Hazardous chemicals in FCMs

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FOOD PACKAGING MATERIALS

❖ Metallic cans

❖ Cardboard and paper

❖ Glass and ceramic

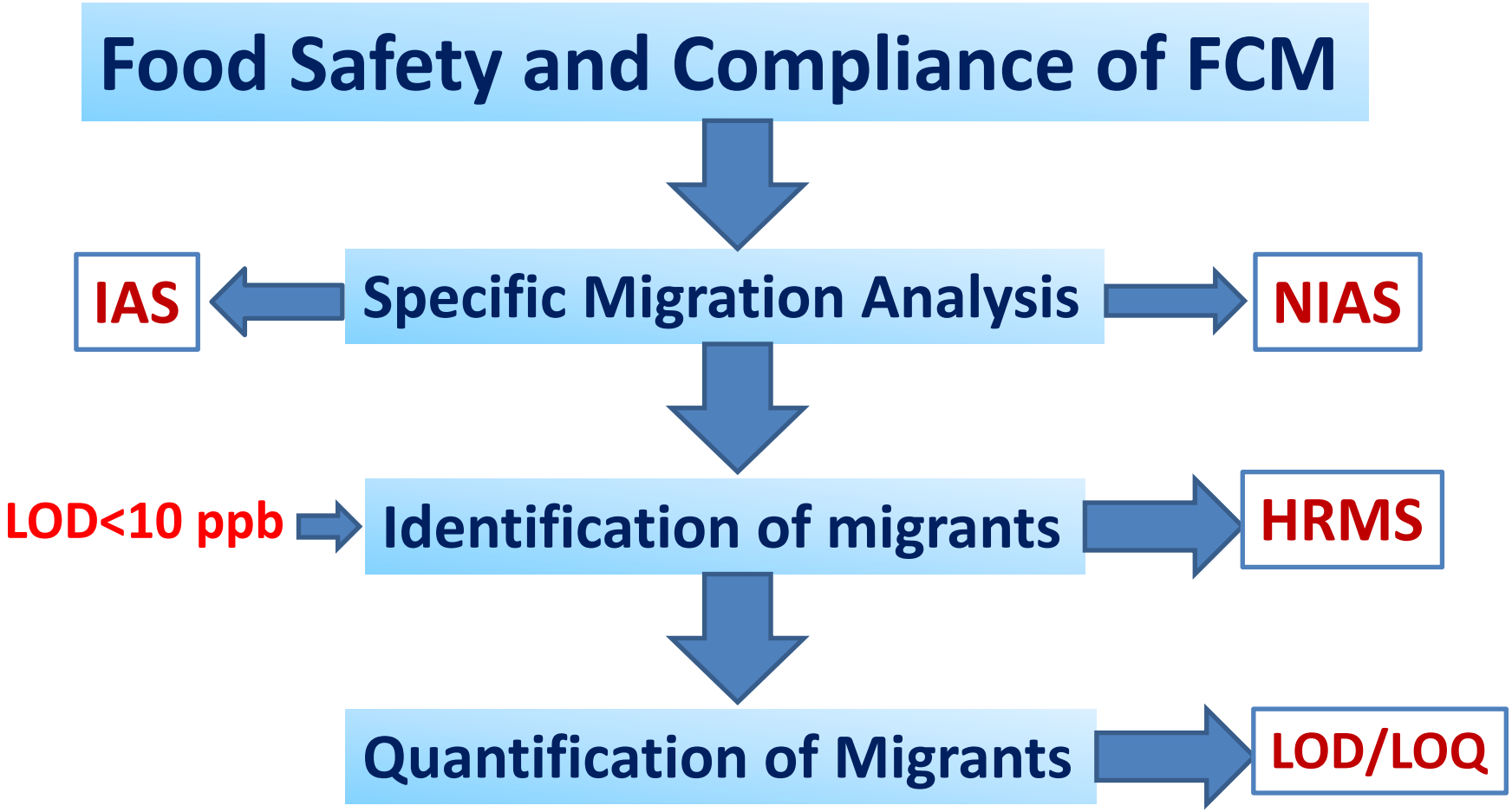
❖ Silicones

❖ Recycled polymers

❖ Conventional plastic polymers (PP, PE, PET,..)

❖ Biopolymers

Targeted and untargeted analysis



Frame Regulation 1935/2004
Plastics Regulation 10/2011/EU (with 16 amendments)

Sources of hazardous substances in FCM

- Plastics (virgin and recycled)
- Paper and board (virgin and recycled)
- Silicons
- Natural materials
- Cork
- Adhesives
- Printing inks
- …

- Monomers
- Additives
- Oligomers
- Metals
- NIAS
- Pesticides
- Mineral oils
- Interaction compounds
- ……

Specific Migration Limits (SML) are enough?

