

# Food Crime

# An Analysts View

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JANE WHITE

GLASGOW SCIENTIFIC SERVICES

# Food Crime

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Legislative Framework

Some Common Issues

Analytical Methods

Analytical Limitations

Evidential Rigor

The Future





# History

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Saw Dust in tea

Watered Beer

Unfit meat

Public Analysts

- Over 150 years
- MChemA - RSC





# Food Crime Unit - FSS

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Organised Crime

Length of Food Chain

Global Market

Intelligence driven





# Legislative Framework

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**Food Safety Act 1990**

**The General Food Regulations 2004**

**EU regulation - 178/2002 –Article 14 – Unfit for human consumption**

**Sampling and Qualification Regulations 2013**

**Secondary Legislation**

**Food And Feed Enforcement Laboratories**



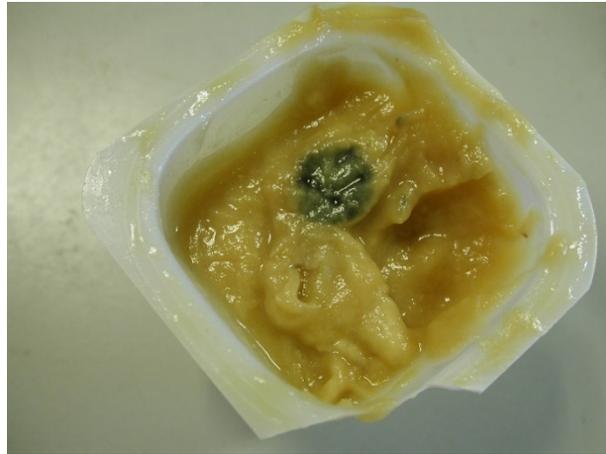
# Injurious to Health

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**Adding or removing a substance so that the food causes harm**

- **Glass in baby food**
- **Melamine in baby milk**
- **Allergens**

# Unfit for Human Consumption



# Nature - Substance - Quality

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# Misleading Description

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**Traditional Dairy Ice cream containing vegetable fat**

**Vodka with 20% alcohol**

**This may also be applicable to pictorial representation**

# Formal Sampling

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Three part sample

- Portion 1 – Enforcement Lab
- Portion 2- Business Operator
- Portion 3 – Reference sample

Homogeneous

Sample size

Laboratory of the Government Chemist

# Common Issues

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## Substitution

- Meat
- Fish
- Cheese
- Wine and Spirits

## Adulteration

- Added water
- Melamine
- Sudan Colours
- Allergens



# Meat

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Species substitution

Breed substitution

Added Water

Protein

MRM

Offal

Country of Origin



# Analysis

## Speciation

- DNA – PCR
- ELISA

## Added Water

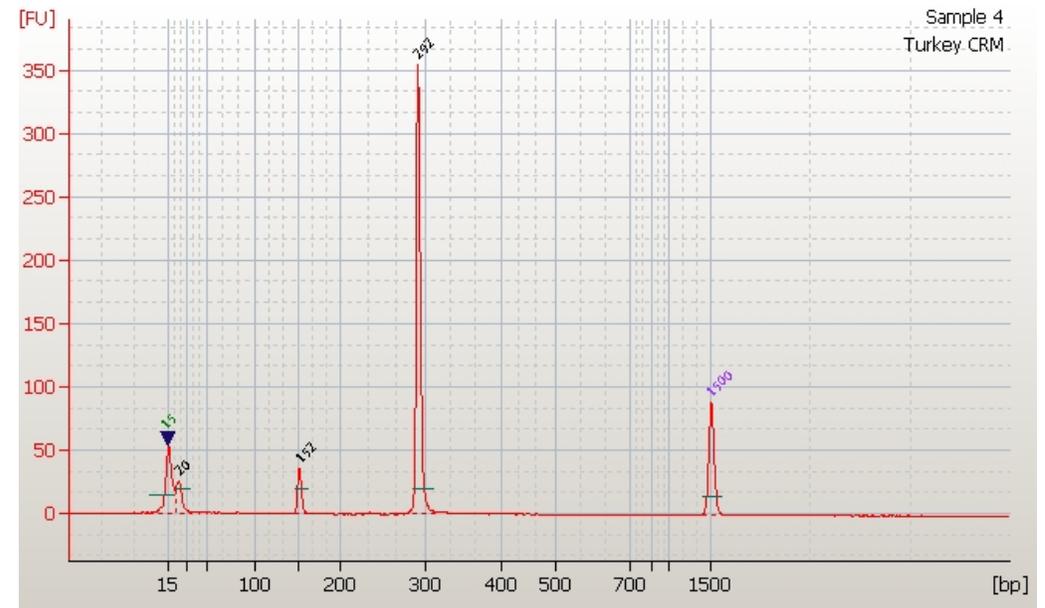
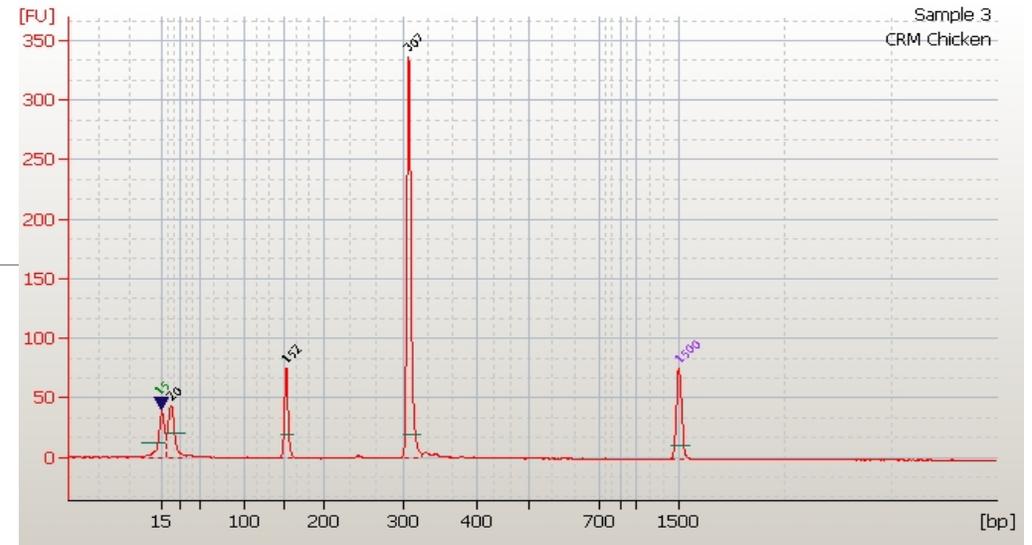
- Nutritional analysis

## MRM/Offal

- Specific Proteins/ Microscopy

## Origin

- Isotope Ratio



# Fish/Shellfish

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**Substitution**

**Illegal fishing/harvesting grounds**

**Unfit**





# Analysis

## PCR

### Freshness

- Histamine – HPLC fluorescence
- TVBN

### Shellfish toxins

- HPLC
- LC/MS/MS

Fish Species	Ddel			HaeIII		
Haddock ( <i>Melanogrammus aeglefinus</i> )	418-462			34-46		404-447
Whiting ( <i>Merlangius merlangus</i> )	114-126	342-378	33-45	100-110	314-347	
Atlantic Cod ( <i>Gadus morhua</i> )	78-105	114-126	232-257	33-45	101-112	308-340



# Alcoholic Drinks

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## Vodka

Industrial alcohol

- Markers for industrial alcohol

## Whisky

Brand Substitution

- Congeners

## Wines

Origin issues

- Lead isotope ratio

# Traceability

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Continuity of evidence

Samples as received

Tamperproof

Paper trail

Recording all your finding

Pictures

Corroboration of results



# Robustness of Analysis

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Accredited Methods

Validation

Appropriate Quality Control

- Spikes
- Labelled standards
- Duplicate analysis
- Proficiency Testing Schemes

Uncertainty of Measurement



# Limitations

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Data Bases

Non Specific Primers

Availability of Standards

Matrix Issues



# Future considerations

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Development of Accessible Data Base

Continuing collaboration between National Reference Laboratories and Official Control Laboratories

Funding of research into rapid - robust techniques

Acceptance that enforcement costs are higher than route analysis

# Questions

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Legacy Flame Retardants,  
Emerging Flame Retardants  
and dioxins: Links and tools  
for risk assessment



## WHERE FLAME RETARDANTS ARE FOUND

In home insulation

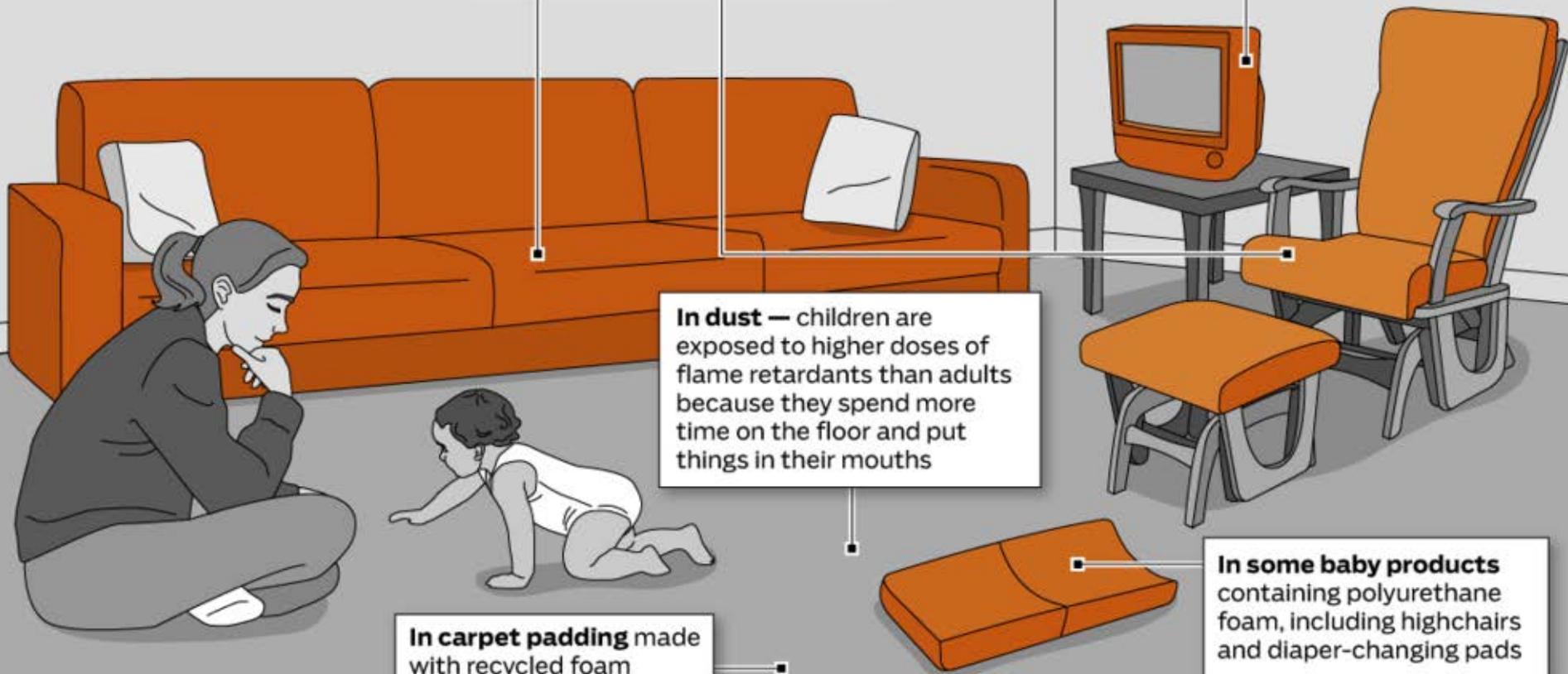
In upholstered furniture containing polyurethane foam — manufacturers add it to meet flammability standards enacted by California but followed nationwide

