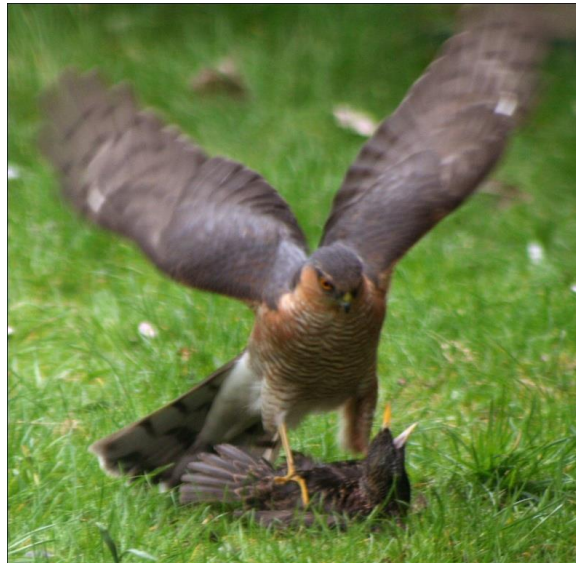


# Using predatory birds to monitor long term trends of PBDEs in the UK

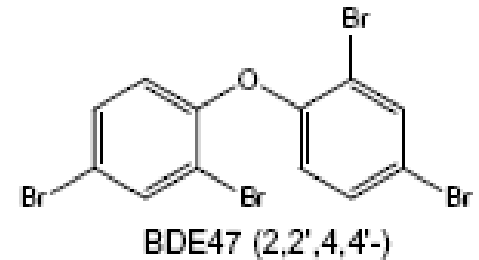
John D. Crosse<sup>1,2</sup>, Richard F. Shore<sup>1</sup>, Richard A. Wadsworth<sup>1</sup>, Kevin C. Jones<sup>2</sup> & M. Glória Pereira<sup>1</sup>

1. NERC Centre for Ecology & Hydrology, Lancaster Environment Centre, Library Avenue, Bailrigg, Lancaster, LA1 4AP, U.K.
2. Lancaster Environment Centre, Lancaster University, Lancaster, LA1 4YQ, U.K.



# Overview

- PBDEs
  - What they are
  - Usage and consumption
  - Environmental occurrence
  - Why we should care
- Environmental monitoring
- Using apex predators (birds and their eggs)
- Results from two UK birds
  - Spatial trends (marine, terrestrial)
  - Temporal trends
  - Toxicity



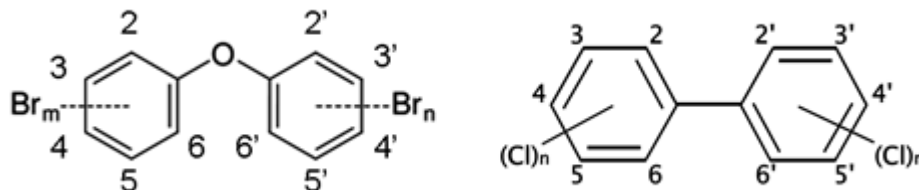
# PBDEs

- Additive flame retardants
  - Not chemically bonded to host matrix
- Disrupt combustion
  - Dilute flammable gases
  - Scavenge free radicals
- Used in high impact plastics, textiles, furniture foam
- Release to environment from product manufacture, use, disposal
  - Continual release through normal usage

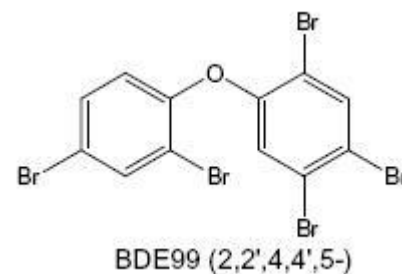


# PBDEs

- Structurally and chemically analogous to PCBs



- 209 theoretical congeners
  - 28, **47**, **99**, **100**, **153**, **154**, **183**, 196, 197, 201, 202, 203, **209**
- Technical products utilise a mixture of congeners
  - PeBDE (99,47), OBDE (183, 209), DeBDE (209)

