Risiken erkennen – Gesundheit schützen

FEDERAL INSTITUTE
FOR RISK ASSESSMENT

Re-use of recycled materials in food contact applications in the perspective of consumer protection

Karla Pfaff

Basic requirements for food contact materials

Regulation (EC) No 1935/2004 on materials and articles intended to come into contact with food

Article 3

Materials and articles shall be manufactured in compliance with good manufacturing practice so that, under normal or foreseeable conditions of use, they do not transfer their constituents to food in quantities which could:

(a) endanger human health;

or

(b) bring about an unacceptable change in the composition of the food;

or

(c) bring about a deterioration in the organoleptic characteristics thereof.

These requirements apply for virgin and recycled materials.

Safety of recycled materials in contact with food

Risks associated with the use of recycled materials come from the possible migration of chemicals such as

- Contaminants which may be introduced by the presence of materials in the input stream which have not been manufactured for food contact applications.
- Incidental contaminants from previous uses including possible misuse.
- Chemicals used in the recycling process.
- Degradation products caused by multiple processing.

Plastics recycling

Regulation 282/2008/EC on recycled plastic materials and articles intended to come into contact with foods

Scope:

Materials and articles intended to come into contact with food which contain recycled plastics.

Excluded are:

- Materials and articles made with substances derived from chemical recycling (by depolymerisation).
- Recycled plastic materials and articles made from unused plastic production offcuts and/or process scraps recycled within the manufacturing site.
- Recycled plastics used behind a functional barrier.

The recycled plastic materials and articles remain subject to Regulation 10/2011/EU on plastics for food contact.

Plastics recycling

Regulation 282/2008/EC

Principles:

- Individual authorisation of recycling processes based on an application and an evaluation by the European Food Safety Authority (EFSA).
- EFSA-guidance for the safety evaluation of recycling processes.
- Starting material: Plastics manufactured according to Regulation 10/2011/EU.
- Plastic input must originate from a closed product loop or it must be demonstrated e.g. in a challenge test, that the process is able to reduce any contamination of the plastic input to a concentration that does not pose a risk to human health.
- Quality of plastic input (level of contamination) must be characterised and controlled in accordance with pre-established criteria.

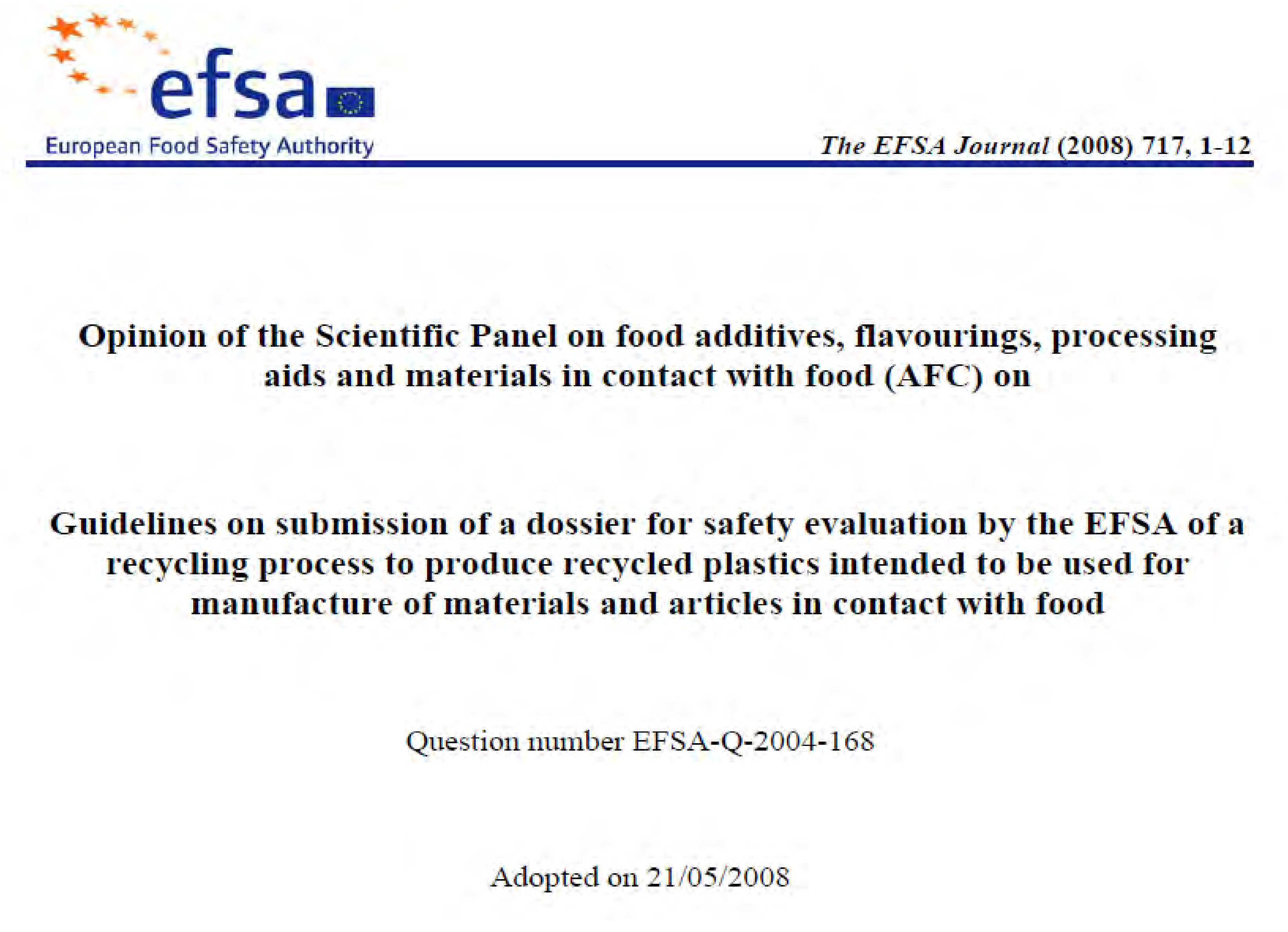
Plastics recycling

Regulation 282/2008/EC

Principles:

- Quality assurance system for plastic recycling processes (e.g. quality control plans, input and recycled plastic characterisation, suppliers' qualification, sorting processes, washing processes, deep cleansing processes, critical control points, analytical protocols).
- Community register of authorised recycling processes within the European community and in third countries.
- Verification that the recycling process corresponds to the conditions of authorisation and that an effective quality assurance system is in place by official controls.

EFSA Guidelines



European Food Safety Authority

The EFSA Journal (2008) 717, 1-12

Opinion of the Scientific Panel on food additives, flavourings, processing aids and materials in contact with food (AFC) on

Guidelines on submission of a dossier for safety evaluation by the EFSA of a recycling process to produce recycled plastics intended to be used for manufacture of materials and articles in contact with food

Question number EFSA-Q-2004-168

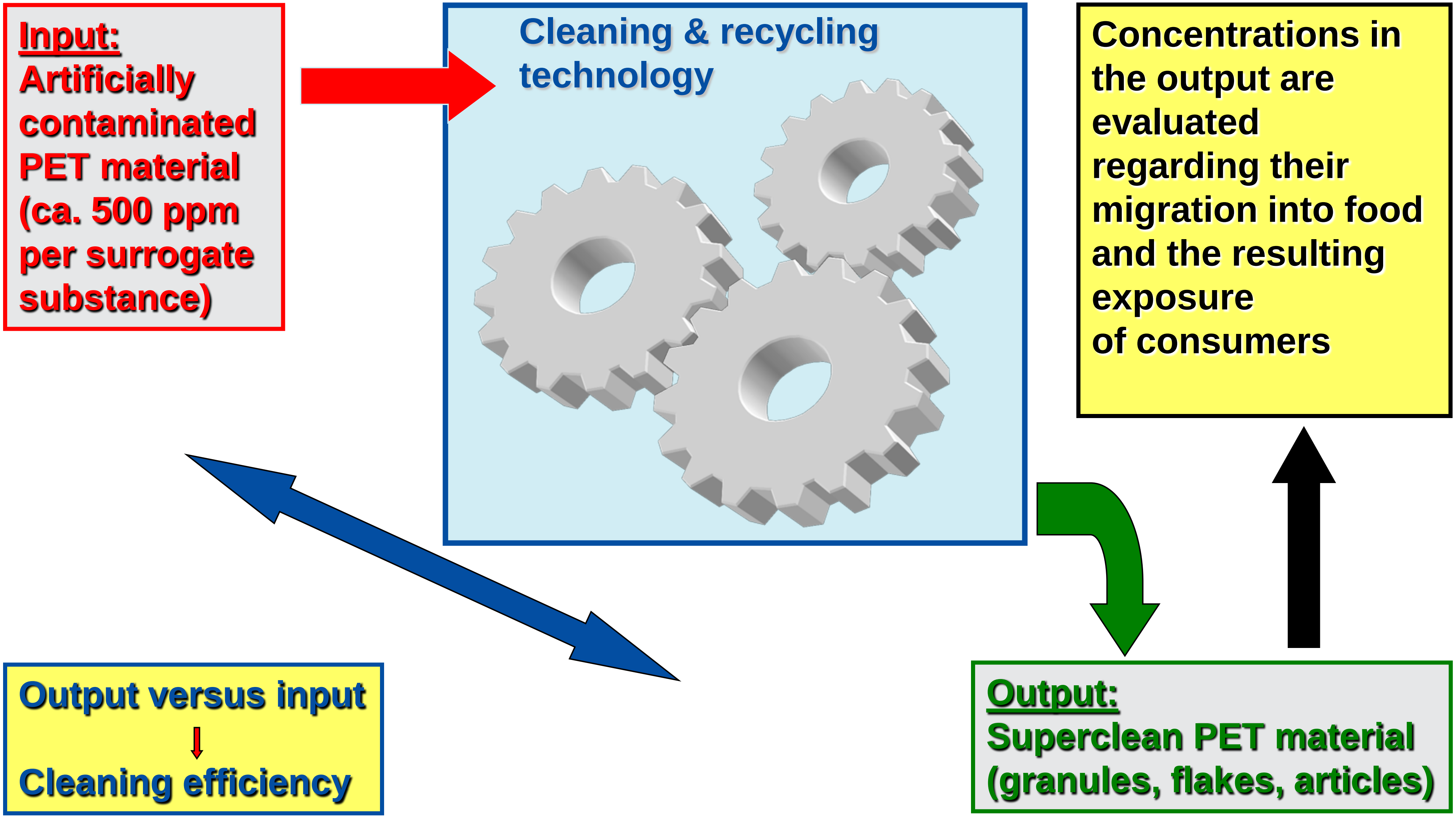
Adopted on 21/05/2008

http://www.efsa.europa.eu/en/efsajournal/doc/717.pdf

EFSA Guidelines

- Administrative information
- Details of the recycling process
- Characterisation of the input material (type and purity of the polymer, fraction of plastics from non-food uses)
- Determination of the decontamination efficiency (“Challenge test”)
- Characterisation of the plastics recyclate
- Compliance with the relevant provisions for food contact materials
- Intended uses (type of food, time and temperature of contact)
- Process analysis und evaluation, identification of critical steps
- Information on the Quality Assurance System

„Challenge Test“



Input:
Artificially contaminated PET material (ca. 500 ppm per surrogate substance)

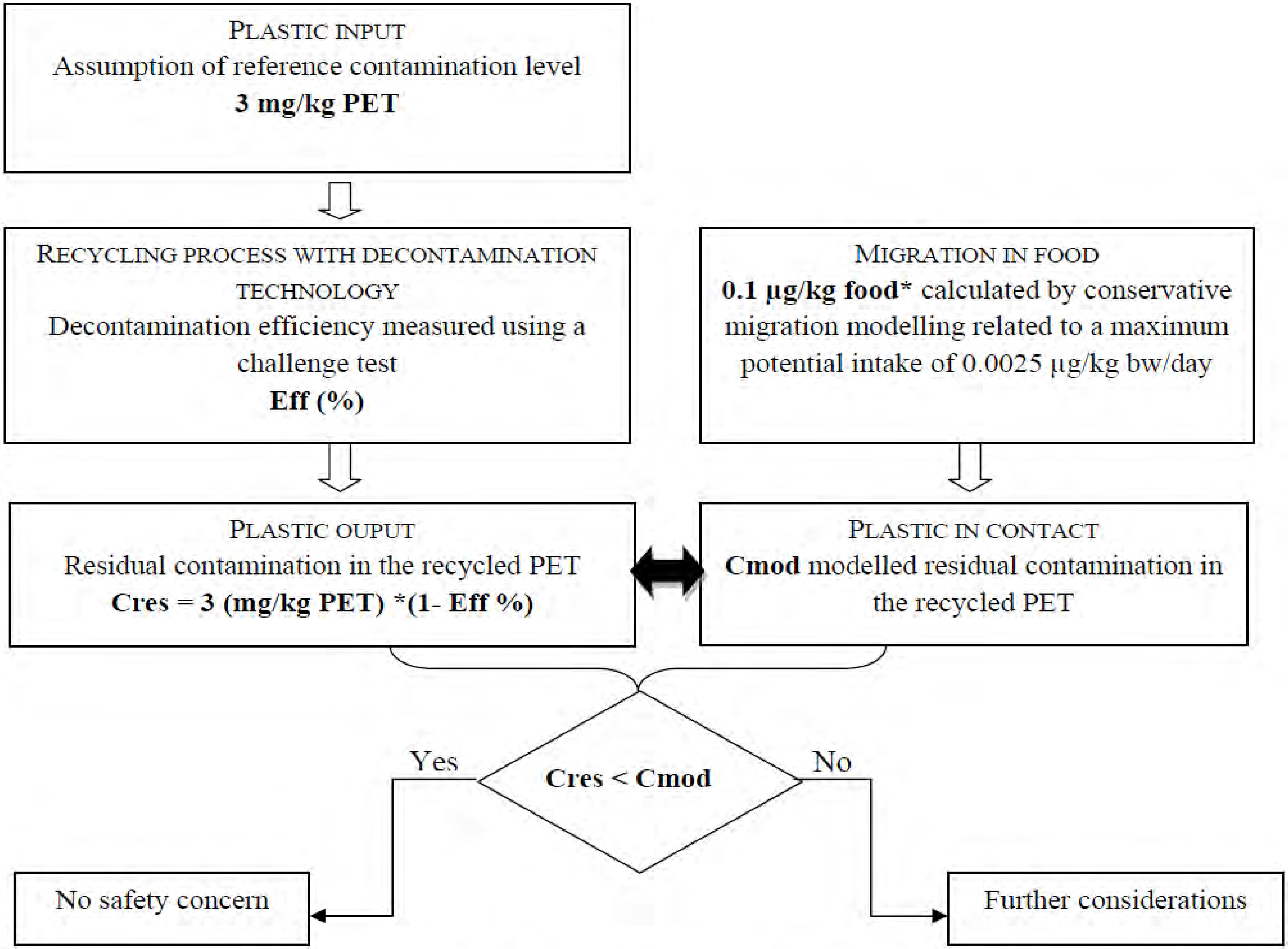
Cleaning & recycling technology

Concentrations in the output are evaluated regarding their migration into food and the resulting exposure of consumers

Output:
Superclean PET material (granules, flakes, articles)

Output versus input
↓
Cleaning efficiency

EFSA criteria for safety evaluation of processes to produce recycled PET for food contact



PLASTIC INPUT
Assumption of reference contamination level
3 mg/kg PET

RECYCLING PROCESS WITH DECONTAMINATION TECHNOLOGY
Decontamination efficiency measured using a challenge test
Eff (%)

MIGRATION IN FOOD
0.1 µg/kg food* calculated by conservative migration modelling related to a maximum potential intake of 0.0025 µg/kg bw/day

PLASTIC OUPUT
Residual contamination in the recycled PET
Cres = 3 (mg/kg PET) *(1- Eff %)

PLASTIC IN CONTACT
Cmod modelled residual contamination in the recycled PET

Cres < Cmod

Yes

No

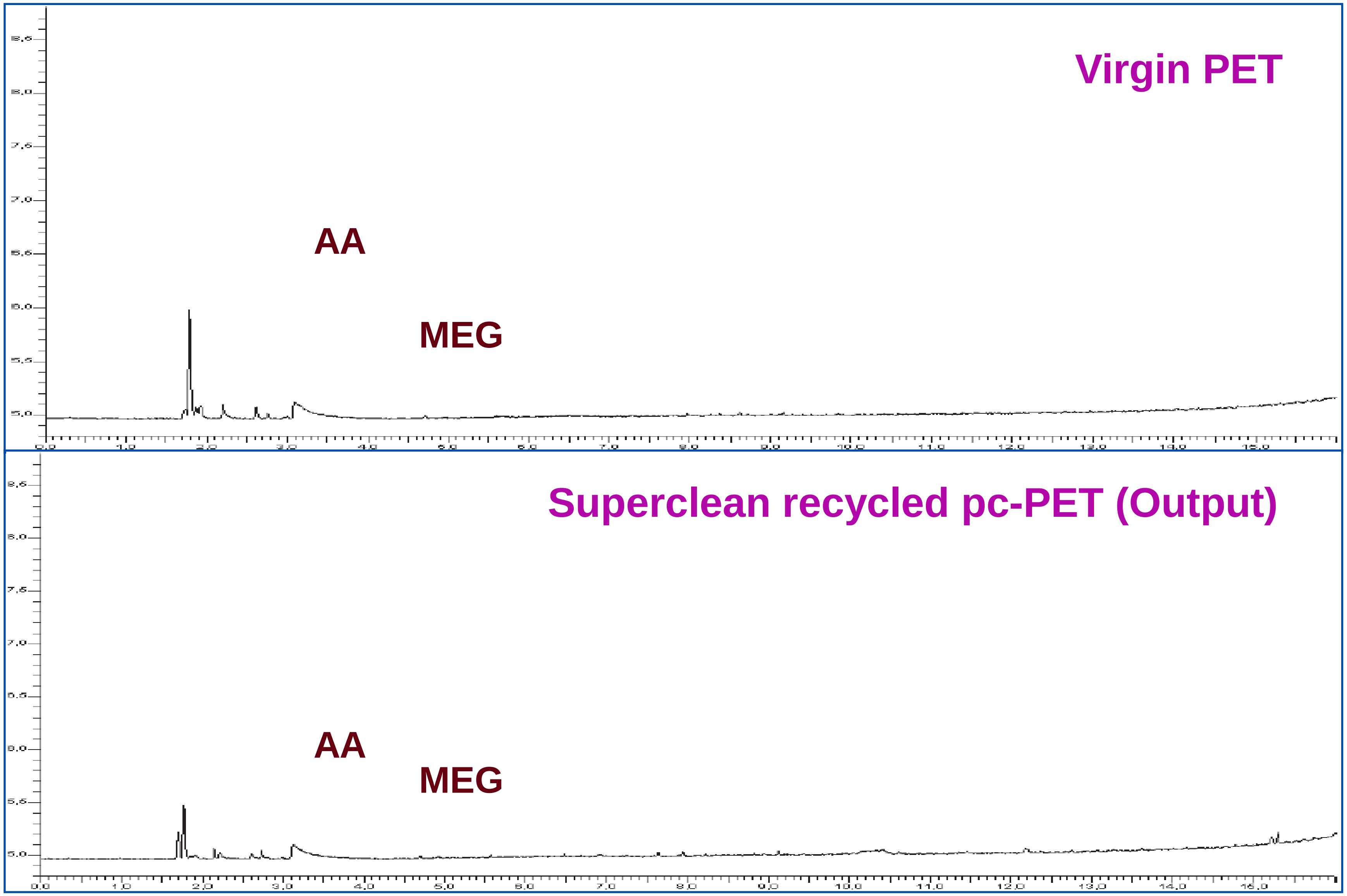
No safety concern

Further considerations

**: Default scenario (Infant). For adults and toddlers, the migration criterion will be 0.75 and 0.15 µg/kg food respectively.*

http://www.efsa.europa.eu/en/efsajournal/doc/2184.pdf

HS-GC analysis of PET for potentially migrating substances



Plastics recycling

- EU legislation has prompted 99 petitions for evaluation of recycling processes since 2009.
- Dossiers arriving at EFSA are predominantly related to PET (ca. 95%).
- Suitability of recycled PET for re-use in food contact is in first instance based on its low diffusivity.
- For PET recycling, processes with high decontamination efficacy are in place.

Recycling of paper and board

- Specific legislation for use of paper and board in food contact is not available.
- BfR recommendation XXXVI lists recycled fibres as raw material with specific requirements laid down in an annex (e.g. migration limits for known contaminants).
- Use of recycled fibres in hot filtration papers, baking paper and absorber pads is not foreseen according to the corresponding BfR recommendations.
- Contamination of the recycling feedstock is caused e.g. by printing inks, glues, and carbonless copy paper.
- For dry, non-fatty foodstuffs having a large surface area (e.g. flour, semolina, rice, breakfast cereals, breadcrumbs), transfer of volatile and hydrophobic substances via the gas phase has to be considered particularly.

Recycling of paper and board

Case 1 - Di-isopropylnaphthalene (DIPN)

- Up to 120 mg/kg in recycled paper from use as solvent in carbonless copy paper (CCP).
- Transfer into food was detected up to 2 mg/kg (pasta, rice).
- Levels in food are not of toxicological concern but present an unwanted contamination.
- By joint action of health and environmental authorities as well as industry, contamination of recycled paper was decreased to 50 mg/kg on average. CCP as recovered paper grade is now separeted from the general input stream and is mainly recycled for sanitary papers.

Recycling of paper and board

Case 2 - Di-isobutylphthalate (DiBP)

- Up to 70 mg/kg in recycled paper from use as plasticiser in dispersion adhesives used for instance in folding boxes and corrugated board for non-food applications and for print products.

- Transfer into food was detected up to 5 mg/kg (pasta, rice).

- Toxic for reproduction, SVHC candidate list, migration limit in food 0.3 mg/kg (BfR)

- **„Initiative for reduction of DiBP in paper and board“** was signed November 2007, joined by 9 industrial associations, addressed to the Federal Institute for Risk Assessment and the Federal Environment Agency.

  No products which contain DiBP - in particular adhesives - should be used in all paper products in order to reach a reduction of the transfer of DiBP into food to a level of < 0.3 mg/kg until 2010. This limit applies from 2011.

Recycling of paper and board

Case 3 – Mineral oil

- Source for the introduction of mineral oil into the recycling system: in first instance inks used in the offset printing of e.g. newspapers or leaflets. Ink preparations contain 20-30% mineral oil as solvent.
- Mineral oils are also introduced from other sources (e.g. adhesives and solvents used in the formulation of paper additives).
- Mineral oil is not significantly removed in the recycling process.
- Mineral oil in newspapers is about 3000 mg/kg; content in unprinted reclycled board is 300-1000 mg/kg (265 mg/kg on an average in „119 sample study“).
- Contamination of food occurs by transfer via gas phase and is limited to volatile components up to about C24.

Mineral oil

Composition:

- ***„Mineral Oil Saturated Hydrocarbons“ (MOSH)***

Paraffinic (open chain, mostly branched) and naphthenic (cyclic) hydrocarbons, distribution of chain length is centered at C17 – C19.

- ***„Mineral Oil Aromatic Hydrocarbons“ (MOAH)***

10 – 25 %, 1 – 4 aromatic rings, partly hydrogenated, mostly highly alkylated (> 97 %).

Max. content in food:

(“119 sample study”, semolina)	MOSH : 100 mg/kg
	MOAH: 16 mg/kg

Data on oral toxicology of the mineral oil mixture is not available.

Mineral oil

Toxicological data available for MOSH :

Genotoxicity, sub/chronical toxicity, cancerogenicity, accumulation in the body.