In the plastic casing of some electronics

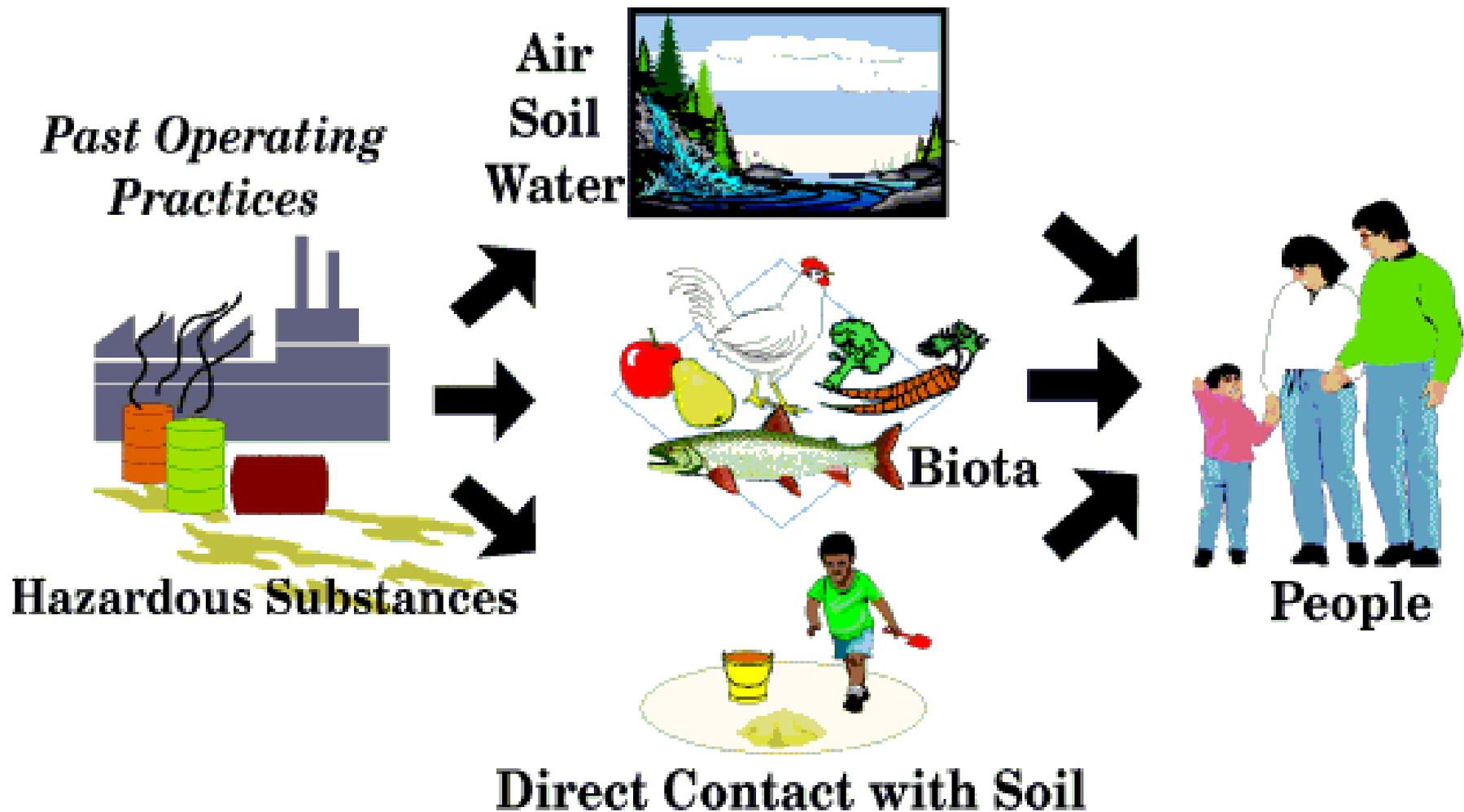
In dust — children are exposed to higher doses of flame retardants than adults because they spend more time on the floor and put things in their mouths

In carpet padding made with recycled foam

In some baby products containing polyurethane foam, including highchairs and diaper-changing pads



# Exposure Pathways



# Terminology

- **Legacy or Established FRs** (BFRs/CFRs/PFRs) are chemicals which are extensively documented regarding production and use as FRs, chemistry, fate, exposures, environment and health issues (i.e. (eco-) toxicity and/or human health effects).
- **Emerging FRs** (BFRs/CFRs/PFRs) are chemicals which are documented regarding production and use as FRs that have been shown to occur/distribute to the environment and/or wildlife, humans or other biological matrices.
- **Novel FRs** (BFRs/CFRs/PFRs) are chemicals which are documented as potential FRs that have been shown to be present in materials or products.
- **Potential FRs** (BFRs/CFRs/PFRs) are chemicals reported to have applications as FRs (e.g. in patents).



Contents lists available at SciVerse ScienceDirect

# Environment International

journal homepage: [www.elsevier.com/locate/envint](http://www.elsevier.com/locate/envint)



## Review

### A novel abbreviation standard for organobromine, organochlorine and organophosphorus flame retardants and some characteristics of the chemicals

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Phosphorus flame retardants

Nomenclature

Abbreviations

Physico-chemical properties

## ABSTRACT

Ever since the interest in organic environmental contaminants first emerged 50 years ago, there has been a need to present discussion of such chemicals and their transformation products using simple abbreviations so as to avoid the repetitive use of long chemical names. As the number of chemicals of concern has increased, the number of abbreviations has also increased dramatically, sometimes resulting in the use of different abbreviations for the same chemical. In this article, we propose abbreviations for flame retardants (FRs) substituted with bromine or chlorine atoms or including a functional group containing phosphorus, i.e. BFRs, CFRs and PFRs, respectively. Due to the large number of halogenated and organophosphorus FRs, it has become increasingly important to develop a strategy for abbreviating the chemical names of FRs. In this paper, a two step procedure is proposed for deriving *practical abbreviations* (PRABs) for the chemicals discussed. In the first step, *structural abbreviations* (STABs) are developed using specific STAB criteria based on the FR structure. However, since several of the derived STABs are complicated and long, we propose instead the use of PRABs. These are, commonly, an extract

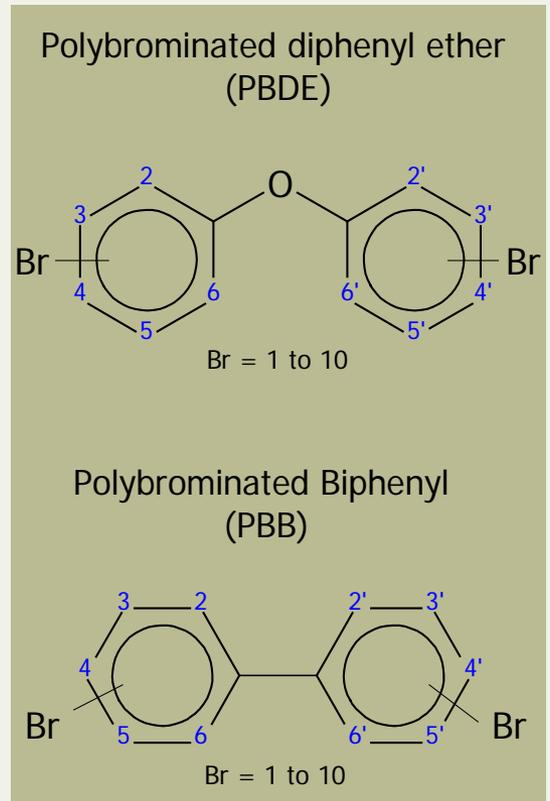
# Legacy BFRs

- Reactive BFRs - Covalently bonded to polymer
  - Tetrabromobisphenol-A
  - Tetrabromophthalic Anhydride
- Additive Flame Retardants - Blended with polymer
  - Polybrominated diphenyl ethers
  - Polybrominated biphenyls
  - Hexabromocyclododecane



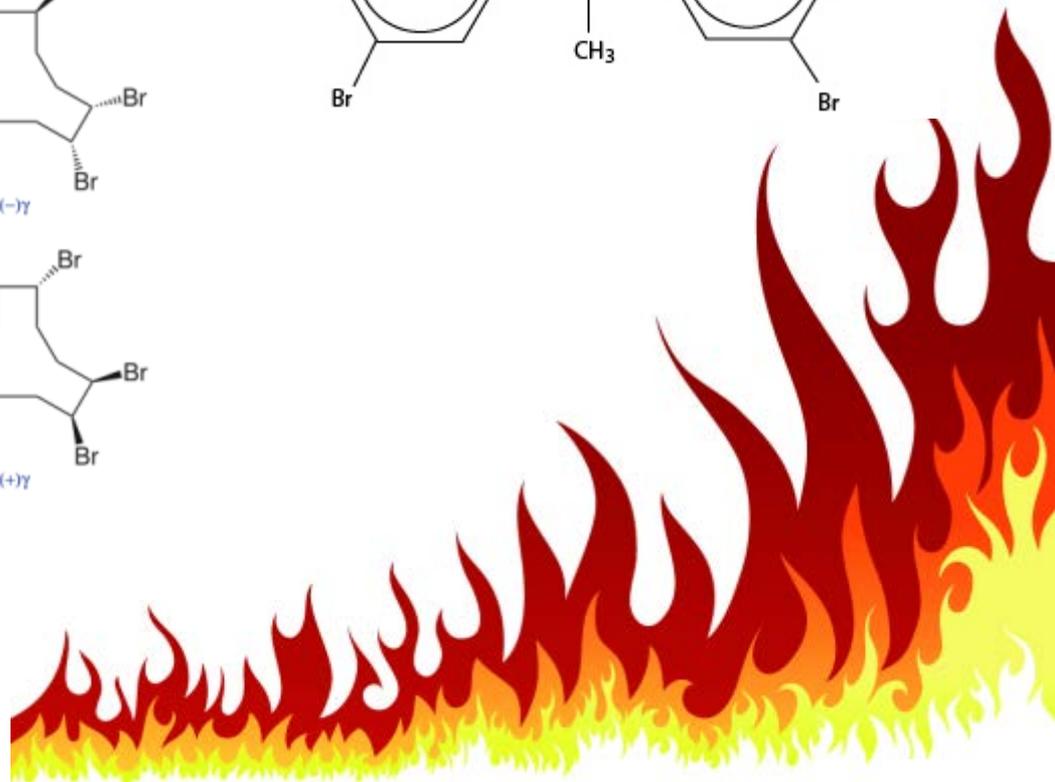
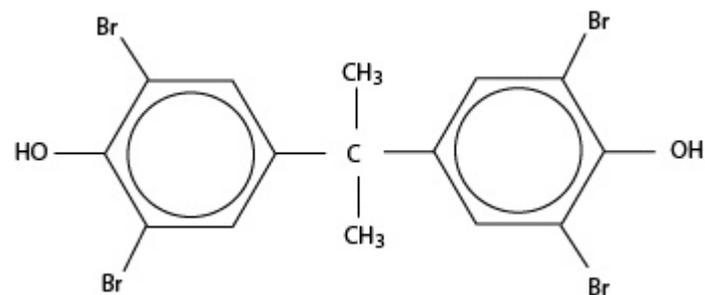
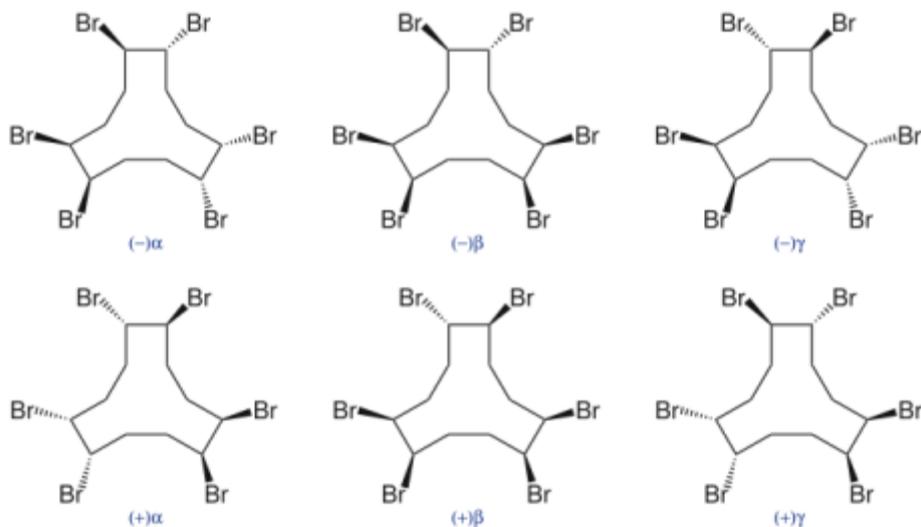
# PBBs and PBDEs

- Additive flame retardants
  - PCBs were used from 1920s-1980s
  - PBBs No longer used - Michigan 1976 Firemaster mixed with cattle feed
  - PBDEs sold in distillation fractions  
Penta, Octa and DecaBDE  
Individual congeners numbered as PCBs
  - Used in...
    - Plastics
    - Upholstery
    - Textiles
    - Foams
    - Wiring
- Can be > 15% w/w !