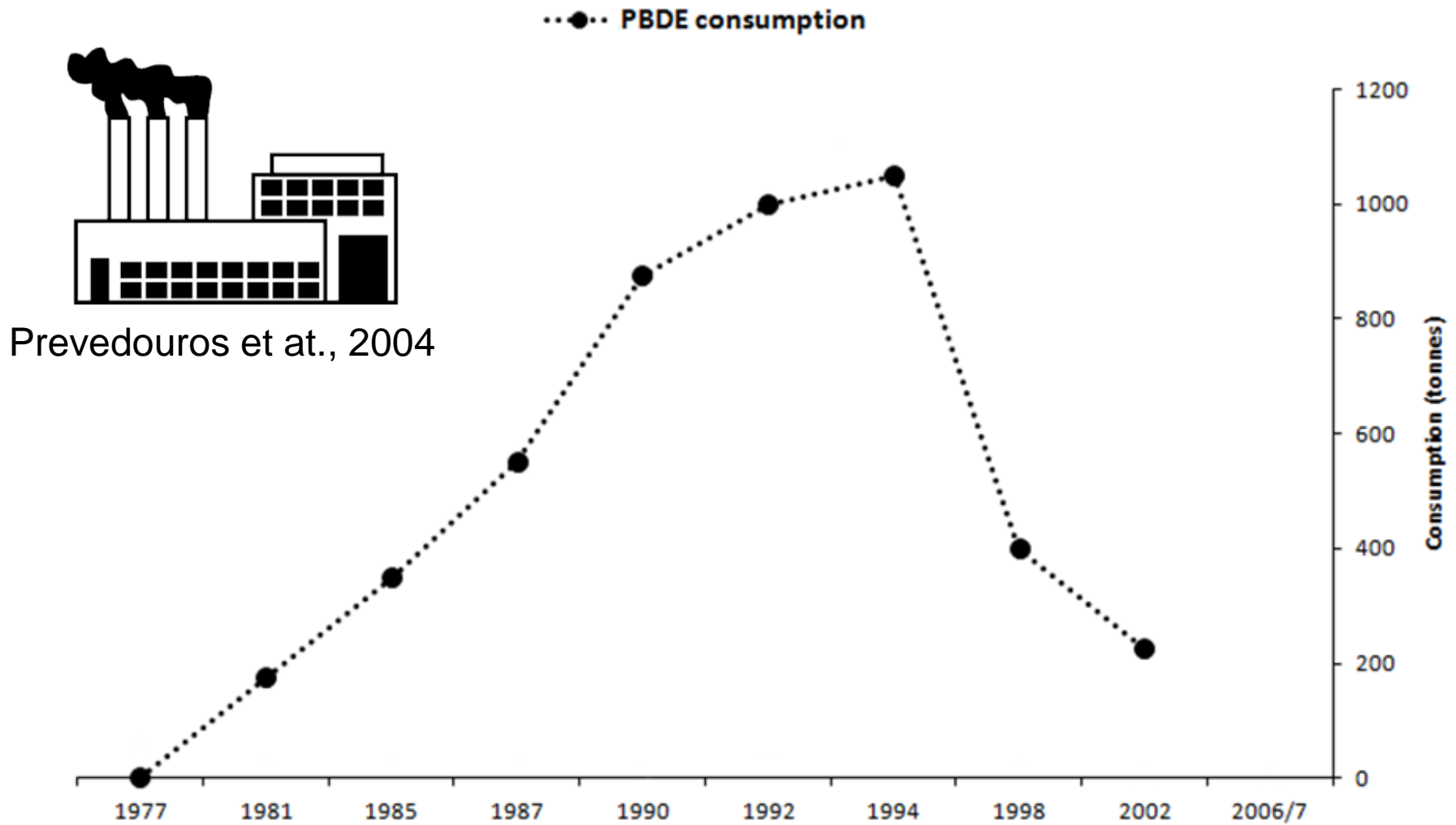


# Drivers for changes in PBDE usage

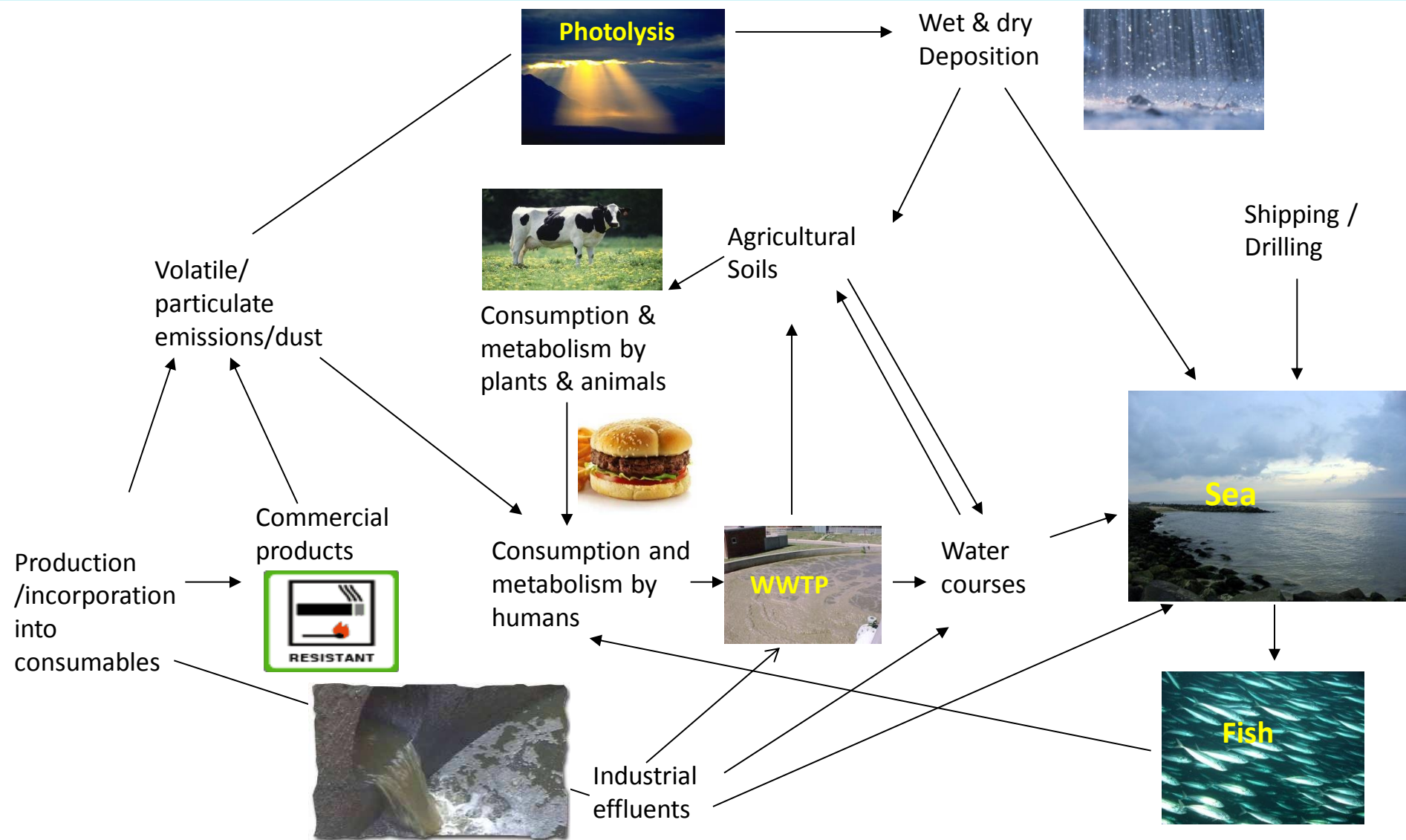
- Series of fire disasters in the UK and Ireland
  - Summerland 1973, Taunton train fire 1978, Woolworth's department store fire 1979, Stardust discotheque fire 1981, Bradford City football stadium fire 1985, King's Cross Underground fire 1987
  - Over 150 people died
  - Rapid spread of fire, production of toxic smoke
- Furniture and Furnishings Fire Safety Regulations (FFFSR), 1988
- RoHS, EEC Directive EEC793/93
- EEC proposes ban on penta- and octa-BDEs, 2001



# PBDE consumption



# Cycling of PBDEs



# PBDEs are everywhere

- Persistent
- Subject to long range transport
- Lipophilic and bioaccumulative