Toxicogical effects (inflammation, histiocytosis) were dependent on the viscosity (chain length) of the mineral oils and on their accumulation in the body.
Accumulation was found in lymph nodes, liver and spleen after oral exposure (90 d-stuy on rats).

Acceptable daily intakes (ADI) differ in several orders of magnitude. For the relevant fraction a temporary ADI of 0.01 mg/kg b.w. is available (JECFA).

SCF (1995): *http://ec.europa.eu/food/fs/sc/scf/reports/scf_reports_37.pdf,*
EFSA (2006): *http://www.efsa.europa.eu/EFSA/efsa_locale-1178620753812_1178620770938.htm,*
JECFA (2002, 2009): *http://whqlibdoc.who.int/trs/WHO_TRS_913.pdf*

Temporary ADI is regularly exceeded by the transfer from recycled paper and board.

Mineral oil

Toxicological data available for MOAH :

Presence of aromatic hydrocarbons in mineral oils – in particular of polycyclic aromatic compounds – results in **mutagenic and cancerogenic effects**.
(Doak et al., 1983; Roy et al., 1988)

- Alkylated aromatic hydrocarbons are insufficiently investigated to date (insufficient data on genotoxicity, no oral studies on cancerogenicity). Data on occurence, metabolism and toxicological effects are limited to few congeners, only.

- Alkylation of aromatic ring systems may influence metabolism and biological activity of the compounds and may result in different toxicological properties:
  Some alkylated aromatics are known to be cancerogenic in animal experiments in contrary to their non alkylated aromatic homologues *(LaVoie et al., 1985; Rice et al., 1987)* or to have a much higher cancerogenic potency *(Coombs et al., 1976)*.

Toxicological evaluation and derivation of tolerable intake is not possible due to the lack of data. The reduction of the contamination is necessary.

Recycling of paper and board

- Recycling processes are not efficient in removal of most contaminants.
- Reduction strategies to minimise transfer of contaminants into food are needed.

Recycling of paper and board

Possible options:

- Use of alternative packaging materials including the use of virgin fiber materials (in combination with suitable printing inks).
- Restrictions in use of recycled paper and board (e.g. exclusion of direct contact with dry food having a high specific surface area).
- Exclusion of newspapers as input material by sorting processes.
- Phasing out printing inks containing mineral oils and switching to other kinds of printing inks (e.g. soya oil-based inks).
- Improving cleaning efficiency in the recycling processes.
- Use of functional barriers
  - Bag-in-Box systems
    i.e. inner bags with barrier function (e.g. PET, aluminum >7 µm)
  - Barrier coatings e.g. based on polyesters, polyacrylates, polyamides.

Thank you for your attention

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Fate of BFR during treatment of plastics from WEEE

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Fraunhofer Institute IVV, Dep. Polymer Recycling, Freising

Fraunhofer
IVV

Contents

Plastics in WEEE

- Polymer types
- BFR and PXDD/F

Thermal treatment

- High-Tech-Principles
- High Tech example
- Effect of low tech

Recycling

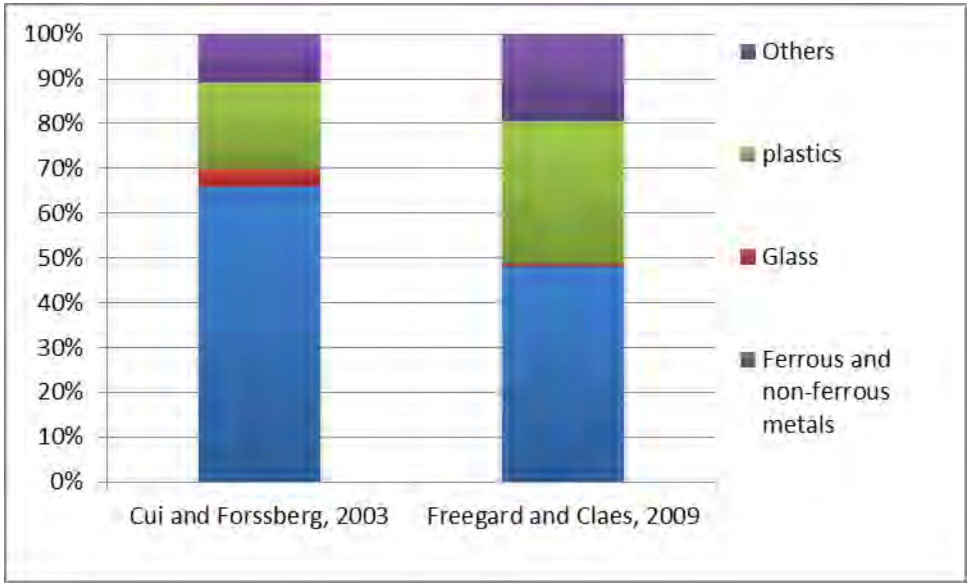
- Current practise (Export)
- Cherry picking
- CreaSolv® approach

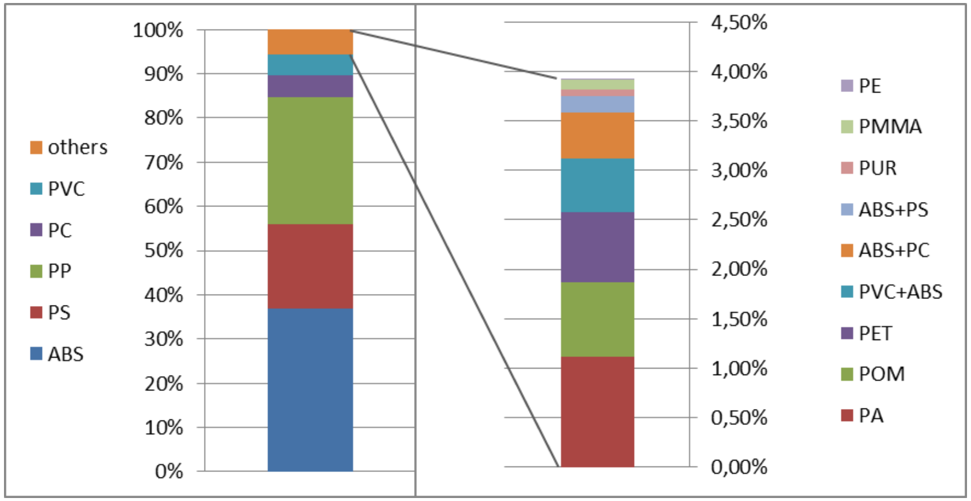
Dumping

Conclusions

Plastics in WEEE

- Polymer share of WEEE rises
- ABS, PS and PP are the dominating polymer types
- Separation / recovery of plastics from WEEE is not state of the art
- Dismantling fractions
- Plastics Shred

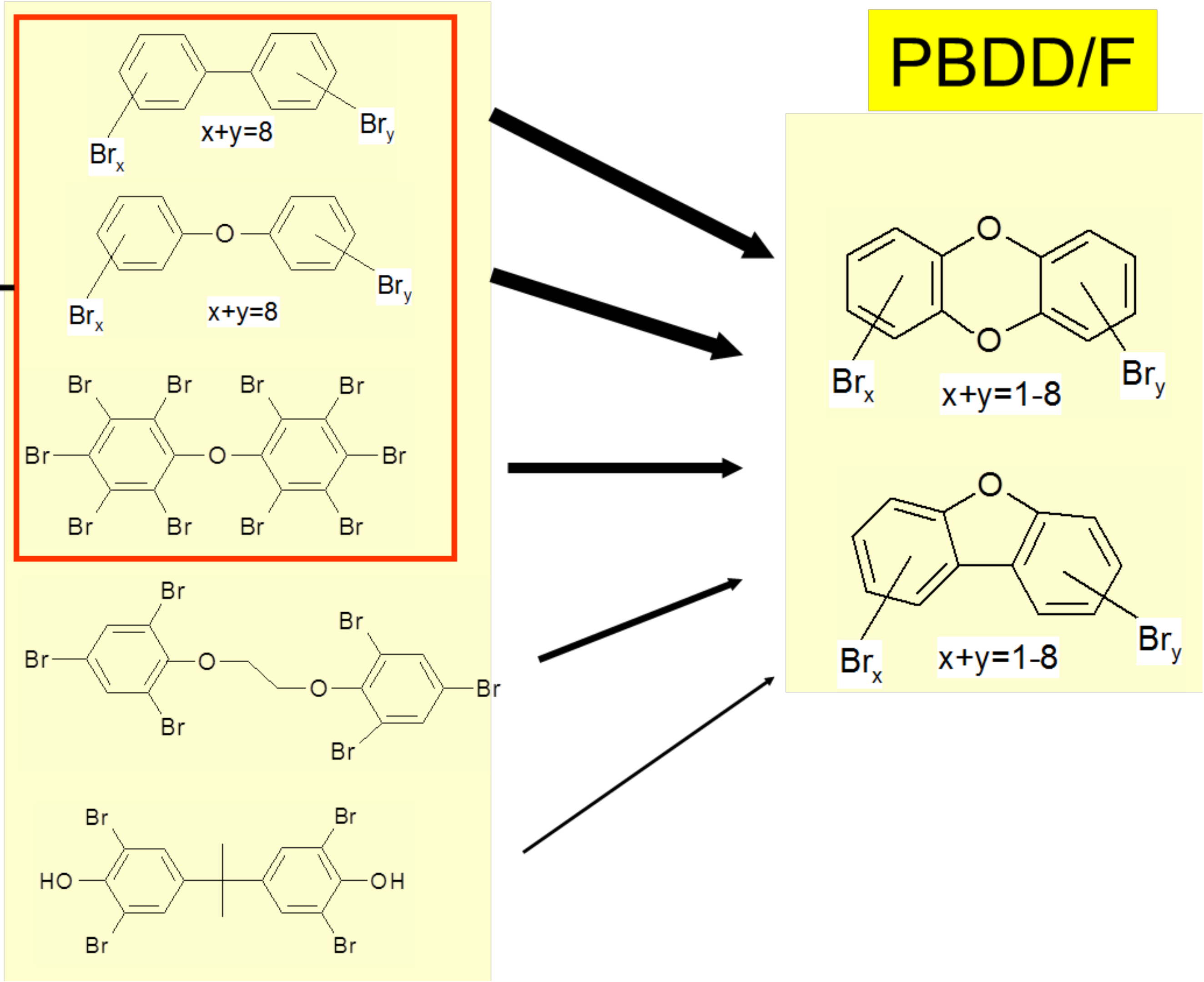




Dimitrakakis, Janz, Bilitewski, Gidarakos (2009)

BFR in WEEE 1

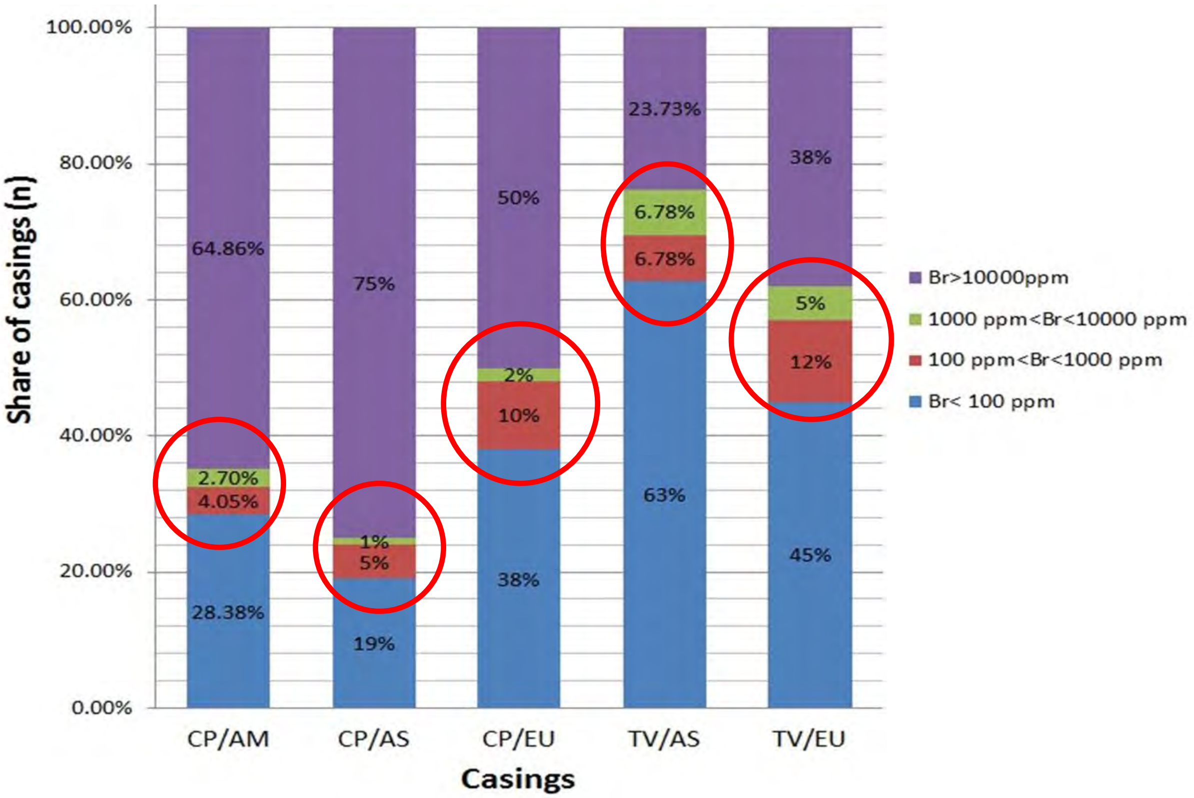
RoHS:
0,1%



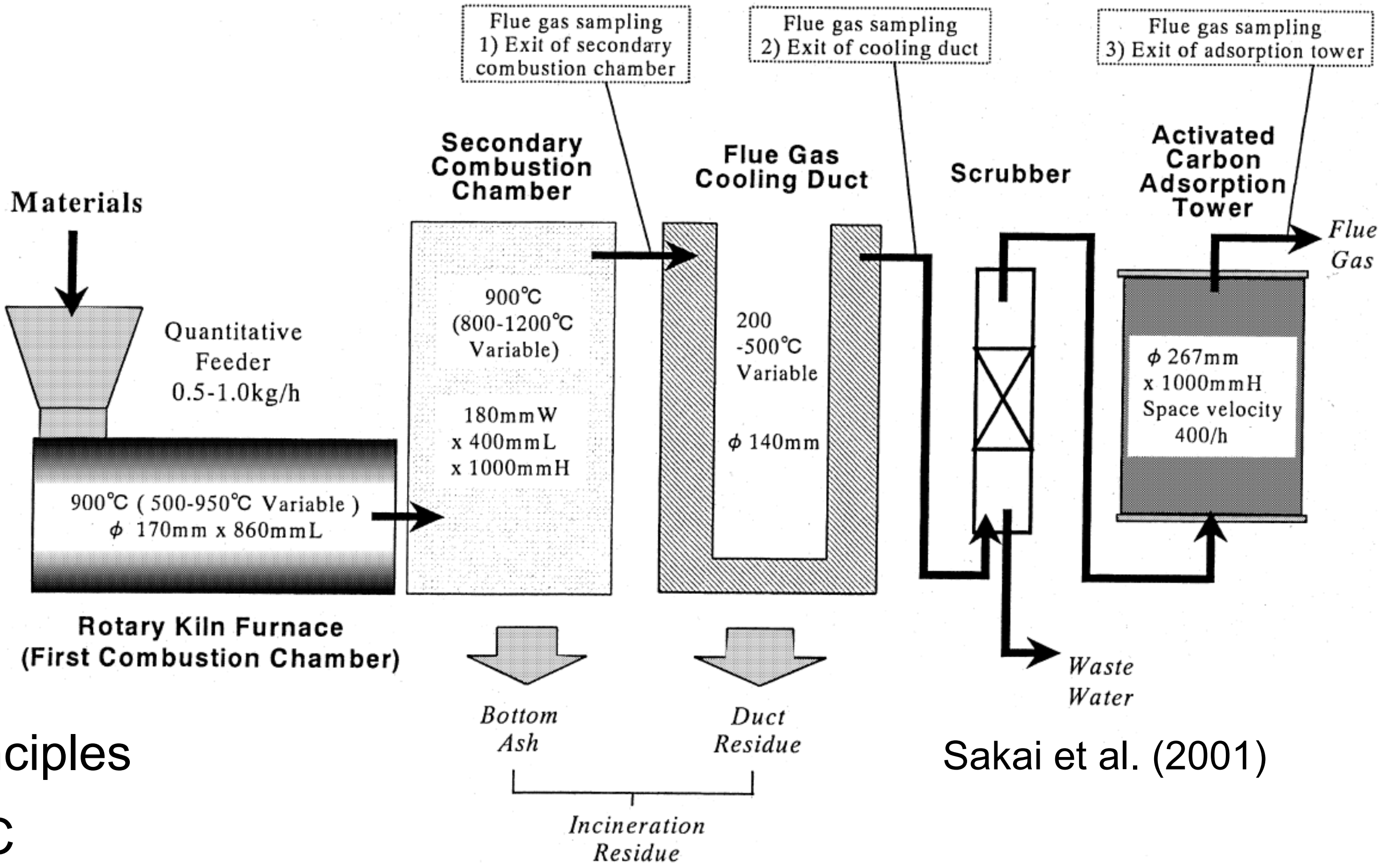
PBDD/F

Contaminants (BFR) in WEEE 2

- No PBB anymore and decreasing amounts of OctaBDE
- Data of a running screening project on BFR in WEEE plastics sampled in Nigeria → still high shares of BFR materials



Thermal treatment BAT/BEP



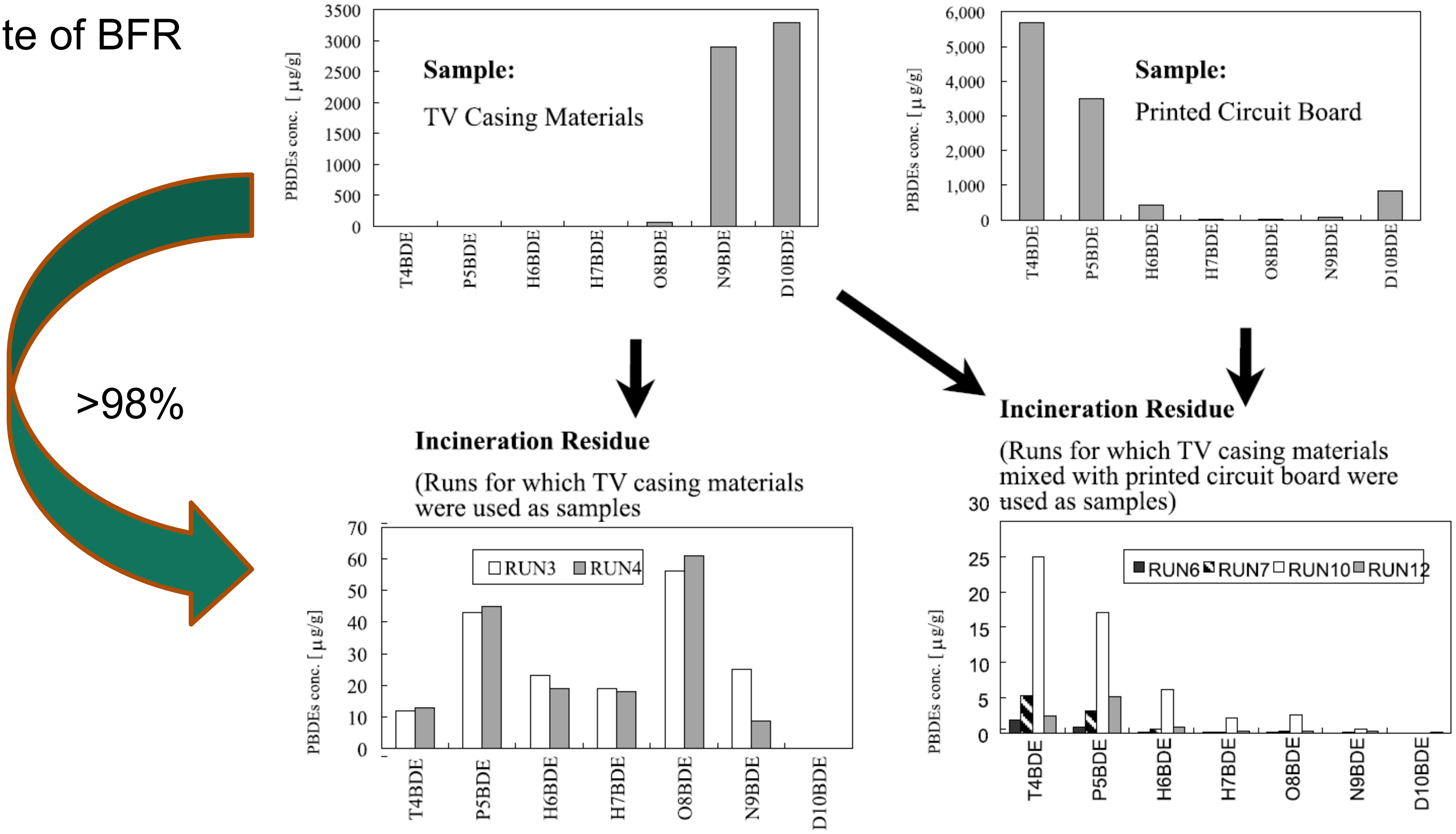
Sakai et al. (2001)

Important principles

- 2 s > 850°C
- Secundary combustion chamber
- Rapid cooling in order to avoid de-novo synthesis of dioxins/furans

Thermal treatment BAT/BEP

Fate of BFR



Incineration Residue

(Runs for which TV casing materials were used as samples

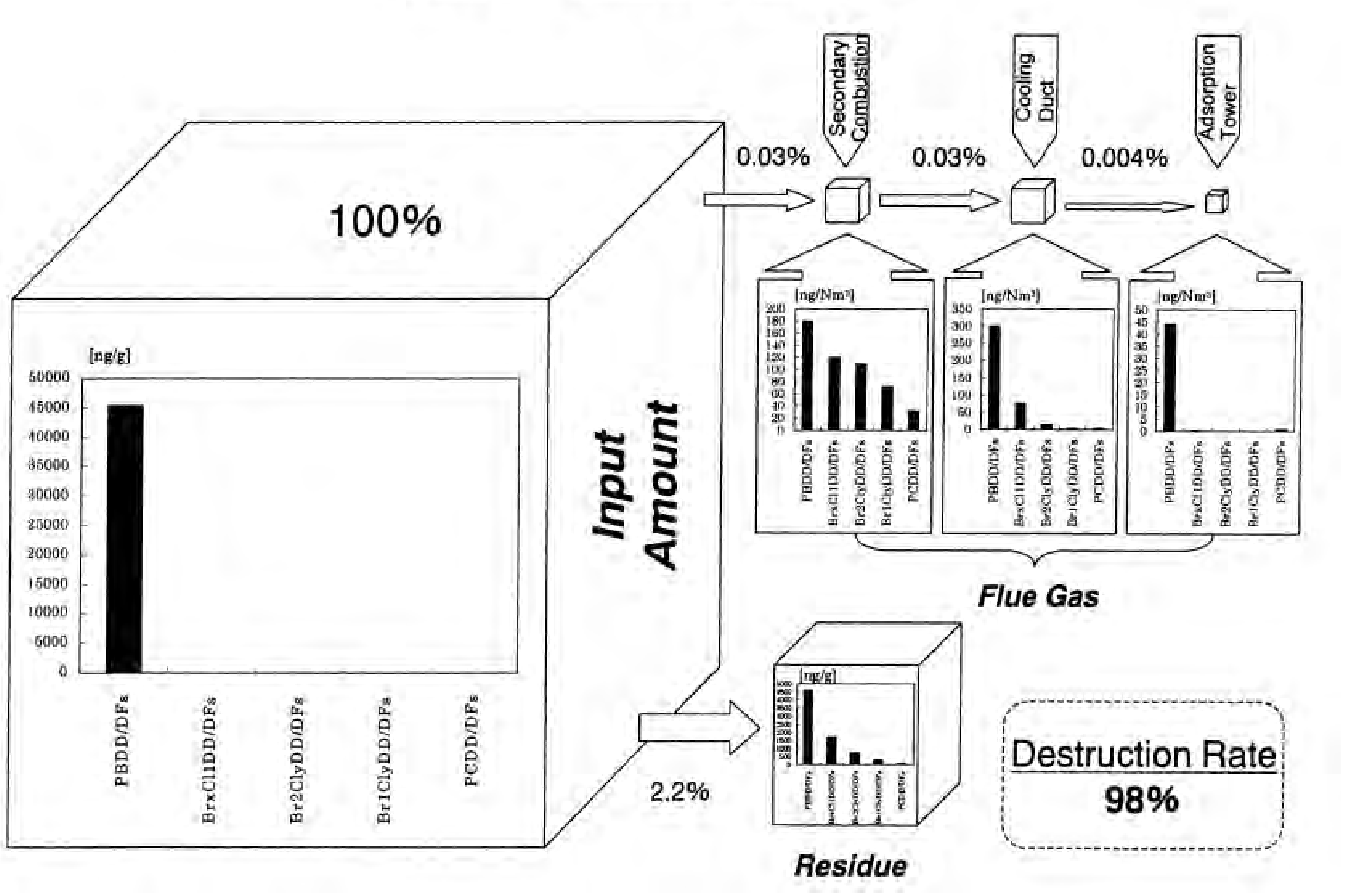
Incineration Residue

(Runs for which TV casing materials mixed with printed circuit board were used as samples)

