Dietary Exposure to PBBs, PBDEs and PBDD/Fs in the United Kingdom

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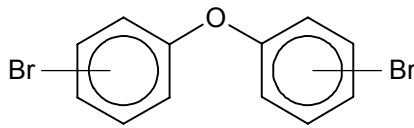
What are PBBs, PBDEs and PBDD/Fs…..

- **Polybrominated diphenyl ethers**
  - Common flame retardants
  - Penta & Octa mix now banned or being phased out

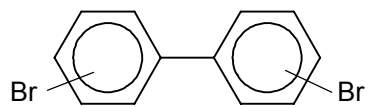
PBDE



Br = 1 to 10

- **Polybrominated biphenyls - PBBs**
  - Legacy flame retardants, now widely banned
  - Little used for over 20 years
  - Michigan “Firemaster” Incident 1973

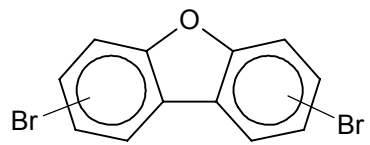
PBB



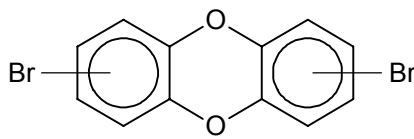
Br = 1 to 10

- **Polybrominated dibenzo-p-dioxins & Polybrominated dibenzofurans - PBDD/Fs**
  - Trace contaminants of BFR products
  - Thermal and photolytic break down products of BFRs
  - **May be MORE toxic than chlorinated dioxins**