- Are toxic

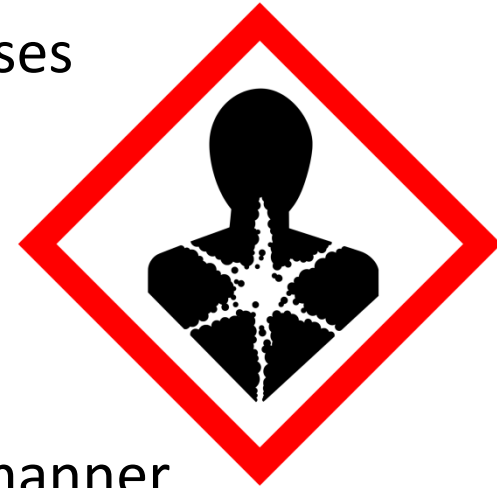


- Found in all environmental compartments
- Found in places where they have never been used
- Found in unborn children
- Growing evidence of toxicity



# Examples of human toxicity

- Chromosomal damage and genotoxicity at low doses
  - (Barber et al., 2006; Llabjani et al., 2011)
- Cytotoxicity
  - (He et al., 2008)
- Apoptosis and genotoxicity in a dose dependant manner
  - (Song et al., 2009;
- Cellular changes in DNA/RNA reflecting a genotoxic mechanism – (Llabjani et al., 2011)
- Competitive binding with T4 to plasma thyroid hormone-transporter transthyretin (TTR)
  - (Athanasidou et al., 2008; Lacorte & Ikonomidou, 2009; Ryden et al., 2012)