Specific migration analysis Examples

- Coffee capsules: Migrants over SML in coffee
- Migration from Silicone molds and bags
- Bamboo tableware
- BPA in recycled PET
- Surfynol (surfactant)

Migration of dihydroxy alkylamines from PP coffee capsules by UPLC-MS-MS

EFSA is evaluating now the toxicity (EFSA-Q-number: EFSA-Q-2019-00763). Deadline: 30/06/2021

Exposure: 60ºC, 10 days. Extraction of coffee: SALLE; Extraction of Tenax: 2 x 3 g ethanol

Migration (µg/kg) of dihydroxy alkylamines from 5 different capsules to real coffee and to Tenax.

Sample	Migration concentration(µg/kg)					
	To Tenax			To Coffee		
	$C_{12amine}$	$C_{13amine}$	$C_{15amine}$	$C_{12amine}$	$C_{13amine}$	$C_{15amine}$
Capsule1	41.3± 1.7	225± 5	117±7	29.5± 1.1	180± 2	75.2± 0.6
Capsule2	35.2± 0.6	501± 40	165±8	31.8± 1.8	492± 21	153± 1
Capsule3	**463± 9**	**1310± 97**	**155±3**	**425± 4**	**1050± 14**	**201± 2**
Capsule4	35.1±0.9	44.3±0.9	33.8±1.6	31.9± 1.3	40.0± 1.9	34.2± 1.0
Capsule5	39.2±0.6	306±18	96.1±4.8	28.3± 1.4	189± 6	83.9± 3.7

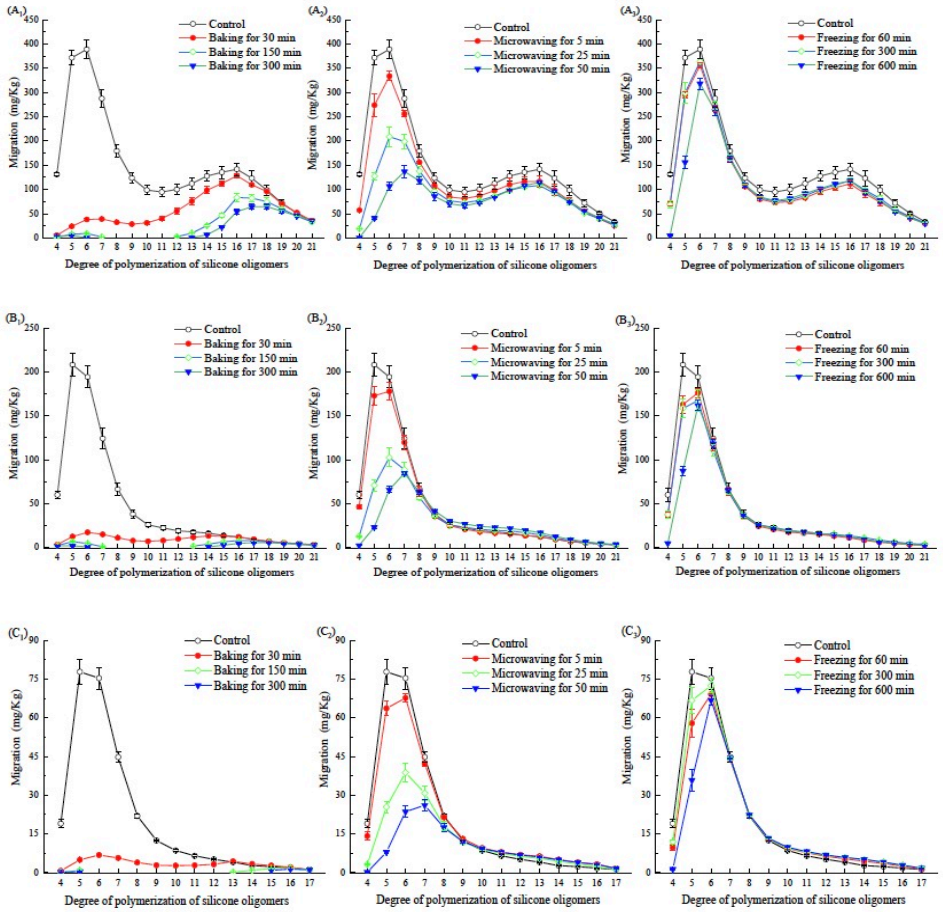
SML

>1.2mg/Kg

Mahdiyeh Otoukesh, Paula Vera, Magdalena Wrona, Cristina Nerin, Zarrin Es'haghi
Migration of dihydroxyalkylamines from polypropylene coffee capsules to Tenax® and coffee by salt-assisted liquid–liquid extraction and liquid chromatography–mass spectrometry. *Food Chemistry* ***2020****, 321,126720 DOI:10.1016/j.foodchem.2020.126720*