Sakai et al. (2001)

Fate of PXDD/F in incineration process

S. Sakai et al. / Chemosphere 42 (2001) 519–531



Thermal treatment in developing countries

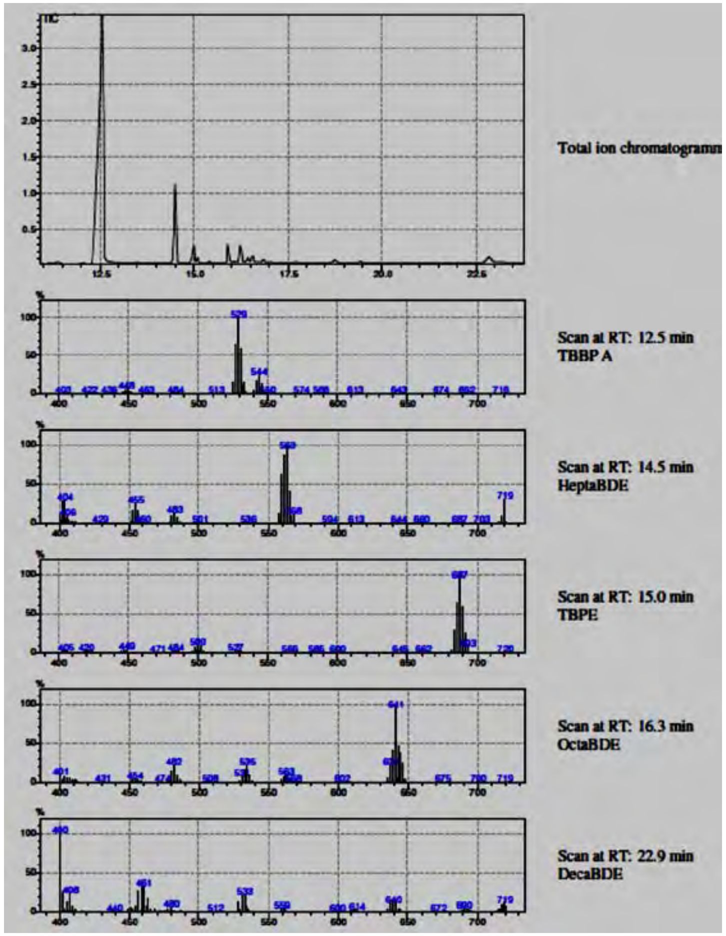
Low-tech incineration provides

- no T controll
- no secundary combustion zone
- no fast cooling device

- High emissions into air, soil and water
- High exposure of workers towards BFR and PXDD/F

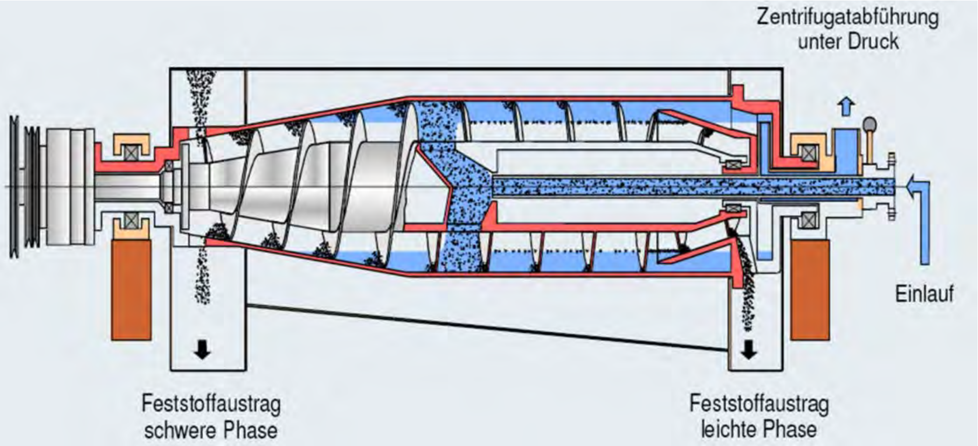
Recycling options – no treatment and export

- Export of WEEE plastics including BFR
- Separate plastics
- Re-extrude and dilute
- Produce new plastic parts and re-distribute globally (RoHS compliance!!)
- Proof of assumption by detection of diferent BFR types (TBBPA, TBPE and PBDE) in a homgeneous plastic part.
- „The global BFR cycle“



Recycling options – Cherry picking (BFR free)

- Separation of BFR containing polymers (e.g. by density or X-ray): BFR increase density of base polymer if applied in percentage range (BFR elimination from TV sets ~95%)
- Does not work to separate low BFR plastics (~1000 ppm bromine)
- Low BFR fraction provides good quality and RoHS compliance



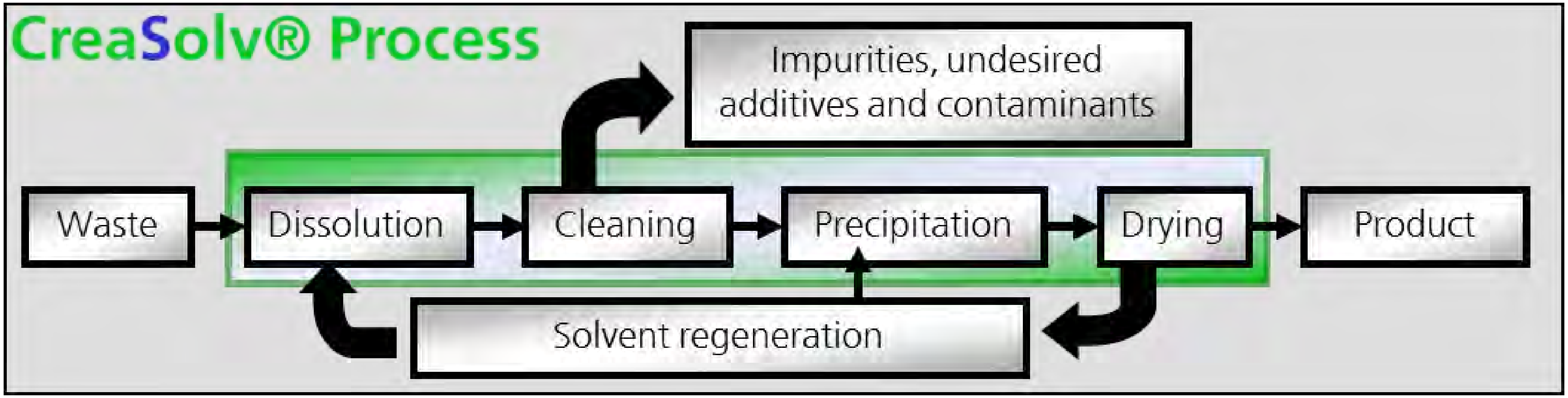
- Treat BFR rich fraction (incineration or CreaSolv®) and recycle and distribute only the low BFR fraction
- Option to take BFR out of the global BFR cycle

Recycling options – CreaSolv®

CreaSolv® enables the separation of BFR from BFR plastics by a solvent based recycling approach.

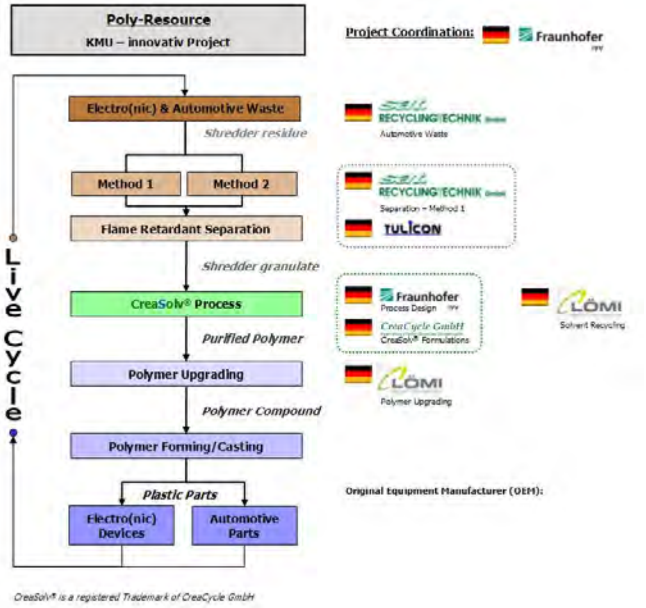
BFR (and PBDD/F) are discharged as a BFR rich residue and may be incinerated. Bromine may be scrubbed from the off-gas and re-used in safe BFR.

Recovery of the maximum amount of polymers without spreading BFR.



Recycling options – CreaSolv®

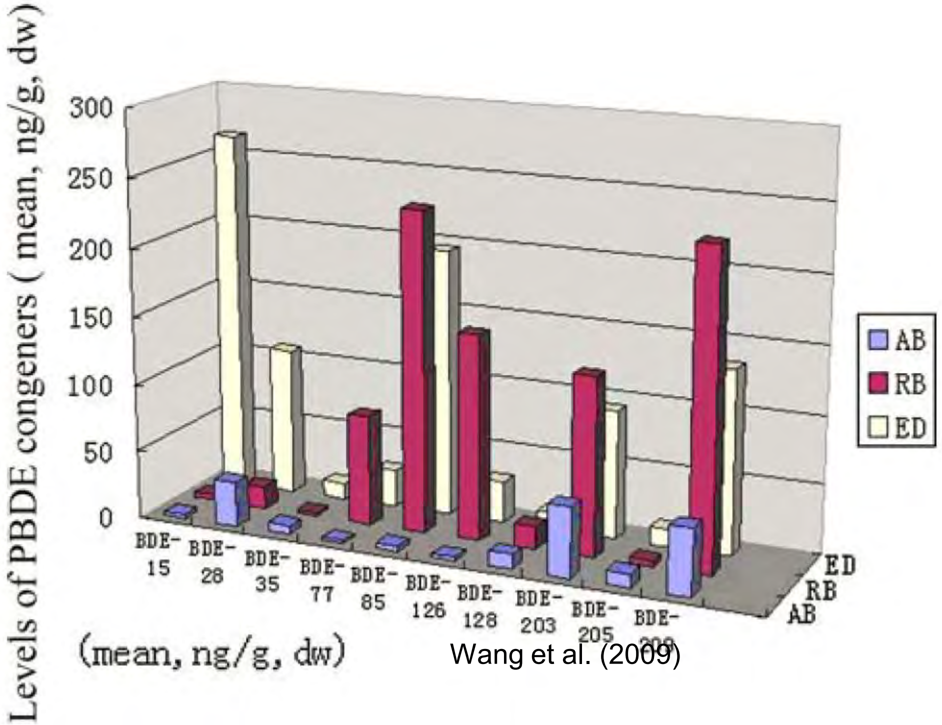
- CreaSolv is not available at industrial scale
- An external evaluation has shown that it is a profitable process at larger scale (5-10.000 tones per anno) (WRAP 2006)
- Current project (PolyRessource) improves economy by
  - Optimising the pre-treatment
  - Changing batch process steps into continous ones
  - Technical upgrade of recycled polymers
- Test of recyclates with 2 OEMs



CreaSolv® is a registered Trademark of CreaCycle GmbH

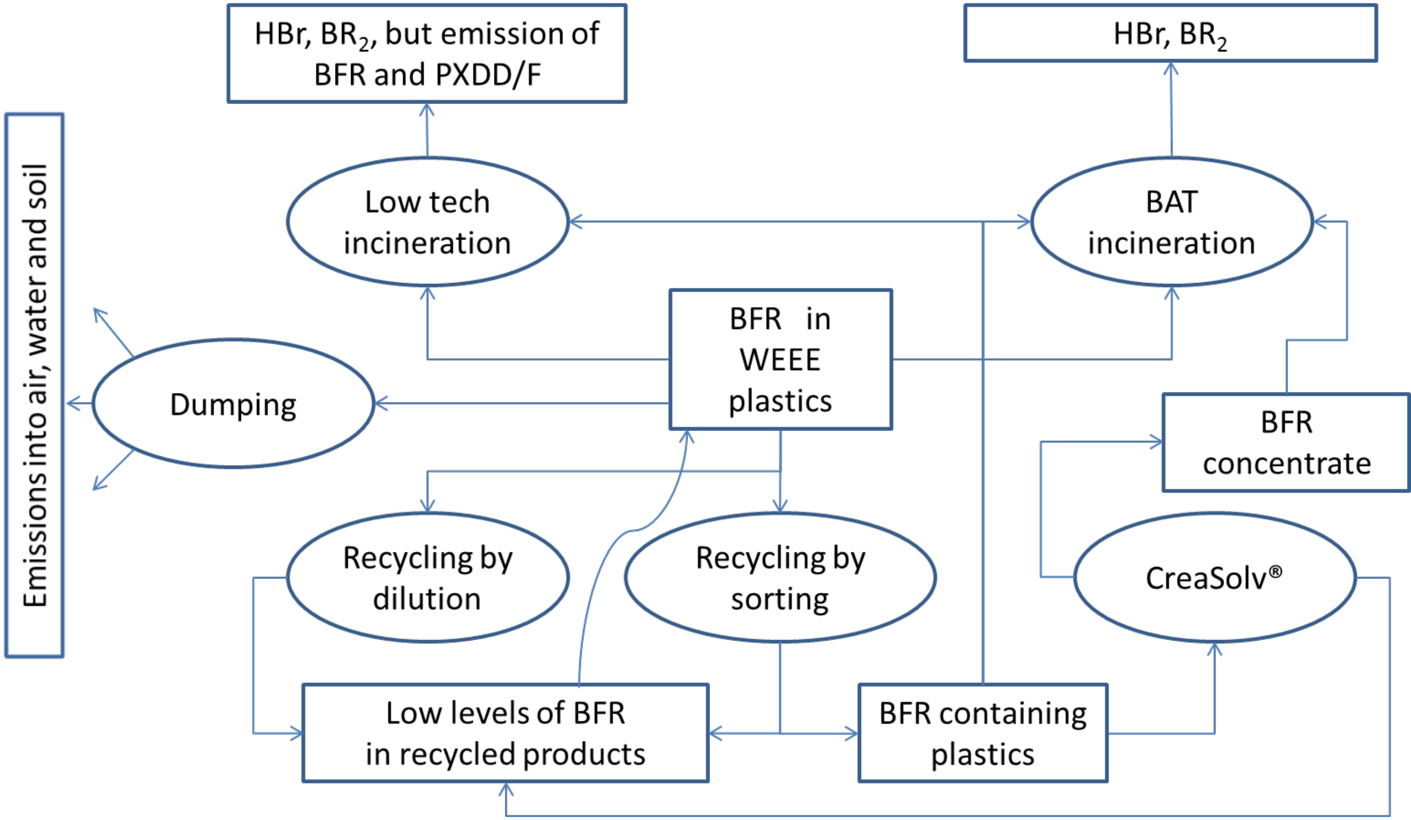
WEEE DUMPING

- Clear indication for degradation
- DecaBDE is the dominating PBDE congener
- BFR transfer into soil, water and air
- Some more information is available in the conference proceedings



Wang et al. (2009)

Conclusions



- Thermal treatment may be a sink of BFR if applied properly
- Current treatment of WEEE distributes BFR all over the globe
- Recycling is possible and recommended, BFR rich side products of recycling activities require a thermal treatment
- Dumping is no option

Fraunhofer IVV

Thank you very much for your attention !!

Literature:

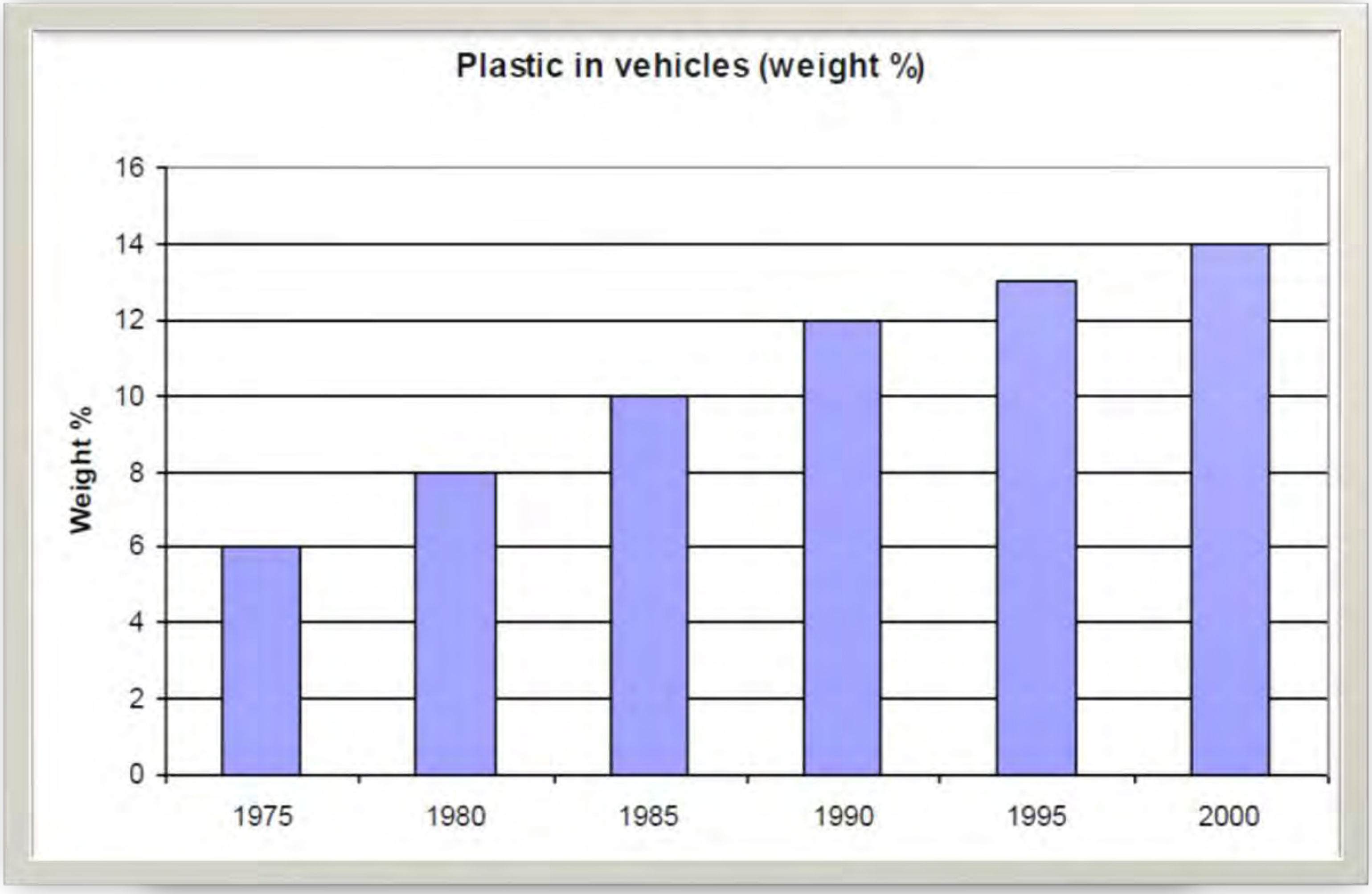
- Guidelines on Best Available Techniques and Best Environmental Practice for the Recycling and Disposal of Articles containing Polybrominated Diphenyl Ethers (PBDEs) under the Stockholm Convention on Persistent Organic Pollutants. UNEP 2012. Draft circulating
- Chicago Tribune

Qualitative and quantitative determination of antioxidants and UV-stabilizers in recycled plastics, before and after recycling

Momina Bibi

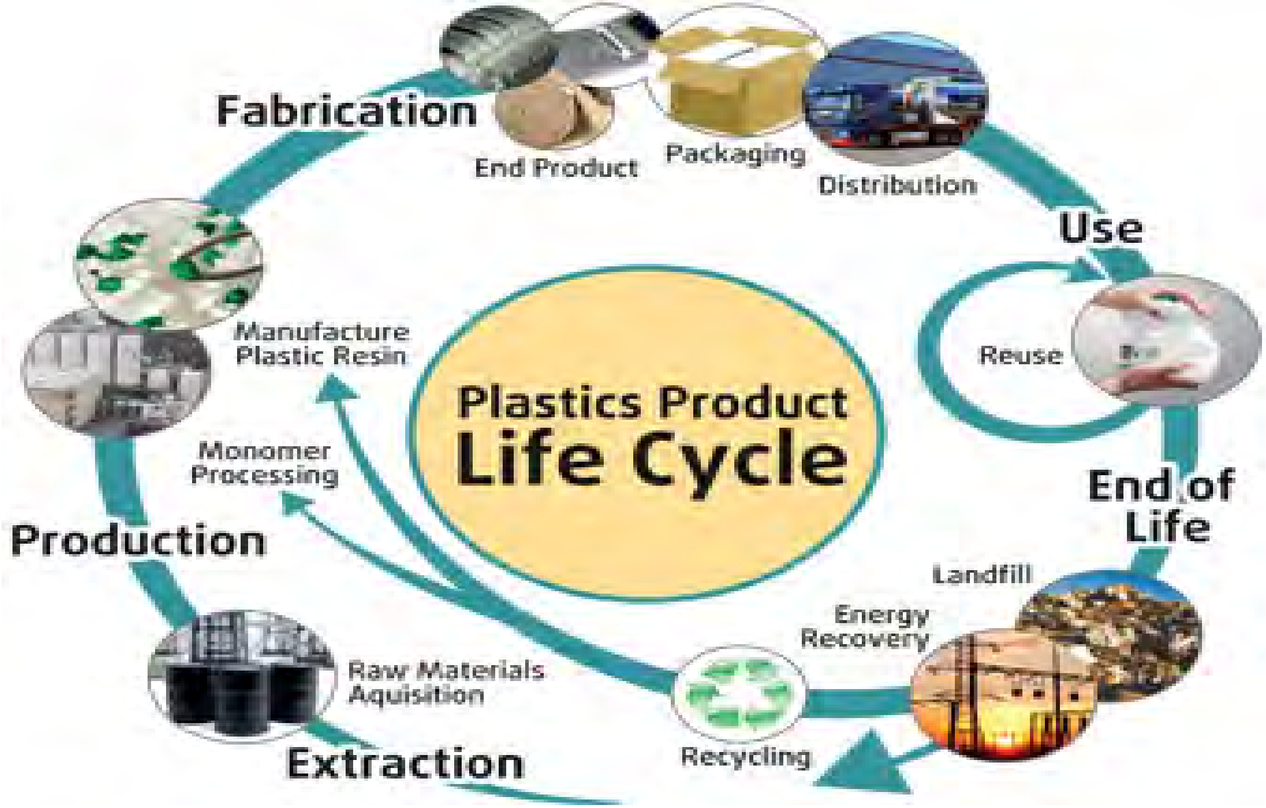
Swedish Environmental Research Institute

Content of Plastic in vehicles



Environmental Issues: Recycling

- EU:50% by 2030



http://www.styron.com/company/sustainability/products_life_cycle.htm

Is recycling good or bad ?