# HBCDD, TBBPA...

- Replacements for PBDEs



# Next steps - new and emerging BFRs

- industrial and commercial demand arising from the restrictions of the previously commonly used BFRs will be filled by an increasing number of alternative flame retardants in order to comply with fire safety regulations



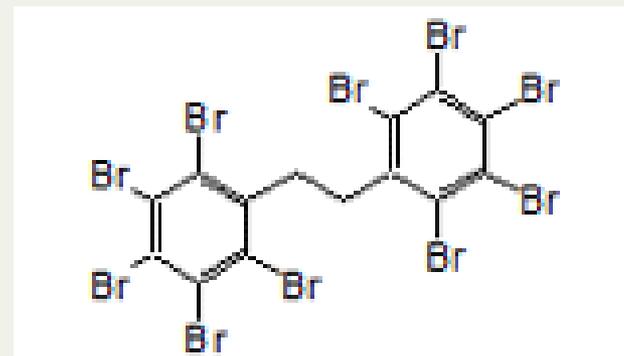
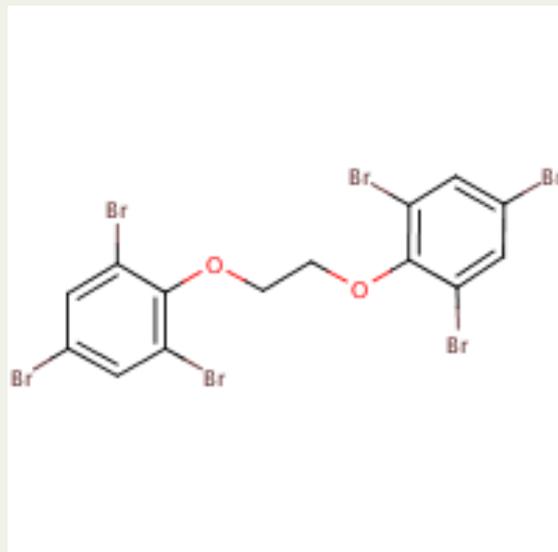
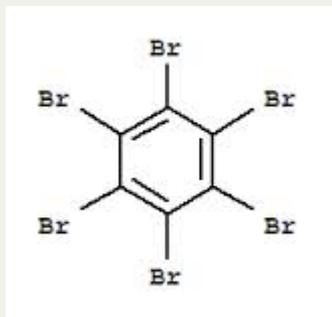
# Emerging FRs

- Many potential BFRs, CFRs and PFRs have been registered (many 100s when congeners and enantiomers are considered)
- Current production volume of BFRs exceeds 200,000 tonnes/year
- 600,000 tonnes/year of chlorinated paraffins in China alone (multiple applications)



## Some emerging FRs already found in the environment and foods

- hexabromobenzene (HBB)
- bis (2,4,6-tribromophenoxy)ethane (BTBPE)
- decabromodiphenylethane (DBDPE)



- similar properties to PBDEs (chemical stability arising from halogenated aromaticity and low aqueous solubility)



European Food Safety Authority EFSA Journal 2012;10(10):2908

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**SCIENTIFIC OPINION**

**Scientific Opinion on Emerging and Novel Brominated Flame Retardants (BFRs) in Food<sup>1</sup>**

**EFSA Panel on Contaminants in the Food Chain<sup>2,3</sup>**

European Food Safety Authority (EFSA), Parma, Italy



European Food Safety Authority EFSA Journal 2012;10(4):2634

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**SCIENTIFIC OPINION**

**Scientific Opinion on Brominated Flame Retardants (BFRs) in Food: Brominated Phenols and their Derivatives<sup>1</sup>**

**EFSA Panel on Contaminants in the Food Chain (CONTAM)<sup>2,3</sup>**

European Food Safety Authority (EFSA), Parma, Italy



European Food Safety Authority EFSA Journal 2011;9(12):2477

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**SCIENTIFIC OPINION**

**Scientific Opinion on Tetrabromobisphenol A (TBBPA) and its derivatives in food<sup>1</sup>**

**EFSA Panel on Contaminants in the Food Chain (CONTAM)<sup>2,3</sup>**

European Food Safety Authority (EFSA), Parma, Italy



European Food Safety Authority EFSA Journal 2011;9(7):2296

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**SCIENTIFIC OPINION**

**Scientific Opinion on Hexabromocyclododecanes (HBCDDs) in Food<sup>1</sup>**

**EFSA Panel on Contaminants in the Food Chain (CONTAM)<sup>2,3</sup>**

European Food Safety Authority (EFSA), Parma, Italy



European Food Safety Authority EFSA Journal 2011;9(5):2156

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**SCIENTIFIC OPINION**

**Scientific Opinion on Polybrominated Diphenyl Ethers (PBDEs) in Food<sup>1</sup>**

**EFSA Panel on Contaminants in the Food Chain (CONTAM)<sup>2,3</sup>**

European Food Safety Authority (EFSA), Parma, Italy



European Food Safety Authority EFSA Journal 2010; 8(10):1789

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**SCIENTIFIC OPINION**

**Scientific Opinion on Polybrominated Biphenyls (PBBs) in Food<sup>1</sup>**

**EFSA Panel on Contaminants in the Food Chain (CONTAM)<sup>2,3</sup>**

European Food Safety Authority (EFSA), Parma, Italy

- tris(2,3-dibromopropyl) phosphate (TDBPP) and dibromoneopentyl glycol (DBNPG)
- genotoxic and carcinogenic
- poor environmental stability and high chemical reactivity
- not expected to occur in foods.



# Commission Recommendation 2014/118/EU

5.3.2014

EN

Official Journal of the European Union

L 65/39

## COMMISSION RECOMMENDATION

of 3 March 2014

on the monitoring of traces of brominated flame retardants in food

(Text with EEA relevance)

(2014/118/EU)

THE EUROPEAN COMMISSION,

- (5) EFSA recommended, for a number of those classes, that further data on levels in food and in humans should be gathered.

Having regard to the Treaty on the Functioning of the European

Levels of BFRs in food of animal origin could be related to the presence of these substances in animal feed, therefore, a recommendation as regards the monitoring of animal feed is likely to follow in 2015



# Prioritisation of emerging BFRs

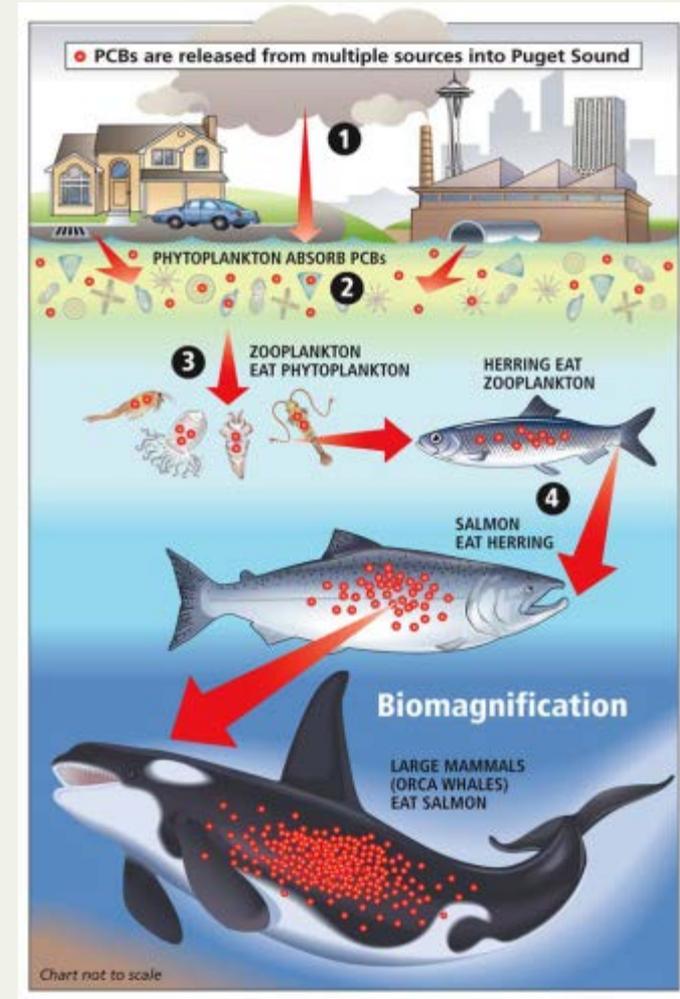
- high overall persistence (>500 days)
- potential for bioaccumulation
- identification in the environment or food



**From the moment they are born  
over 200 chemicals course through  
their veins.**

Killer chemicals in  
the environment

[bonvictor.blogspot.com](http://bonvictor.blogspot.com)



# Top 10 emerging BFRs

- hexabromobenzene (HBB),
- 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE),
- 5,6-dibromo-1,10,11,12,13,13-hexachloro-11-tricyclo[8.2.1.0<sup>2,9</sup>]tridecene (DBHCTD),
- 1,2,3,4,7,7-hexachloro-5-(2,3,4,5-tetrabromophenyl)-bicyclo[2.2.1]hept-2-ene (HCTBPH),
- pentabromotoluene (PBT),
- pentabromobenzyl acrylate (PBB-Acr),
- pentabromoethylbenzene (PBEB)
- 1,2,4,5-tetrabromo-3,6-dimethylbenzene (TBX)
- decabromodiphenyl ethane (DBDPE)
- octabromotrimethylphenyl indane (OBTMPI)



# Risk assessment - Impact of exposure

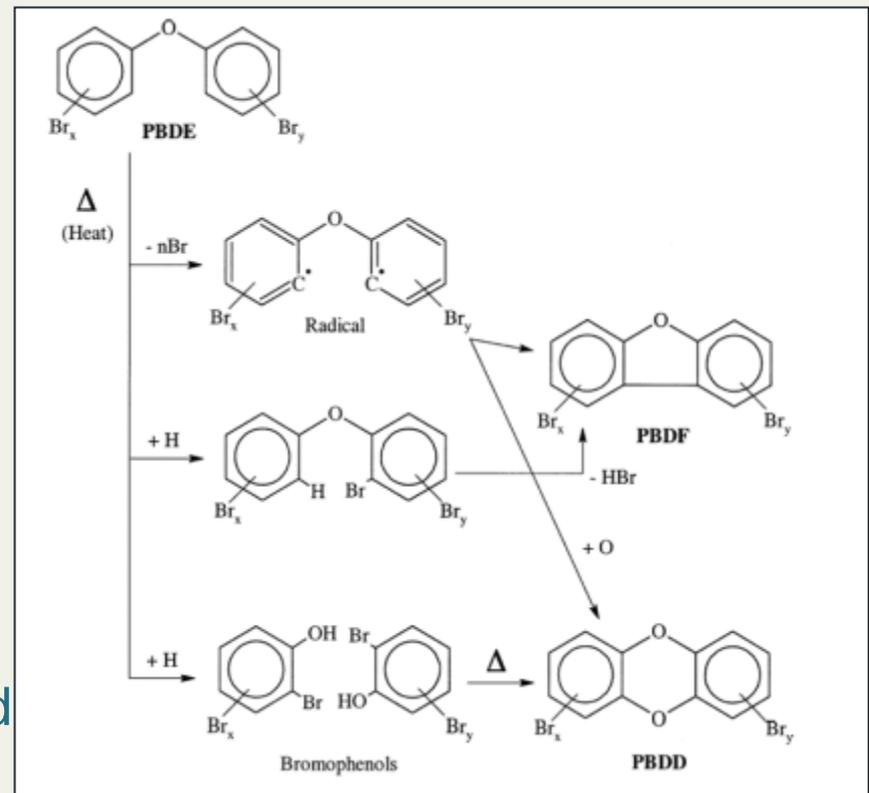
- links between exposure to chemicals in the environment and resulting human and environmental health effects
  - Risk assessment of environmental contaminants
  - Pathways of environmental contaminants in the environment

