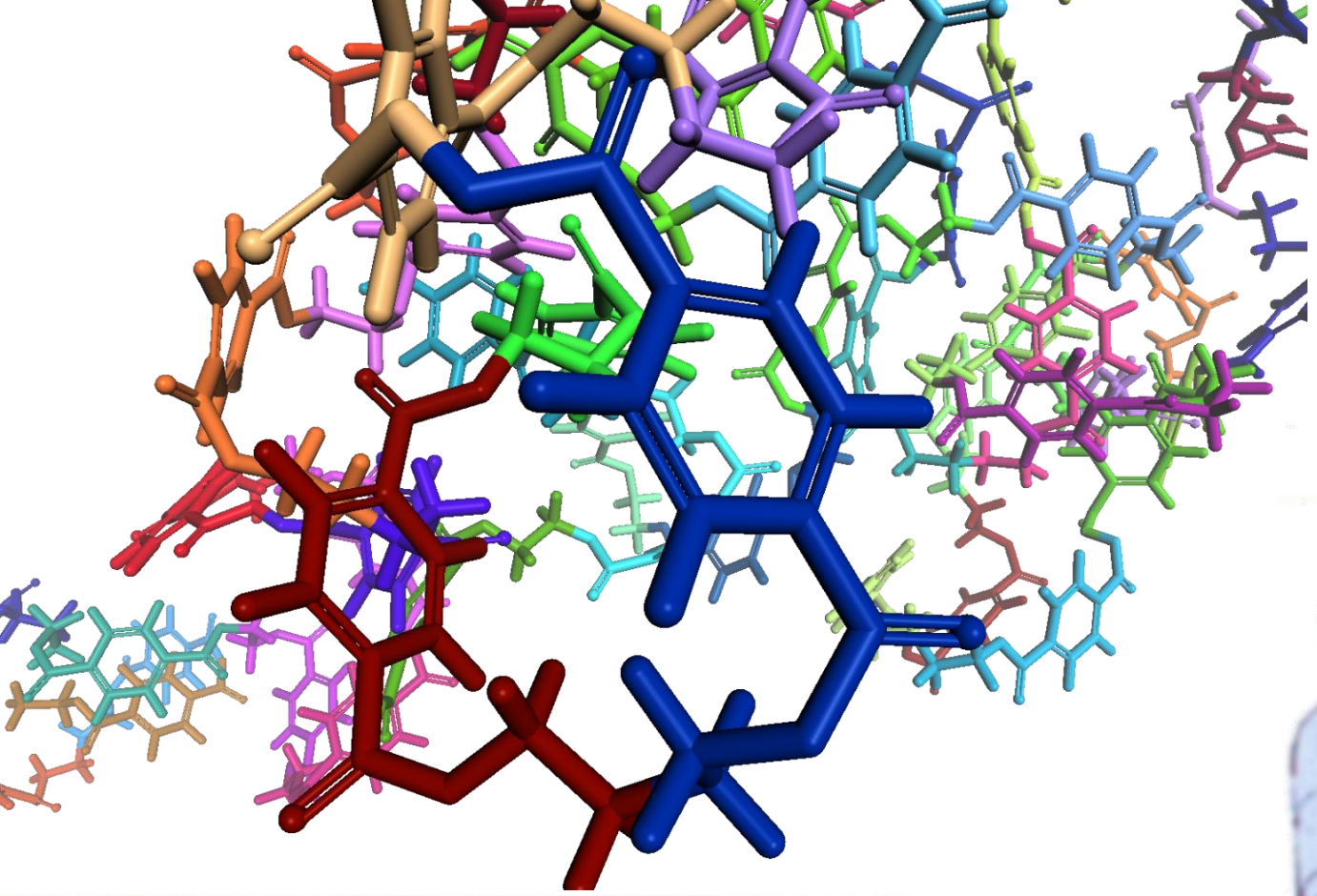
PVC (Polyvinyl chloride)		
	• Inertia • Good stretchability • Machinability • Excellent memory • Resistance to stress-cracking • Transparency	• Tray containers • Boxes • Bottles • Flasks • Blister packs • Sheets for thermoforming • Food-contact films



EVOH
polyvinyl alcohol

Complexes (Combination of materials using PE, PP, PVC, PET, EVOH, PVDC, aluminium, paper or cardboard).	Structure adapted to application: complementary properties • Barrier to aroma, perfume and gas	• Flexible and rigid packaging with special barrier properties • Closures for heat sealing • Tubes • Packing in modified atmosphere or vacuum

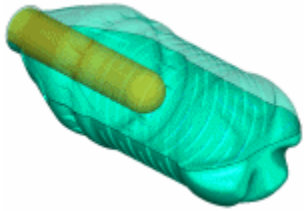




PET

(Polyethylene terephthalate)

- (A)PET (amorphous):
  - Transparent • Perfume compatible
  - Shiny • Impact resistant
  - Resistant to internal pressure
  - Resistant to stress-cracking
  - Gas barrier
  - Tray containers • Boxes • Bottles
  - Lids
  - Thermoforming sheets
  - Films • Flasks • Pots
- (C)PET (crystallised):
  - same properties as (A)PET but not transparent
  - Temperature resistant to 220° C
  - Oven trays (220°C)
  - Blister packs • Bottles
  - Films • Flasks • Pots
- PETG (glycol): amorphous, same properties as (A)PET
  - Tray containers • Lids
  - Thermoforming sheets



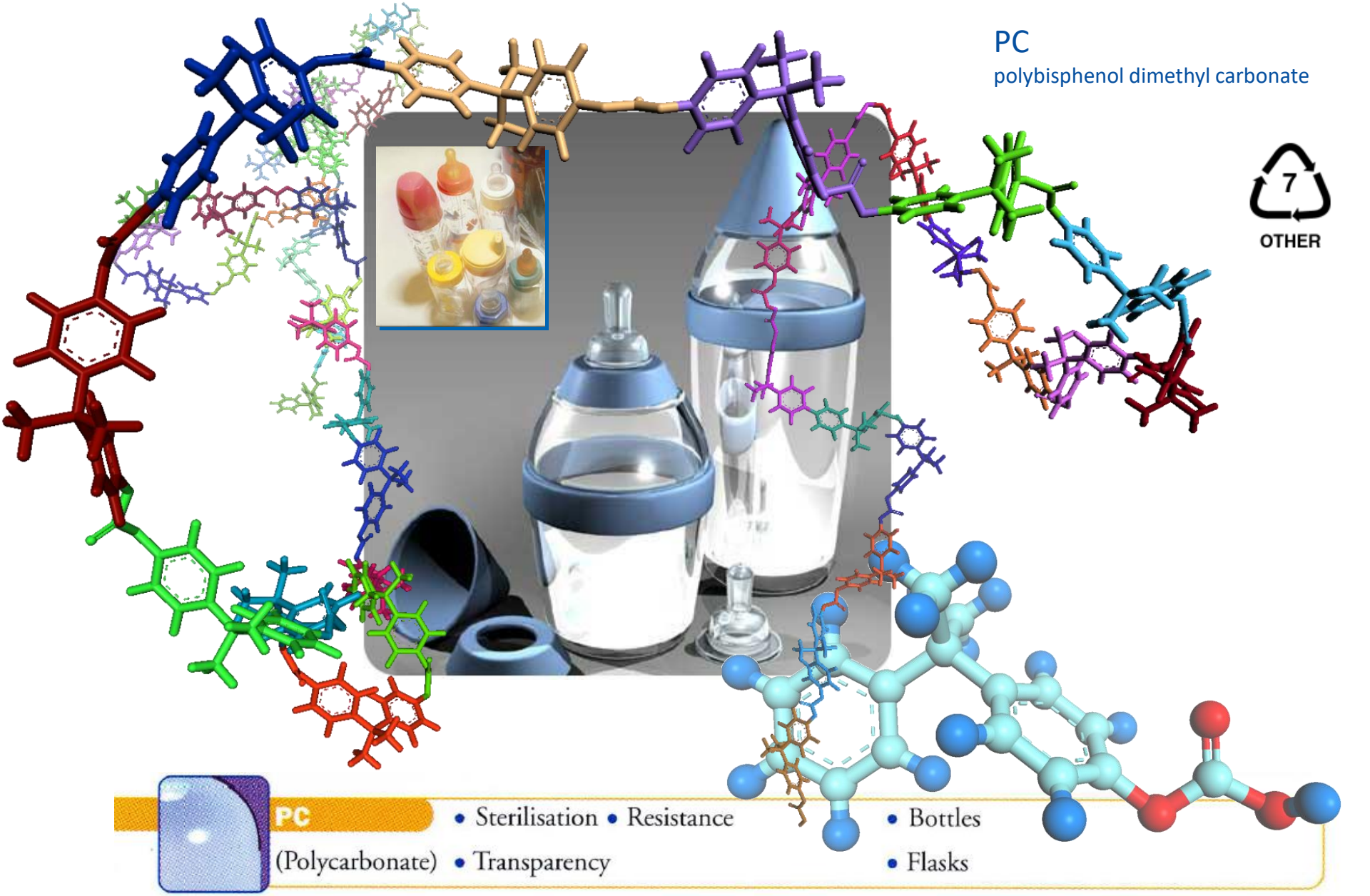
PET/PEN copolymer

- Gas barrier
- UV barrier
- Bottles
- Flasks

PET

Polyethylene terepthalate

POLYCARBONATES



MIGRATION CLASSES

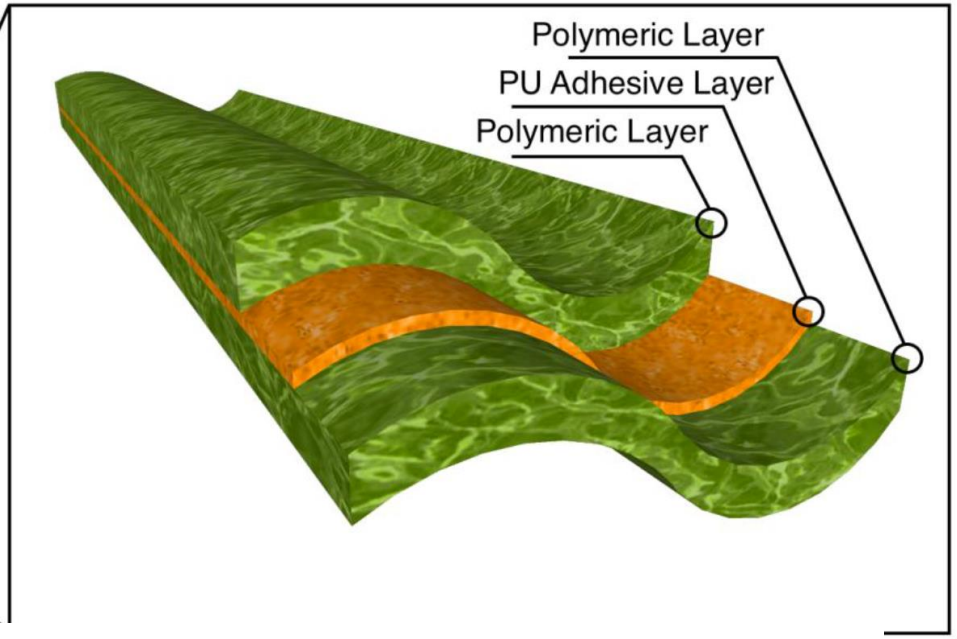
Polymer	Formulation level	Degradation products	Interactions with fatty food	Interactions with alcohols and acids	Contamination risk
PET	+	++ (acetaldéhyde, cyclic trimer)	-	+	+
PE	+++++	+++ (carbonyled compounds)	++++	-	+++++
PP	+++++	+++ (carbonyled compounds)	+++	-	+++++
PS	+++	++ phenol, benzaldehyde, acetophenone	+++	non documented	+++(+)
PVC	+++ à ++++++ (si plastifié)	++ HCl	+++	non documented	+++ to ++++++

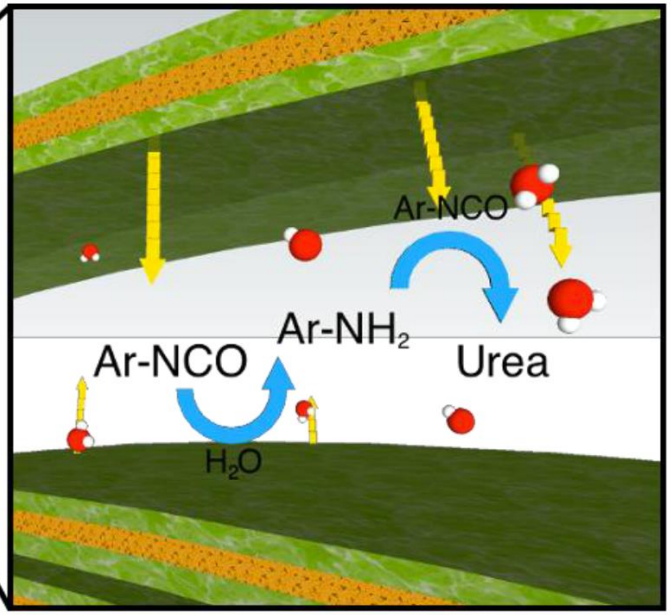
CONTAMINATION SOURCES

Polyurethane based
Sylil terminated polyether based
Butyl rubber based
Natural rubber water-based adhesives
Carboxylated-SBR water-based adhesives
Epoxies
Modified acrylics
Cyanoacrylates

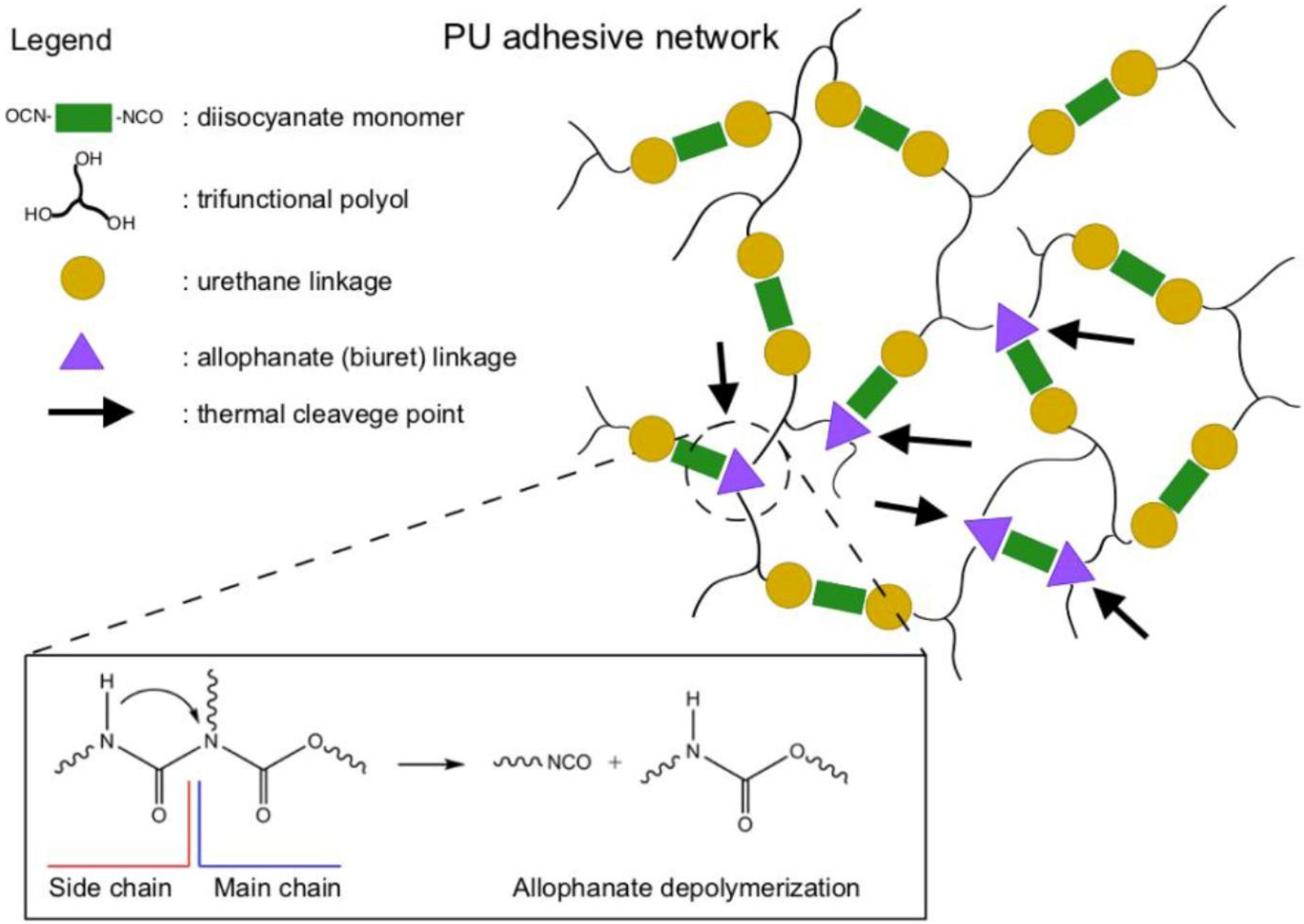
Component	Formulation level	Exposed contact surface	Interaction with food	Contamination risk
Plastic layer in contact withfood	+++	+++++	+ to +++	+++++
Layer non-intented to be in contact with food	+++	+++++	-	+++
Cap, lid	+++	++	- to +	++
Gasket	+++++	+	- to +	+ to ++
Varnish	+++ to +++++	+++++	-	+++
Ink	+++++	+ to +++	-	+ to +++

Laminates

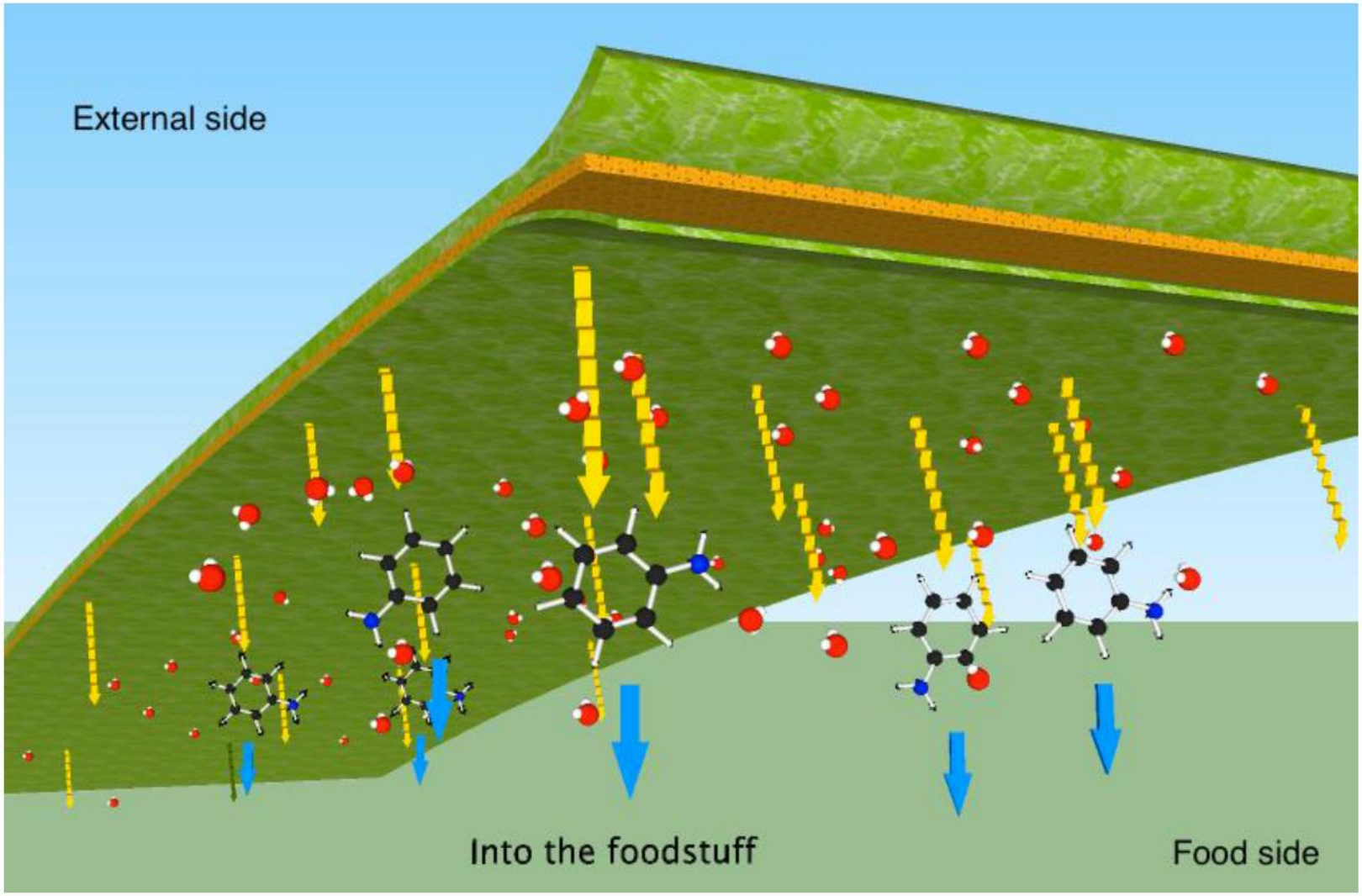

Polymeric Layer
PU Adhesive Layer
Polymeric Layer


Ar-NCO
Ar-NH2
Urea
Ar-NCO
H2O

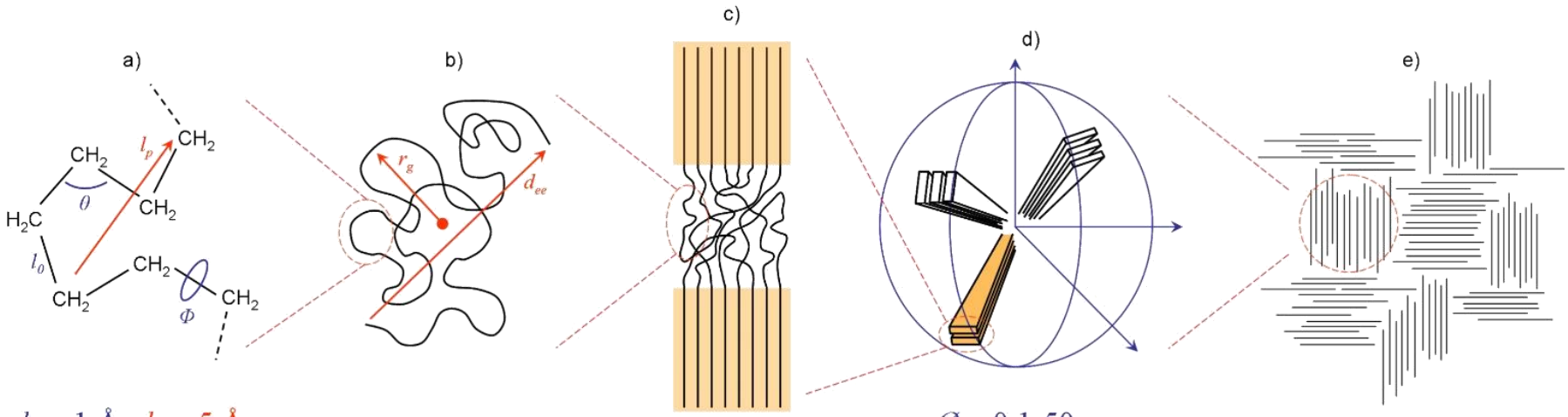
Polyurethane adhesive



MIGRATION FROM LAMINATES



UNIVERSAL PROPERTIES OF LINEAR POLOLYMERS



$l_0 \sim 1$ Å ; $l_p \sim 5$ Å

l_0: bond length
l_p: persistence length
Φ: torsion angle
r_g: gyration radius
dee: end-to-end distance

$\varnothing \sim 0{,}1\text{-}50$ µm

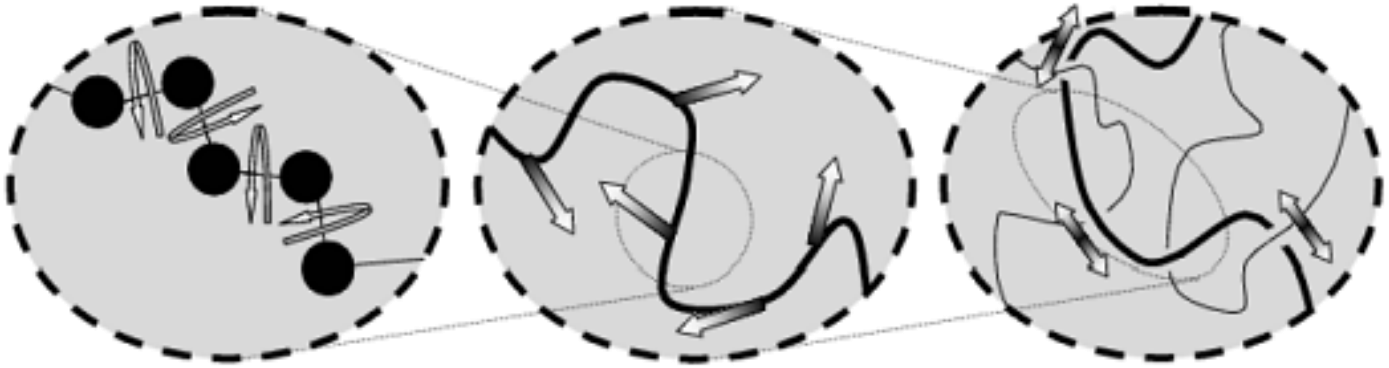
a) Chemical structure
b) Intermingled chains
c) Semi-crystalline structure
d) Poly-crystalline structure
e) Heterogeneous material

CORRESPONDING MOTIONS (RELAXATIONS)

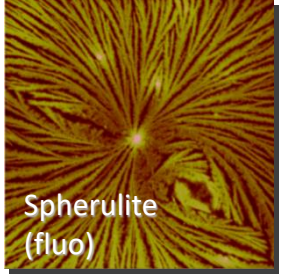
Local reorientations (shaft motions)

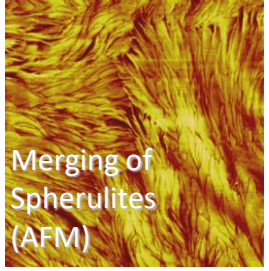
Local translation (between entanglements)

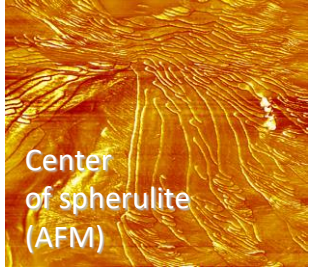
full translation

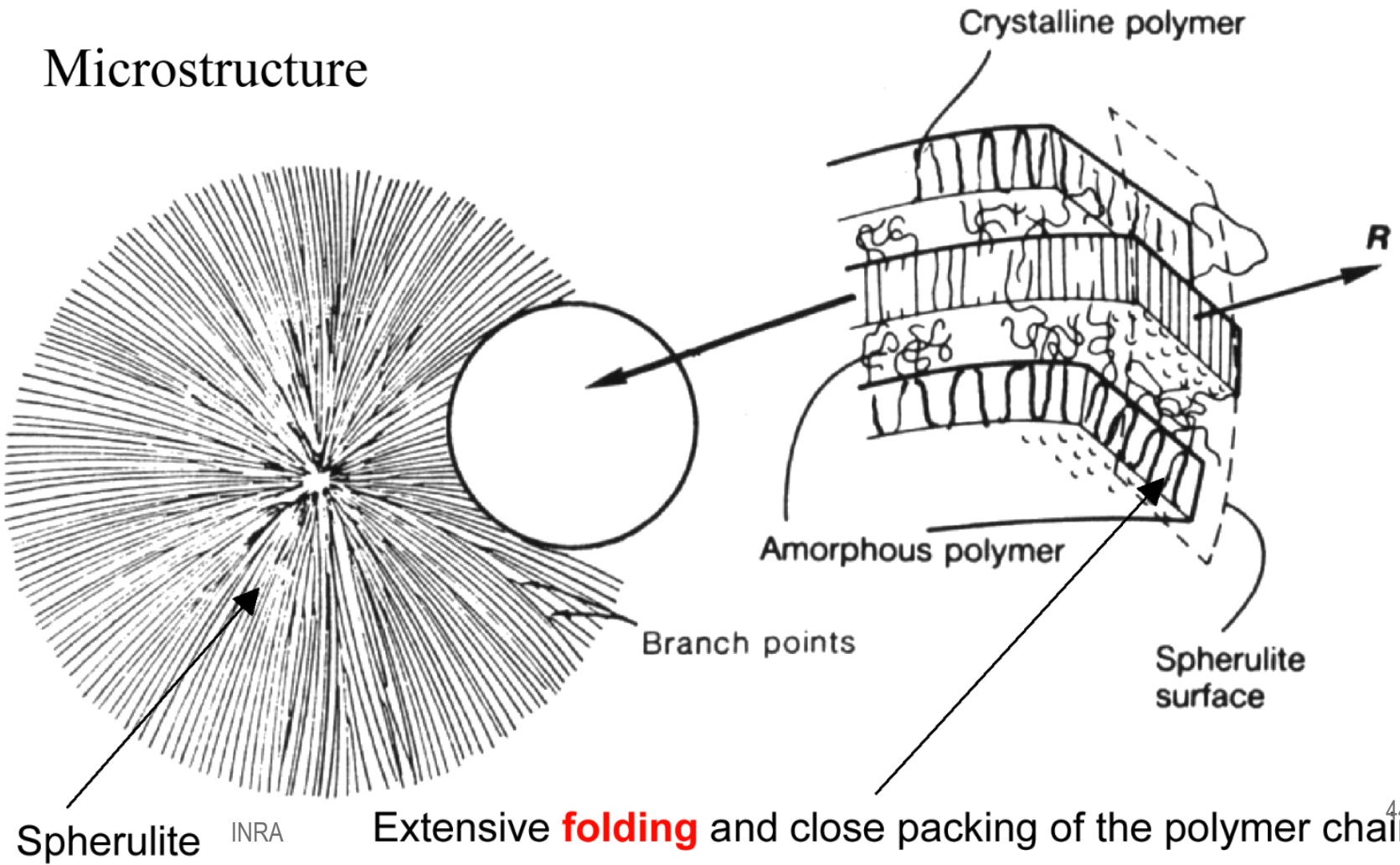


POLY CRYSTALLINE STRUCTURE









INRA

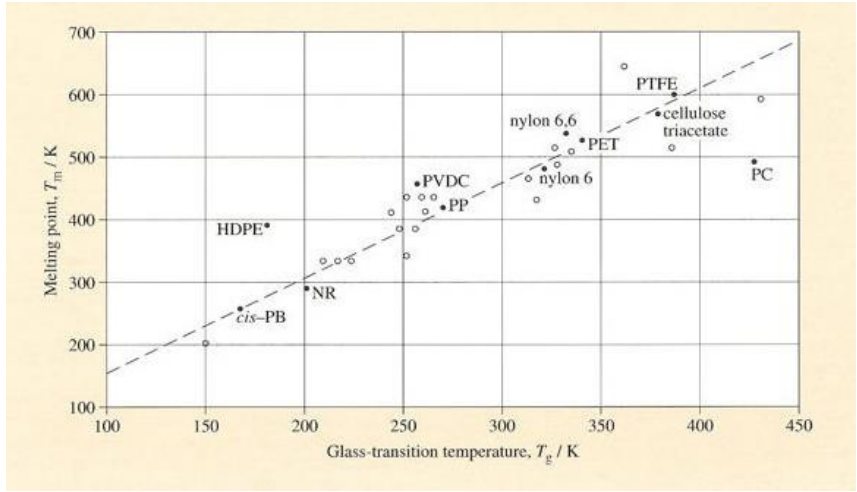
Extensive **folding** and close packing of the polymer chain

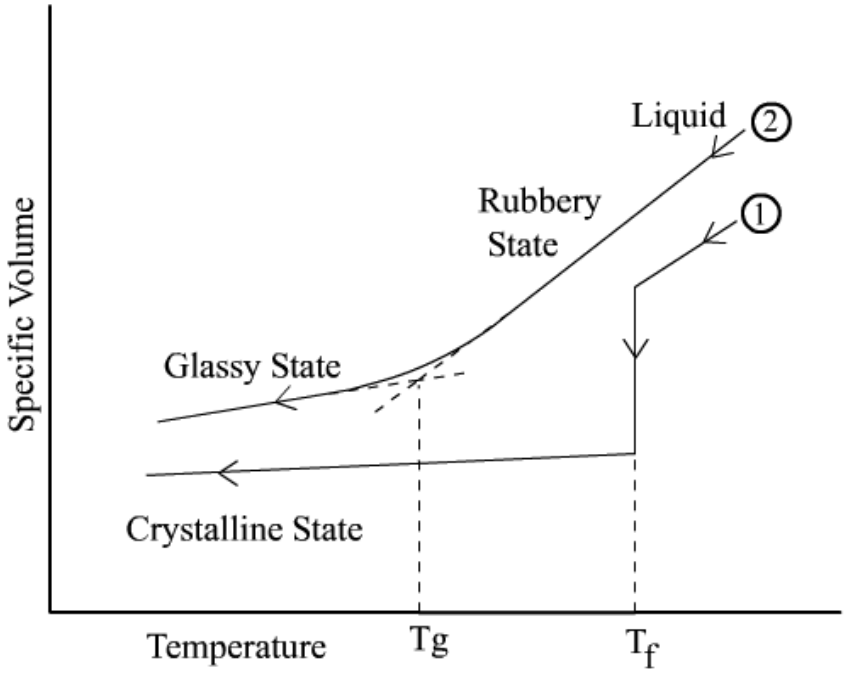
Critical temperatures for polymers

Glass transition temp. T_g

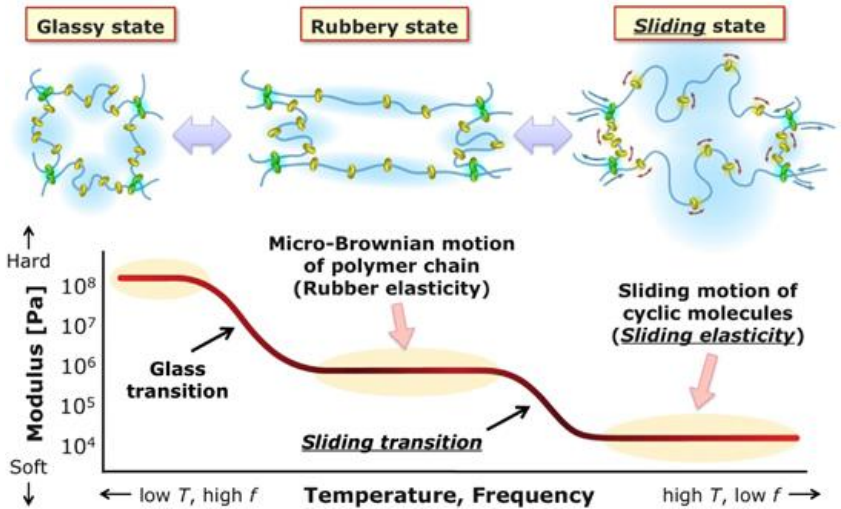
Melting point T_m

$$T_g \approx \frac{2}{3} T_m$$



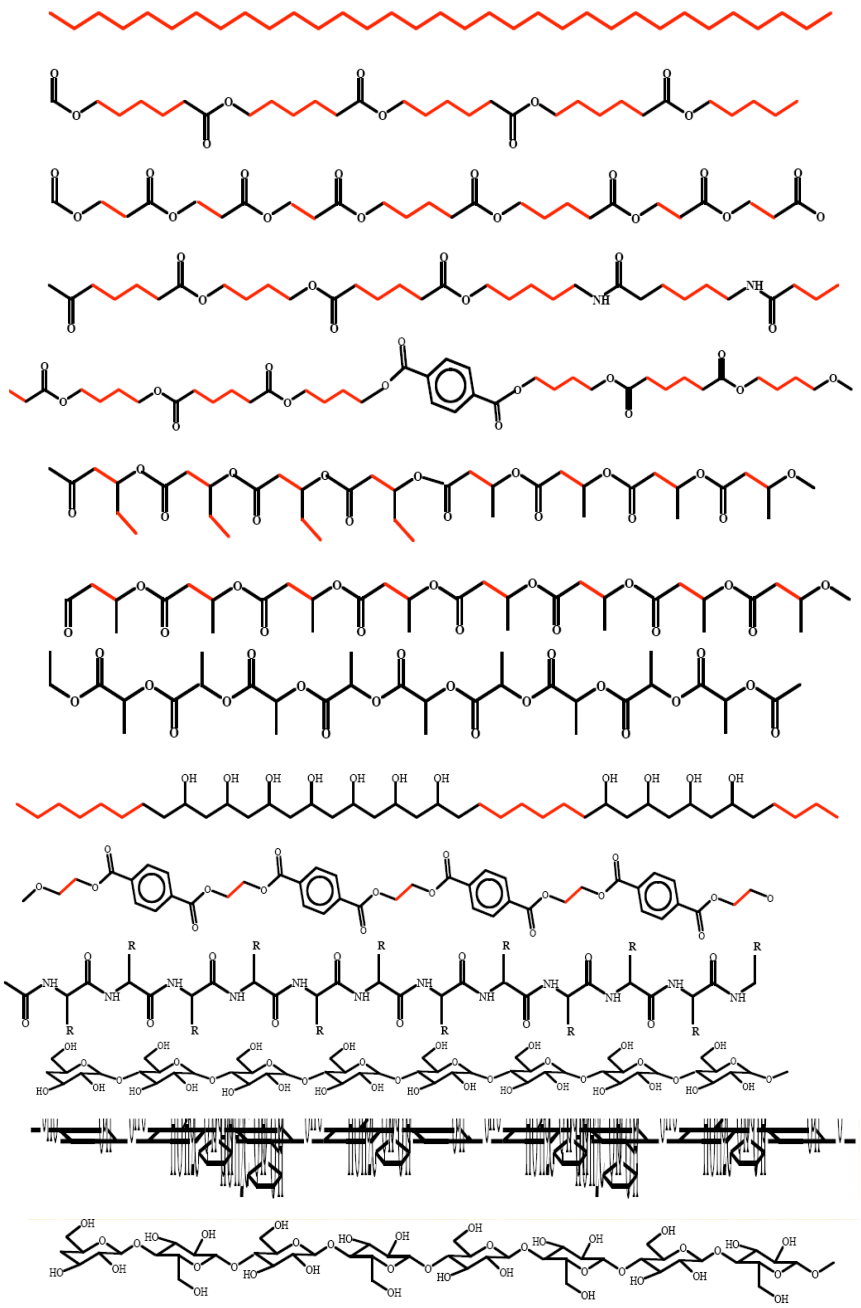


$$T_g = T_{g\infty} - \frac{K}{\langle M_n \rangle}$$



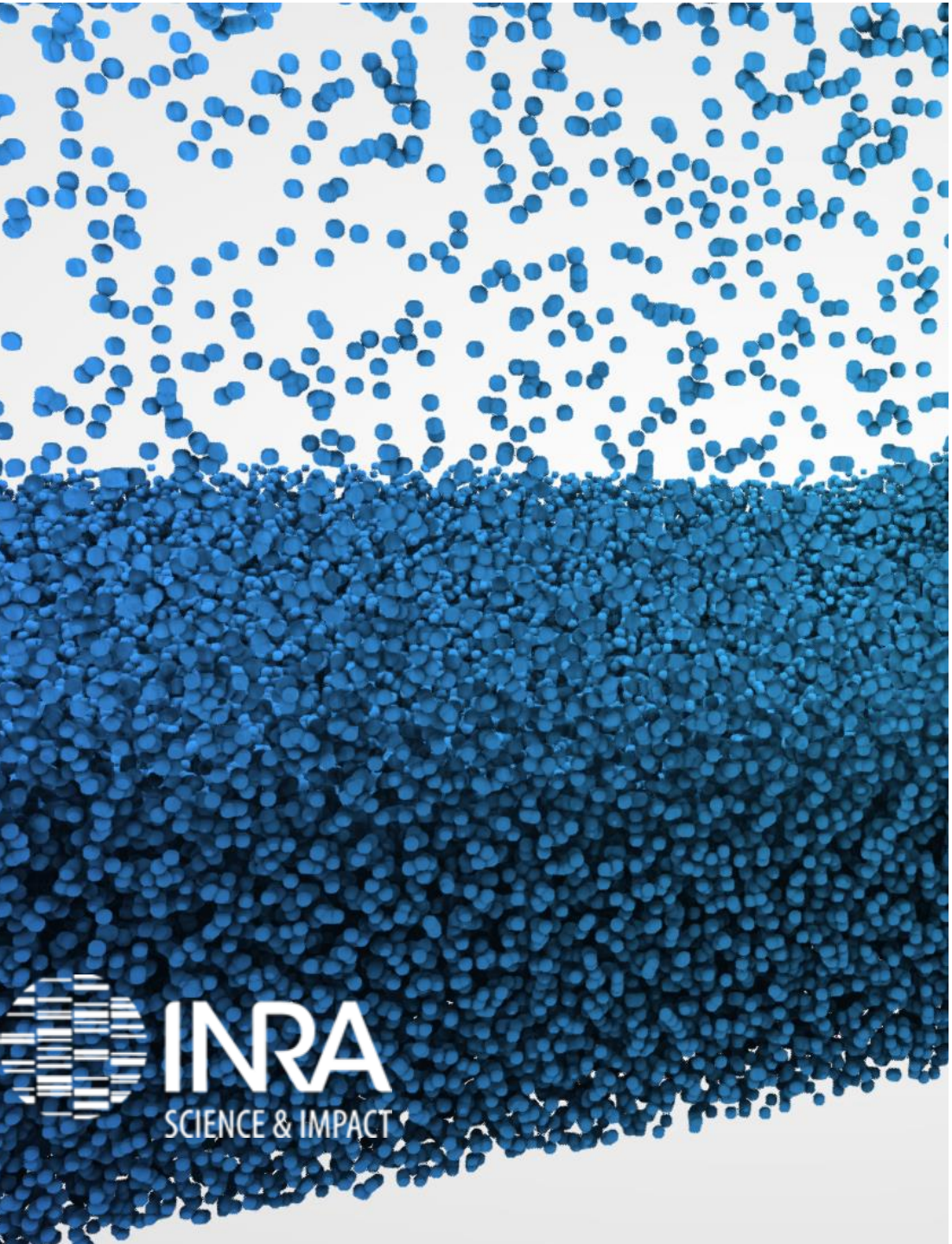
TOWARDS BIODEGRADABLE POLYMERS

e.g.



polarity

polymer	Tg (°C)	Tm (°C)
PE	-120	60
PCL	-60	60
PBSA	-45	114
PEA	-30	112
PBAT	-30	110
$PHBV_{15}$	+5	145
PHB	+10	175
PLA	+58	+152
EVOH	+60	+190
PET	+90	+270
Proteins	>200 @0% RH	Degradation before melting
Starch		
Hemicelluloses		
Cellulose		



PERMEATION

OVERVIEW OF

BARRIER PERFORMANCES

TABLE 12.1
Degree of Protection Required by Various Foods and Beverages (Assuming 1 Year Shelf Life at 25°C)

Food/Beverage	Maximum Amount of O_2 Gain (ppm)	Other Gas Protection Needed	Maximum Water Gain or Loss	Requires High Oil Resistance	Requires Good Barrier to Volatile Organics
Canned milk and flesh foods	1–5	No	3% Loss	Yes	No
Baby foods	1–5	No	3% Loss	Yes	Yes
Beers and wine	1–5	<20% CO_2 (or SO_2) loss	3% Loss	No	Yes
Instant coffee	1–5	No	2% Gain	Yes	Yes
Canned soups, vegetables and sauces	1–5	No	3% Loss	No	No
Canned fruits	5–15	No	3% Loss	No	Yes
Nuts, snacks	5–15	No	5% Gain	Yes	No
Dried foods	5–15	No	1% Gain	No	No
Fruit juices and drinks	10–40	No	3% Loss	No	Yes
Carbonated soft drinks	10–40	<20% CO_2 loss	3% Loss	No	Yes
Oils and shortenings	50–200	No	10% Gain	Yes	No
Salad dressings	50–200	No	10% Gain	Yes	Yes
Jams, jellies, syrups, pickles, olives, vinegars	50–200	No	10% Gain	Yes	No
Liquors	50–200	No	3% Loss	No	Yes
Condiments	50–200	No	1% Gain	No	Yes
Peanut butter	50–200	No	10% Gain	Yes	No

Source: Adapted from Salame, M., The use of low permeation thermoplastics in food and beverage packaging, in: *Permeability of Plastic Films and Coatings*, Hopfenberg, H.B. (Ed.), Plenum, New York, p. 275, 1974.

Example 12.1

A breakfast cereal has an initial moisture content m_i of 2.5%. The COP is the critical moisture content m_c of 8% due to loss of crispness (Robertson, 2011a). The equilibrium moisture content m_e at 25°C is 14.8% and the pseudo-equilibrium moisture content m'_e obtained by extension of the linear portion of the isotherm is 11%; the slope of the line (*b*) is 0.147 g H_2O/g solids/unit a_w (see Figure 12.4).

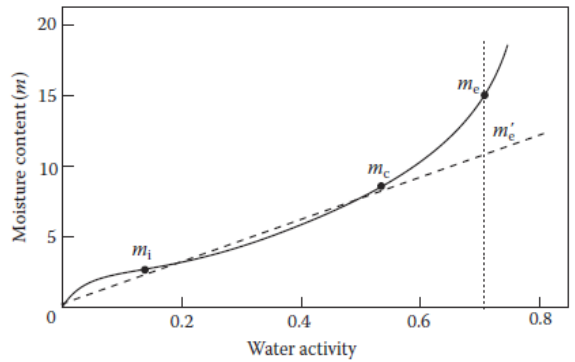


FIGURE 12.4 Schematic of a typical moisture sorption isotherm for breakfast cereal with a superimposed straight line of slope *b*. Initial (m_i), critical (m_c) and equilibrium (m_e) moisture contents are indicated together with the pseudo-equilibrium (m'_e) moisture content used for package shelf life calculations.

Calculate the shelf life of the cereal if it is packaged in a bag of 50 µm LDPE or 50 µm OPP. The weight of dry cereal in the package is 400 g and the dimensions of the bags are 20 cm × 30 cm. The packed product is to be stored at 25°C and 75% RH.

$$\text{Surface area of the bags is } 20 \times 30 = 600 \text{ cm}^2 = 0.06 \text{ m}^2$$

$$\text{Vapour pressure of pure water at } 25°C = 2.3756 \text{ cm Hg}$$

Data from a plastic film supplier indicated that WVTRs determined at 25°C/75% RH were

$$50\,\mu\text{m LDPE} = 8.0 \text{ g m}^{-2}\text{day}^{-1}$$

$$50\,\mu\text{m OPP} = 1.35 \text{ g m}^{-2}\text{day}^{-1}$$

These WVTRs must be converted into water vapor permeances *P*/*X* by dividing by the driving force for water vapor transfer. The saturated water vapor pressure at 25°C is (from Table 4.10) 2.376. Thus, the driving force at 25°C/75% RH is

$$2.376 \times 0.75 = 1.782 \text{ cm Hg}$$

For LDPE film,

$$\frac{P}{X} = \frac{8.0\text{g}}{\text{m}^2\,\text{day}} \times \frac{1}{1.782(\text{cmHg})}$$
$$= 4.489\,\text{g}H_2O\text{m}^{-2}\,\text{day}^{-1}(\text{cmHg})^{-1}$$

For OPP film,

$$\frac{P}{X} = \frac{1.35\text{g}}{\text{m}^2\,\text{day}} \times \frac{1}{1.782(\text{cmHg})}$$
$$= 0.758\,\text{g}H_2O\text{m}^{-2}\,\text{day}^{-1}(\text{cmHg})^{-1}$$

Substituting into Equation 12.10 for cereal packed in LDPE film,

$$\ln\frac{11-2.5}{11-8} = 4.489 \cdot \frac{0.06}{400} \cdot \frac{2.3756}{0.147} \cdot \theta_s \qquad (12.12)$$

Solving for shelf life θ_s,

$$\theta_s = \frac{[\ln 2.833]}{1.088 \times 10^{-2}}$$
$$= \frac{1.0413}{1.088 \times 10^{-2}}$$
$$= 96 \text{ days}$$

If the cereal were packed in OPP film instead,

$$\theta_s = \frac{[\ln 2.833]}{1.837 \times 10^{-3}}$$
$$= 567 \text{ days}$$

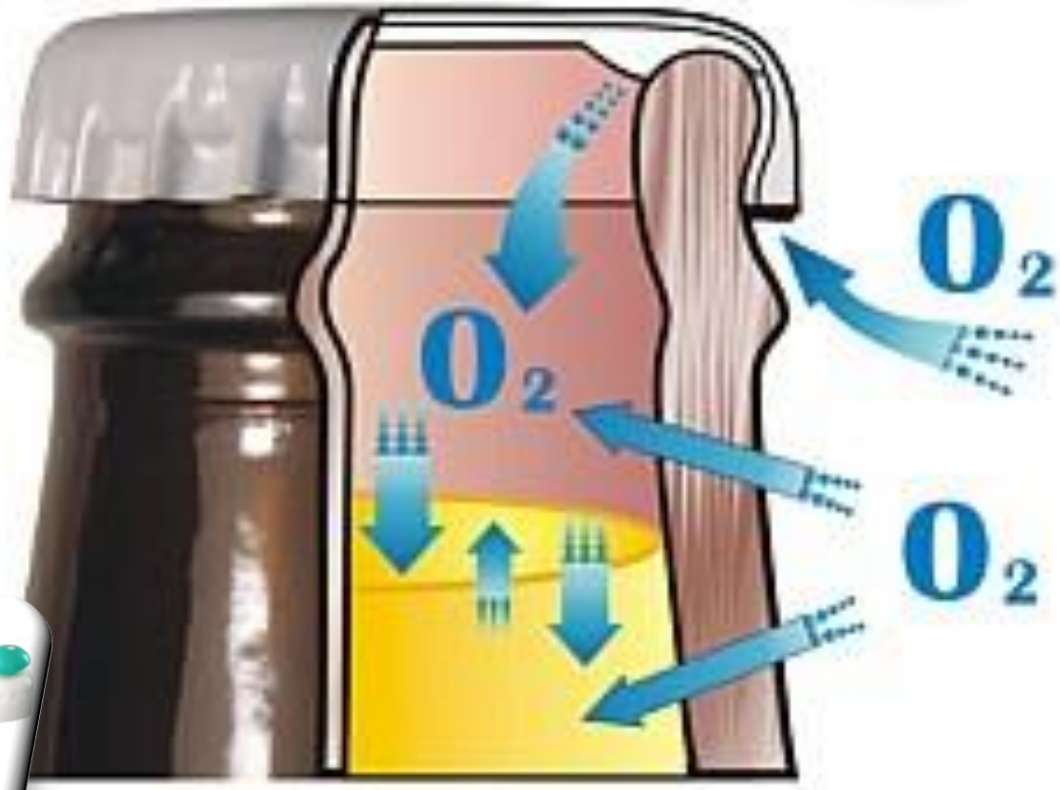
The shelf life is inversely related to the water vapor permeances of the film; since *P*/*X* for LDPE is 5.9 times that for OPP, the shelf life in the latter film is 5.9 times that in the former. If the required shelf life were, say, 300 days, then Equation 12.10 could be recalculated using t_s = 300 and solved for *P*/*X*. From this, the corresponding WVTR could be calculated and the film supplier requested to supply a film that met this specification at 25°C and 75% RH.

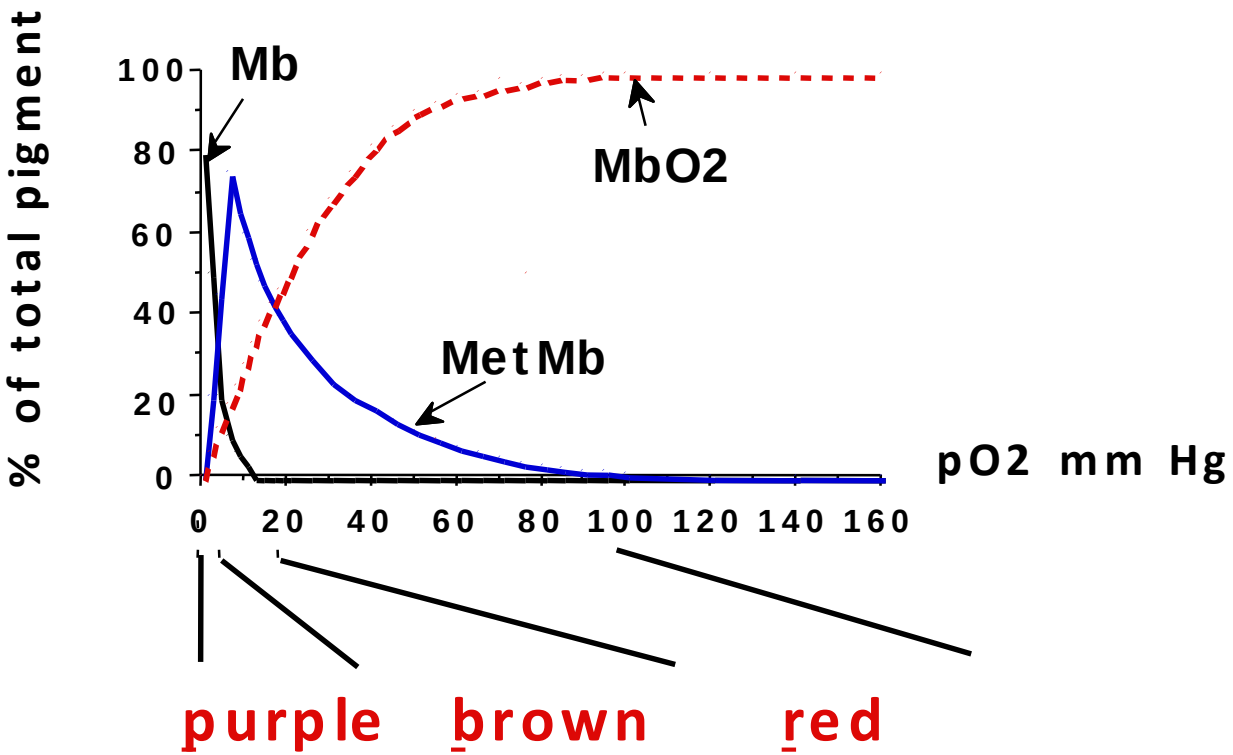
As noted earlier, the shelf lives calculated earlier will be longer than what would be achieved in practice because the pseudo-equilibrium moisture content m'_e used in the calculations is less than the actual equilibrium moisture content, which is the real driving force for water vapor transport. Because of the simplifying assumptions made in the earlier calculations, the calculated shelf lives should be verified by actual shelf life testing.

HOW TO ADAPT PACKAGING DESIGN
TO FOOD PRODUCT SPECIFICATIONS ?