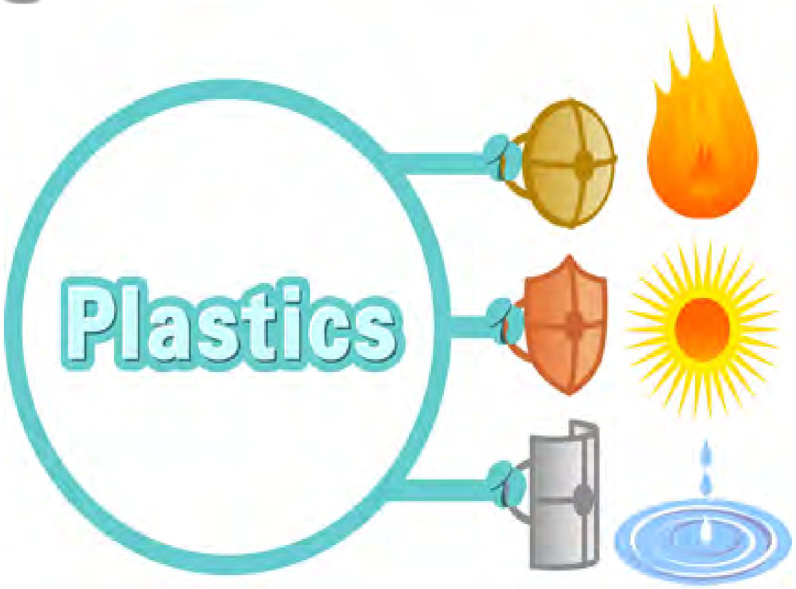
should we put our heart in this

- How much knowledge do we have concerning

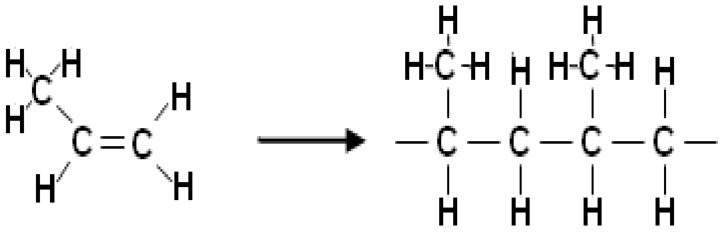
1. Chemical content ?
2. Fate of those?
3. Toxicity?
4. And do we have any other options?

Additivs in plastic

- Antibakteriell Agent
- Antioxidants
- Fillers
- Flame retardants
- Heat stabilizers
- Plasticizers
- UV –stabilizers

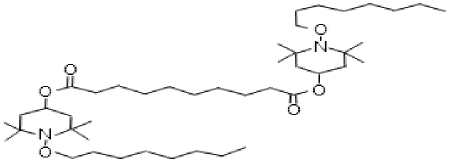


1.Polypropen, (PP)

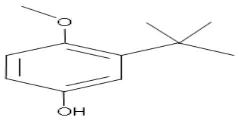


Antioxidants and UV stabilizers

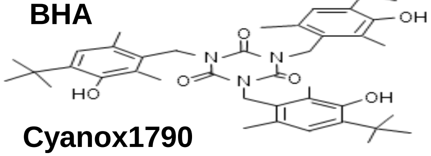
Compounds	MW g / mol	LogKow	Mode of action
BHA	180,3	3,2	antioxidant
BHT	220,4	5,3	antioxidant
BHT-CHO	234,3	4,4	antioxidant metabolite
Cyanox 1790	699,9	10	antioxidant
Irgafos 168	646,9	15,5	antioxidant
Irganox 1010	1 177,6	19,4	antioxidant
Irganox 1076	530,9	13,8	antioxidant
Lowinox	358,5	7,4	antioxidant
Quinone	220,3	3,4	antioxidant metabolite
Tinuvin 123	737,2	<10	UV-stabilizer
Tinuvin 770	480,7	6,3	UV-stabilizer
Tinuvin 99-2	451,6	7,3	UV-stabilizer



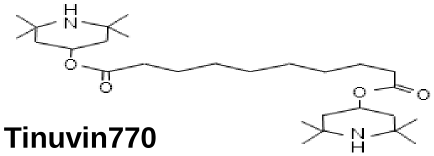
Tinuvin123



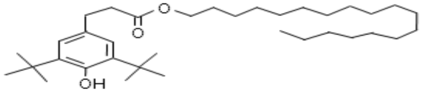
BHA



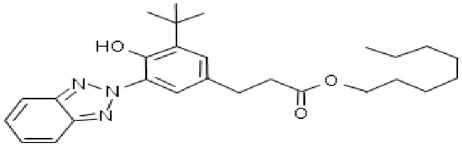
Cyanox1790



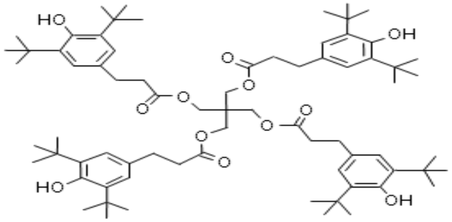
Tinuvin770



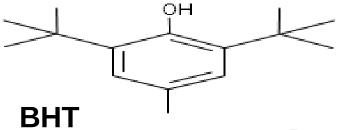
Irganox1076



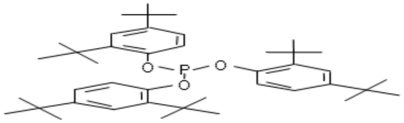
Tinuvin99-2



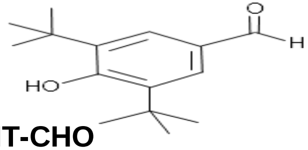
Irganox1010



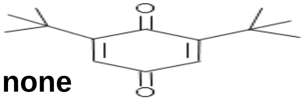
BHT



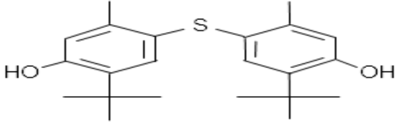
Irgafos168



BHT-CHO



Quinone



Lowinox

[Momina Bibi]

Studies on the additivs toxicity

- BHT: Increase risk of cancer in rats.
- DNA damage induced by various BHT metabolites.
- Tinuvin 123: Behave as a Parkinson toxin in rats.
- BHA:Enhancing effect of gastric squamous cell carcinogenesis

Noguerol et al.2010. Liquid chromatographic methods to analyze hindered amine light stabilizers (HALS) levels to improve safety in polyolefins.

Jackson-Lewis et al, 2000. Effects of a unilateral stereotaxic injection of Tinuvin 123 into the substantia nigra on the nigrostriatal dopaminergic pathway in the rat. Brain

Oikawa et al, 1998. Oxidative DNA damage and apoptosis induced by metabolites of BHT. Biochemical Pharmacology

Purpose of the study

- Fate of antioxidants and UV-stabilizers.
  - . In Polypropen polymer
- Development of the extraction method
  - . Compare two different extraction methods
- Development of the analytical method
  - . Qualitative and quantitative

Sample matrix

- **Car bumpers**

Mixed

processed once

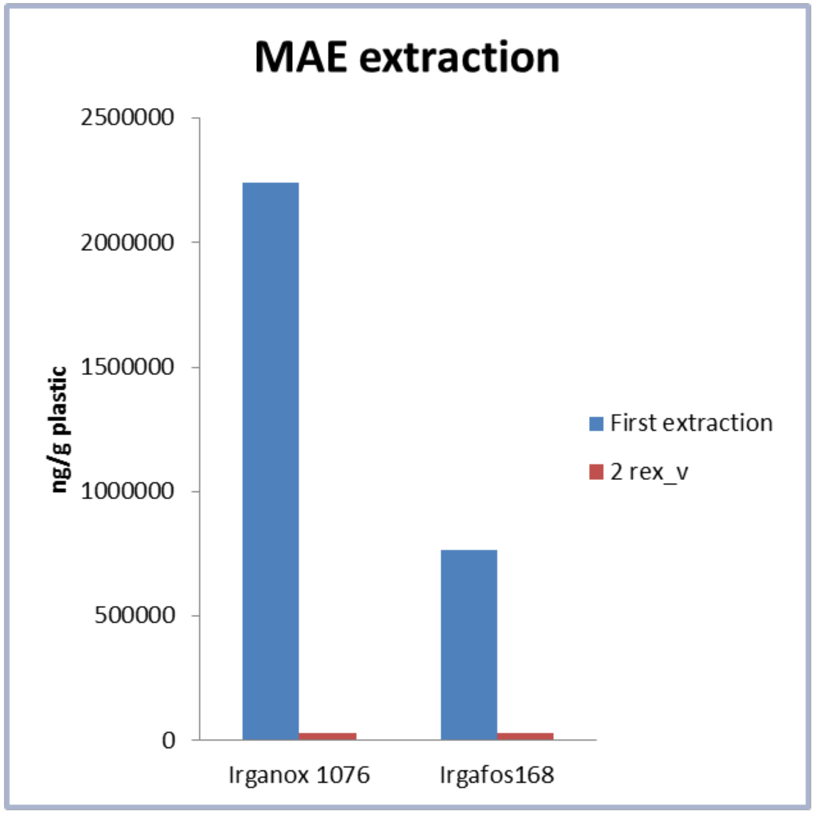
processed twice

METHOD VALIDATION

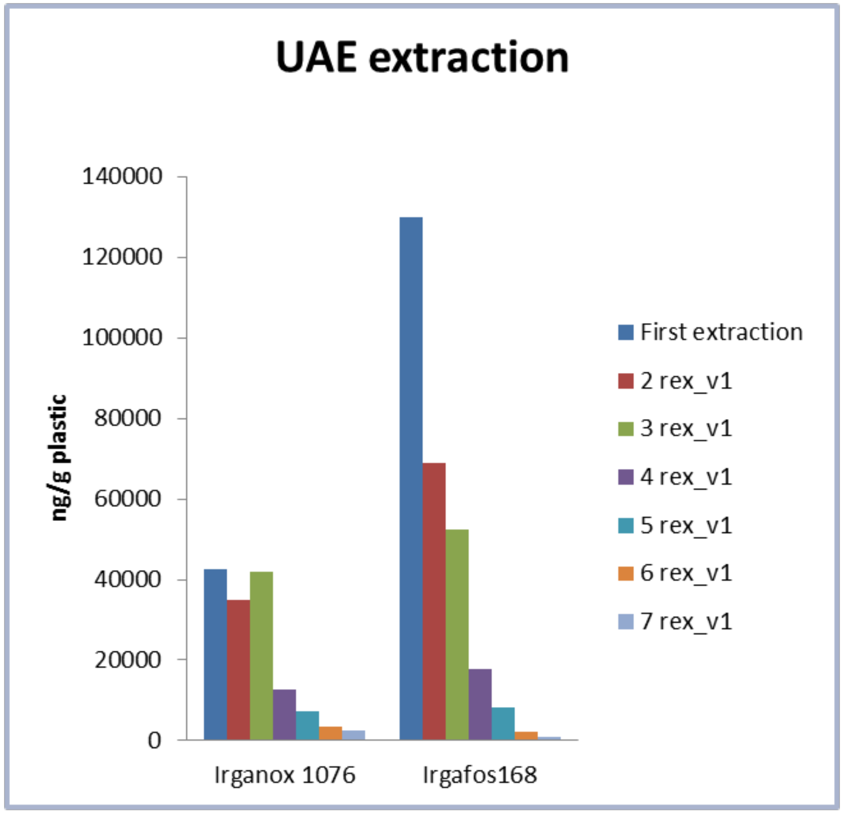
- Repeatability and reproducibility:
  - Instrument LC-ESI-MS/MS
  - Extraction methods UAE,MAE
- Limit of detection and Limit of quantitation:
  - **LOD** 0,008-3,6 ng/ml
  - **LOQ** 0,018-8,5 ng/ml
- Recovery:
  - Instrument
  - Extraction method

Analytical method for extraction

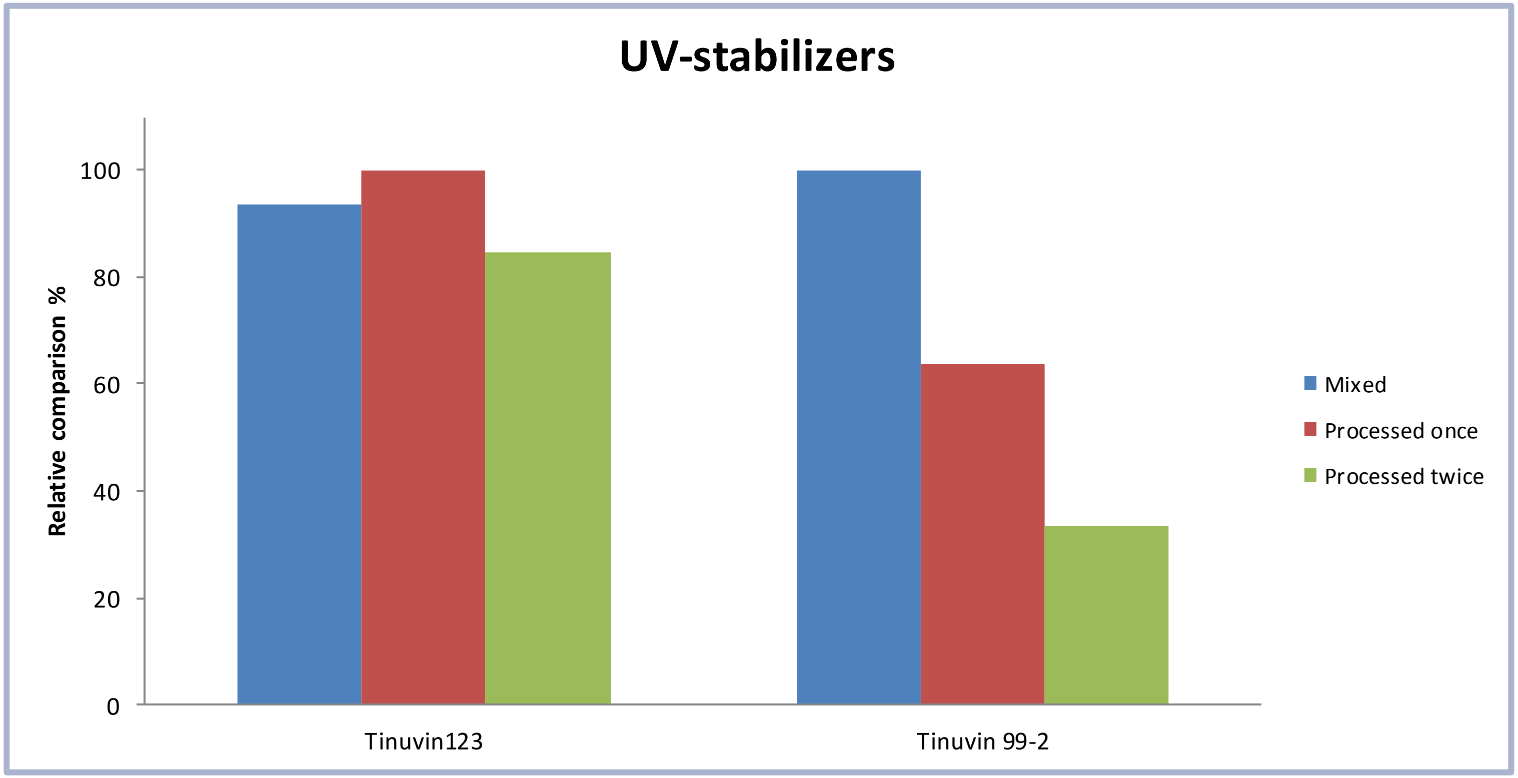
- Microwave-Assisted Extraction (MAE)



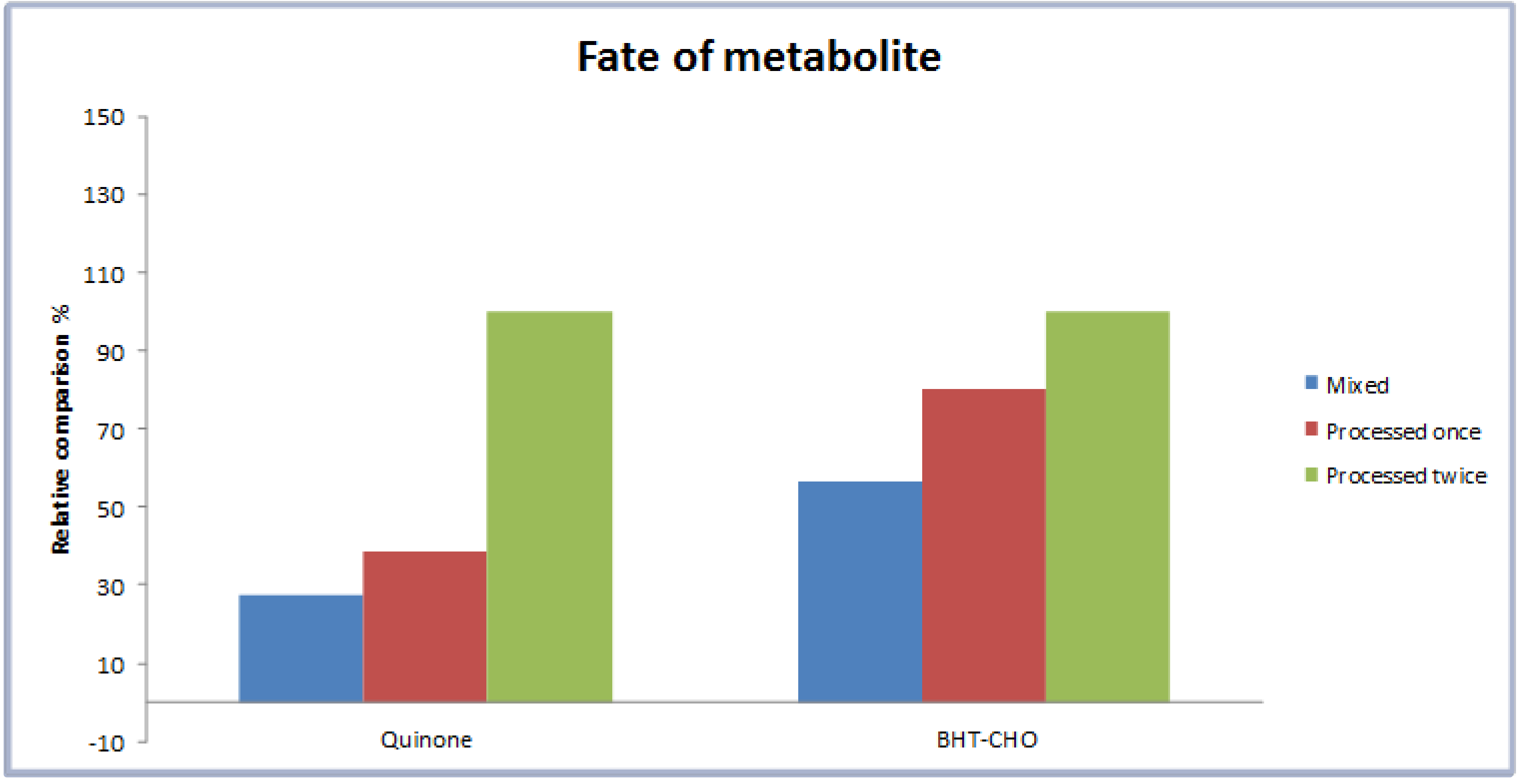
- Ultrasonic Assisted Extraction (UAE)