- Emerging contaminants
- Health effects
- Diet and health

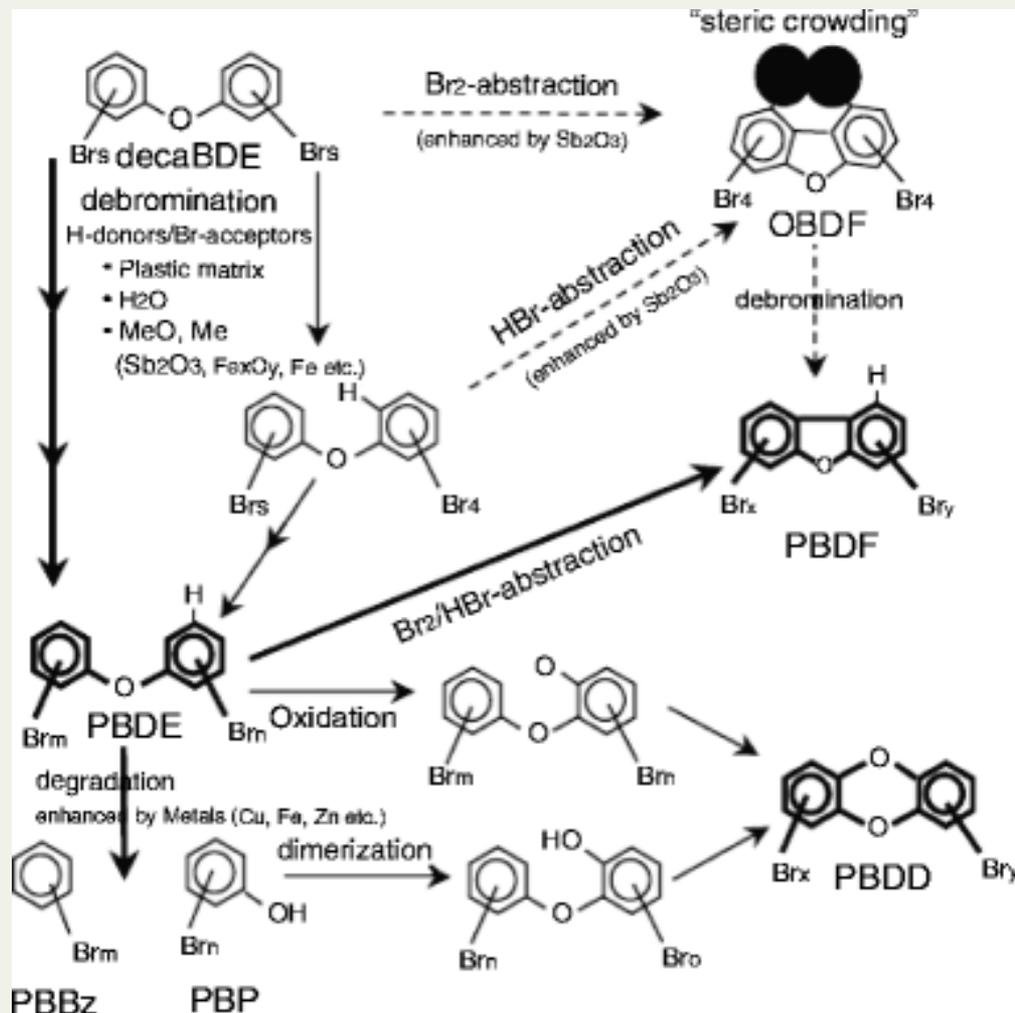


# BFRs can form Brominated Dioxins and Furans (PBDD/Fs)

- PBDD/Fs
  - 210 congeners
  - Thermal breakdown products of brominated organics
  - Formed from burning of BFRs in plastics
  - Highly toxic and persistent
  - Mimic hormones - Thyroxine
  - Some congeners more toxic than 2,3,7,8-substituted chlorinated dioxins



# Various mechanisms



## Formation of polybrominated dibenzofurans (PBDFs) after heating of a salmon sample spiked with decabromodiphenyl ether (BDE-209)

Walter Vetter • Paul Bendig • Marina Blumenstein • Florian Hägele • Peter A. Behnisch • Abraham Brouwer

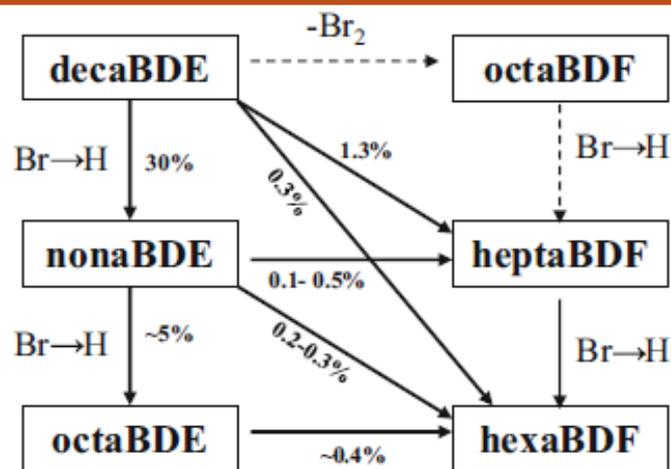


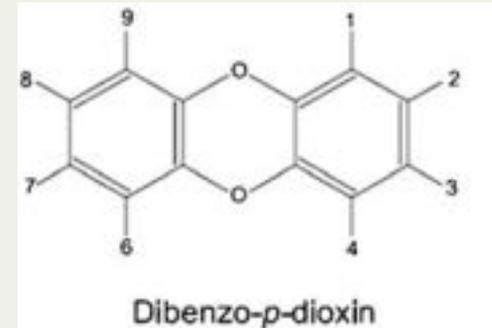
Fig. 3 Transformation scheme for polybrominated diphenyl ethers decaBDE (BDE-209, nonaBDE (BDE-206, BDE-207/208) and octaBDE (BDE-196, BDE-199) by hydrodehalogenation (*left panel*) and by dehydrohalogenation into octa- to hexabromodibenzofurans (*right panel*) along with the conversion rates observed by the heating of the corresponding PBDEs in 1 g of fish for 30 min. *Dashed arrows* represent potential pathways not verified by the experiments. *Ranges* represent compound-specific variations of the isomers mentioned above

Mixed Cl- and Br- dioxins may be formed where there is also a source of chlorine

PXDD; PXDF; PXB

# PXDD/Fs and PXBs

- Between 7-11 of 13 measured congeners detected (biosolids, CLOs, MBMAs, PLA2 and RWW 1 and 2)
- Total sum 0.2-3.0 ng/kg DS (compared to 4.9-4369 ng/kg DS for PCDD/Fs)
- Small subset of the potentially large number of laterally substituted mixed halogenated congeners



# Dealing with mixtures



- Easy for chlorinated dioxins!

- WHO-TEQ - a simplified expression of the toxicities of the different PCBs and dioxins as one number

$$\text{WHO-TEQ} = \sum[\text{PCDD}_i \times \text{TEF}_i] + \sum[\text{PCDF}_i \times \text{TEF}_i] + \sum[\text{PCB}_i \times \text{TEF}_i]$$

# PCDD/F, PBDD/F and PBrCIDD/F congeners

Substitution :

Compound	Mono	Di	Tri	Tetra	Penta	Hexa	Hepta	Octa	Total
PBDD	2	10	14	22	14	10	2	1	75
PBDF	4	16	28	38	28	16	4	1	135
PCDD	2	10	14	22	14	10	2	1	75
PCDF	4	16	28	38	28	16	4	1	135
PBrCIDD	0	14	84	254	420	452	252	74	1550
PBrCIDF	0	28	168	496	840	880	504	134	3050
Grand Total PXDD/F congeners									5020

# Formation

- Thermal
  - *de novo*
  - *formation from precursors*
- Chemical
- Photochemical
- Biological - condensation reactions of naturally occurring bromophenols\*



# Toxicity of PBDD/Fs and PBrCIDD/F

## As for PCDD/Fs

- Lethality
- Wasting
- thymic atrophy
- Teratogenesis
- reproductive effects
- Chloracne
- Immunotoxicity
- enzyme induction
- decrease in T4 and vitamin A
- increased hepatic porphyrins



# Toxicity and occurrence of PXBs

Environment International 44 (2012) 118–127



ELSEVIER

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Environment International

journal homepage: [www.elsevier.com/locate/envint](http://www.elsevier.com/locate/envint)



Review

## Mixed poly-brominated/chlorinated biphenyls (PXBs): Widespread food and environmental contaminants

Jerzy Falandysz <sup>a,\*</sup>, Martin Rose <sup>b</sup>, Alwyn R. Fernandes <sup>b</sup>

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<sup>b</sup> *Food and Environment Research Agency, Sand Hutton, York YO41 11Z, UK*

# Toxicity of PBDD/Fs and PBrCIDD/F (2)

TOXICOLOGICAL SCIENCES 133(2), 197–208 2013  
doi:10.1093/toxsci/kft070  
Advance Access publication March 14, 2013

## REVIEW

### Polybrominated Dibenzo-*p*-Dioxins, Dibenzofurans, and Biphenyls: Inclusion in the Toxicity Equivalency Factor Concept for Dioxin-Like Compounds

Martin van den Berg,<sup>1,\*</sup> Michael S. Denison,<sup>†</sup> Linda S. Birnbaum,<sup>‡</sup> Michael J. DeVito,<sup>‡</sup> Heidelore Fiedler,<sup>§</sup> Jerzy Falandysz,<sup>¶</sup> Martin Rose,<sup>||</sup> Dieter Schrenk,<sup>|||</sup> Stephen Safe,<sup>|||</sup> Chiharu Tohyama,<sup>#</sup> Angelika Tritscher,<sup>\*\*</sup> Mats Tysklind,<sup>††</sup> and Richard E. Peterson<sup>‡‡</sup>

- Use same TEFs as for chlorinated dioxins – interim basis
- Data on exposure is needed



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Environment International

journal homepage: [www.elsevier.com/locate/envint](http://www.elsevier.com/locate/envint)

# Characterisation of chlorinated, brominated and mixed halogenated dioxins, furans and biphenyls as potent and as partial agonists of the Aryl hydrocarbon receptor



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Risk assessment

CYP1A1

Potency

## ABSTRACT

The Aryl hydrocarbon receptor (AhR) binds a variety of chlorinated and brominated dioxins, furans and biphenyls. Mixed halogenated variants have been recently identified in food at significant levels but full characterisation requires potency data in order to gauge their impact on risk assessment. Rat H4IIE and human MCF-7 cells were treated with various mixed halogenated ligands. Antagonist properties were measured by treating cells with various concentrations of TCDD in the presence of EC<sub>25</sub> of the putative antagonist. Measurement of CYP1A1 RNA was used to quantify the potency of agonism and antagonism. The PXDDs were found to be slightly less potent than the corresponding fully chlorinated congeners with the exception of 2-B,3,7,8-TriCDD which was 2-fold more potent than TCDD. PXDFs and non-ortho-PXBs were found to be more potent than their chlorinated congeners whilst several mono-ortho-substituted PXBs were shown to have partial agonistic properties. REPs were produced for a range of mixed halogenated AhR-activating ligands providing a more accurate estimation of potency for risk assessment. Several environmentally abundant biphenyls were shown to be antagonists and reduce the ability of TCDD to induce CYP1A1. The demonstration of antagonism for AhR ligands represents a challenge for existing REP risk assessment schemes for AhR ligands.