FOOD PRODUCT DESIGN

PERMEATION ISSUES



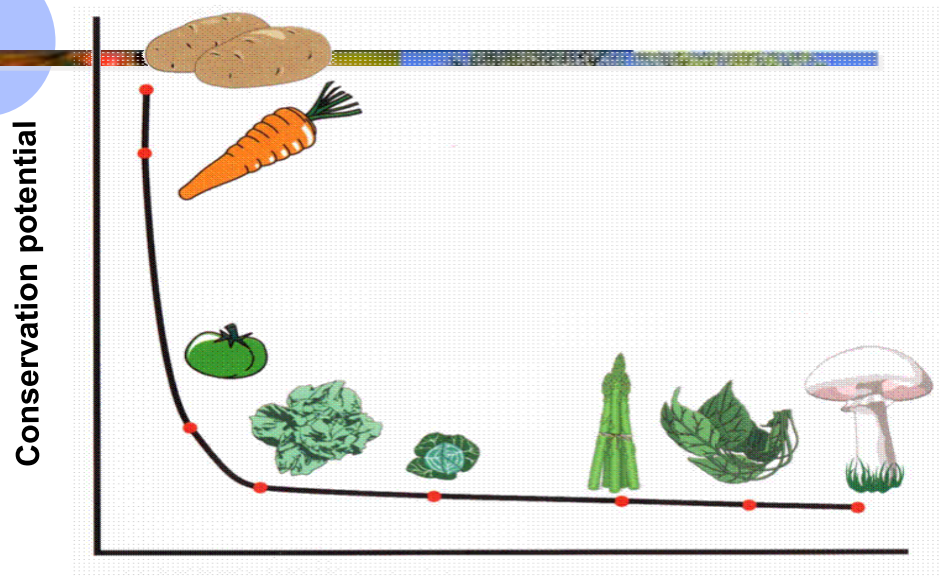


(Ledward, 1970)

Schaeffer (1992)

A COMPLEX CONTROL OF GAS COMPOSITION

ALIVE PRODUCTS



Growth of microorganisms

Respiratory catabolism

CO_2

O_2

H_2O

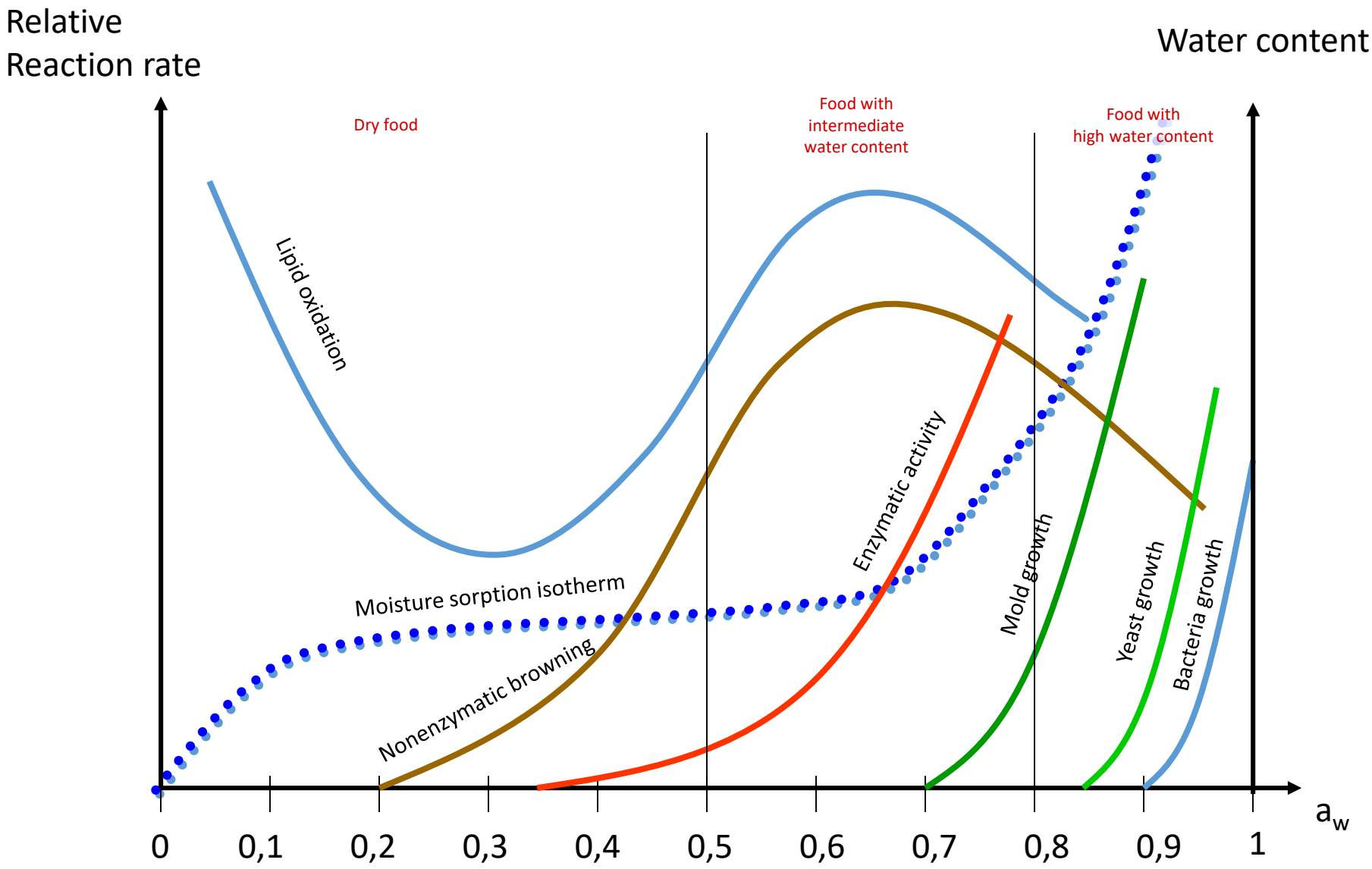
Transpiration

C_2H_4

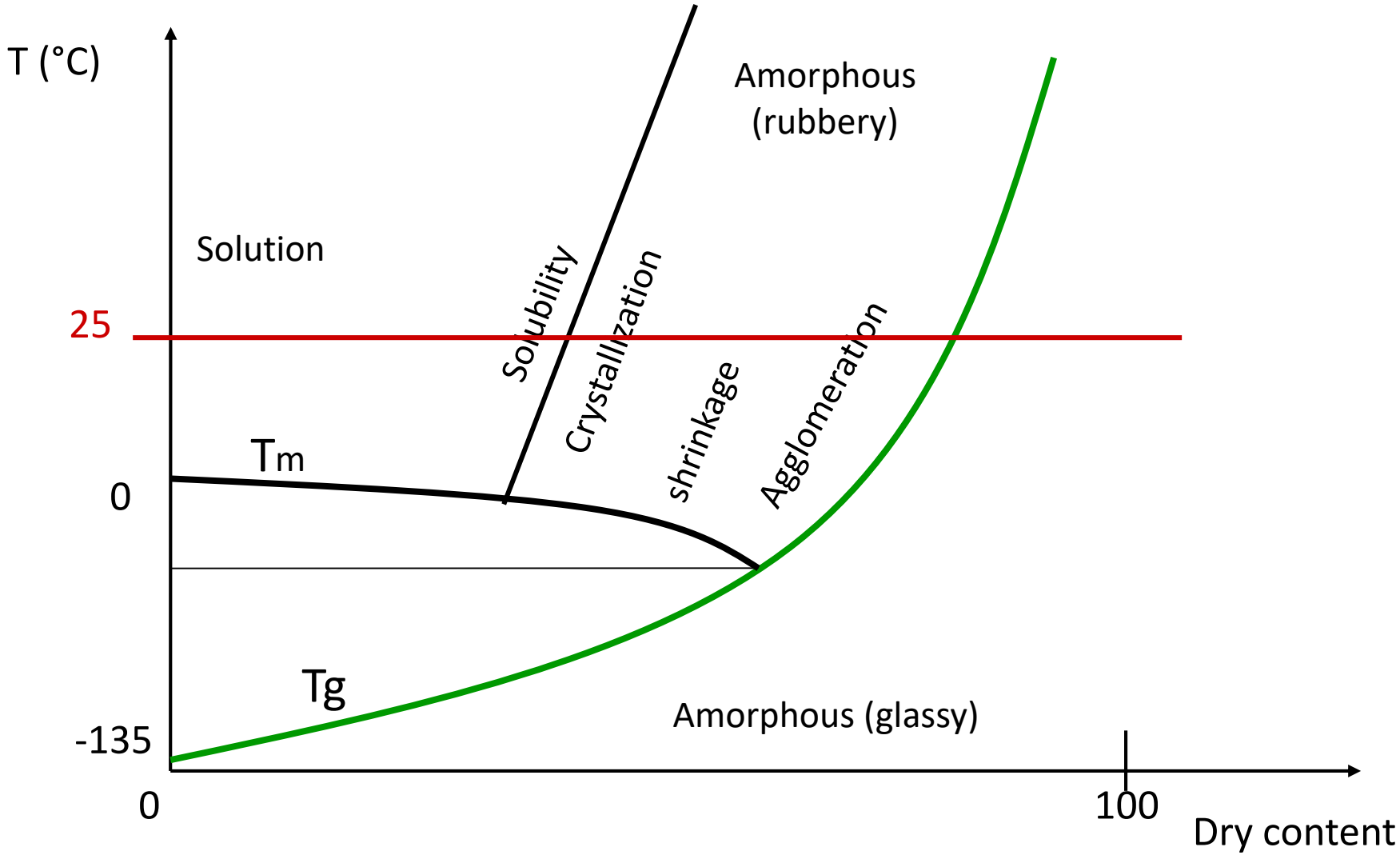
Temperature

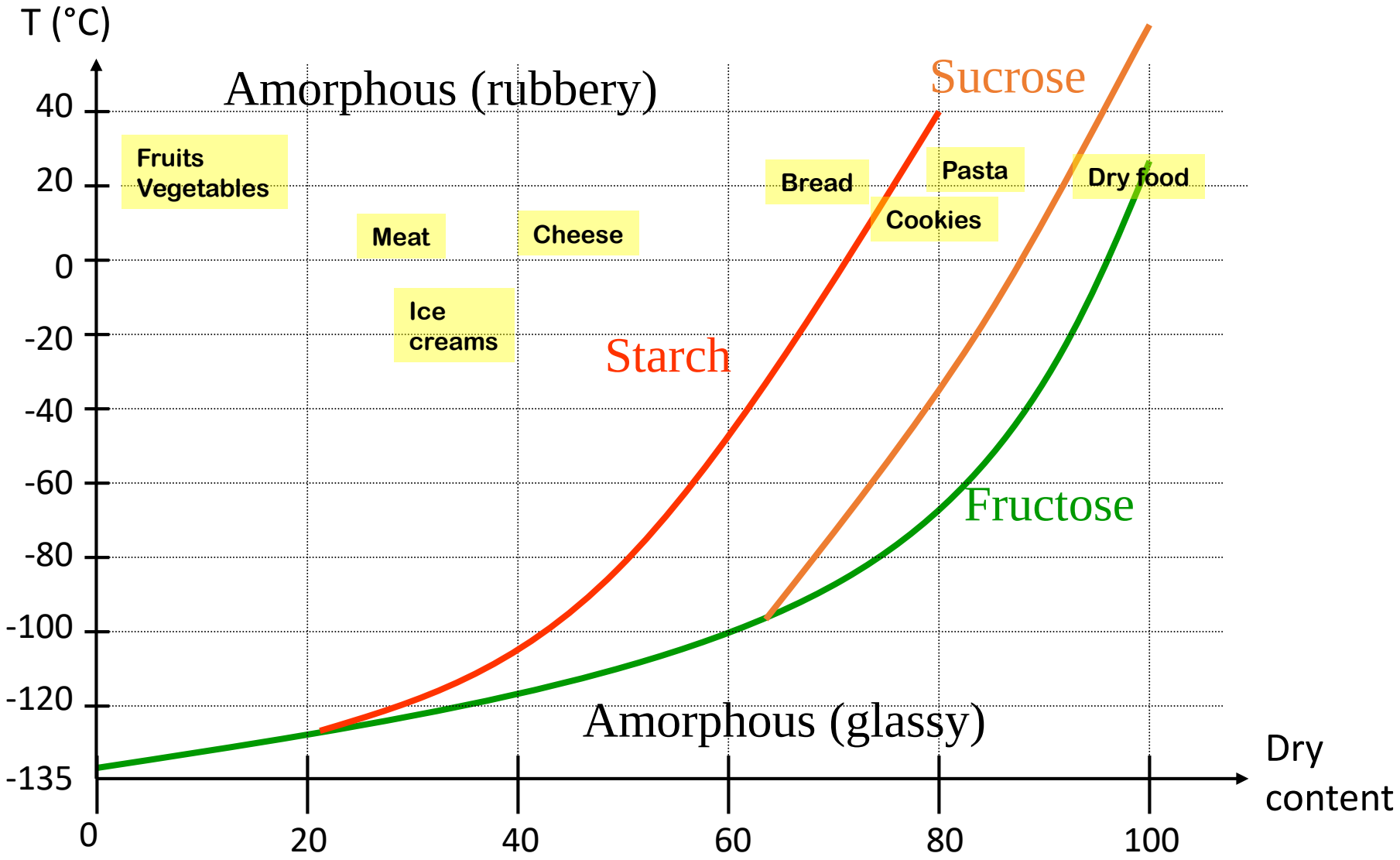
Gaseous atmosphere

RH

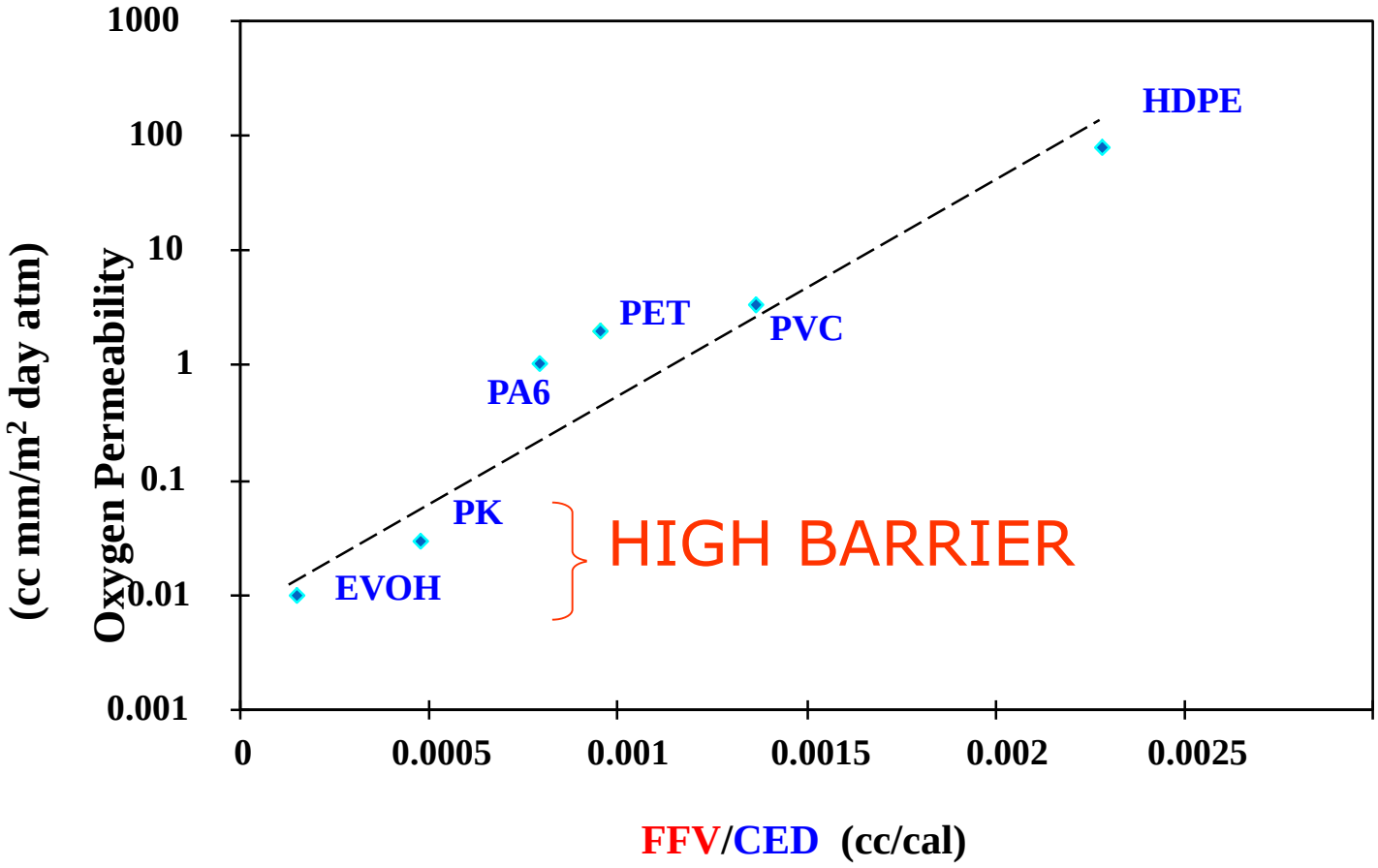


Global Food Stability Map (adapted from Labuza et al., 1969)


T (°C)
Amorphous
(rubbery)
Solution
Solubility
Crystallization
shrinkage
Agglomeration
25
Tm
0
Tg
-135
Amorphous (glassy)
0
100
Dry content


T (°C)
40
20
0
-20
-40
-60
-80
-100
-120
-135
Amorphous (rubbery)
Sucrose
Fruits
Vegetables
Meat
Cheese
Bread
Pasta
Dry food
Cookies
Ice
creams
Starch
Fructose
Amorphous (glassy)
Dry
content
0
20
40
60
80
100

HIGH BARRIER: FFV/CED



High Barrier Requires:

- ↓ **FFV : Fractional Free Volume**
- ↑ **CED : Cohesive Energy Density**

SELECTIVITY

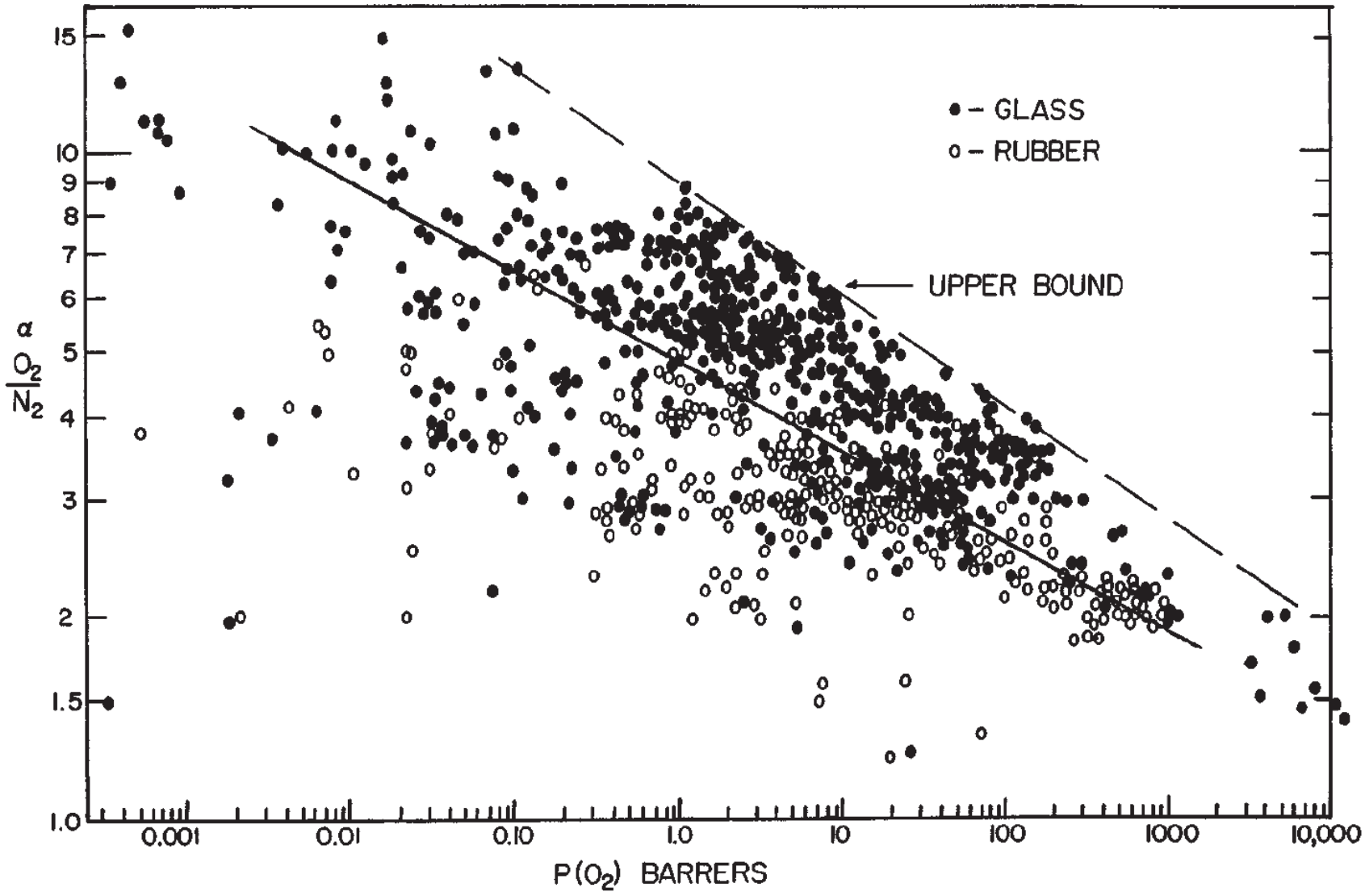
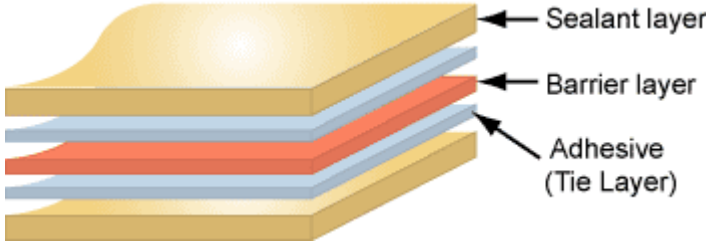


FIG. 22-73 Plot of separation factor versus permeability for many polymers, O_2/N_2. Abscissa—"Fast Gas Permeability, $\rho(O_2)$ Barrers." Ordinate—"Selectivity, α (O_2/N_2)."

Perry's Handbook

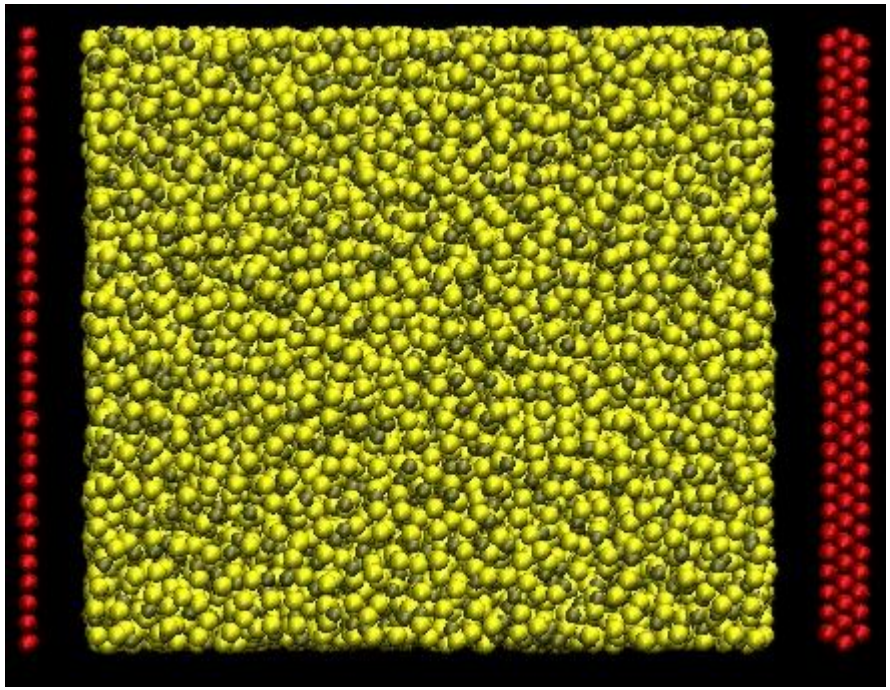
It is well known that traditional polymers are permeable to gazes such as oxygen, CO_2, vapor This property can become critical for food conservation or storage of gaseous beverages. This is the reason why, in most of the cases, multilayers structures are used. They are composed of a core barrier material and inert outerlayers like polyolefin. Typical Barrier materials are highly crystalline like EVOH, Polyamide, polyester. Aluminium foil or Carton can also be used (example Tetrapak).

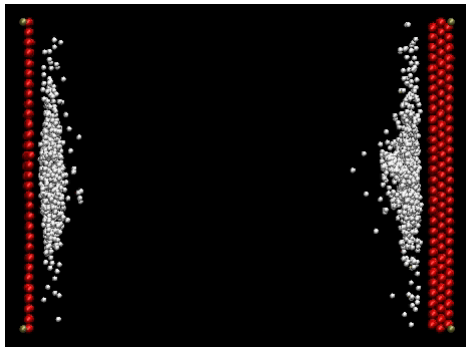


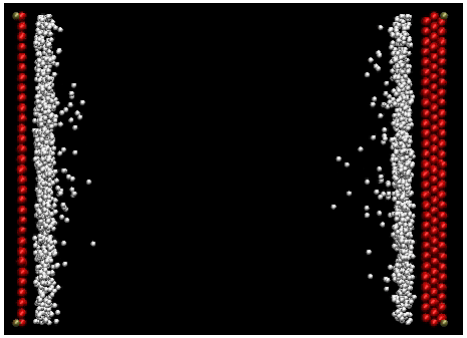
MATERIALS	Applications	Recyclability
PA/PE	Applications: ham, meat cheese, pasta... PA provides oxygen barrier and outer abrasion resistance whereas PE provides sealability and flexibility.	blends require to be compatibilized
PA/EVOH/PE	PA6 provides mechanical strength and abrasion resistance, EVOH provides oxygen barrier, PE provides sealability and protects EVOH against moisture.	

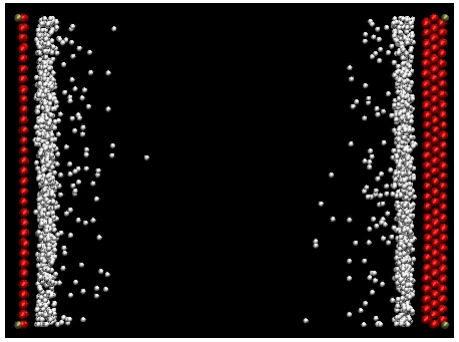
SORPTION AND DIFFUSION OF HE

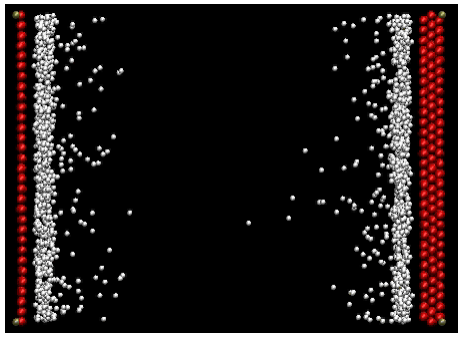
IN ENTANGLED POLYMERS



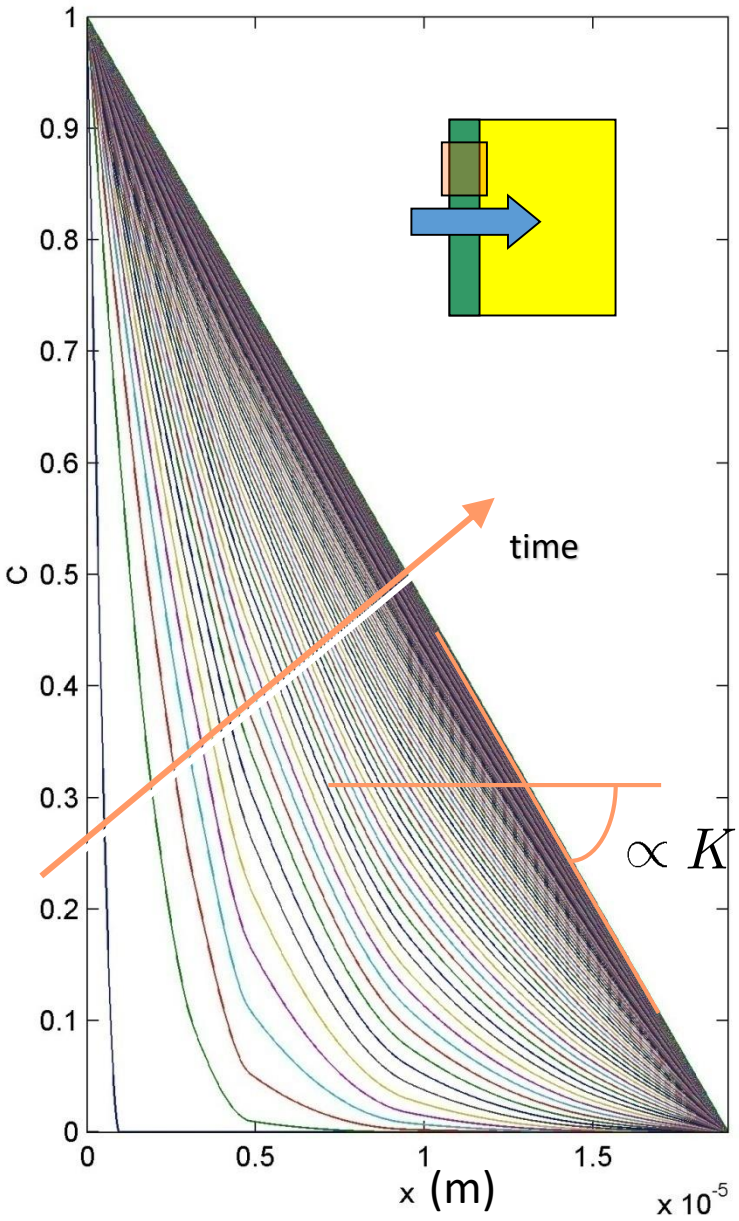


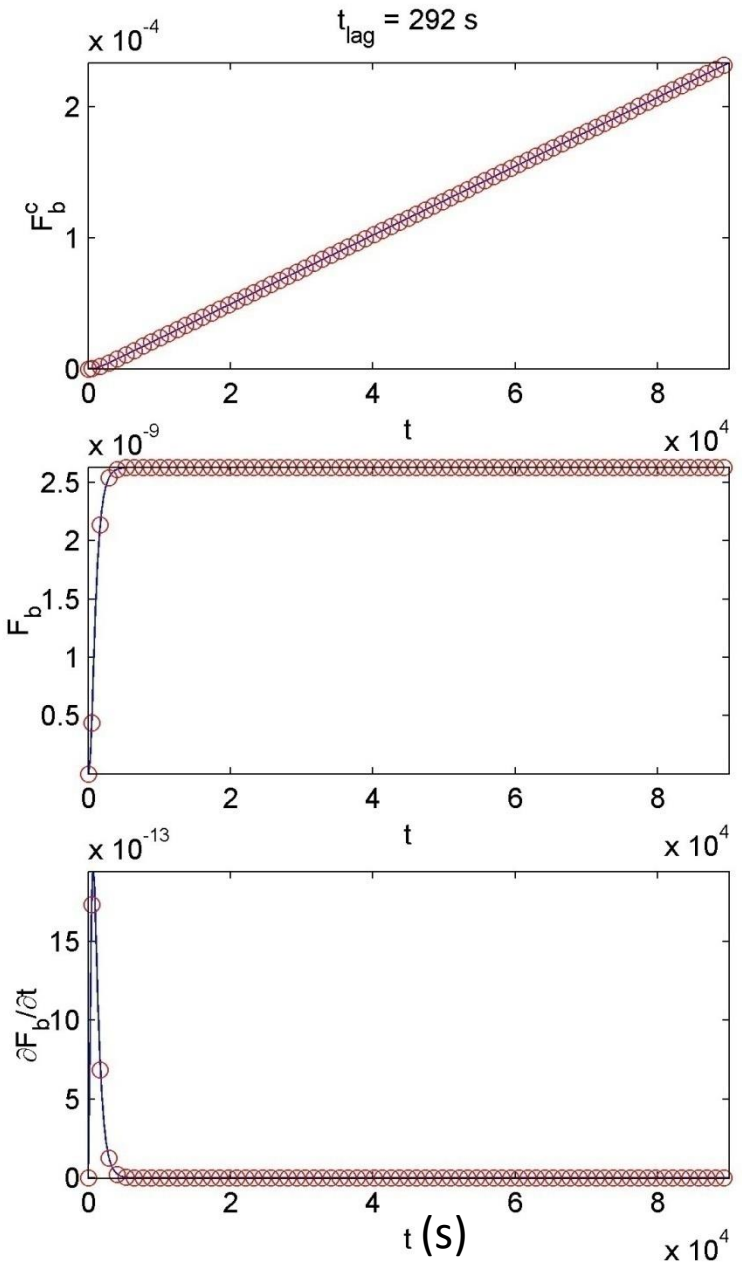




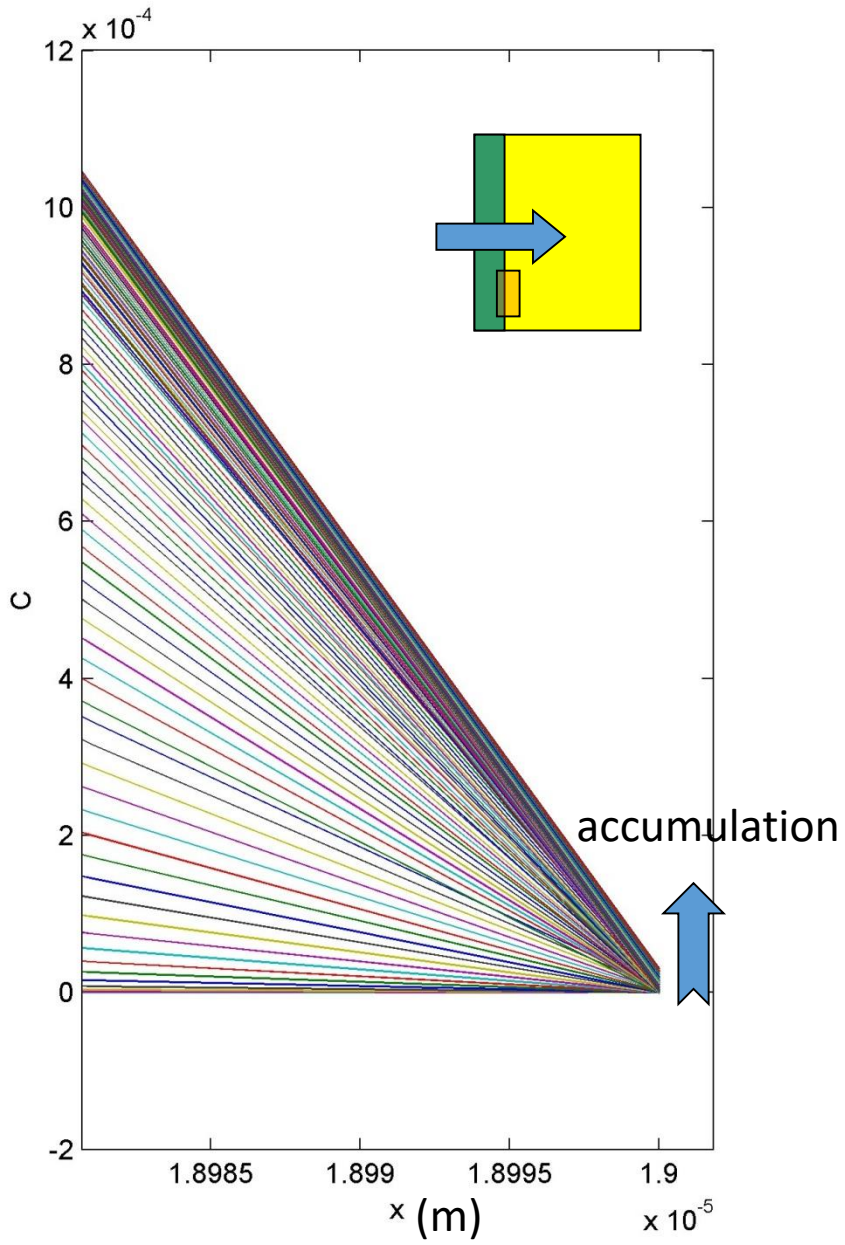


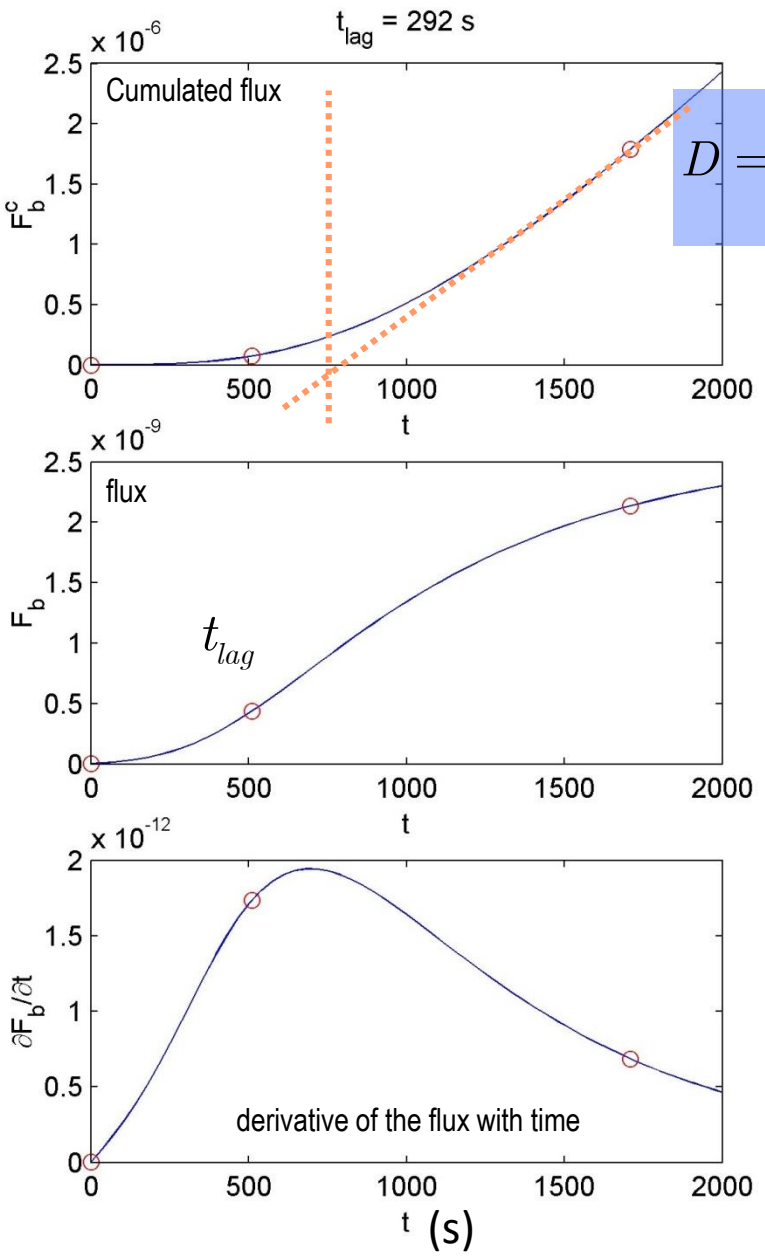
PERMEATION


C
x (m)
x 10^-5
time
∝ K


t_lag = 292 s
x 10^-4
F_b^c
t
x 10^-9
x 10^4
F_b
t
x 10^-13
x 10^4
∂F_b/∂t
t (s)
x 10^4

PERMEATION

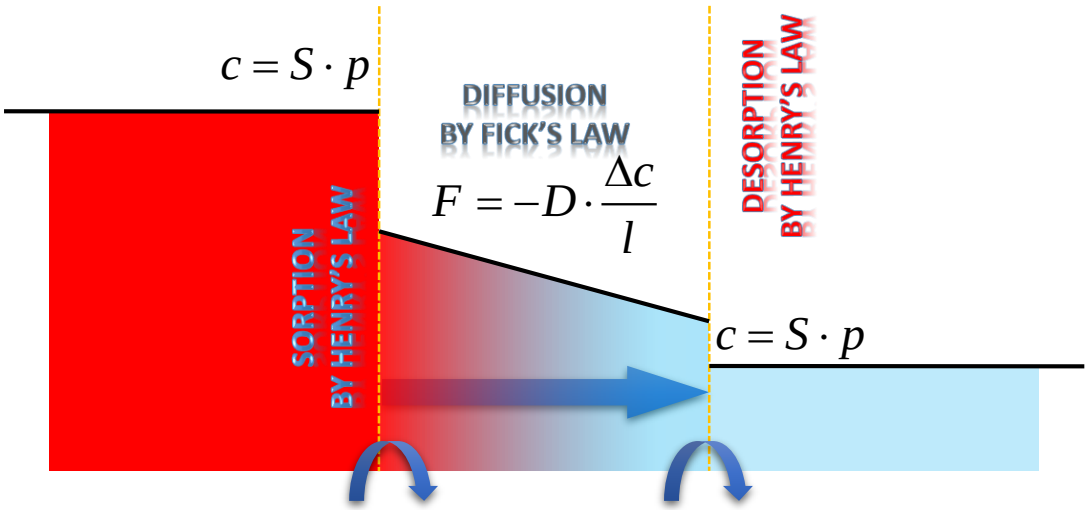




$$D = \frac{l^2}{6 \cdot t_{lag}}$$

PERMEABILITY

gas	M ($g \cdot mol^{-1}$)	velocity @0°C ($m \cdot s^{-1}$)	velocity @15°C ($m \cdot s^{-1}$)	velocity @25°V ($m \cdot s^{-1}$)
O_2	32	425	436	444
N_2	28	454	467	475
He	4	1202	1256	1256.2
CO_2	44	363	372	379
H2O	18	567	582	592
Ait	28.8	448	460	461



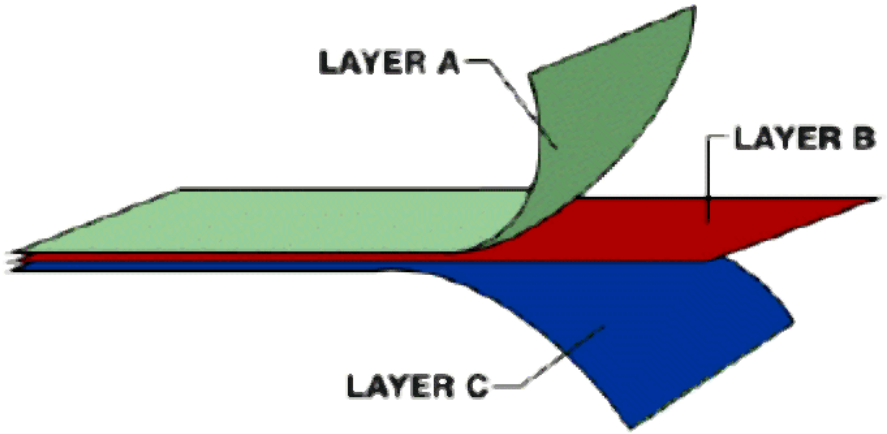
$$F = -D \cdot S \cdot \frac{\Delta p}{l} = \frac{q}{A \cdot t}$$

$$P = D \cdot S \sim \left[\frac{L^2}{\theta}\right] \cdot \left[\frac{\theta^2}{L^2}\right] \sim [\theta] \text{ s in SI}$$

Units of permeability, permeance, and Gas Transmission Rate

		Common Units	SI	Fundamental dimension	
Amount of mass	q	g, cm^3(STP), mol	kg	M	Mass
Thickness	l	cm/ mil	m	L	Length
Time	t	h, d	s	θ	Time
Area	A	cm^2, in^2	m^2	L^2	Length
Partial pressure	p	atm, psi, mmHg	Pa	F/L^2	Force/length

$$P_T = \frac{L_T}{\Re_T} = \frac{\sum_{i=1}^{n} l_i}{\sum_{i=1}^{n} \Re_i} = \frac{\sum_{i=1}^{n} l_i}{\sum_{i=1}^{n} \frac{l_i}{P_i}}$$



Polymer	Thickness (μm)	P_i at 25°C	Ep (kcal/mol)
LDPE	18	1.900	10.2
Nylon 6	10	25.0	10.5
PP	20	620	11.5

$$L_T = 18 + 10 + 20 = 48\ \mu m$$

$$\sum_{1}^{3} \frac{\ell_i}{P_i} = \frac{\ell_1}{P_1} + \frac{\ell_2}{P_2} + \frac{\ell_3}{P_3} = \frac{18}{1900} + \frac{20}{25} + \frac{20}{620} = 0.4417 \frac{m^2 \cdot d\ kPa}{cc}$$

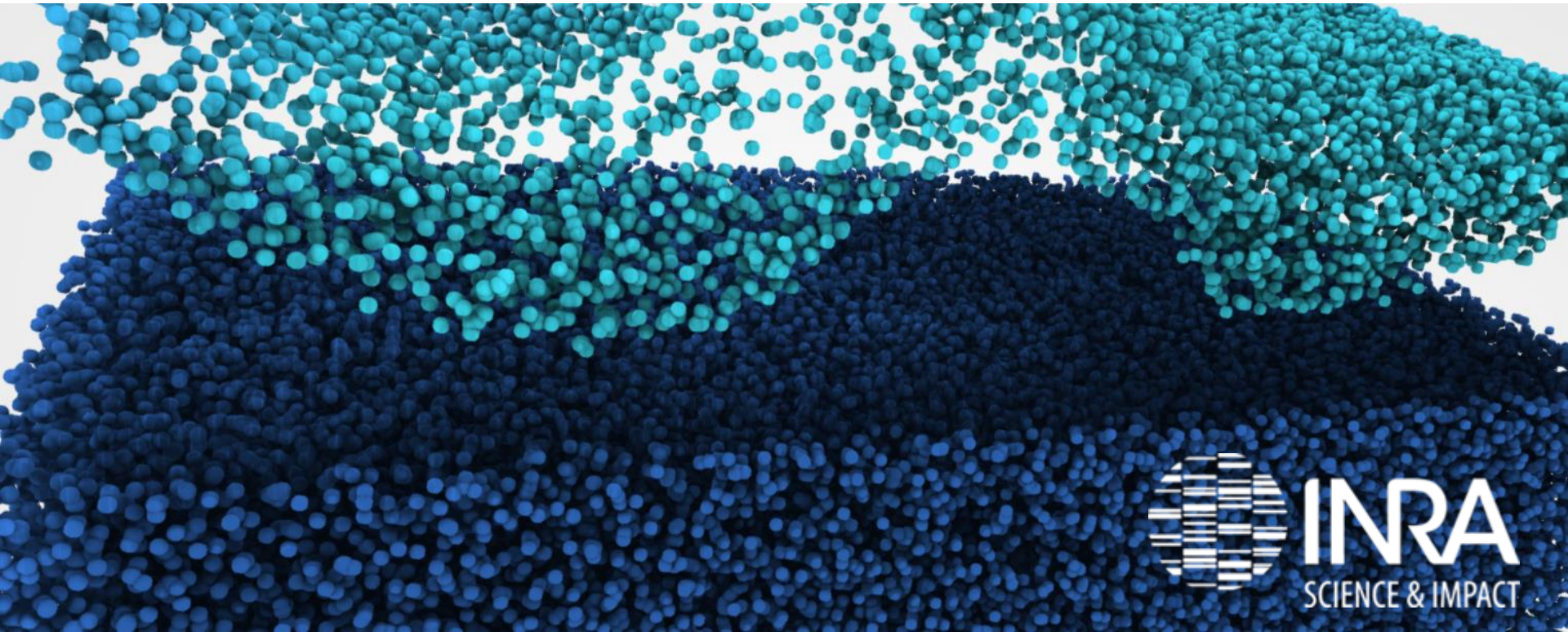
$$P_T = \frac{48}{0.4417} = 109 \frac{cc \cdot \mu m}{m^2 \cdot d \cdot kPa}$$

Permeability of some polymers at 25° C

Polymer	Permeant	10^{15} Permeability ($kg\ m^{-1}\ kPa^{-1}\ s^{-1}$)	10^{12} Diffusivity ($m^2\ s^{-1}$)	10^{3} Solubility ($kg\ m^{-3}\ kPa^{-1}$)
PA 6	Nitrogen	0.023	0.025	0.94
PETP	Nitrogen	0.063	0.13	0.48
PVC	Carbon dioxide	0.52	0.21	2.5
PIB	Nitrogen	3.1	4.5	0.69
	Carbon dioxide	77	5.8	13
CR	Nitrogen	11	25	0.44
	Carbon dioxide	300	24	16
NR	Nitrogen	76	110	0.69
	Carbon dioxide	1900	110	18
	n-Propane	2500	21	120
HDPE	Helium (30°C)	1.9	360	0.0055
	Oxygen (30°C)	5.4	22	0.25
	Nitrogen (30°C)	1.7	12	0.14
	Carbon dioxide	31	16	2.0
LDPE	Isobutene (30°C)	680	4.7	140
	n-Hexane (30°C)	6200	2.5	2500
	Water	540	23	24

ADDITIVES

THERMOPLASTICS, ELASTOMERS



FOOD APPLICATIONS

PLATICS ADDITIVES

Innovative Solutions for Packaging

NON FOOD APPLICATIONS

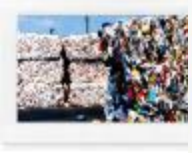


Table 16.13 Examples of Processing and Service Aids Used in Food-Packaging Materials

Technical function	Example	Use level, wt%, polymer
Antioxidant	Tetrakis[methylene (3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate)]methane	0.25 (Polystyrene)
	Tris(2,4-di- *tert*-butylphenyl) phosphite	0.2 (Polyolefins)
Stabilizer	Di(*n*-octyl)tin *S,S′*-bis(isooctylmercaptoacetate)	1.5 (PVC)
	Epoxidized soybean oil	6 (PVC)
	Stearoylbenzoylmethane	0.5 (PVC)
	Cuprous iodide	0.01 (Nylon 6,6)
Plasticizer	Di(2-ethylhexyl) phthalate	40 (PVC)
	Di(2-ethylhexyl) adipate	20 (PVC)
	Acetyltributyl citrate	5 (PVDC)
Lubricant	*N,N′*-Ethylenebisstearamide	1 (PVC)
	Pentaerythritol adipate-stearate	1 (PVC)
Processing agent	Styrene/butadiene/methacrylate copolymer	2 (PVC)
Melt fracture eliminator	Vinylidene fluoride-hexafluoropropylene copolymer	0.1 (Polyethylene)
Slip agent	Fatty acid amides (erucamide, oleamide)	0.2 (Polyolefins)
Antistatic agent	*N,N′*-Bis (2-hydroxyethyl)alkyl-$C_{14–18}$-amine	0.15 (Polyolefins)
Blowing agent	Azodicarbonamide	0.15 (Polyethylene)
Antiblock agent	Silica, talc	0.2 (Polyethylene)
Impact modifier	Butadiene/styrene/methacrylate copolymers	10 (PVC)
Clarifying agent	Dibenzylidene sorbitol	0.25 (Polyolefins)
Light stabilizer	2-Hydroxy-4-*n*-octoxybenzophenone	0.5 (Polyolefins)
	Dimethylsuccinate-(4-hydroxy-2,2,6,6-tetra-methyl-1-piperidyl)-ethanol polycondensate	0.25 (Polyolefins)
Coupling agent	3-(triethoxylsilyl)propylamine	0.5 (Nylon 6,6)
Filler, extender	Calcium carbonate, clay, talc	>5 (Various polymers)
Reinforcing agents	Glass, fiber, mica, calcium silicate	>5 (Various polymers)
Colorant	Titanium dioxide, ferric oxide, carbon black, ultramarine blue, phthalocyanine blue	0.1–5 (Various polymers)

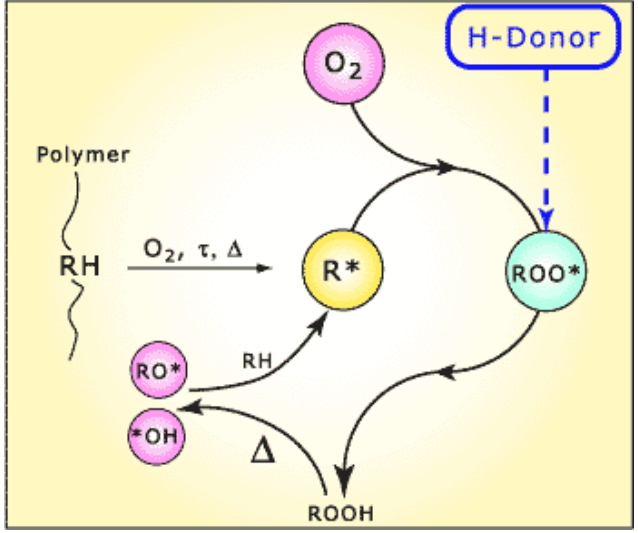
Source: Compiled from FDA (1987) and British Plastics Federation (1980).

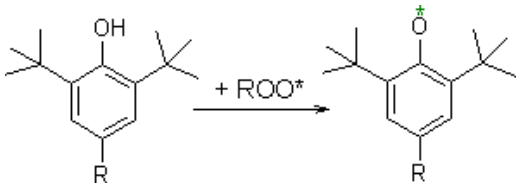
COMMON ADDITIVES AND CONCENTRATION RANGES IN INITIAL MATERIALS

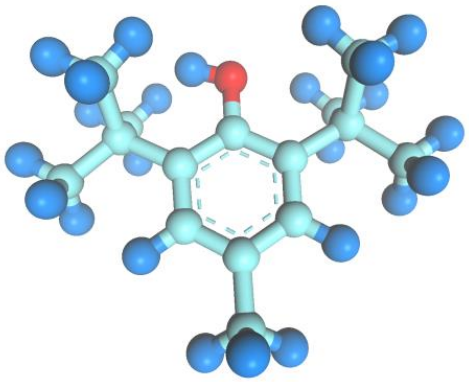
	PE	PP	PS	PVC	PET	PVA	PC	Epoxy	PA
Antioxidant	B	B	B	x					B
Heat stabilizer				B/C		B			
UV stabilizer	B/C	B/C	C	C				C	
Antistatic agent	X	X	X	x	x	x	x		x
Shock agent	x	X	X	x	x	x	x		
Initiator			D	D		D			
Catalyst	D	D			D		D		D
Lubricant	X	X	X	x	x			x	
Plasticizer	A		A	A		A			
Charges	A	A	A	A	A	A	A	A	A

A >10 000 $mg \cdot kg^{-1}$ – B = 100-5000 $mg \cdot kg^{-1}$ – C = 100-500 $mg \cdot kg^{-1}$
D = 1-100 $mg \cdot kg^{-1}$ – E < 1 $mg \cdot kg^{-1}$, x ou X variable amounts (with x>X),

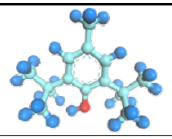
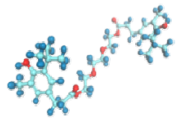
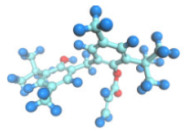
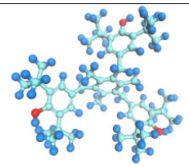
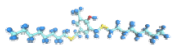
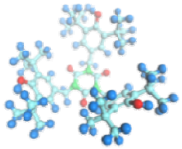
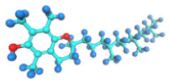
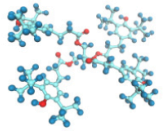
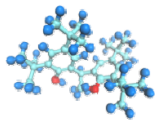
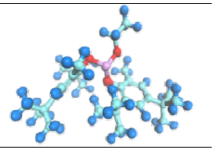
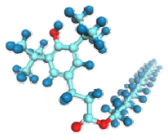
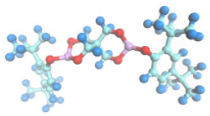
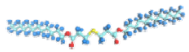
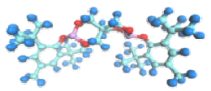
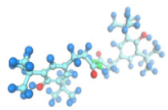
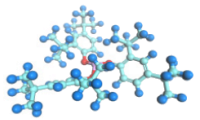
ANTIOXIDANTS



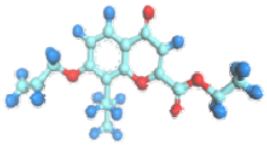
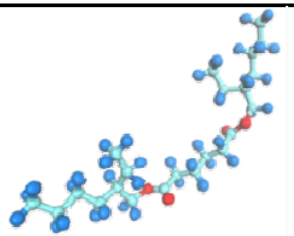
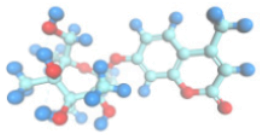
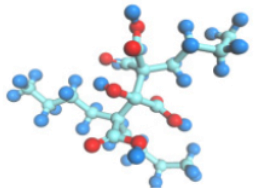
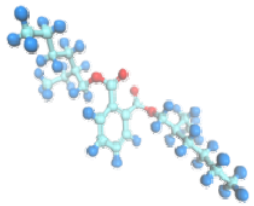


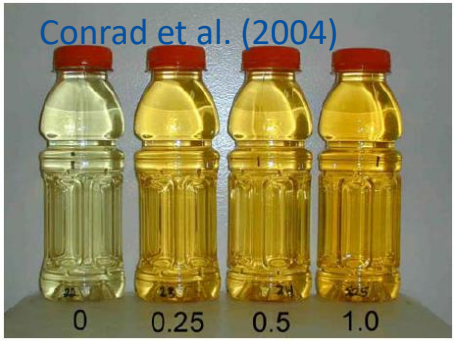


The 2,6-ditert-butyl-4-hydroxytoluene (BHT, B121) is the simplest phenolic antioxidant. It yields a stable phenoxy radical i) by mesomery, ii) steric effect due to large tert-butyl, and iii) captodative effect.

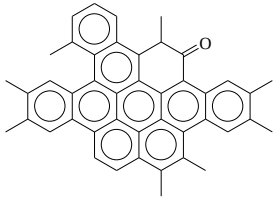
nom	*CAS Formule M (g·mol^{-1})*	*Structure 3D*	*nom*	*CAS Formule M (g·mol^{-1})*	*Structure 3D*
2,6-Di(tert-butyl)hydroxytoluène (BHT)	128-37-0 C15 H24 O 220.35		Acide 3-(1,1-diméthyléthyl)-4-hydroxy-5-méthyl-Benzènepropanoïque (Irganox 245)	36443-68-2 C34 H50 O8 586.76	
Monoacrylate de 2,2'-Méthylenebis(4-méthyl-6-tert-butylphénol) Irganox (3052)	61167-58-6 C26 H34 O3 394.55		4,4',4''-[(2,4,6-triméthyl-1,3,5-benzènetriyl)tris(méthylène)]tris[2,6-bis(1,1-diméthyléthyl)-phénol (Irganox 1330)	1709-70-2 C54 H78 O3 775.20	
2-méthyl-4,6-bis[(octylthio)méthyl]-phénol (Irganox 1520)	110553-27-0 C25 H44 O S2 424.75		Isocyanurate de s-Triazine-2,4,6(1H,3H,5H)-trione, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-(8CI); 1,3,5-Tri(3,5-di-tert-butyl-4-hydroxybenzyle) (Irganox 3114)	27676-62-6 C48 H69 N3 O6 784.08	
3,4-dihydro-2,5,7,8-tetraméthyl-2-(4,8,12-triméthyltridecyl)- 2H-1-Benzopyran-6-ol (Irganox 231)	59-02-9 C29 H50 O2 430.71		Benzène propanoate de 3,5-bis(1,1-diméthyléthyl)-4-hydroxy-, 1,1'-[2,2-bis[[3-[3,5-bis(1,1-diméthyléthyl)-4-hydroxyphényl]-1-oxopropoxy]méthyl]-1,3-propanediyle] (Irganox 1010)	6683-19-8 C73 H108 O12 1177.63	
1,1-Bis(3,5-di-tert-butyl-2-hydroxyphényl)éthane (Isonox 129)	35958-30-6 C30 H46 O2 438.68		bis[2,4-bis(1,1-diméthyléthyl)-6-méthylphényl] éthyl ester (Irgafos 38)	145650-60-8 C32 H51 O3 P 514.72	
2,6-Di-tert-butyl-4-(octadécanoxycarbonyléthyl)phénol (Irganox 1076)	2082-79-3 C35 H62 O3 530.86		2,4,8,10-Tetraoxa-3,9-diphosphaspiro[5.5]undécane, 3,9-bis[2,4-bis(1,1-diméthyléthyl)phénoxy]- (Ultranox 626,640)	26741-53-7 C33 H50 O6 P2 604.69	
Propionate de 3, 3'-thiobis-, didodécyle (Irganox 800)	123-28-4 C30 H58 O4 S 544		Diphosphite de Bis(2,6-di-tert-butyl-4-méthylphényl)pentaérythritol (Mark PEP 36)	80693-00-1 C35 H54 O6 P2 632.75	
3,5-bis-(1, 1-diméthyléthyl)-4-hydroxynenzène propionate d'hydrazine (Irganox 1024)	32687-78-8 C34 H52 N2 O4 552.79		1,1',1''- Phosphite de 2,4-bis(1,1-diméthyléthyl)-Phénol (Irgafos 168)	31570-04-4 C42 H63 O3 P 646.92	

PLASTICIZERS

nom	CAS Formule M (g·mol^{-1})	Structure 3D	nom	CAS Formule M (g·mol^{-1})	Structure 3D
Acide 4*H*-1-Benzopyran-2-carboxylique	248595-13-3 C18 H20 O5 316.35		Adipate de Di(2-éthylhexyle (DEHA)	103-23-1 C22H42O4 370.57	
4-Methylumbelliferyl-beta-D-galactopyranoside	6160-78-7 C16H18O8 338.31		Citrate de tributyl-acétyle	77-90-7 C20 H34 O8 402.88	
2-diéthylhexyl)phtalate (DEHP)	117-81-7 C24H38O4 390.56				

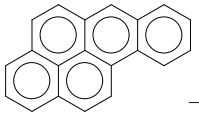


test containers with red drink after three days of UV exposure.