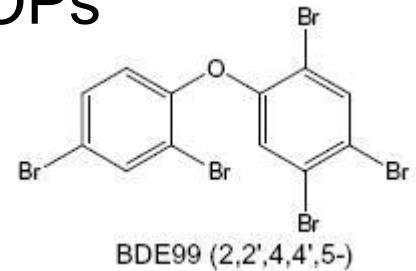
# Specific examples in predatory birds

- Henny et al., (2009)
  - Osprey
  - Reduced productivity (concs >1ug/g ww)
- McKernan et al., (2009)
  - American kestrel
  - Decreased pipping and hatching success (concs 10-20ug/g)
- Fernie et al., 2005, 2008, 2009 ; Marteinson et al., 2010
  - American kestrel - Concs 0.2 – 2.1 ug/g
  - Delayed hatching, reduced pair bonding, shell thinning
- Llabjani et al., 2012
  - DNA/RNA effects
  - Low doses ( $10^{-9}$ ,  $10^{-12}$  M)

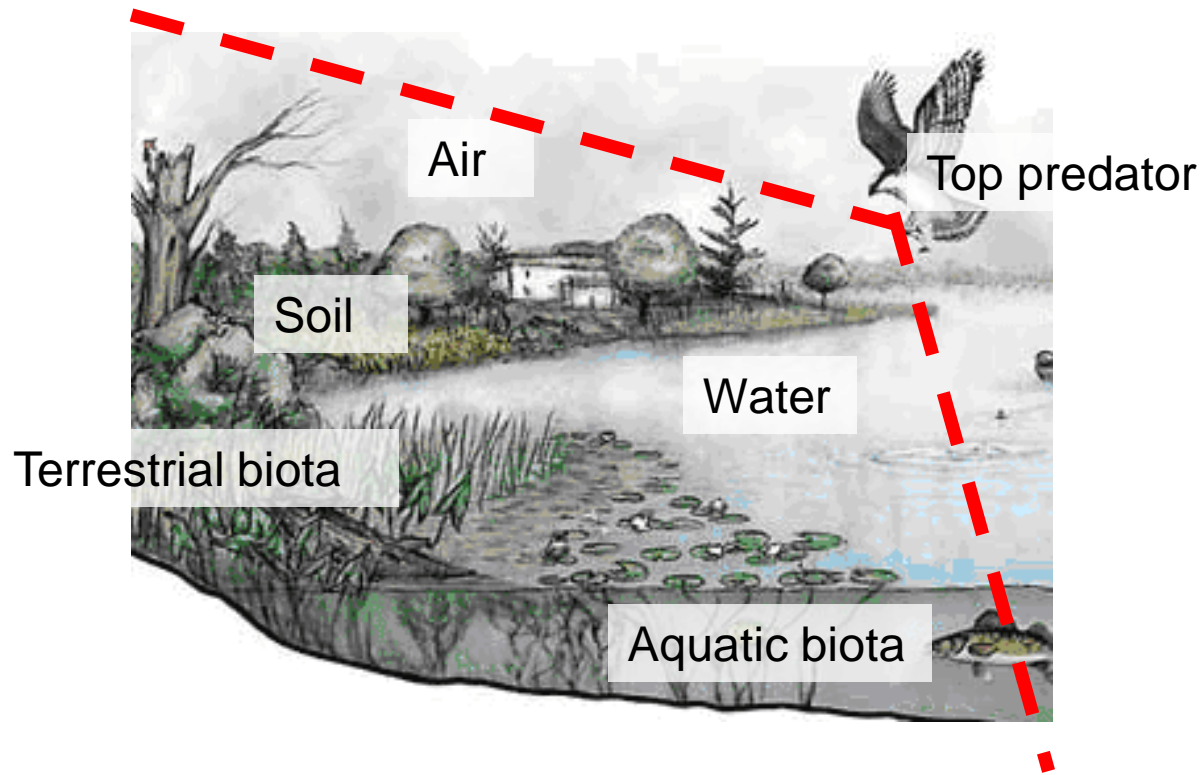


# Legislation

- Penta and Octa BDE mixtures now 'banned'
- Inclusion into the Stockholm Convention on POPs
  - Tetra, Penta, Hexa, Hepta BDEs
  - Annex A (Elimination)
    - OC pesticides and PCBs
- Deca BDE now prohibited in EU in electrical goods
  - ~80% of usage
  - Subject to voluntary phase-outs in the US
- All formulations still in circulation in consumer goods
- Reoccurrence through recycled plastic?