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# Toxicity of PXDD/Fs and PXBs

- Ah activity demonstrated
- Broadly similar order of magnitude compared with PCDD/Fs and PCBs
- Some congeners may be more toxic - e.g. tri substituted congeners; some non-2,3,7,8-congeners



Contents lists available at ScienceDirect

# Environment International

journal homepage: [www.elsevier.com/locate/envint](http://www.elsevier.com/locate/envint)



## Mixed halogenated dioxins/furans (PXDD/Fs) and biphenyls (PXBs) in food: Occurrence and toxic equivalent exposure using specific relative potencies



Alwyn R. Fernandes <sup>a,\*</sup>, David Mortimer <sup>b</sup>, Richard J. Wall <sup>c</sup>, David R. Bell <sup>d</sup>, Martin Rose <sup>a</sup>, Melanie Carr <sup>a</sup>, Sean Panton <sup>a</sup>, Frankie Smith <sup>a</sup>

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Congener-selective

### ABSTRACT

The occurrence of nineteen mixed halogenated (bromo-chloro) dibenzo-*p*-dioxins, dibenzofurans (PXDD/Fs) and biphenyls (PXBs) in a range of foods ( $n > 100$ ) was investigated. The analytical methodology used dual activated carbon column fractionation with high resolution mass spectrometric measurement (13,500–15,000 res). Occurrence was observed in most commonly consumed foods but the most frequent detections of these environmental contaminants were made in shellfish and offal. The concentrations of the individual compounds were condensed into toxic equivalents (TEQs) using recently reported relative potency values. Although representing only a small subset of the full range of toxic PXDD/Fs and PXBs, the TEQs estimated for these compounds ranged from 0.2% to approximately 15% (depending on the food matrix) of the corresponding TEQ for the fully chlorinated analogues. This finding is of great toxicological importance as it implies that a potentially greater magnitude of TEQ could be associated with the full range of toxic PXDD/Fs and PXBs, thus making a significant contribution to dioxin-like toxicity from the diet, to human exposure.

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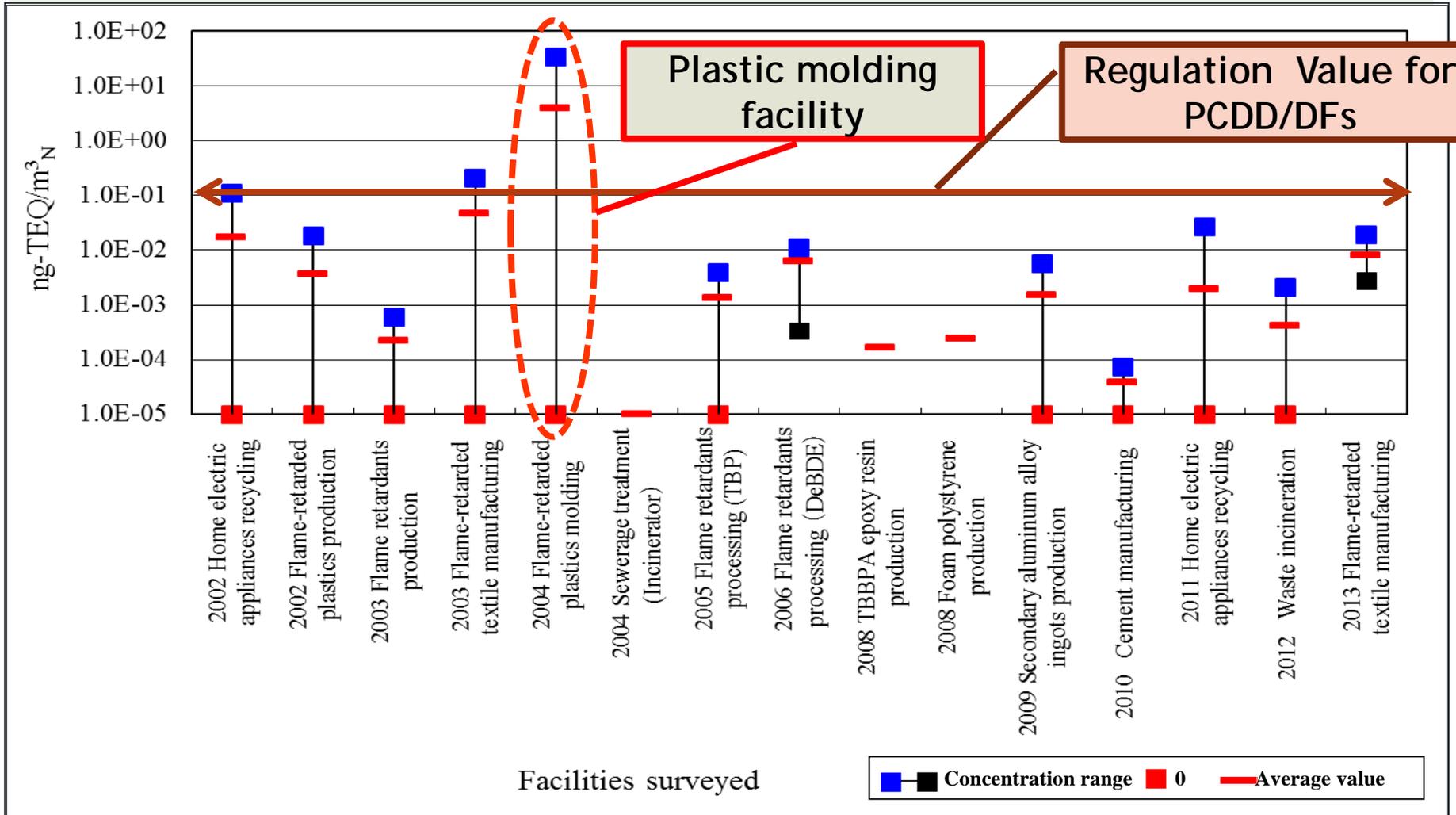
## PXDD/Fs and PXBs in food

- These compounds are found in foods!
- Lower levels
- Many more congeners, only very few measured
- Potential for TEQ to be significant if all could be measured and summed

# Relationship between BFRs and PBDD/Fs

- Clear linear relation between PBDEs and PBDD/Fs in emission sources from industrial processes such as fabric and furniture manufacture (Shin-ichi Sakai, BFR 2015 April 2015)

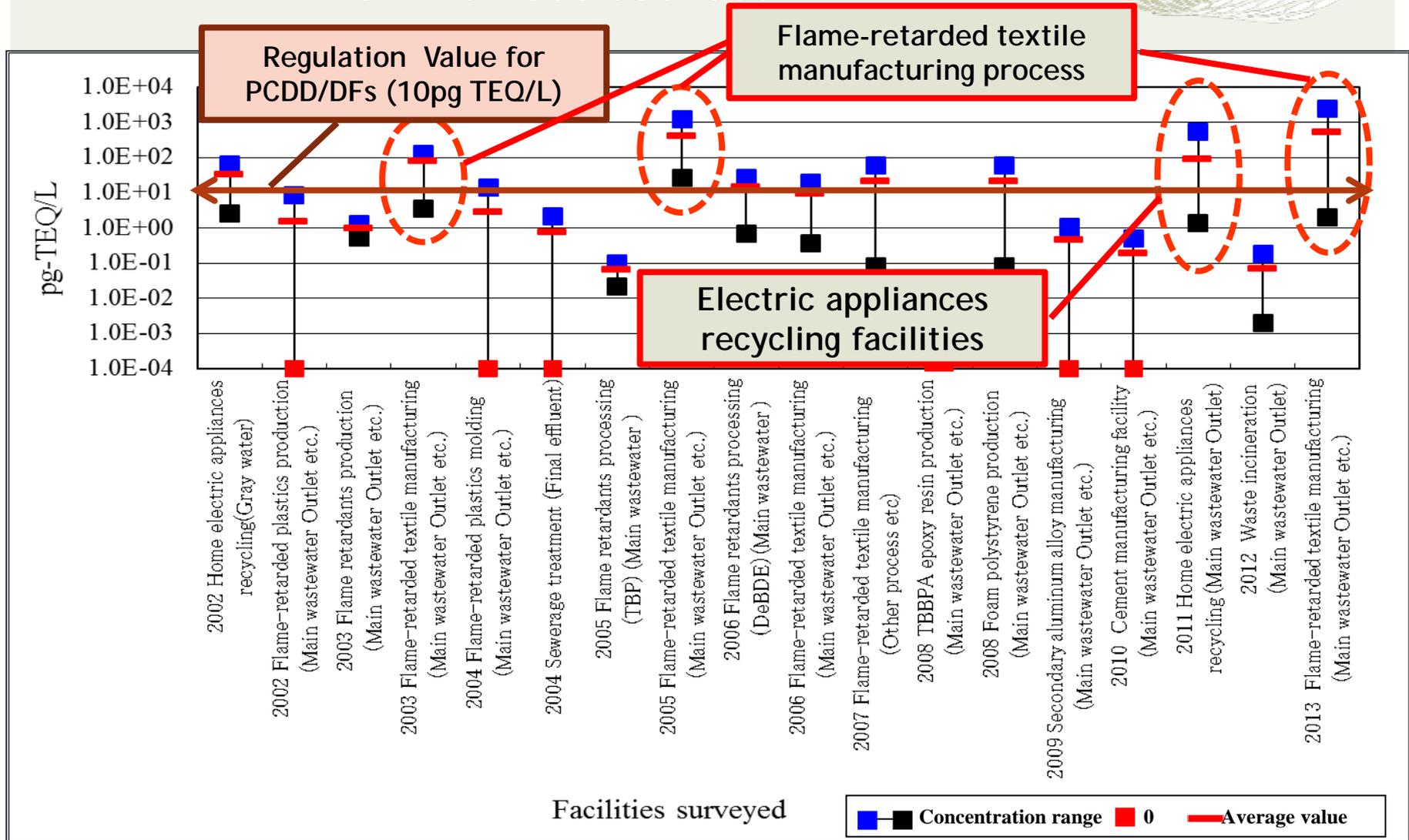
# Levels of PBDD/DFs in emission gas from various sources



TEQ estimation approach on a trial basis

TEQs for the PBDD/DF congeners were calculated using WHO-TEFs (1998 or 2006) of their chlorinated counterparts.