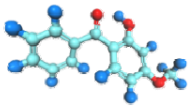
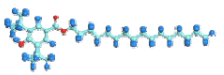
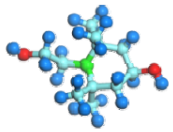
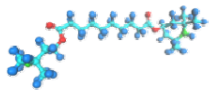
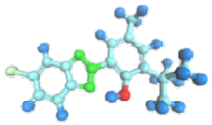
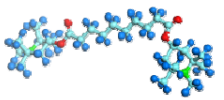
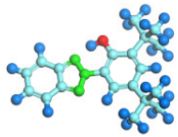
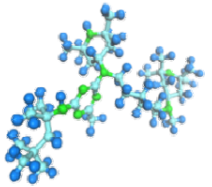
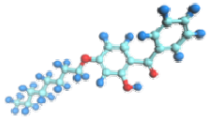
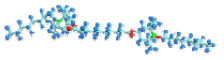
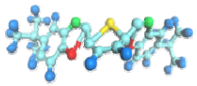
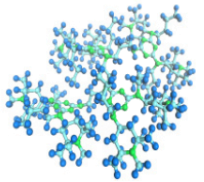
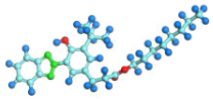
Carbon black PM 42080

Benzo[a]pyrene, carcinogenic impurity (< 0,25 mg/kg C)

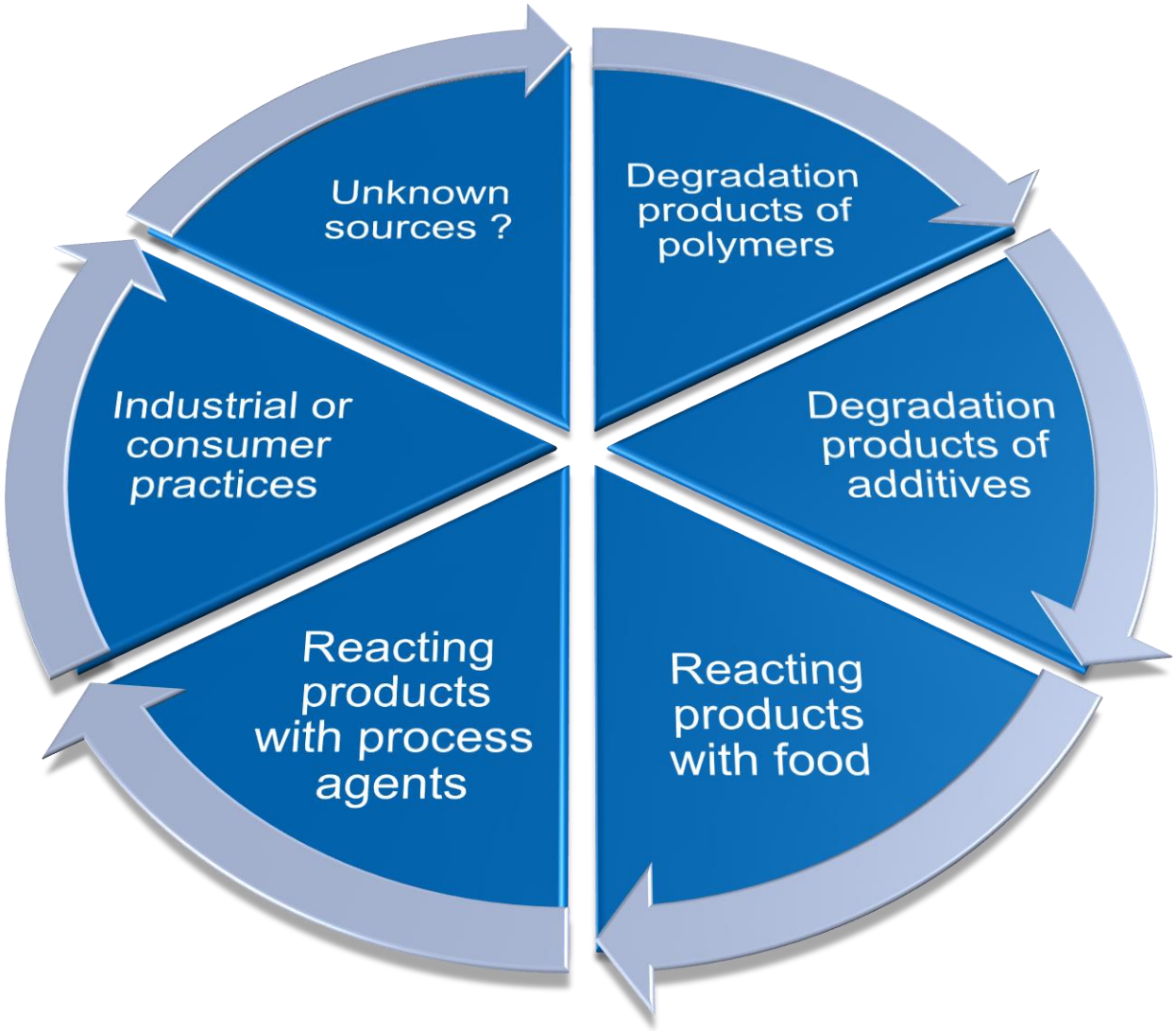


specifications for the HAP

ANTIUV

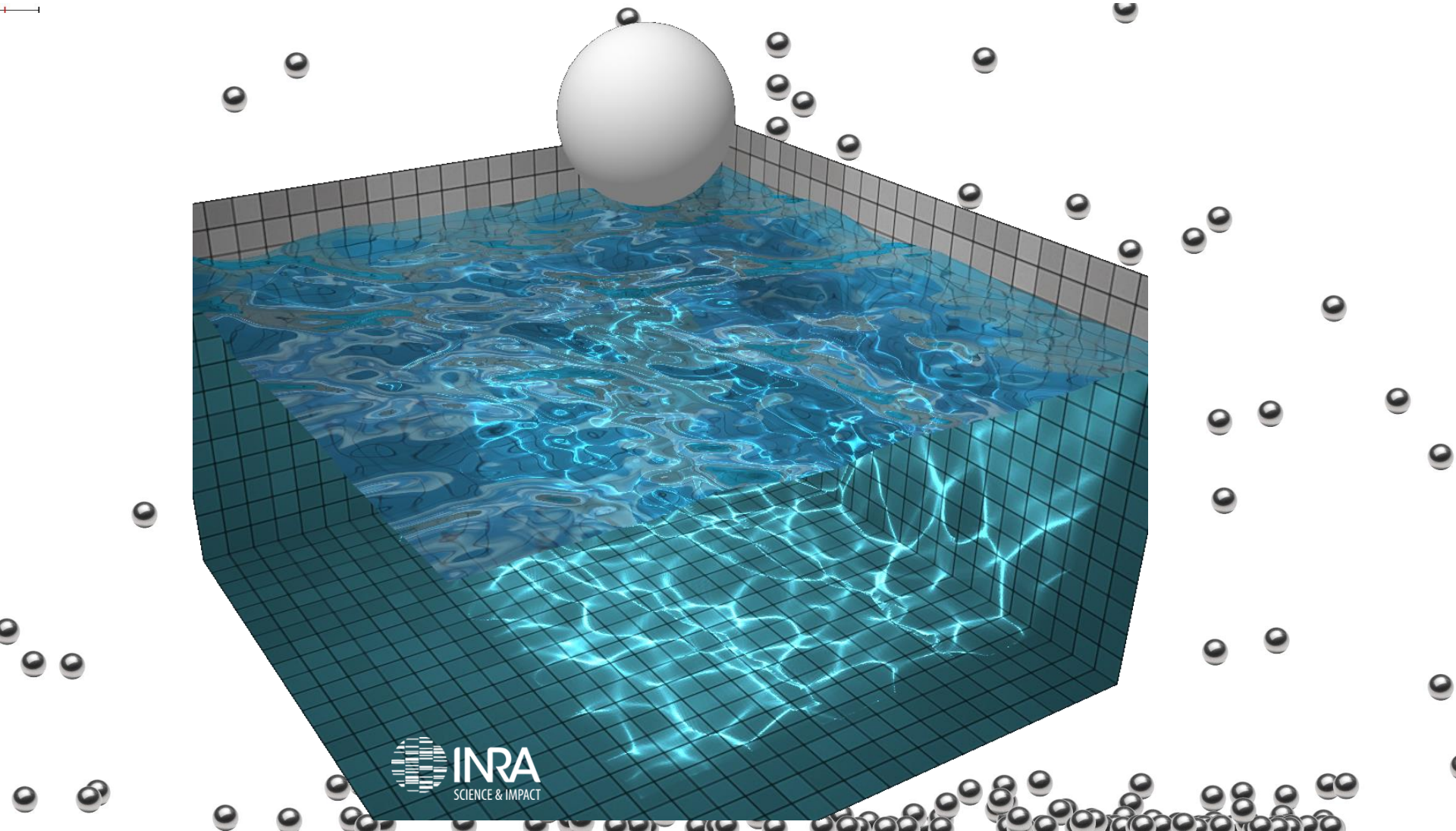
nom	*CAS Formule M ($g \cdot mol^{-1}$)*	*Structure 3D*	*nom*	*CAS Formule M ($g \cdot mol^{-1}$)*	*Structure 3D*
2-Hydroxy-4-methoxybenzophénone (Chimassorb 90)	131-57-7 C14 H12 O3 228.24		Acide 3,5-bis(1,1-diméthyléthyl)-4-hydroxy-benzoïque (Cyasorb 2908)	67845-93-6 C31 H54 O3 474.76	
1-(2-Hydroxyéthyl)-2,2,6,6-tetraméthyl-4-hydroxypiperidine (Tinuvin 622)	52722-86-8 C11 H23 N O2 201.31		Décanoate de 1,10-bis(2,2,6,6-tetraméthyl-4-pipéridinyle) (Tinuvin 770)	52829-07-9 C28 H52 N2 O4 480.72	
2-(5-chloro-2H-benzotriazol-2-yl)-6-(1,1-diméthyléthyl)-4-méthyl-Phénol (Tinuvin 326)	3896-11-5 C17 H18 Cl N3 O 315.80		Didécanoate de 1,10-bis(1,2,2,6,6-pentaméthyl-4-piperidinyle) (Tinuvin 292)	41556-26-7 C30 H56 N2 O4 508.78	
2-(2H-benzotriazol-2-yl)-4,6-bis(1,1-diméthyléthyl)-Phénol (Tinuvin 320)	3846-71-7 C20 H25 N3 O 323.43		Poly[[6-[(1,1,3,3-tetraméthylbutyl)amino]-1,3,5-triazine-2,4-diyl][(2,2,6,6-tetraméthyl-4-piperidinyl)imino]-1,6-hexanediyl[(2,2,6,6-tetraméthyl-4-piperidinyl)imino]] (Chimassorb 944)	71878-19-8 (C35 H66 N8)n n·598.96	
2-hydroxy-4-(octyloxy)-(6CI,8CI); 2-Benzoyl-5-octyloxyphénol benzophénone (Chimassorb 81)	1843-05-6 C21 H26 O3 326.43		Didécanoate de 1,10-bis[2,2,6,6-tetraméthyl-1-(octyloxy)-4-piperidinyle] (Tinuvin 123)	122586-52-1 C44 H84 N2 O6 737.15	
2,2'-(2,5-thiophénediyl)bis[5-(1,1-diméthyléthyl)-Benzoxazole (Uvitex OB55)	7128-64-5 C26 H26 N2 O2 S 430.56		N2,N2'-1,2-ethanediylbis[N2-[3-[[4,6-bis[butyl(1,2,2,6,6-pentaméthyl-4-piperidinyl)amino]-1,3,5-triazin-2-yl]amino]propyl]-N4,N6-dibutyl-N4,N6-bis(1,2,2,6,6-pentaméthyl-4-piperidinyl)-1,3,5-Triazine-2,4,6-triamine (Chimassorb 119)	106990-43-6 C132 H250 N32 2285.61	
2-(3'-tert-Butyl-2'-hydroxy-5'-(2-octyloxycarbonyléthyl)phényl)benzotriazole (Tinuvin 99)	84268-23-5 C27 H37 N3 O3 451.60				

NON INTENTIONALLY ADDED SUBSTANCES



MIGRATION ISSUES

PAST CRISES, DIFFUSION-SOLUBILIZATION, REGULATION




INRA
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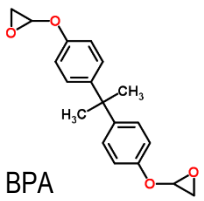
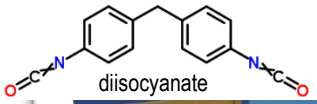
SAFEMAT
MATÉRIAUX AU CONTACT
DES ALIMENTS


BPA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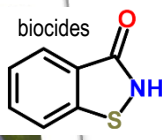
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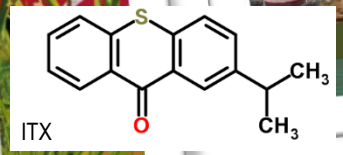
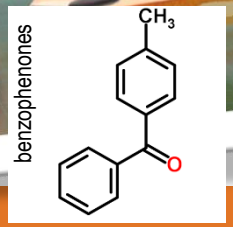
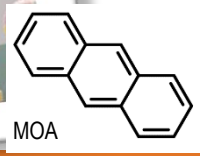

ITX


benzophenones


MOA


Is it safe?
How to assess it?
How to grant it?
OPEN
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RAPID ALERT SYSTEM FOR FOOD & FEED

http://ec.europa.eu/food/food/rapidalert/index_en.htm

RASFF
Rapid Alert System for Food and Feed

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European Commission

HEALTH AND CONSUMERS
Food

EUROPA > European Commission > DG Health and Consumers > Overview > Food and Feed Safety

General Food Law | Animal Nutrition | Labelling & Nutrition | Biotechnology | Novel Food | Chemical Safety | Biological Safety | Official controls | Food waste | Food improvement agents

Rapid Alert System for Food and Feed (RASFF) - Introduction

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Publications

Rapid Alert System for Food and Feed

What's New?

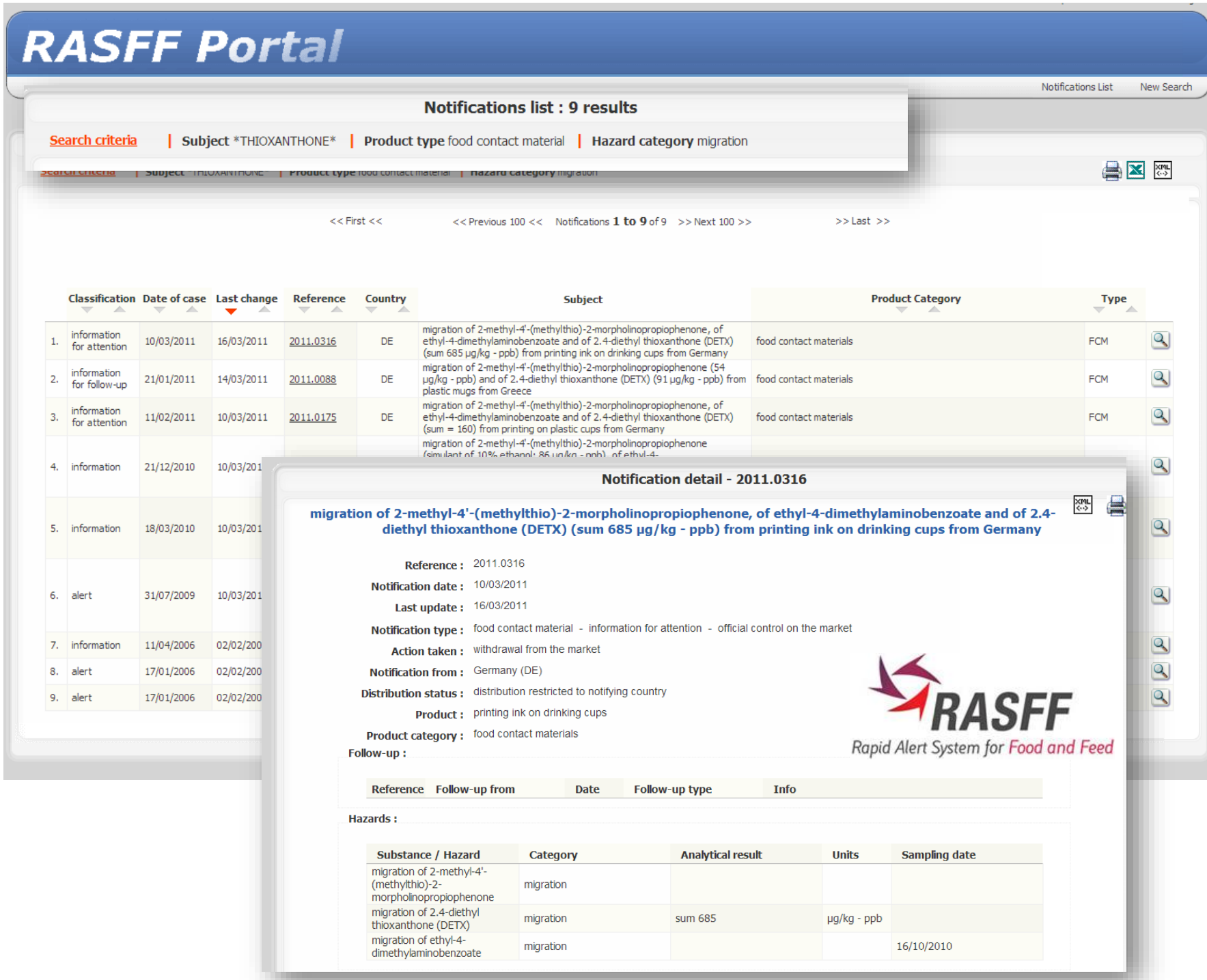
Rapid Alert System for Food and Feed (RA
Press release on 2012 RASFF annual rep
Questions and answers on 2012 RASFF a

Welcome to the RASFF porta

The Rapid Alert System for Food and Feed (RA
exchange information about measures take
information helps Member States to act mor
feed.

Read more about the legal basis of RASF
Who are the members of RASFF?
RASFF - Keeping an eye on your food -

The effectiveness of RASFF is ensured by kee
Commission, EFSA, EFTA surveillance authorit
structured way by means of templates.



RASFF Portal

Notifications List New Search

Notifications list : 9 results

Search criteria | Subject *THIOXANTHONE* | Product type food contact material | Hazard category migration

<< First << << Previous 100 << Notifications 1 to 9 of 9 >> Next 100 >> >> Last >>

	Classification	Date of case	Last change	Reference	Country	Subject	Product Category	Type
1.	information for attention	10/03/2011	16/03/2011	2011.0316	DE	migration of 2-methyl-4'-(methylthio)-2-morpholinopropiophenone, of ethyl-4-dimethylaminobenzoate and of 2.4-diethyl thioxanthone (DETX) (sum 685 µg/kg - ppb) from printing ink on drinking cups from Germany	food contact materials	FCM
2.	information for follow-up	21/01/2011	14/03/2011	2011.0088	DE	migration of 2-methyl-4'-(methylthio)-2-morpholinopropiophenone (54 µg/kg - ppb) and of 2.4-diethyl thioxanthone (DETX) (91 µg/kg - ppb) from plastic mugs from Greece	food contact materials	FCM
3.	information for attention	11/02/2011	10/03/2011	2011.0175	DE	migration of 2-methyl-4'-(methylthio)-2-morpholinopropiophenone, of ethyl-4-dimethylaminobenzoate and of 2.4-diethyl thioxanthone (DETX) (sum = 160) from printing on plastic cups from Germany	food contact materials	FCM
4.	information	21/12/2010	10/03/201			migration of 2-methyl-4'-(methylthio)-2-morpholinopropiophenone (simulant of 10% ethanol: 86 µg/kg - ppb), of ethyl-4-		
5.	information	18/03/2010	10/03/201					
6.	alert	31/07/2009	10/03/201					
7.	information	11/04/2006	02/02/200					
8.	alert	17/01/2006	02/02/200					
9.	alert	17/01/2006	02/02/200					

Notification detail - 2011.0316

migration of 2-methyl-4'-(methylthio)-2-morpholinopropiophenone, of ethyl-4-dimethylaminobenzoate and of 2.4-diethyl thioxanthone (DETX) (sum 685 µg/kg - ppb) from printing ink on drinking cups from Germany

Reference : 2011.0316
Notification date : 10/03/2011
Last update : 16/03/2011
Notification type : food contact material - information for attention - official control on the market
Action taken : withdrawal from the market
Notification from : Germany (DE)
Distribution status : distribution restricted to notifying country
Product : printing ink on drinking cups
Product category : food contact materials

RASFF
Rapid Alert System for Food and Feed

Follow-up :

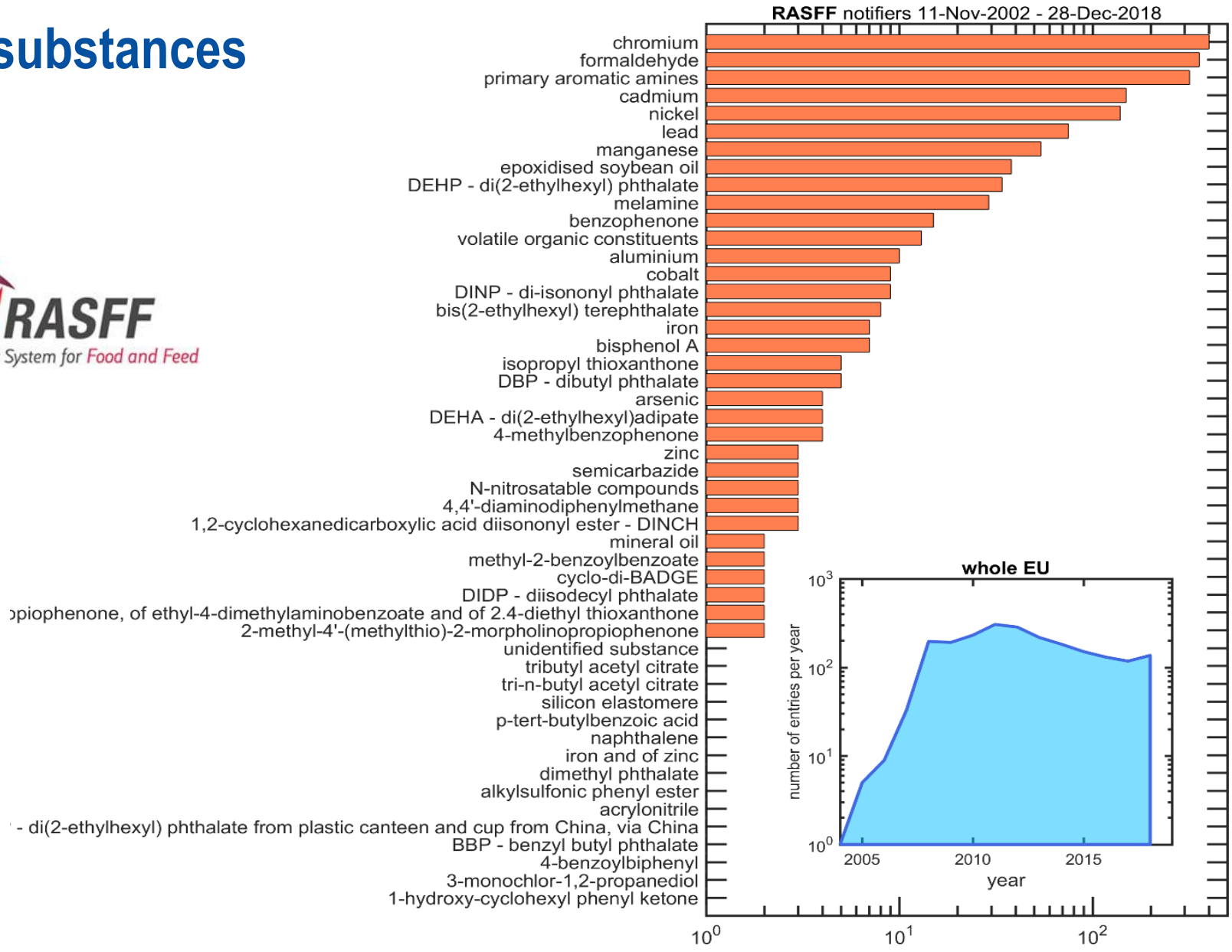
Reference	Follow-up from	Date	Follow-up type	Info

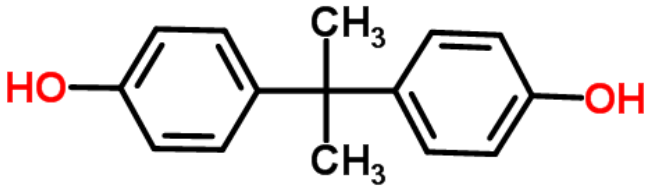
Hazards :

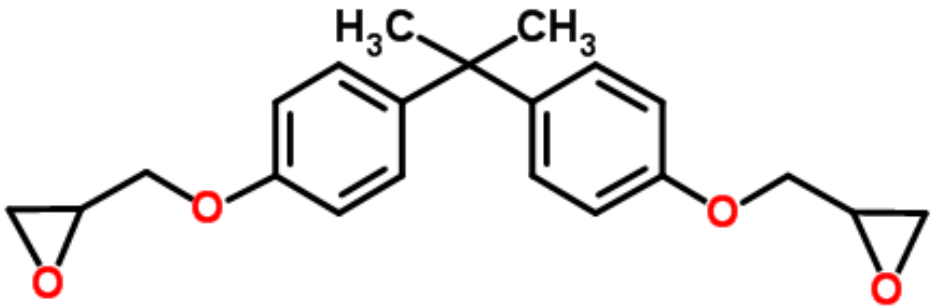
Substance / Hazard	Category	Analytical result	Units	Sampling date
migration of 2-methyl-4'-(methylthio)-2-morpholinopropiophenone	migration			
migration of 2.4-diethyl thioxanthone (DETX)	migration	sum 685	µg/kg - ppb	
migration of ethyl-4-dimethylaminobenzoate	migration			16/10/2010

List of substances

RASFF
Rapid Alert System for Food and Feed







BISPHENOLS

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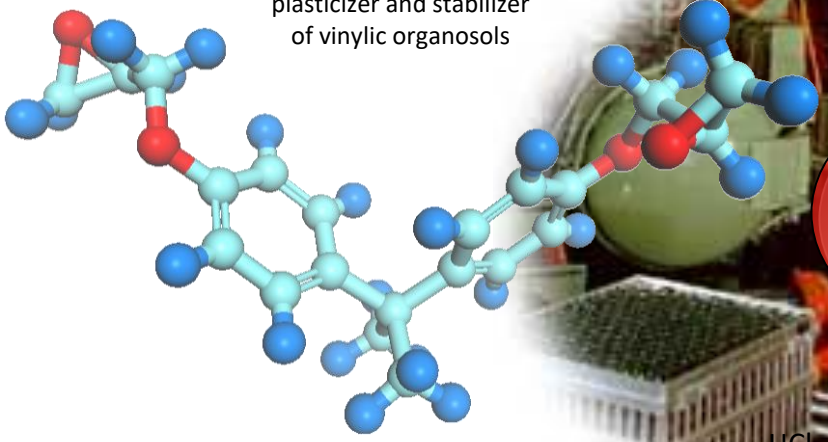
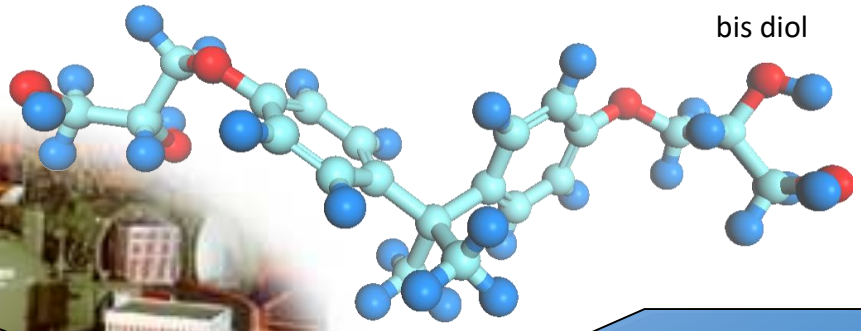
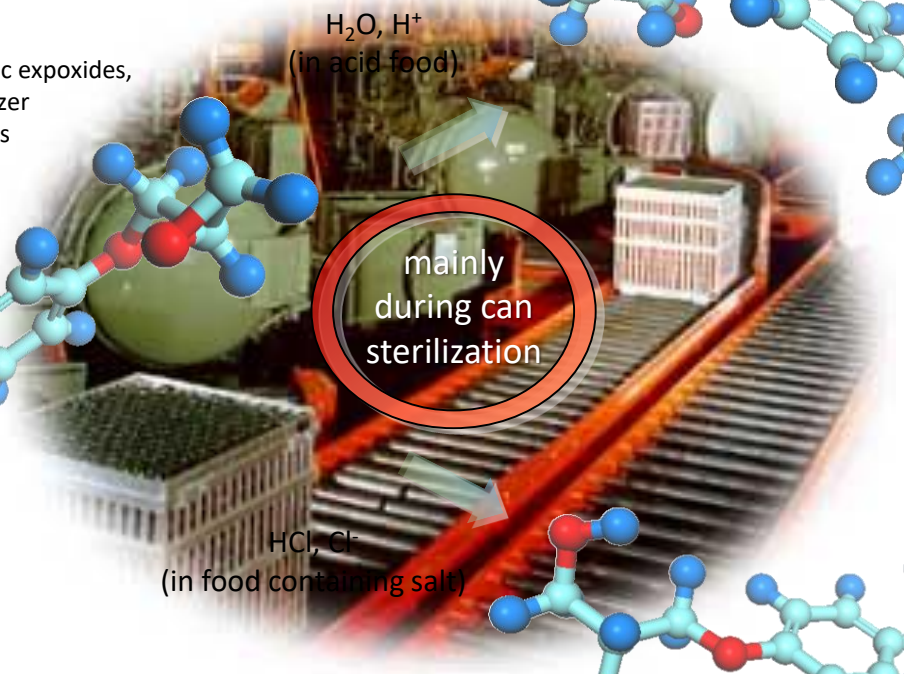
EPOXIDE=reactive migrants

Badge
= starting substance of phenolic expoxides, plasticizer and stabilizer of vinylic organosols



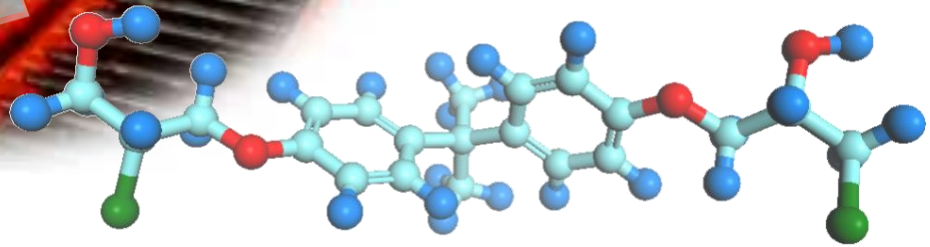


bis diol



MUTAGENESIS
RINGS

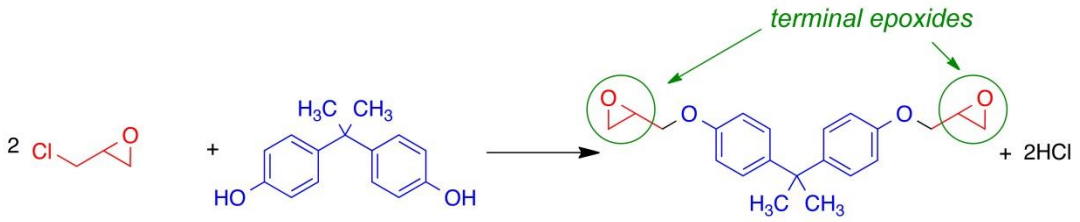
chlorohydrine



MUTAGENESIS
OXY GROUP

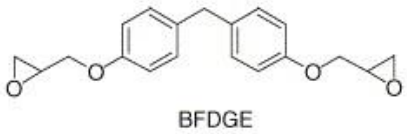
MUTAGENESIS
CHLOROHYDRINES

Cottier 1997, 1999, Paseiro 1995, Philo 1997

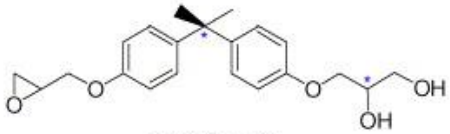


epichlorohydrin bisphenol A bisphenol A diglycidylether hydrogen chloride

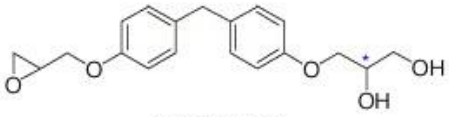
BADGE



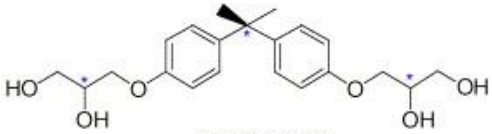
BFDGE



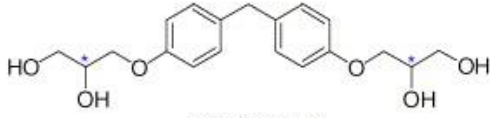
BADGE.H_2O



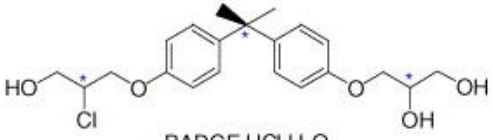
BFDGE.H_2O



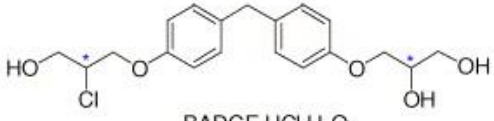
BADGE.2H_2O



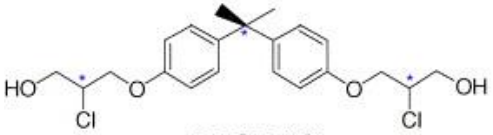
BF DGE.2H_2O



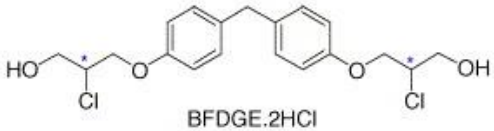
BADGE.HCl.H_2O



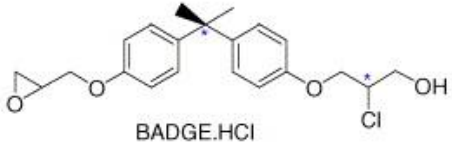
BADGE.HCl.H_2O



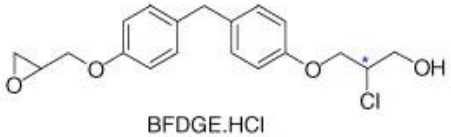
BADGE.2HCl



BFDGE.2HCl



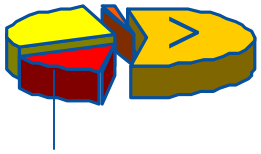
BADGE.HCl



BFDGE.HCl

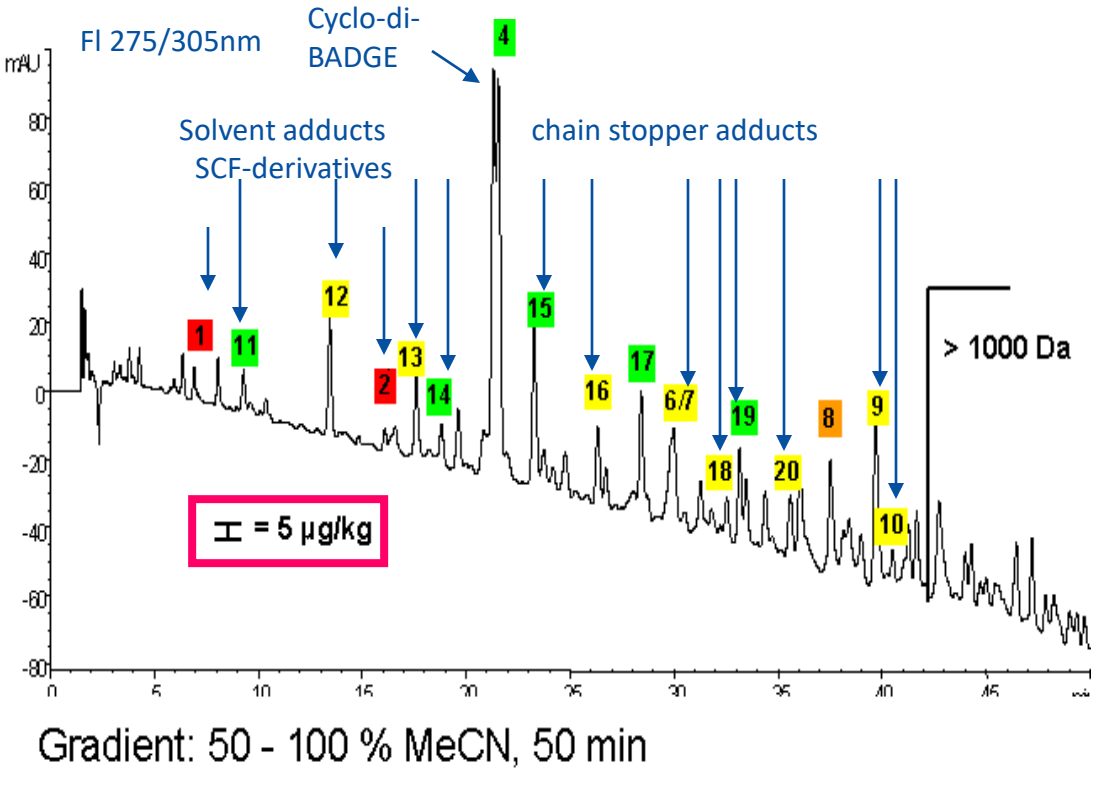
SCREENING OF MIGRANTS FROM CAN COATINGS <1000 Da

SAMPLE: STANDARD EPOXY-COATING, MECN-EXTRACT



resin components < 1000 Da

‚Structured Non-Target'-Screening

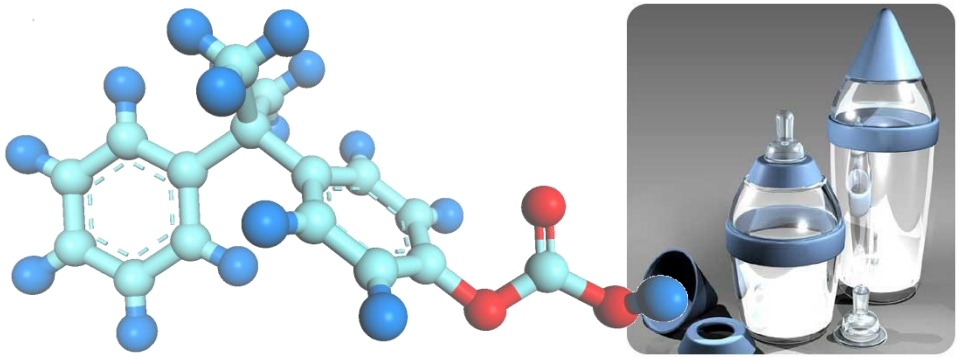


#	M +1	Substances (originated from the resin)
1	359	BADGE·H_2O
2	341	BADGE
3	643	BADGE(n=1)·H_2O
4	569	Cyclo-DiBADGE
5	625	BADGE(n=1)
6	927	BADGE(n=2)·H_20
7	491	BADGE·tBuPh*
8	909	BADGE(n=2)
9	775	BADGE(n=1)·tBuPh
10	641	BADGE·2tBuPh
11	477	BADGE·H2O·BuEtOH**
12	403	BADGE·EG*** (+)
13	459	BADGE·BuEtOH
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, 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



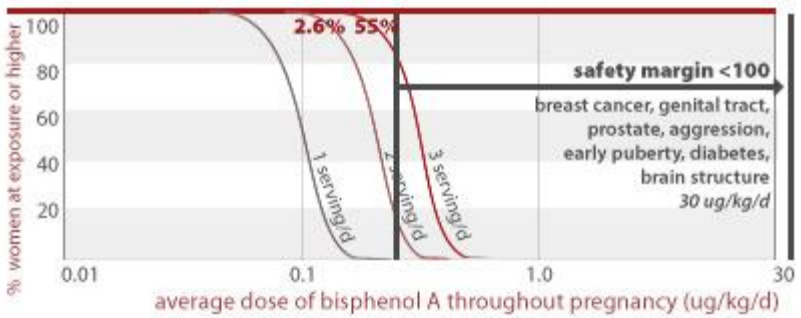
Background: There is increasing concern that exposure to man-made substances that mimic endogenous hormones may adversely affect mammalian reproduction. Although a variety of reproductive complications have been ascribed to compounds with androgenic or estrogenic properties, little attention has been directed at the potential consequences of such exposures to the genetic quality of the gamete.

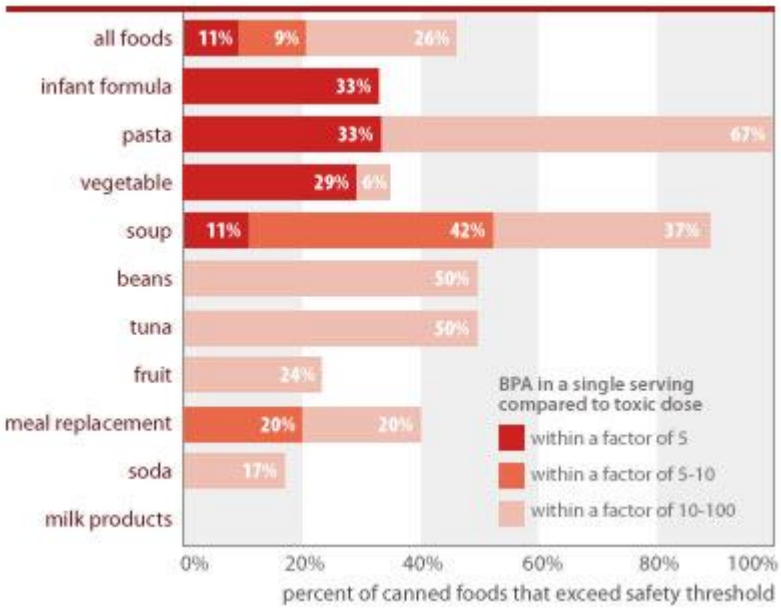
Results: A sudden, spontaneous increase in meiotic disturbances, including aneuploidy, in studies of oocytes from control female mice in our laboratory coincided with the accidental exposure of our animals to an environmental source of bisphenol A (BPA). BPA is an estrogenic compound widely used in the production of polycarbonate plastics and epoxy resins. We identified damaged caging material as the source of the exposure, as we were able to recapitulate the meiotic abnormalities by intentionally damaging cages and water bottles. In subsequent studies of female mice, we administered daily oral doses of BPA to directly test the hypothesis 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.

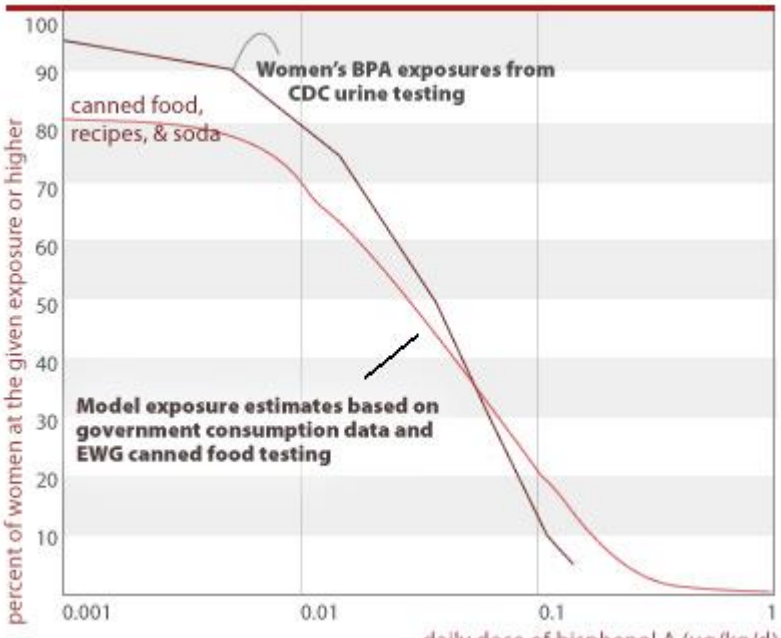
Conclusions: Both the initial inadvertent exposure and subsequent experimental studies suggest that BPA is a potent meiotic aneugen. Specifically, in the female mouse, short-term, low-dose exposure during the final stages of oocyte growth is sufficient to elicit detectable meiotic effects. These results 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.

BPA

PRESENCE IN FOOD



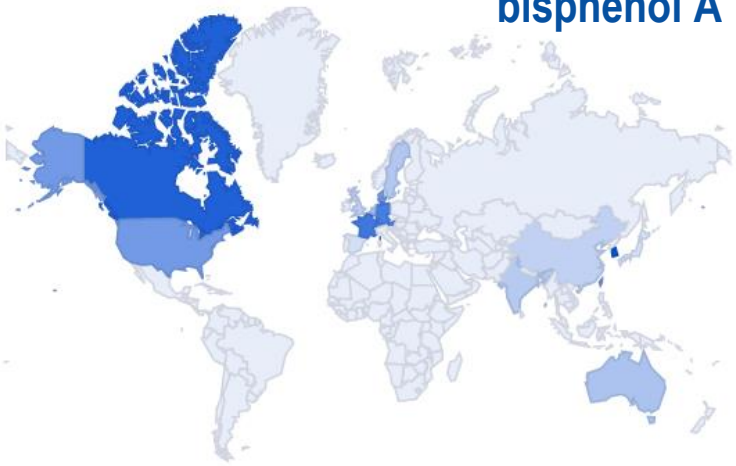




Source: Chemical analyses of 97 canned foods by Southern Testing and Research Division of Microbac Laboratories, Inc., North Carolina

Google Trends – 2003-present

bisphenol A



Termes associés ?

Les plus fr... | En progre...

bpa bisphenol a	100
bpa	95
bisphenol a bottles	60
bisphenol a plastic	55
bisphenol a biberon	55
biberon bisphenol	50
sans bisphenol a	50
biberon sans bisphenol	40
bisphenol a free	35
bisphenol a baby	35

Epilogue

L'EXPRESS ACTUALITÉ ÉCONOMIE FINANCE PE
ENTREPRISE EMPLOI CULTURE ST

Actualité | Photos | Vidéos | Blogs | Express Yourself | Tendances | Elysée 2012

À la une | Politique | Monde | Economie | Société | Education | Médias | High-Tech | Sport | Sciences et s

Actualité > Politique

L'Assemblée unanime interdit les contenants alimentaires avec du bisphénol A

publié le 12/10/2011 à 17:11, mis à jour à 19:23

afp.com/Mychèle Daniau

PARIS - A l'unanimité, l'Assemblée a voté mercredi l'interdiction du bisphénol A dans les contenants alimentaires, objet d'une proposition de loi socialiste soutenue par le gouvernement.

La mesure s'appliquera à compter de 2014, mais dès 2013 pour les contenants alimentaires de produits destinés aux enfants de moins de 3 ans, conformément à un amendement introduit par le ministre de la Santé, Xavier Bertrand, lors des débats jeudi dernier.

Le bisphénol A, composant chimique très répandu dans les objets de la

Toutes les dépêches

CAN: le Soudan qualifié, carton plein de la Côte d'Ivoire dans le groupe B

Wall Street finit en légère baisse: Dow Jones -0,05%, Nasdaq -0,16%

RÉPUBLIQUE FRANÇAISE

JOURNAL OFFICIEL

LOIS ET DÉCRETS

Mercredi 26 décembre 2012 / N° 300

LOI no 2012-1442 du 24 décembre 2012 visant à la suspension de la fabrication, de l'importation, de l'exportation et de la mise sur le marché de tout conditionnement à vocation alimentaire contenant du bisphénol A.

« Cette suspension prend effet, dans les mêmes conditions, au **1er janvier 2015** pour **tout autre conditionnement, contenant ou ustensile comportant du bisphénol A et destiné à entrer en contact direct avec des denrées alimentaires.**

« Avant le 1er juillet 2014, le Gouvernement remet au Parlement un rapport évaluant les substituts possibles au bisphénol A pour ses applications industrielles au regard de leur éventuelle toxicité. »

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

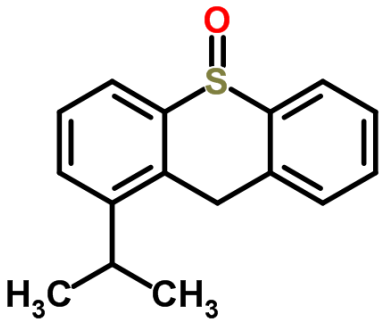
Nonylphenol
NP

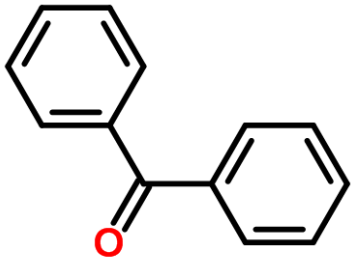
?

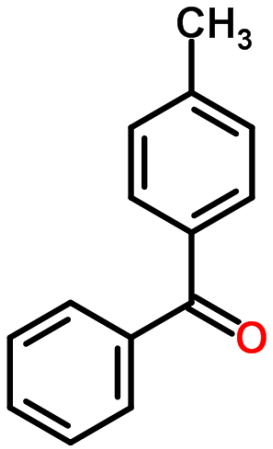
Semicarbazide/SEM

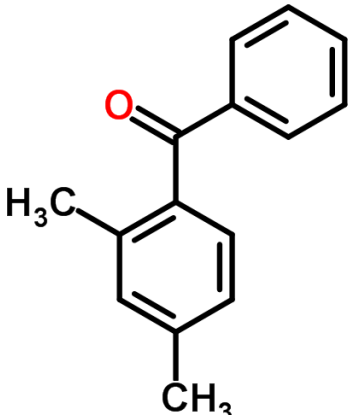
Organic solvents/
residues

Bisphenol A diglycidyl
ether (BADGE)

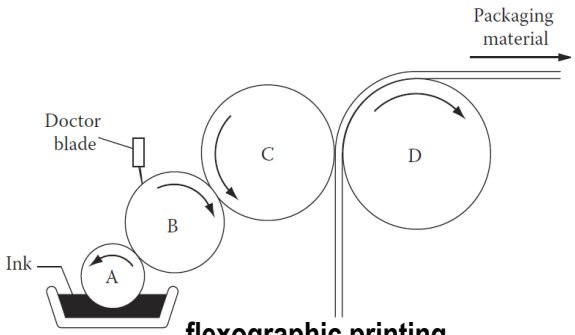




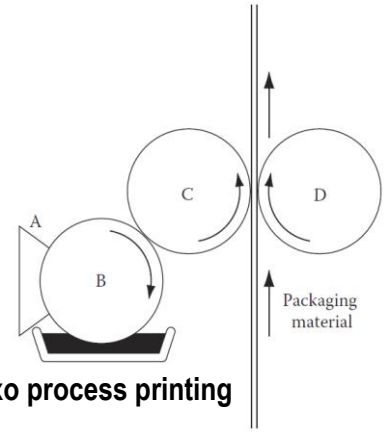




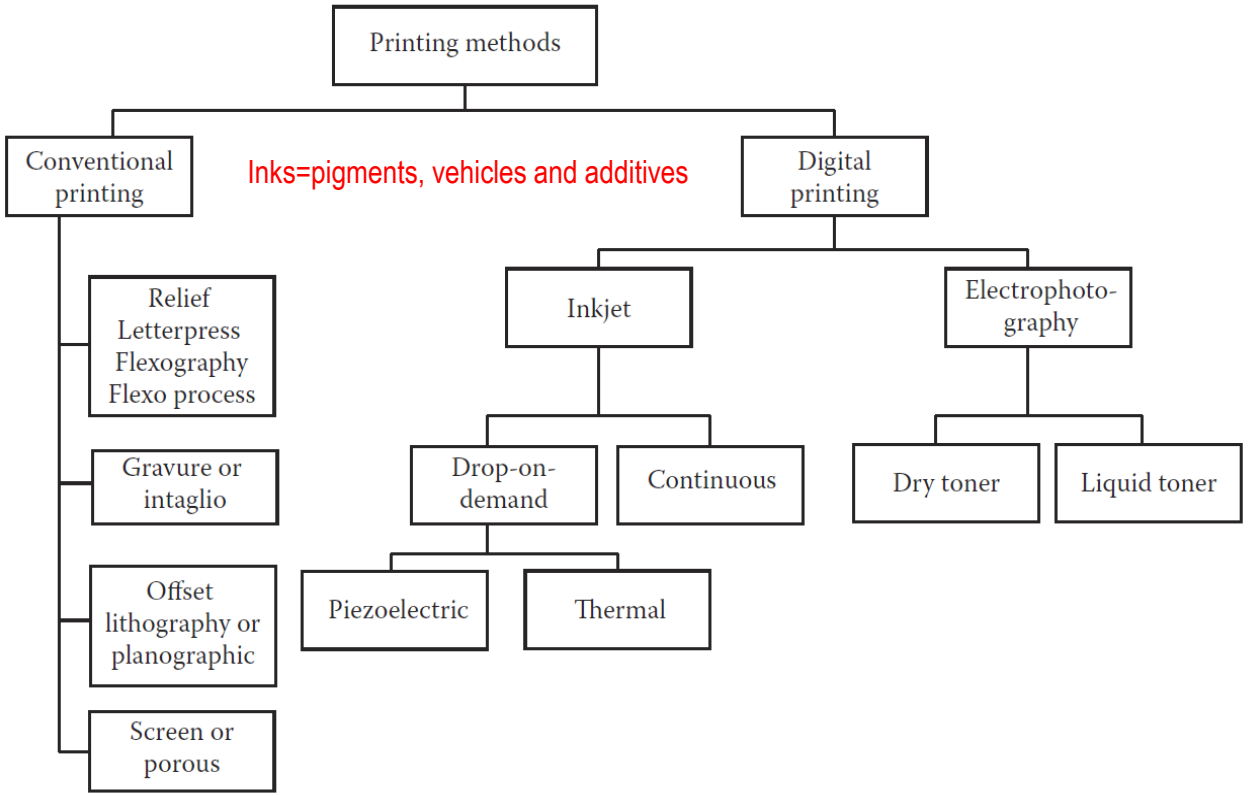
PHOTOINITIATORS

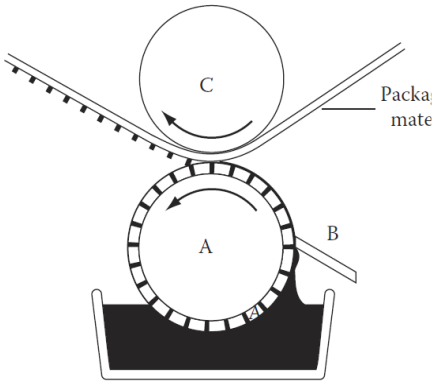


flexographic printing

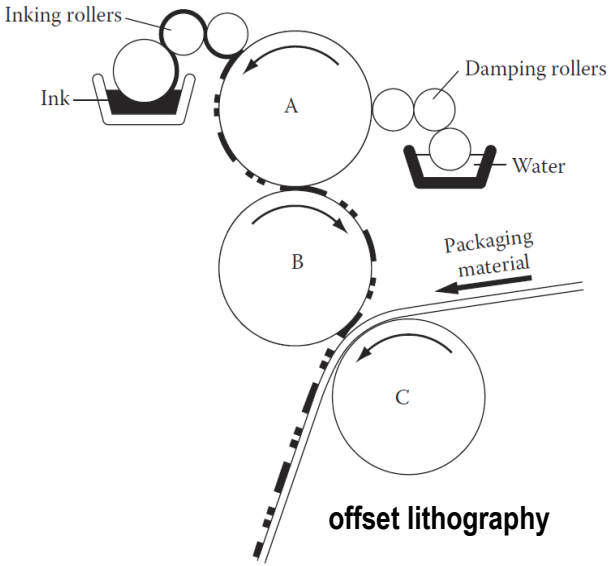


flexo process printing

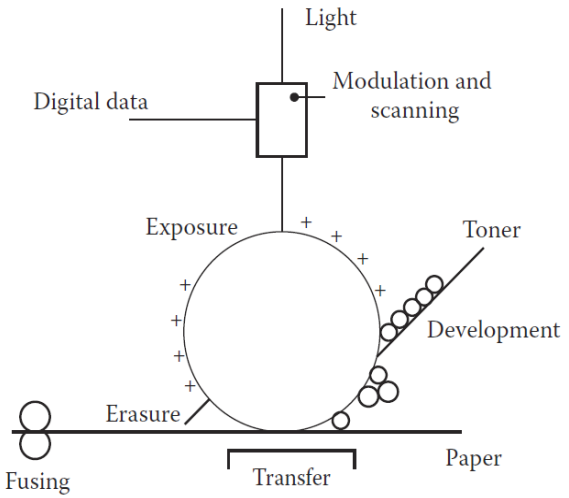




rotagravure printing



offset lithography



digital electrophotography.

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

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 component used in the offset printing process of the Tetra Pak cartons.

They broadened their net on Tuesday, sweeping hundreds of packets of milk off supermarket shelves and out of depots around Italy. Police said they also searched lorries in their effort to root out the four Nestle products under investigation.

Nestle, the world's biggest food company, said it had decided to recall all liquid infant formula milks packed in offset printed cartons in Italy, France, Spain and Portugal.

BOTTOM LINE SAFE

A spokesman at Nestle's corporate headquarters in Switzerland said a new packaging process had been put in place to prevent the contamination and that the recall would not have a significant impact on the company's results at a group level.

Nestle shares were down 0.5 percent at 1615 GMT in a slightly higher overall Swiss market.

Tetra Pak spokeswoman Patricia O'Hayer said ITX was not recognised as a toxic substance on any official list and was not on the World Health Organisation lists of toxic substances that should not come into contact with food.