Migration from Silicone molds

Baking MW Freezing



Oligomers <1000Da

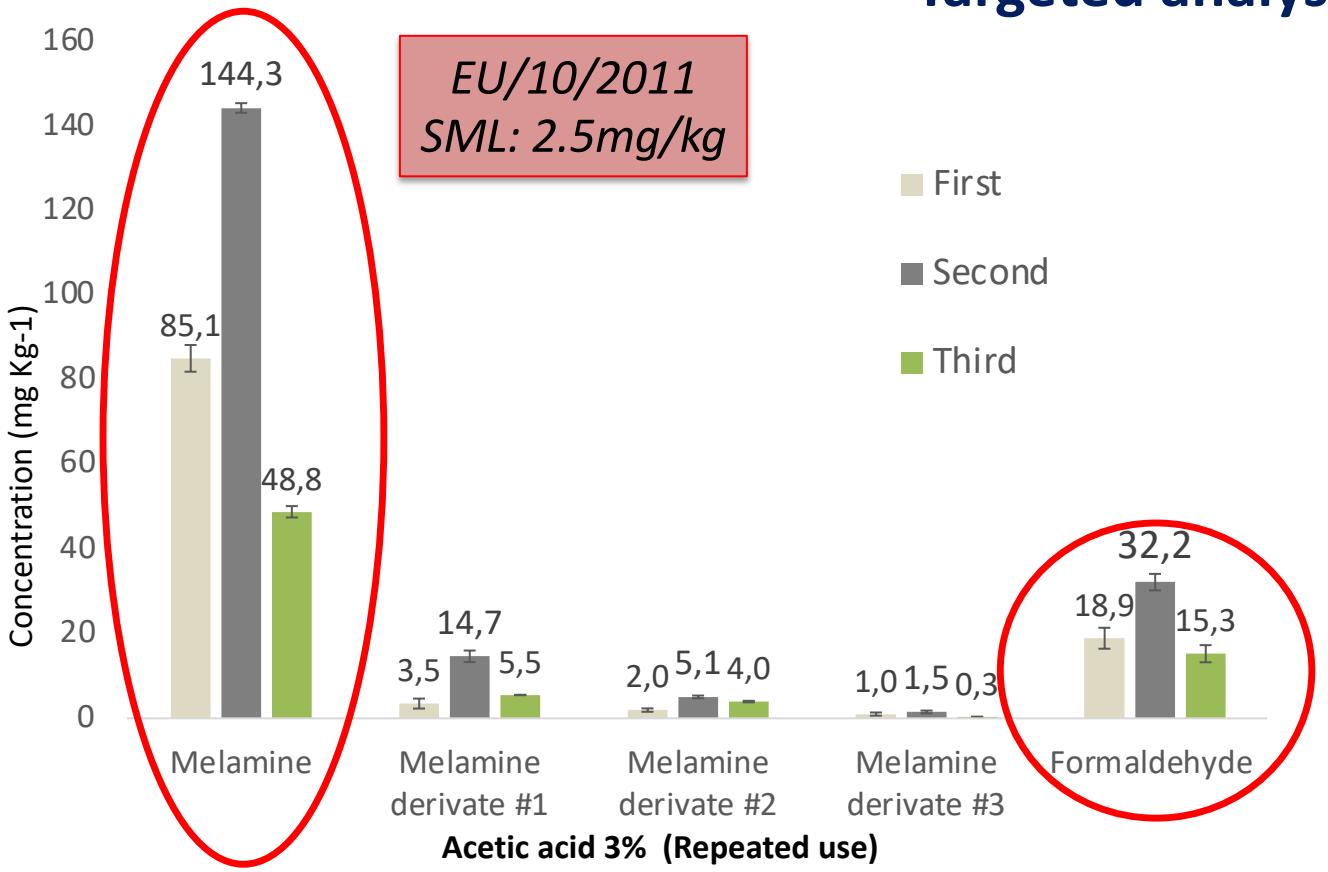
Isoctane	2671.40 mg/Kg
Ethanol 95%	884.20 mg/Kg
Tenax	97.2 mg/Kg