# Environmental sampling



- Occupy a high trophic position
  - Representative of a whole ecosystem

# PBMS

- Long term, national scale
- Funded by CEH, NE, EA, CRRU, RSPB
- Chemical surveillance and monitoring in *sentinel* species
- SGARs, POPs, Trace & toxic metals, PAHs
- Aims: identify hazards, assess risk, quantify environmental drivers, inform policy, evaluate mitigation, assess risks to high priority species
- Tissue and egg archive for monitoring and research



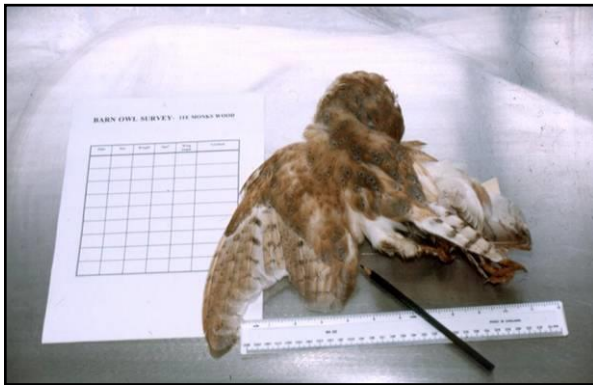
# Predatory birds as Biomonitoring tools

- Why use predatory birds?
  - High trophic position
  - Integrated sentinel – more representative of the ecosystem as a whole
  - Sparrowhawks = terrestrial
  - Gannets = Marine
- Why use eggs?
  - Consistent media
  - Easy to collect
  - Long running archive ~1970-present
  - Good accumulators of lipophilic contaminants





# How it works



**Volunteer  
submission**

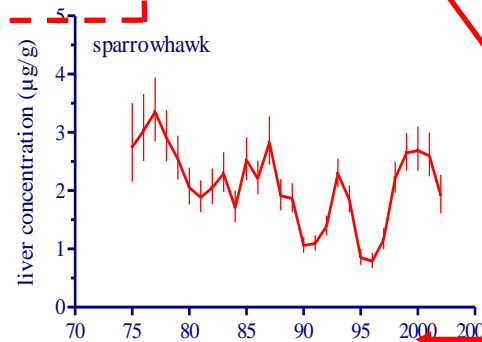
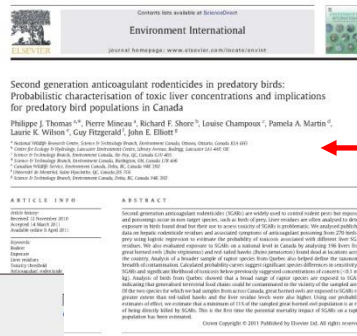
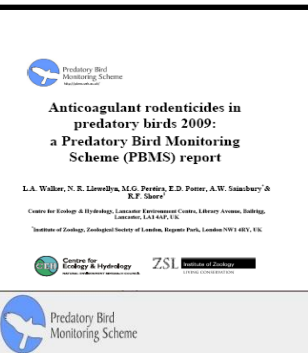