"We have studied the toxicological data available, and that confirms that it is not toxic," she told Reuters.

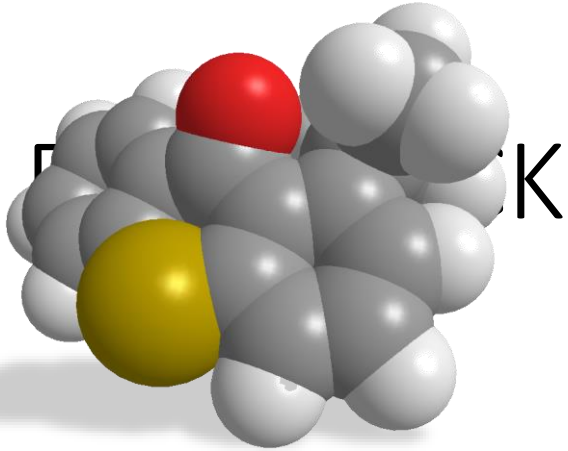
O'Hayer said Tetra Pak removed the printing technology in question in October to prevent any printing compound, even if not dangerous, from seeping into a product.

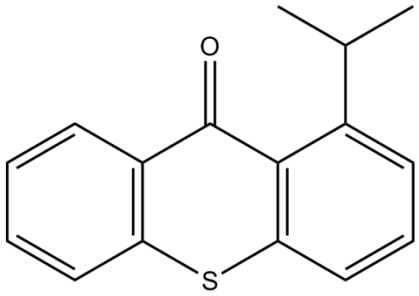
"We had no indication that this was in any way a cause for concern," she said.

This is the second time Nestle has run foul of Italian authorities this year.

In October, Italy's antitrust authority fined seven producers of baby formula including Nestle a total of 9.743 million euros for running a cartel in Italy to keep prices much higher than in many European countries.

IS [illegible]CK





isopropyl thioxanthone

photoinitiator used in UV, curing resins, inks, coatings and adhesives
M=241 g·mol^{-1}

INFACT Canada
Infant Feeding Action Coalition
Protecting, Promoting & Supporting Breastfeeding

BOYCOTT Nestlé BOYCOTT

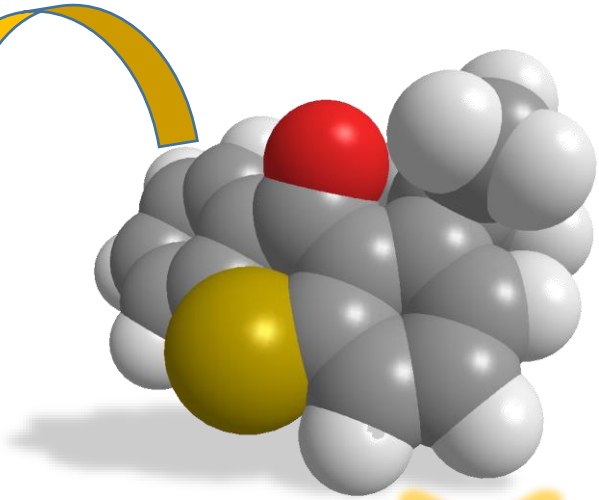
December 15, 2005

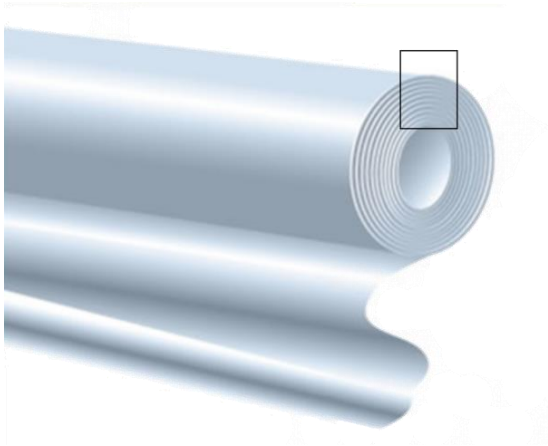
DETAILS EMERGE IN TAINTED NESTLÉ FORMULA SCANDAL

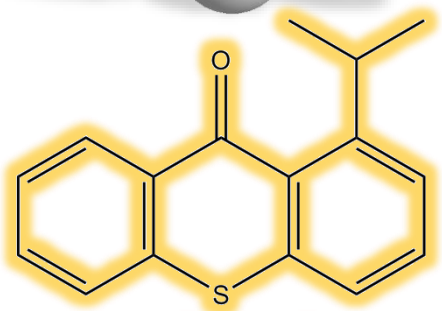
The discovery of contamination in various Nestlé baby food brands has caused a huge stir in Europe. Millions of litres of formula have been pulled from the shelves and a top official in the Italian government has threatened legal action against the corporation's CEO. It is now clear that the contamination was caused by IsopropilThioxanthone (ITX), a fixative of printing ink used on liquid milk cartons (produced by TetraPack, a large company that serves many other food companies for different kinds of foods and beverages). It is also apparent that Nestlé has been less than responsible is recalling potentially contaminated baby formula, prompting government intervention and seizures of the product. This episode demonstrates yet again Nestlé's willingness to preserve its own profits at the expense of infant health, and the inherent dangers presented by mass-produced baby food.

July 2005: First tests of Nestlé ready-to-feed liquid formula in the Marche region of Italy show contamination by ITX. Further tests were ordered on other Nestlé products: Nidina 1 for infants, Nidina 2 for babies 6 to 12 months, Latte Mio and Mio Cereali for children 1 to 3 years.

RAPPEL







isopropyl thioxanthone

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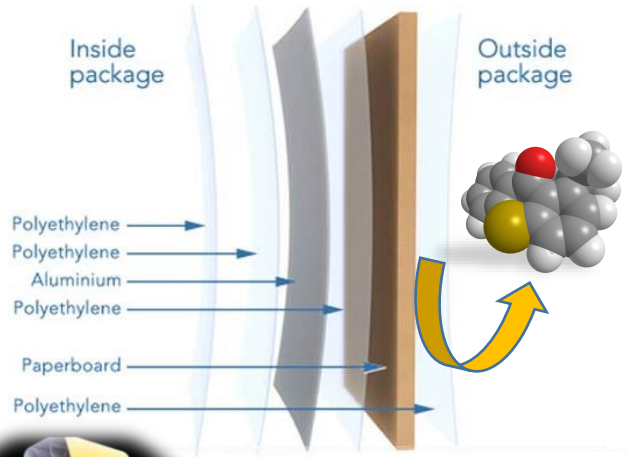
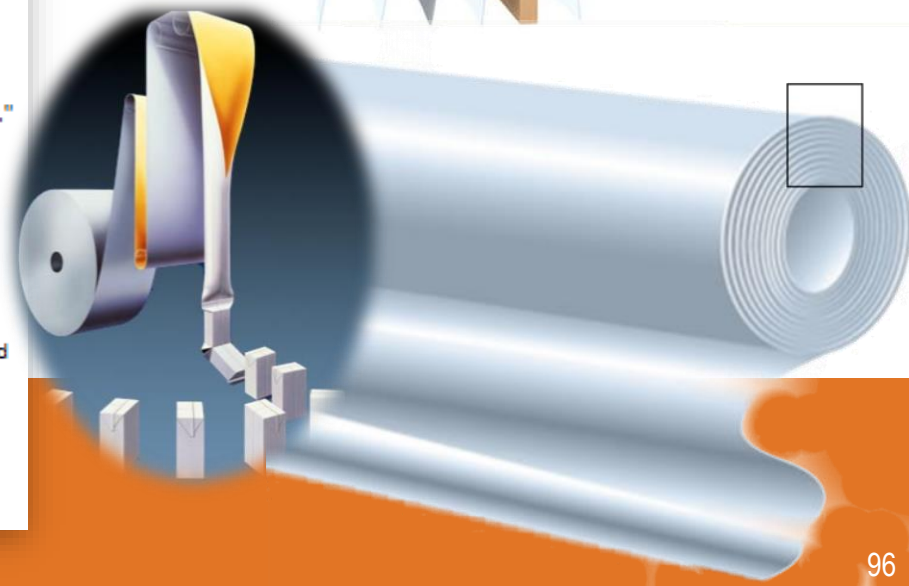




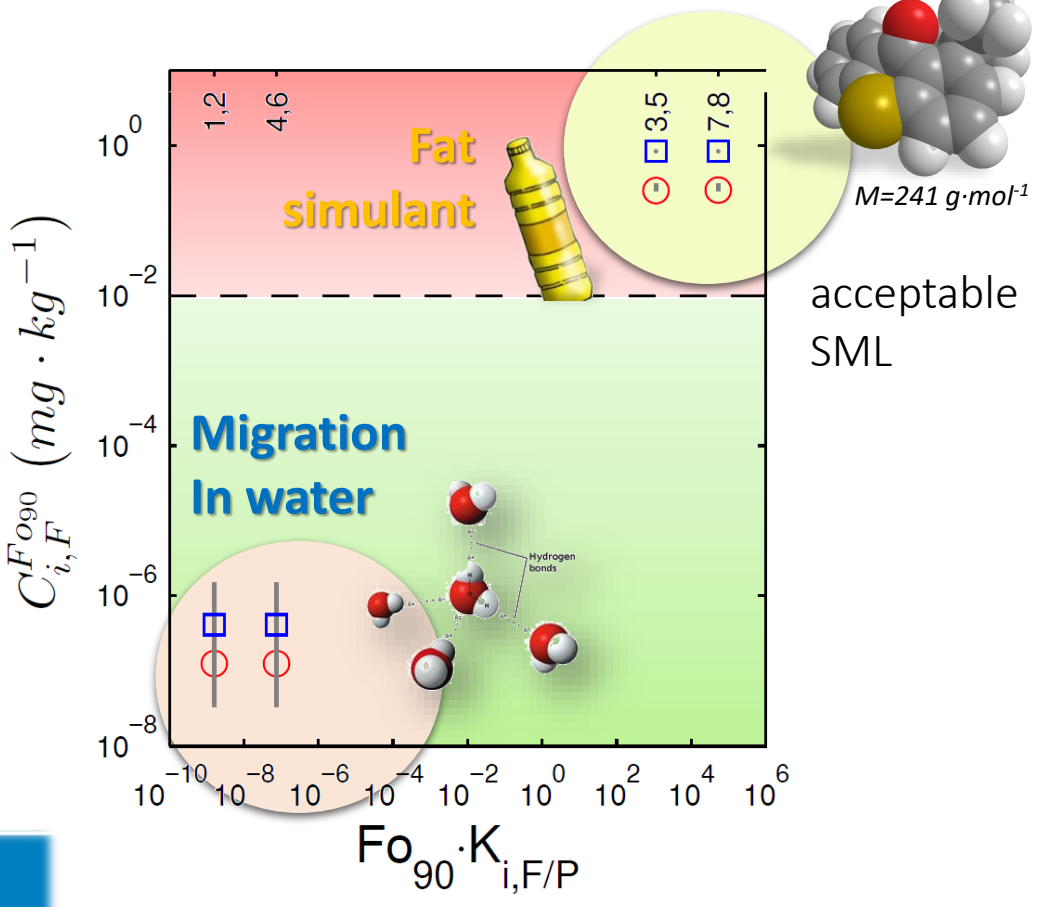
REUTERS AlertNet FOUNDATION

SCIENCE & IMPACT

MODELING WOULD HAVE BEEN ABLE TO PREDICT ITX VALUES IN FOOD?

.*Food Additives and Contaminants Part a-Chemistry Analysis Control Exposure & Risk Assessment*, **2009**, 26(12), 1556-1573.

	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[a]	$\overline{C}^0_{i,P}$ [a] (mg·kg^{-1})	100 ± 10
Conservative initial concentration[b]	$\left(C^0_{i,P}\right)^+$ [b] (mg·kg^{-1})	300
Likely diffusion coefficient[c]	$\overline{D}_{i,P}$ [c] (m^2.s^{-1})	$8.4\cdot10^{-16}$ [$7.6\cdot10^{-16}$ $9.2\cdot10^{-16}$]
Conservative diffusion coefficient[d]	$D^+_{i,P}$ [d] (m^2.s^{-1})	$3.9\cdot10^{-14}$
Likely partition coefficient[e]	$\overline{K}_{i,F/P}$ (-)	$1.4\cdot10^{-9}$ [$3.7\cdot10^{-10}$ $5.1\cdot10^{-9}$]
Conservative partition coefficient	$K^+_{i,F/P}$ (-)	10^3

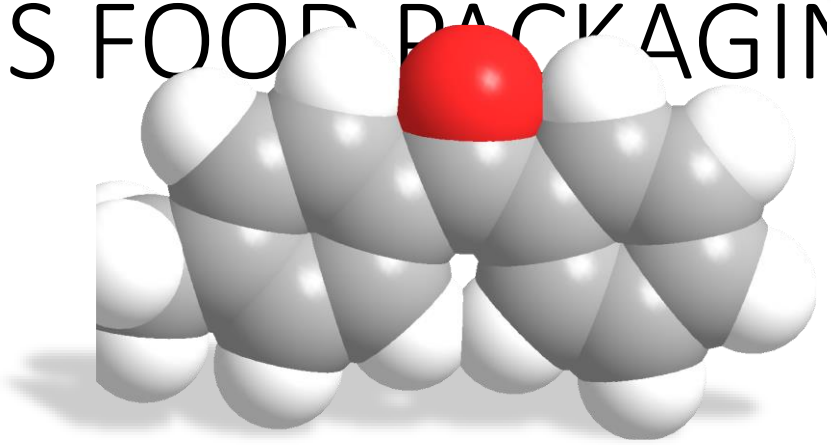


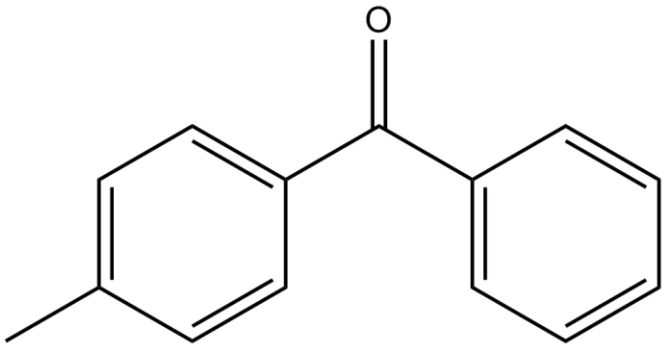
M=241 g·mol^{-1}

acceptable SML

	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

IS FOOD PACKAGIN





4-methyl benzophenone

LE VEILLEUR@

Quelques fois on ne voit pas tout..

Contact

Accueil > Actu, France > Lidl a rappelé des milliers de boîtes de céréales en février

Lidl a rappelé des milliers de boîtes de céréales en février

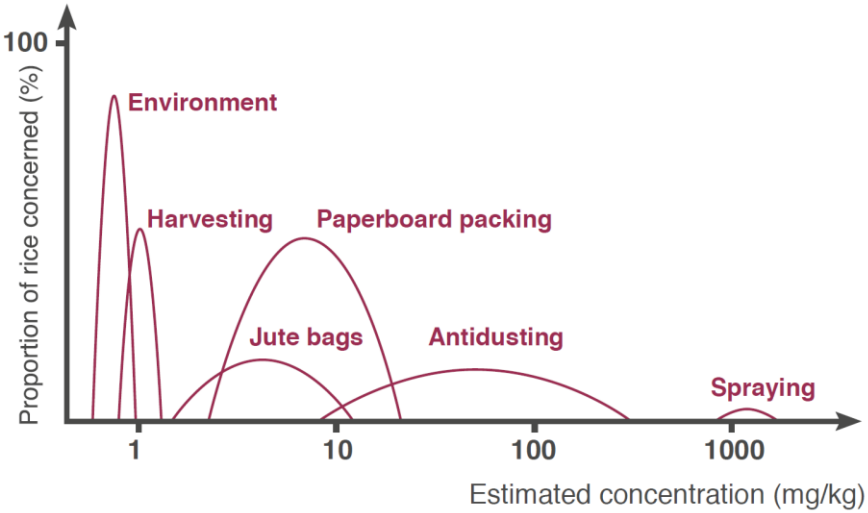
02/04/2009 Allez aux commentaires Commenter

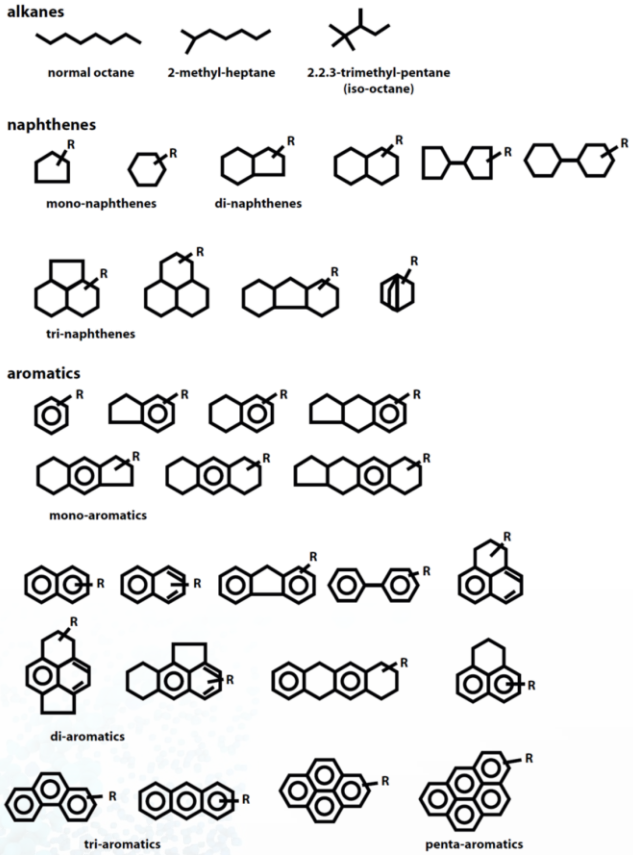
Des milliers de paquets de céréales pour le petit déjeuner "muësli" ont été retirés en février des rayons des 1 400 magasins Lidl de France, suite à la contamination de ces céréales par une composante toxique utilisée dans l'encre des emballages, indique, jeudi 2 avril, Lidl.

"Nous avons été informés le 6 février par notre maison-mère qu'il fallait retirer de la vente deux références, des muesli au chocolat et des muesli aux fruits. Les marchandises ont été retirées le 9 février", déclare Jérôme Gresland, directeur des achats de Lidl pour la France, confirmant une information du Canard enchaîné. Des sites comme 60 millions de consommateurs ou rappelsproduits.fr permettent aux consommateurs s'informer sur les produits – steaks hachés avariés, circuits hydrauliques de voiture défectueux, saucisson contenant des salmonelles – rappelés par les constructeurs et fabricants.

Le signalement de la maison-mère était consécutif à une alerte du système d'alerte européen pour les denrées alimentaires (RASFF), après qu'un contrôle sanitaire a mis en évidence en Allemagne la présence de 4-méthyle benzophénone (4-MBP) dans des céréales, a précisé M. Gresland. L'EFSA a fait savoir le 4 mars que "la consommation régulière de produits fortement contaminés" par la molécule incriminée pouvait présenter "dans des cas extrêmes un risque pour certains enfants". La branche française de Lidl a décidé de son propre chef de retirer les produits de ses rayons, "par précaution", a souligné M. Gresland.

"A aucun moment la Direction générale de la concurrence, de la consommation, et de la répression des fraudes (DGCCRF) ne nous a demandé de procéder à un rappel des produits" déjà vendus, a-t-il dit. "La DGCCRF a pris contact avec nous début mars, trois semaines après le retrait des produits de la vente", a-t-il.

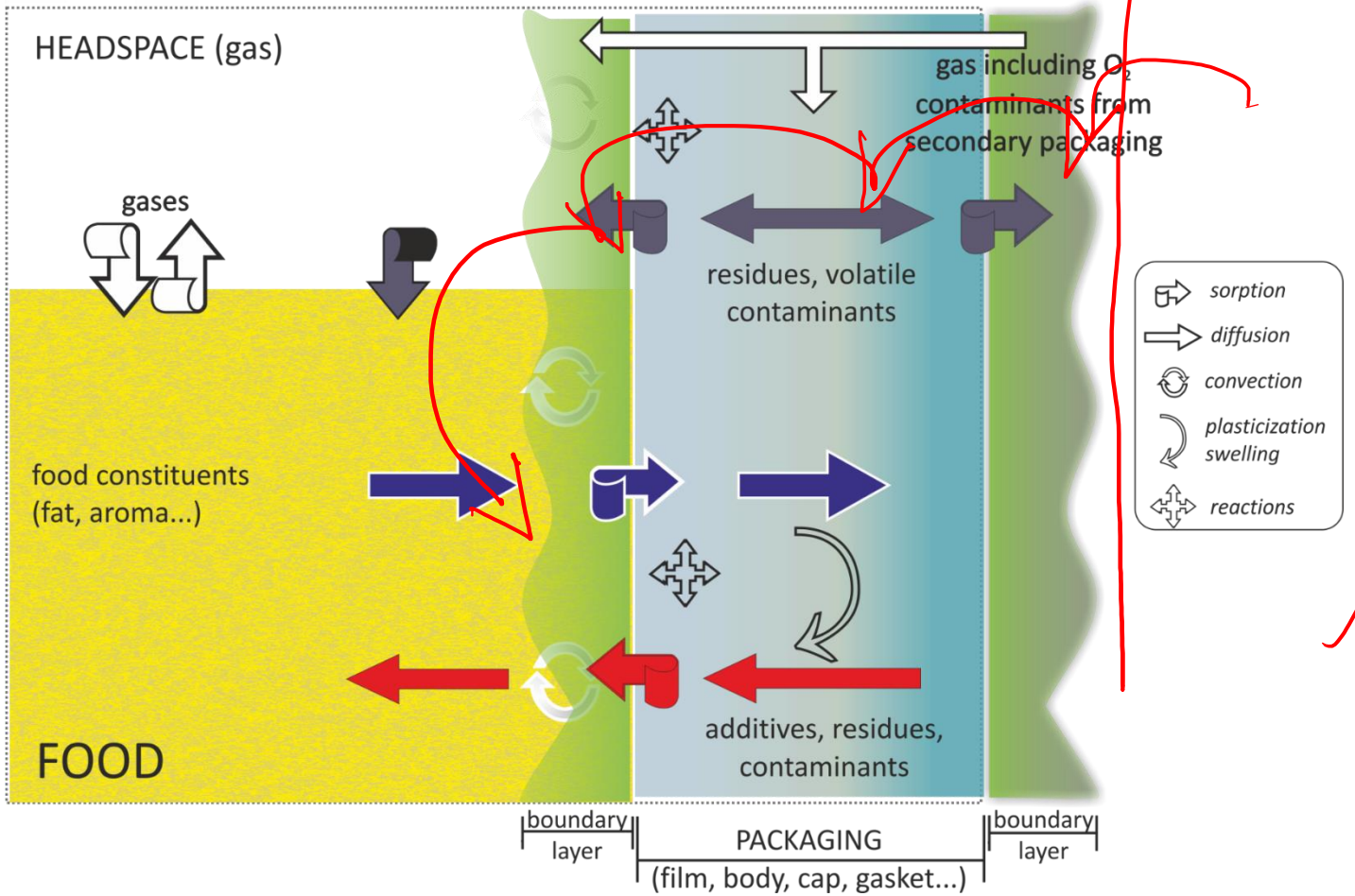




MINERAL OILS

Coupled mass transfer

between the food product and the packaging material

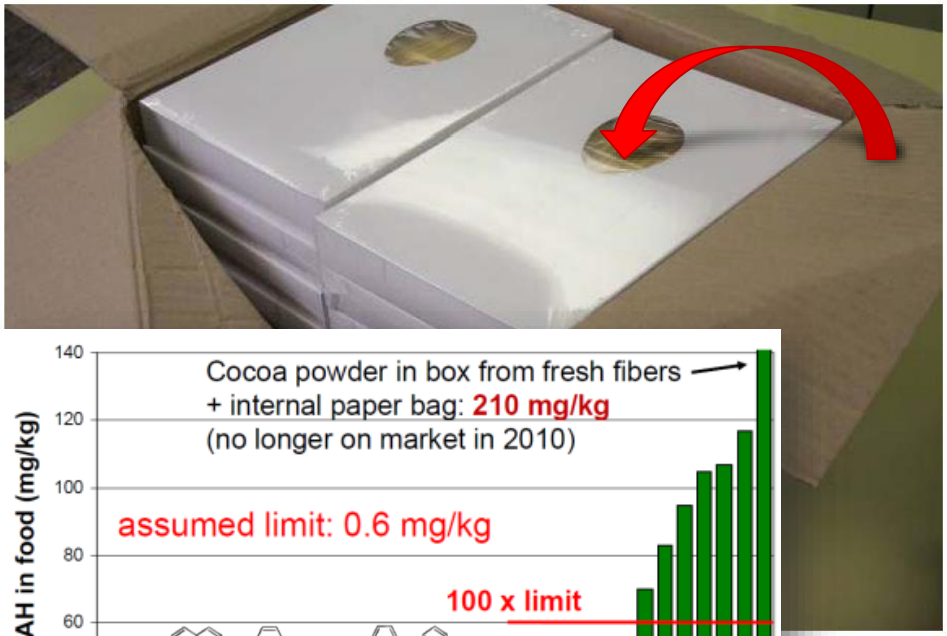


CONTEXT: EXAMPLES NOT COVERED BY SPECIFIC MEASURES: NON-SPECIFICALLY REGULATED MATERIALS, DRY AND AQUEOUS FOOD FALSELY CONSIDERED SAFE

CONTAMINATION OF NODDLES BY RECYCLED FIBERS OF SECONDARY PACKAGING

After 65 days of contact, 6.1 mg/kg of paraffins found in noodles stored in boxes in top and bottom positions. Estimated migration at shelf life (2 years) : 10 mg/kg

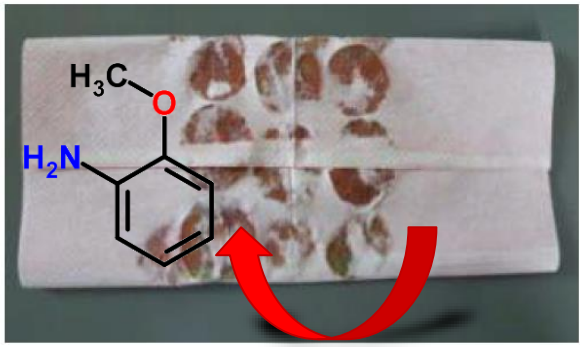
(Biedermann *et al.*, 2011; Packaging Technol & Sci 2011, 24, 281-290)



CONTAMINATION OF FRESH FRUITS BY PRINTED TABLE NAPKIN

Migration of o-anisidine (primary aromatic amine): printed paper 17.5 µg/l → kiwi: 5.3 µg/l (migration rate: 17 %)

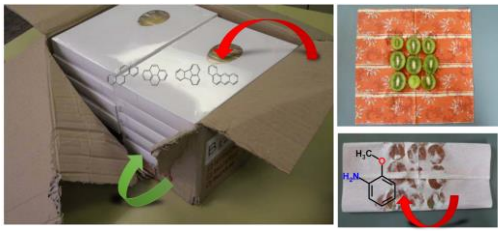
(Helling, 2011)



MOH SURVEY

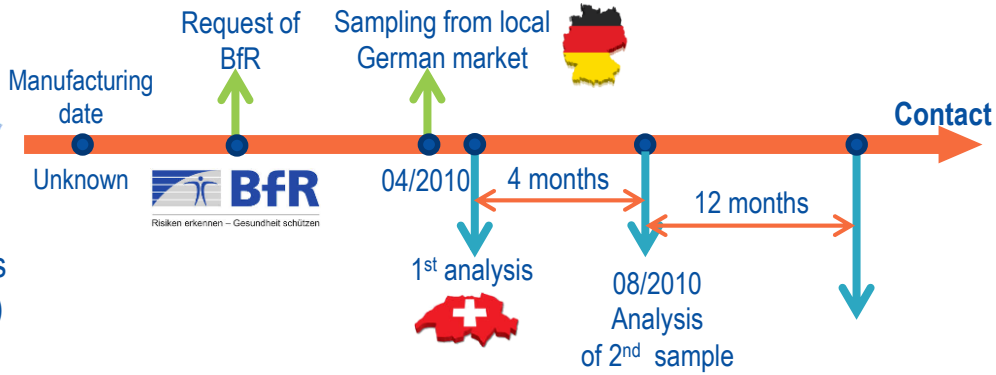
FOOD WATCH – October 2015

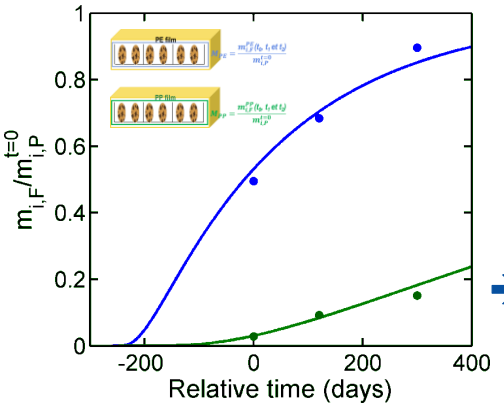
http://www.foodwatch.org/fr/presse/communiques-de-presse/page-detail-communiques-de-presse/des-hydrocarbures-dans-nos-assiettes-foodwatch-tire-le-signal-dalarme/



SOURCES DE CONTAMINATION DES ALIMENTS
PAR LES HUILES MINÉRALES

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



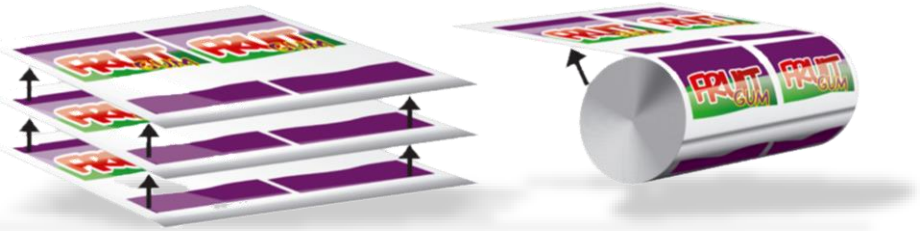


$$\rightarrow \frac{M_{PE}}{M_{PP}} \propto \frac{D_{i,PE}}{D_{i,PP}}$$

Ubiquitous contaminants
Mineral Oils, Printing inks, adhesives

PRINTING INKS
(EUPIA guidelines to be revised)

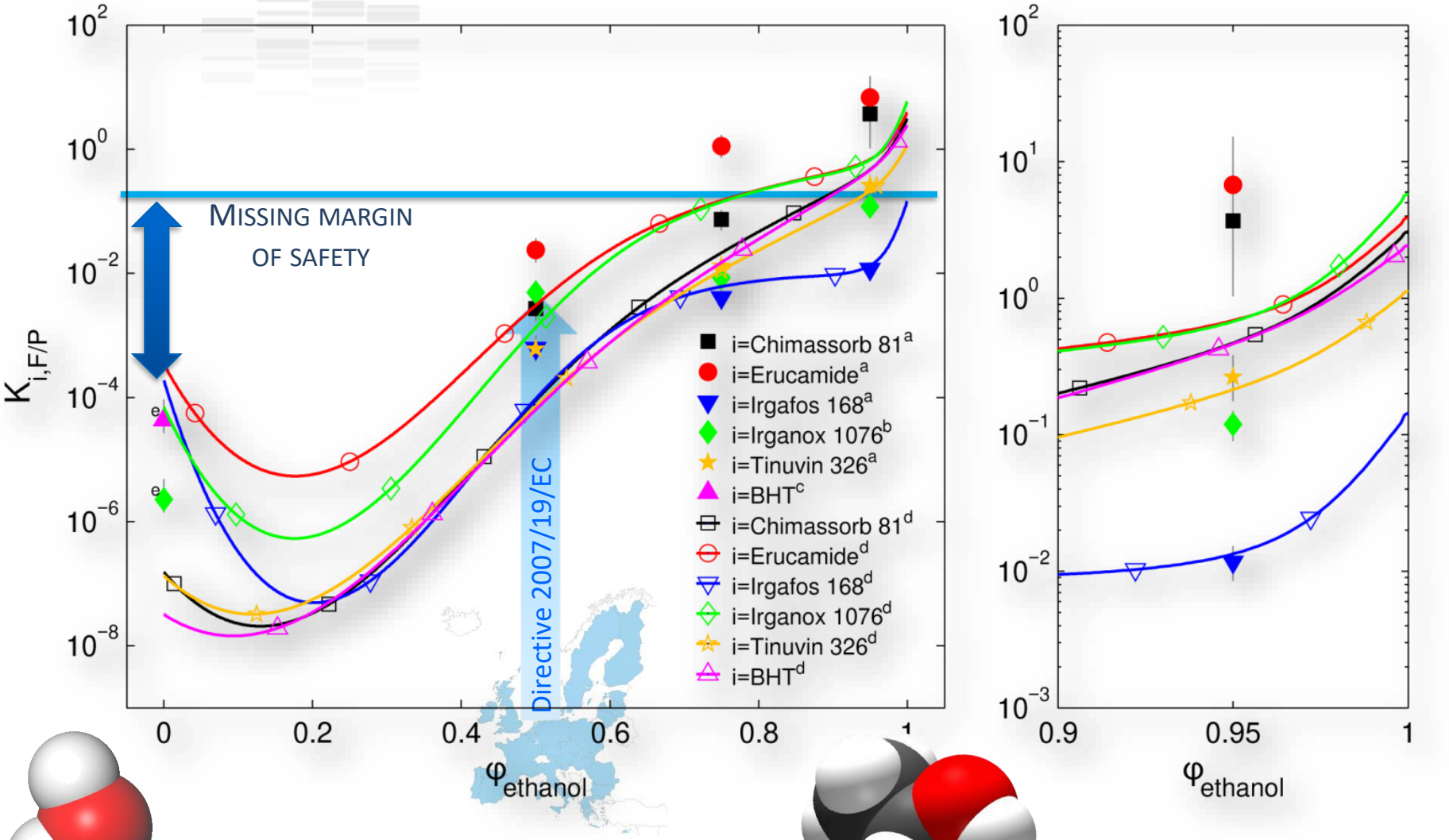
- Exclusion/Negative lists
- Recommended substances
- Purity/traceability requirements
- Migration (less than 10 ppb for non evaluated substances) and risk assessments
- Inks prepared according to GMP
- No-direct contact with food
- No “visible’ Set-off in stacks and reels



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

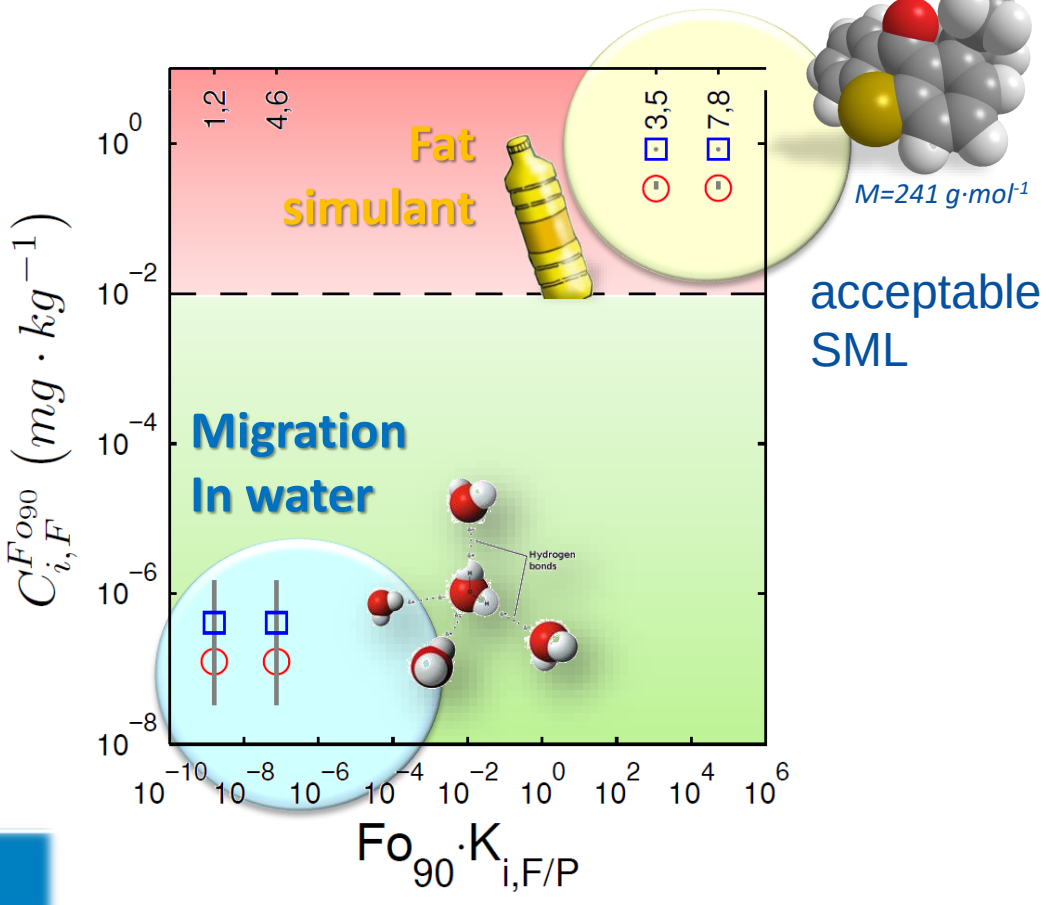
PARTITION COEFFICIENTS WITH WATER/ETHANOL AND POLYETHYLENE



MODELING WOULD HAVE BEEN ABLE TO PREDICT ITX VALUES IN FOOD?

.*Food Additives and Contaminants Part a-Chemistry Analysis Control Exposure & Risk Assessment*, **2009**, 26(12), 1556-1573.

	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[a]	$\overline{C}^0_{i,P}$ [a] ($mg \cdot kg^{-1}$)	100 ± 10
Conservative initial concentration[b]	$\left(C^0_{i,P}\right)^+$ [b] ($mg \cdot kg^{-1}$)	300
Likely diffusion coefficient[c]	$\overline{D}_{i,P}$ [c] ($m^2.s^{-1}$)	$8.4 \cdot 10^{-16}$ [$7.6 \cdot 10^{-16}$ $9.2 \cdot 10^{-16}$]
Conservative diffusion coefficient[d]	$D^+_{i,P}$ [d] ($m^2.s^{-1}$)	$3.9 \cdot 10^{-14}$
Likely partition coefficient[e]	$\overline{K}_{i,F/P}$ (-)	$1.4 \cdot 10^{-9}$ [$3.7 \cdot 10^{-10}$ $5.1 \cdot 10^{-9}$]
Conservative partition coefficient	$K^+_{i,F/P}$ (-)	10^3



	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

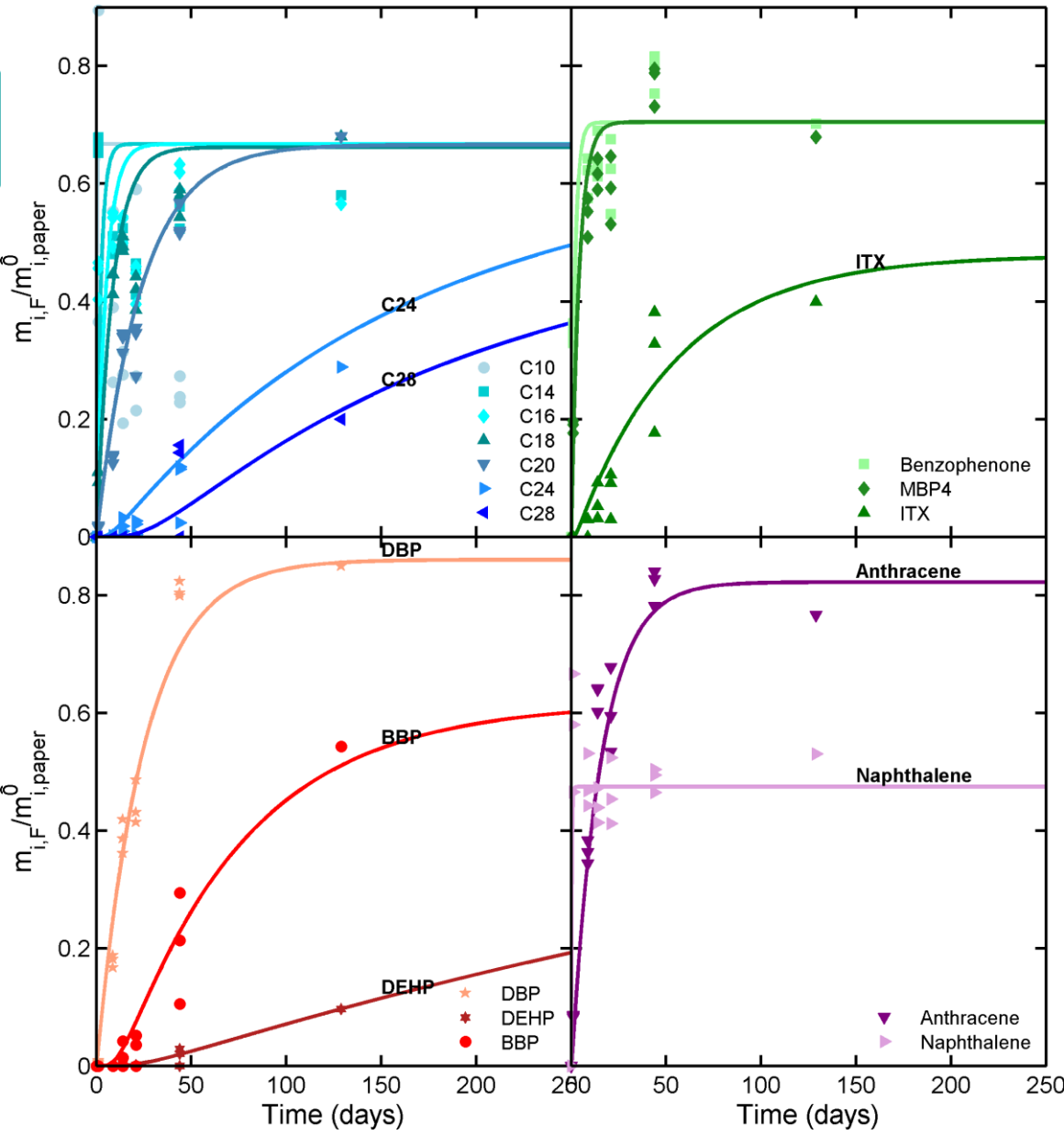
PREDICTIONS vs EXPERIMENTS

Nguyen *et al.* 2014, submitted to I&EC, FAC

Experimental results at 60°C, *i*=1…15 → **Detailed modeling with FMECAengine**

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

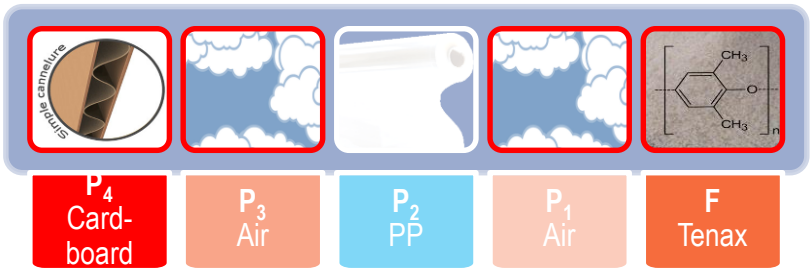
0 to 120 days



https://github.com/ovitrac/FMECAengine

TWO EXTREME CASES

Type 1 : desorption in gaseous phase (exponential without delay)



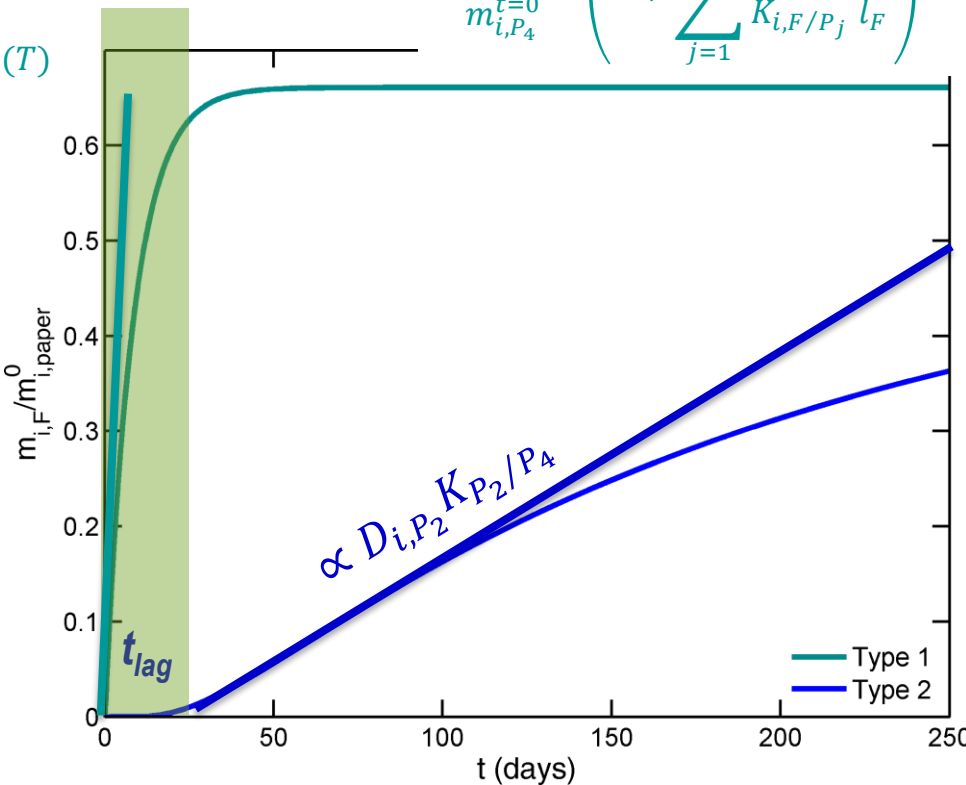
$$\frac{C_{i,P_4}^{t=0} - C_{i,P_4}(t)}{C_{i,P_4}^{t=0} - C_{i,P_4}^{eq}}$$

$$\xrightarrow[t\to 0]{} \frac{P_i^{vsat}(T) V_i \gamma_{i,P_4}^{v}(T) h_e}{(1-\varepsilon_{P_4}) RT l_{P_4}} (1 + K_{P_4/F} L_{P_4/F}) t$$

$$\frac{dm_{i,F}(t)}{dt}\Big|_{t\to 0} \propto P_i^{vsat}(T)$$

$$\frac{m_{i,F}^{eq}}{m_{i,P_4}^{t=0}} = \left(1 + \sum_{j=1}^{4} \frac{1}{K_{i,F/P_j}} \frac{l_{P_j}}{l_F}\right)^{-1}$$

Type 2 : diffusion through the PP layer



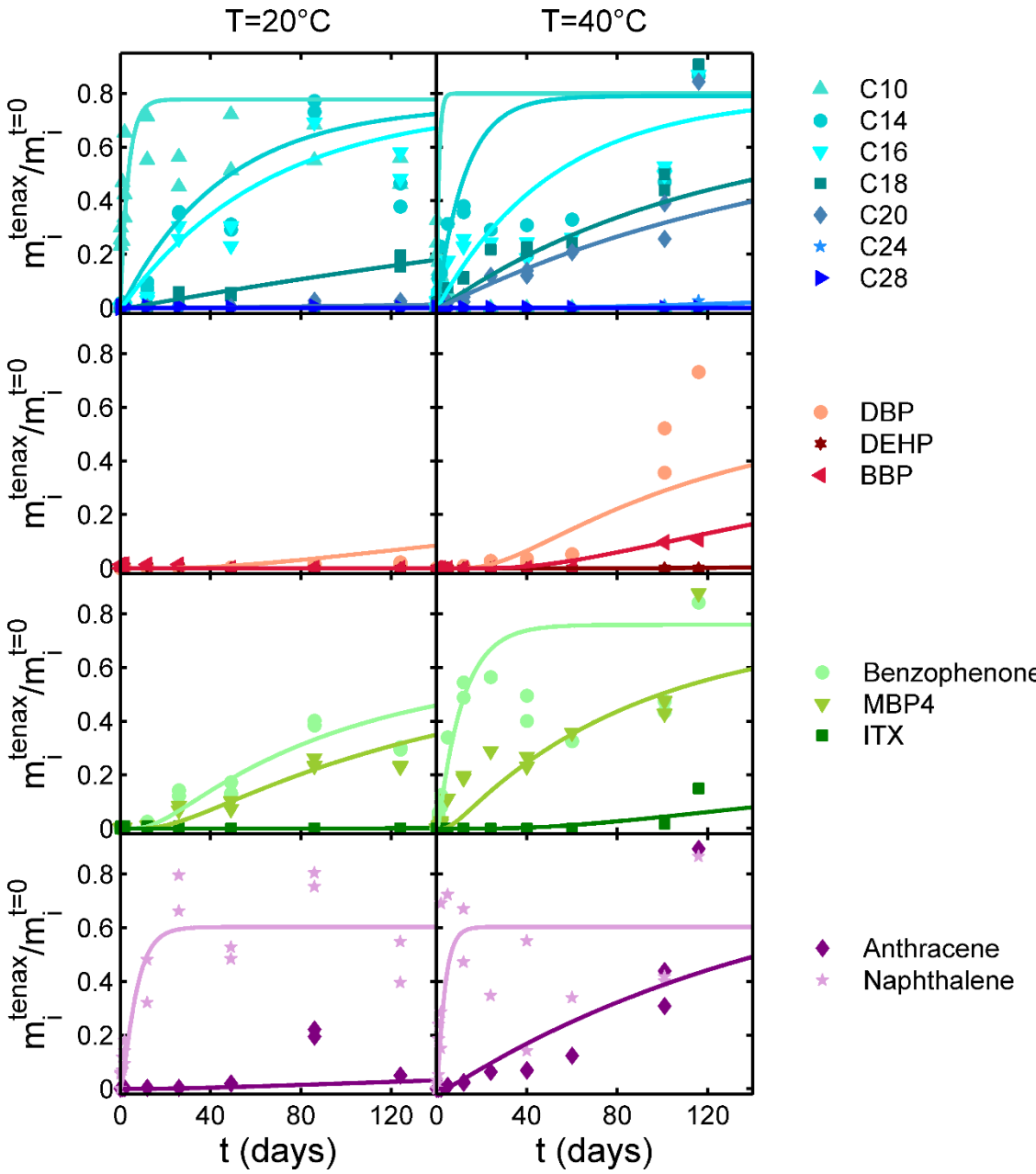
AMBIENT TEMPERATURES

Nguyen *et al.* 2016, submitted to FAC

Experimental results at 60°C, *i*=1…15 → **Detailed modeling** with FMECAengine

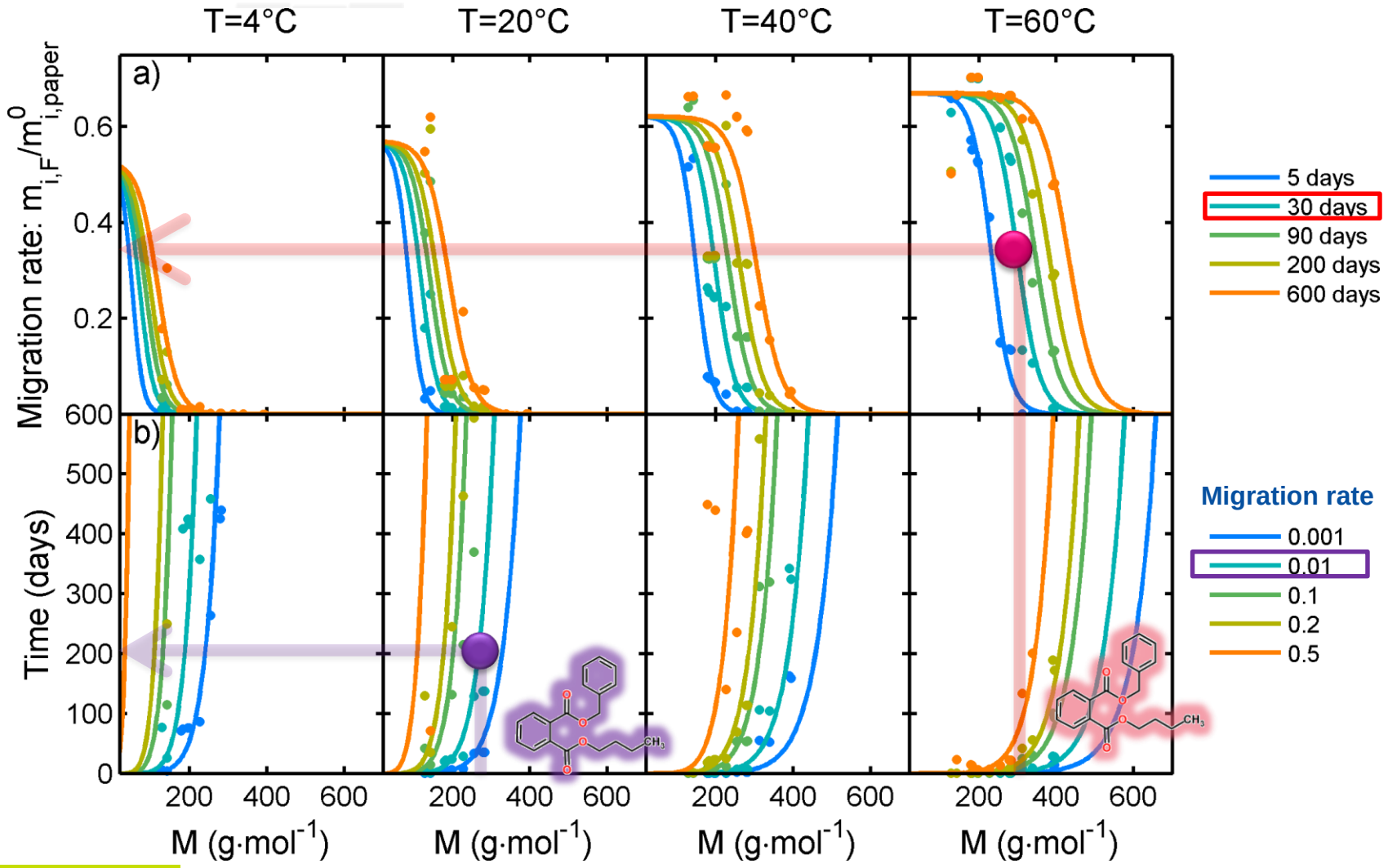
$$\frac{m_{i,F}^{(t)}}{m_{i,P}^{0}} = \frac{V_F}{m_{i,P}^{0}} \int_0^t C_{i,F}^{(t)} \, d\tau$$

0 to 160 days



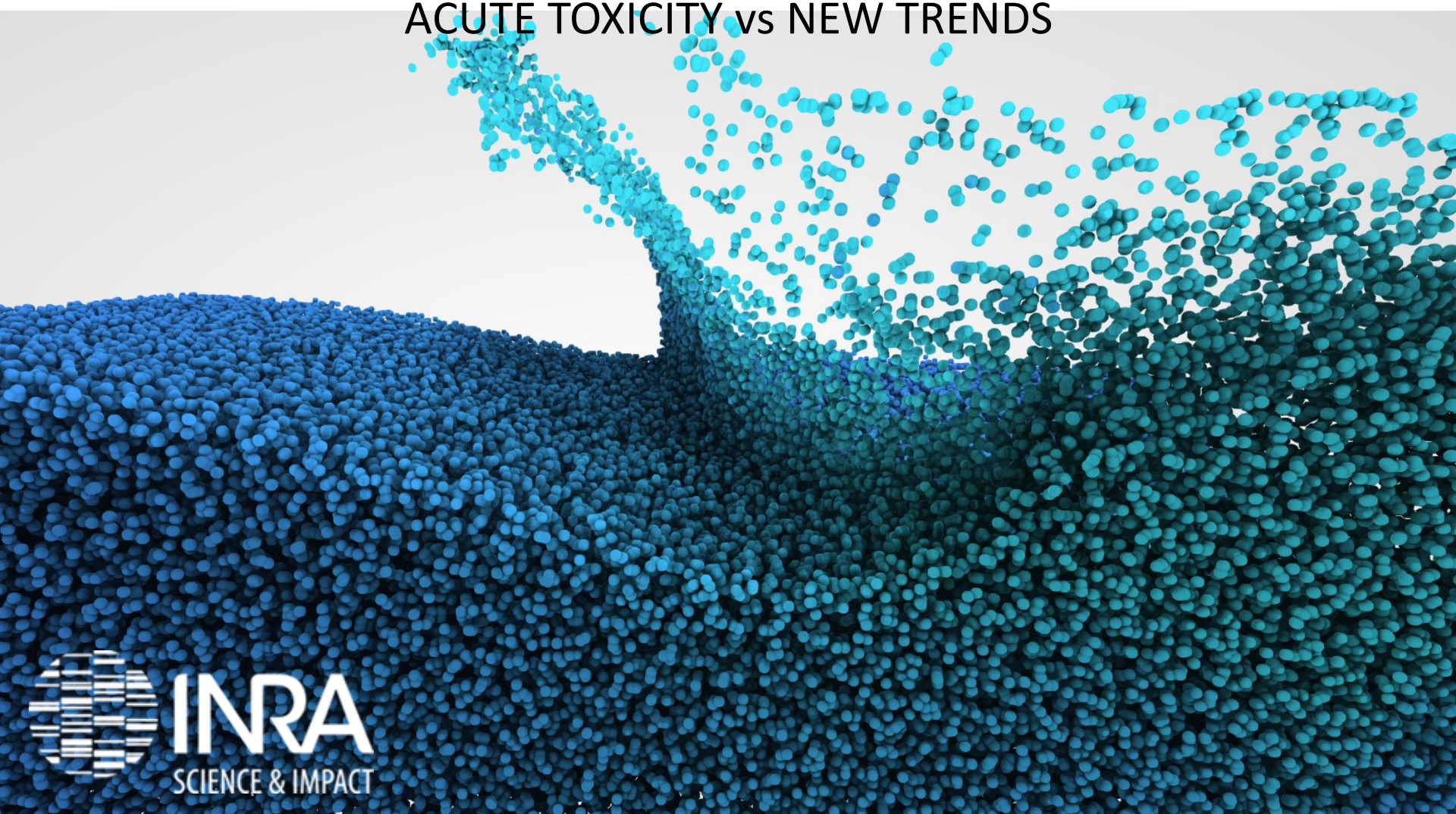
https://github.com/ovitrac/FMECAengine

ISO-MIGRATION: TIME x TEMPERATURE x M
ISO-TIME: CONTAMINATION x TEMPERATURE x M

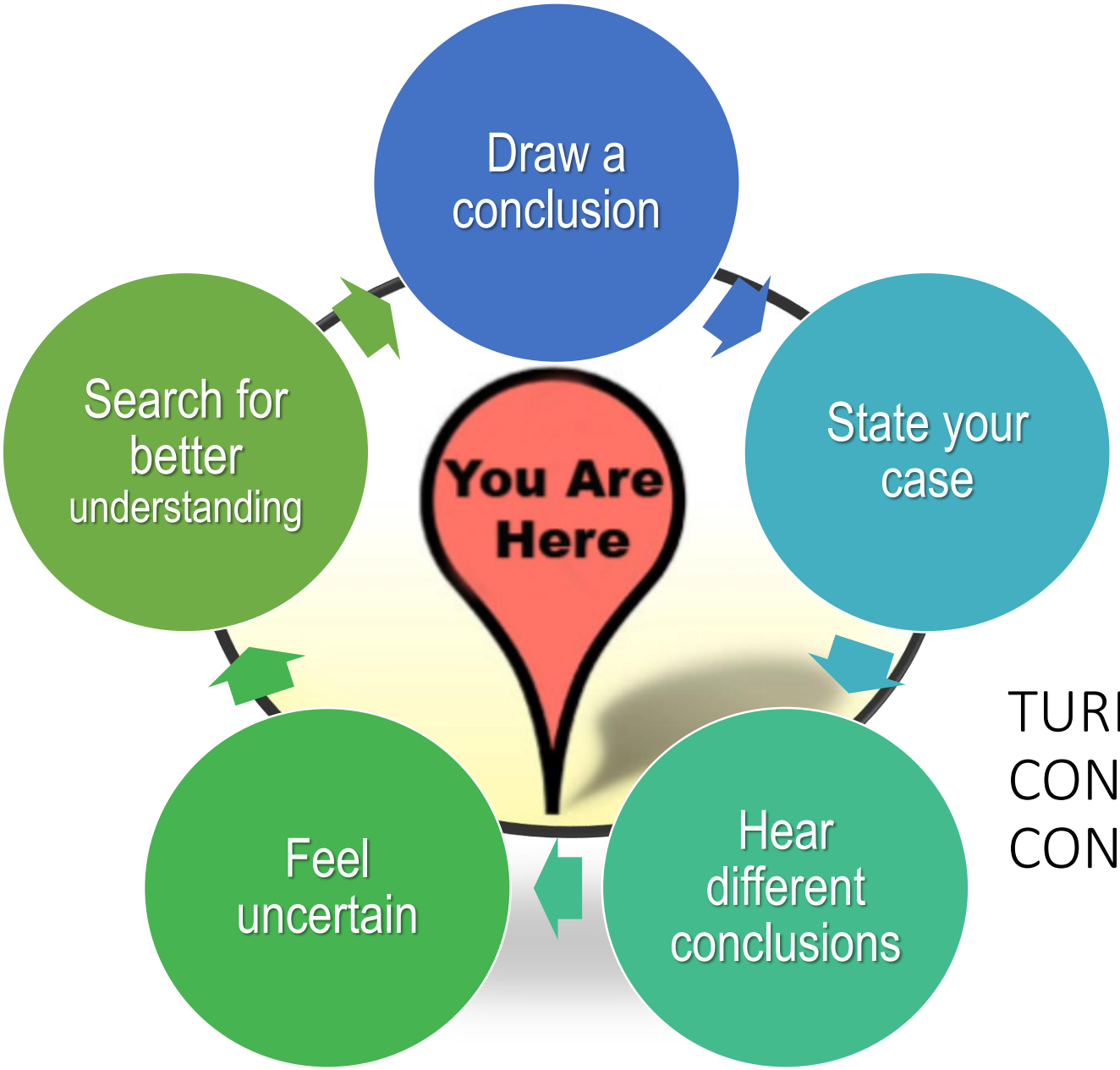


TOXICITY

ACUTE TOXICITY vs NEW TRENDS



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



TURN INTO CONSTRUCTIVE CONTROVERSY

Chemicals leaching into food from packaging raise safety concerns

Scientists, in BMJ paper, warn of potential long-term damage of exposure to synthetics, including formaldehyde in drinks bottles

Sarah Boseley, health editor
The Guardian, Wednesday 19 February 2014

Jump to comments (449)

Article history

World news
Food safety

Business
Food & drink industry

Science
Food science · Chemistry

Society
Health · Cancer · Diabetes

UK news

Environment
Pollution · Plastic bags

More news

Packaged burger and chips. Synthetic chemicals in packaging include phthalates, known to disrupt hormone production. Photograph: Martin Godwin for the Guardian

Synthetic chemicals which are used in the processing, packaging and storing of the food we eat could be doing long-term damage to our health, environmental scientists warn.