PBDF



Br = 1 to 8

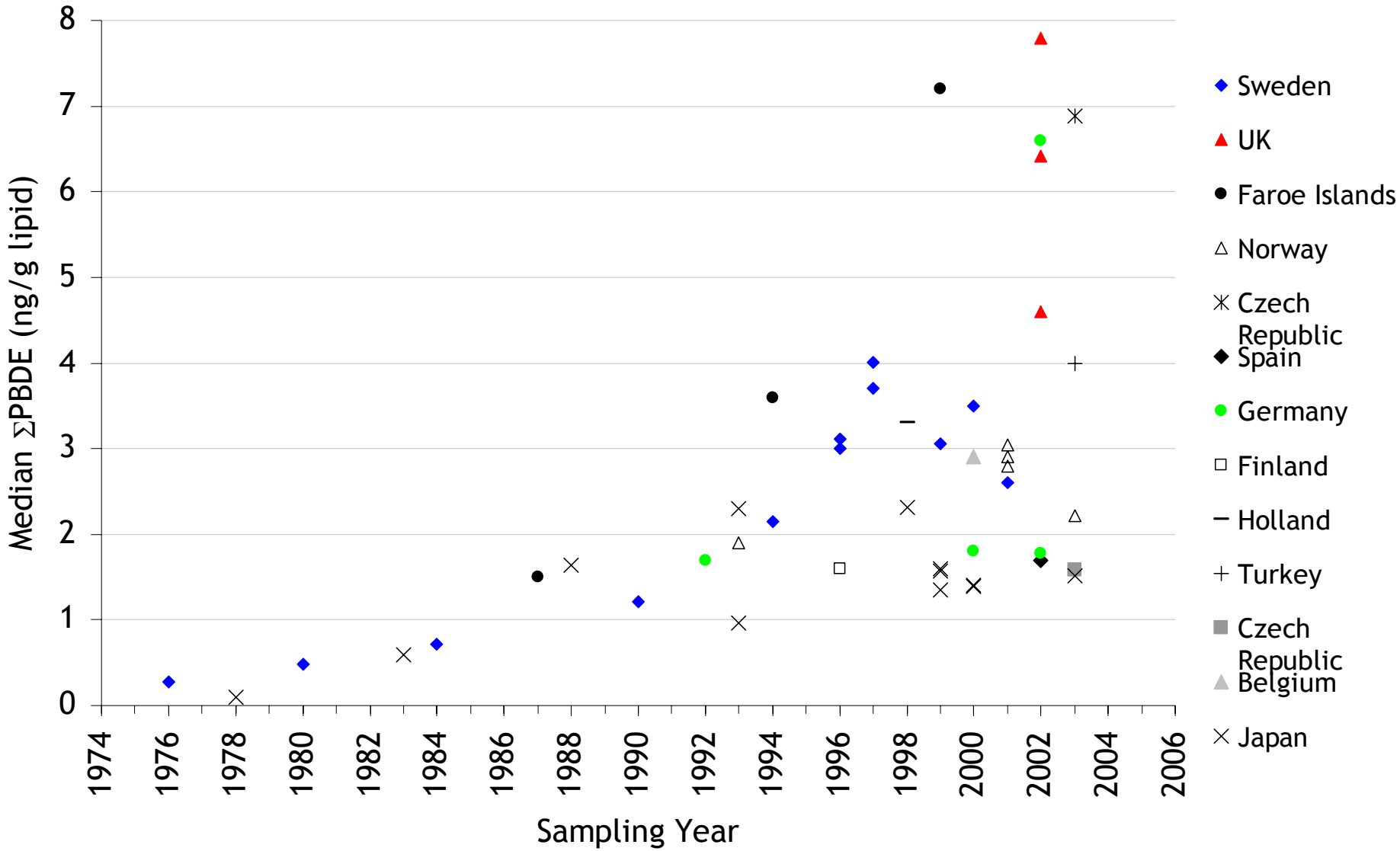


PBDD

Why do we want to look for PBDEs in food?

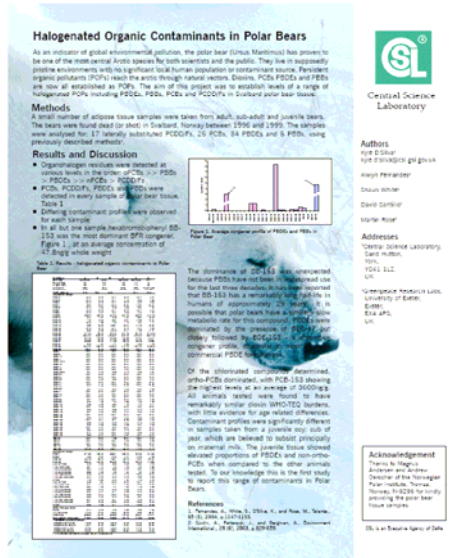
- PBDEs are environmental contaminants - but are they significant contaminants in the UK diet?
- No dietary exposure data from structured surveys for United Kingdom
- What congeners are we exposed to?
- PBDEs ‘appear’ to be increasing in humans, is this due to diet?…

PBDEs in human breast milk



Why look for PBBs and PBDD/Fs in food?

- PBBs
  - Polar bears BB-153 dominant BFR
  - PBBs very persistent ($t_{1/2}$ = 29 years*)
  - No data on dietary exposure


Halogenated Organic Contaminants in Polar Bears

Methods

Results and Discussion

Central Science Laboratory

Authors

Addresses

Acknowledgement

- PBDD/Fs
  - Only a handful of studies on PBDD/Fs in any matrices
  - Dietary exposure is probably the primary exposure route
  - Which congeners are we exposed to, if any?

*Blanck, H.M., Marcus, M., Hertzberg, V., Tolbert, P. E., Rubin, C., Henderson, A. K., and Zhang, R. H., Environmental Health Perspectives., 108 (2), 2000, p.147-152.

Aims of study

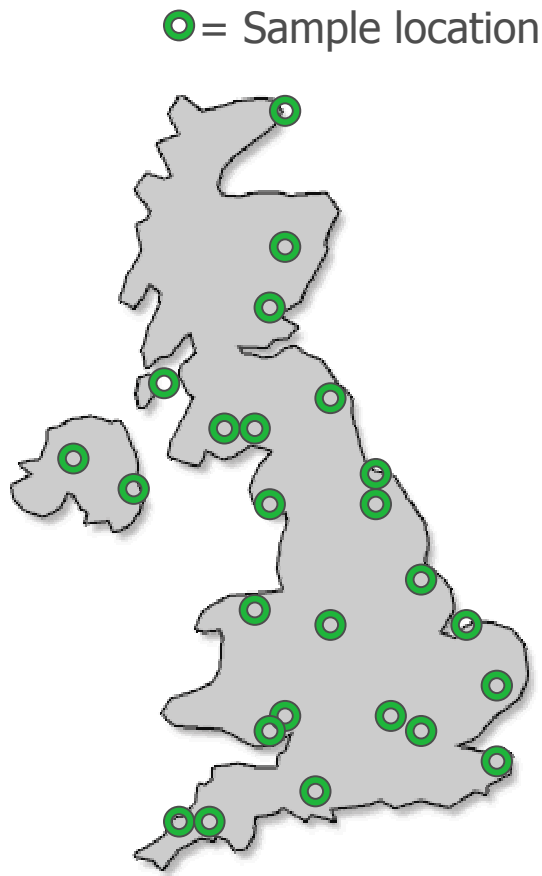
1. Develop suitable methods for PBDEs, PBBs and PBDD/Fs in food