Cramer Class III < 90 mg/Kg

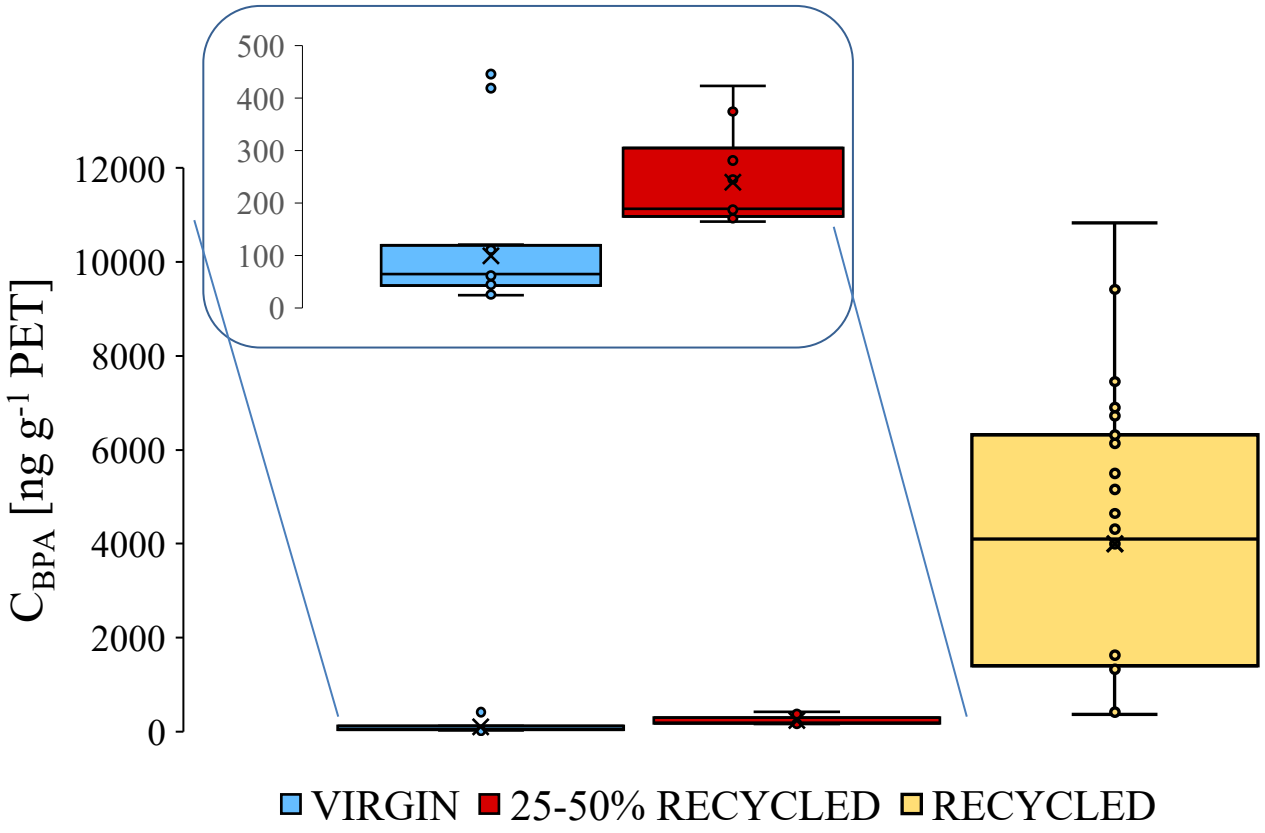
Yi-Qi Liu, Magdalena Wrona, Qi-Zhi Su, Paula Vera, Cristina Nerín* and Chang-Ying Hu
Influence of cooking conditions on the migration of silicone oligomers from silicone rubber baking molds to food simulants. *Food Chemistry* ***2021****, 347,128964, DOI:10.1016/j.foodchem.2020.128964*

Quantification: Melamine and formaldehyde (3 sequential migrations)