The concerns have been raised in the Journal of Epidemiology and Community Health, part of the British Medical Journal group.

The scientists claim that tiny amounts of synthetic chemicals leach into food. While these minute quantities in themselves do no harm, no one knows how safe we are from a lifetime's exposure to the chemicals, such as formaldehyde, through eating food previously wrapped or stored in plastics.

In a commentary piece in the journal the scientists note that some of the chemicals that could cause concern are regulated but this does not prevent their being used widely in food packaging. They say that people who eat packaged or processed foods are likely to be chronically exposed to low levels of these substances throughout their lives.

Far too little is known about the long-term impact and especially about our exposure to such chemicals at critical points in human development, such as in the womb and during early childhood.

More on this story

China's toxic air pollution resembles nuclear winter, say scientists
Air pollution now impeding photosynthesis and potentially wreaking havoc on country's food supply, experts warn

Air pollution: European commission launches legal action against the UK

Air pollution: how big a problem is it for

Forbes.com

Geoffrey Kabat
Contributor

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I write about the science and politics of health risks.
full bio →

OP/ED 8/20/2013 @ 8:00AM | 13,109 views

How Abysmal Scientific Research Is Used To Scare America's Parents

14 comments, 2 called-out + Comment Now + Follow Comments

Much that is published in scientific journals is of astonishingly poor quality.

We have become accustomed to a steady barrage of reports of hazards lurking in our environment that MAY pose a threat our health and that of our children.

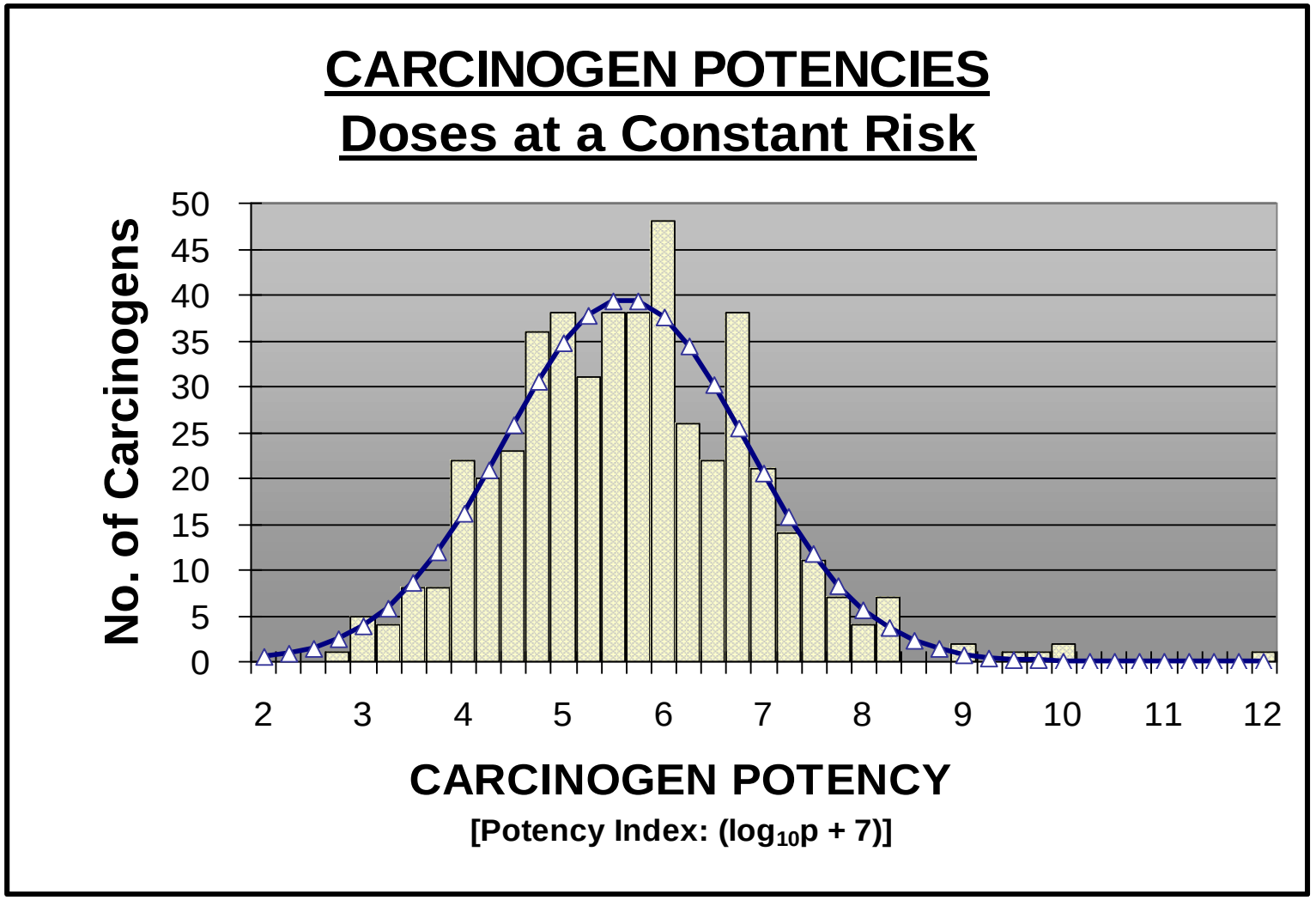
These include, among others, low-level radiation exposure from nuclear power plants and nuclear waste; possible water contamination from hydraulic fracturing; and exposure to a wide range of chemicals, including pesticides and industrial pollutants, in food, water, air, and consumer products.

Potential hazards like these need to be studied and will be studied, but the public needs to realize that much that is published in scientific journals, and even in reputable journals, can be of astonishingly poor quality and is of absolutely no relevance to non-researchers. But, far from these papers being ignored, they often get seized on by the media and high-lighted as if they provided serious, actionable evidence of a hazard.

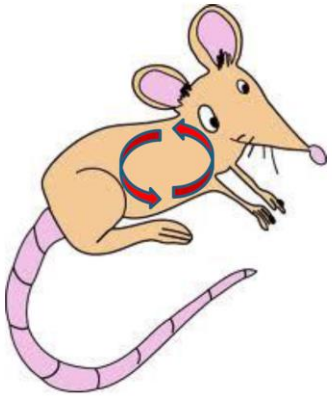
How can this happen? How do mediocre or plain-wrong studies get accepted for publication in scientific journals? In essence the explanation is simple. Scientists and scientists-in-training need to find questions to work on and need to publish their results in order to put themselves on the map and to advance in their careers. Journals want to publish articles on topics that appear to be important and that will engage readers.

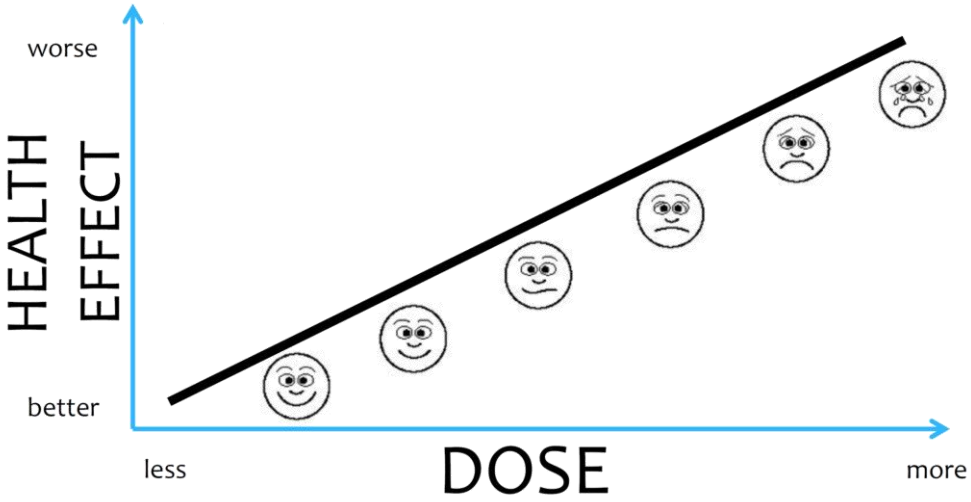
CONFERENCES AND MORE

Threshold of Regulation based on acute toxicology concepts



ACUTE TOXICOLOGY





Reference Dose

LOAEL

NOAEL

Max Tolerated Intake

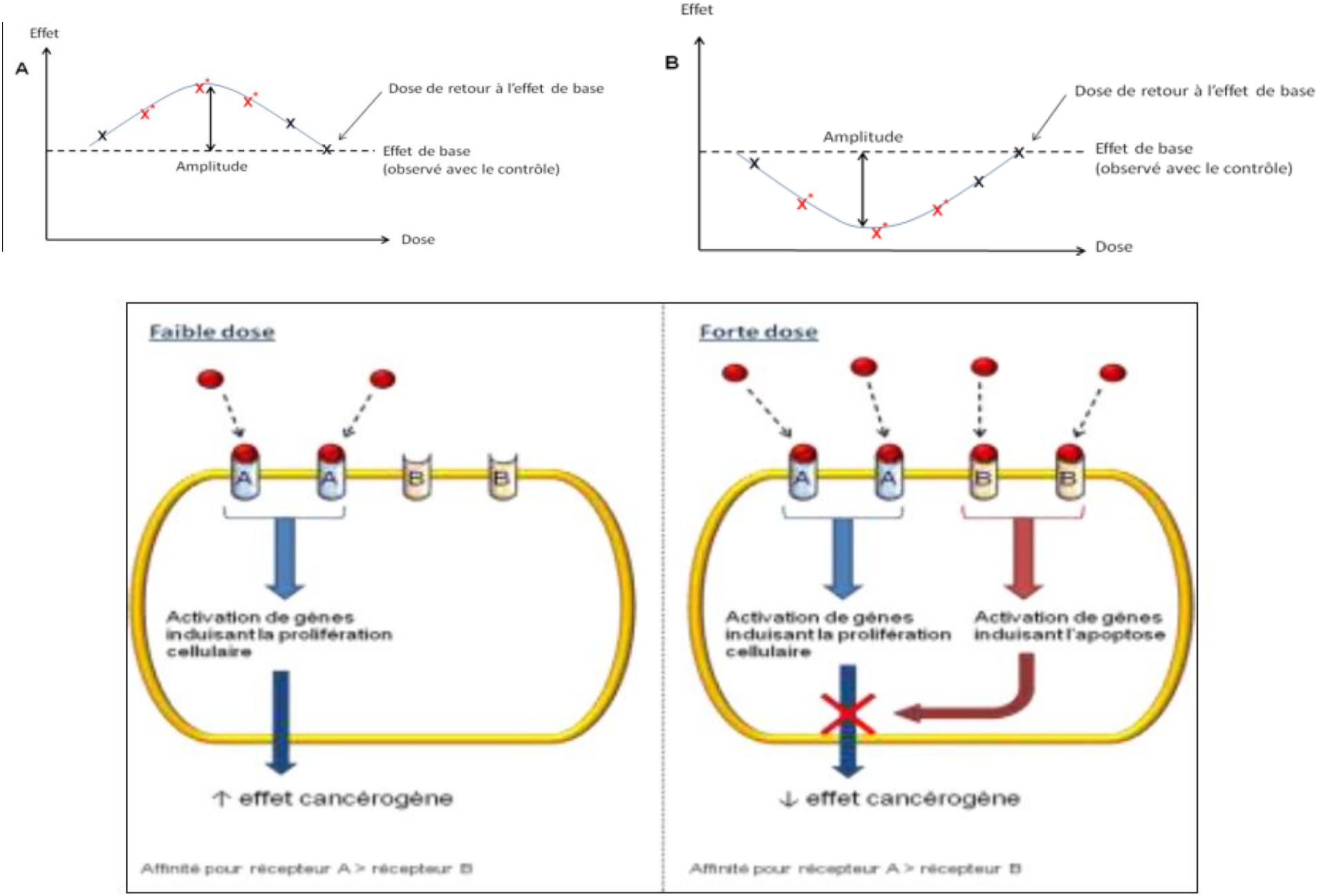
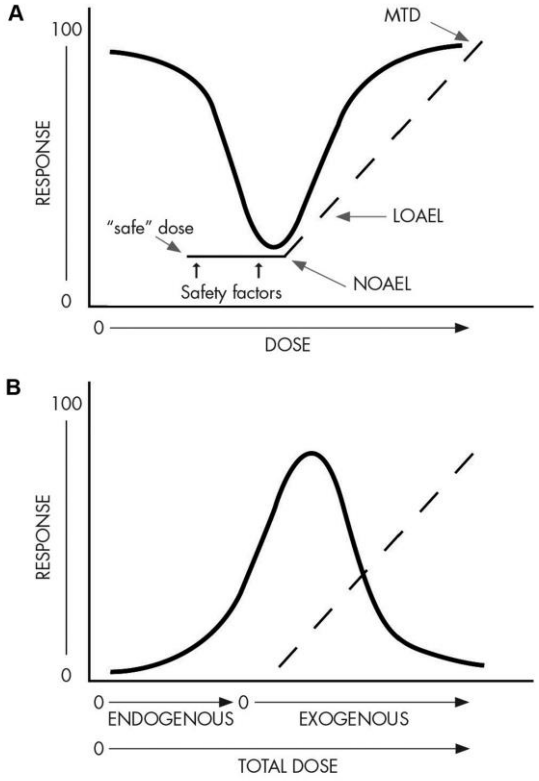


Figure 3 : Equilibre entre effets prolifératifs et pro-apoptotiques selon la dose

800 studies



Hormones and Endocrine-Disrupting Chemicals: Low-Dose Effects and Nonmonotonic Dose Responses

Laura N. Vandenberg, Theo Colborn, Tyrone B. Hayes, Jerrold J. Heindel, David R. Jacobs, Jr., Duk-Hee Lee, Toshi Shioda, Ana M. Soto, Frederick S. vom Saal, Wade V. Welshons, R. Thomas Zoeller, and John Peterson Myers

Center for Regenerative and Developmental Biology and Department of Biology (L.N.V.), Tufts University, Medford, Massachusetts 02155; The Endocrine Disruption Exchange (T.C.), Paonia, Colorado 81428; Laboratory for Integrative Studies in Amphibian Biology (T.B.H.), Molecular Toxicology, Group in Endocrinology, Energy and Resources Group, Museum of Vertebrate Zoology, and Department of Integrative Biology, University of California, Berkeley, California 94720; Division of Extramural Research and Training (J.J.H.), National Institute of Environmental Health Sciences, National Institutes of Health, U.S. Department of Health and Human Services, Research Triangle Park, North Carolina 27709; Division of Epidemiology and Community Health (D.R.J.), School of Public Health, University of Minnesota, Minneapolis, Minnesota 55455; Department of Preventive Medicine (D.-H.L.), School of Medicine, Kyungpook National University, Daegu 702-701, Korea; Molecular Profiling Laboratory (T.S.), Massachusetts General Hospital Center for Cancer Research, Charlestown, Massachusetts 02129; Department of Anatomy and Cellular Biology (A.M.S.), Tufts University School of Medicine, Boston, Massachusetts 02111; Division of Biological Sciences (F.S.v.S.) and Department of Biomedical Sciences (W.V.W.), University of Missouri-Columbia, Columbia, Missouri 65211; Biology Department (T.Z.), University of Massachusetts-Amherst, Amherst, Massachusetts 01003; and Environmental Health Sciences (J.P.M.), Charlottesville, Virginia 22902

TABLE 1. Low-dose definitions and cutoff doses: BPA and DEHP as examples

Chemical	Estimated range of human exposures	Doses below the NOAEL	Doses below the LOAEL	Administered doses (to animals) that produce blood levels in typical humans
BPA	0.4–5 μg/kg · d (679)	No NOAEL was ever established in toxicological studies (38)	<50 mg/kg · d (38)	~400 μg/kg · d to rodents and nonhuman primates (4, 253)
DEHP	0.5–25 μg/kg · d (680)	<5.8 mg/kg · d (681, 682)	<29 mg/kg · d (681, 682)	Unknown

Estimates of human exposure are made from consumer product consumption data but do not take into account that there are unknown sources of these chemicals. DEHP, Bis(2-ethylhexyl) phthalate.

Endocrine Reviews, 2012, 33(3):378–455

• LOW-DOSE EFFECT SUBSTANCES

Hormones and Endocrine-Disrupting Chemicals: Low-Dose Effects and Nonmonotonic Dose Responses

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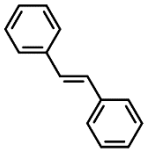
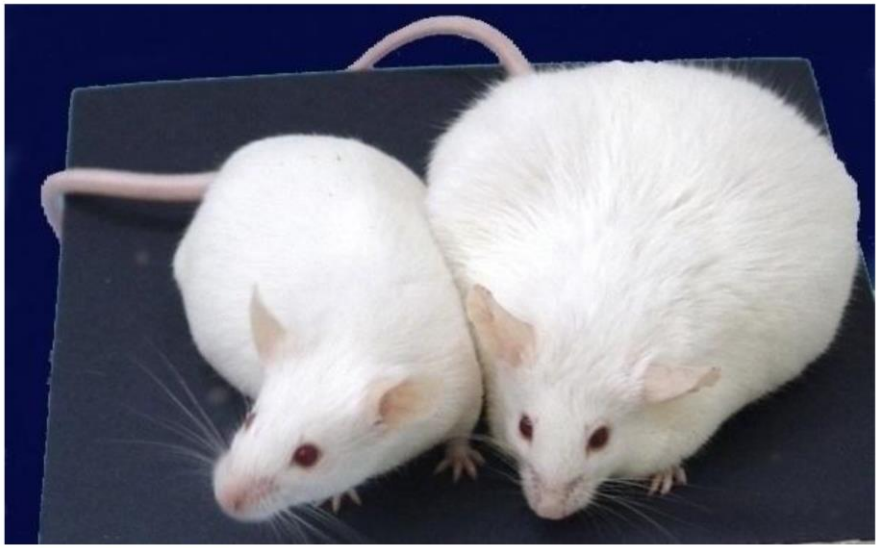
TABLE 4. Select examples of EDCs whose potential low-dose effects on animals remain to be studied

Chemical	Use	EDC action	Low-dose cutoff
Antiseptics and preservatives			
Butyl paraben	Preservative (cosmetics)	Estrogenic, antiandrogenic	2 mg/kg · d (EPA)
Propyl paraben	Antimicrobial preservative found in pharmaceuticals, foods, cosmetics, and shampoos	Estrogenic activity	LOAEL 10 mg/kg · d, NOEL 6.5 mg/kg · d (Europa)
Cosmetics and personal care products			
2,4-Dihydroxybenzophenone	UV absorber in polymers, sunscreen agent	Estrogenic activity	Not identified
3-Benzylidene camphor	UV blocker used in personal care products	Estrogenic activity	0.07 mg/kg · d (710)
4,4′-Dihydroxybenzophenone	UV light stabilizer used in plastics, cosmetics, adhesives, and optical fiber	Estrogenic activity	Not identified
Benzophenone-2	Used in personal care products such as aftershave and fragrances	Estrogenic activity, changes in T_4, T_3, and TSH levels, alterations in cholesterol profile	NOEL 10–333 mg/kg · d (711)
Benzophenone-3	UV filter	Estrogenic, PPARγ activator	200 mg/kg · d (Europa)
Multiple use (other)			
Melamine	Flame-retardant additive and rust remover; used to make laminate, textile, and paper resins; metabolite of cyromazine	Affects voltage-gated K^+ and Na^+ channels and Ca^{2+} concentrations in hippocampal neurons	63.0 mg/kg · d (FDA)
Resorcinol	Used in the manufacturing of cosmetics, dyes, flame retardants, hair dye formulations, pharmaceuticals, skin creams, and tires	Alters T_4 and TSH levels	80.00 mg/kg · d (Europa)
Pesticides			
Aldrin[a]	Insecticide	Estrogenic activity	0.025 mg/kg · d (Health Canada)
Alachlor	Herbicide	Decreases serum T_4, binds PR, weakly binds ER	1 mg/kg · d (EPA)
Amitrole	Herbicide	Decreases thyroid hormone	0.12 mg/kg · d (FAO)
Bitertanol	Fungicide	Alters aromatase	30 mg/kg · d (EPA)
Carbendazim	Fungicide	Affects FSH, LH, and testosterone levels; alters spermatogenesis and Sertoli cell morphology	8 mg/kg · d (712)
Diazinon	Insecticide	Alters glucocorticoids	0.065 mg/kg · d (CDC)
Endrin[a]	Insecticide	Stimulates glucocorticoid receptor	0.025 mg/kg · d (CDC)
Fenoxycarb	Insecticide	Alters acetylcholinesterase	260 mg/kg · d (CDC)
Mirex[a]	Insecticide	Decreases testosterone levels	0.075 mg/kg · d (CDC)
Zineb	Fungicide	Alters T_4 and dopamine levels	LOAEL 25 mg/kg · d (EPA)
Ziram	Fungicide	Alters norepinephrine levels	1.6 mg/kg · d (EPA)
Resins			
Bisphenol F	Used in polycarbonates	Alters T_4, T_3, and adiponectin levels, has estrogenic activity	LOAEL 20 mg/kg · d (713)
Styrene	Precursor to polystyrene	Alters dopamine	200 mg/kg · d (EPA)



DIETHYLSTILBESTROL

- HIGH DOSE: 10 000 PPB EXPOSURE
- LOW DOSE: 1 PPB EXPOSURE



Newbold RR, Padilla-Banks E, Jefferson WN, Heindel JJ 2008 Effects of endocrine disruptors on obesity. Int J Androl 31:201–208

CONTROVERSY O OF PACKAGING MATERIA

Nat. Rev. Endocrin. 6 (2010), 237

Water Research 46(2012), 571-583

Editorial

Nature Reviews Endocrinology 6, 237 (May 2010) |

Subject Category: Epidemiology

The perils of plastic

Vicky Heath About the author

A 'round-robin' spam e-mail that is circulating on servers worldwide claims that drinking bottled water that has been left in a warm car can cause breast cancer. Is this warning just an urban myth or does it hold a grain of truth? The FDA, it seems, is erring on the side of caution; earlier this year, the organization revised its position on the safety of bisphenol A (BPA), a chemical used in the manufacture of plastics. Previously deemed safe for food-contact use, the FDA has now expressed "some concern" about the potential health risks that BPA poses to fetuses, infants and young children.

"The plastics industry has a responsibility to ensure that its products are safe..."

Is society compromising its health for the conveniences of modern living? Industrial chemicals, such as BPA, are literally everywhere: in homes, in the workplace, even the great outdoors. They cannot possibly all be avoided. Given the current recommendations of the FDA and the Endocrine Society, a multidisciplinary approach is clearly needed—one that involves scientists, clinicians, policy makers and the chemicals industry—with the aim of gathering reliable data to form the basis of national and international public-health policies. In the meantime, the use of plastics and other man-made substances should be closely monitored in groups known to be at the greatest risk. Perhaps that e-mail is not spam after all.

[…]

Genotoxic and estrogenic activities in PET-bottled water have been reported. Chemical mixtures in bottled water have been suggested as the source of these toxicological effects. […]

Formaldehyde, acetaldehyde and antimony are clearly related to migration from PET into water. However, several studies have shown other theoretically unexpected substances in bottled water. The origin of these compounds has not been clearly established (PET container, cap-sealing resins, background contamination, water processing steps, NIAS, recycled PET, etc.).

[….]

ESTROGENIC COMPOUNDS FROM PET??

2 RECENT STUDIES (Italian and German) on drinking water

1) **involving a recombinant yeast–based in vitro assay** (March 2009 in *International Journal of Hygiene and Environmental Health*) ➔**estrogenic activity was assessed in 30 PET–bottled mineral water samples. Ninety percent of the samples tested negative for estrogenic activity. Of the remaining samples, most showed measurements corresponding to a range of 14–23 ng/L estradiol equivalents—similar to the estrogen burden posed by treated drinking water derived from groundwater and river water (15 and 17 ng/L estradiol equivalents, respectively).**

2) **Involving mud snails (*Potamopyrgus antipodarum*) (10 March 2009, *Environmental Science and Pollution Research*) ➔ PET-housed snails produced up to twice as many embryos as glass-housed snails..**

Reference = glass bottle water with same water.

epidemiologist at the University of Rochester School of Medicine and Dentistry in New York.

"This is coming at a good time because the use of bottles for consuming water is getting very bad press now because of its carbon footprint," she says. "It's just another nail in the coffin of bottled water, the way I see it."

Wagner and a colleague used genetically engineered yeast to analyse 20 samples of mineral water. Nine samples came out of glass bottles, nine were bottled in PET plastic and two were in cardboard, juice-like boxes.

The specialised yeast, which change colour in the presence of estrogen-like compounds, revealed estrogenic activity in seven of the nine plastic bottles (and both cardboard samples), compared with just three of the nine glass ones.

Overall, Wagner says, levels of these compounds in the water were surprisingly high.

l'augmentation du niveau d'obésité dans les populations occidentales. Plusieurs centaines de substances sont actuellement classées parmi les perturbateurs endocriniens.

Où les trouve-t-on ?

Ces molécules sont principalement détectées dans l'eau, puis dans toute la chaîne alimentaire. De plus, comme viennent de le montrer Martin Wagner et Jörg Oehlmann de l'université Goethe de Frankfort [1], peut-être aussi dans le plastique des bouteilles d'eau minérales en polyéthylène téréphtalate (PET).

RISK ASSESSMENT

efsa

European Food Safety Authority

http://www.efsa.europa.eu

Scientific Committee

Senior scientists, with experience of work within scientific bodies, covering all disciplines across EFSA's areas of responsibility.

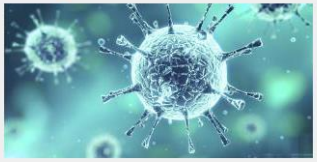
AHAW

Panel on Animal Health and Welfare
Experts in toxicology, toxicity, epidemiology, chemistry, exposure assessment, and microbiology.

ANS

Panel on Food Additives and Nutrient Sources Added to Food
Experts in toxicology, toxicity, epidemiology, chemistry, exposure assessment, and microbiology.

BIOHAZ



Panel on Biological Hazards
Experts in epidemiology, microbiology, pathology, and exposure assessment.

CONTAM

Panel on Contaminants in the Food Chain
Experts in chemistry, exposure assessment, toxicology, epidemiology, and statistics

CEF

Panel on Food Contact Materials, Enzymes, Flavourings and Processing Aids
Panel on Food Contact Materials, Enzymes, Flavourings and Processing Aids

GMO

Panel on Genetically Modified Organisms
Experts in food and feed safety assessment, environmental sciences, molecular characterisation, and plant science.

NDA

Panel on Dietetic Products, Nutrition and Allergies
Experts in nutrition, human medicine, exposure assessment, toxicology

PLH

Panel on Plant Health
Experts in pest risk assessment, plant pathology, epidemiology, and ecology.

FEEDAP

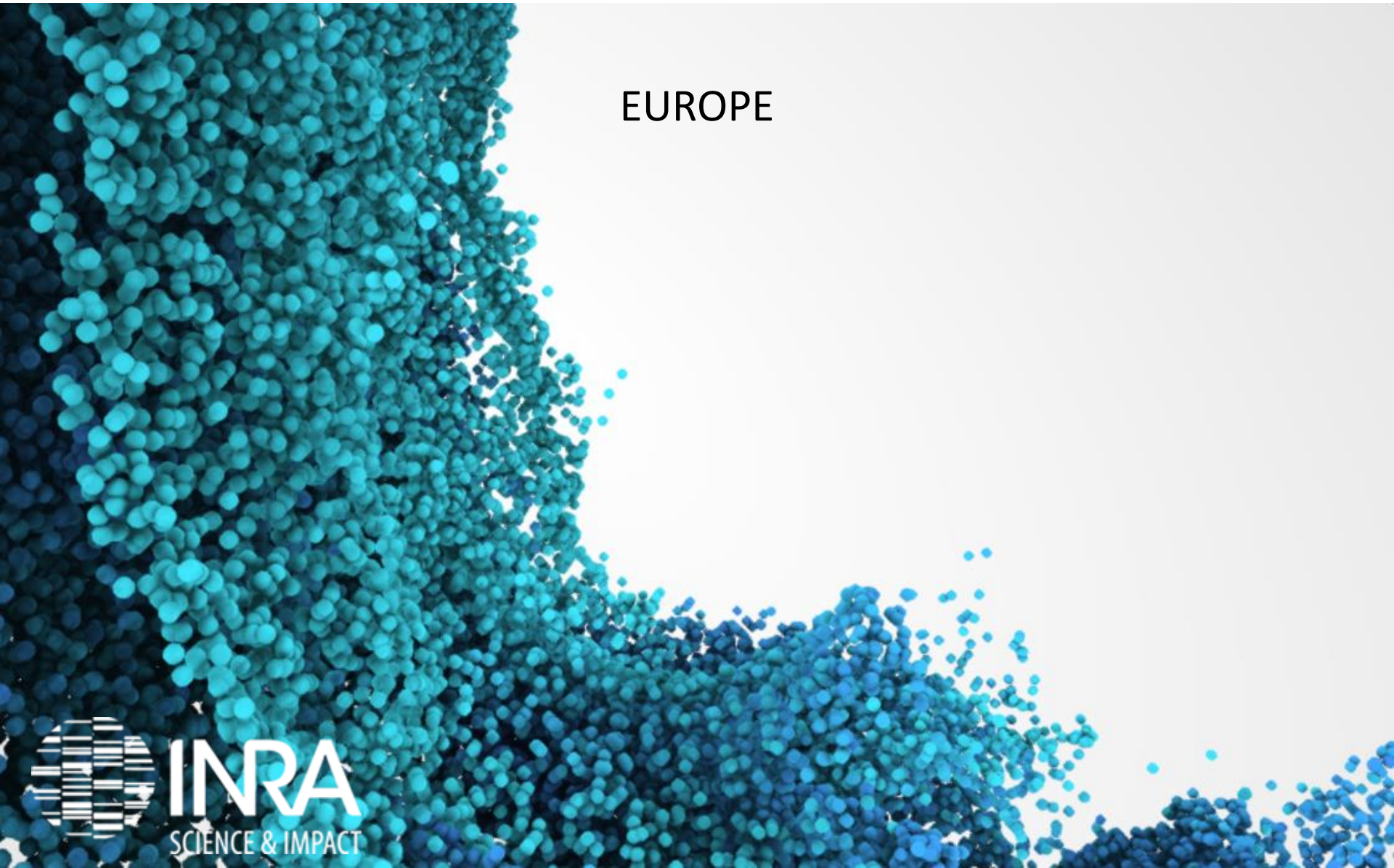
Panel on Additives and Products or Substances used in Animal Feed
Experts in animal nutrition, toxicology, microbiology, exposure assessment, and

PPR

Panel on Plant Protection Products and their Residues
Experts in chemistry, toxicology,

INRA

REGULATION



PRINCIPLES OF FOOD INERTIA: A LONG HISTORY

L'ART DE CONSERVER,

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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

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 révèlerait 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-

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

YOUR ROLE

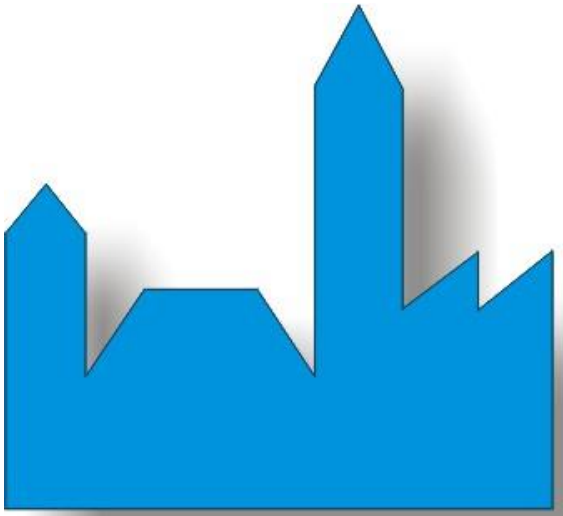
ROUTINE ASSESSMENT

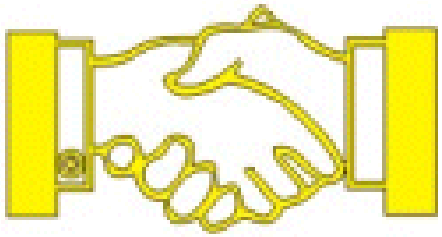
	Scientifc risk assessment	Risk balancing	Risk Tradeoff
role ↓		Conflict Evaluative	Conflicts cognitive, evaluative, normative
Routine	Conflict: cognitive	Targets: BfR, anses, ISTITUTO SUPERIORE DI SANITÀ, FOOD STANDARDS AGENCY, efsa European Food Safety Authority	Targets:DG SANCO, industry stakeholders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

WHAT IS RISK?

Risk is a function of perception and representation

REGULATION=TRANSFER OF RESPONSABILITIES





EXPERTISE, DIAGNOSIS

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 perform safety assessments of substances used to manufacture FCMs involving the European Food Safety Authority
- rules on labelling including an indication for use (e.g. as a coffee machine, a wine bottle, or a soup spoon) or by reproducing the appropriate symbol. For more information, please refer to the following document on Symbols for labelling food contact materials.
- for compliance documentation and traceability

Regulation on Good Manufacturing Practices

Regulation (EC) No 2023/2006 ensures that that the manufacturing process is well controlled so that the specifications for FCMs remain in conformity with the legislation:

- premises fit for purpose and staff awareness of critical production stages
- documented quality assurance and quality control systems maintained at the premises, and
- selection of suitable starting materials for the manufacturing process with a view to the safety and inertness of the final articles

Good manufacturing rules apply to all stages in the manufacturing chain of food contact materials, although the production of starting materials is covered by other legislation.

II. EU legislation on specific materials

In addition to the general legislation, certain FCMs — ceramic materials, regenerated cellulose film, plastics (including recycled plastic), as well as active and intelligent materials — are covered by specific EU measures. There are also specific rules on some starting substances used to produce FCMs.

[Expand All]

- Plastic Materials
- Active and Intelligent Materials
- Recycled Plastic Materials
- Ceramics
- Regenerated Cellulose Film

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

Overview of Community legislation (last update 20/10/2009)

1935/2004/EC

GMP

Inertie

EU REGULATION

(EC) No 1935/2004 Framework

2023/2006/EC Good Manufacturing practice *(applicable to all Food Contact Materials)*

2007/42/EC Regenerated Cellulose Film

84/500/EEC Ceramics

2005/31/EC 1st amendment

Regulation 10/2011/EC

Plastic Materials + Coatings

Elastomers and Rubbers

(EC) No 450/2009 Active and intelligent materials

93/11/EEC Nitrosamines

Thermopl.

2002/72/EC Monomers Additives

2004/1/EC 1st amendment

2004/19/EC 2nd amendment

2005/79/EC 3rd amendment

2007/19/EC 4th amendment

2008/39/EC 5th amendment

(EC) No 975/2009 6th amendment

78/142/EEC Vinyl Chloride

80/766/EEC VC in PVC analysis

81/432/EEC VC in food analysis

Joints

372/2007/EC Transitional migration limits for plasticizers in gaskets in lids

82/711/EEC Migration Testing

93/8/EEC 1st amendment

97/48/EC 2nd amendment

Test

(EC) No 282/2008 Recycled Plastics

1895/2005/EC BADGE/BFDGE/ NOGE

85/572/EC List of simulants

Vernis

PET

Paper and Board

Glass

Wood

Cork

Metals and alloys

Textiles

Adhesives

Ion-exchange resins

Printing inks

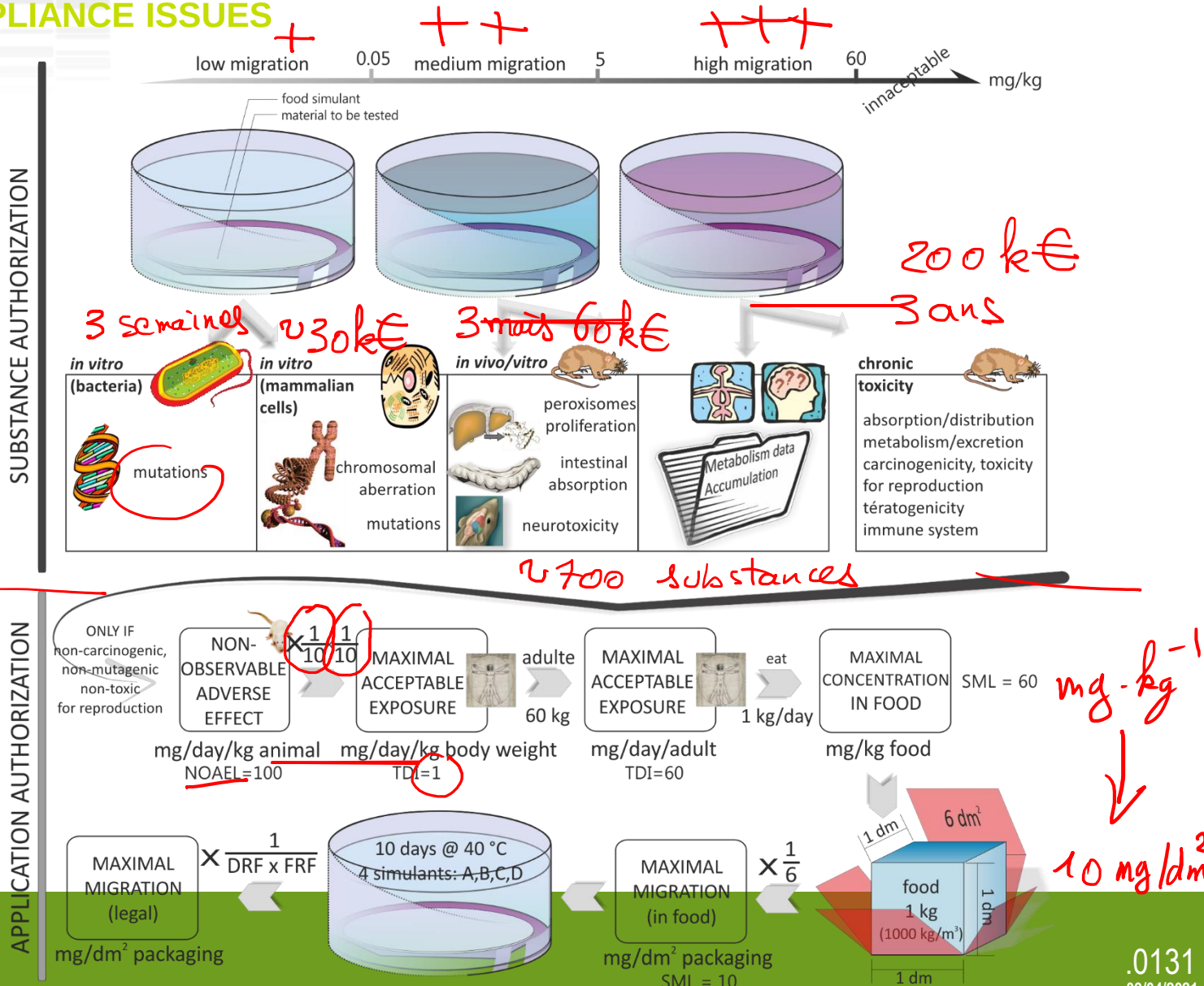
Silicones

Varnishes and coatings

Waxes

SPECIFIC RULES FOR PLASTICS

COMPLIANCE ISSUES



nouvelle substance

ITX

liste +

3 semaines ~30k€

3 mois 60k€

200 k€

3 ans

~700 substances

mg · kg⁻¹

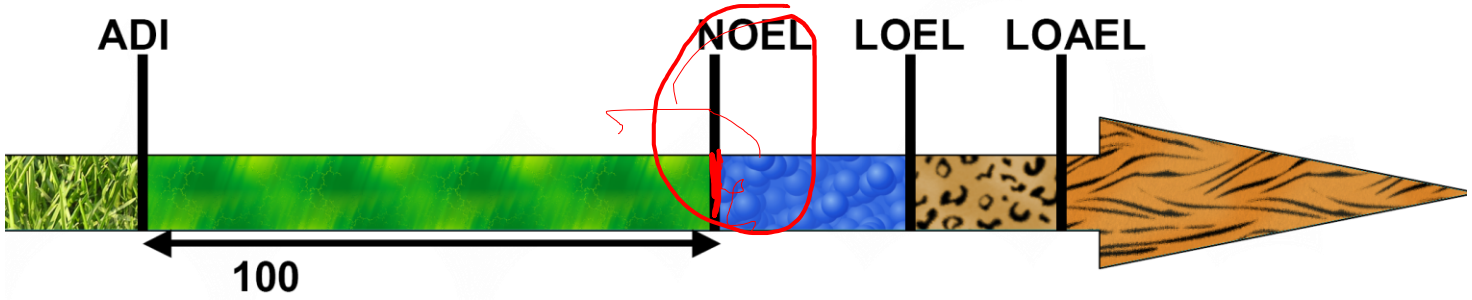
10 mg/dm²

Risk assessment vs risk management

502 substances (including 230 monomers and 272 additives) among the 937, which are positively listed in EU directives on plastics in contact with food, are subjected to (SML)

EFSA: **Risk Assessment**
ADI = NOEL/100 (per kg body weight)

DG SANCO: **Risk Management**
SML= 60 * ADI (mg intake per person per day from an assumed 1 kg packaged food)



ADI = Acceptable Daily Intake
SML = Specific Migration Level
NOEL = No Observed Effect Level
LOEL = Lowest Observed Effect Level
LOAEL = Lowest Observed Adverse Effect Level

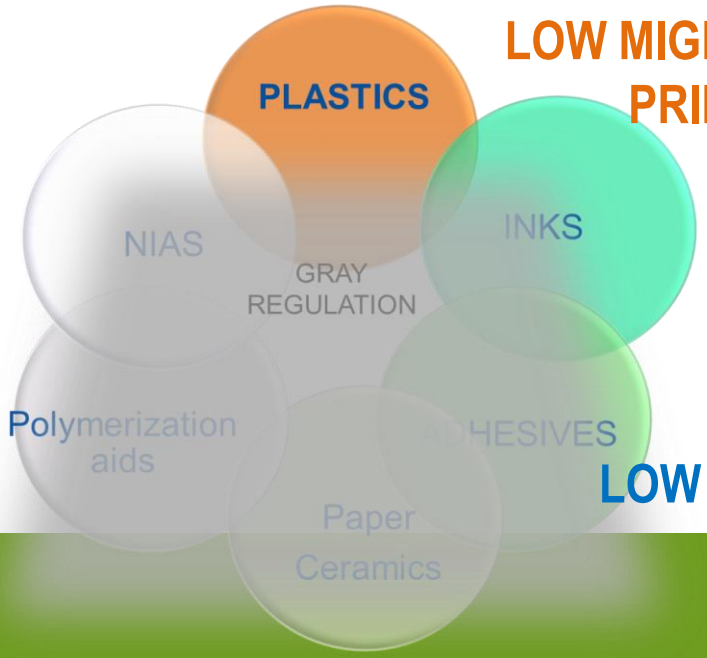
SPECIFIC EU RULES FOR PLASTICS FOR FOOD CONTACT

Materials can be regulated alone or in combination with other materials

- list of substances
- purity standard for substances
- **overall migration limits: OML (60 mg/kg or 10 mg/dm^2)**
- **specific migration limits: SML**
- other rules ensuring safety and inertness
- **compliance, sampling, analytical methods, migration modeling**
- traceability
- declaration of compliance

Plastic materials

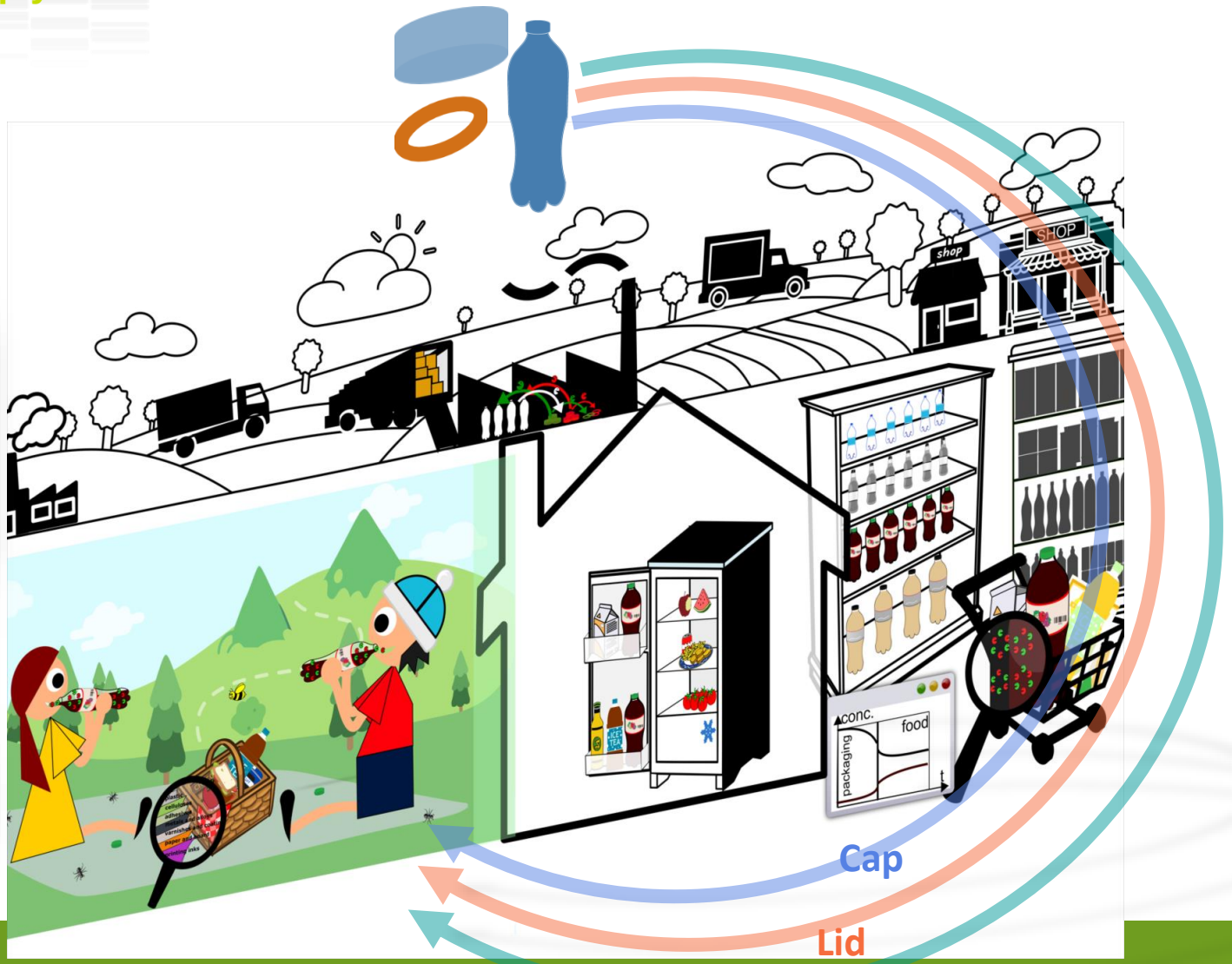
- exclusively plastics
- Plastic multilayers or layers tied with adhesives
- Plastic layers, coatings forming gaskets
- Plastic layers in multi-materials



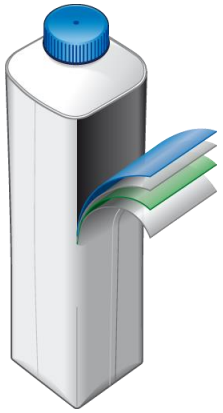

plastic
celluloses
adhesives
metals and alloys
varnishes and coatin

CHAINED STEPS, COMBINED MATERIALS

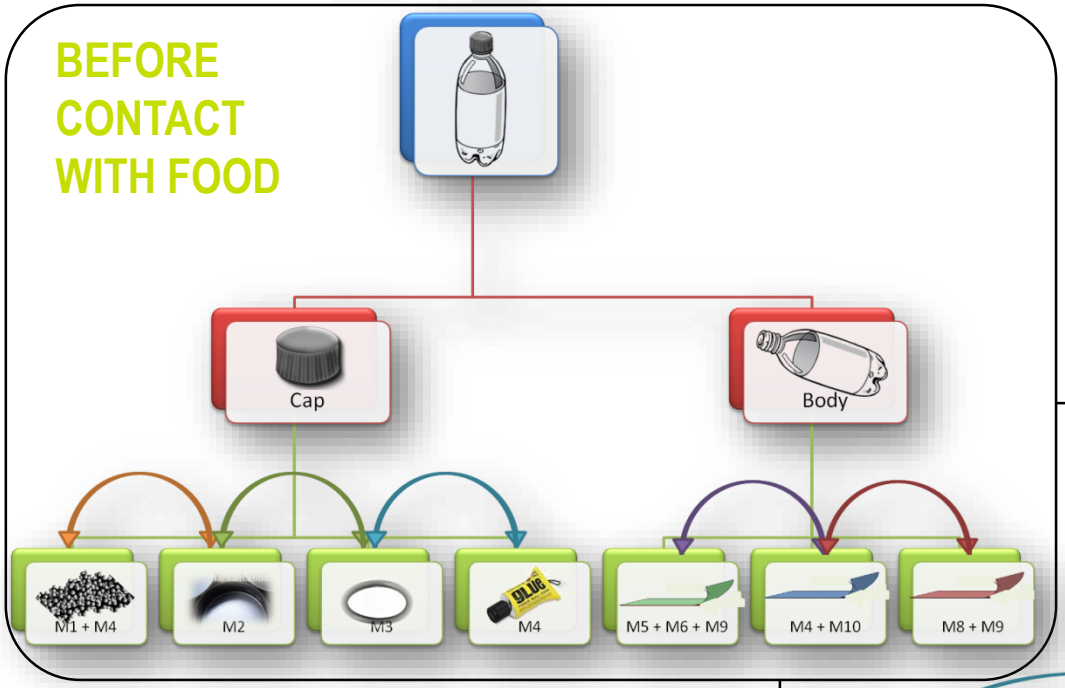
Supply chain



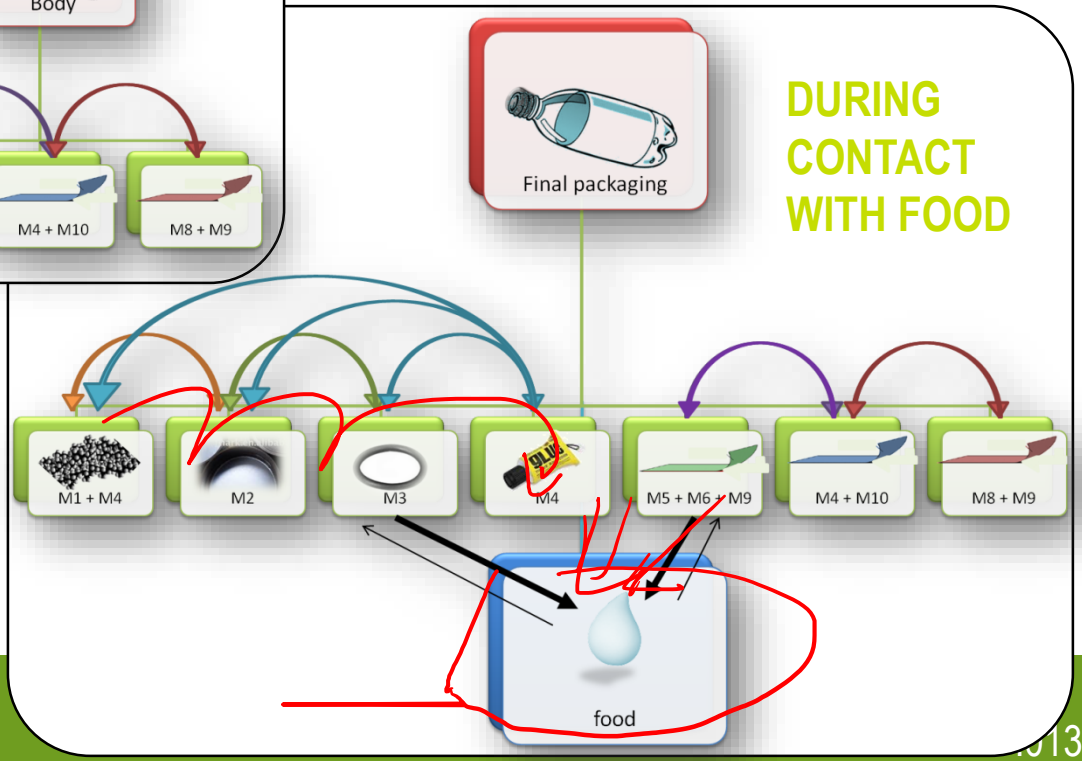
CROSSED-MASS TRANSFER BETWEEN MATERIALS



BEFORE CONTACT WITH FOOD

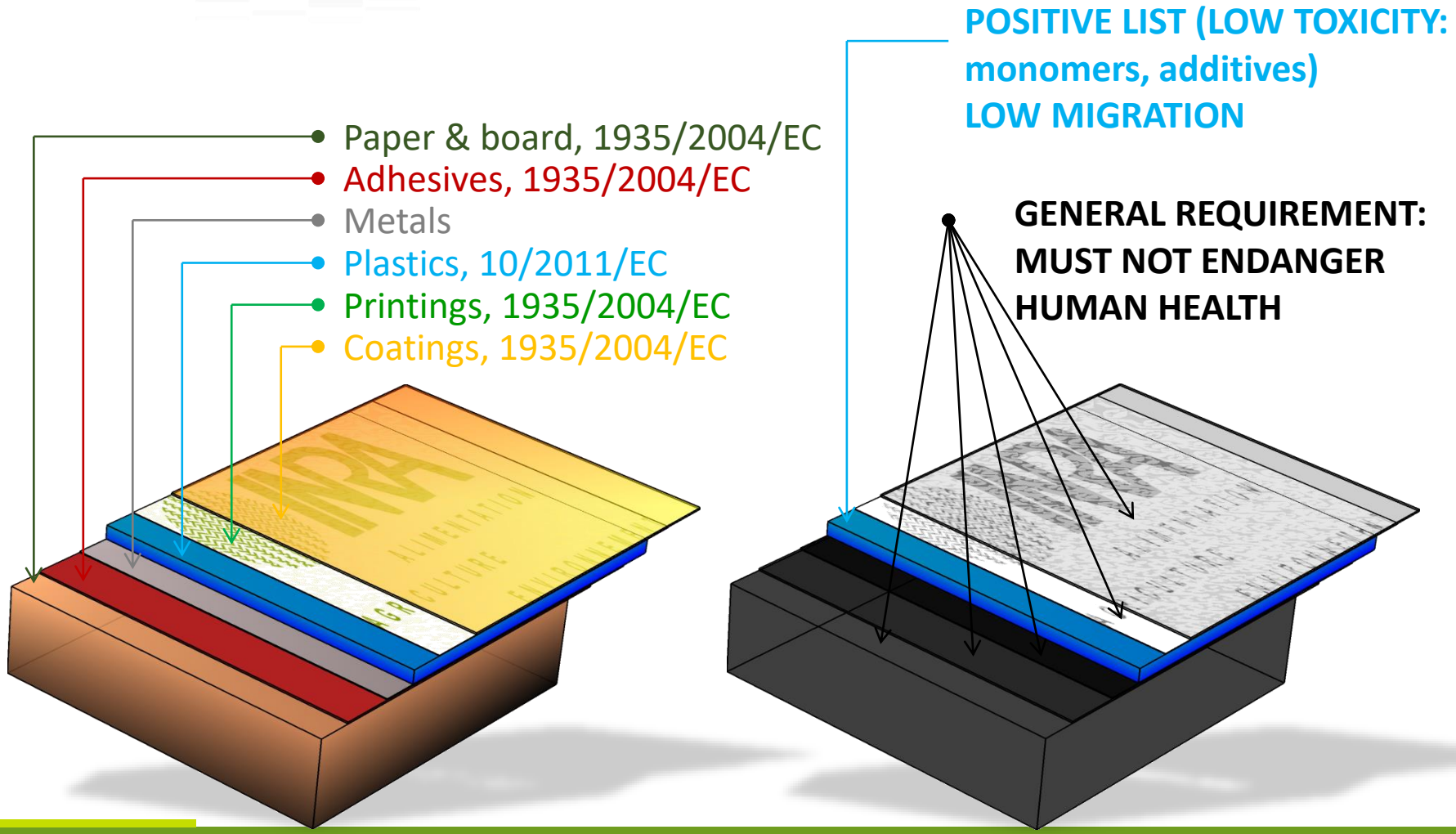


DURING CONTACT WITH FOOD

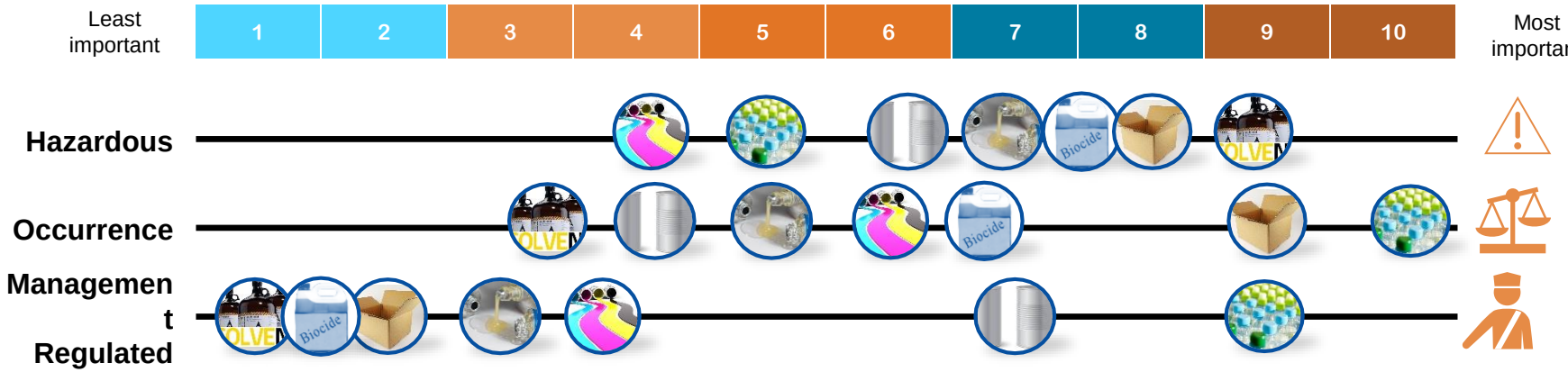


HETEROGENEOUS EU REGULATIONS

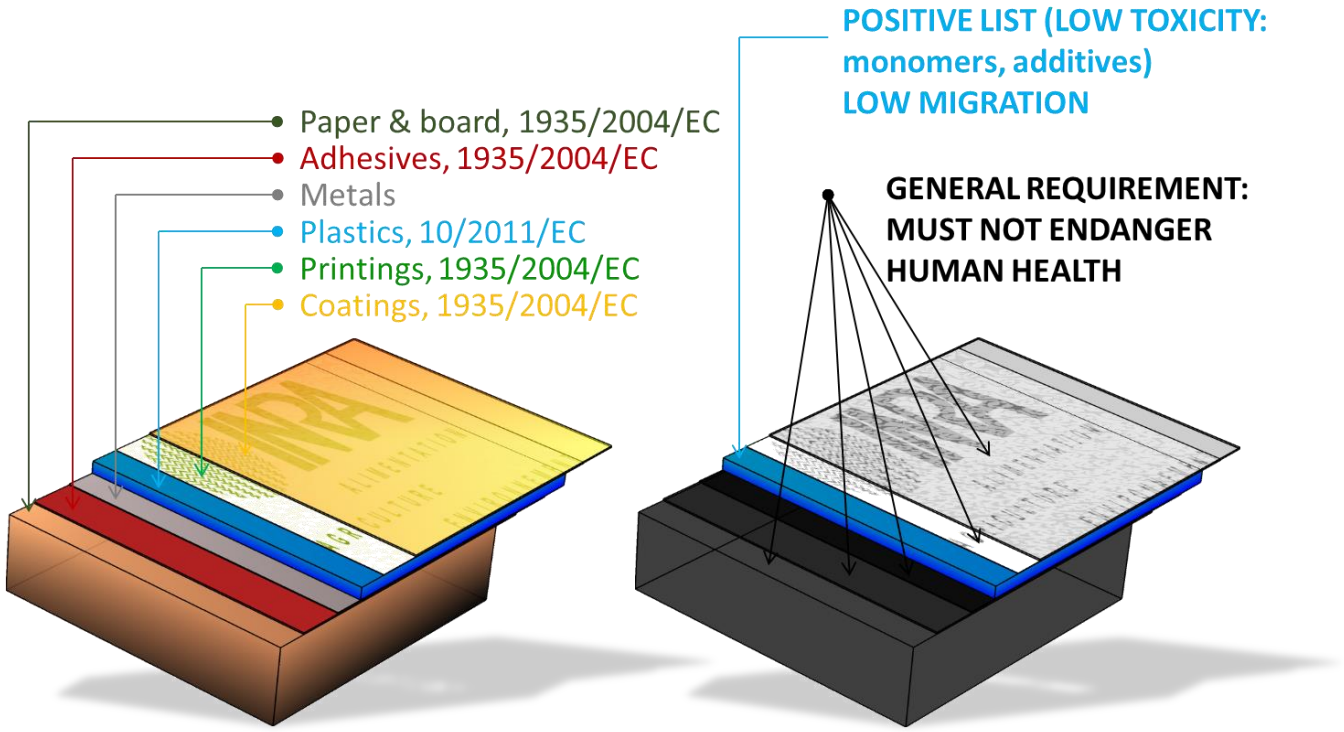
Variable concepts



17 groups of materials listed in Annex 1 of regulation 1935/2004/EC are still not covered by specific measures.
They must be produced according to **Good Manufacturing Practices** (Regulation 2023/2006/EC)
incl. 3 pillars: quality assurance system, quality control system, documentation.