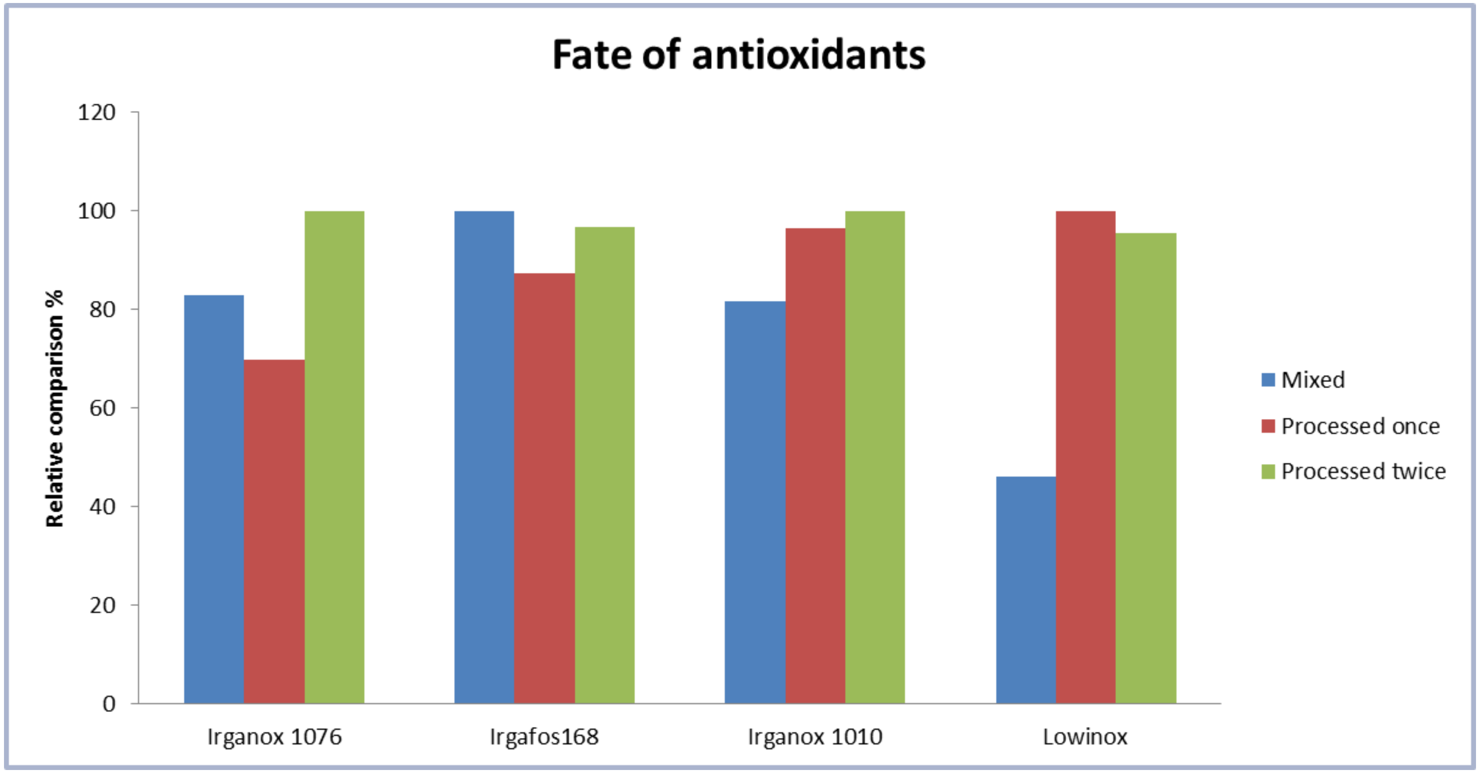
Fate of antioxidants and UV-stabilizers



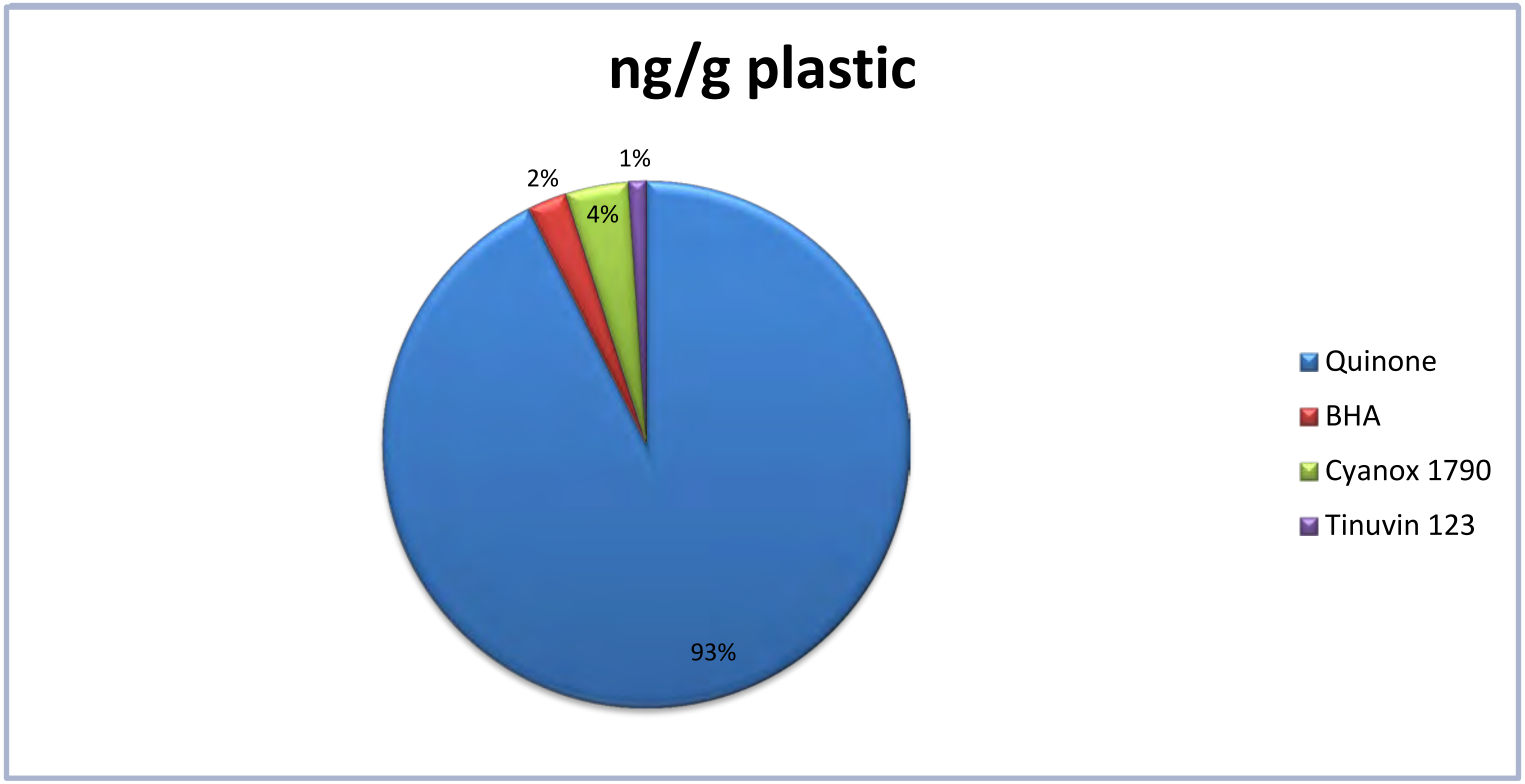
Fate of antioxidants and UV-stabilizers



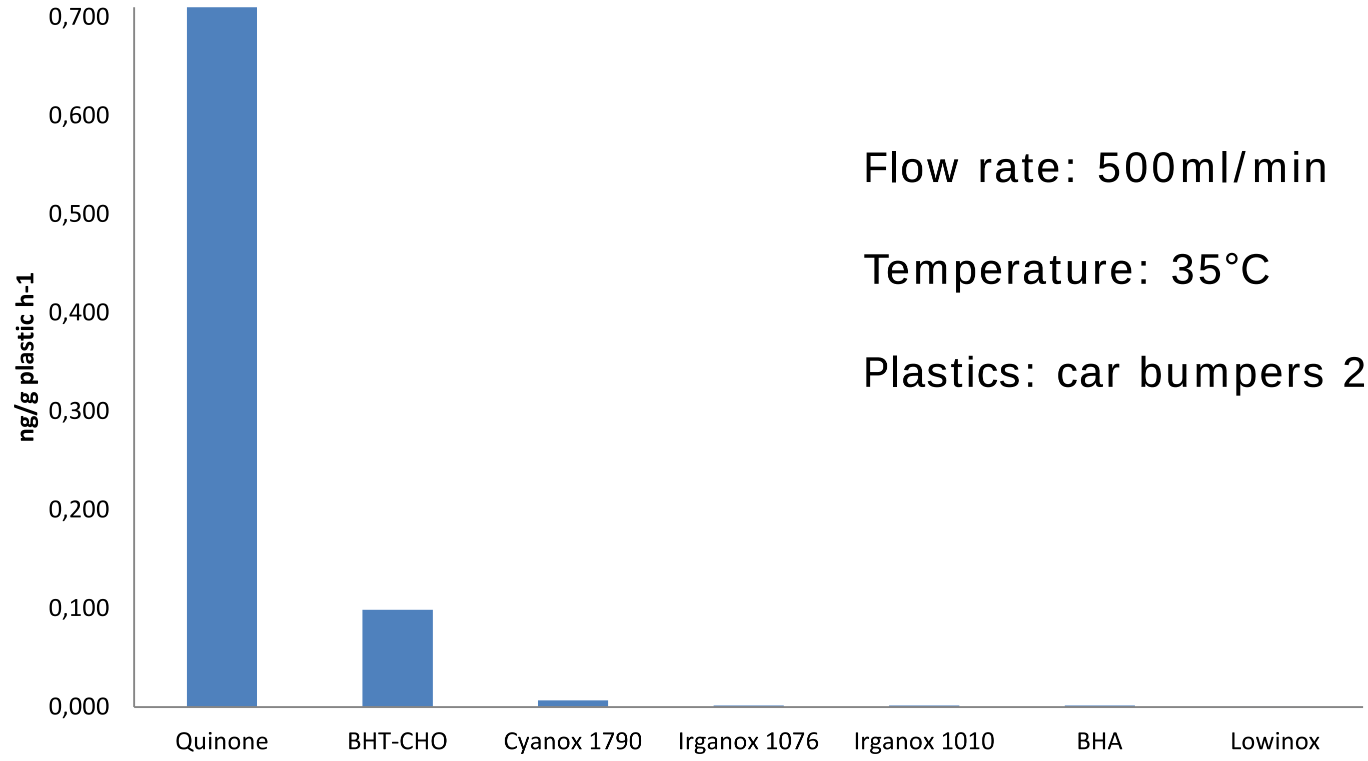
Fate of antioxidants and UV-stabilizers



Quantity of antioxidants and UV-stabilizers in processed plastic



Emissions to air



Flow rate: 500ml/min

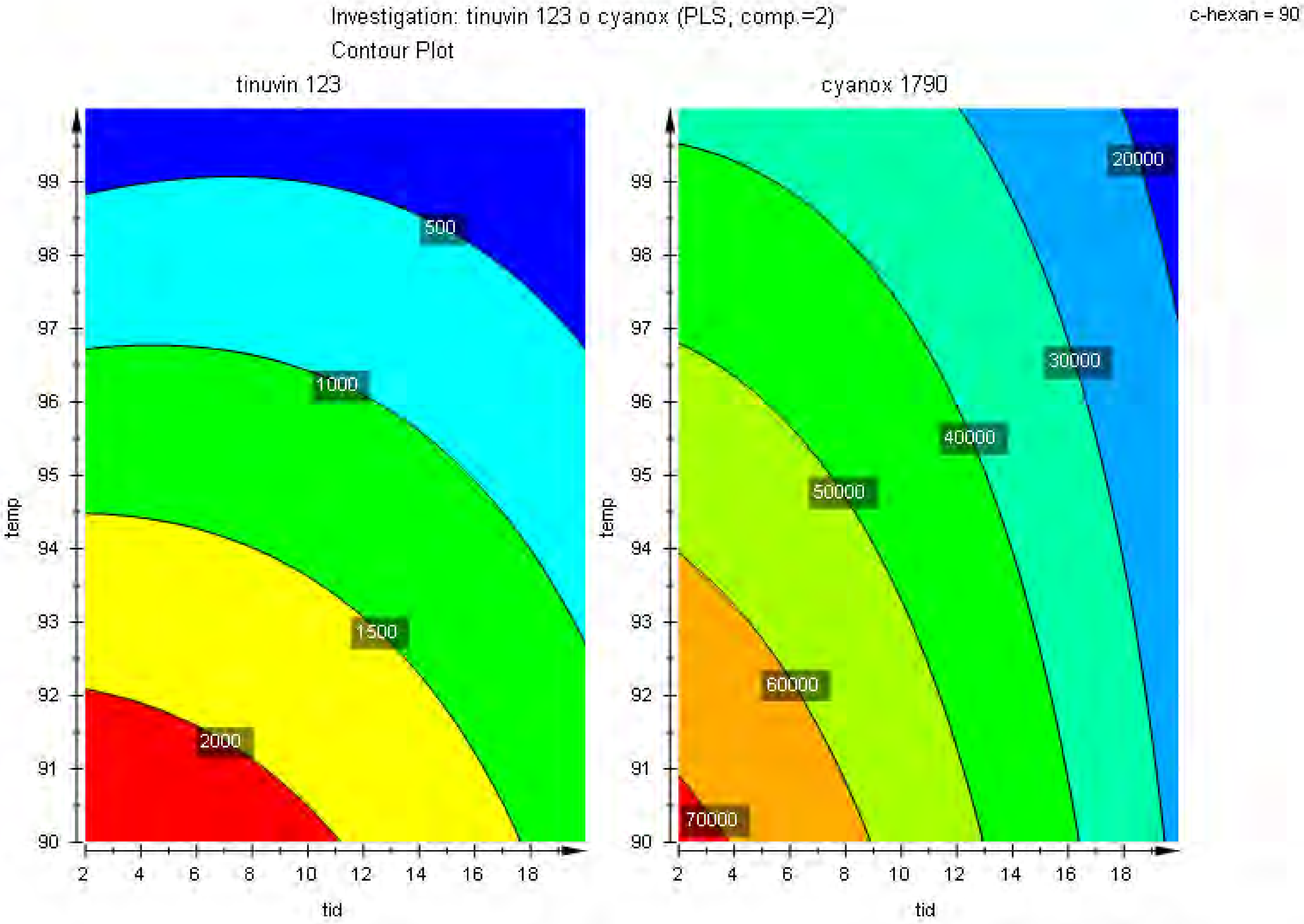
Temperature: 35°C

Plastics: car bumpers 2

Conclusions

1. MAE efficient extraction technique.
2. UV-stabilizers decreases.
3. Antioxidant metabolite increases.
4. Further investigation of some antioxidants are required.
5. Comparison to reference material.
6. Further investigation of emissions to the air.


THANK
YOU


Investigation: tinuvin 123 o cyanox (PLS, comp.=2)
Contour Plot
c-hexan = 90
tinuvin 123
cyanox 1790
temp
tid
99
98
97
96
95
94
93
92
91
90
2
4
6
8
10
12
14
16
18
500
1000
1500
2000
20000
30000
40000
50000
60000
70000

Tow extraction method

A. One (g) of powder in 20 ml , c-hexane / IPA 70 / 30 % + IS

B. 90 / 10 %

A. 60 min in 65°C

B. 6min in 90°C

A. Filtered with glass fiber filter

[Mom]

Analytical method for Identification and quantification

LC / MS / MS

- **Column:**

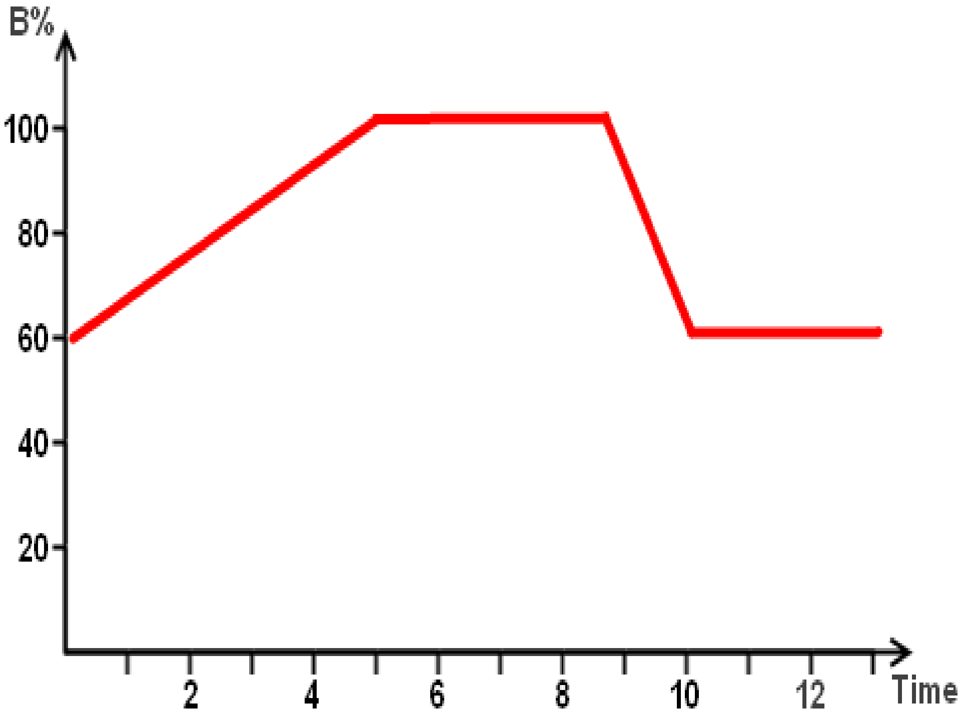
  C8 , column 50 x 3 mm, i.d. 5µm

- **Flow: gradient**
- **Mobile phase:**

  A: H2O 5mM **acetic acid**

  B :MeOH 5mM **acetic acid**

- **Ionization technique: ESI**



Extraction method repeatability and reproducibility

	Different samples			
	MD	EE	volvo 1	volvo 2
	RSD%	RSD %	RSD %	RSD %
BHA	70.62	4.67	2.40	30.33
Cyanox 1790	59.23	3.04	48.21	120.0
Irganox 1076	56.6	43.43	22.83	32.33
Irganox 1010	67.92	38.57	20.51	22.18
Lowinox	18.40	30.63	9.04	20.85
Tinuvin123	101.8	19.81	37.54	40.49
BHT-CHO	15.47	5.76	18.12	36.03
Irgafos168	26.49	10.40	17.23	51.90

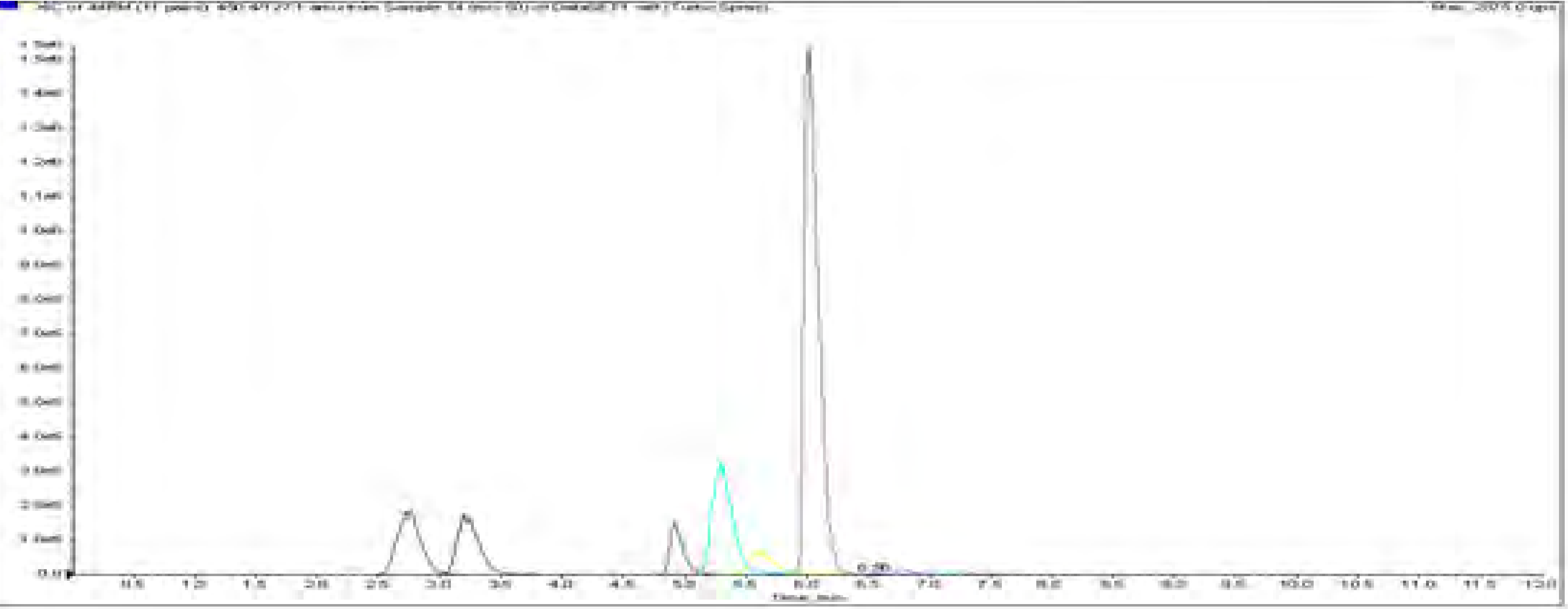
Limit of detection and Limit of quantitation

1. Five separate blanks
2. Throughout the entire analytical chain.
3. Area which is significantly higher than that detection decision (LC) 95% of the time .
4. Lc=2.132*SD
5. LOD=2*Lc
6. LOQ=10*Lc

Limit of detection and Limit of quantitation

		[a]Blank(ng/ml)		
Compound	**SD**	**Lc**	**LOD**	**LOQ**
BHA	-	-	No Peak	No Peak
BHT-CHO	-	-	No Peak	No Peak
Cyanox 1790	-	-	No Peak	No Peak
Irganox 1010	0.846	1.8	3.6	8.46
Irganox 1076	0.002	0.004	0.008	0.018
Lowinox	-	-	No Peak	No Peak
Tinuvin 123	-	-	No Peak	No Peak
Tinuvin 99-2	0.017	0.037	0.074	0.173

a=5


0.5
1.0
1.5
2.0
2.5
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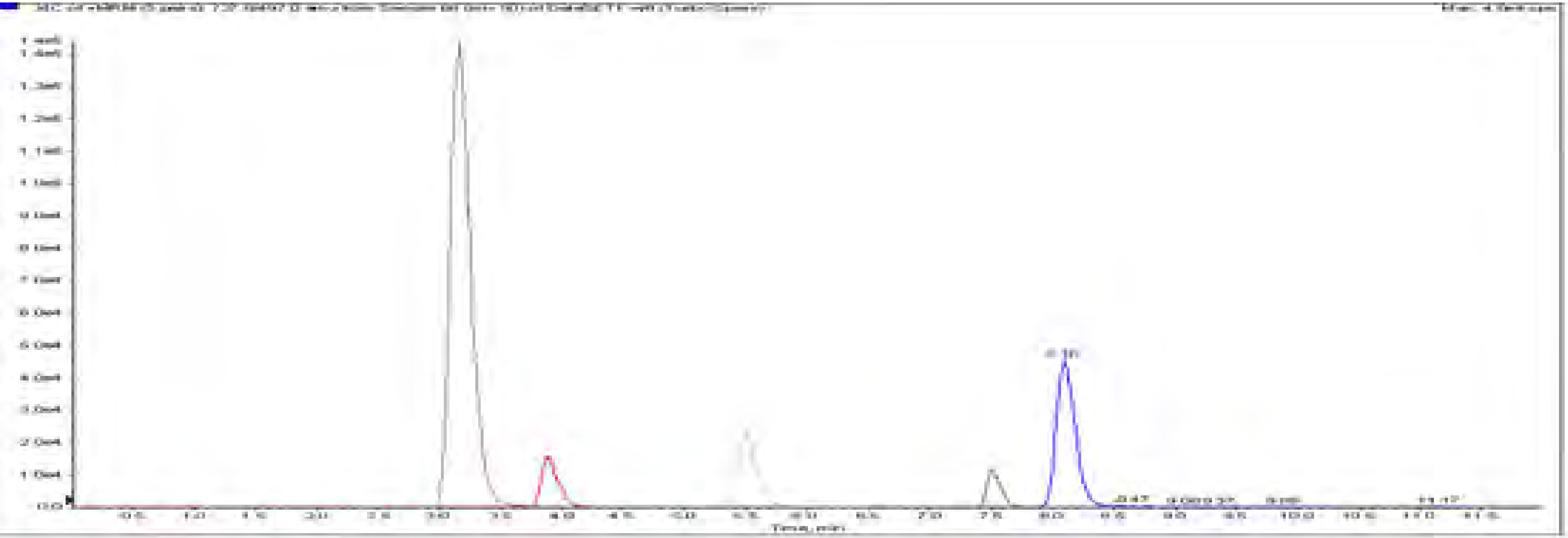
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
12.0
Time, min


0.5
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4.5
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7.0
7.5
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8.5
9.0
9.5
10.0
10.5
11.0
11.5
Time, min

Obstacles

Recycled paper-paperboard for food contact materials: contaminants suspected, migration models and healthy concerns.

Francesca Tiberto, Nicoleta Suciu, Marco Trevisan

Institute of Agricultural and Environmental Chemistry
Piacenza, Italy

nicoleta.suciu@unicatt.it

Summary

- ✓ Introduction
- ✓ Objectives
- ✓ First part: determination of the contaminants
- ✓ Second part: migration tests
- ✓ Conclusions

Introduction

Food packaging is the most common way to:

- store foods at different environmental conditions;
- extend the shelf-life of the products;
- safeguard foods from natural agents;
- protect foods from any type of external pollution.

packaging is necessary to preserve the quality and the ***safety*** of the foods.

In some cases packaging can become a new source of contaminants that can affect the organoleptic properties of the foods and make them hazardous to the food consumers.

it is necessary to *control* the composition of the packaging and assess the <u>potential migrations</u> of the compounds to the foods.

Food contact materials: why *recycled* paper-paperboard?