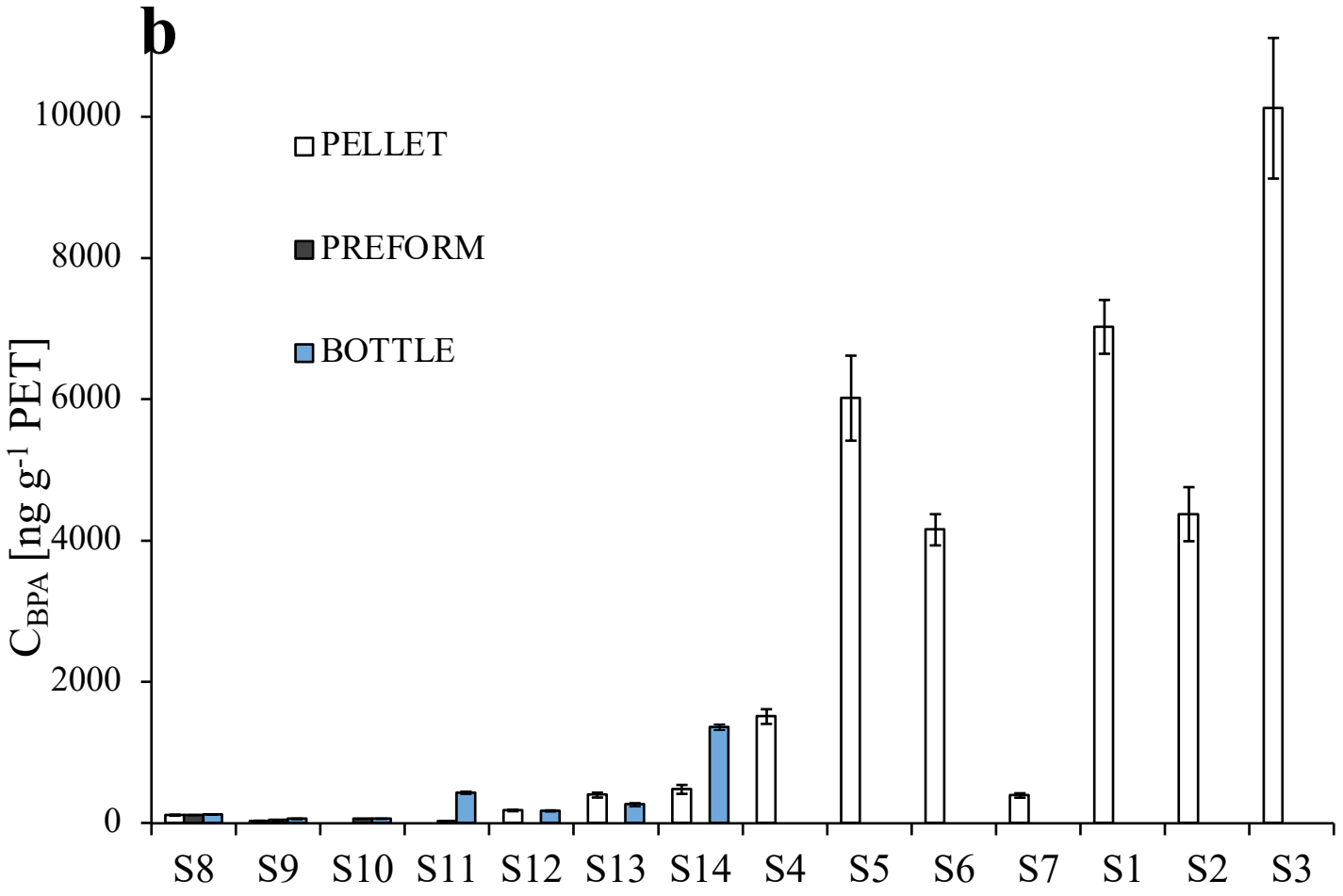
Targeted analysis by UPLC-QqQ



BPA in recycled PET



BPA in recycled PET



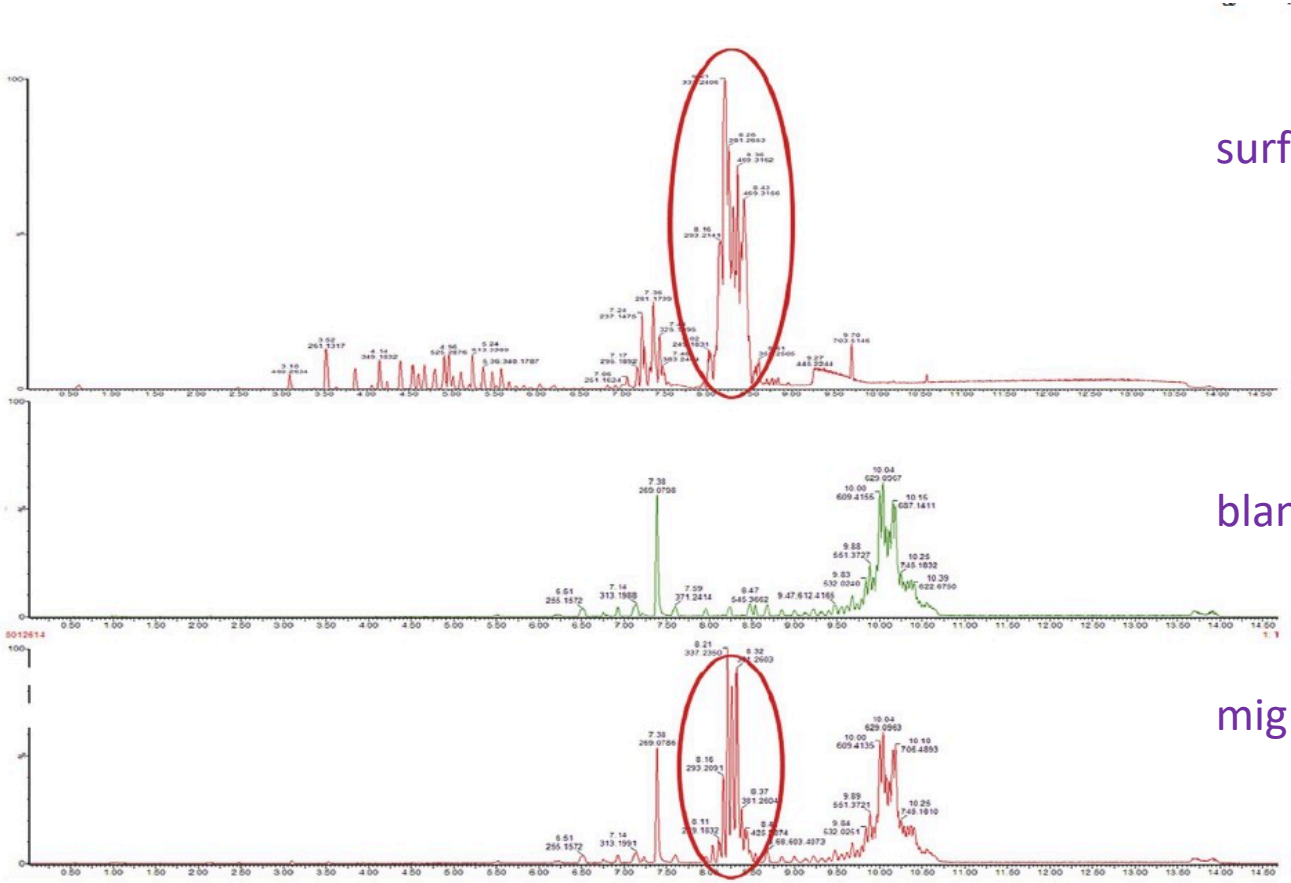
N. Dreolin, M. Aznar, S. Moret and C. Nerín. Development and validation of an LC-MS/MS method for the analysis of bisphenol a in polyethylene terephthalate. *Food Chem.* ***2019****, 274, 246-253; DOI:10.1016/j.foodchem.2018.08.109*

Reprotoxicity of some migrants

(Studies carried out on boar spermatozoa and artificial insemination of saws)