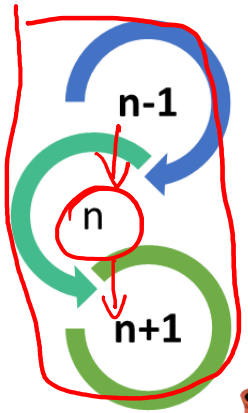

Least important
1
2
3
4
5
6
7
8
9
10
Most important
Hazardous
Occurrence
Management Regulated
Biocide
SOLVENT


Plastics
Printing inks
Adhesives
Solvents, polymerization aids
Biocides
Coatings
Paper and board


Paper & board, 1935/2004/EC
Adhesives, 1935/2004/EC
Metals
Plastics, 10/2011/EC
Printings, 1935/2004/EC
Coatings, 1935/2004/EC
POSITIVE LIST (LOW TOXICITY: monomers, additives)
LOW MIGRATION
GENERAL REQUIREMENT:
MUST NOT ENDANGER
HUMAN HEALTH

Chain of responsability along the supply chain

Material vs Information flux



PE

traceability

Upstream

e.g. Adhesive industry

Retailer

Fromage

PA

Converters

Quality Control

Packaging filler

Quality Control

Consumer

Information on composition

Information

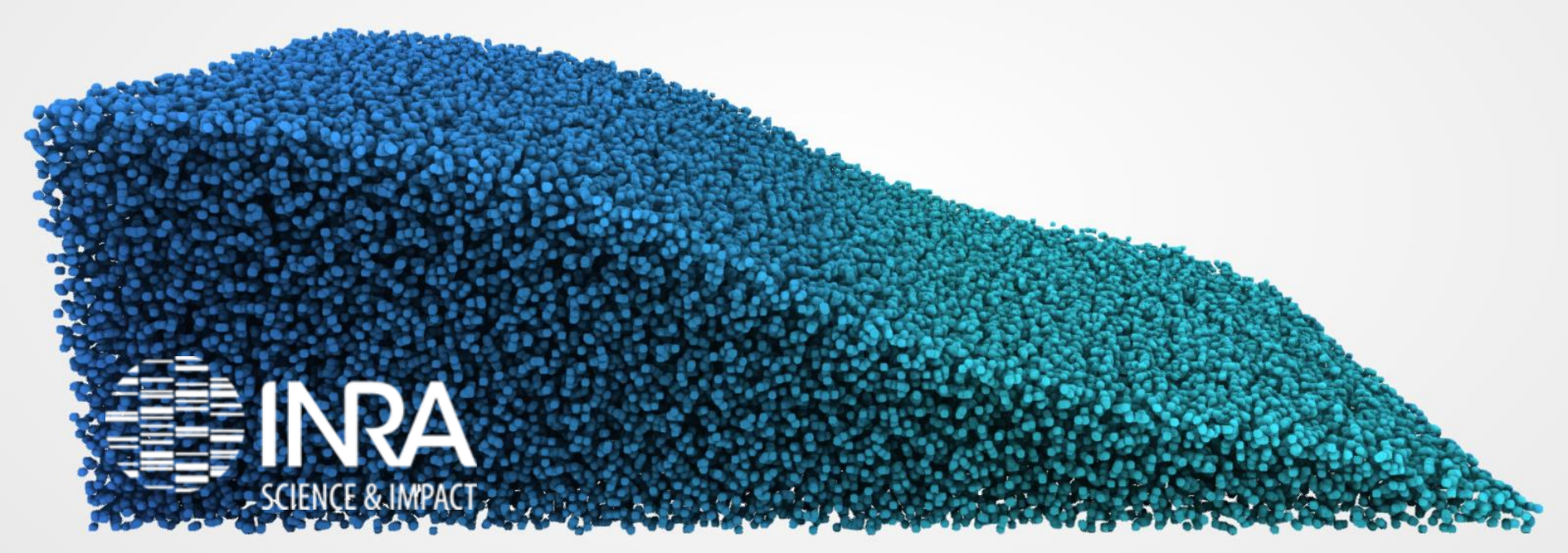
Trigger initiation/update

Trigger initiation/update

Information on final use

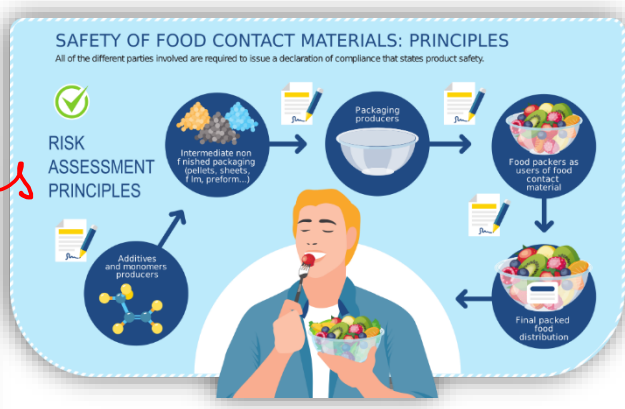
DIFFUSION IN POLYMERS

OVERVIEW, BARRIER PROPERTIES, MIGRATION ISSUES



Is migration modeling a trusted science?

EU REGULATION
10/**2011**/EC on plastics



FDA U.S. FOOD & DRUG ADMINISTRATION

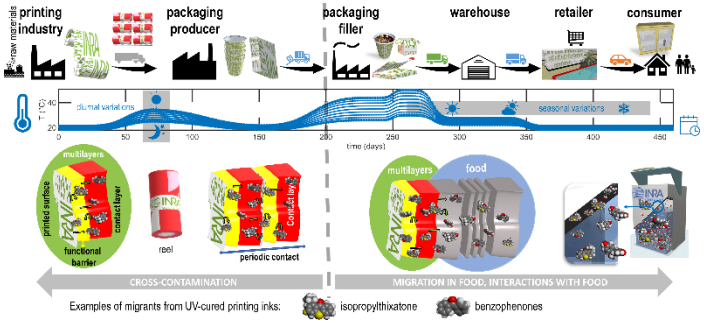
"We have reviewed the proposed recycling process as well as the information you obtained from surrogate testing and migration modeling, which were submitted to demonstrate the capability of the proposed recycling process to remove potential contaminants from PCR-PET. **Based on our review of these data, we have determined that the proposed recycling process, as described in the subject submission**, …."

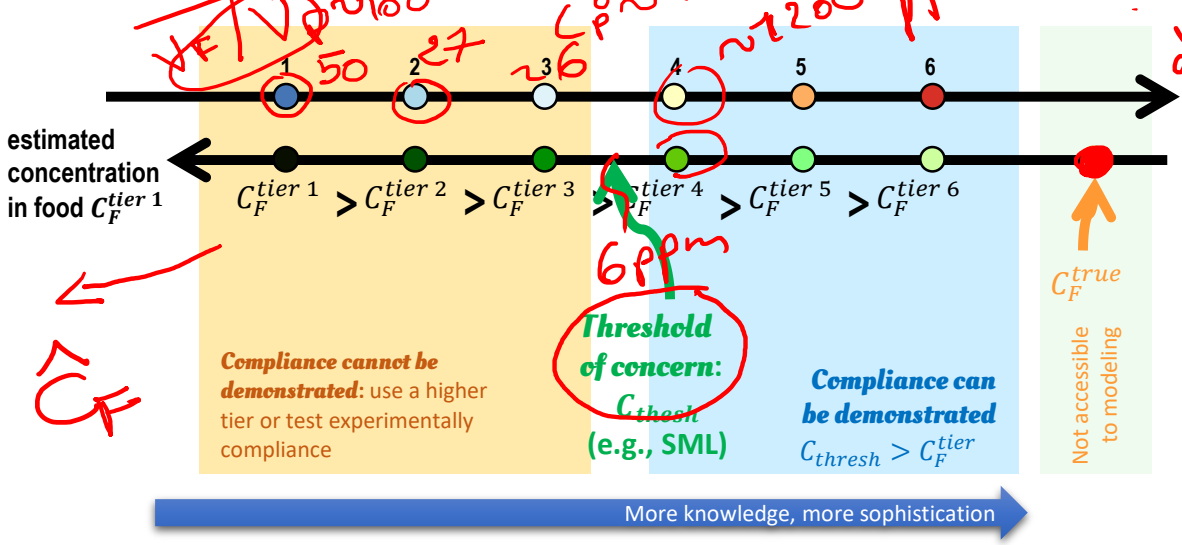
https://www.fda.gov/Food/IngredientsPackagingLabeling/PackagingFCS/RecycledPlastics/default.htm

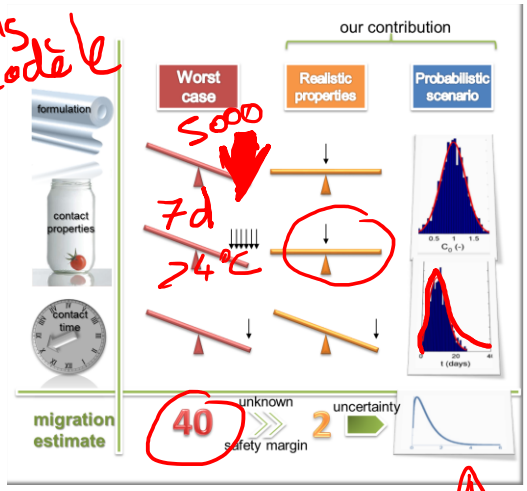
18 As migration testing is complex, costly and time consuming it should be admissible that compliance can be demonstrated also by calculations, including modelling, other analysis, and scientific evidence or reasoning if these render results which are at least as severe as the migration

The principles of migration modeling = Tier modeling

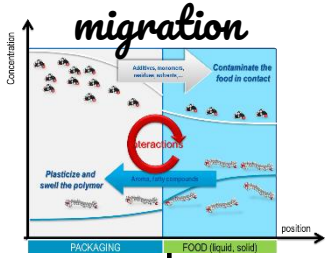
- ***conservatism***: modeling overestimates real migration.
- ***reliability***: mass transfer pathways and substances obey to well-described mechanisms
- ***consistency***: $D_{i,P}$ and $K_{i,F/P}$ are enough known with enough conservatism.
- ***parsimony***: sophisticated and refined scenarios should be considered only when simplified ones fail.
- ***proportionality***: non-compliance cannot be demonstrated by calculation.







Migration pathways where modeling is applied



direct contact

without food

heat curing

UV curing

with food

liquid

solid

without contact

paper & board

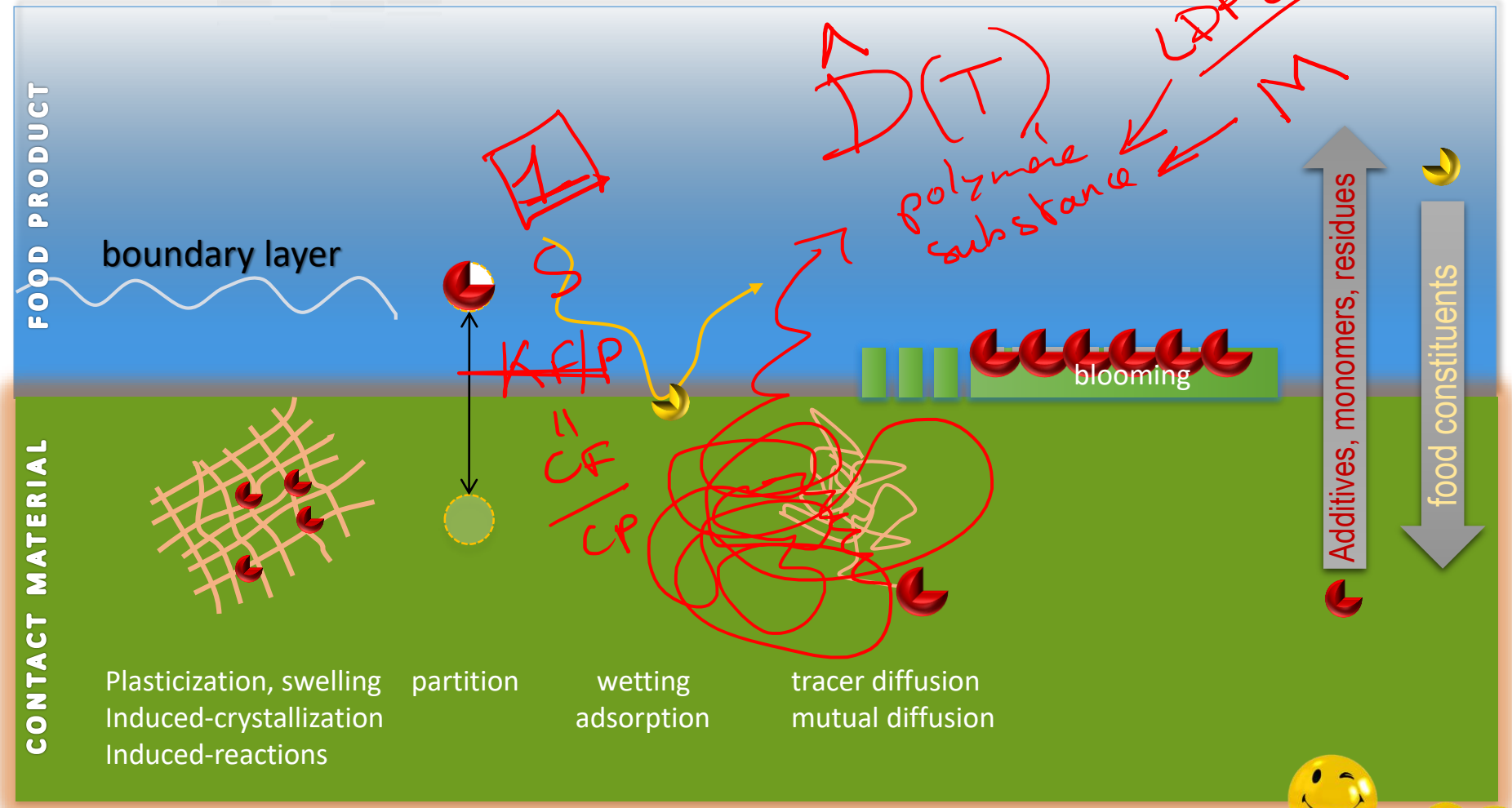
others

additive

food constituent

MIGRATION ISSUES

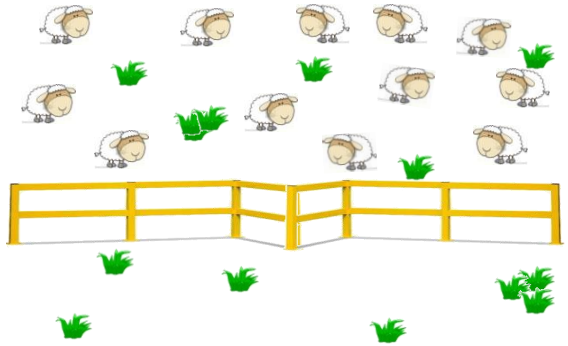
CROSSED MASS TRANSFER OF FOOD CONTACT MATERIALS AND FOOD CONSTITUENTS

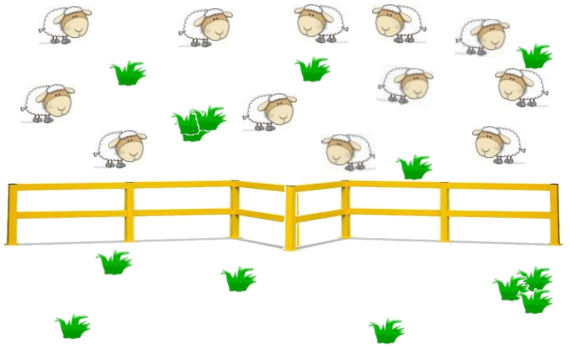


D small

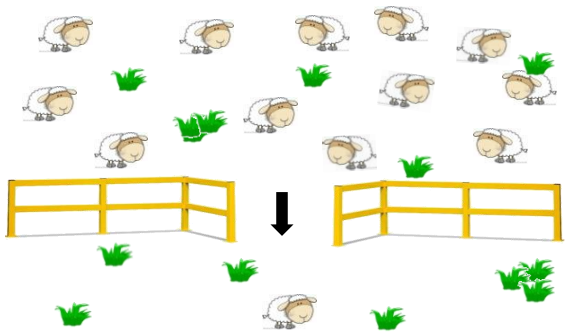
D large

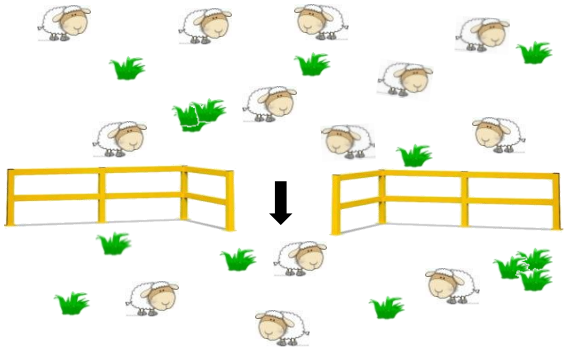
t_0 = 0 hour

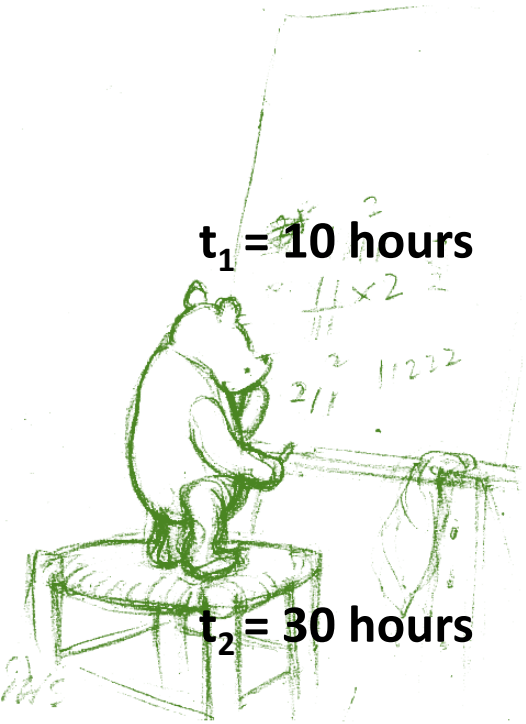




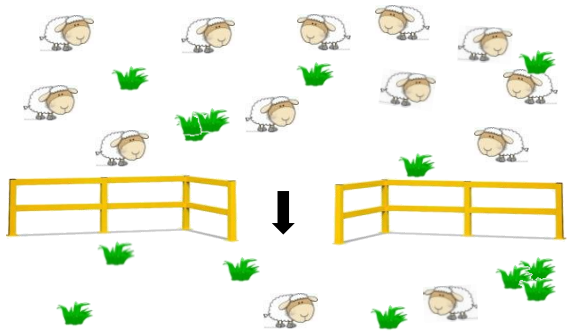
t_1 = 10 hours

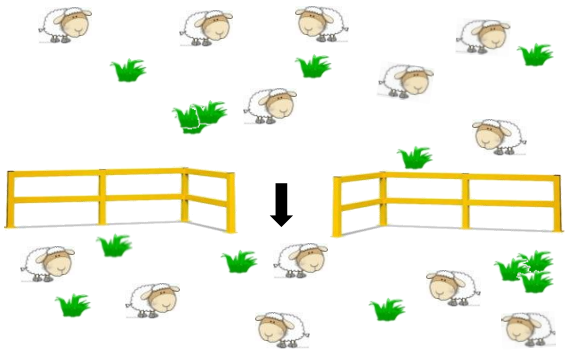






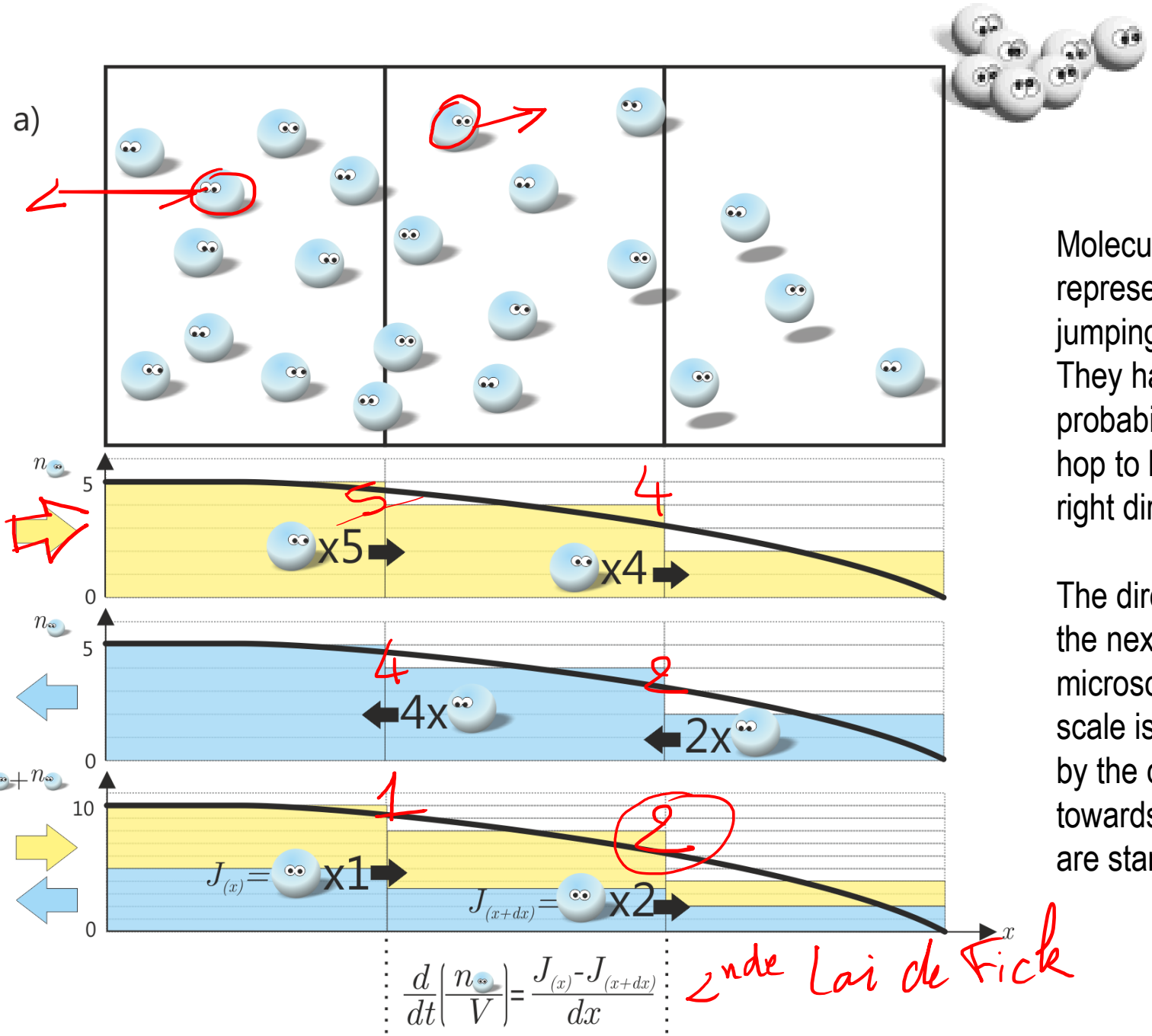
t_2 = 30 hours





$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right)$$

MOLECULAR DIFFUSION

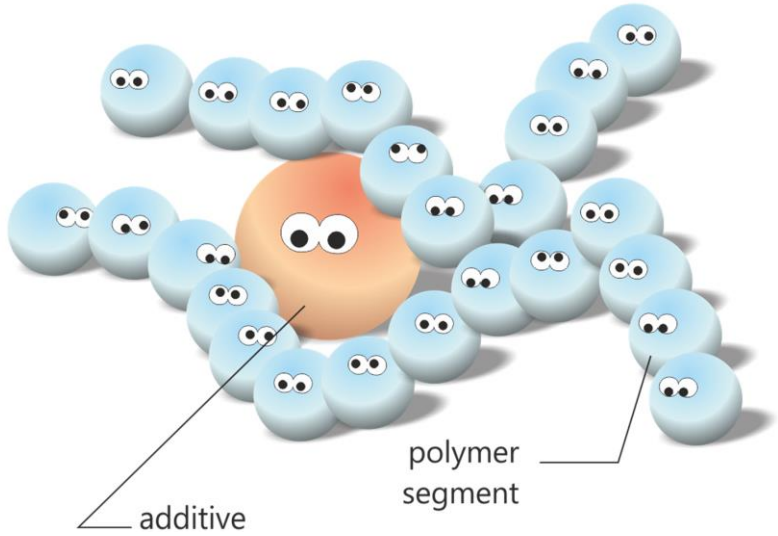


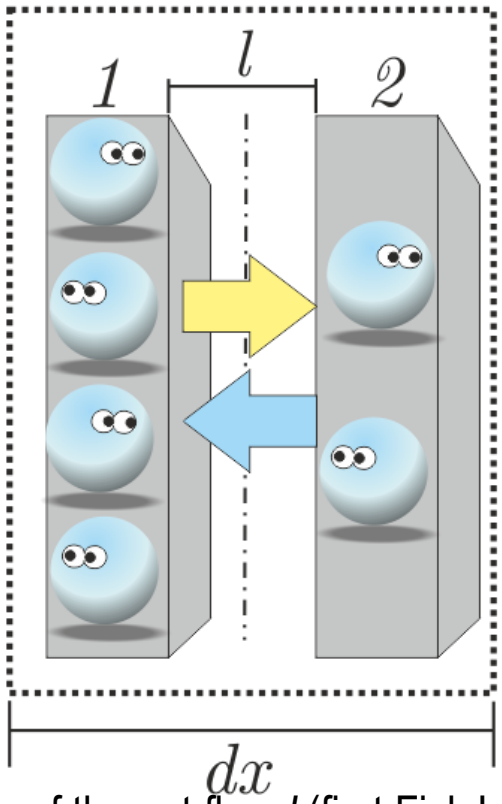
Molecules are represented as jumping beads. They have equal probabilities to hop to left and right directions.

The direction of the next hop at microscopic scale is indicated by the direction towards beads are staring.

MICROSCOPIC RANDOM-WALK

Mutual diffusion of additive
Among polymer segments





$$j_{\rightarrow} = \nu \cdot n^1 = \frac{1}{2} \cdot \nu \cdot n^1$$

$$j_{\leftarrow} = \nu \cdot n^2 = \frac{1}{2} \cdot \nu \cdot n^2$$

$$\frac{dc}{dx} = \frac{n^2/l - n^1/l}{l}$$

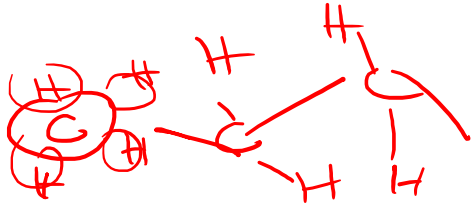
$$J = j_{\rightarrow} - j_{\leftarrow} = -\frac{1}{2} \cdot \nu \cdot l^2 \cdot \frac{dc}{dx}$$

D

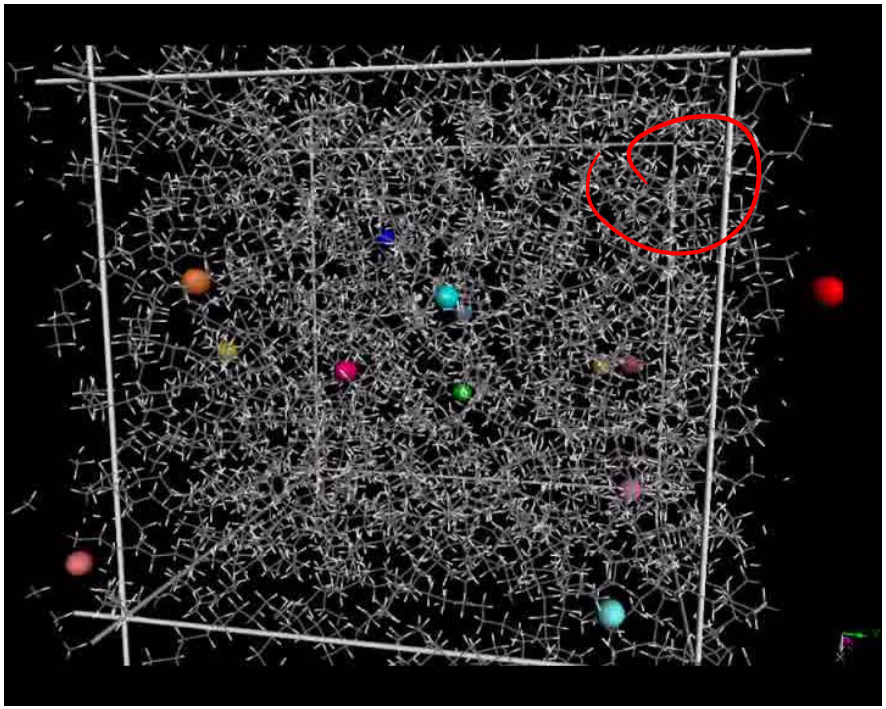
Interpretation of the net flux *J* (first Fick Law) as the microscopic exchange of molecules at frequency *v* between states 1 and 2 separated by a distance *dx*.

DIFFUSION IN POLYETHYLENE (0.5 NS SIMULATION, T=298 K)

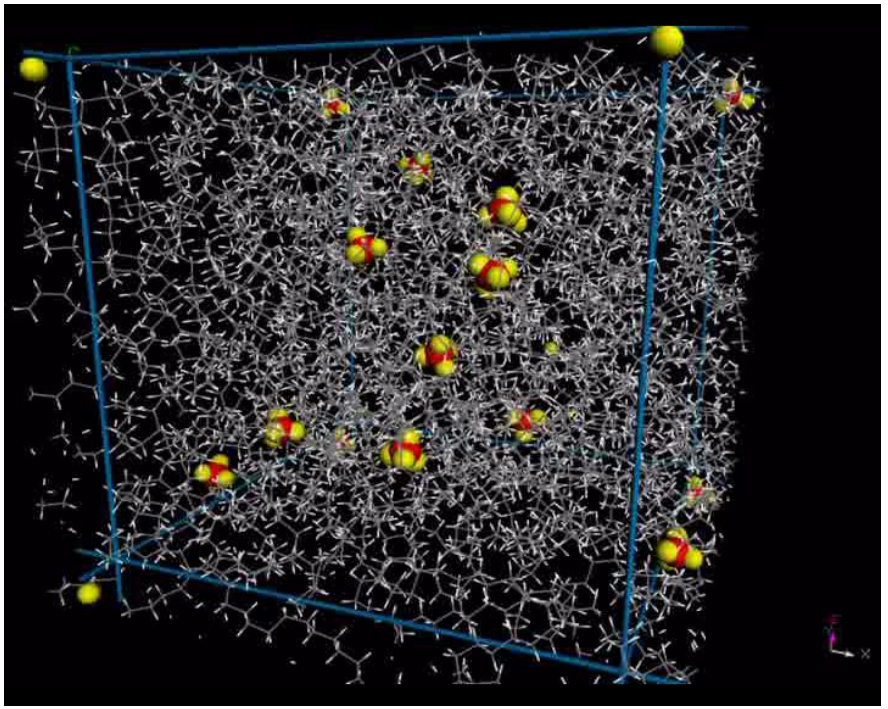
LDPE @ 25°C



10 molecules of helium



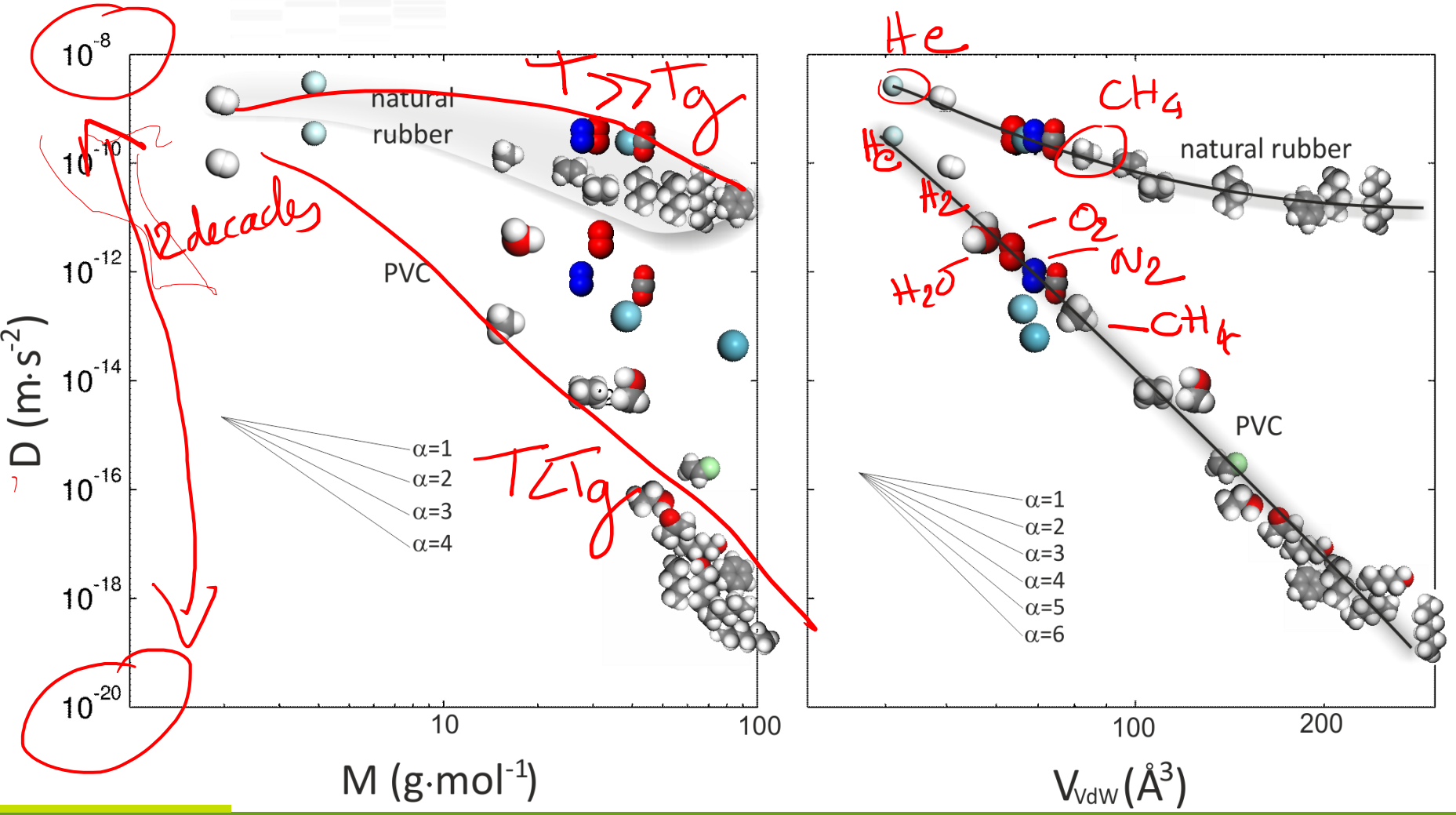
10 molecules of methane



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

SCALING D WITH SOLUTE SIZE

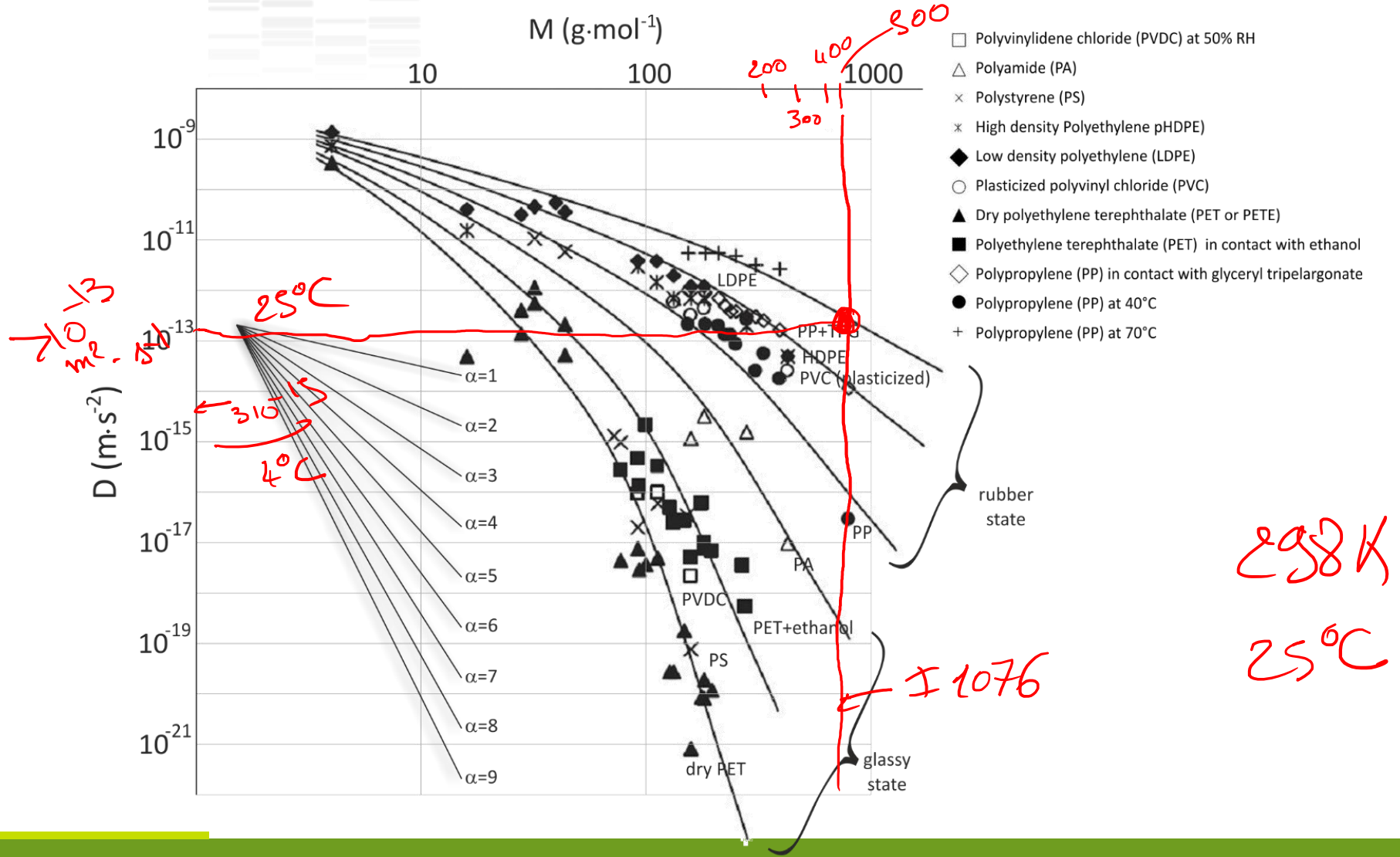
STIFF DIFFUSANTS



From: A. R. Berens, Pure Appl. Chem., **1981**, 53, 365

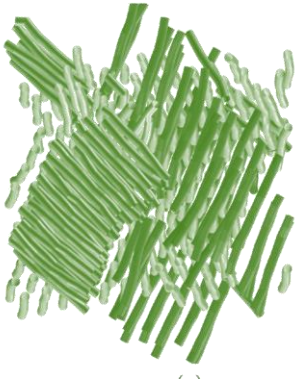
SCALING EXPONENTS

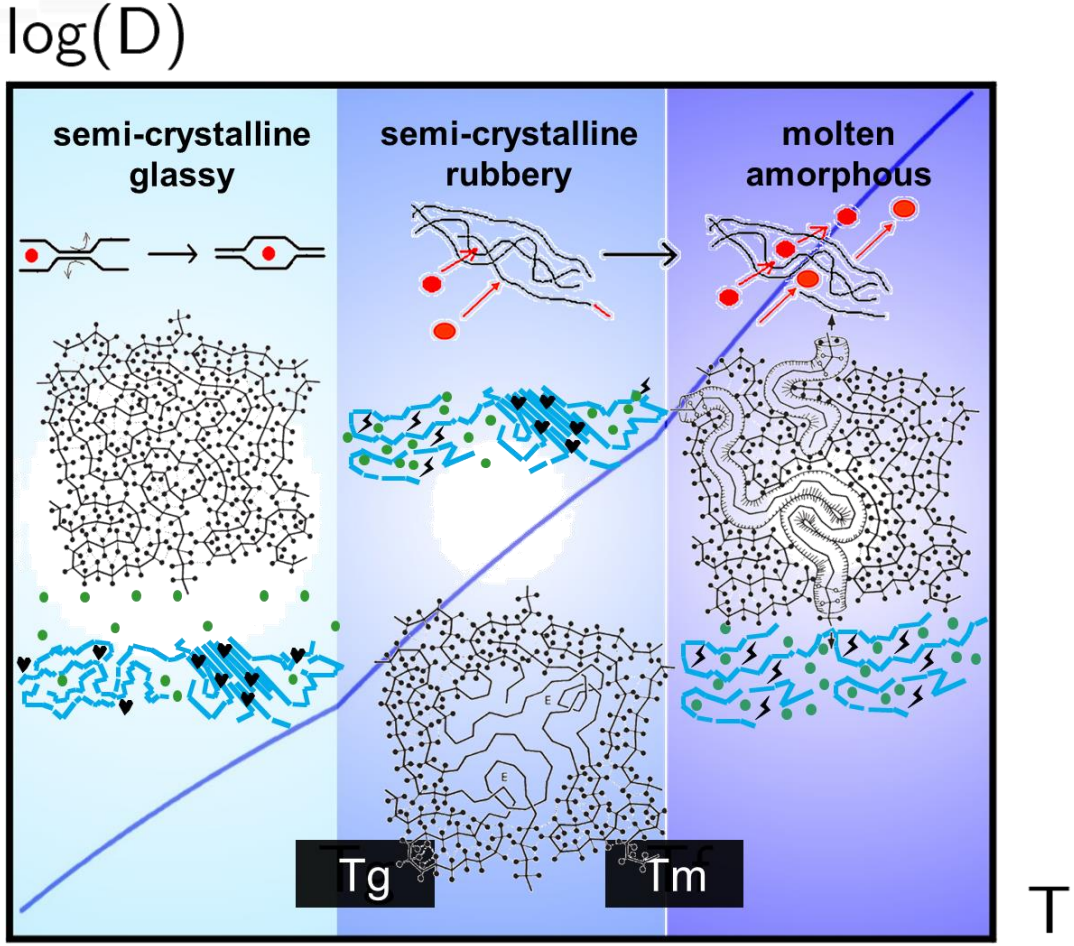
FOR VARIOUS POLYMERS

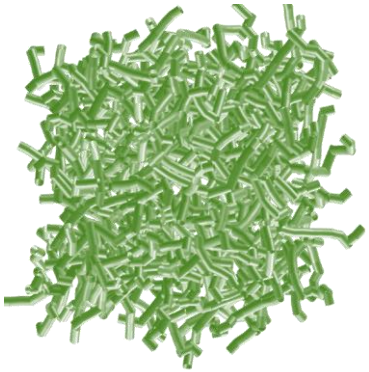


ACTIVATION OF DIFFUSION BY TEMPERATURE

BELOW TG, ABOVE TG





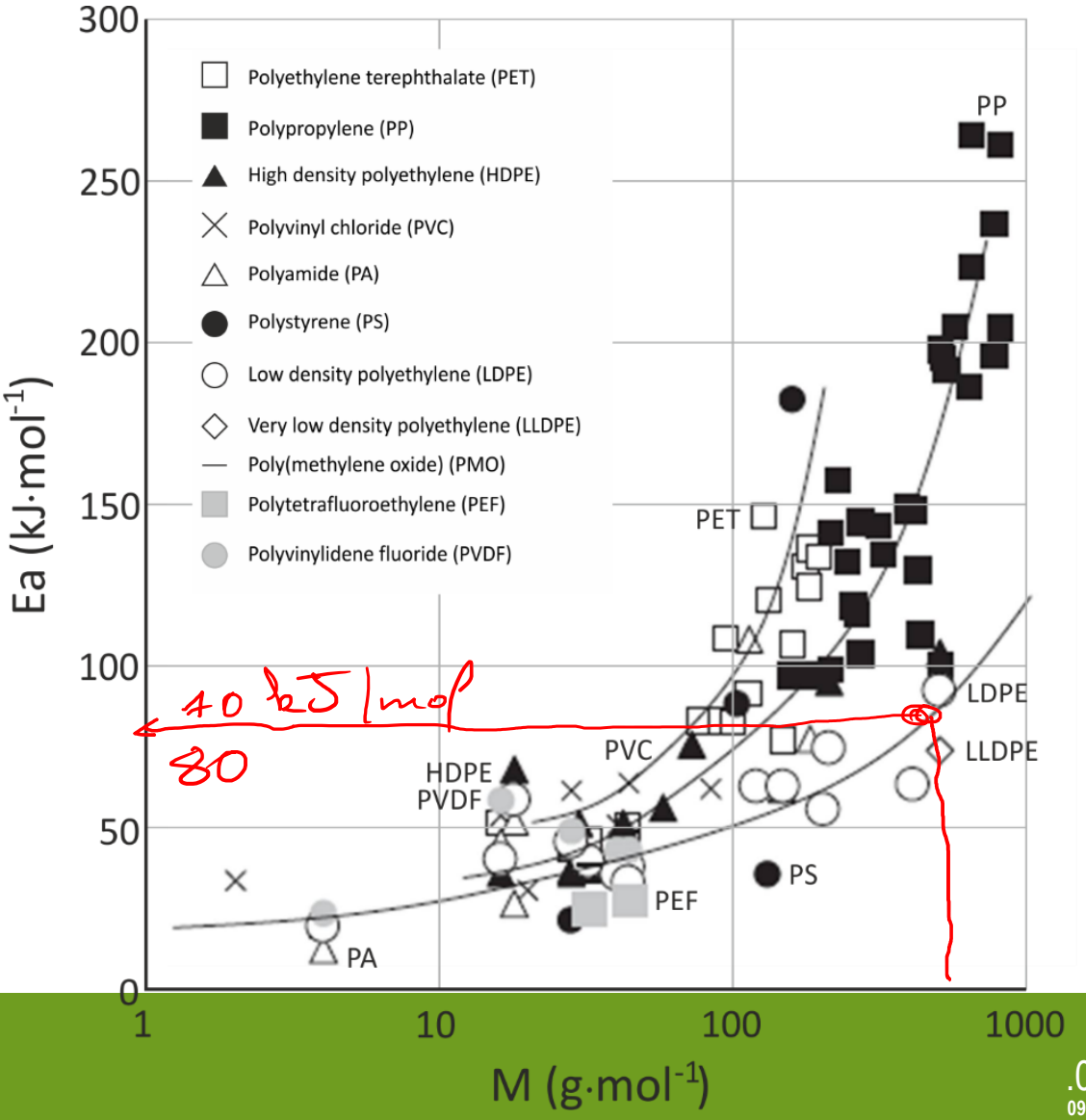


For each temp. range: $D = D_0 \cdot \exp\left(\frac{-Ea}{R \cdot T}\right)$

SCALING ACTIVATION ENERGY

VARIOUS DIFFUSANTS IN VARIOUS POLYMERS

$$\mathrm{Ea}(M) \approx \mathrm{Ea}(M_0) + ln(M/M_0)$$



Crit. Rev. Food Sci. Nut. 2015 (Fang & Vitrac)
http://www.tandfonline.com/doi/full/10.1080/10408398.2013.849654

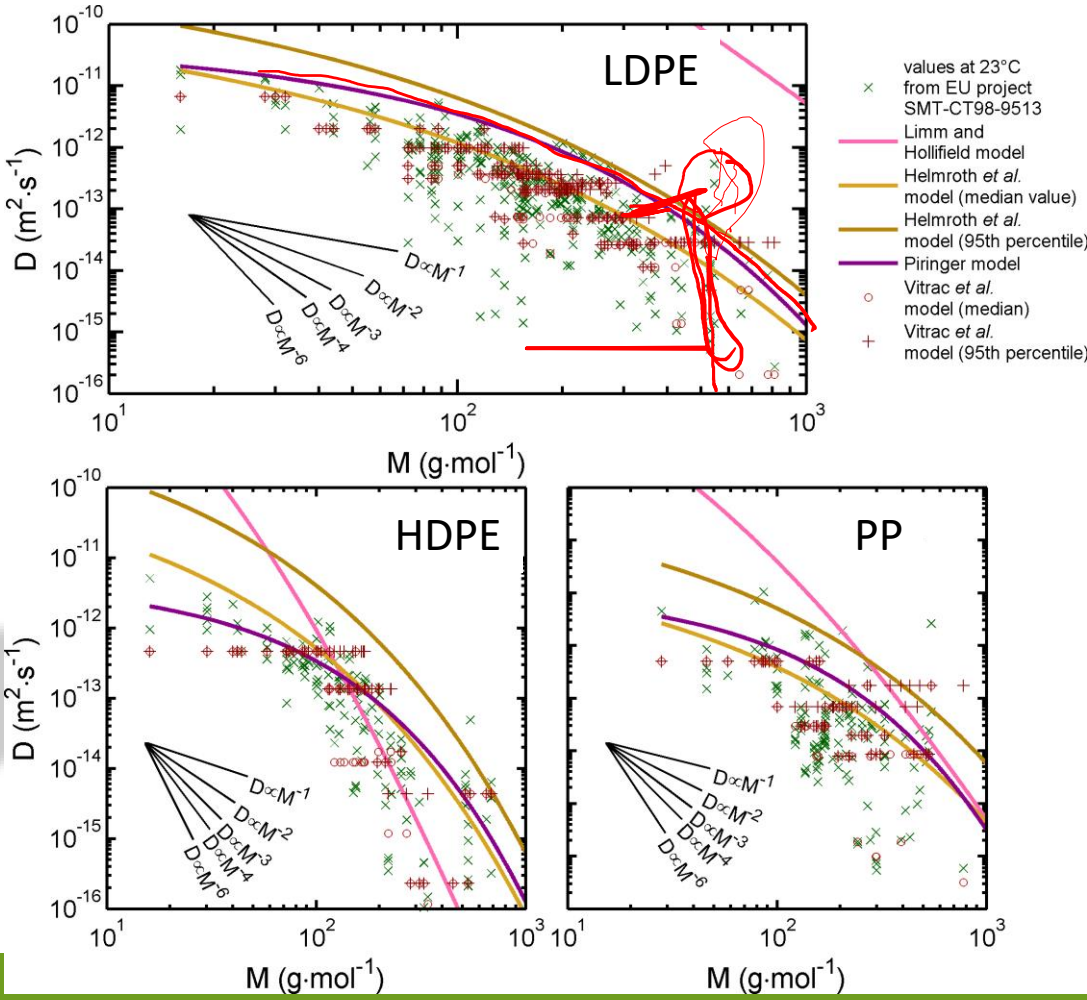
OVERESTIMATING D VALUES

PIRGINGER EQUATION

$$\ln D_{(M,T)} = A'_P - 0.1351 M^{2/3} + 0.003M - \frac{\tau + 10454}{RT}$$

Polymer	A'$_P$	τ (K)
LDPE,LLDPE	11	0
HDPE	14	1565
PP (homo and random)	13	1565
PP (rubber)	11	0
PS	0	0
HIPS	1	0
PET	6	1565
PBT	6	1565
PEN	5	1565
PA	2	0
PVC	0	0