- A way to minimize the amount of worldwide wastes, preserve natural resources.
- In Europe about half of the paper/board production is directly/indirectly concerned by food-contact materials.
- They are usually perceived by consumers as *safe/healthy* due to the natural origin of the wood.
- Unintentionally added compounds due to the incorporation of recycled pulp, additives used to make recycled materials suitable for food packaging must be considered as potential hazardous migrants.
- Lack of specific laws: necessary an approach like plastic food-contact materials?
- Reg. (UE) N. 1935/2004 only affirms that recycled paper can just be used for solid dry foods (salt, sugar, pasta, rice, flour,…).

⇨ **an increasing lobby which recommends the *«not use»* of waste paper packaging for food contact applications.**

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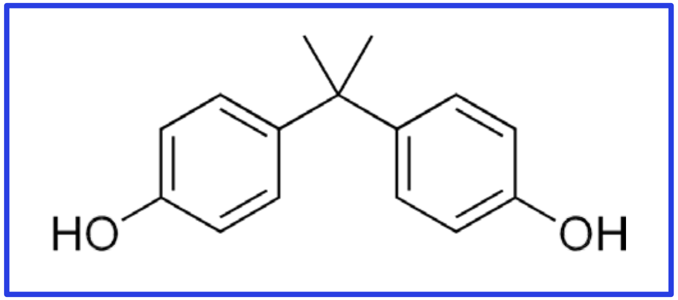
[1] Reg. (UE) N. 10/2011, Reg. PIM (Plastic Implementation Measure)

Contaminants investigated (1)

Bisphenol A, BPA



- ✓ polycarbonate plastics, epoxy resins for cans, microwave containers, baby's bottles, …

- ✓ founded in wastewaters from wastepaper recycling plants

contaminant in recycled fibers?

- ✓ Biochemical changes in brain, immune-modulatory effects, enhance susceptibility to breast tumours

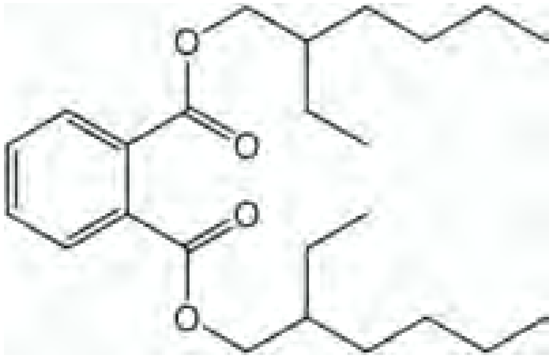
- ✓ TDI of **0.05 mg/kg b.w./day** – NOAEL 5 mg/kg b.w./day (uncertainty factor: 100) [2]

---

[2] EFSA, 2010.

Contaminants investigated (2)

Bis(2-ethylhexyl)phthalate, DEHP



- ✓ Since 1930 industrial success as additive to PVC to increase flexibility

Exponential applicability

adhesives, lacquers, waxes, inks, cosmetics, insecticides,…

present in paper-paperboard food packaging: contamination of raw materials and/or process

- ✓ Endocrine disruption properties, reducing man fertility
- ✓ TDI of **0.05 mg/kg bw/day** - NOAEL of 5 mg/kg bw/day (uncertainty factor: 100) [3]

---

[3] EFSA, 2010.

Contaminants investigated (3)

Nonylphenol monoethoxylate, NMP - Nonylphenol diethoxylate, NDP

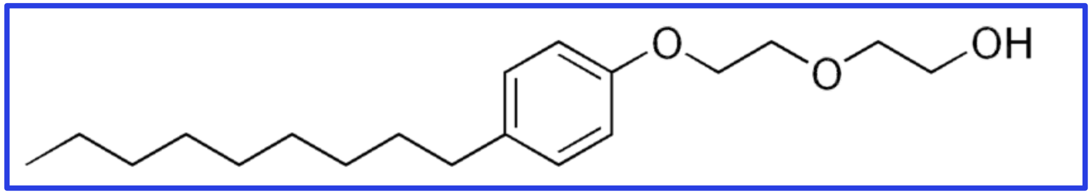
✓ Environmental ubiquitous contaminants (aquatic systems): contamination of raw materials?

✓ in lubricants, detergents, resins, plasticizers, herbicides, cosmetics,…

used as *dispersing/stabilizing agents* in paper food packaging process

✓ oestrogenic activity - endocrine disrupting effects in vitro/in vivo experiments

activity on the reproductive system /carcinogenics



Objectives

Assess real degree of **suitability** of some *recycled* paper-paperboard packaging available on the market.

The experimental study was divided into 2 sequent parts:

1. determination of **contaminants concentrations** in recycled paper-paperboard samples;
2. carrying out **migration tests** of the identified contaminants in a food (NaCl) and in a food simulant (Tenax).

The first part was conducted to know the *real composition* of the samples about the contaminants – they can derive from raw materials, manufacturing process and environment.

The second part had the aim of estimate the *potential transfer* of the contaminants investigated in the first part, considering different conservation's conditions.

First part: materials and methods (1)

Solvents and reagents

- ✓ **BPA**: methanol (0,06-25 mg L^{-1})
- ✓ **DEHP**: hexane (0,5-60 mg L^{-1})
- ✓ **NMP, NDP**: hexane (0,1-10 mg L^{-1})

STANDARD SOLUTIONS

Extraction method

Extraction in triplicate

- Removal outside printed surface → cut into small pieces (ca. 0,5x1 cm)
- **Soxhlet extraction** (with anhydrous sulfate)
  - **BPA**: ethanol, 15 cycles, 2,5 g paper material
  - **DEHP**, **NMP**, **NDP**: hexane:acetone (4:1), 6 hours, 1 g paper material
- Rotavapor → 10 ml hexane → evaporation under N_2 stream → 1 ml I.S.

Internal standards (I.S.): anthracene-d$_{10}$, perylene-d$_{12}$ (1 mg L^{-1})

First part: materials and methods (2)

GC-MS analysis

- Agilent Technologies gas chromatograph 6890 series
- Supelco SLB-5ms type column
- high grade helium - carrier gas

GC-MS analyses
in triplicate

- Identification of contaminants: **TOTAL ION MONITORING MODE**
- Quantification of contaminants (except DEHP): **SELECTED ION MONITORING MODE (SIM)**
- Final measurements using internal standards calibration curves

First part:
paper and paperboard samples

Sample no.	Product	Contact	Type of paper	Percentage of recycled material
1	Cereals box	Indirect	Recycled	100%
2	Eggs box	Direct	Recycled	100%
3	Salt box	Direct	n.s.	n.s.
4	Sugar box	Direct	n.s.	n.s.
5	Take-away pizza box 1	Direct	n.s.	n.s.
6	Frozen pizza box 1	Indirect	Recycled	ca. 90%
7	Soy box	Direct	n.s.	n.s.
8	Lentils box	Direct	n.s.	n.s.
9	Barley box	Direct	n.s.	n.s.
10	Pasta box	Direct	Recycled	ca. 40%
11	Rice-pasta box	Direct	n.s.	n.s.
12	Rice box	Indirect	Recycled	100%
13	Napkins	-	Recycled	100%
14	Polenta	Indirect	Recycled	80-90%
15	Take- away pizza box 2	Direct	n.s.	n.s.
16	Frozen pizza box 2	Indirect	Recycled	ca. 90%
17	Salt box 2	Direct	n.s.	n.s.

n.s. Not specified.

First part: results

Sample no.	DEHP (mg Kg^{-1})	NMP (mg Kg^{1})	NDP (mg Kg^{-1})
1	11.66±0.45	0.23±0.01	0.61±0.05
2	2.42±0.20	x	0.46±0.08
3	9.68±1.22	0.10±0.01	0.38±0.02
4	75.23±18.65	0.33±0.06	0.54±0.07
5	<LOD	<LOD	0.27±0.02
6	2.27±1.87	0.11±0.03	0.38±0.07
7	2.22±1.23	0.33±0.06	0.36±0.03
8	1.10±0.49	x	0.22±0.02
9	<LOD	<LOD	x
10	x	x	0.25±0.01
11	3.19±0.71	x	0.20±0.00
12	3.55±1.67	0.69±0.13	0.11±0.09
13	<LOD	<LOD	0.19±0.01
14	16.27±2.52	0.19±0.03	0.62±0.03
15	<LOD	x	0.13±0.01
16	45.16±1.93	0.26±0.08	0.30±0.24
17	8.08±1.78	<LOD	0.28±0.17

Compound	Recovery (%)
DEHP	89
NMP	101±4
NDP	108±2

x = identified, but not quantified (between LOD and LOQ - LOD was considered as being three times lower that LOQ).

First part: discussion

Not all samples contain the selected contaminants

- **DEHP** was detected in twelve samples: except sample no. 4 and no. 16, all paper materials show DEHP concentrations range from 1.10 and 16.27 mg Kg^{-1}

concentrations detected with the method presented **confirm** the results of the literature.

- **NMP** was founded in thirteen samples and quantified in eight, **NDP** was detected in all tested samples and quantified in all samples, except no. 9.

detected levels are slightly higher than literature values - considering the *virgin nature* of the samples investigated.

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Second part:
migration tests

Materials

- ✓ FOOD: NaCl
- ✓ SIMULANT: Tenax TA 60-80 mesh (modified polyphenylene oxide, MPPO)
- ✓ PAPER SAMPLE: no. 1 (Cereal box)
- ✓ TARGET CONTAMINATS: DEHP, NMP, NDP

Test design

Paperboard exposed to matrix in glass dishes (basal area 0.25 dm^2) wrapped in aluminum foil

Test conditions	Contact matrix	g/dm^2
10 days (20±2)°C	NaCl	10/0.25
10 days 40°C	Tenax	1/0.25

Second part: extraction method

- Twice **solid-liquid extraction** under agitation, at environmental temperature → filtration

NaCl: methanol
TENAX: hexane

Extraction and recovery in triplicate

- Rotavapor → 10 ml hexane → evaporation under N_2 stream → 1 ml I.S.[2]

Contaminant	NaCl recovery (%)	Tenax recovery (%)
DEHP	79±10	103±19
NMP	106±8	120±16
NDP	104±11	125±19

---

[2] Internal Standards

Second part: results

Contaminant	Paper concentration (μg dm^2)	Migration (μg dm^2)
DEHP	46.64 ± 1.80	0.64 ± 0.52
NMP	0.92 ± 0.04	nm
NDP	2.44 ± 0.20	nm

NaCl

Contaminant	Paper concentration (μg dm^2)	Migration (μg dm^2)
DEHP	46.64 ± 1.80	5.04 ± 1.48
NMP	0.92 ± 0.04	0.68 ± 0.24
NDP	2.44 ± 0.20	1.8 ± 1.28

TENAX

nm: not significant migration

Second part: discussion

Contaminant	% Migration NaCl	% Migration Tenax
DEHP	1	11
NMP	nm	72
NDP	nm	74

nm: not significant migration

MIGRATION IN TENAX > MIGRATION IN NaCl

Consider much more long time of contact matrix - paper for migration in NaCl due to its shelf-life

⇓

migration tests will be **continue** considering 1, 2 and 3 months to assess transfer of contaminats under conditions much similar to the reality

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Conclusions (1)

- ✓ A procedure for **analysing four chemical contaminants** in recycled paper-paperboard materials has been developed
- ✓ applicability of the method was illustrated using commercial products
- ✓ selected contaminants are generally present in the tested samples at levels in agreement with the literature

recycled fibers have a great influence on the amount of chemicals present in the end-products.

- ✓ a **migration's study** was introduced: comparison of migration behaviors of contaminants after 10 days of contact with NaCl and Tenax

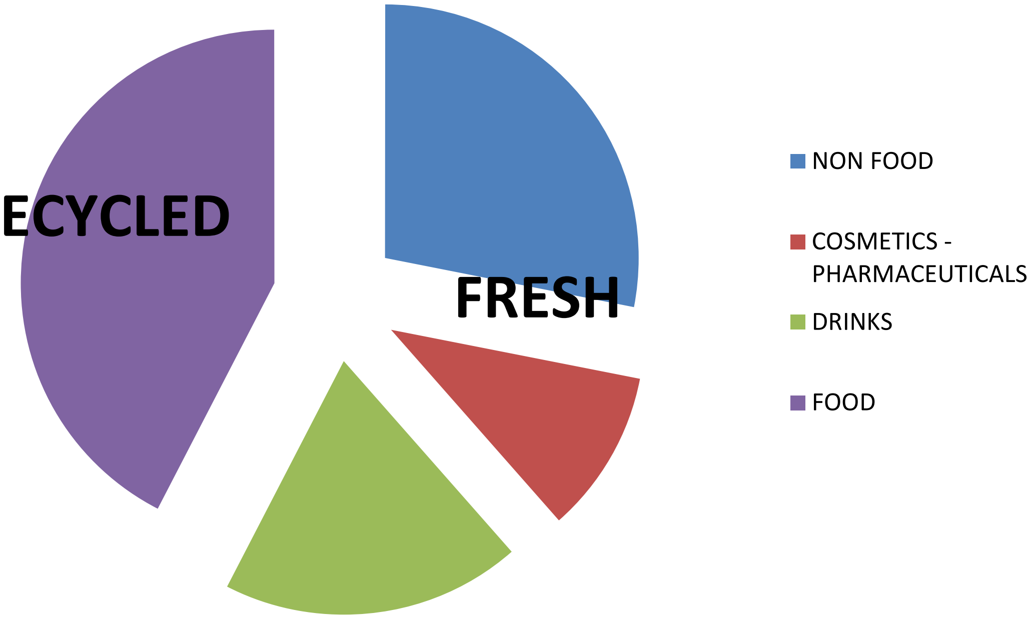
much more migration in Tenax due to its high absorbent power
results obtained confirm literature levels

THE WORK IS COMING ALONG WITH THE COMPLETION OF MIGRATION STUDIES

✓ Paperboard detection and migration tests for BPA
✓ Migration tests for long time

Conclusions (2)

The results of the study suggests that it is recommendable a **higher care** for the use of recycling paper-paperboard as food packaging.



PAPER-BASED PACKAGING DESTINATION

WHY DON'T FOCUS MORE - EVEN ALL- RECYCLED PAPER-PAPERBOARD TO NON-FOOD SECTORS?

Thank you for your attention!

Emerging risks in recycling and waste: Perfluorinated compounds in plastic pellets and nanomaterials in contaminated soil

Damià Barceló, Naif Abdullah Al-Harbi, Hrissi K. Karapanagioti,
Antoni Ginebreda,Marta Llorca, Josep Sanchís

Summary

1. Introduction
2. Case Studies Presentation and Objectives
3. Perfluorinated compounds in sea plastic pellets
4. Nanomaterials in contaminated soils
5. Conclusions

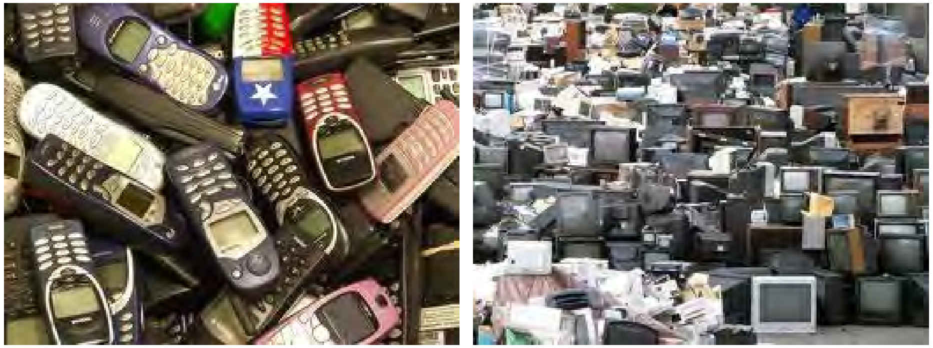
Introduction

According to the **European Parliament over 1.8 billion tonnes of waste are generated each year in Europe** (3.5 tonnes per person) and less than a third of it is recycled.

United States produces approximately 200 million tons of garbage each year, according to the Environmental Protection Agency.

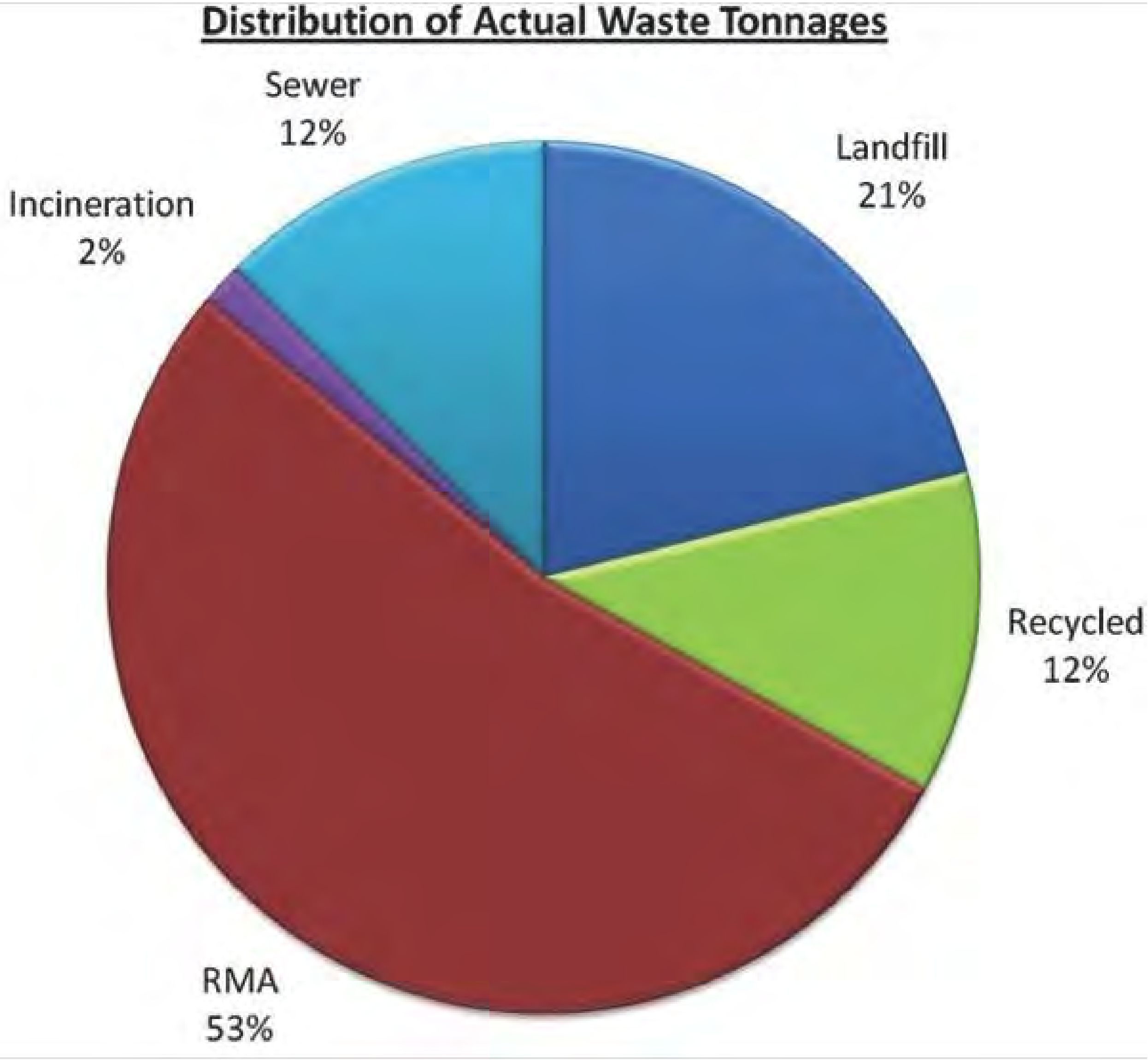
Chemicals

Plastic wastes



e-Wastes

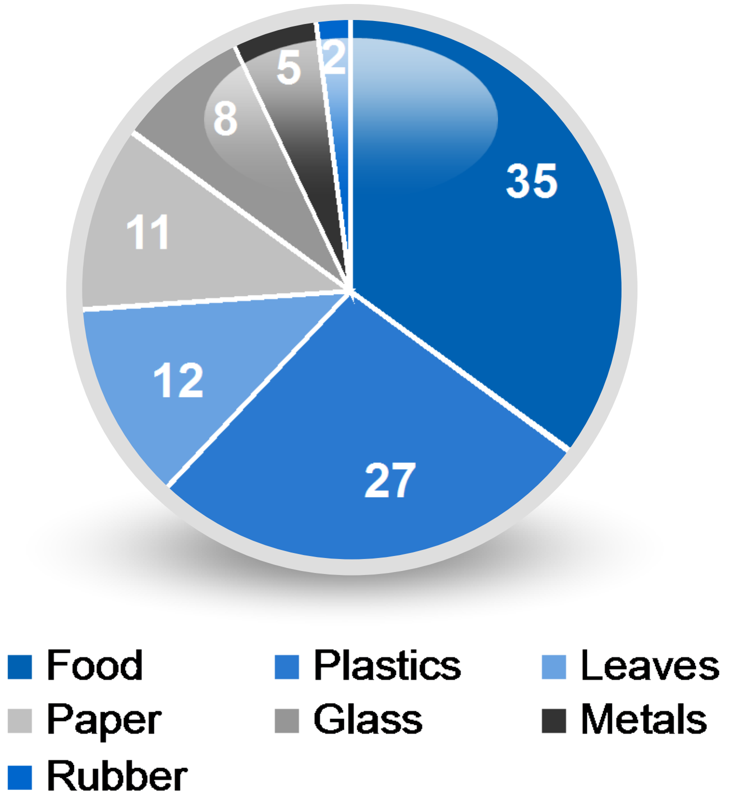
Introduction



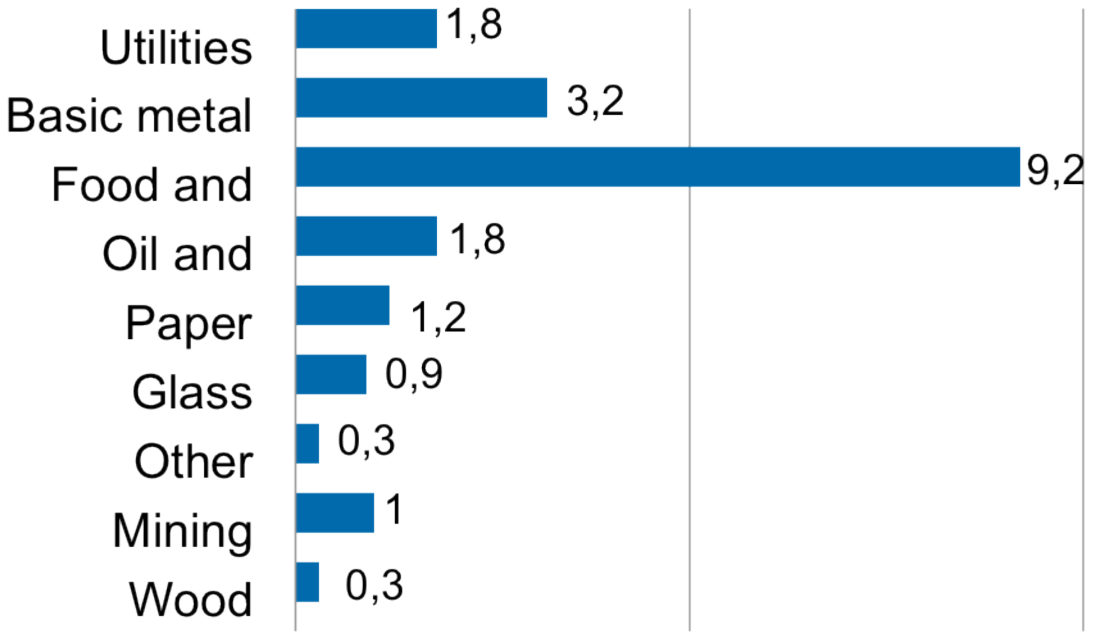
Introduction

Composition of solid urban wastes vs. Industrial wastes

Distribution in percentage of URBAN wastes in EU



INDUSTRIAL wastes in million tonnes (Source CBS) in EU



Case study presentation

The lack of recycling constitutes a new source of emerging contaminants to the environment and some materials could act as adsorbents able to stabilize and transport persistent organic pollutants.