**PM examination**

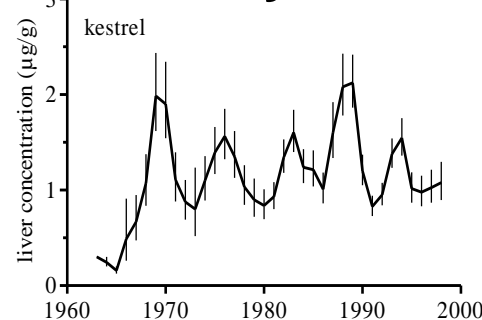


**Sample  
archive**

**Publication**



**Data analysis**



**Chemical analysis**



# Study 1 - Gannets

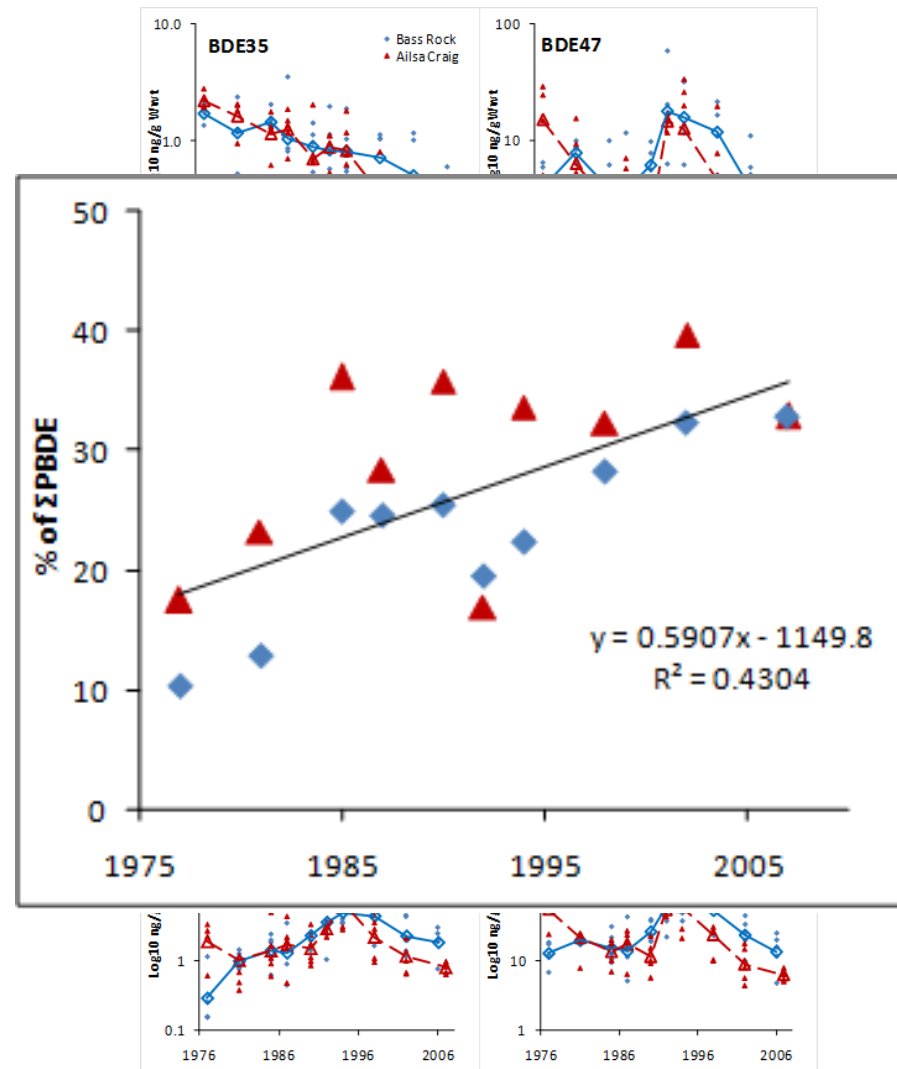
- Marine sentinels
  - Two colonies; Bass Rock and Ailsa Craig
  - Historically contaminated waters
  - Eggs from 1977-2007
- Specific aims
  - Spatial differences
  - Temporal trends
    - PBDE concentration
    - PBDE congeners