2. Analyse archived Total Diet Survey (TDS) samples using methods

3. Use consumption data (National Food Survey) to calculate exposure and trends

The Total Diet Study (TDS)

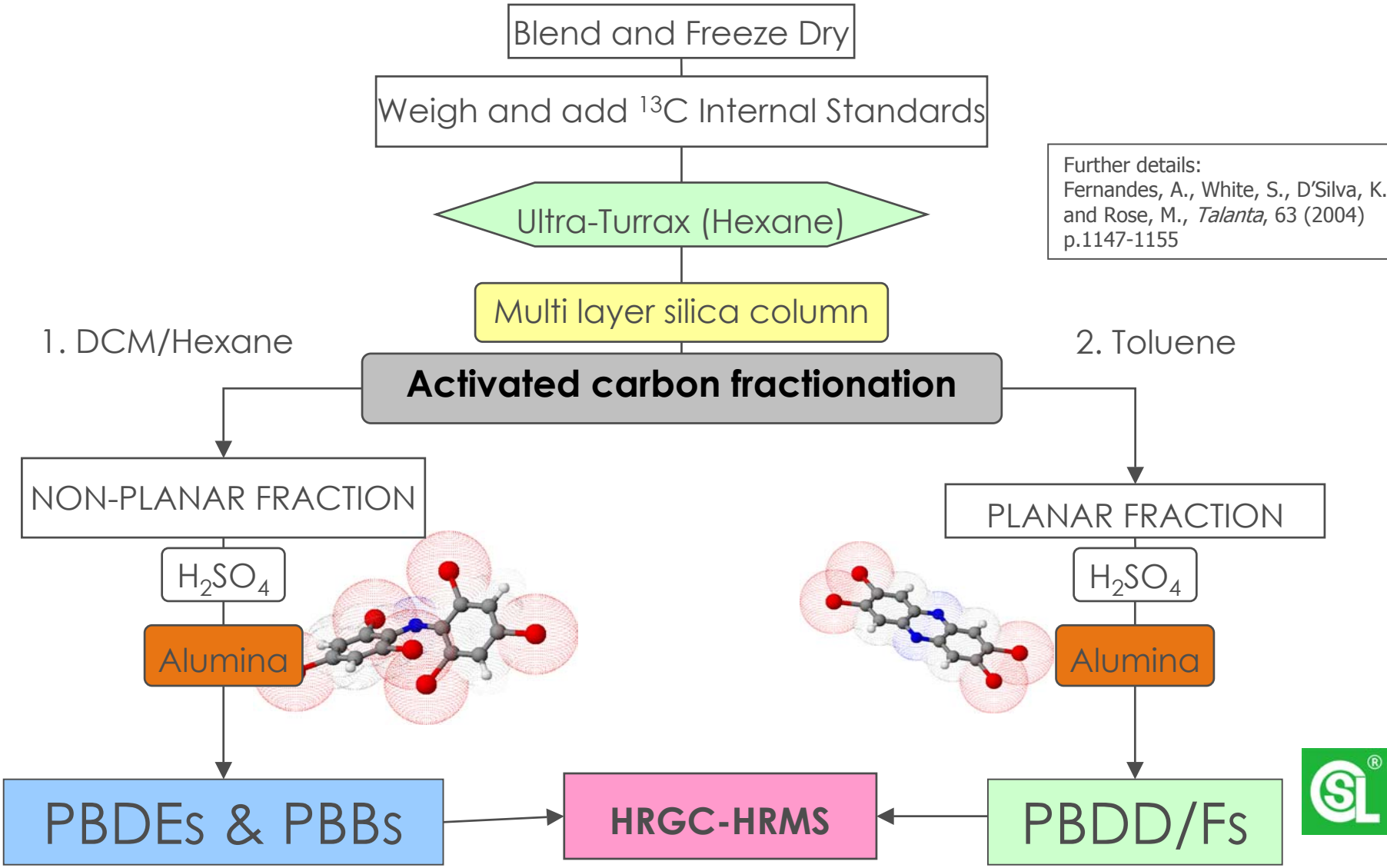
- 119 categories of food
- 24 random locations
- 1 item from each category
- Purchased throughout year
- Food prepared for consumption
- Large sample size; 480 samples
- 20 composites per year



Analytical considerations

- Archived samples from 1992, 1997, 2000 & 2001 TDS studies
- TDS sample sizes were small (5-50g)
- Method must be multi-residue:
  - PBDEs – 34 congeners
  - PBBs – 5 congeners
  - PBDD/Fs – 11 congeners
- All analytes must be determined from single sample aliquot