Tests done by direct contact between spermatozoa and the substance

- BADGE (from epoxy and adhesives): causes misscarriages
- Surfynol (a surfactant): kill spermatozoa
- Nonylphenol (degradation of antioxidants): affect spermatozoa
- Others…

Migration of surfynol



surfynol

blank

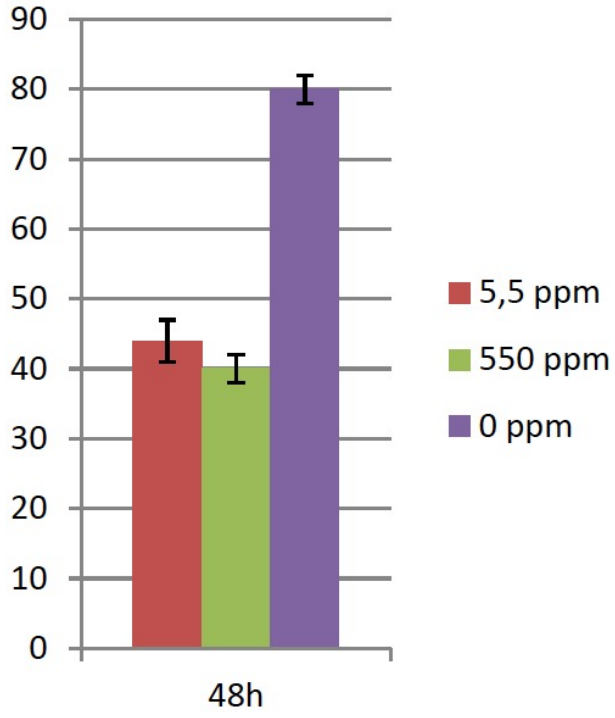
migration

Fig. 1. UPLC-MS-Q-TOF of Surfynol (A), blank (B) and migration to acetic acid 3% (C) after exposure to plastic multilayer containing Surfynol.