Two case studies will be presented

- Perfluorinated compounds in sea plastic pellets
- Occurrence of nanomaterials in contaminated soil

Objectives

- **To develop analytical methods for their determination in environmental samples based on liquid chromatography and tandem mass spectrometry**
- **To assess their occurrence in the environment in order to create enough data to create the basis of a future risk assessment**

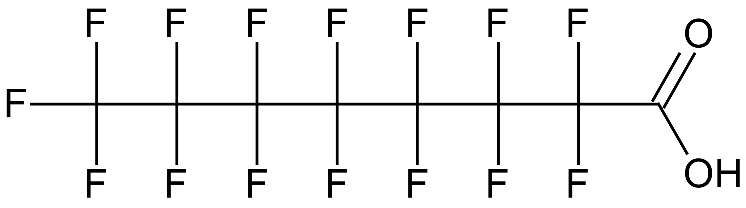
Case study I

Perfluorinated compounds in sea plastic pellets

Perfluorinated compounds in sea plastic pellets

Perfluoroalkyl substances (PFASs) or perfluorinated compounds (PFCs)

Perfluorinated = fully fluorinated



Ex. Perfluorooctanoic acid (PFOA , C-8)

Very stable (C-F bond energy 485 kJ/mol)

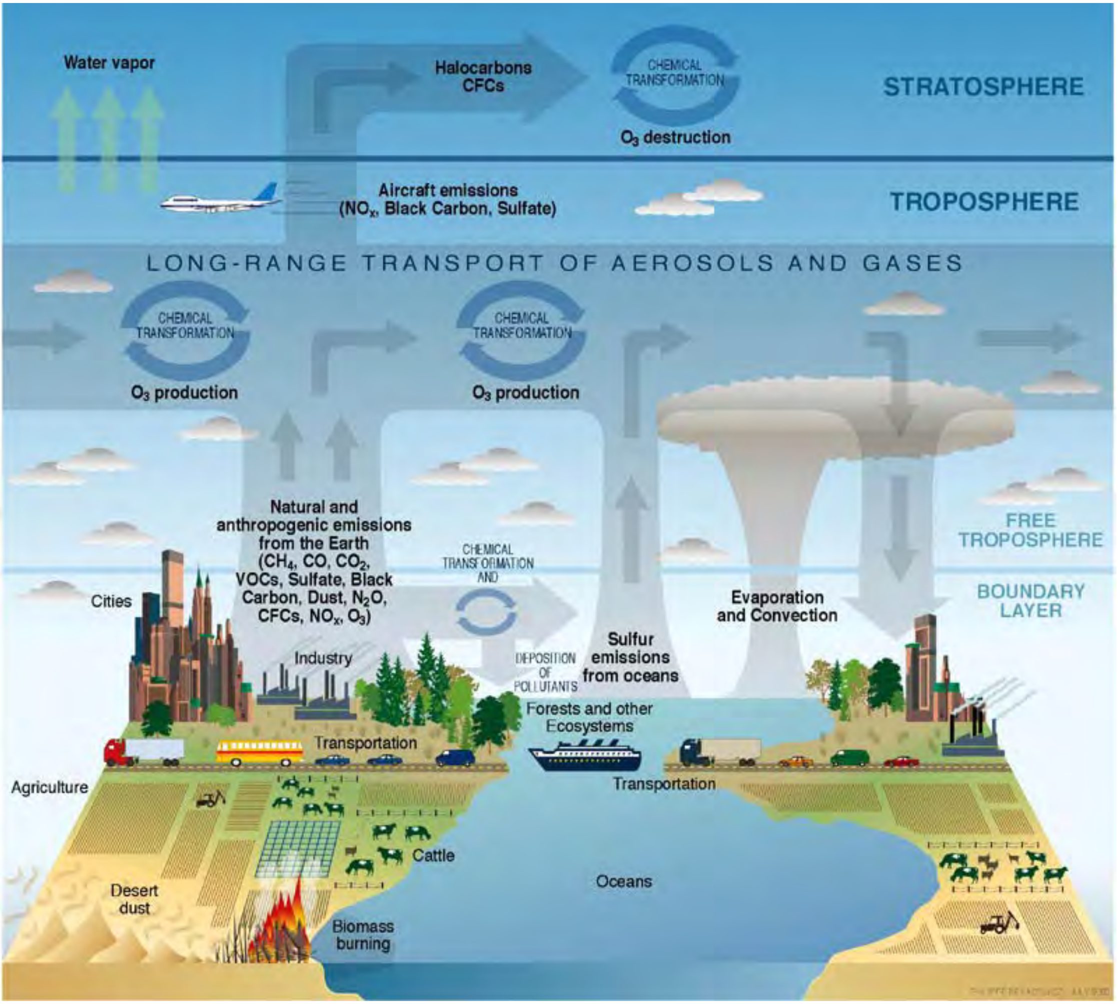
(C-C 346, C-N 305, C-O 358, C-Cl 327 kJ/mol

Properties

- Thermally stable (in excess of 150° C)
- Resists degradation (acid, alkali, oxidizing agents, bio…)
- Hydrophobic and oleo phobic (3 phases in Kow)
- Good surfactants, lubricants
- Non-flammable
- Chemically inert

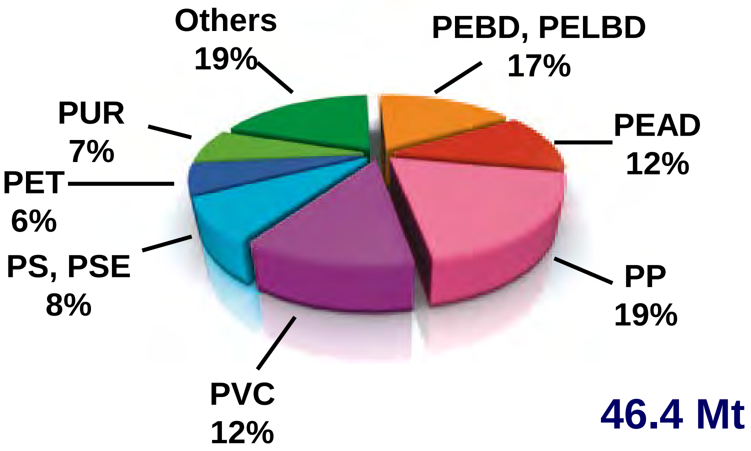
Perfluorinated compounds in sea plastic pellets

Due to PFASs properties are used in a plethora of industrial applications



Perfluorinated compounds in sea plastic pellets

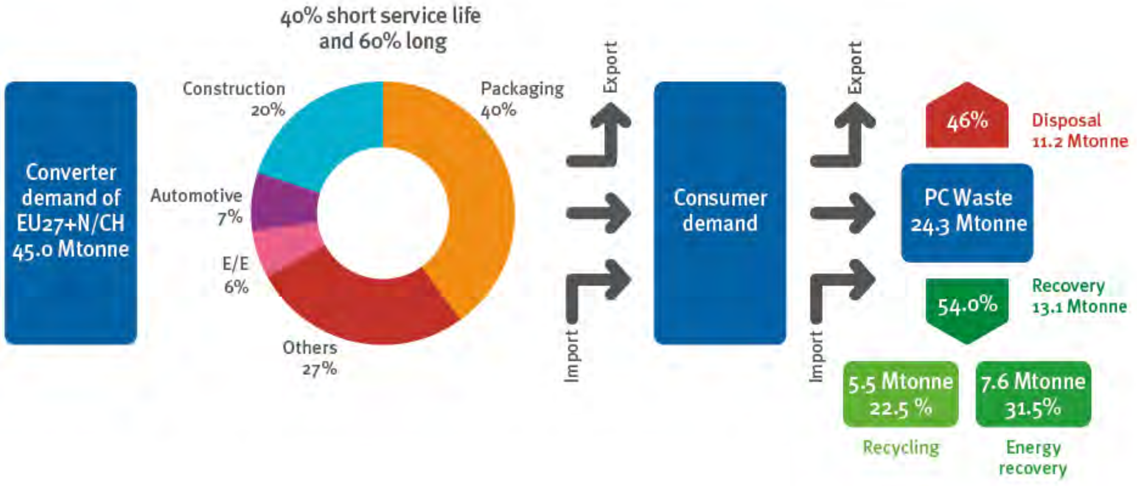
Plastic European demand (2010)



European plastics production in 2010

~ 57 Mt

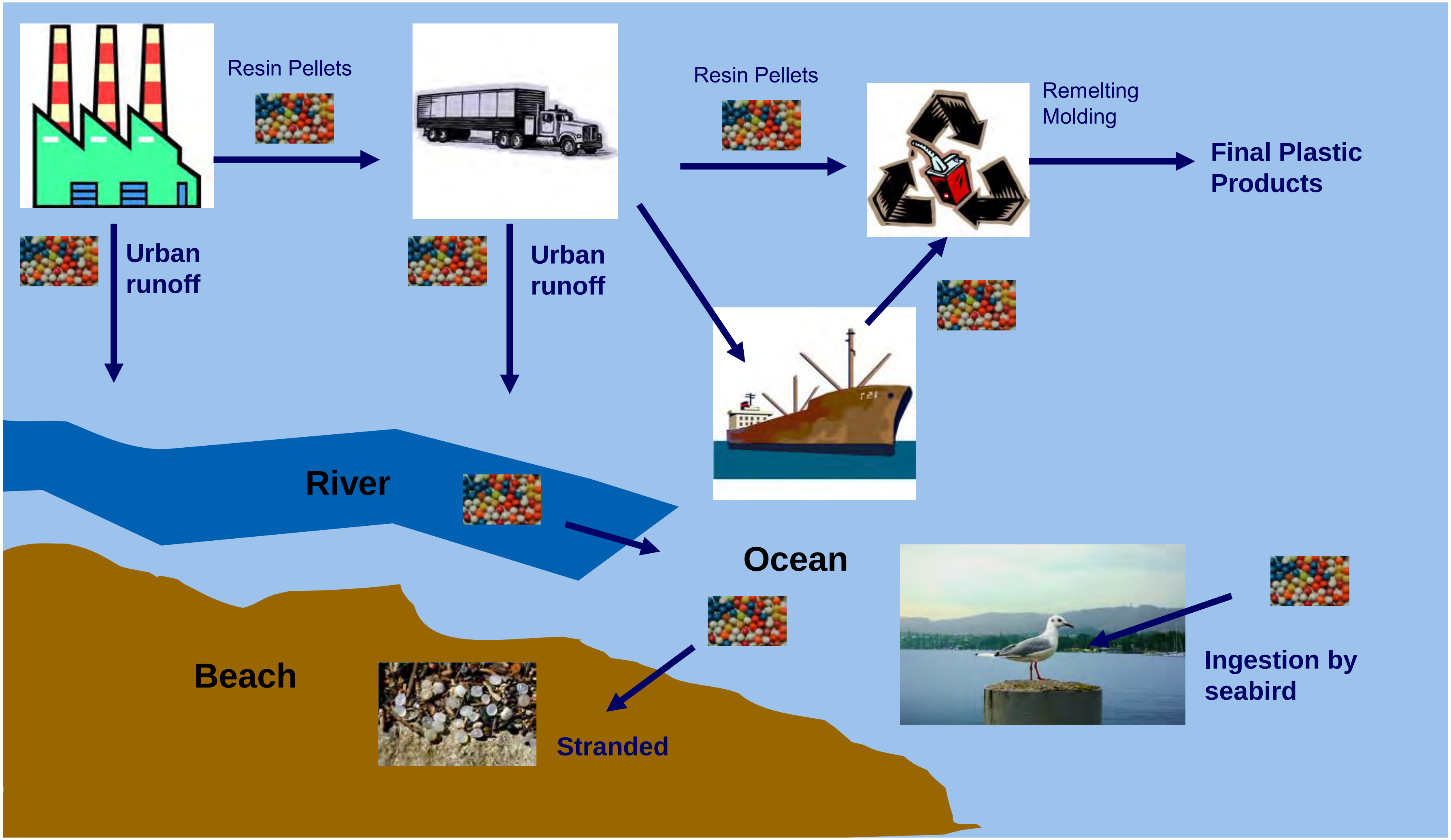
Plastics, value chain during its lifecycle



Plastics Europe Market Research Group (PEMRG)

Perfluorinated compounds in sea plastic pellets

Plastic Resin Pellets in the ocean



Resin Pellets

Resin Pellets

Remelting
Molding

Final Plastic Products

Urban runoff

Urban runoff

River

Ocean

Beach

Stranded

Ingestion by seabird

Perfluorinated compounds in sea plastic pellets

- Plastic pellets (small granules 1-5 mm diameter) are therefore widely distributed in the ocean all over the world.
- The environmental concerns related to these wastes are:
  - as source of contamination
  - the accumulation and transport of persistent organic pollutants that is done while they float on the sea surface.
- They are hydrophobic organic material thus they are favourable medium for persistent organic contaminants.
- Pellets demonstrating a certain degree of erosion are expected to have enough contact area with water contaminants and thus, reach the equilibrium with the pollutants in the water phase.
- Nowadays, monitoring media which can easily collected and shipped with low cost is important for monitoring diffuse pollution.
- In this context a new analytical approach has been developed **to assess 18 PFASs in plastic pellets in the Mediterranean Sea**, and these data was compared with contamination in sediments from the same sampling areas.

Perfluorinated compounds in sea plastic pellets

Sampling - Mediterranean Sea (Greece)

Sampling Poing	Sample type	Sampling site	Possible contamination source
Corfu Island	Plastic Pellet	Beach surface	International Airport and harbour
	Sediment	Beach face	
Lavrio beach	Plastic Pellet	Beach surface	Mazut and natural gas power plant; DOW chemicals plant; near to Athens city
	Sediment	Beach face	
Kato Achaia beach	Plastic Pellet	Beach surface	Harbour
	Sediment	Beach face	
Leros Island	Plastic Pellet	Beach surface	Airport and harbour
	Sediment	Beach face	
Loutropyrgos	Plastic Pellet	Beach surface	Oil refineries (Aspropyrgos and Elefsina); Near to Athens city
	Sediment	Near shore zone	
Pagasitikos Gulf	Sediment	Beach face	Central Greece International Airport Cement Industry (Aget Heracles Industry)
Amvrakikos Gulf	Sediment	Bottom of the sea	National Airport of Preveza-Lefkada Air force base (Mazona lagoon)
Aliveri	Sediment	Bottom of the sea	Cement plant (Heracles); Near to Athens city

Perfluorinated compounds in sea plastic pellets

Analytical method

Sample pre-treatment and SPE

- 1 g sea sand (or Plastic Pellet) + I.S. + 10 mL MeOH
- 1h Ultrasonic bath
- Centrifugation 20’ 4000 rpm, 25ºC
- Supernatant dried under N_2
- Reconstitution in 50 mL Water and SPE (Oasis WAX)
- 150 µL (MeOH/Water)+ I.S

Chromatography

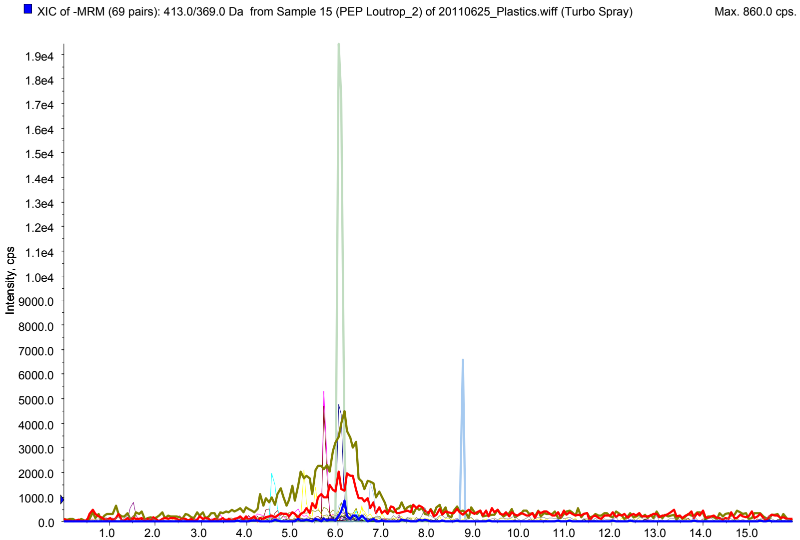
Mobile phase (A) aqueous ammonium acetate 20mM

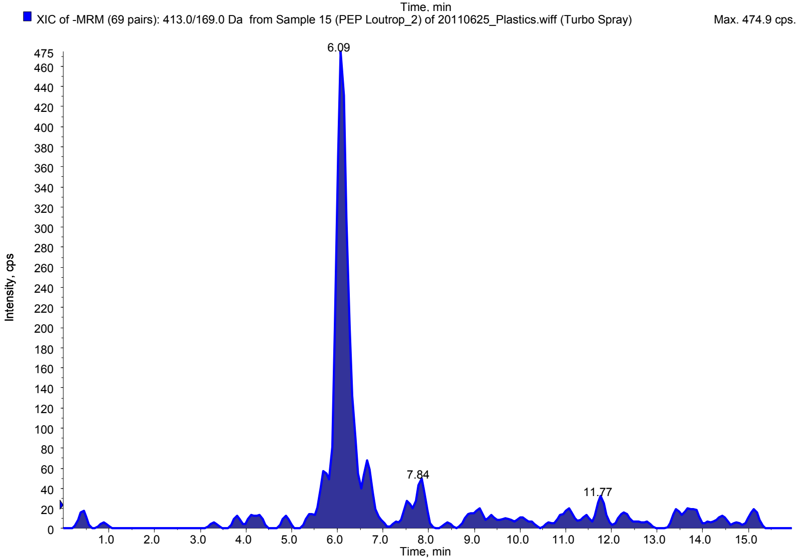
(B) MeOH.

Flow rate: 0.5 mL/min and 10 µL injection volume.

Mass spectrometry

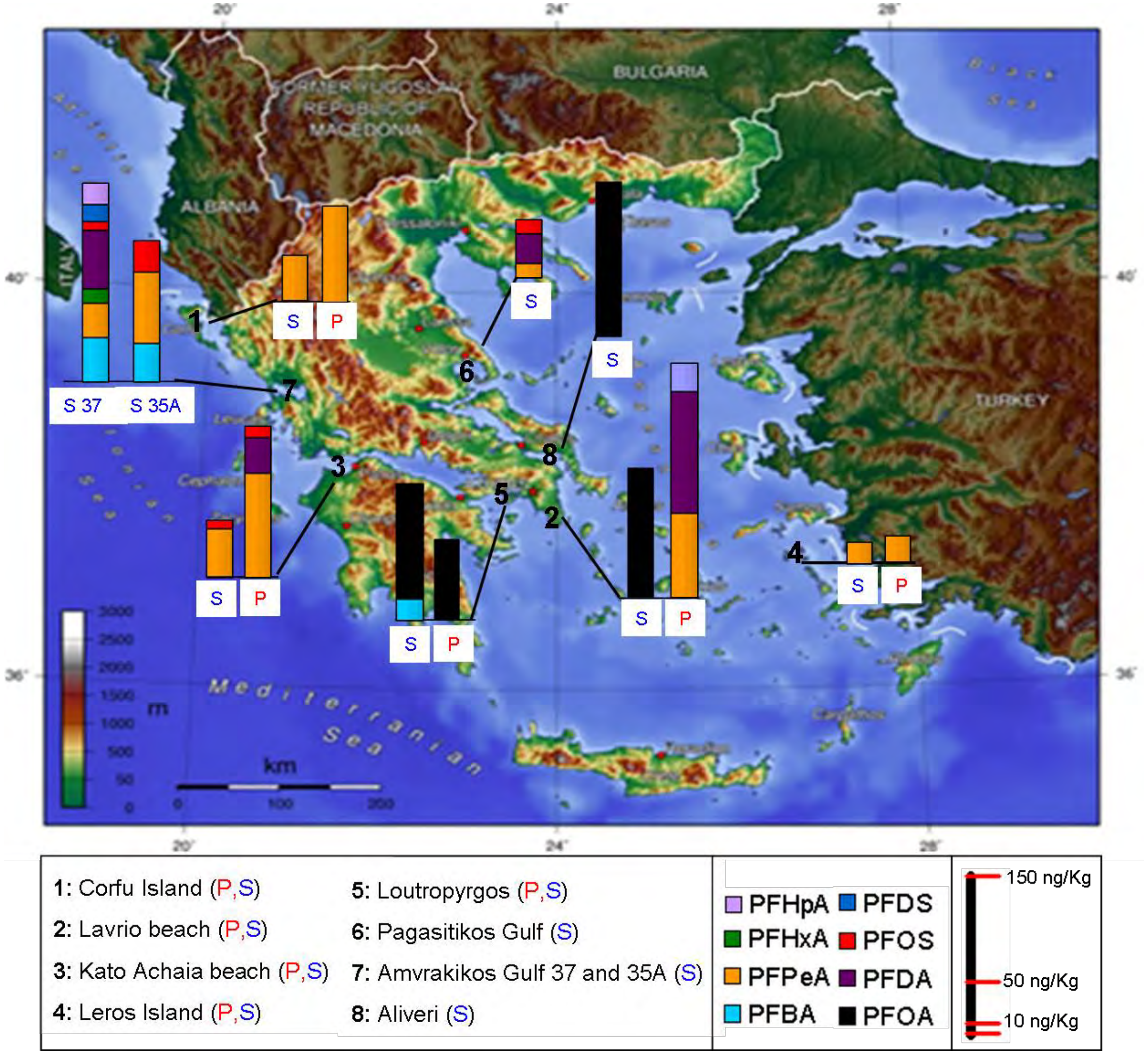
Mass spectrometer (QLIT-MS/MS) 4000 QTRAP (Applied Biosystems), equipped with a Turbo Ion Spray source employed in the negative electrospray ionization mode (ESI(-)).


XIC of -MRM (69 pairs): 413.0/369.0 Da from Sample 15 (PEP Loutrop_2) of 20110625_Plastics.wiff (Turbo Spray) Max. 860.0 cps.


XIC of -MRM (69 pairs): 413.0/169.0 Da from Sample 15 (PEP Loutrop_2) of 20110625_Plastics.wiff (Turbo Spray) Max. 474.9 cps.