# Levels of PBDD/DFs in effluent from various sources



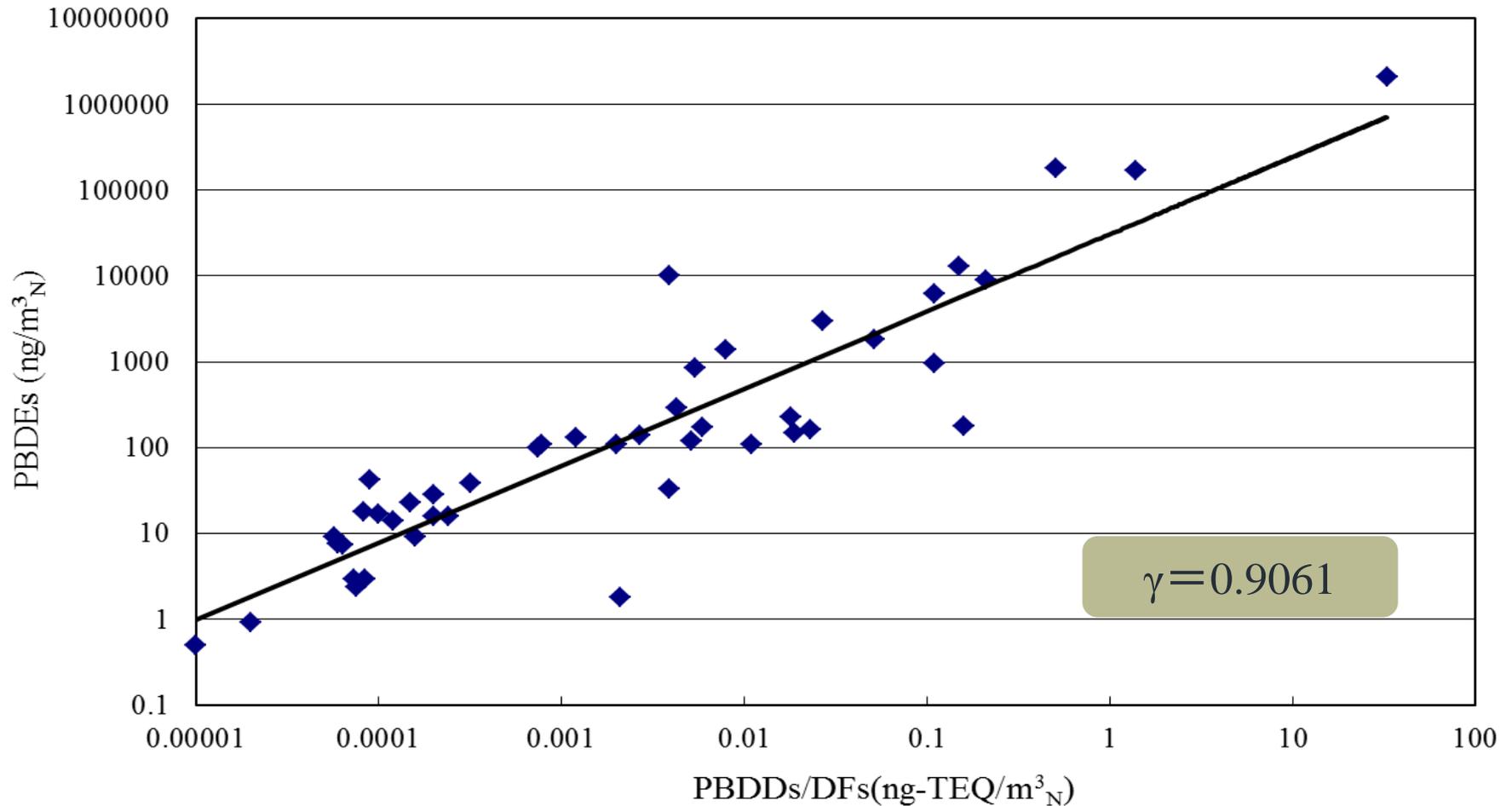
TEQ estimation approach on a trial basis

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# Correlation between PBDD/DFs(TEQ) and PBDEs

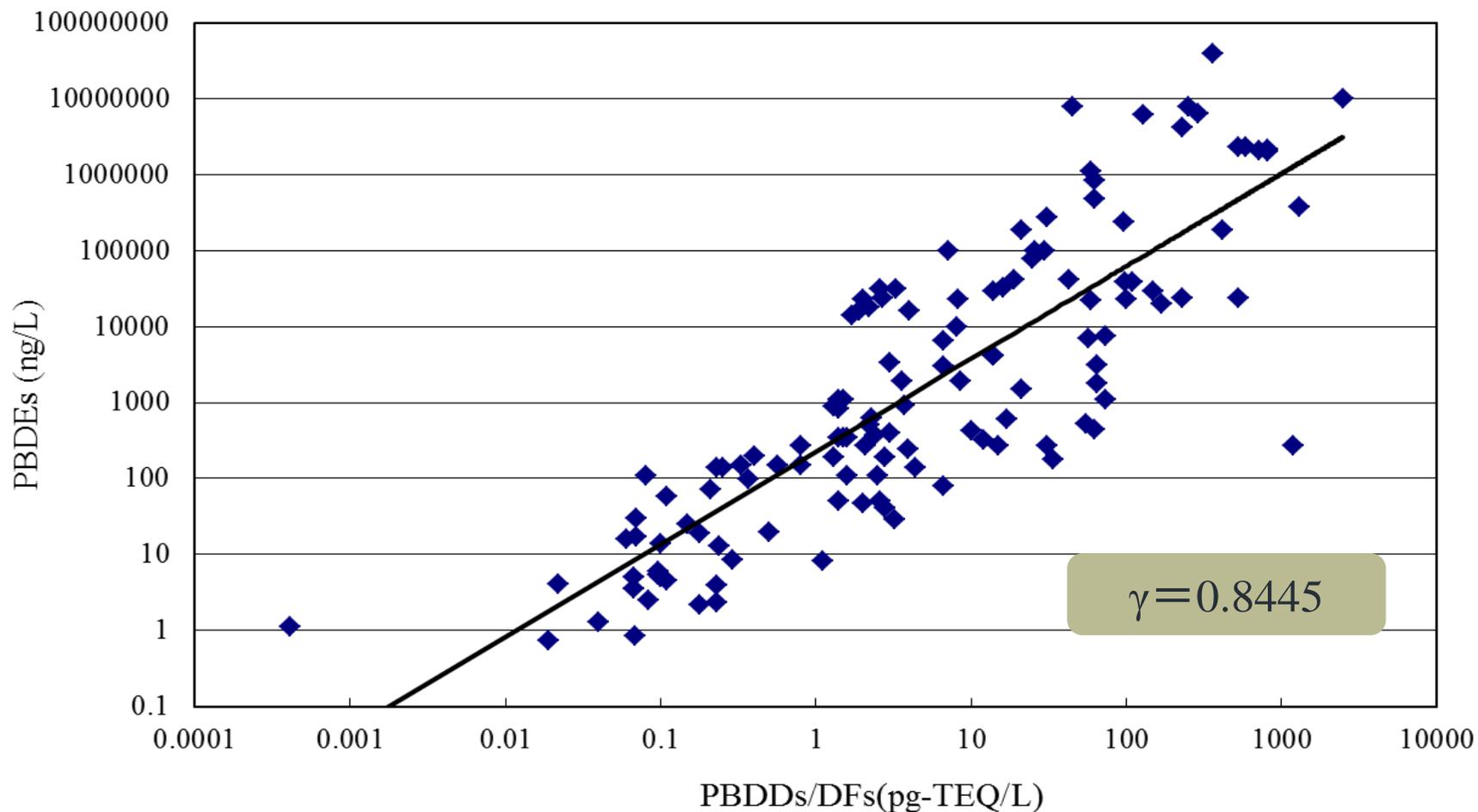


## Emission gas



# Correlation between PBDD/DFs (TEQ) and PBDEs

Effluent





This research project is funded by the Food Standards Agency



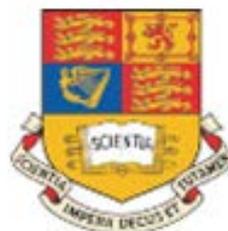
## Contaminants in recycled waste materials used in agriculture: implications for food production



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# Introduction

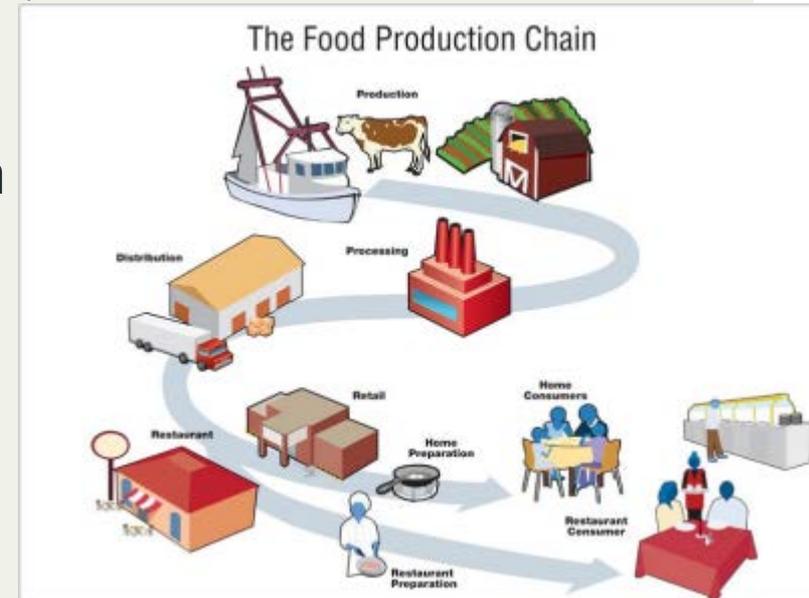
- Recycled wastes are used across Europe as animal bedding or soil improvers/fertilisers



# Need to confirm safety with respect to food chain

- Priority emerging contaminants need to be considered
  - e.g. PFCs (Transfer to wheat: Wen *et al.* (2014) Environmental Pollution 184, 547-544)

- Transfer pathways to the food chain
  - uptake by crops
  - ingestion of wastes-amended soil and
  - contaminated foliage by grazing livestock
  - Ingestion of recycled animal bedding



- Development of methodology and quality standards to assess waste materials

# Recycled Waste - Livestock Bedding Materials



- Recycled waste wood (RWW)
  - Dried paper sludge (DPS)
    - Paper sludge ash (PSA)

# Biowastes



- Dewatered, mesophilic anaerobically digested biosolids



- Compost-like-output (CLO) - mechanically separated composted organic fraction of MSW

# Combustion Products



- Meat and bone meal ash (MBMA)
- Poultry litter ash (PLA)
- Paper sludge ash (PSA)

# Penta- and octa- PBDEs, Deca-BDE and PCNs

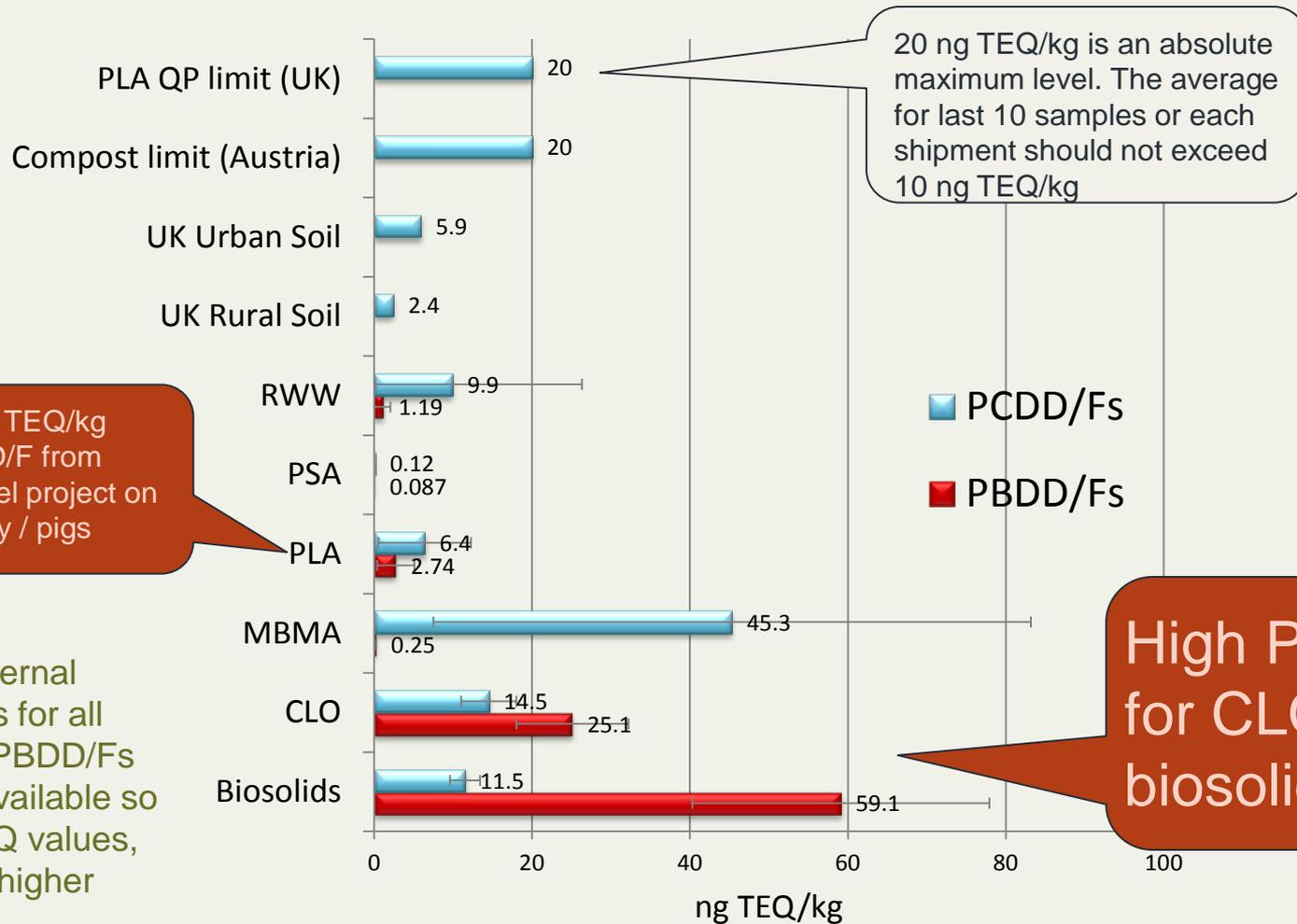
- Expanding use of deca-BDEs in Europe since the prohibition of preparations containing penta and octa-BDE by the European Union in 2003 (EU, 2003)
- PCNs have not been produced in the UK for over 35 years