Method Step 1: Extract and purify



Further details:
Fernandes, A., White, S., D'Silva, K., and Rose, M., *Talanta*, 63 (2004) p.1147-1155

Method Step 2: Analysis of extracts

- HRGC-HRMS, Triple sector, EI (Autospec Ultima NT)
- Selected Ion Monitoring
- Two ions monitored for each analyte
- Mass Resolution 10,000
- Quantification - Isotope dilution methodology
- 60m DB5-MS, thin film (0.1µm) column
- PTV injector - 10 µL injections

- Instrumental LODs as low as 50 fg on column for 2378TBDD
- **Only technique suitable for PBDD/Fs**

Benefits of Method

Freeze dry

Extract, purify
and concentrate

Results for:

PBDEs

PBBs

PBDD/Fs

250ml Milk

5-50g solids

25µl
Extract

- **Concentration Factor = 10,000**
- **50 analytes from one sample**

Method Performance

Analyte	Method Precision (RSD)	Typical Recovery	Method LOD (Lipid Weight)
PBDEs	11%	50-110%	0.05 µg/Kg (ppb)
PBBs	10%	50-110%	0.05 µg/Kg (ppb)
PBDD/Fs	10%	30–80%	0.1 - 6.0 ng/Kg (ppt)

Precise, Accurate, Robust

Total Diet Study Results

>60 composites analysed from 4 TDS studies for 50 separate analytes:

- PBDEs determined above LOQ in **EVERY** sample
- PBBs occasionally detected
- PBDDs rarely detected above LOQ
- PBDFs occasionally detected

PBBs in the UK diet

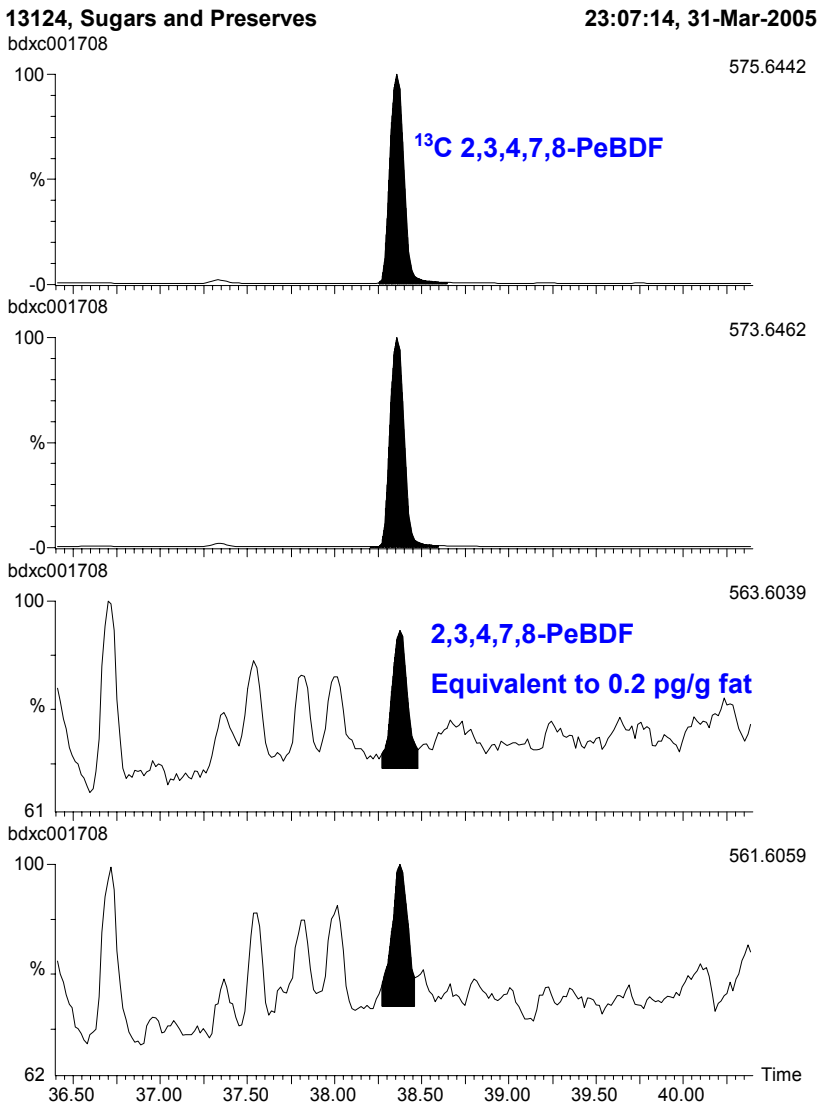
- PBBs rarely detected
- BB-153 was the dominant congener
- UK dietary exposure to PBBs :