    - BDE209 was not analysed as a 209 was not detected by Leslie et al., 2011 in a subsample of these eggs
- Toxicity
  - Shell thickness





# Study 1 - Results

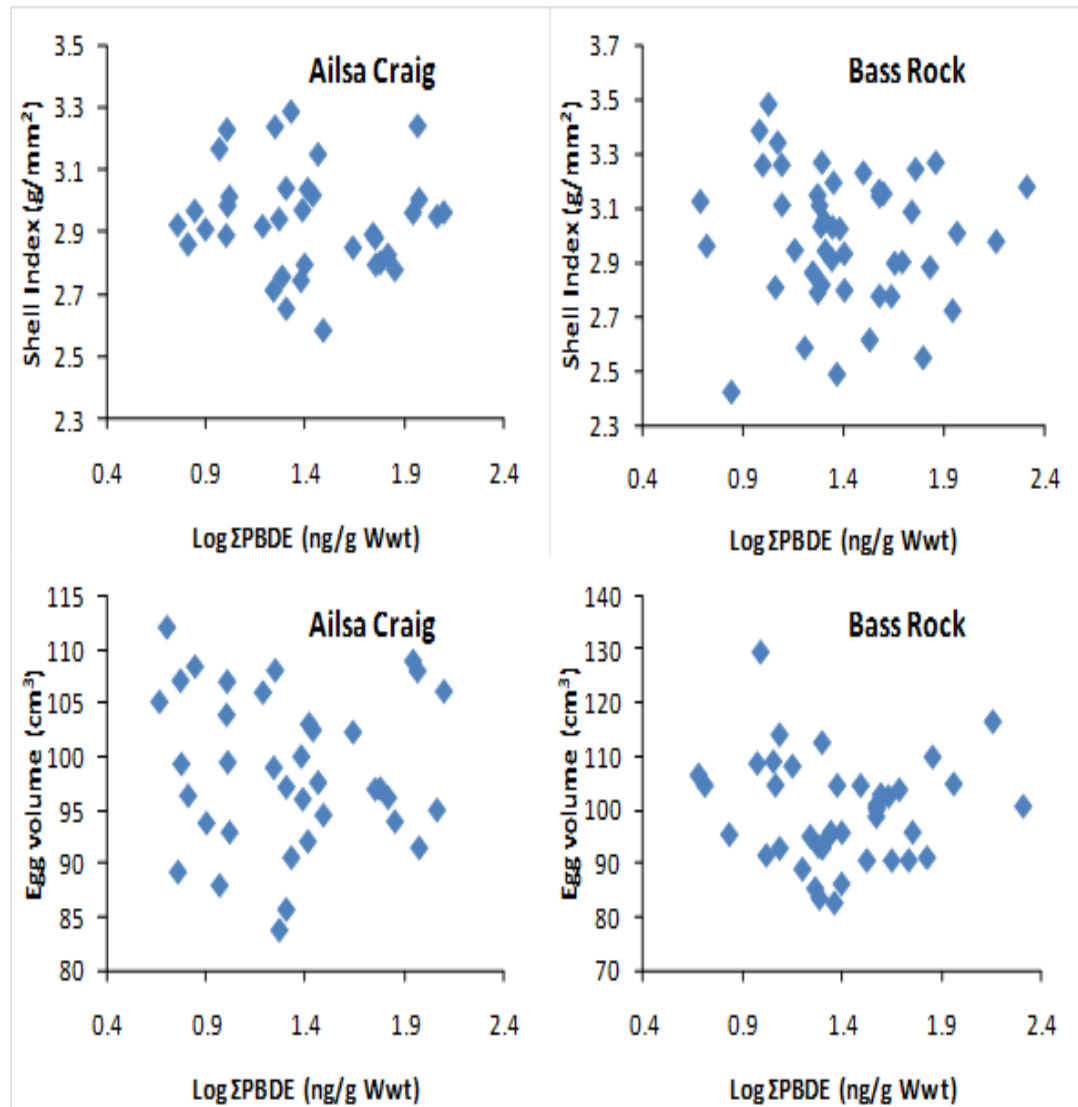
- Congener profile
  - PeBDE dominated
- Spatial trends
  - No significant spatial trends
  - $\Sigma$ PBDE or congeners
- Temporal trends
  - Significant temporal trends
  - Rapid increase from 1980s
  - Peak in 1994, before declining
  - Higher brominated congeners increase over time