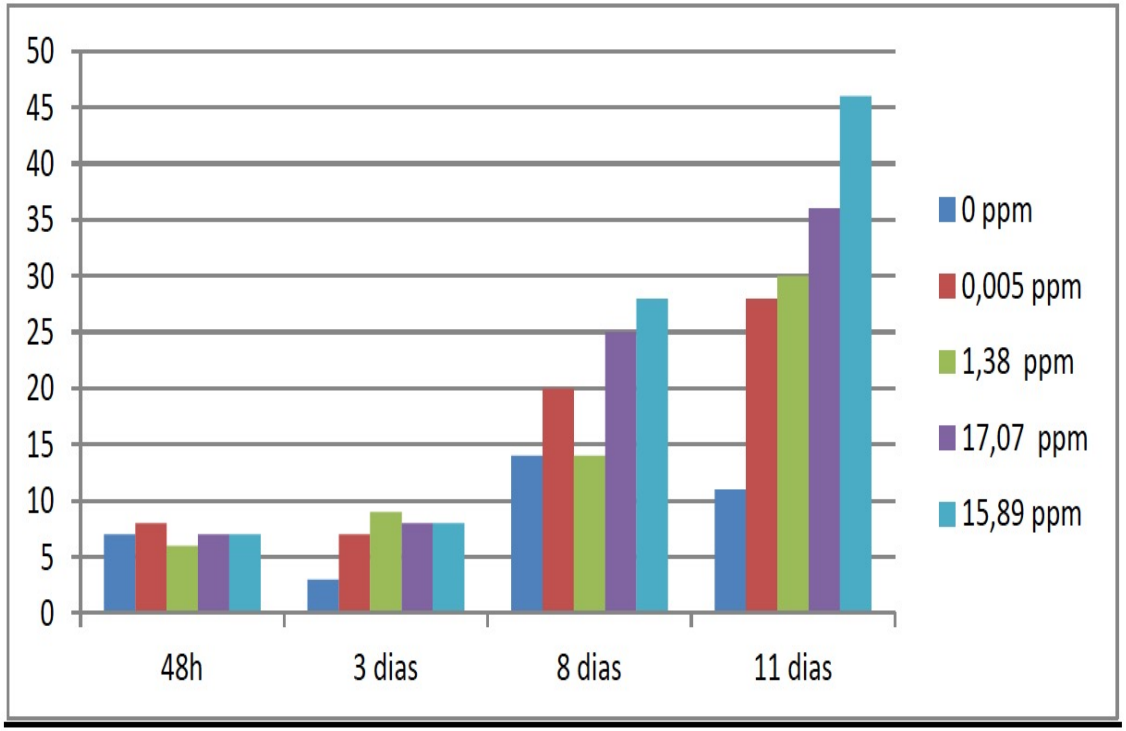
Migration of surfynol

Compound/migration mg/Kg	Mass Q-TOF	LOD	Ethanol 10% PE(35 µm)-adh(4 g/m^2)-PET(12 µm)	Ethanol 10% PE(60 µm)-adh(4 g/m^2)-PET(12 µm)	Ethanol 10% PE(90 µm)-adh(3 g/m^2)-PET(12 µm)	AC 3% PE(35 µm)-adh(4 g/m^2)-PET(12 µm)	AC 3% PE(60 µm)-adh(4 g/m^2)-PET(12 µm)	AC 3% PE(90 µm)-adh(3 g/m^2)-PET(12 µm)
1-hexanol-2-ethyl		0.001	0.005	0.003	<LOD	0.011	0.007	0.003
2,4,7,9-Tetramethyl-5-decyne-4,7-diol (sum of isomers)	249.1827	0.012	1.38	0.58	<LOD	0.72	0.33	0.14
2,4,7,9-Tetramethyl-5-decyne-4,7-diol ethoxylate n=1 m=1*(sum of isomers)	337.2353	0.012	17.07	11.08	2.90	13.40	6.42	5.67
2,4,7,9-Tetramethyl-5-decyne-4,7-diol ethoxylate n=2 m=1*(sum of isomers)	381.2614	0.012	15.89	8.81	1.68	12.70	4.77	4.40