Contaminant	Biosolids	CLO	MBMA	PLA	PSA	RWW	Literature values (Biosolids)
	(µg/kg DS)						
Polybrominated diphenyl ethers (PBDEs)	90-103 <sup>a</sup>	41-60 <sup>a</sup>	0.26-0.28 <sup>a</sup>	0.22-0.33 <sup>a</sup>	0.087 <sup>a</sup>	0.52-4.34 <sup>a</sup>	108 <sup>bcd</sup>
	77-88 <sup>b</sup>	35-56 <sup>b</sup>	0.21-0.22 <sup>b</sup>	0.20-0.26 <sup>b</sup>	0.17 <sup>b</sup>	0.45-3.8 <sup>b</sup>	
Deca-BDE 209	4198-6693	1650-1723	0.62-0.70	<0.17-3.0	1.4	11.0-246	13-288 <sup>a</sup> 1030 <sup>e</sup>
Polychlorinated naphthalenes (PCNs)	0.54-0.74 <sup>f</sup>	0.69-1.2	0.045-0.108	0.088-0.061	0.039	0.088-1.2	5-190 <sup>erg</sup>

<sup>a</sup>sum penta- and octa-; <sup>b</sup>sum 28, 47, 99, 153, 154, 183; <sup>c</sup>median for 11 WWTP sludges; <sup>d</sup>Knoth *et al.* (2007);

<sup>e</sup>Clarke and Smith (2011) *Environ Int* 37, 226–247; <sup>f</sup>sum; <sup>g</sup>Smith (2009) *Philos T Royal Soc A* 367, 3871-3872

# PCDD/Fs and PBDD/Fs



30 ng TEQ/kg PCDD/F from parallel project on poultry / pigs

20 ng TEQ/kg is an absolute maximum level. The average for last 10 samples or each shipment should not exceed 10 ng TEQ/kg

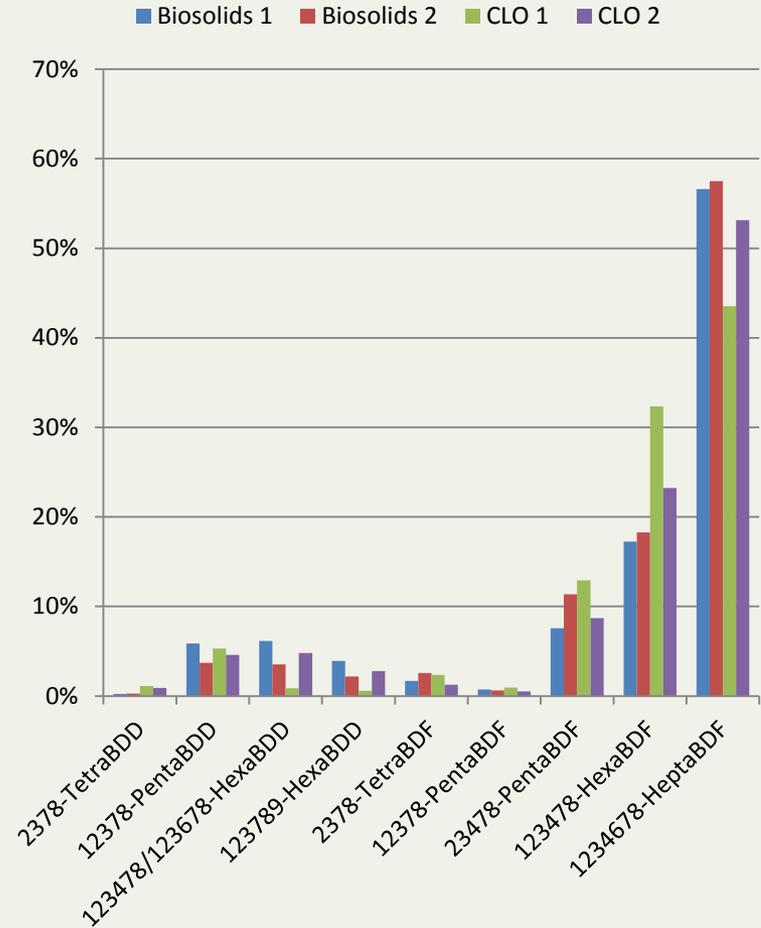
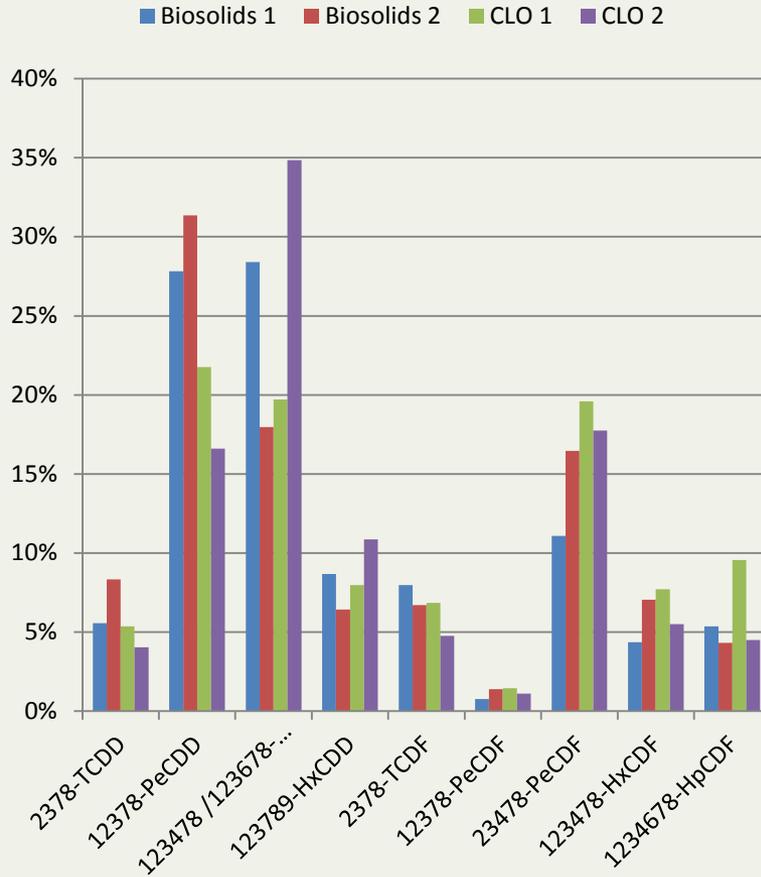
High PBDD/Fs for CLO and biosolids

Note: internal standards for all relevant PBDD/Fs are not available so true  $\Sigma$ TEQ values, could be higher

# PCDD/F and PBBD/F in biowastes

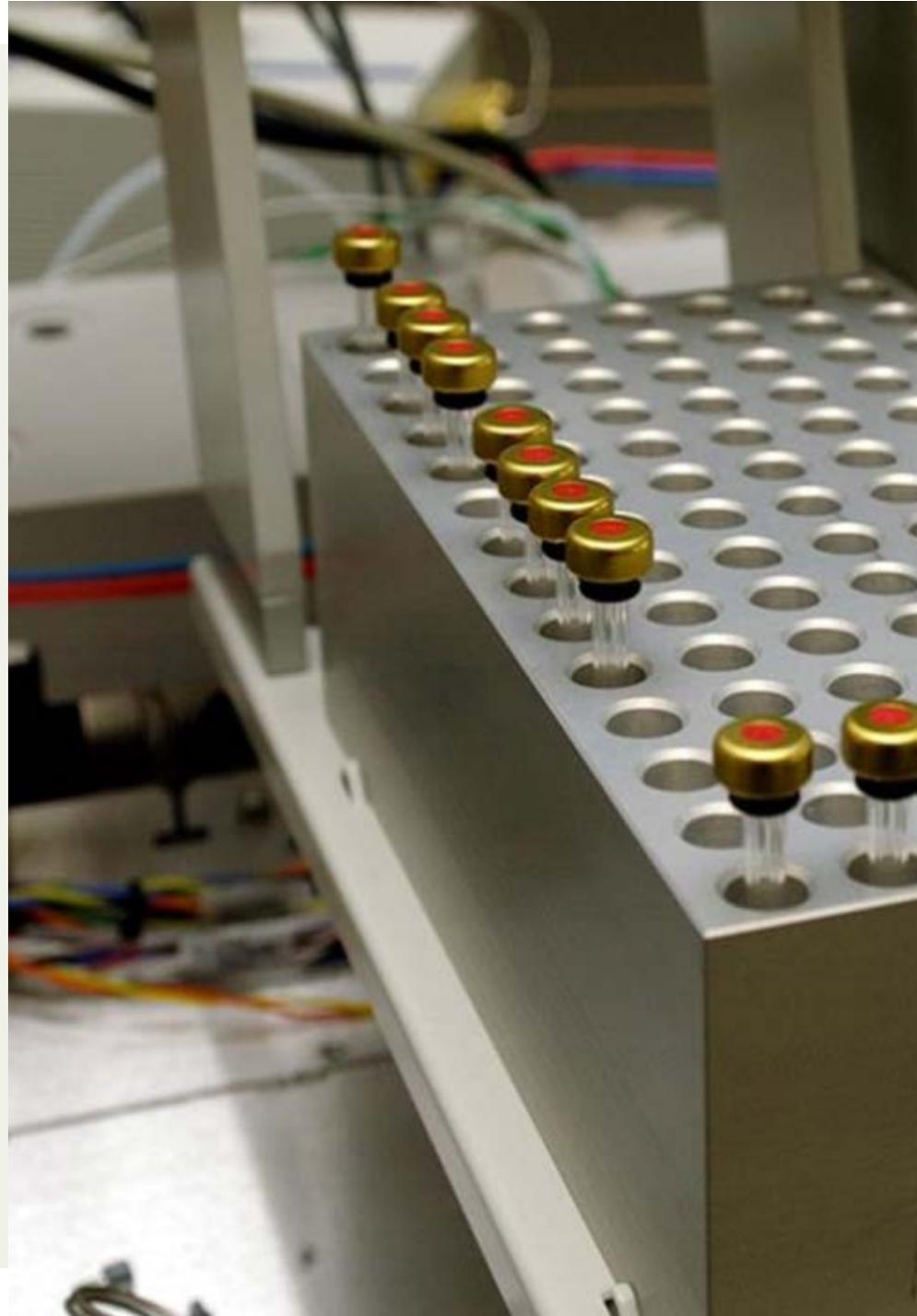


% total TEQ



# Measurement

- Challenging!
- Many congeners
- Few analytical standards
- Even fewer  $^{13}\text{C}$  analogues



# Seeing the whole picture

Should the TEF / TEQ scheme apply to other Ah agonists we know about and those we don't know about?