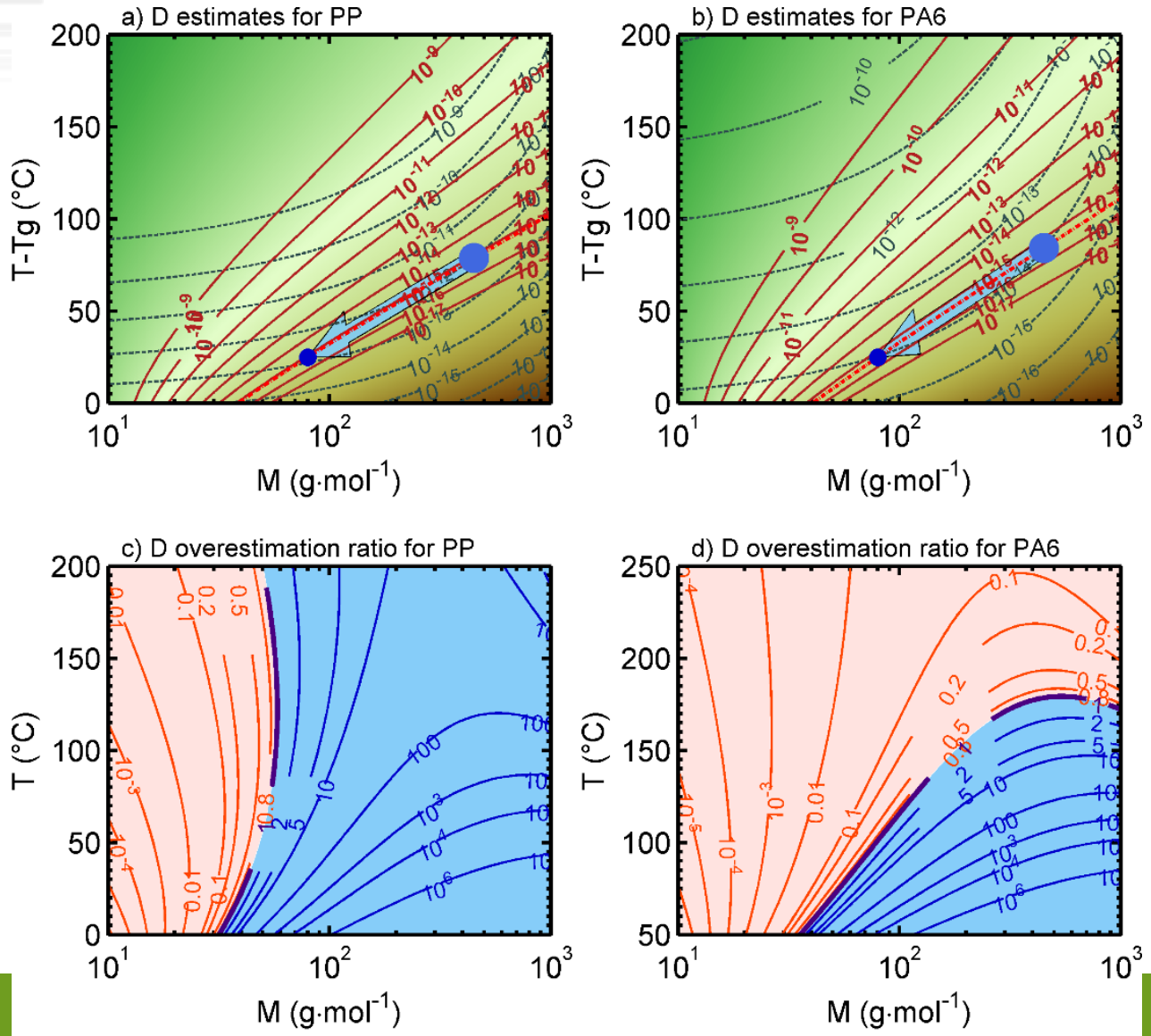
SAFETY MARGIN



ROBUSTNESS OF THE PIRINGER EQUATION

RUBBER POLYMERS (T>Tg)

- **Tg~0°C (PP)**
- **Tg~50°C (PA)**



Crit. Rev. Food Sci. Nut. 2015 (Fang & Vitrac)
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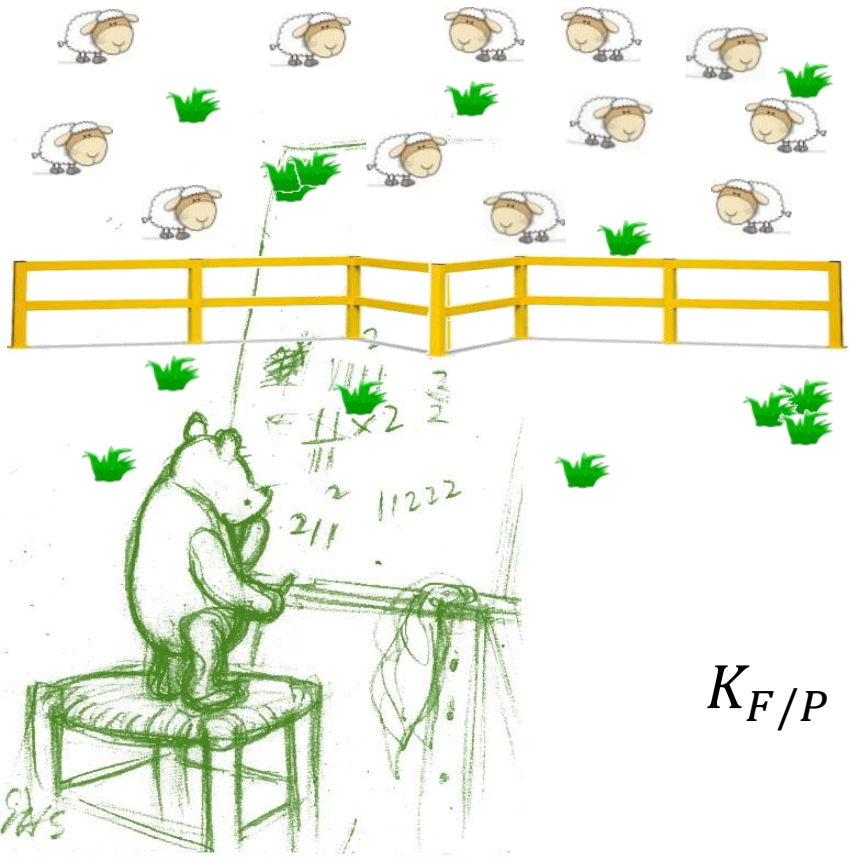
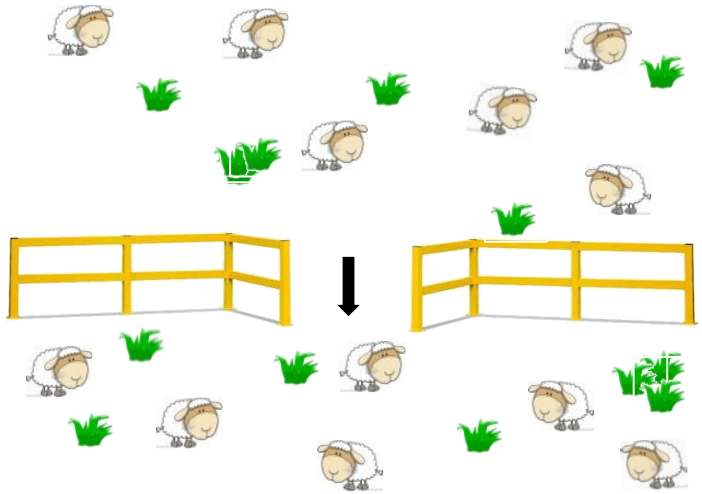
INTUITIVE DEFINITION OF PARTITION COEFFICIENTS

initial state

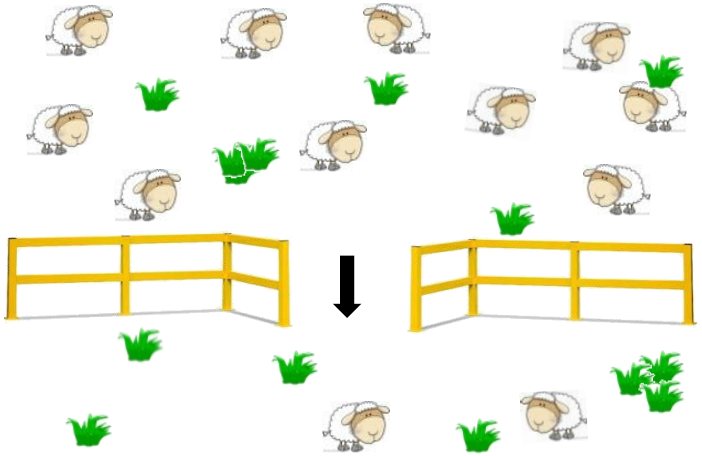


$$K_{F/P} = \frac{C_F^{eq}}{C_P^{eq}} = 1$$



thermodynamical equilibrium

$$K_{F/P} = \frac{C_F^{eq}}{C_P^{eq}} < 1$$

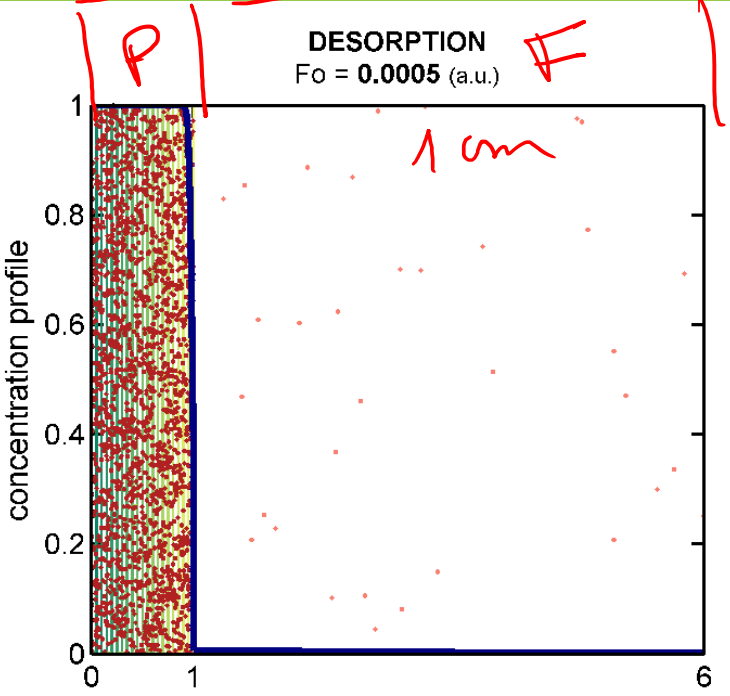


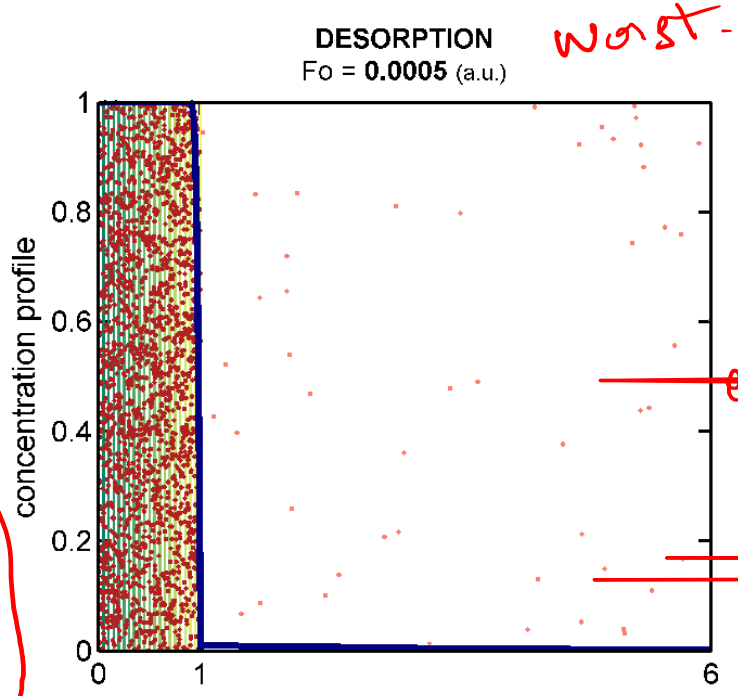
EFFECT OF PARTITION COEFFICIENT ON MIGRATION

50 times for chemical affinity for P

50 times for chemical affinity for F

$K_{i,F/P}$ = 1/50 | 50





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

MIGRATION MODELING

AUTHORIZED IN EU, US, China

At each stage of manufacture, supporting documentation, substantiating the declaration of compliance, should be kept available for the enforcement authorities. Such demonstration of compliance may be based on migration testing. As migration testing is complex, costly and time consuming it should be admissible that compliance can be demonstrated also by calculations, including modelling, other analysis, and scientific evidence or reasoning if these render results which are at least as severe as the migration testing. Test results should be regarded as valid as long as formulations and processing conditions remain constant as part of a quality assurance system.

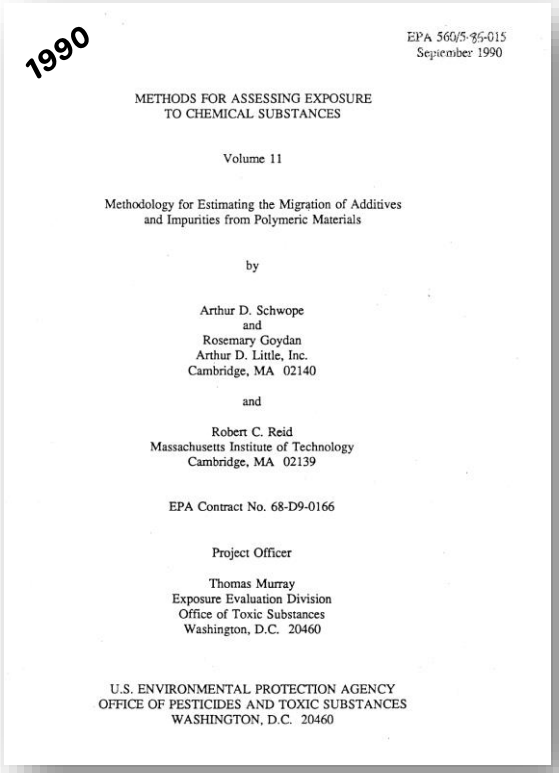
To screen for specific migration the migration potential can be calculated based on the residual content of the substance in the material or article applying generally recognised diffusion models based on scientific evidence that are constructed such as to overestimate real migration.

Migration modeling is well accepted in the US, Europe and China

Revisions and to extensions to non-plastic materials are pending

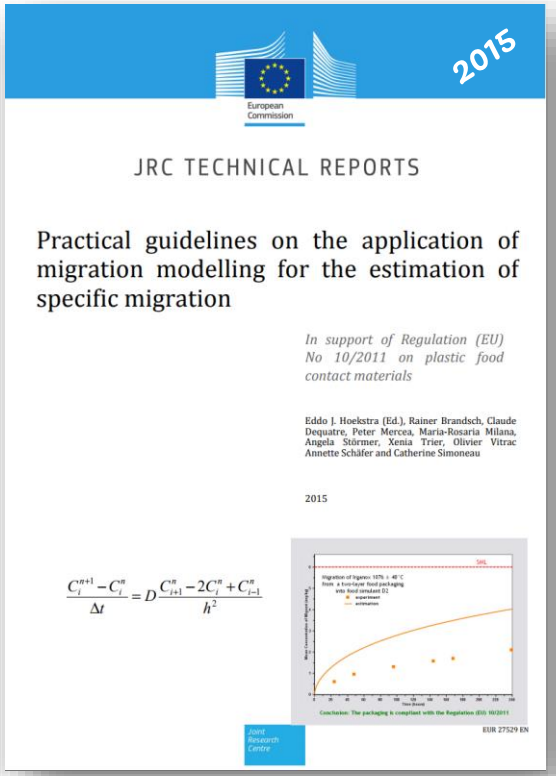
US guidance

Methodology for Estimating the Migration of Additives and Impurities from Polymeric Materials



https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P100BCMB.TXT

Europe guidance

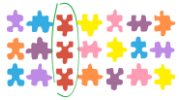


http://publications.jrc.ec.europa.eu/repository/handle/JRC98028

The five principles of migration modeling

- *The first principle* ("**conservatism**") is that modeling and related calculations should overestimate the real migration or contamination.

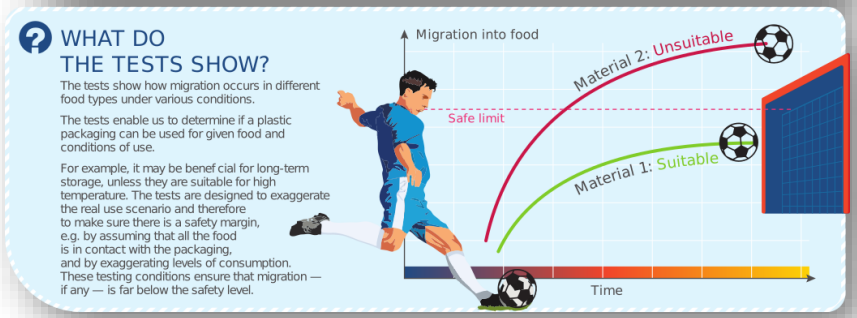
- *The second principle* ("**reliability**") implies that the foreseen mass transfer pathways and substances obey well-described mechanisms, accepted conditions (e.g., uniform distribution), and proper implementation in software.



- *The third principle* ("**consistency**") is that inputs in the model are known or guessed in a way that fulfills the requirements of the first principle.

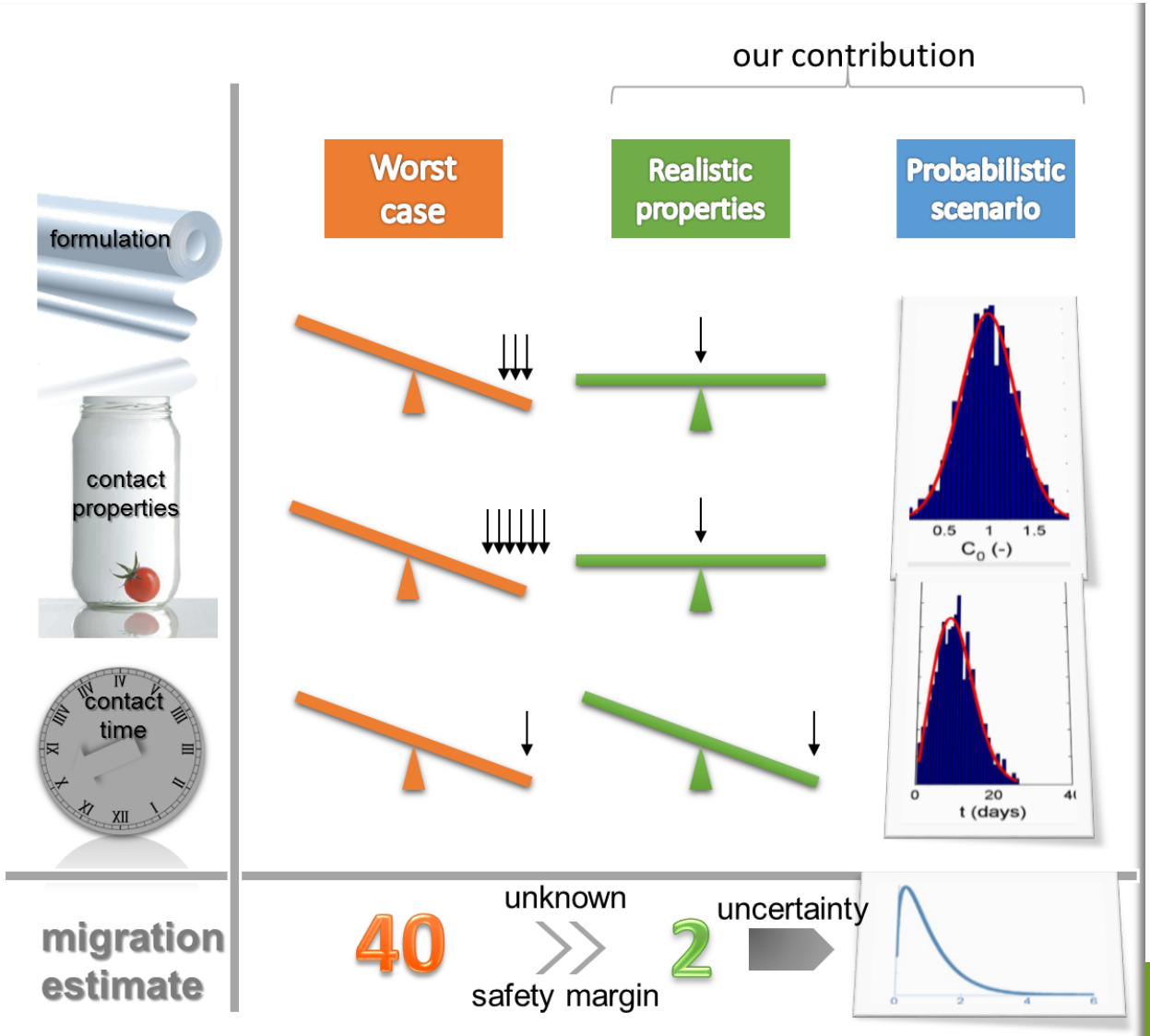
- *The fourth principle* ("**parsimony**") states that sophisticated and refined scenarios should be considered only when simpler ones cannot demonstrate compliance or safety.

- *The fifth and final principle* ("**proportionality**") is that non-compliance cannot be demonstrated by calculation.



HOW TO OVERESTIMATE MIGRATION

MODELING CAN DEMONSTRATE COMPLIANCE BUT NOT NON-COMPLIANCE

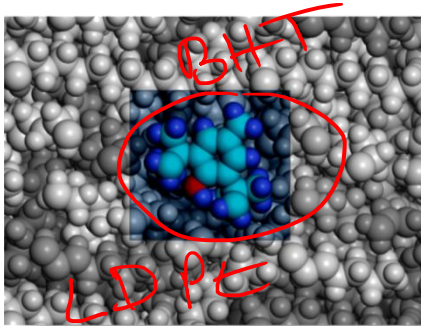


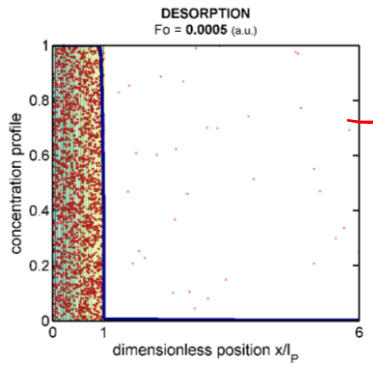
MIGRATION MODELING

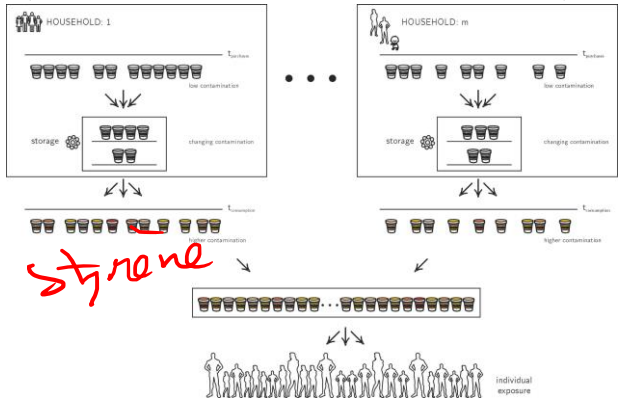
STATE OF THE ART (from lab to industry, from lab to food safety agencies)

properties | migration | exposure

Probabilistic (equilibrium) | Probablistic/deterministic | Probabilistic (no equilibrium)

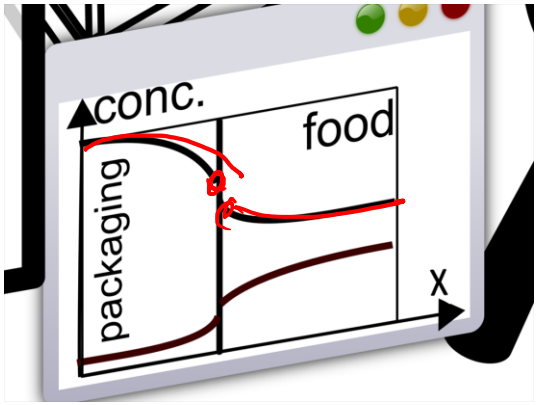


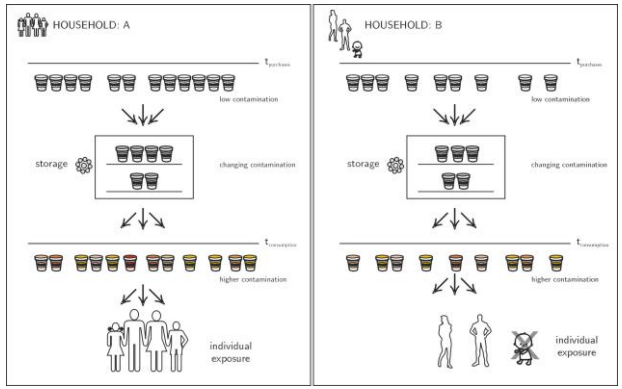




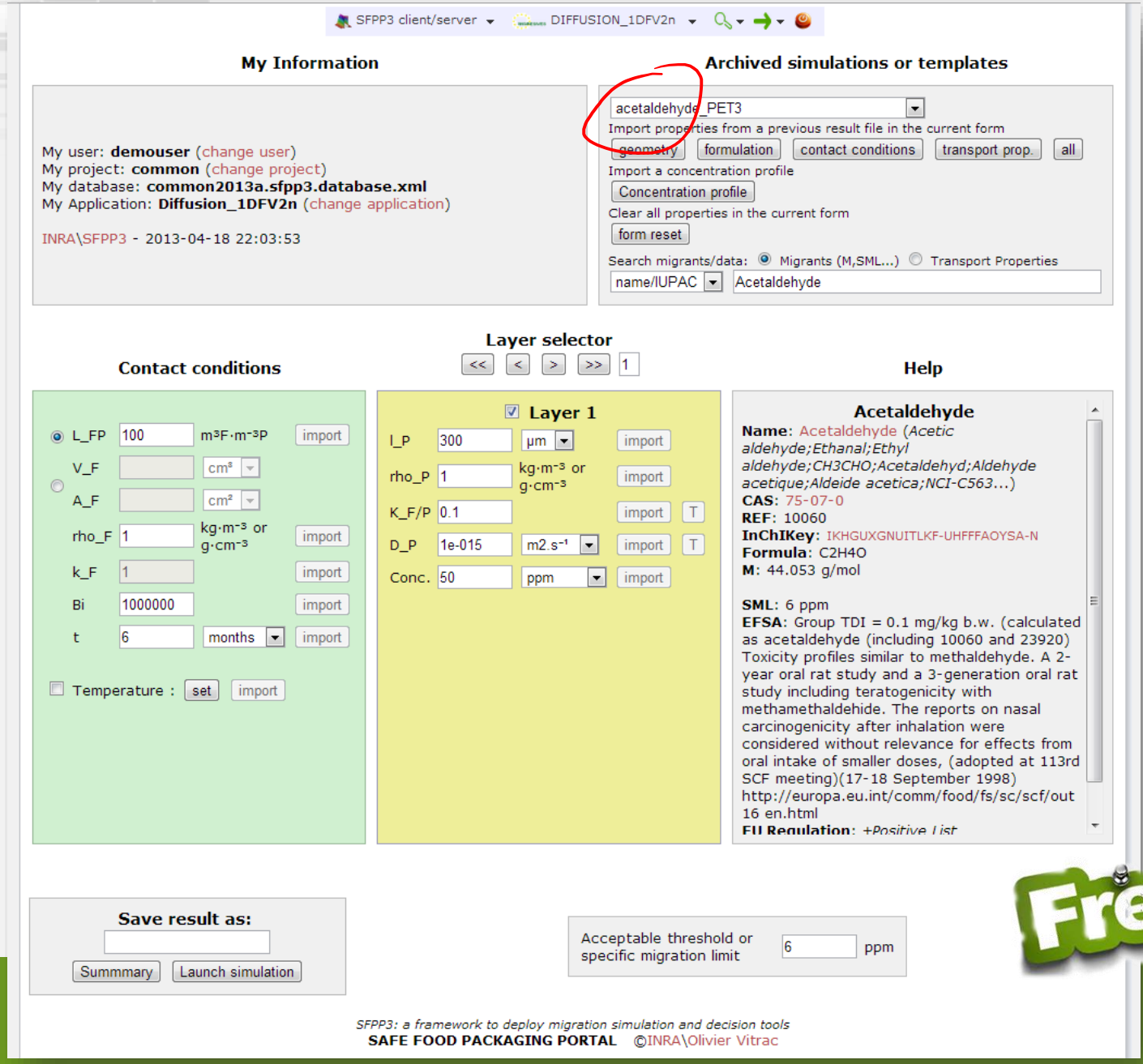
Free energy perturbation

$$\exp\left(-\frac{F_1 - F_0}{k_B T}\right) = \left\langle \exp\left(-\frac{U_1 - U_0}{k_B T}\right)\right\rangle$$





ALL SOFTWARE ARE BUILT ON SIMILAR ASSUMPTIONS



http://modmol.agroparistech.fr/SFPP3/SFPP3_migresives/

New trends: OPEN-SOURCE codes

https://github.com/ovitrac/FMECAengine

open source initiative

GitHub | This repository | Search | Explore | Features | Enterprise | Blog | Sign up | Sign in

ovitrac / FMECAengine | Watch 1 | Star 1 | Fork 2

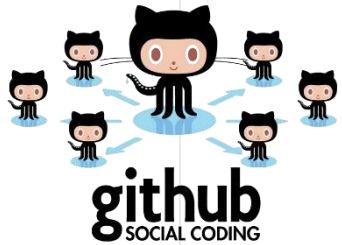
branch: master | FMECAengine / senspatankarC.m

ovitrac on 10 May 2014 Major Update - 10/05/2014

1 contributor

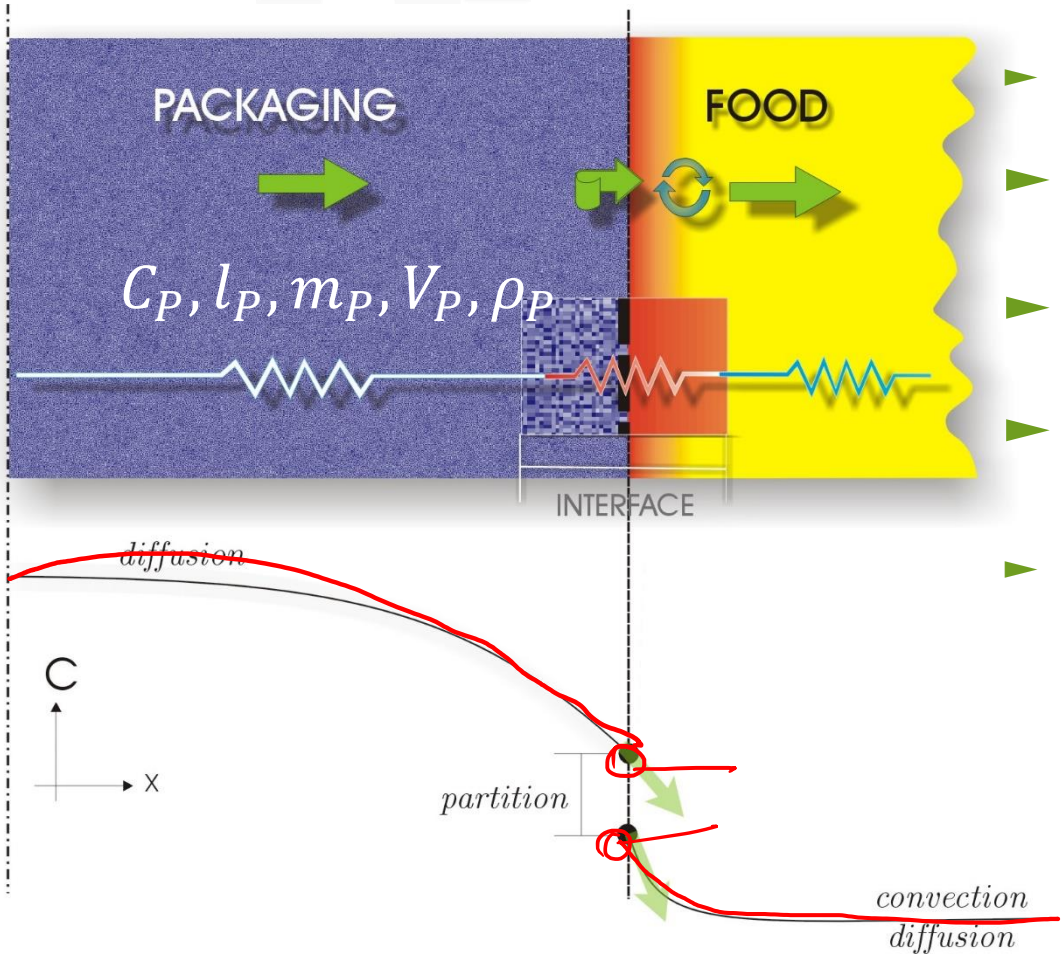
Executable File | 275 lines (252 sloc) | 10.03 kb | Raw | Blame | History

```
function res = senspatankarC(F,ploton,dispon)
%SENSPATANKAR simulates transfer and reactions through n layers using a modified Patankar Method (see p 45)
%   the dimensionless formulation is similar to SENSN
%   all data are normalized according the reference layer or equivalently according to the layer with the lowest D/a value
%   IT IS THE RESPONSABILITY OF THE USER TO PROVIDE THE APPROPRIATE DIMENSIONLESS NUMBERS
%   a wrapper used for the online version is available in ../www/home/diffusion_1DFVn.m

% MS-MATLAB-WEB 1.0 - 25/09/09 - Olivier Vitrac - rev. 05/05/14

% Revision history
% 01/10/07 improve speed
% 16/03/09 add restart
% 29/04/11 add F.restart.CF
% 26/10/11 replace xmesh/xmesh(end) xmesh/F.lrefc(end) in the interpolation (thanks to Nicolas)
% 08/05/14 method = 'pchip'  for compatibility with Matlab 2014

% definitions
global timeout
timeout         = 800; % s
% options               = odeset('RelTol',1e-4,'AbsTol',1e-4,'Stats','yes','Initialstep',1e-5,'Maxstep',.05,'Maxorder',5);
options         = odeset('RelTol',1e-4,'AbsTol',1e-4,'Initialstep',1e-8,'Maxstep',.01,'Maxorder',2);
Fdefault        =       struct(...
                                'Bi'            ,       1e3,... Biot [hm.L1/D]
                                'k'                     ,       [1 1 1 1],...[0.5 3 2],...      ki, i=1 (layer in contact with the
                'D'         ,   [1e-16 1e-14 1e-14 1e-14],... diffusion coefficient
                'k0'        ,   1,... 0 = liquid
                'l'         ,   [50 20 10 120]*1e-6,...[50 20 10 120]*1e-6,... m
                                'L'                     ,       200/1800,...    dilution factor (respectively to iref)
                                'C0'            ,       [0 500 500 0],...       initial concentration in each layer
                                'options'       ,       options...
                                        ); % if iref is missing, it is indentified
%lines to be deleted (OV: 09/04/11, incomplete pieces of code)
%               'kR'        ,   [.1 .1 .1 .1],...
```



DIMENSIONLESS FORMULATION

MONOLAYER / DIFFUSION + SORPTION



- C_F, m_F, V_F, ρ_F
- $K_{F/P} = \frac{C_F^{eq}}{C_P^{eq}}$
- $Fo = \frac{D_P t}{l_P^2}$
- $L_{P/F} = \frac{m_P}{m_F} = \frac{\rho_P V_P}{\rho_F V_F}$
- $Bi = \frac{R_D}{R_H} = \frac{resitance\ to\ diffusion\ in\ P}{resistance\ to\ mass\ transfer\ in\ F}$

MASS BALANCE

FROM TOTAL MIGRATION TO PARTITION CONTROLLED MIGRATION

Intial state

packaging

$$\rho_P \cdot V_P \cdot C_P^{t=0}$$

SI=kg·m^{-3} SI=m^3 SI=kg·kg^{-1}

=

food

$$\rho_F \cdot V_F \cdot C_F^{eq}$$

+

packaging

$$\rho_P \cdot V_P \cdot C_P|_{eq}$$

Equilibrium state

food

$$C_F^{eq} = \frac{1}{\frac{1}{L_{P/F}} + \frac{1}{K_{F/P}}} C_P^{t=0}$$

geometry effect

$$L_{P/F} = \frac{\rho_P V_P}{\rho_F V_F}$$

partitioning

$$K_{F/P} = \frac{C_F^{eq}}{C_P^{eq}}$$

5000

$= \frac{5000}{101}$

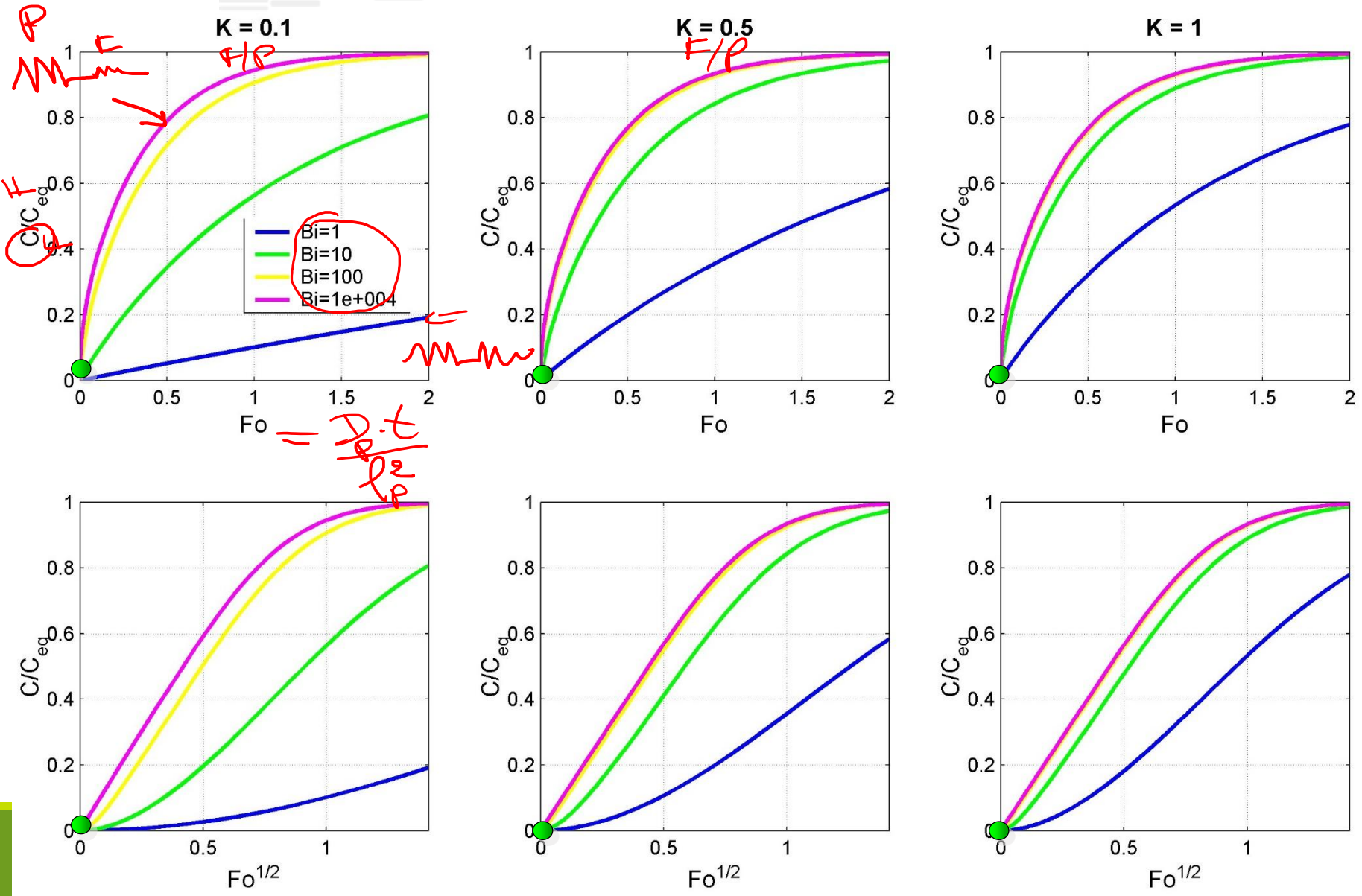
$= \frac{5000}{100}$

$L_{F/P}$ 100 1

C =concentration, l =thickness, m =mass, volume, ρ =density
K =partition coefficient (relative to mass concentration), L =dilution factor, Fo =Fourier number
Ddiffusion coefficient, Bi =mass Biot number, h =surface mass transfer coefficient coefficient

DIMENSIONLESS MIGRATION KINETICS

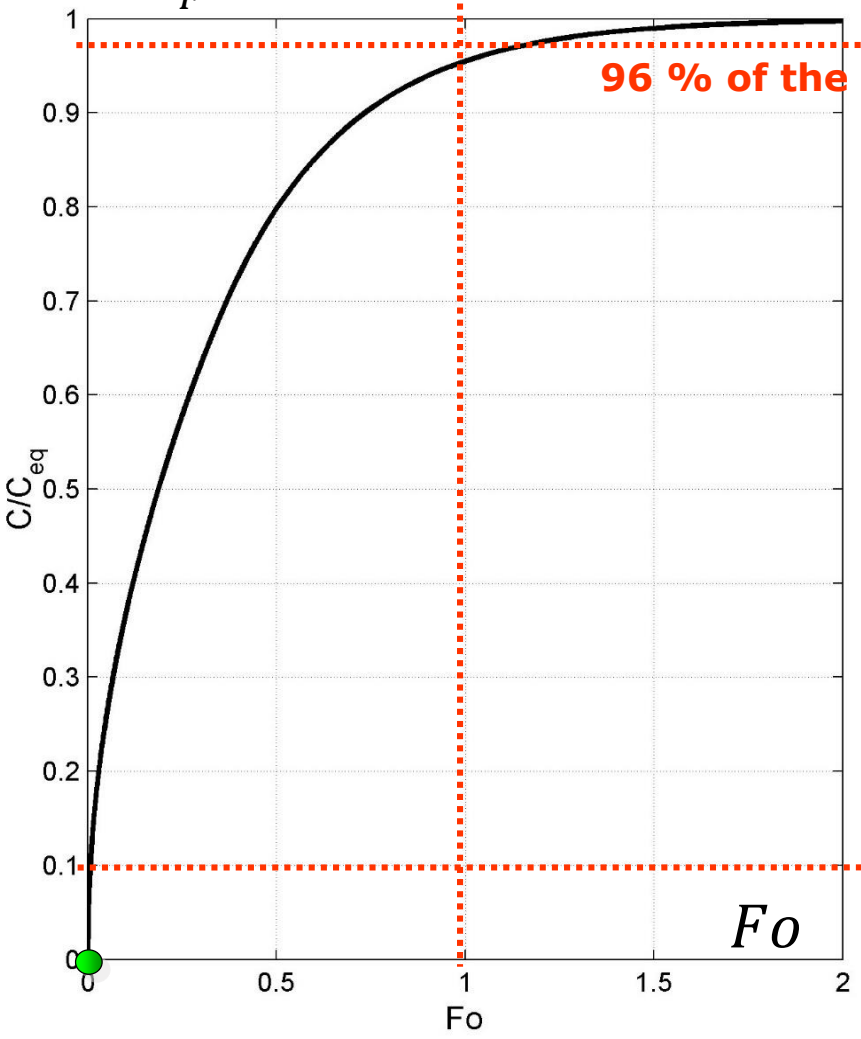
MONOLAYER MATERIAL

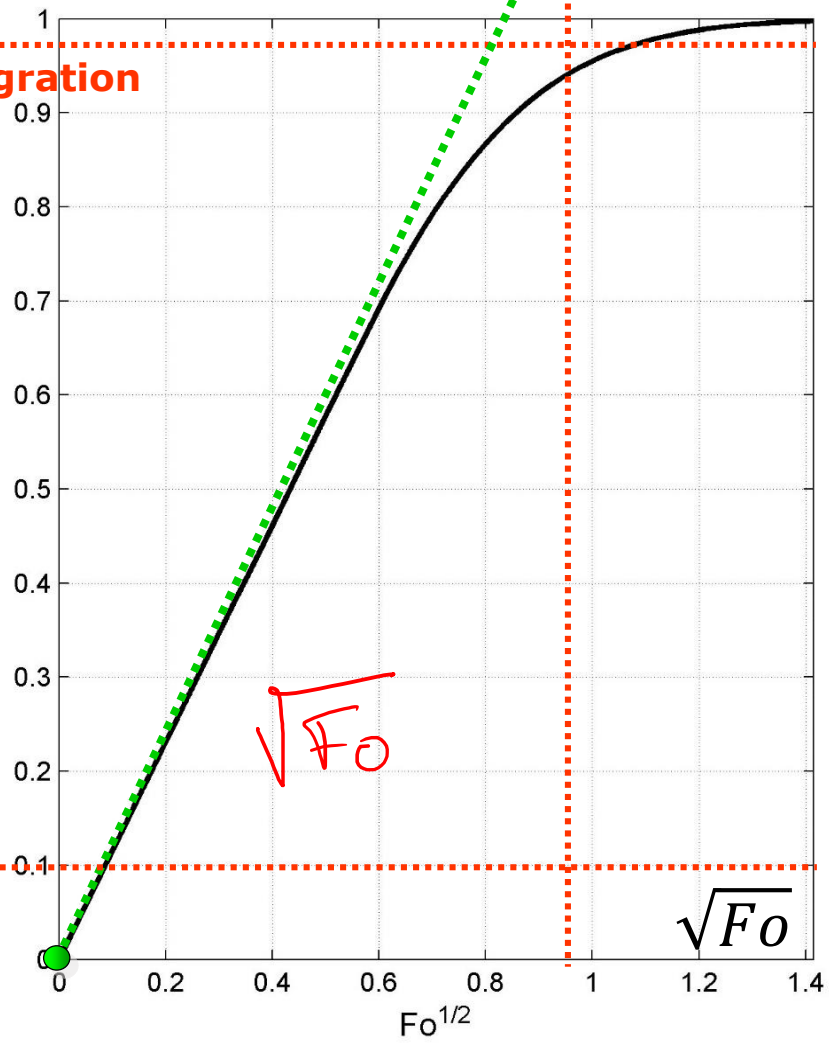


DIMENSIONLESS MIGRATION KINETICS

MONOLAYER MATERIAL / WORST CASE

$$M = \frac{C_F^{(Fo)}}{C_F^{eq}}$$

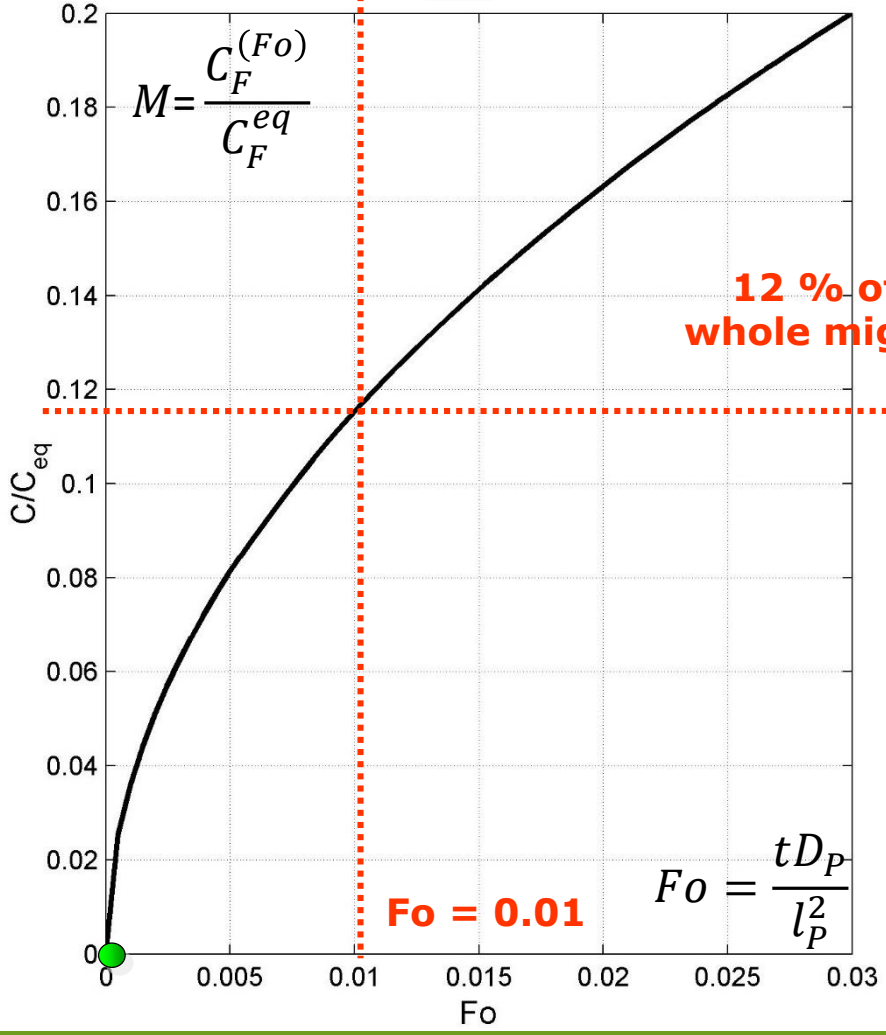




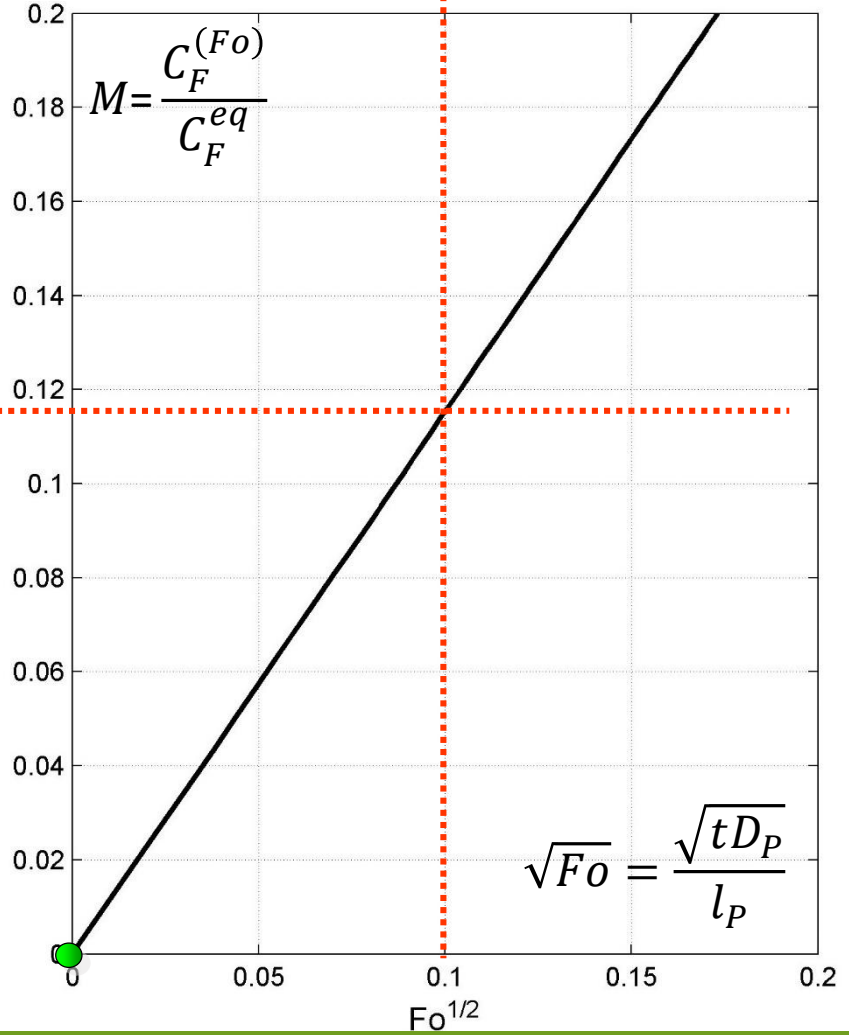
$$K_{F/P} = \frac{C_F^{eq}}{C_P^{eq}} \to \infty,\ L_{P/F} = \frac{m_P}{m_F} = \frac{\rho_P V_P}{\rho_F V_F} \to 0,\ Bi = \frac{R_D}{R_H} \to \infty$$

DIMENSIONLESS MIGRATION KINETICS

MONOLAYER MATERIAL



12 % of the whole migration



- $K_{F/P} = \frac{C_F^{eq}}{C_P^{eq}} \to \infty,\ L_{P/F} = \frac{m_P}{m_F} = \frac{\rho_P V_P}{\rho_F V_F} \to 0,\ Bi = \frac{R_D}{R_H} \to \infty$

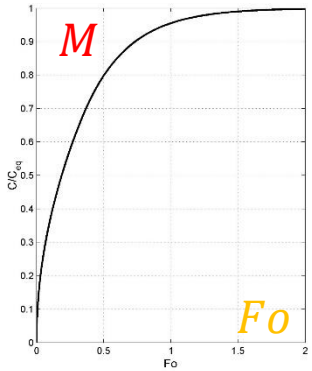
RULES OF THUMB FOR WORST CASE SCENARIOS

MONOLAYER MATERIAL

$M=\frac{C_F^{(Fo)}}{C_F^{eq}}$ Dimension-less migration (migration ratio)	$Fo=\frac{tD_P}{l_P^2}$ Dimension-less time
$\approx 100\%$	1
$\approx 50\%$	0.2
$\approx 10\%$	0.01

Time to reach a given migration ratio: $t = Fo\frac{l_P^2}{D_P}$

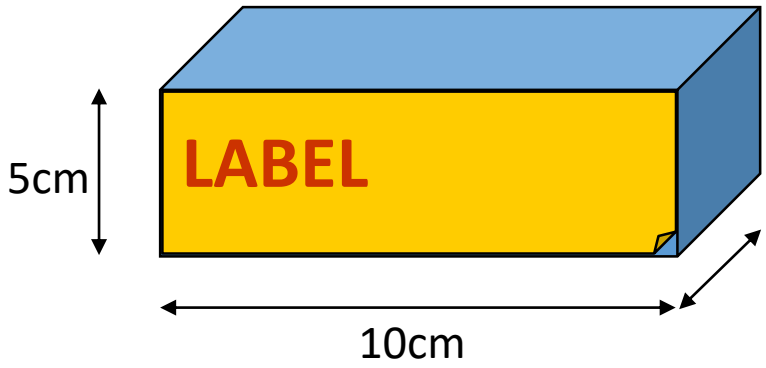
Concentration in food at time t: $C_F(t) = M(Fo) \cdot C_F^{eq} = M(Fo) \cdot \frac{K \cdot L}{K+L} \cdot C_P^{t=0}$

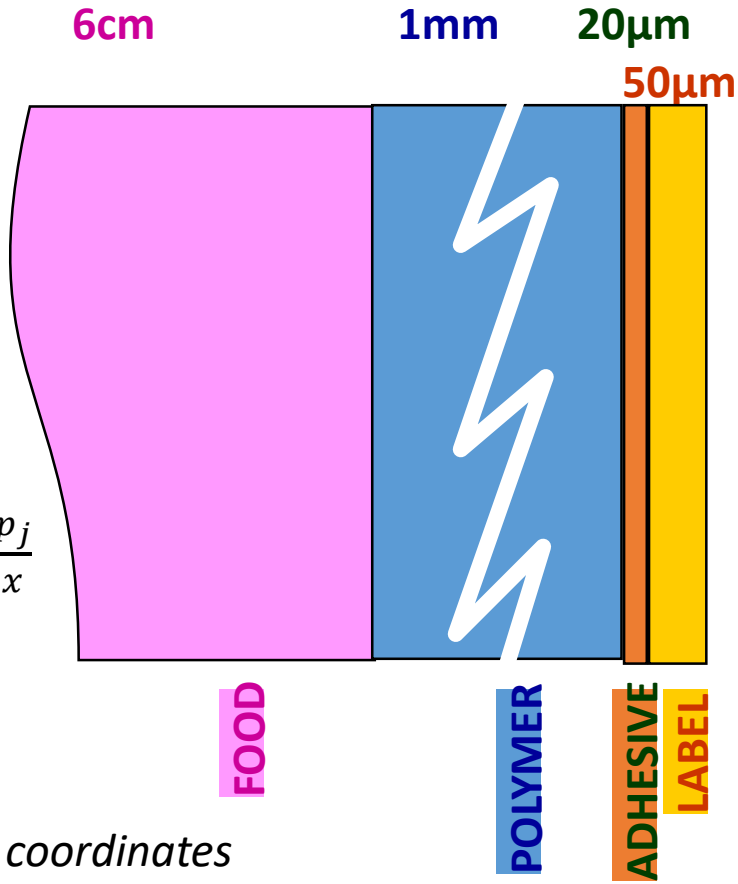


$K_{F/P} = \frac{C_F^{eq}}{C_P^{eq}} \to \infty,\ L_{P/F} = \frac{m_P}{m_F} = \frac{\rho_P V_P}{\rho_F V_F} \to 0,\ Bi = \frac{R_D}{R_H} \to \infty$