Effect of Surfynol on reproduction



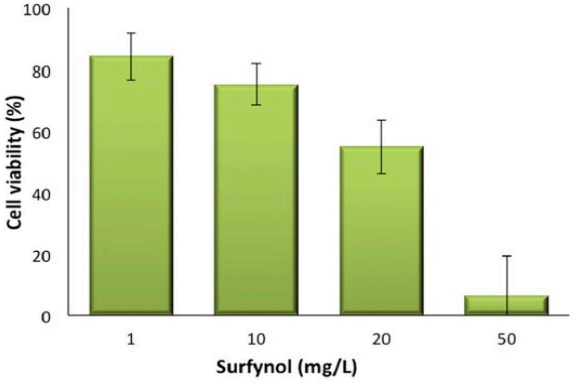
Penetration test



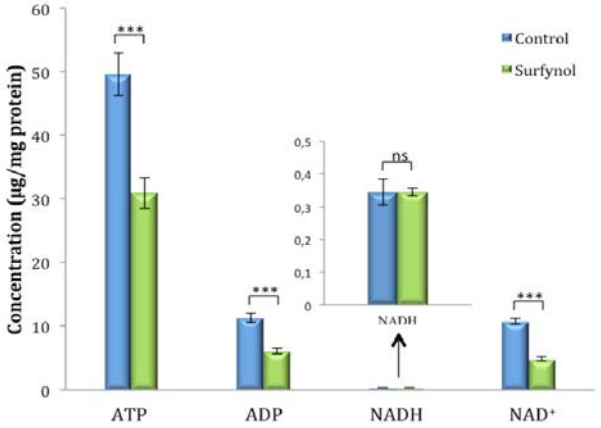
Reacted acrosome (FITC-PNA+)%

Cristina Nerín, Elena Canellas, Paula Vera, Estefanía Garcia-Calvo, José Luis Luque-Garcia, Carmen Cámara, Raquel Ausejo, Joaquín Miguel, Noelia Mendoza. A common surfactant used in food packaging found to be toxic for reproduction in mammals. Food and Chemical Toxicology, **2018**;, 113, 115-124

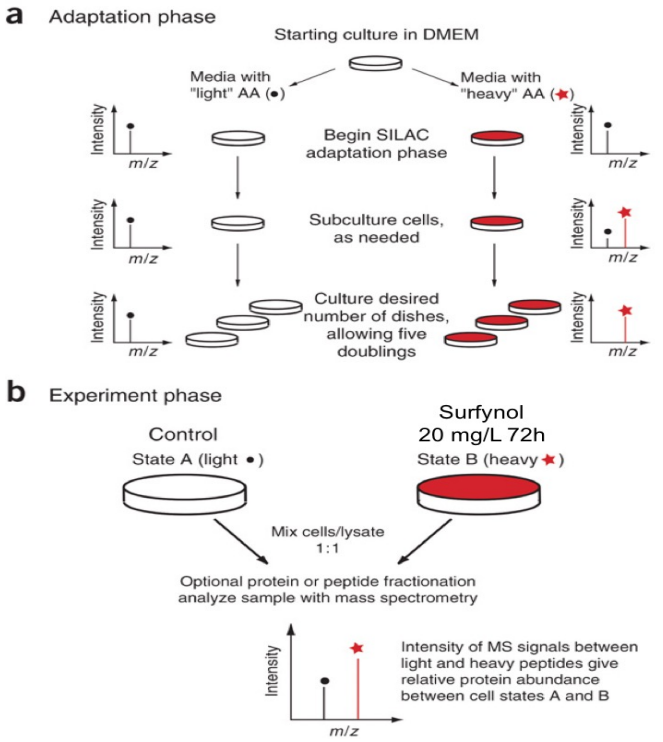
Toxicity of Surfynol: Effect on cells



Cell viability of NTERA-2 cells exposed to different concentrations of Surfynol



NTERA-2 cells exposed to 20mg/L surfynol



108 proteins altered upon surfynol exposure,
34 of which upregulated
74 downregulated

Estefania Garcia-Calvo, Andres Machuca, Cristina Nerín, Noelia Rosales-Conrado, Daniela S. Anunciação, Jose L. Luque-Garcia. *Food and Chemical Toxicology* ***2020****, 146, 111849, DOI:10.1016/j.fct.2020.111849*

Conclusions

- To ensure the safety of food packaging materials is a **difficult task**, as **many unknowns often migrate. Identification is compulsory** for using the material as food conta**ct.**
- Many migrants and some of them **toxic compounds are detected** and quantified. **Legislation needs re-evaluation in depth**.
- **Oligomers often migrate** at quite high levels. Most of them should be lower than 10 ppb. Oligomers **are not degraded** to their original components. Toxicity of oligomers should be studied.
- Sophisticated **laboratories and a high experience are required** for identification of migrants**.**
- **A high investment in pure** standards is also required for quantitative purposes. **Standards of most of NIAS including oligomers are not commercially available.**

R+D+i Projects

(the latest ones)

- **NATURALPACK (INTERREG)**
- **MIGRESIVES Project (EU, VI FP, Collective Research Project)**
- **NAFISPACK Project (EU, VII FP)**
- **SAFEMTECH (EU, IAPP, Marie Curie)**
- AGL-04363 and AGL- 2012-37886 (Spanish Ministry of R&D&i)
- 4 INNPACTO Projects (Spain)
- ACTIBIOPACK
- NANOFLEXIPACK
- AGL-2015
- RTI2018-097805-B-I00
- RTC2019-007161-2
- **FOODYPLAST (EU)**
- Several Companies…

- Instituto de Investigación en Ingeniería de Aragón (I3A)
- Gobierno de Aragón

Grupo GUIA (T-10) and
Fondo Social Europeo

GUIA group, University of Zaragoza, Spain

THANK YOU VERY MUCH FOR YOUR ATTENTION!

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