**For complete picture or a holistic risk assessment....**

$$\text{TEQ} = \Sigma[\text{PCDD}_i \times \text{TEF}_i] + \Sigma[\text{PCDF}_i \times \text{TEF}_i] + \Sigma[\text{PCB}_i \times \text{TEF}_i]$$

$$+ \Sigma[\text{PBDD}_i \times \text{TEF}_i] + \Sigma[\text{PBDF}_i \times \text{TEF}_i] + \Sigma[\text{PBB}_i \times \text{TEF}_i]$$

$$+ \Sigma[\text{PXDD}_i \times \text{TEF}_i] + \Sigma[\text{PXDF}_i \times \text{TEF}_i] + \Sigma[\text{PXB}_i \times \text{TEF}_i]$$

$$+ \Sigma[\text{PCN}_i \times \text{TEF}_i] \dots\dots\dots$$



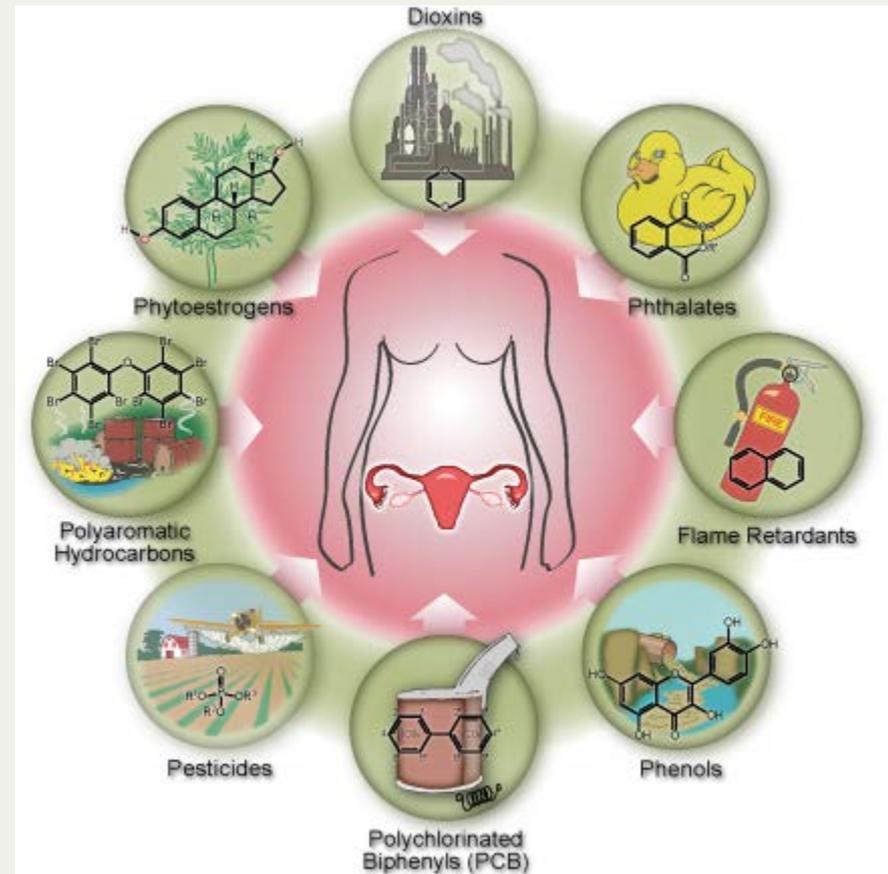
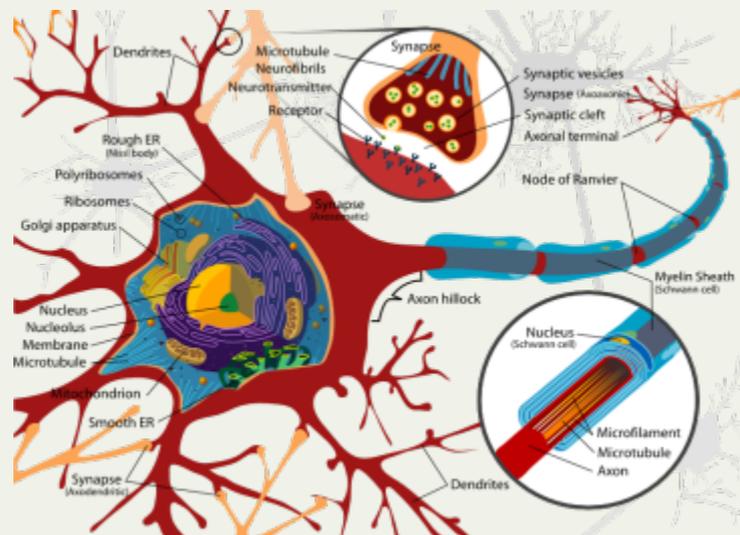
# Other aspects to consider for risk assessment

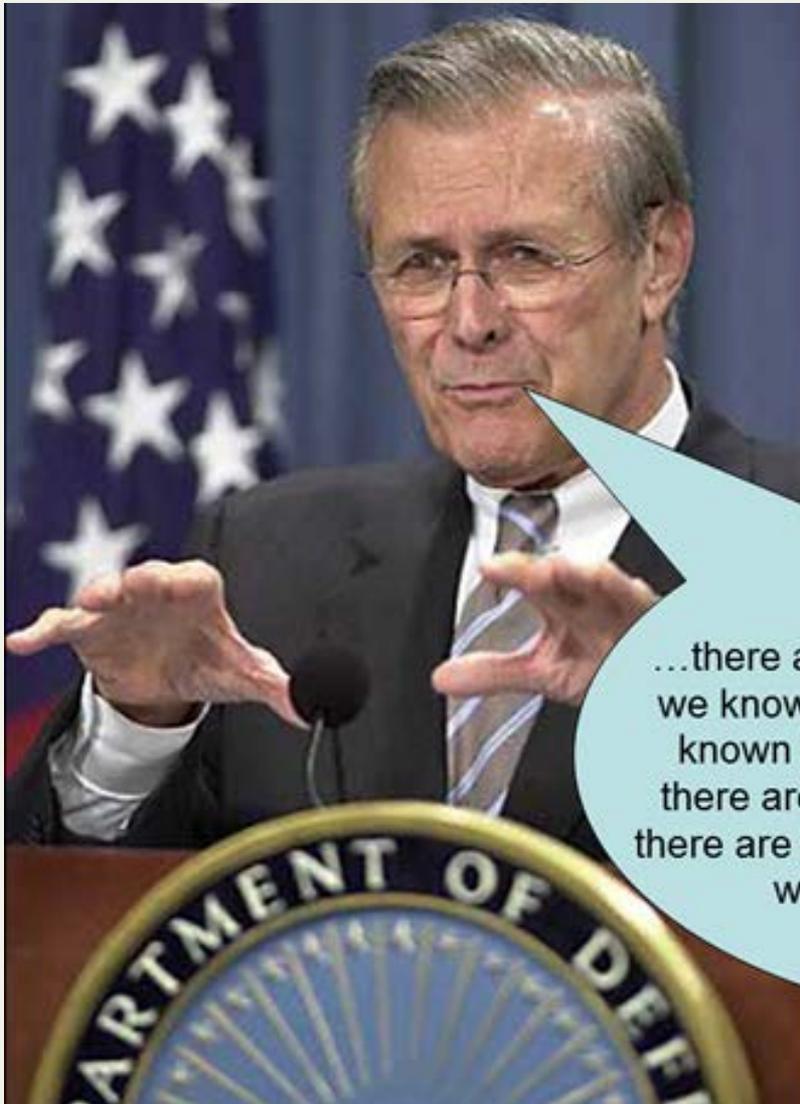
## Endocrine activity

- Many of these compounds + many more are endocrine active

## Neurotoxicity

Etc.....





# The Rumsfeld Theorem

...there are known knowns; there are things we know we know. We also know there are known unknowns; that is to say we know there are some things we do not know. But there are also unknown unknowns -- the ones we don't know we don't know.

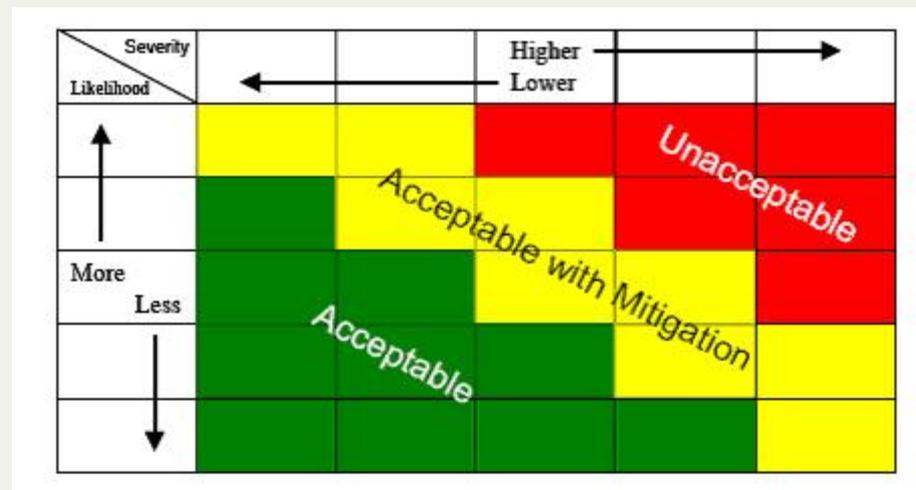
# Analytical future

- Need next generation MS
- Need to combine MS with measurement of biological effect e.g. cell based or receptor assays
- Need to be aware of impact of clean-up methods



# Risk assessment

- Needs to be holistic
- Dioxins first chemicals to be assessed as mixtures, but still a very simple model
- Need to include all Ah receptor agonists
- Endocrine activity?
- Neurotoxicity?
- Etc?



# More information on recycled materials in agriculture



**Investigation of the Potential Transfer and Uptake of Contaminants into Food Arising From The Use of Recycled Waste in Agriculture**

THE PROJECT

Biosolids and other waste-derived materials in agriculture for decades and the impacts on human health from emerging chemical contaminants

**Welcome Message**

This programme of experimental research funded by the Food Standards Agency, under the Environmental Contaminants research programme, aims to investigate wider controlled use of transfer of organic contaminants to soil due to dairy cattle ingesting recycled waste material as an soil conditioner on pasture.

We also measure the uptake of organic contaminants by cereals and cereals grown in soil and waste-derived soil conditions.

**What is the Project about**

A variety of waste materials are recycled in agriculture with the benefit of reducing pressure on resources. Recycled waste materials, such as untreated waste wood shavings or paper sludge from paper recycling mills, can be effectively used as animal bedding in livestock production. Nutrient-rich waste materials such as sewage sludge (biosolids) or outputs from the combustion of waste biomass (e.g. meat and bonemeal ash (MBMA) and poultry litter ash (PLA)) can be applied to land as agricultural fertilisers and soil conditioners in grassland and crop production, closing the nutrient loop and reducing the use of manufactured fertilisers.

Paper sludge ash (PSA) is an effective desiccant in bedding for cattle, and is also

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## What is the Project About

**Study Duration:** February 2014 to March 2016  
**Project Lead:** Professor Stephen Smith, Imperial College London  
**Consortium Members:** Imperial Consultants (Lead) University of Reading The Food and Environment Research Agency (FERA)



**Visit the Food Standards Agency (FSA) site to learn more about our funder.**

## Background

This project aims to generate robust scientific evidence that the following will not compromise food safety:

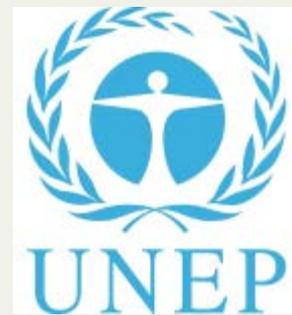
- rearing dairy cattle on bedding made from recycled waste
- using waste-derived fertilisers or liming agents for grassland or for arable land used for root crops or cereals

The project also aims to identify or validate control measures needed to protect the

<http://www.foodagrirecoveredwaste.org/>

# Acknowledgement

- All my colleagues in the environmental contaminants team at Fera, especially Alwyn Fernandes
- FSA have funded a significant amount of work done within the team
- EFSA, WHO, UNEP etc for providing drivers



# BFR

8th International Symposium on Flame Retardants

# YORK 2017

[www.bfr2017.co.uk](http://www.bfr2017.co.uk)