MODELING EXISTS ALSO FOR

MULTILAYERS
ARBITRARY COORDINATE SYSTELS
CHAINED STEPS





Henry isotherm: $p = kC$, k=Henry coefficient

Diffusive flux: $J_j = -D_j \cdot \rho_j \cdot \frac{\partial C_j}{\partial x} = -\frac{D_j \cdot \rho_j}{k_j} \cdot \frac{\partial p_j}{\partial x} = -\alpha_j \cdot \frac{\partial p_j}{\partial x}$

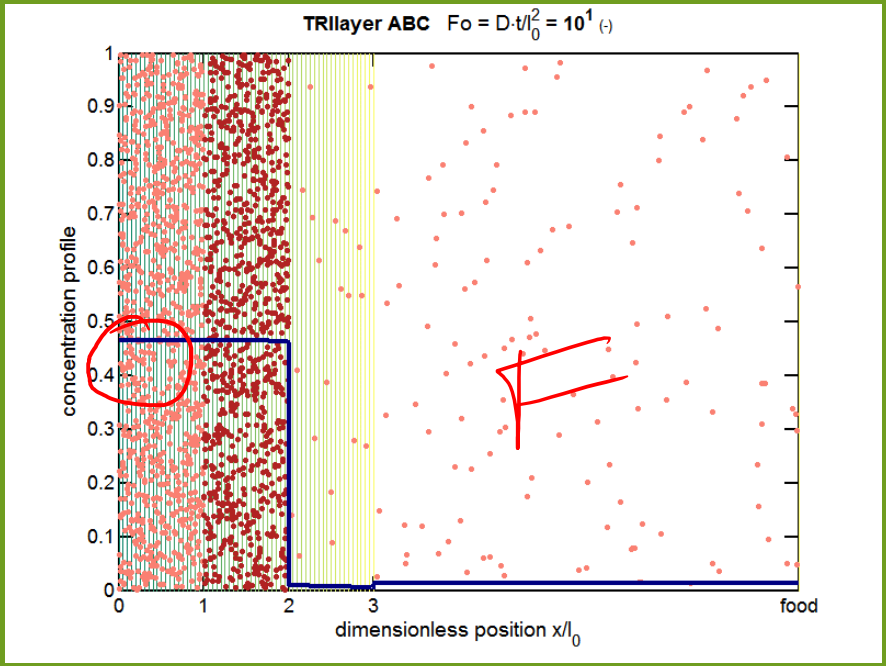
Transport equation: $\delta_j \cdot \frac{\partial p_j}{\partial t} = \frac{1}{x^m} \frac{\partial}{\partial x}\left(x^m \cdot \alpha_j \cdot \frac{\partial p_j}{\partial x}\right)$

$\alpha_j = \frac{D_j \cdot \rho_j}{k_j} = D_j \cdot \delta_j$

cartesian ($m = 0$), cylindrical (($m = 1$), spherical ($m = 2$) coordinates

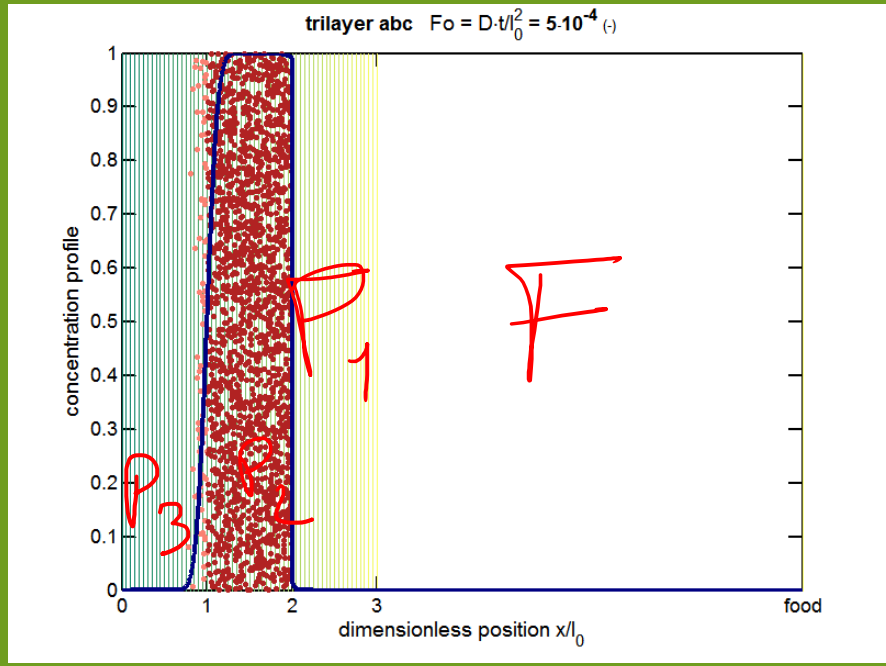
SIMULATION OF MULTILAYER MATERIALS

Functional barrier = barrier to diffusion + sorption



prop	Layer 3	Layer 2	Layer 1	Food
C_0	0	1	0	0
l/l_0	1	1	1	100
D/D_0	1	1	0.1	10^4
k/k_0	1	50	1	1

Idem + low chemical affinity for the food

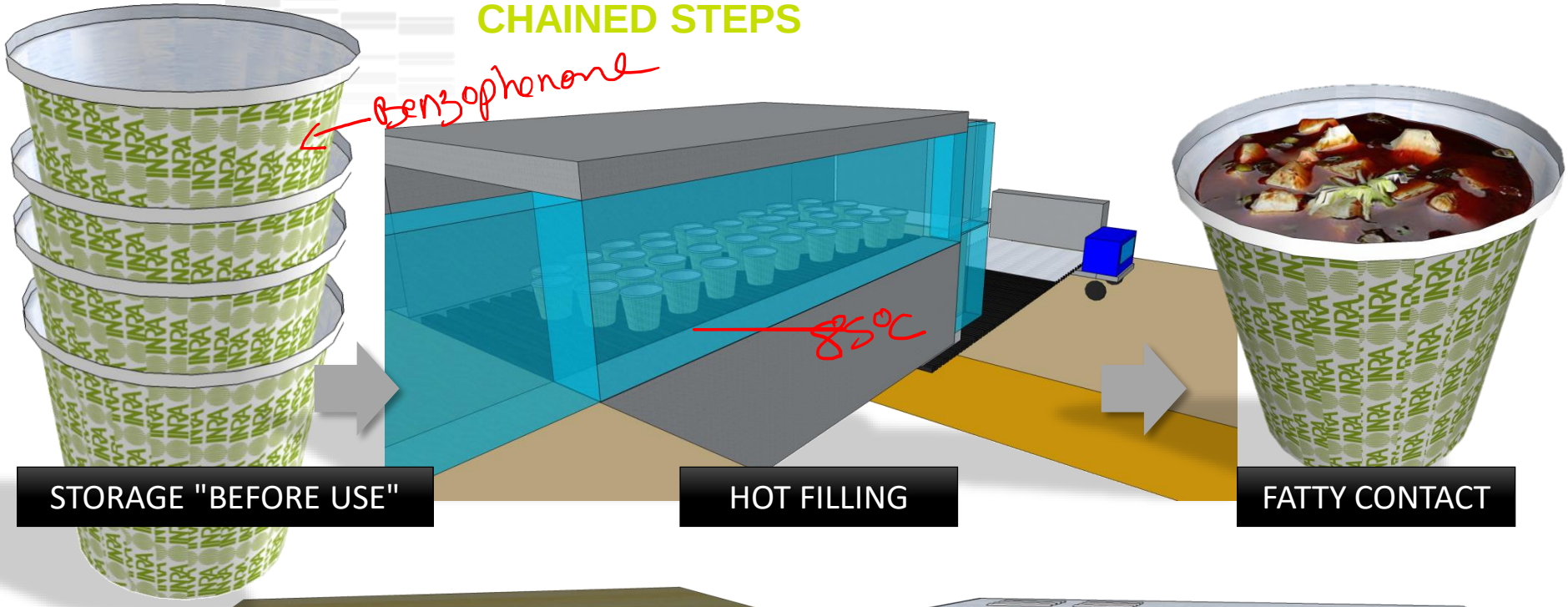


prop	Layer 3	Layer 2	Layer 1	Food
C_0	0	1	0	0
l/l_0	1	1	1	100
D/D_0	1	1	0.1	10^4
k/k_0	1	50	1	20

INRA SCIENCE & IMPACT

MODELING EXISTS ALSO FOR

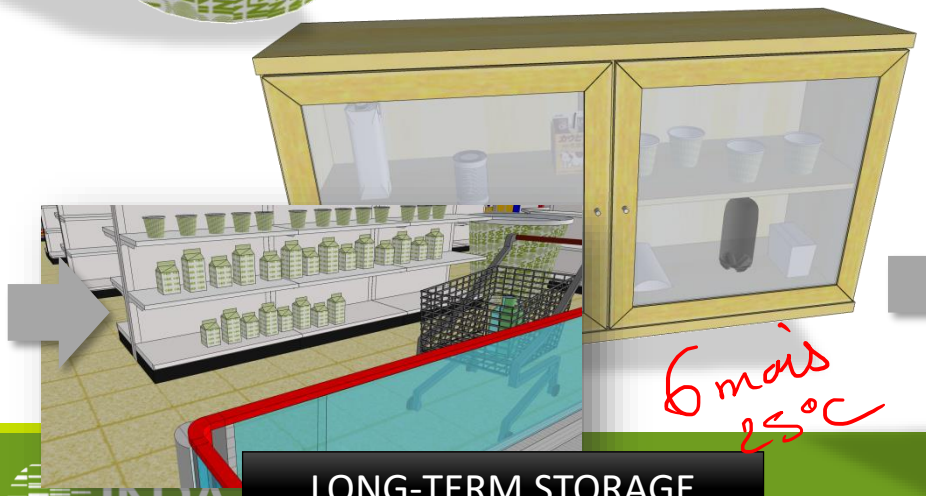
CHAINED STEPS



STORAGE "BEFORE USE"

HOT FILLING

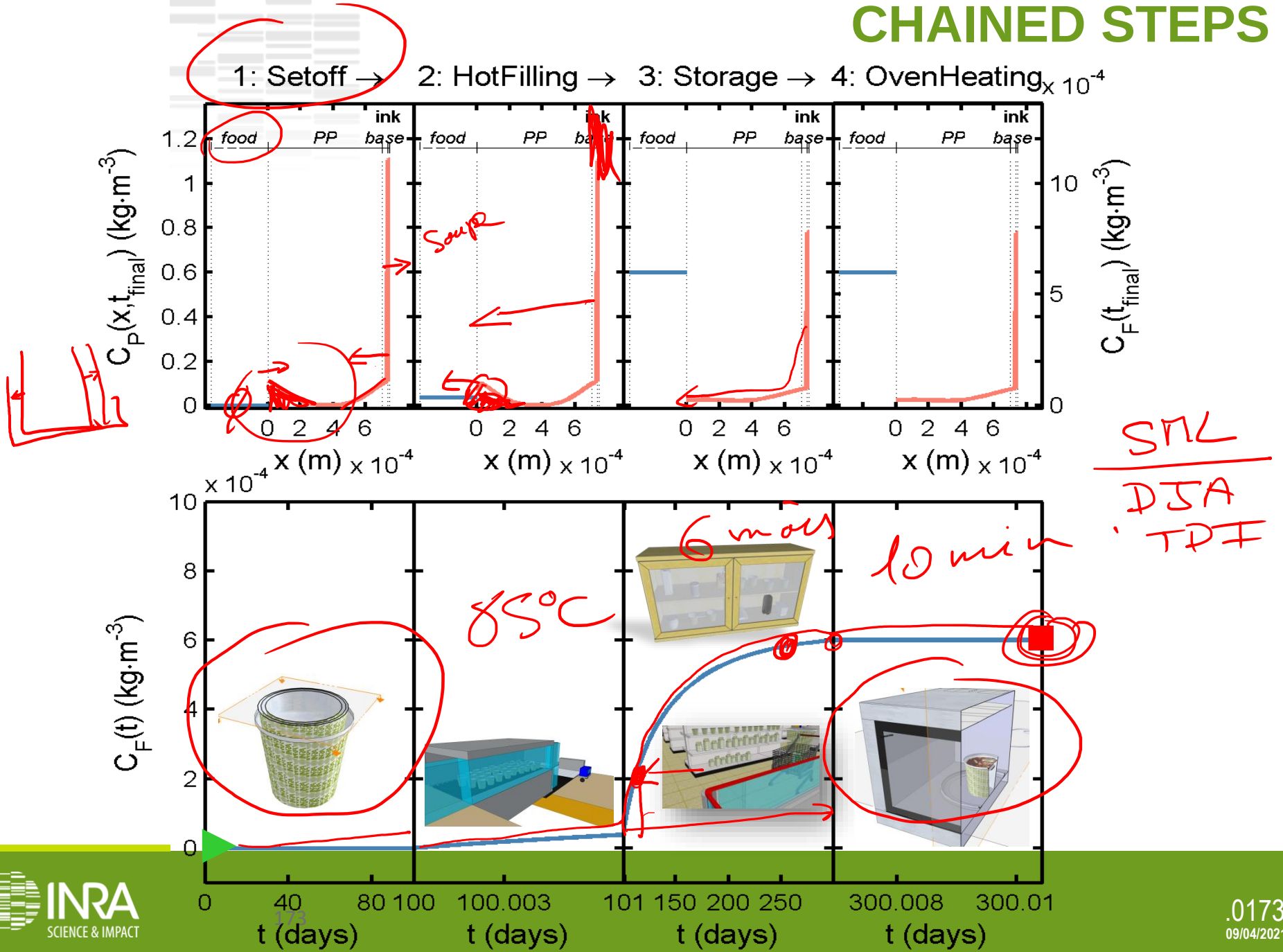
FATTY CONTACT



LONG-TERM STORAGE

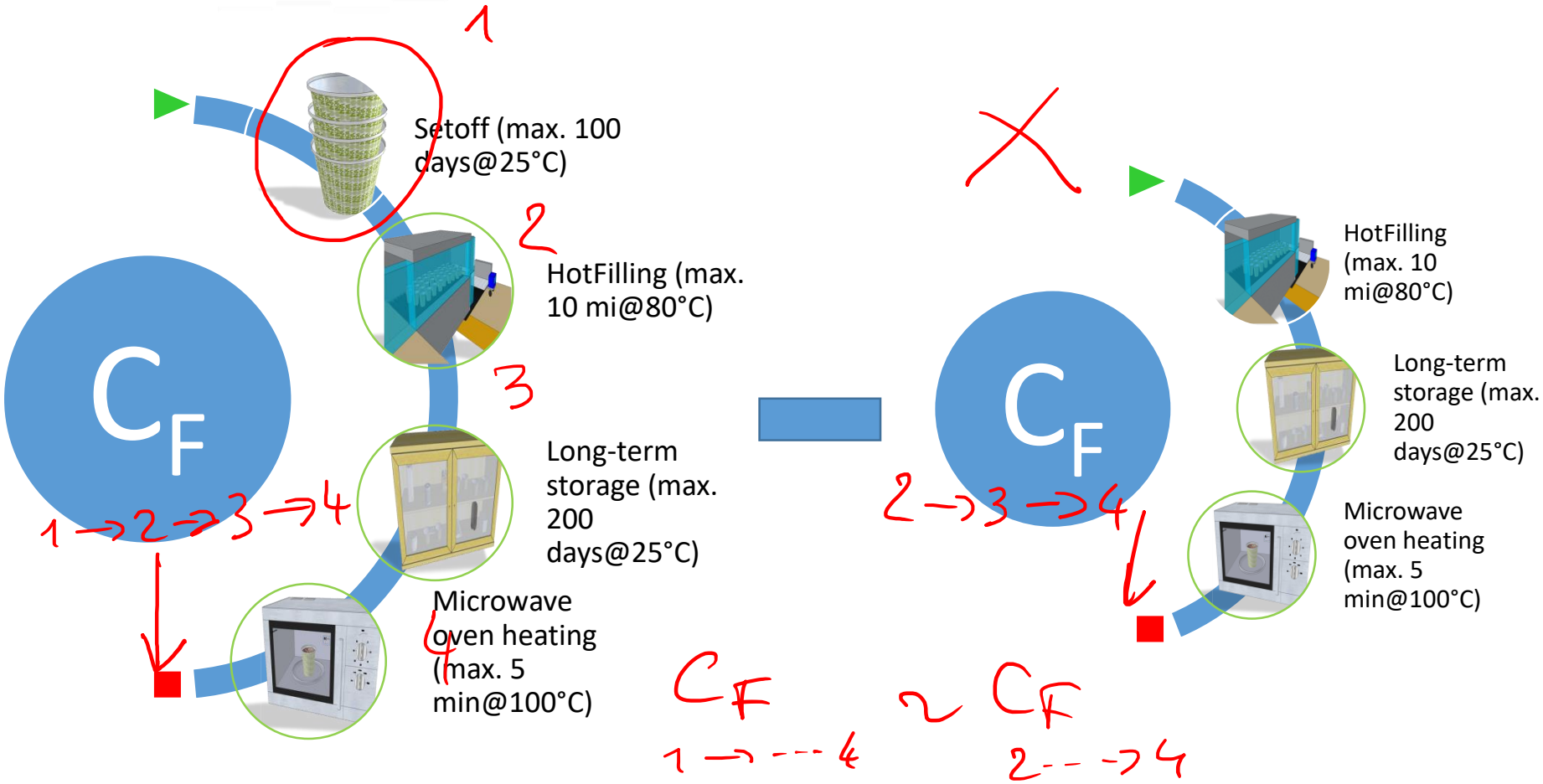
MICROWAVE OVEN HEATING

CHAINED STEPS



ASSESSING THE SEVERITY OF A SINGLE STEP

CASE OF "SETOFF" STEP

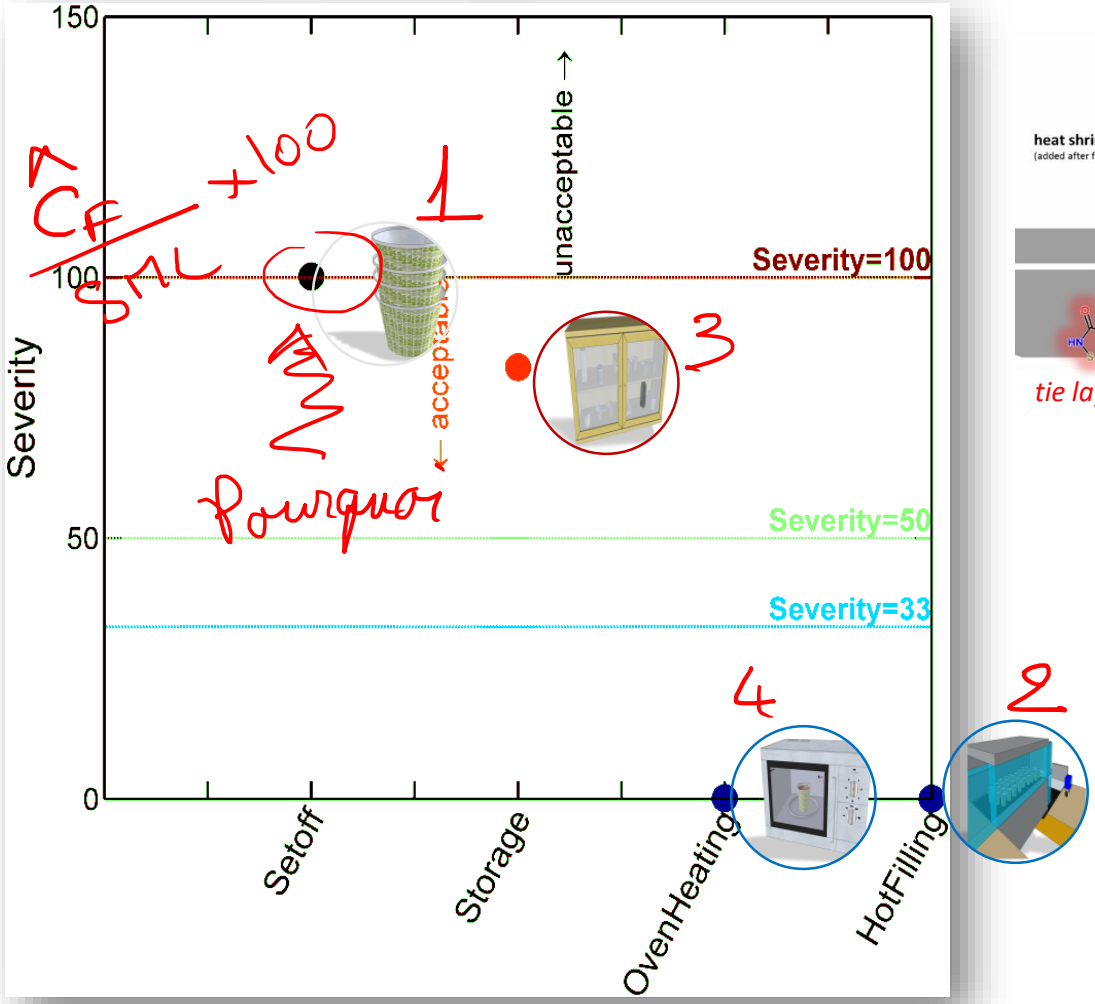


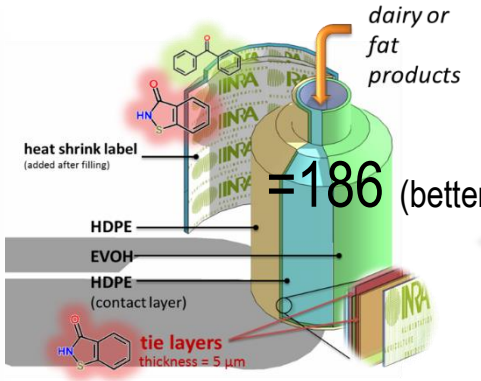
Full methodology described in *AIChE J.* 2013, **59**(4), 1183-1212

$$\text{Severity}\left(\hat{C}_F\left(\text{step } i\right)\right) = f\left(\max\left(\underbrace{C_{F_M}\big|_{1\to 2\to\cdots\to M} - C_{F_M}\big|_{1\to 2\to\cdots\to M/i}}_{\text{comparison with step } i \text{ removed}}, \underbrace{C_{F_i}\big|_i}_{\text{step } i \text{ alone}}\right)\right)$$

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

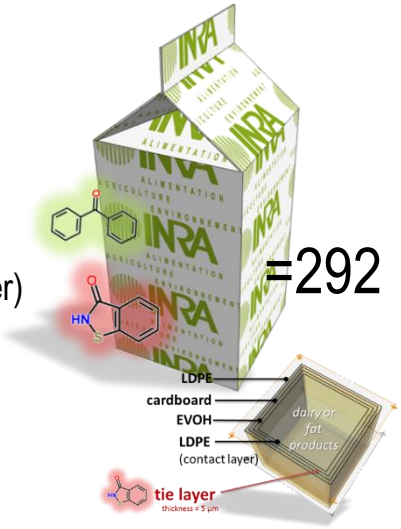
CASE OF "SETOFF" STEP



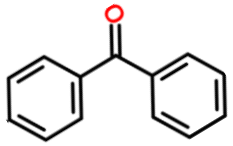


=186 (better)

tie layer = EVA



=292



=115
(almost acceptable)

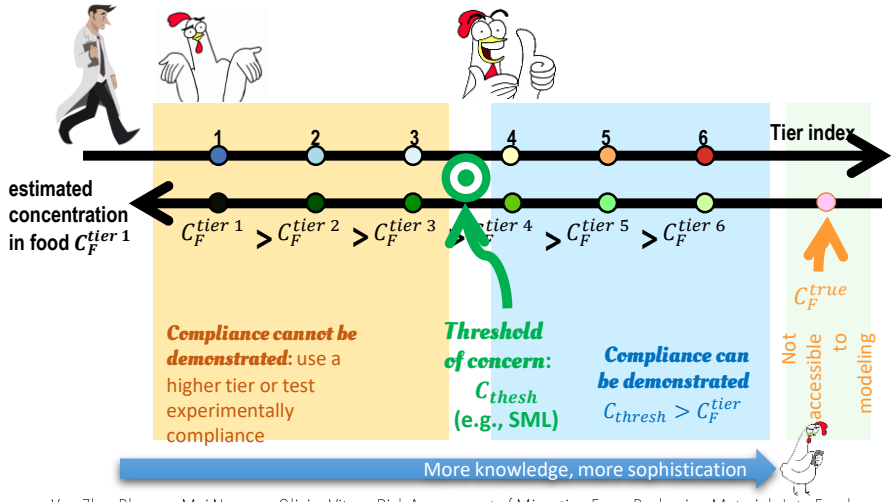
=124

Parsimony vs. sophistication

During the last decade migration modeling became high throughput, multiscale and connected to chemometric approaches

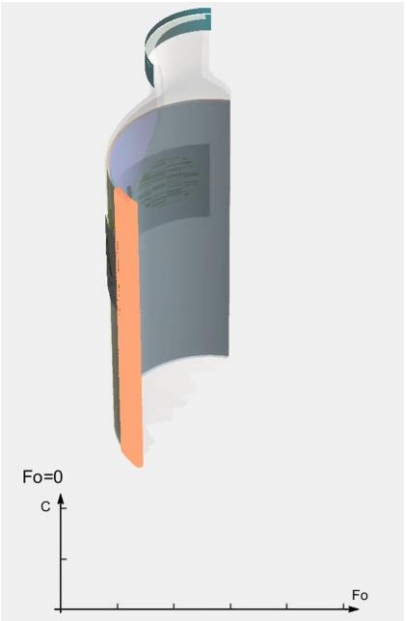
What is the goal?

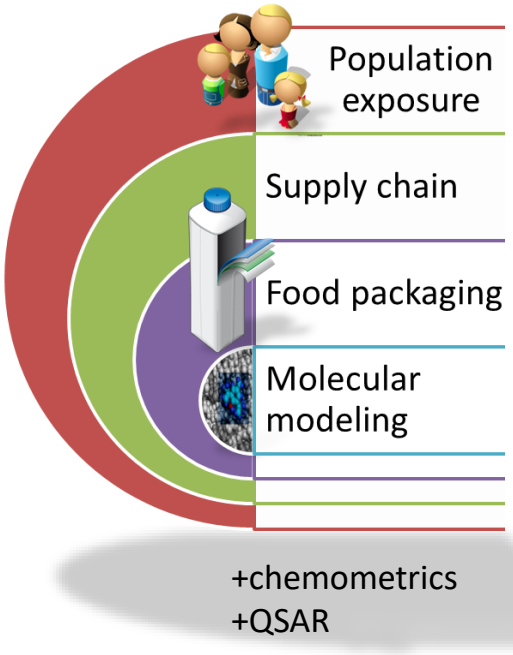
The art of migration modeling consists in building a sequence of scenarios so that the last scenario provides a value lower than the threshold of concern while being large than the real concentration (unknown).



Yan Zhu, Phuong-Mai Nguyen, Olivier Vitrac, Risk Assessment of Migration From Packaging Materials Into Food, Reference Module in Food Science, Elsevier, 2019, https://doi.org/10.1016/B978-0-08-100596-5.22501-8.

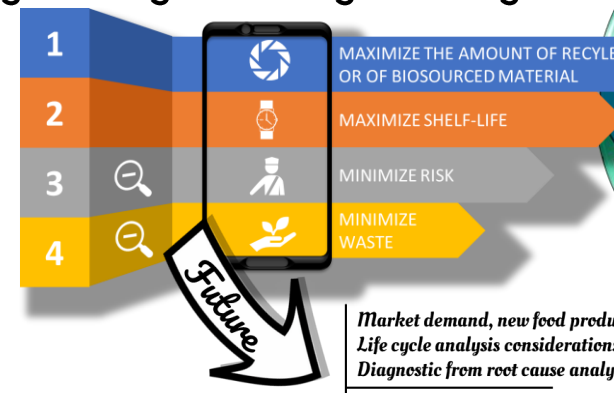
Multiscale modeling

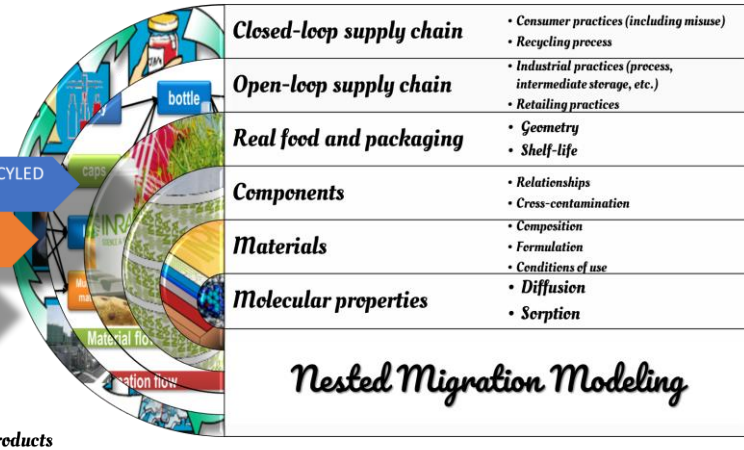




Beyond concurrent design, integrated engineering

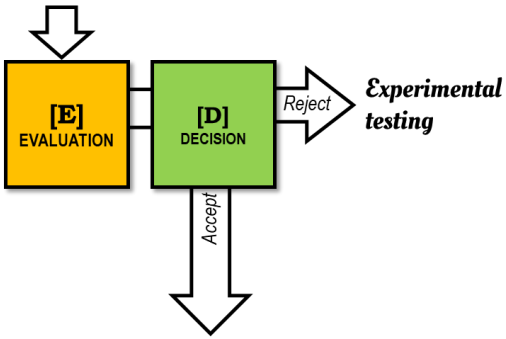
Multicriteria optimization





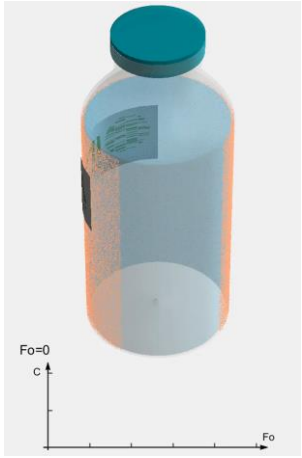
Present

New substance
New material
New recycling process
New food packaging



Experimental testing

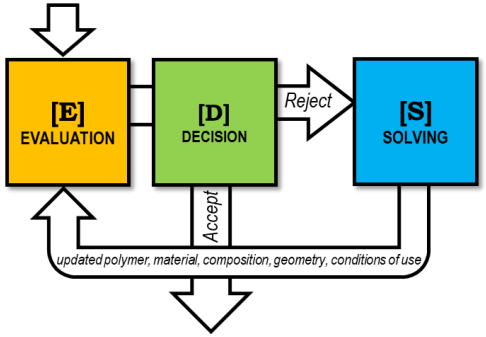
Compliant food contact material (FDA, EU, Chinese rules)



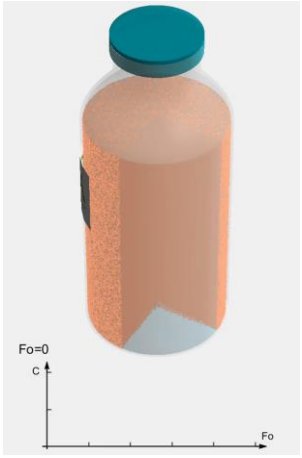
Future

Market demand, new food products
Life cycle analysis considerations
Diagnostic from root cause analysis, seek of preventive actions

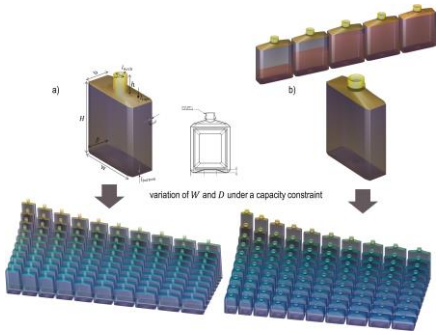
Computer-aided drafting



Rapid prototyping and compliance
Good manufacturing and design practices
Safer food products
Improved shelf-life
Eco-designed packaging

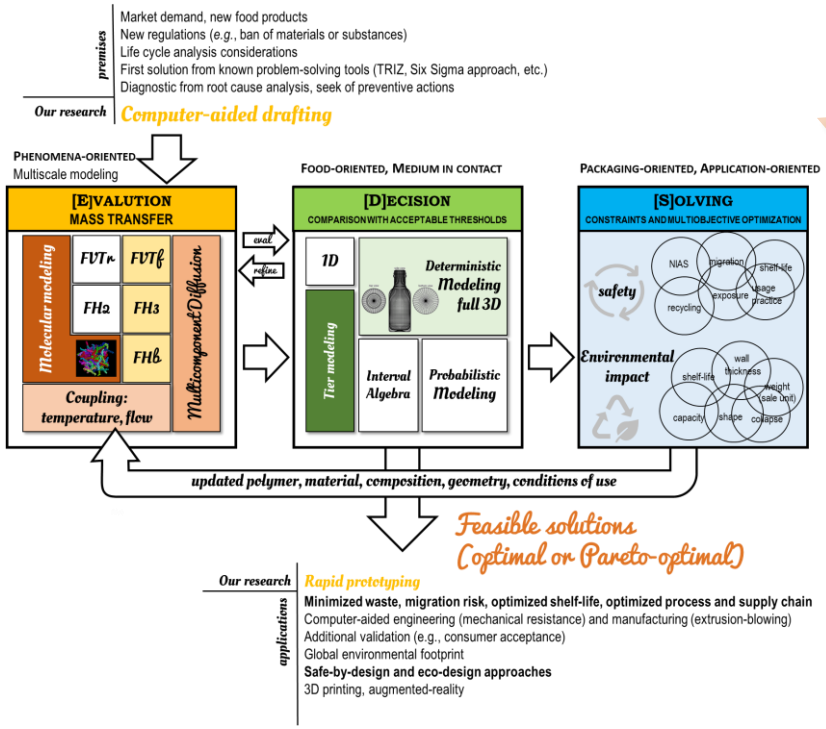


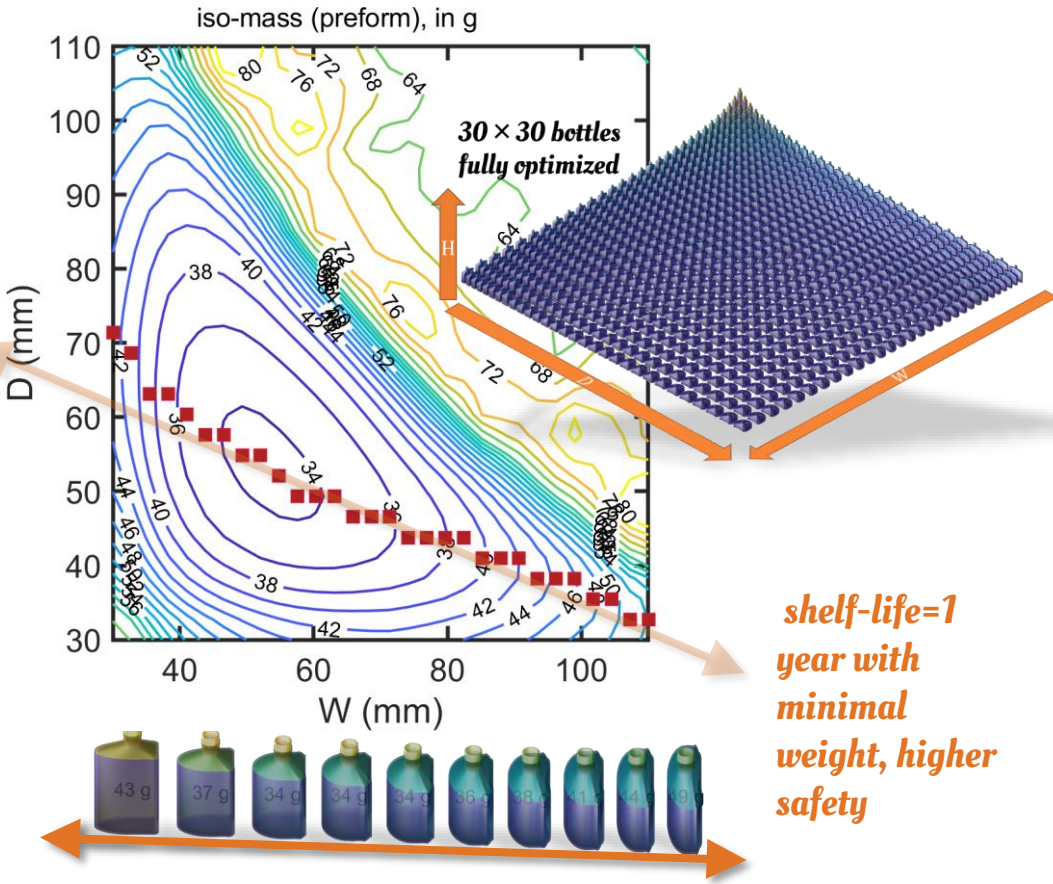
Integrated engineering



Example: redesign of PET bottle for alcoholic beverages (optimized shape, recycled content, reduced weight, improved shell-life)

3D prototype printed the same day





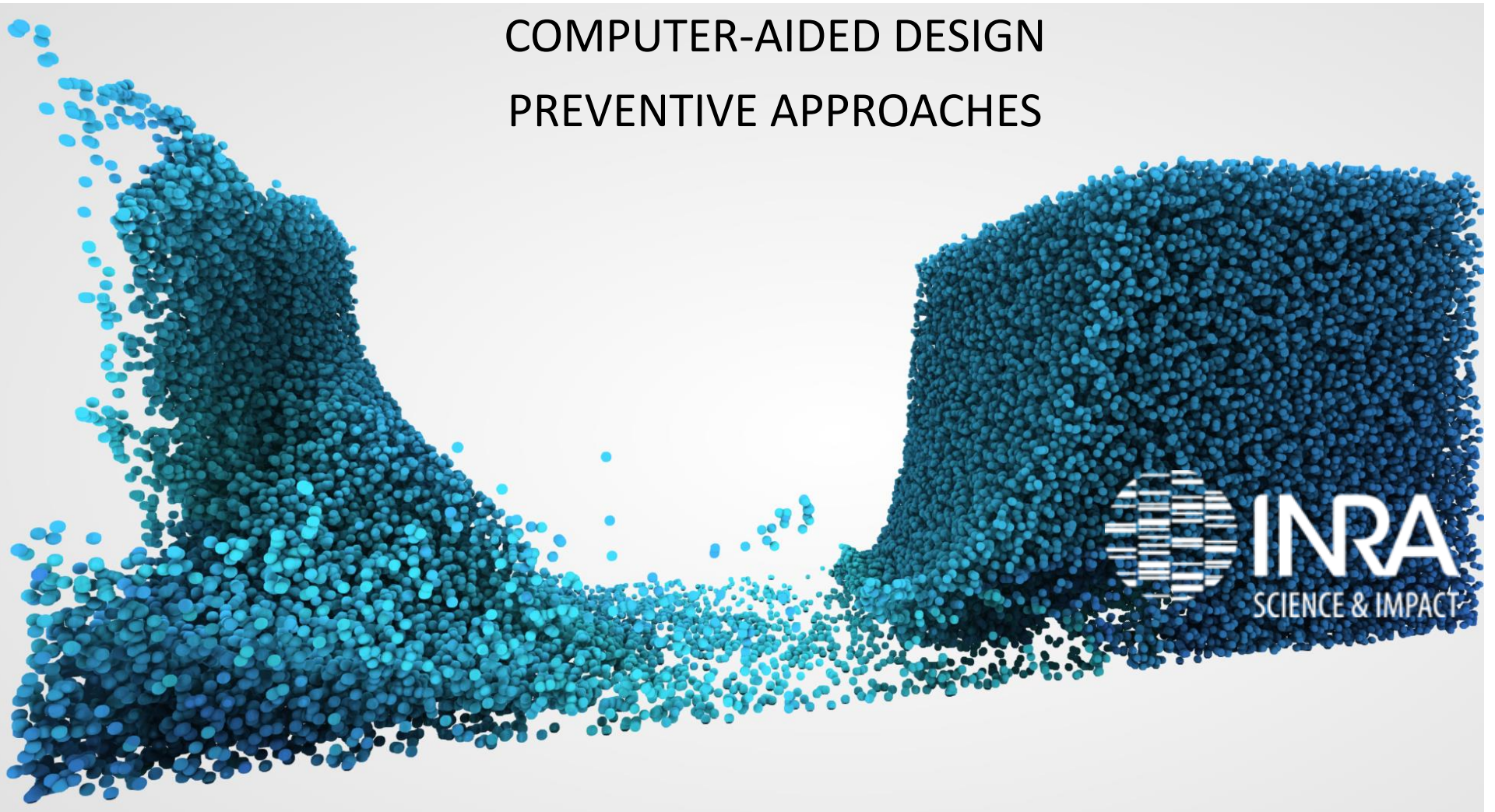
shelf-life=1 year with minimal weight, higher safety

Zhu, Y., Guillemat, B., et Vitrac, O. (2019). Rational Design of Packaging: Toward Safer and Ecodesigned Food Packaging Systems. *Frontiers in Chemistry, 7(349).*

CONCLUSIONS

COMPUTER-AIDED DESIGN

PREVENTIVE APPROACHES



FOOD PACKAGING DESIGN

leaks (sealants, stoppers)

microbial barrier

aroma

syrups

texturing, stabilizing agents

sweeteners

foaming agents

concentrates

preservatives

UV filter

vegetal extracts

coloring

pulps

other additives

acidifying

vitamins

oxygen barrier

carbonates

water

salts

vapor control

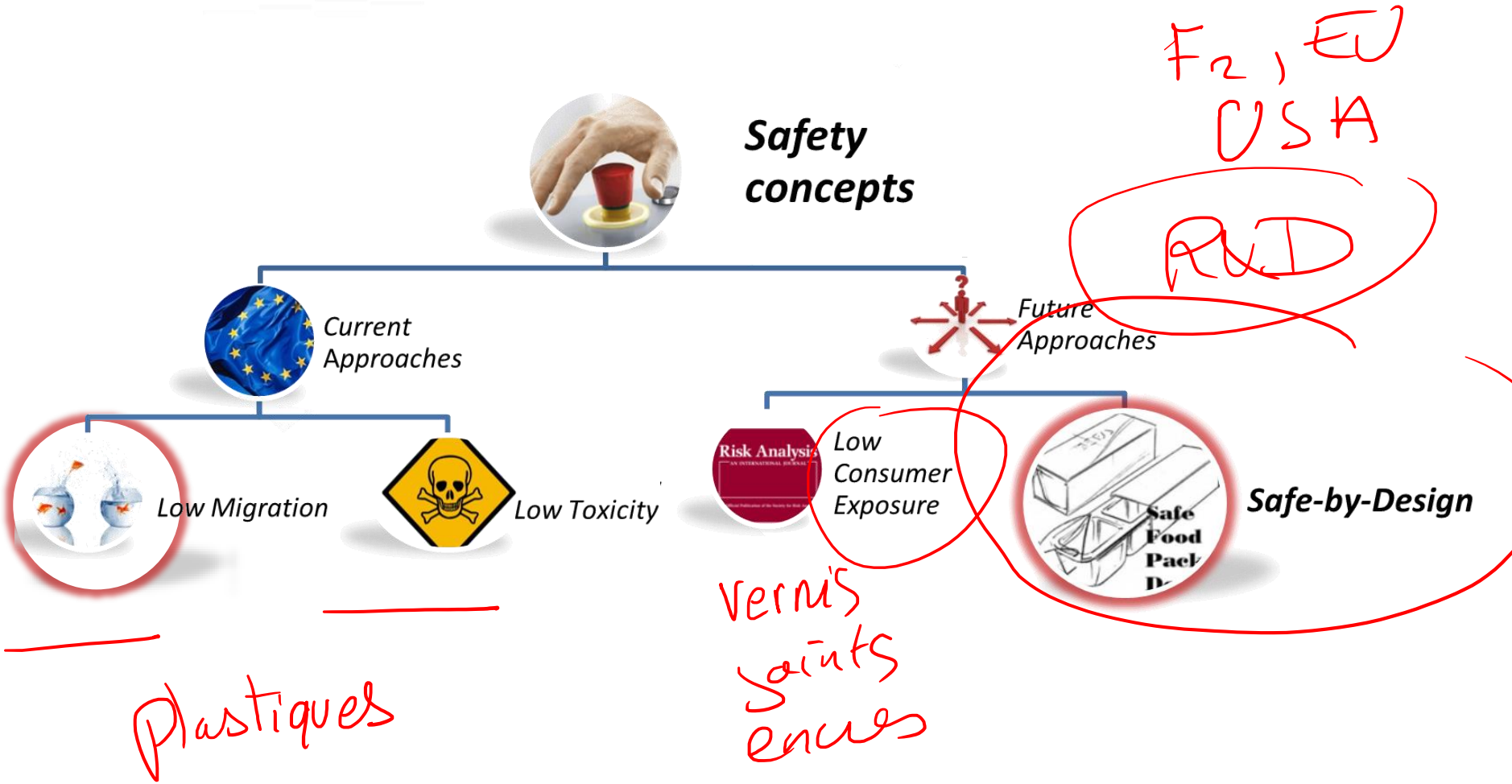
fibers

use, retailing properties

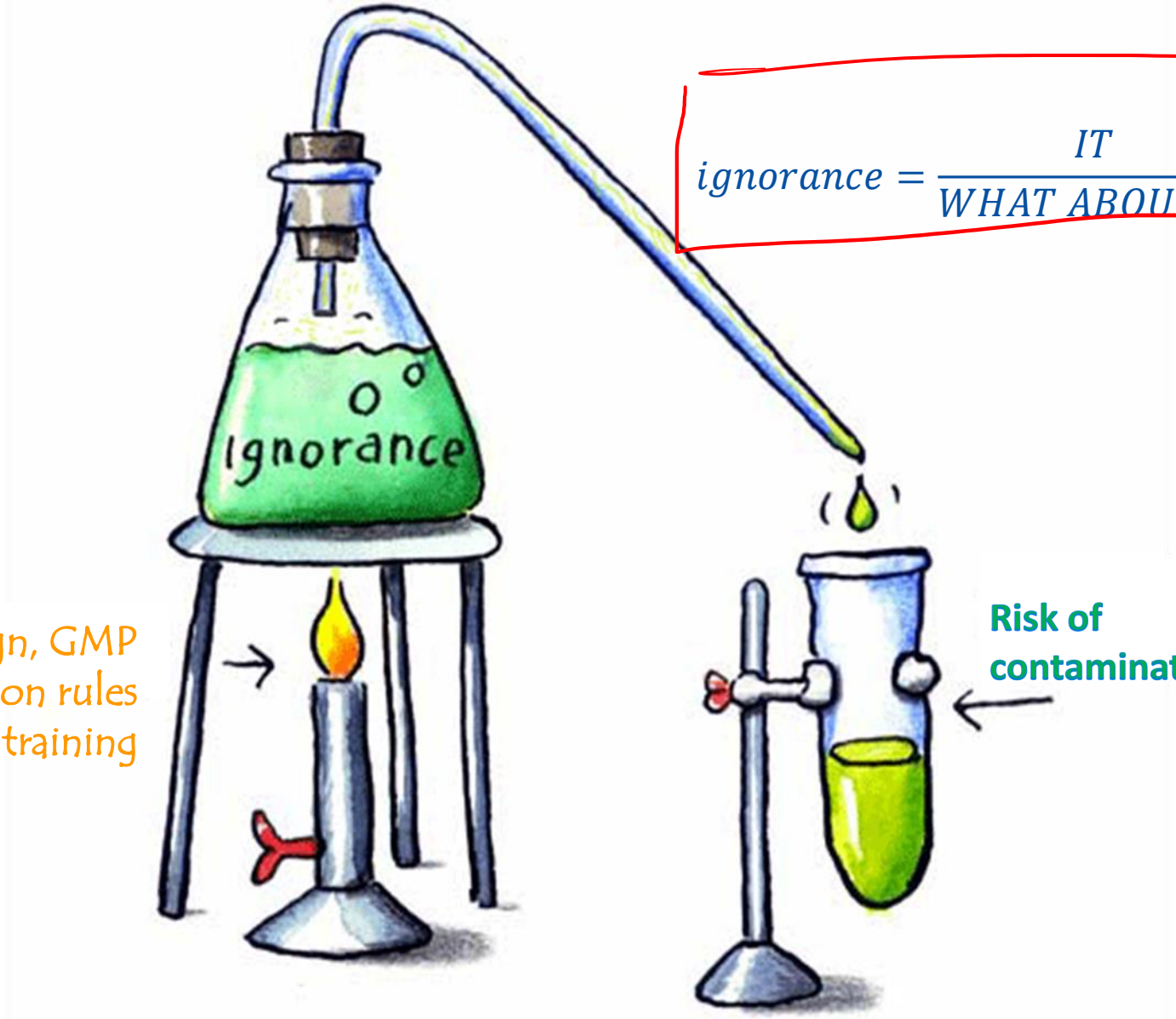

food safety
foodstuff
lesgislation
best practices
shelf life
PACKAGING REQUIREMENTS
consummer convenience
production parameters
ecological aspects

TOWARDS NEW CONCEPTS

PREVENTIVE APPROACHES OF FOOD SAFETY



HUMAN RISK



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

poor design, GMP
weak regulation rules
poor training

Risk of contamination

TOWARDS NEW CONCEPTS

DEVELOPING COOPERATION BETWEEN STAKEHOLDERS

1435/2004

n−1 n n+1

Raw material supplier	Part supplier	Component supplier	Final product	Retailer	Consumer
Polymer flakes	plastic film	body	bottle	retailer 1	consumer 1
Additives	glue	cap		retailer 2	consumer 2
Process aids	ink	label		retailer 3	consumer 3
Catalysts					

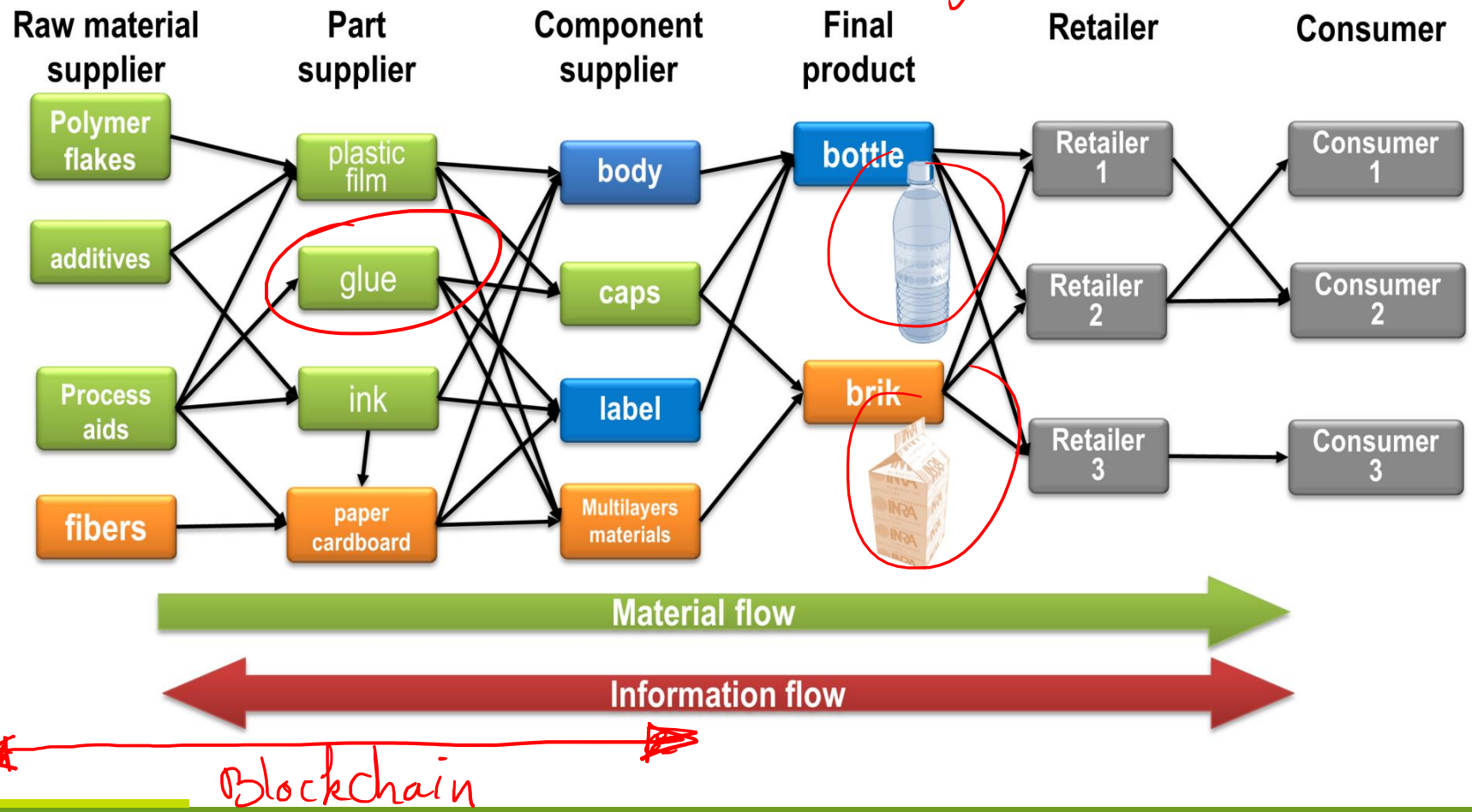
Material flow

Information flow

TOWARDS NEW CONCEPTS

DEVELOPING COOPERATION BETWEEN STAKEHOLDERS

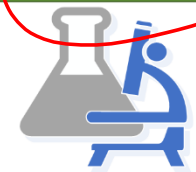
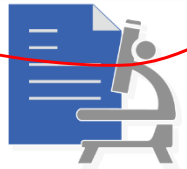
20 refs

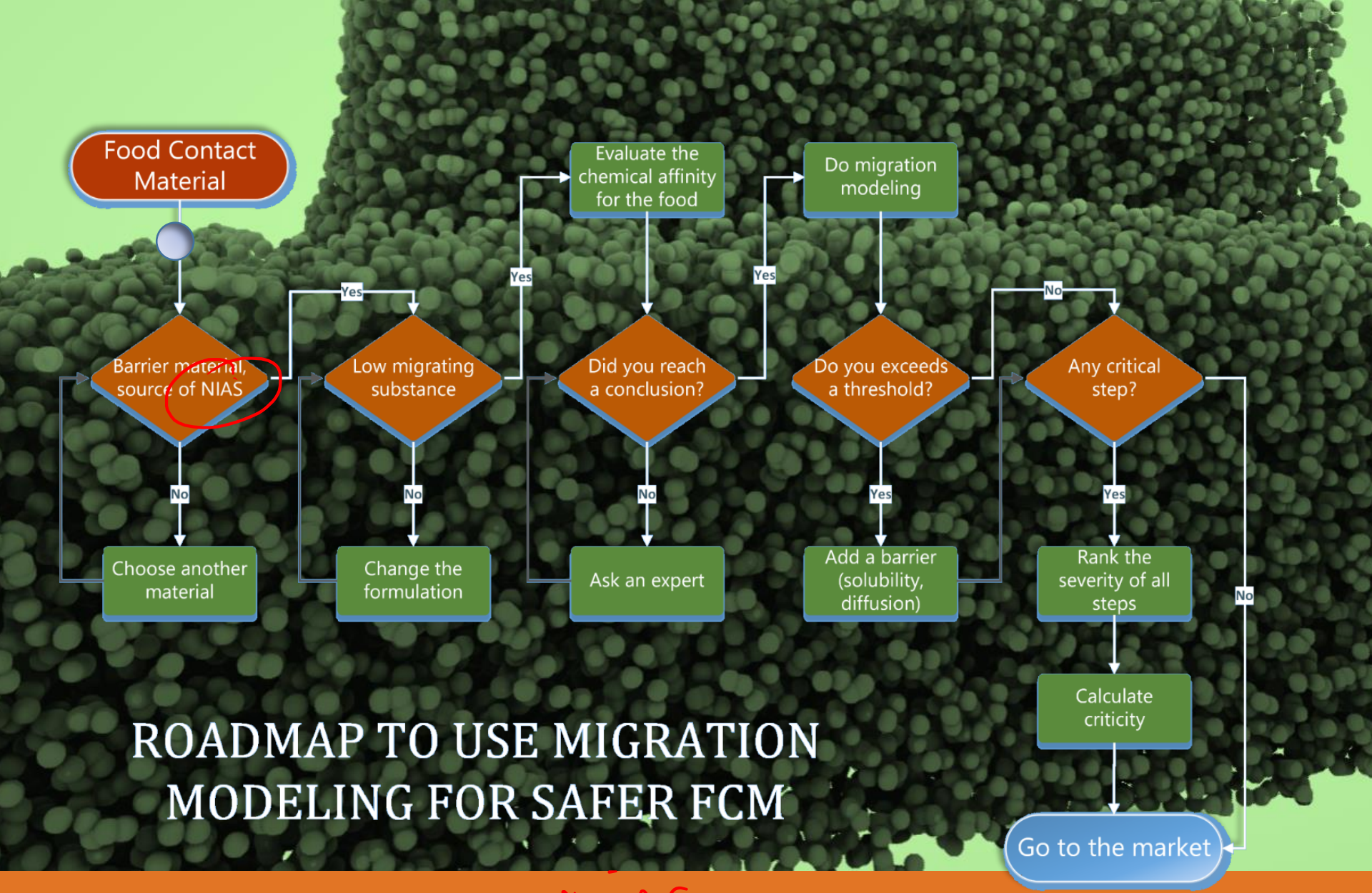


MAIN STEPS TO REVIEW

FMECA « milk for infants stored in a brick »

Collaborative research project SAFEFOODPACK DESIGN

Phase	Formulation	Design	Process	Informations	Mechanisms
					
	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


Food Contact Material
Barrier material, source of NIAS
Low migrating substance
Evaluate the chemical affinity for the food
Did you reach a conclusion?
Do migration modeling
Do you exceeds a threshold?
Any critical step?
Choose another material
Change the formulation
Ask an expert
Add a barrier (solubility, diffusion)
Rank the severity of all steps
Calculate criticity
Go to the market
Yes
No
ROADMAP TO USE MIGRATION MODELING FOR SAFER FCM
NIAS