1992	<0.1	ΣPBB ng/day
1997	0.1	ΣPBB ng/day
2000	0.1	ΣPBB ng/day
2001	<0.1	ΣPBB ng/day

PBDD/Fs in the UK diet

- Highest levels detected were lower brominated PBDFs in sugar & preserves
- Possible process contaminants?
- Dietary exposure low:

Year	PBDD/Fs WHO-TEQ* pg/day
1992	0.1
1997	0.8
2000	6.5
2001	0.3



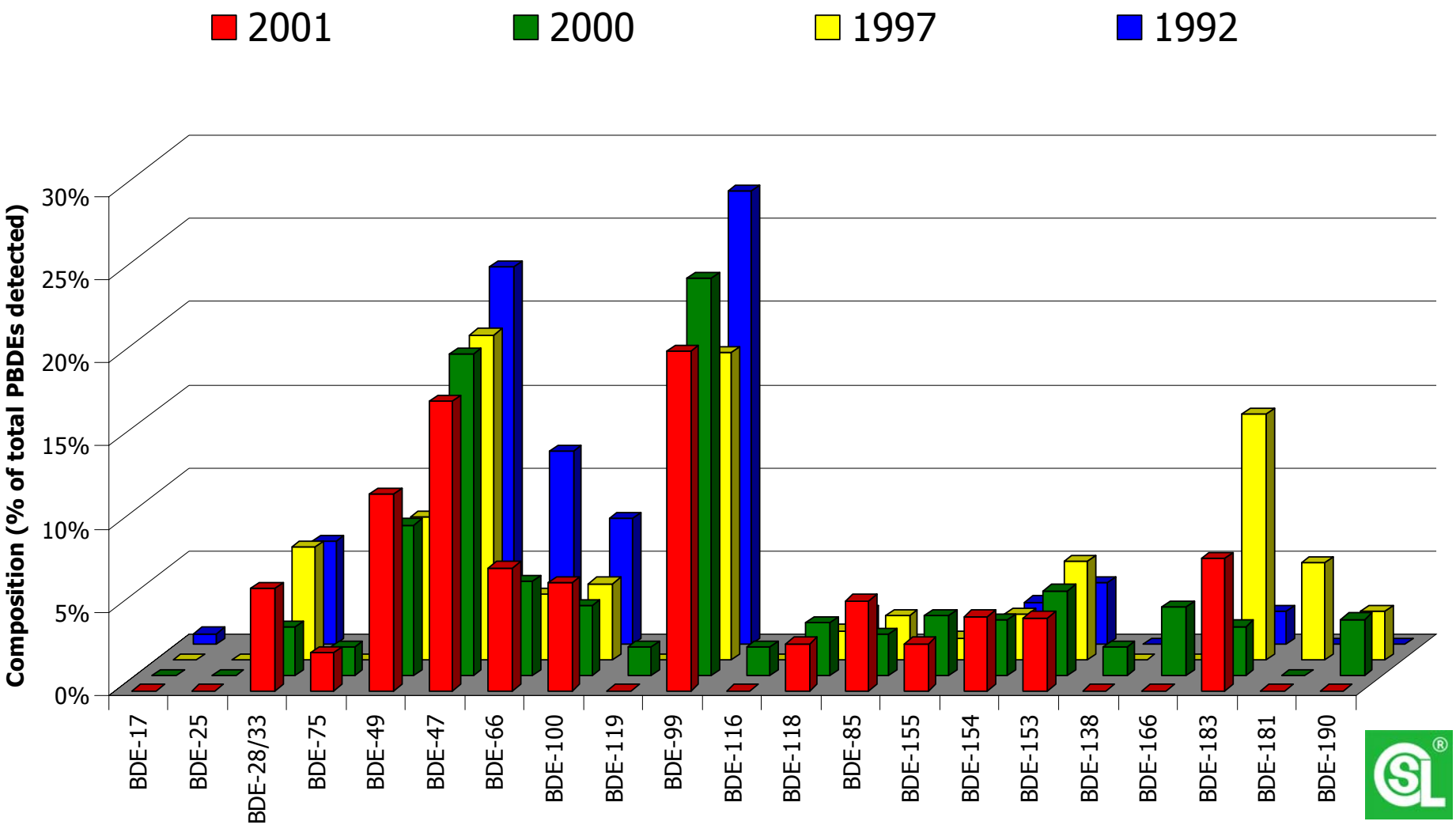
PBDEs in the UK Diet

- All food groups contains PBDEs
- Exposure not just from fish and meat
- Vegetables and fruit also contribute to total exposure
- Out of 34 PBDEs analysed only 21 were routinely present above LOQ
- Greatest dietary exposure is from congeners:

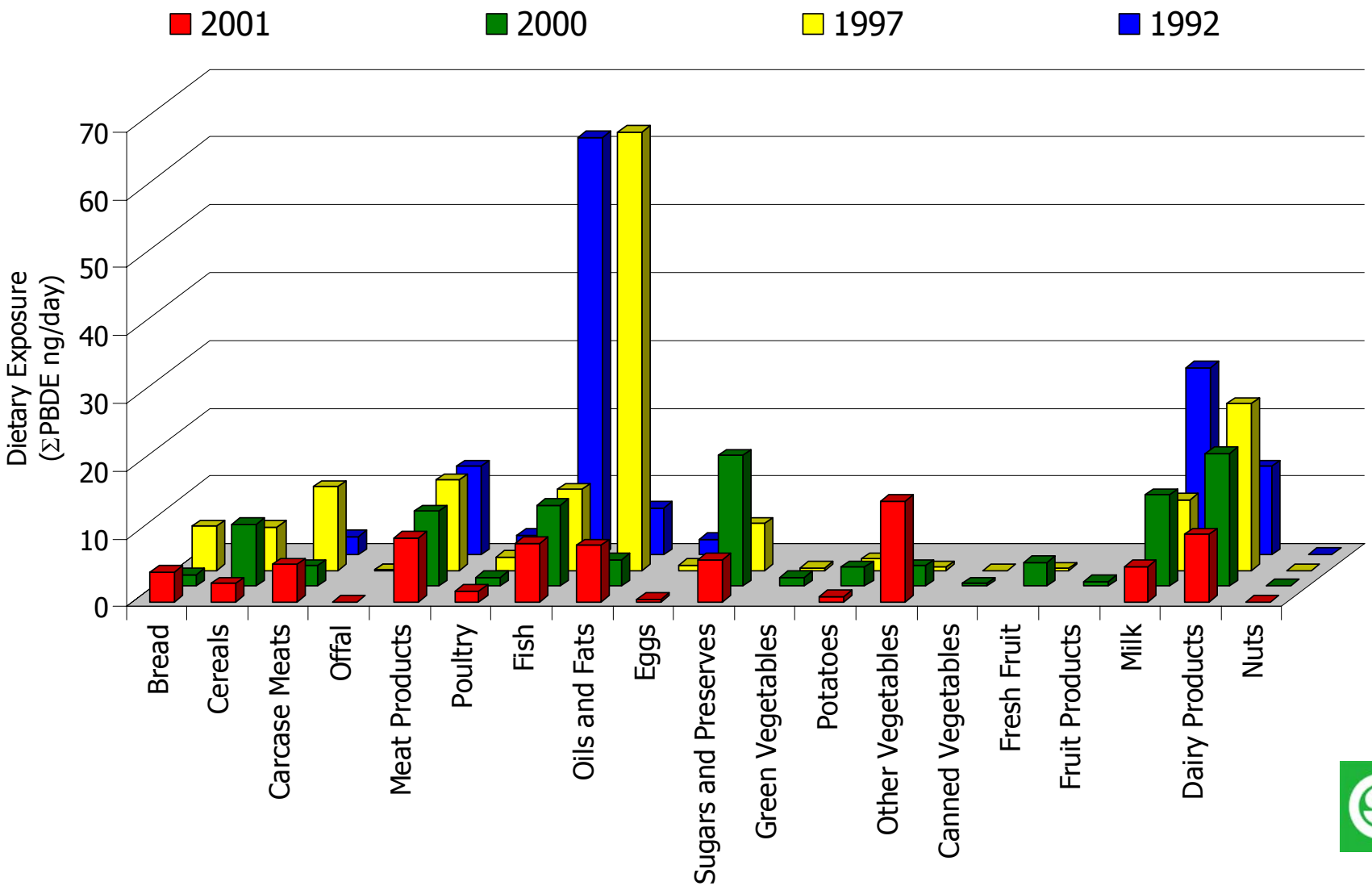
BDE-99 BDE-47 >>

BDE-100 BDE-66 BDE-49 BDE-183

PBDE Congener Composition (% of total PBDE exposure)