Perfluorinated compounds in sea plastic pellets

Results: Sampling sites (Greece) and accumulated concentration of PFASs in sediments (S) and plastic pellets (P), expressed as ng/Kg



1: Corfu Island (P,S)
2: Lavrio beach (P,S)
3: Kato Achaia beach (P,S)
4: Leros Island (P,S)
5: Loutropyrgos (P,S)
6: Pagasitikos Gulf (S)
7: Amvrakikos Gulf 37 and 35A (S)
8: Aliveri (S)

🟪 PFHpA
🟦 PFDS
🟩 PFHxA
🟥 PFOS
🟧 PFPeA
🟪 PFDA
🟦 PFBA
⬛ PFOA

Perfluorinated compounds in sea plastic pellets

Results

PLASTIC PELLET SAMPLES

Concentration range: 11 to 116 ng/Kg

(most of the compounds detected at quantificable concentrations)

PFPeA = 24 - 98 ng/Kg (four samples)
PFHpA = 28 ng/Kg (one sample)
PFOA = 76 ng/Kg (one sample)
PFDA = 35 and 116 ng/Kg (two samples)
PFOS = 11 ng/Kg (one sample)

The highest concentration were found at Lavrio beach and Kato Achaia beach

SEDIMENT SAMPLES

Concentration range: 8.2 to 146 ng/Kg

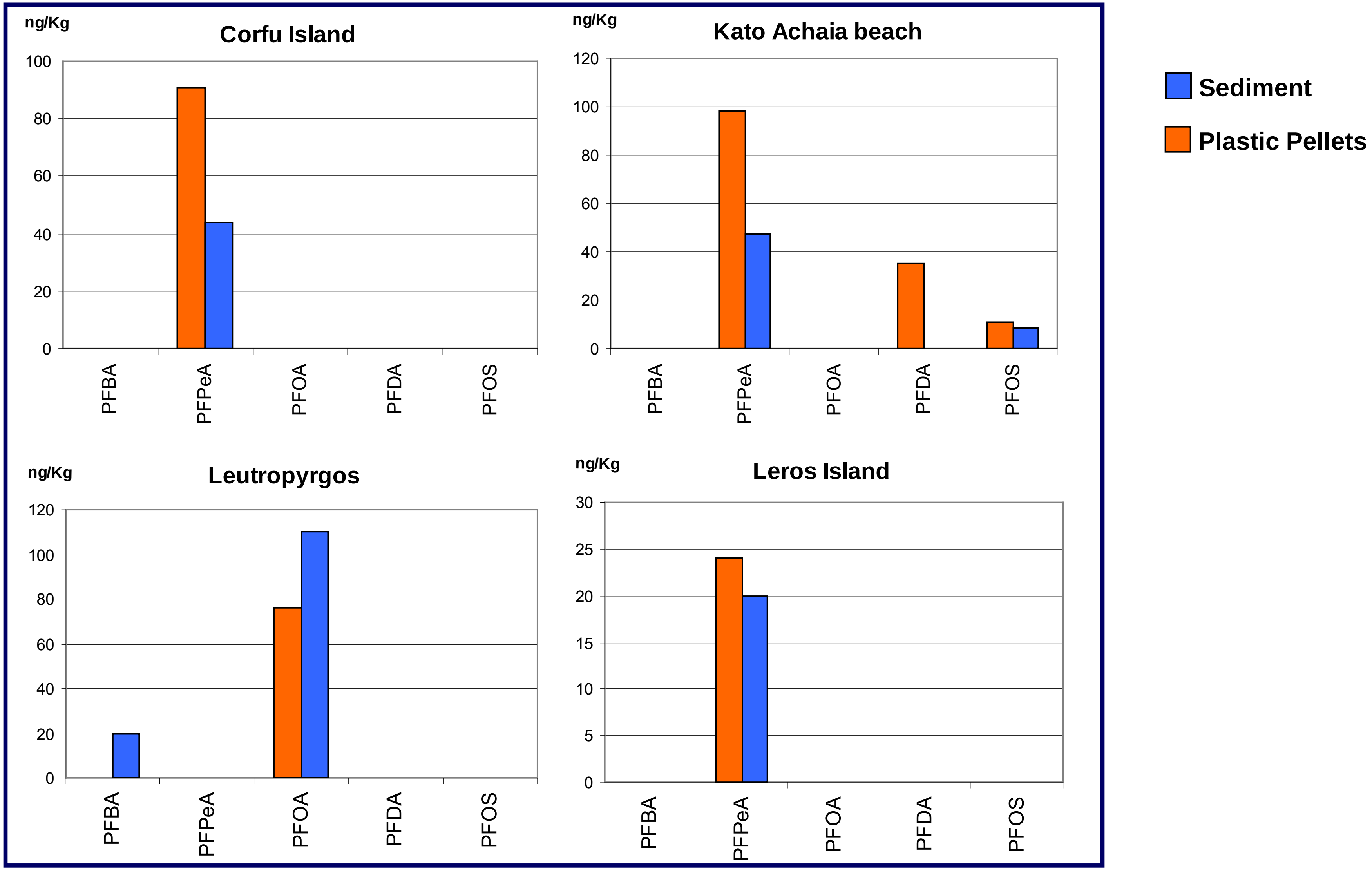
(most of the compounds detected at quantificable concentrations)

PFBA = 20 – 42 ng/Kg (three samples)
PFPeA = 14 – 68 ng/Kg (seven samples)
PFHxA = 13 ng/Kg (one sample)
PFHpA = 20 ng/Kg (one sample)
PFOA = 110 - 146 ng/Kg (three samples)
PFDA = 28 – 56 ng/Kg (two sample)
PFOS = 8.2 – 14 ng/Kg (three samples)
PFDS = 15 ng/Kg (one sample)

The highest concentration were found at Amvrakikos Gulf and Aliveri beach (this samples from the bottom of the sea)

Perfluorinated compounds in sea plastic pellets

Results: Relationship between plastic pellets and sediment samples



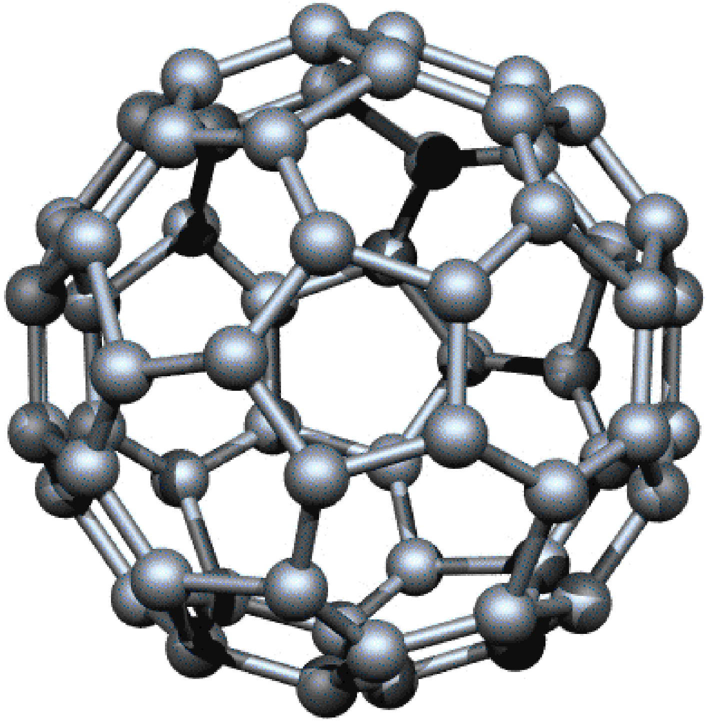
Perfluorinated compounds in sea plastic pellets

Conclusions

- **Main results from beach sediments** (Corfu Island, Kato Achaia beach, Loutropyrgos and Leros Island) indicates that more contaminated areas were Corfu, Leros , Loutropyrgos and areas near harbours
    - **Airports** (Cordu and Leros Islands) due to the combustible
    - **Harbors** due to the combustible and the use of paints and surface treatments for water repellence for ship and doc protection
    - **Oil refinery** (near to Loutropyrgos)
- The prevalent compound in sediment samples was PFPeA
- **Plastic pellet concentrations > Sediment concentrations from beach**, indicating the higher accumulation capacity of plastic pellets
- The similar pattern of PFASs in plastic pellets and sediment beach samples indicates that the residence time of plastic pellets in water is high enough to accumulate these compounds from the water and did not come from longer distances.

Case study II

Nanomaterials in contaminated soils



Fullerenes in contaminated soil

Nanomaterials (NMs)

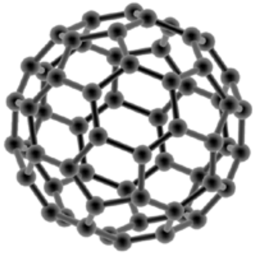
On 18 October 2011, the European Commission adopted the following definition of a nanomaterial

A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the **size range 1 nm – 100 nm**.

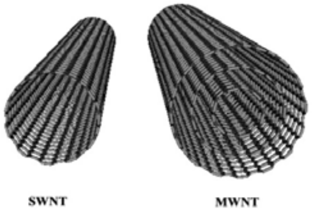
In specific cases and where warranted by concerns for the environment, health, safety or competitiveness the number size distribution threshold of 50% may be replaced by a threshold between 1 and 50%.

Fullerenes in contaminated soil

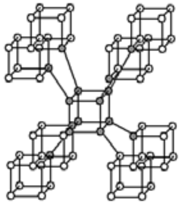
CARBON BASED NMs



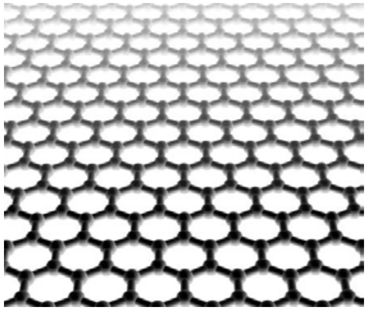
- Fullerenes



- Carbon nanotubes (CNT)
  - Single wall CNTs (SWCNT)
  - Multi wall CNTs (MWCNT)



- Nanodiamonds



- Graphone

Fullerenes in contaminated soil

Sources of FULLERENES

- **Natural fullerenes**
  - Volcanic eruptions
  - Forest fires
  - Minerals

Shungite

Chondrite

Cretaceous–Tertiary boundary sediments

- **Incidental Emission**
  - Car and plane brakes
  - Car emmisions
  - Industrial processes

CURRENTLY MAIN SOURCE

- **Nanotechnology**
  - Microelectronics
  - Consumers products
  - Nanomedicine

FUTURE MAIN SOURCE????

Fullerenes in contaminated soil

Analysis traditionally make use of laser-desorption mass spectrometry

(+) Simple sample preparation
(+) Good ionization of fullerenes
(-) Poor quantification
(-) Fullerene self-generation issue

There is a need for developing new chromatographic methods

(+) Further matrix separation
(+) Better limits of detection
(+) Solid quantification
(-) Need for extraction → poor recovery yields

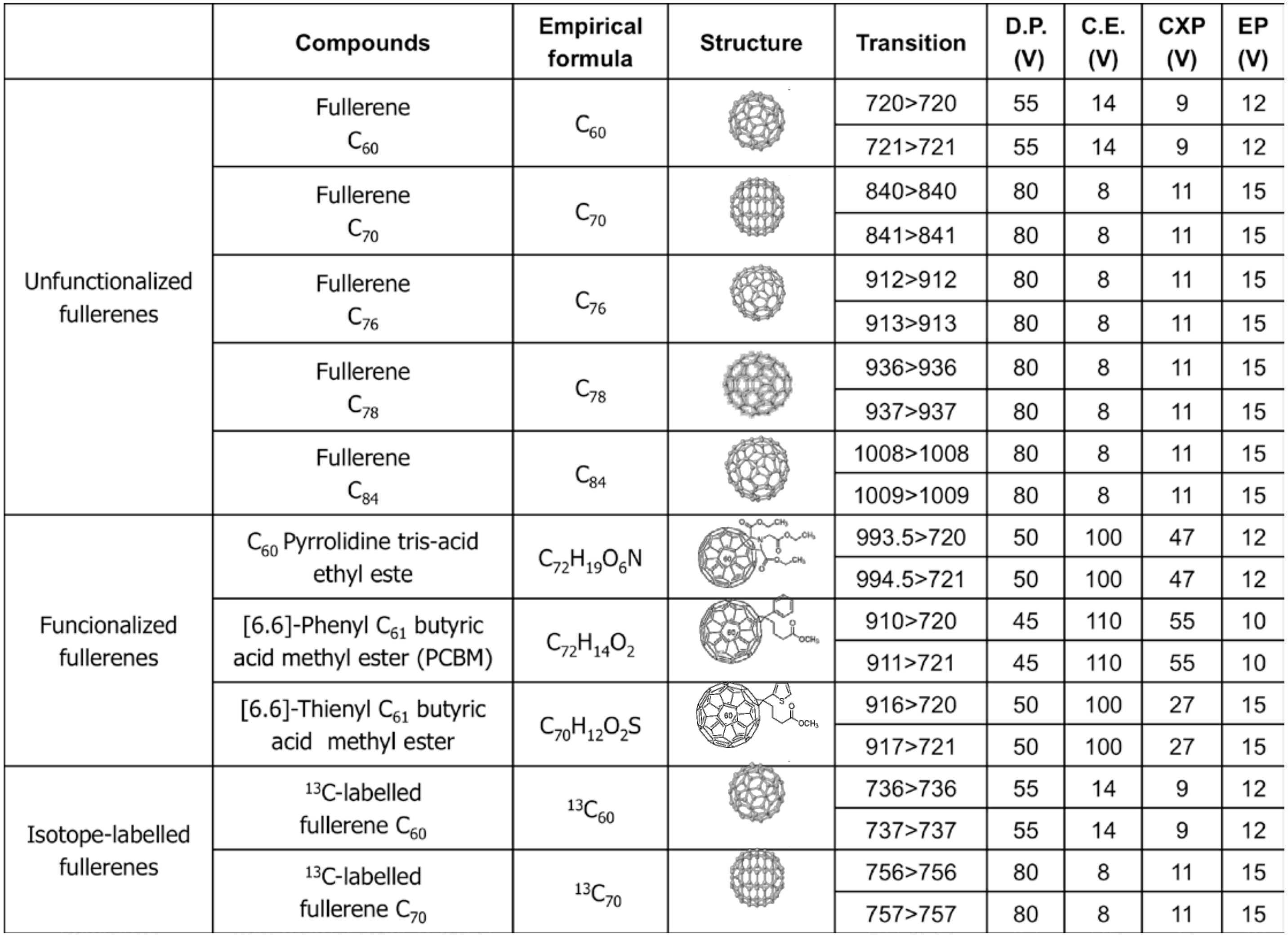
The extraction of fullerenes from high complex matrices (as those with a high content of ash) is a challenge issue, because then recovery yields are too low and matrix too strong.

In this context, the main objectives of the present work were:

- Develop a quantitative method
- Assess the contents of fullerenes in different areas of Saudi Arabia

Fullerenes in contaminated soil

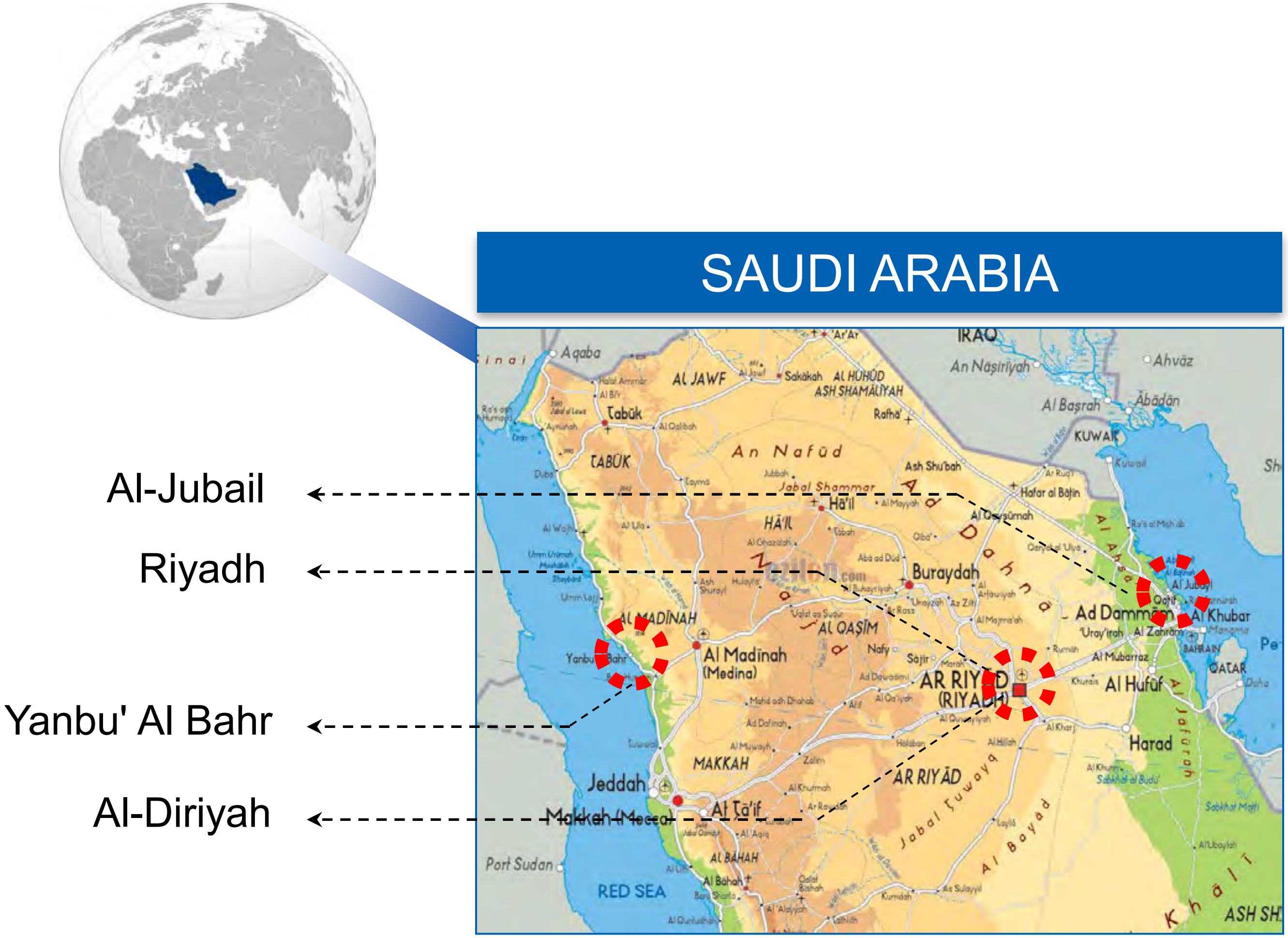
Selected analytes



	Compounds	Empirical formula	Structure	Transition	D.P. (V)	C.E. (V)	CXP (V)	EP (V)
Unfunctionalized fullerenes	Fullerene C_{60}	C_{60}		720>720	55	14	9	12
				721>721	55	14	9	12
	Fullerene C_{70}	C_{70}		840>840	80	8	11	15
				841>841	80	8	11	15
	Fullerene C_{76}	C_{76}		912>912	80	8	11	15
				913>913	80	8	11	15
	Fullerene C_{78}	C_{78}		936>936	80	8	11	15
				937>937	80	8	11	15
	Fullerene C_{84}	C_{84}		1008>1008	80	8	11	15
				1009>1009	80	8	11	15
Funcionalized fullerenes	C_{60} Pyrrolidine tris-acid ethyl este	$C_{72}H_{19}O_6N$		993.5>720	50	100	47	12
				994.5>721	50	100	47	12
	[6.6]-Phenyl C_{61} butyric acid methyl ester (PCBM)	$C_{72}H_{14}O_2$		910>720	45	110	55	10
				911>721	45	110	55	10
	[6.6]-Thienyl C_{61} butyric acid methyl ester	$C_{70}H_{12}O_2S$		916>720	50	100	27	15
				917>721	50	100	27	15
Isotope-labelled fullerenes	^{13}C-labelled fullerene C_{60}	$^{13}C_{60}$		736>736	55	14	9	12
				737>737	55	14	9	12
	^{13}C-labelled fullerene C_{70}	$^{13}C_{70}$		756>756	80	8	11	15
				757>757	80	8	11	15

Fullerenes in contaminated soil

Soils from Saudi Arabia: Sampling locations



SAUDI ARABIA

Al-Jubail

Riyadh

Yanbu' Al Bahr

Al-Diriyah

Samples were taken from **4 sample locations.**

Fullerenes in contaminated soil

Soils from Saudi Arabia: Sampling locations

Riyadh	TOWN (outside)	5 samples
	DOWNTOWN (inside)	5 samples
	INDUSTRIAL AREA	5 samples
Al-Diriyah	NEIGHBORHOOD 1	7 samples
	NEIGHBORHOOD 2	4 samples
	NEIGHBORHOOD 3	1sample
Yanbu' Al Bahr	OLD CITY (inside)	5 samples
	OLD CITY (outside)	5 samples
	INDUSTRIAL CITY (inside)	5 samples
	INDUSTRIAL CITY (outside)	4 samples
Al Jubail	INDUSTRIAL AREA (inside)	4 samples
	INDUSTRIAL AREA (outside)	4 samples
	OLD CITY	4 samples

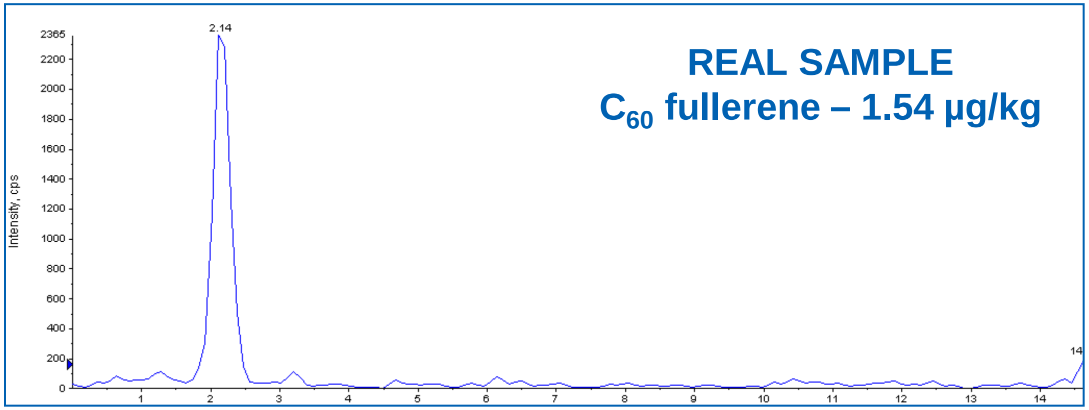
58 SAMPLES

Fullerenes in contaminated soil

Ultrasound assisted extraction with toluene during **8 hours** show good performance in most of the samples, **however for some of them with high contents of ash C_{60} was detected but the quantification was not possible**

Four samples present quantifiable concentrations of C_{60} fullerene:

- Riyadh (outside)
- Riyadh (outside)
- Al-Jubail (industrial area)
- Yanbu' Al Bahr (old city)



REAL SAMPLE
C_{60} fullerene – 1.54 µg/kg

Fullerenes in contaminated soil

Some of the samples presented C_{60} but other fullerenes were not detected, indicating that the origin is combustion processes from cars or from industrial areas.

Positive samples from cities can be directly related to traffic engines. The range of concentrations was 0.15 and 2.15 ng/g

Industrial areas were suspected to be contaminated with both C_{60} and C_{70}, but quantification was not achieved because a strong ion suppression and low recovery rates

Positive samples from industrial areas presented also C_{60} and the concentrations found were higher that in city areas presenting values between 4.35-6.83 ng/g

Conclusion

- Two analytical method have been developed and applied to the analysis of emerging contaminants in the environment.
- In case of plastic pellets, perfluoroalkyl substances were analysed in comparison to sediments from same sampling areas. Good correlation was found between both matrices, but plastic pellets presented higher concentrations.
- Plastic are relevant sources of contamination because during the first periods these materials acts as a source of contaminants. In addition are highly persisten materials that can act stabilizing other contaminants, such as POPs.
- On the other hand, sea plastic pellets are possible passive samplers of the diffuse pollution in an area, as in the examples presented here for PFASs
- Carbon based materials are an emerging class of contamination because the increasing amount of combustion processes and is expected by the nanotechnology.
- In this case the presence of fullerenes was studied in different areas of Saudi Arabia and the results showed that this type of contamination can be associated to some industrial processes and traffic engines but not to the nanotechnology. However the method presented here should be refined to overcome some limitations associated to highly contaminated samples with ash.