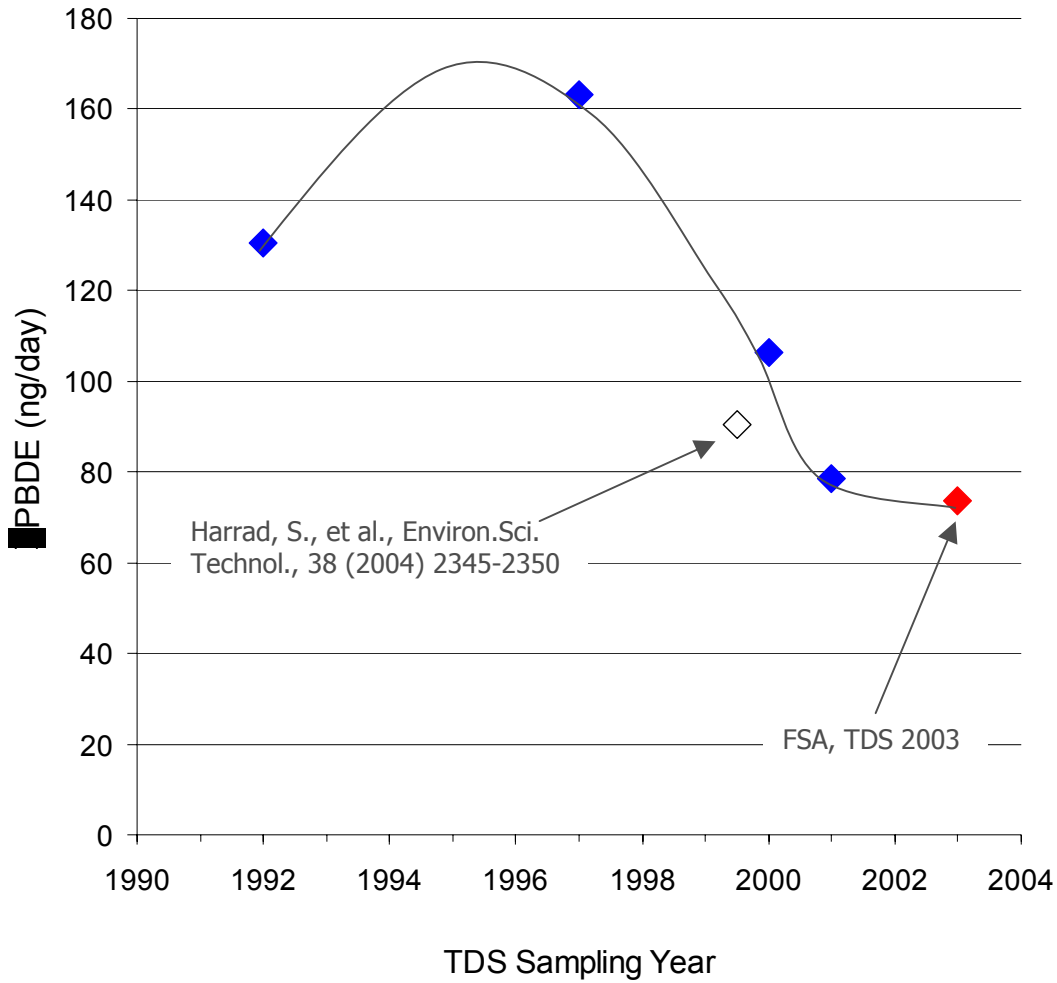


Sources of PBDE exposure



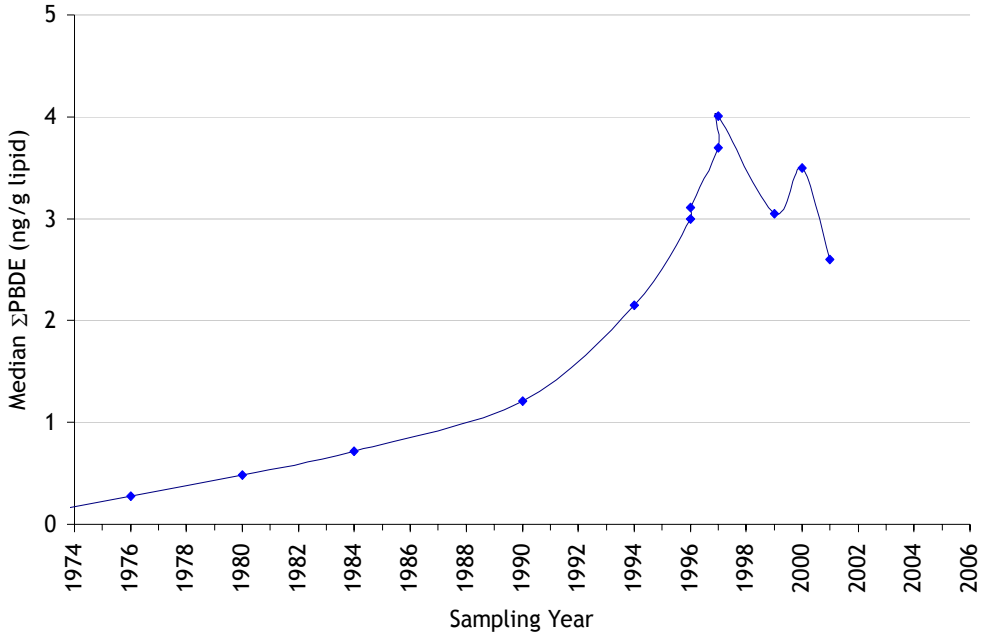
Trends in UK dietary exposure to PBDEs

- PBDEs “appear” to be **decreasing** in the diet
- Exposure maxima possibly between 1993 and 1996?
- Is there other evidence to support environmental decrease of PBDEs?



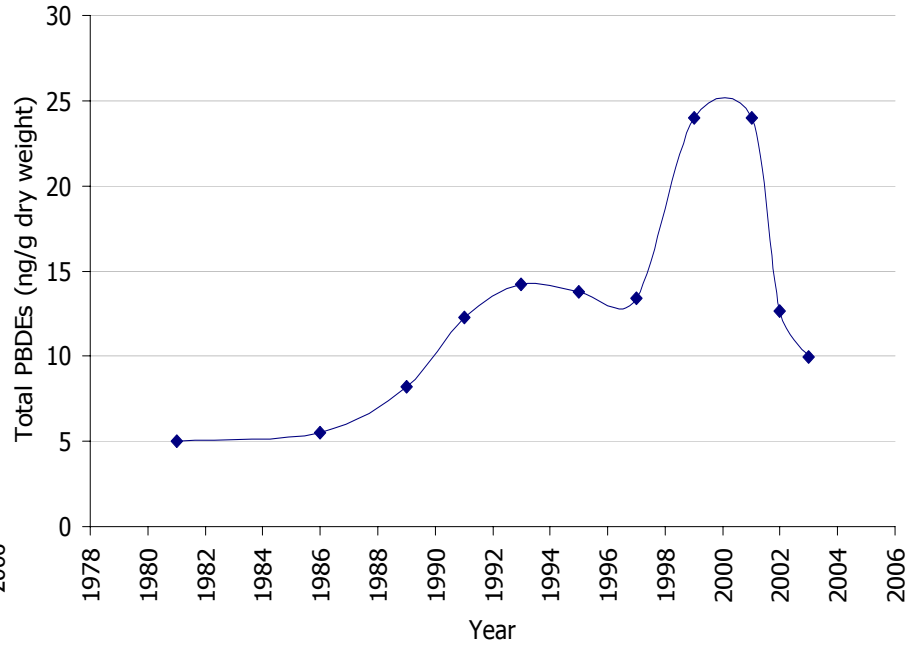
Have PBDEs passed their maxima?

PBDEs in Swedish Human Milk



Lind, Y., et al., Environmental Research, 93 (2003) 186-194.
Noren, K. & Meironyte, D., Chemosphere, 40 (2000) 1111-1123.

PBDEs in Mussels from the Seine, France



Johansson, I., et. al., 3rd International Workshop on Brominated Flame Retardants - BFR 2004, Toronto, Canada, June 6-9, (2004) p.217-220

In Summary

- Average dietary exposure to PBBs is negligible <0.1ng/day.
- Dietary exposure to PBDD/Fs is generally very low, but several assumptions:
  - TriBDFs and TriBDDs excluded from WHO-TEQ
  - PBDD/F WHO-TEQ assumes same toxicity as PCDD/Fs
- Dietary exposure to PBDEs “appears” to be falling. Are the levels significant?:
  - LOAEL PBDEs estimated at 40,000 ng/kg/day
  - Dietary exposure ΣPBDE 70-160 ng/day

Further work

- Re-assessment of PBDE congeners routinely surveyed
- Improvement of analysis for BDE-209
- Need more data points relating to dietary exposure
  - Another UK TDS - Preferred
  - Another market basket study – Good correlation & cheaper?
- Other exposure vectors must be accurately quantified
  - Inhalation
  - Occupational exposure
- Require accurate TEFs for PBDD/Fs
- Tri-BDFs should be assessed for their toxicology

Acknowledgements

- Food Standards Agency
- Seedcorn Program - CSL
- Martin Rose, Shaun White - CSL
- Jim McQuaid - Leeds University

Any questions?