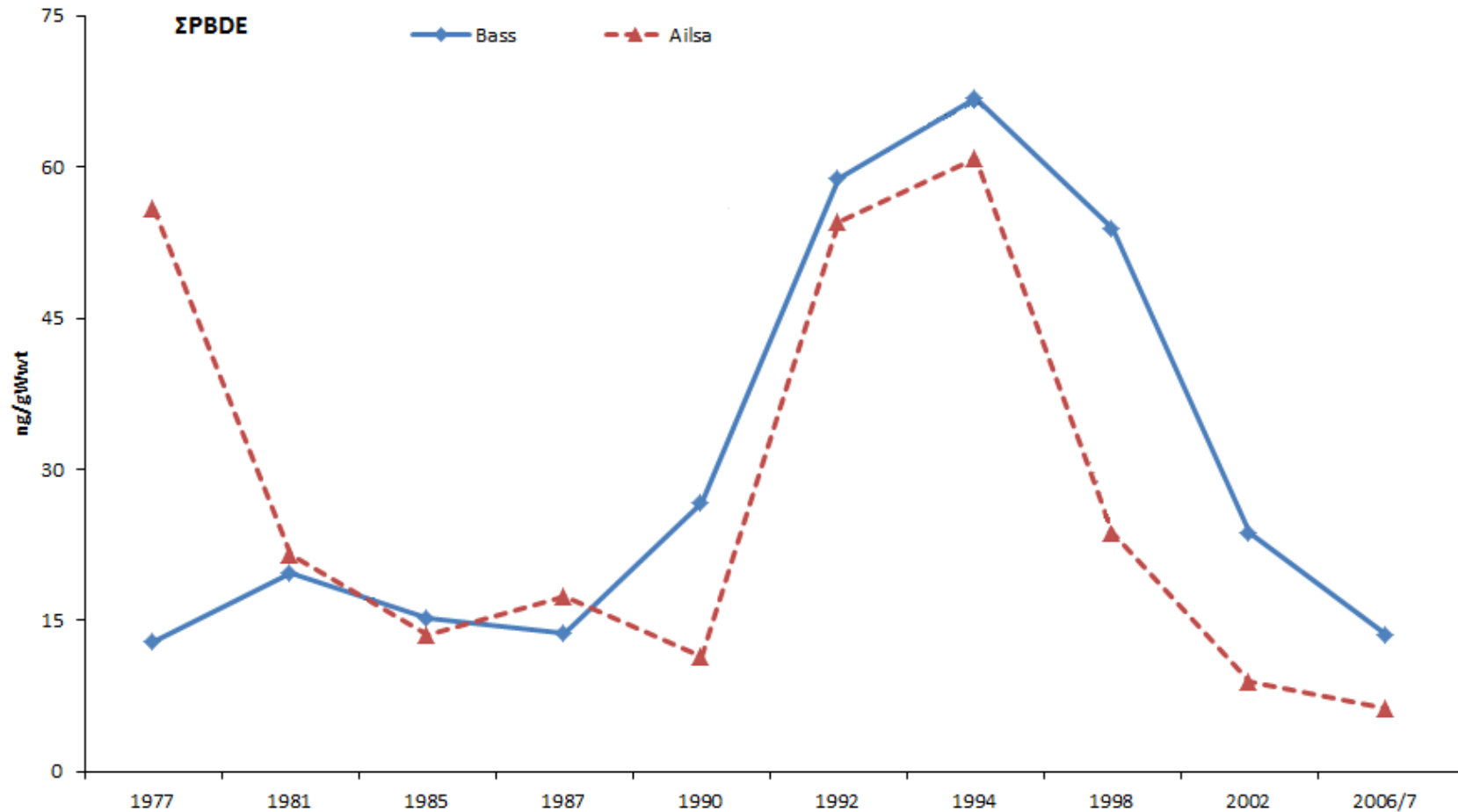
# Study 1 - Results

- Toxicity

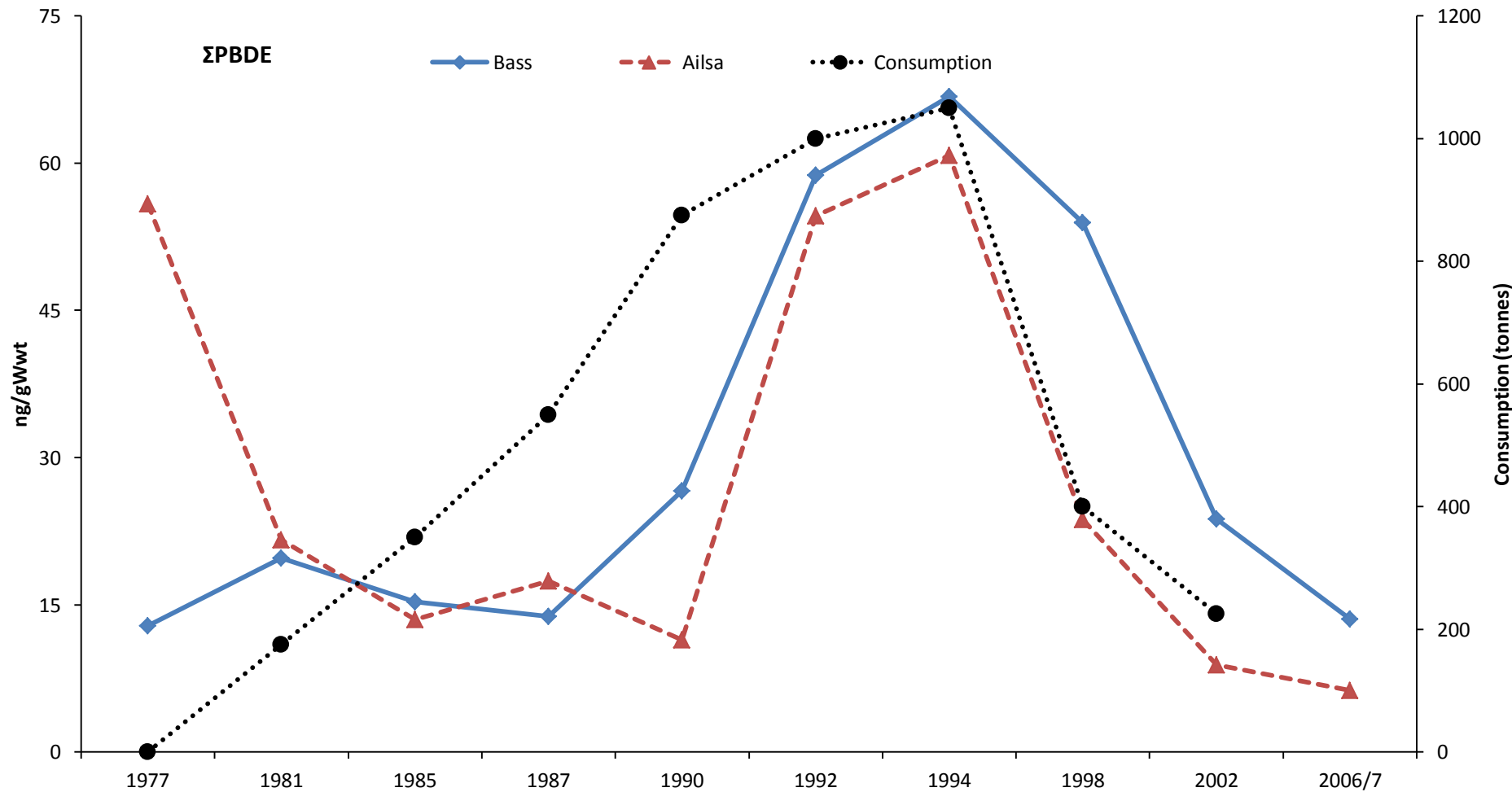
- Overall concentrations relatively low
- 12.9 - 66.8 ng/g in eggs from Bass Rock
- 6.3 to 60.8 ng/g in eggs from Ailsa Craig
- No effect on eggshell thickness or volume



# Study 1 - Results

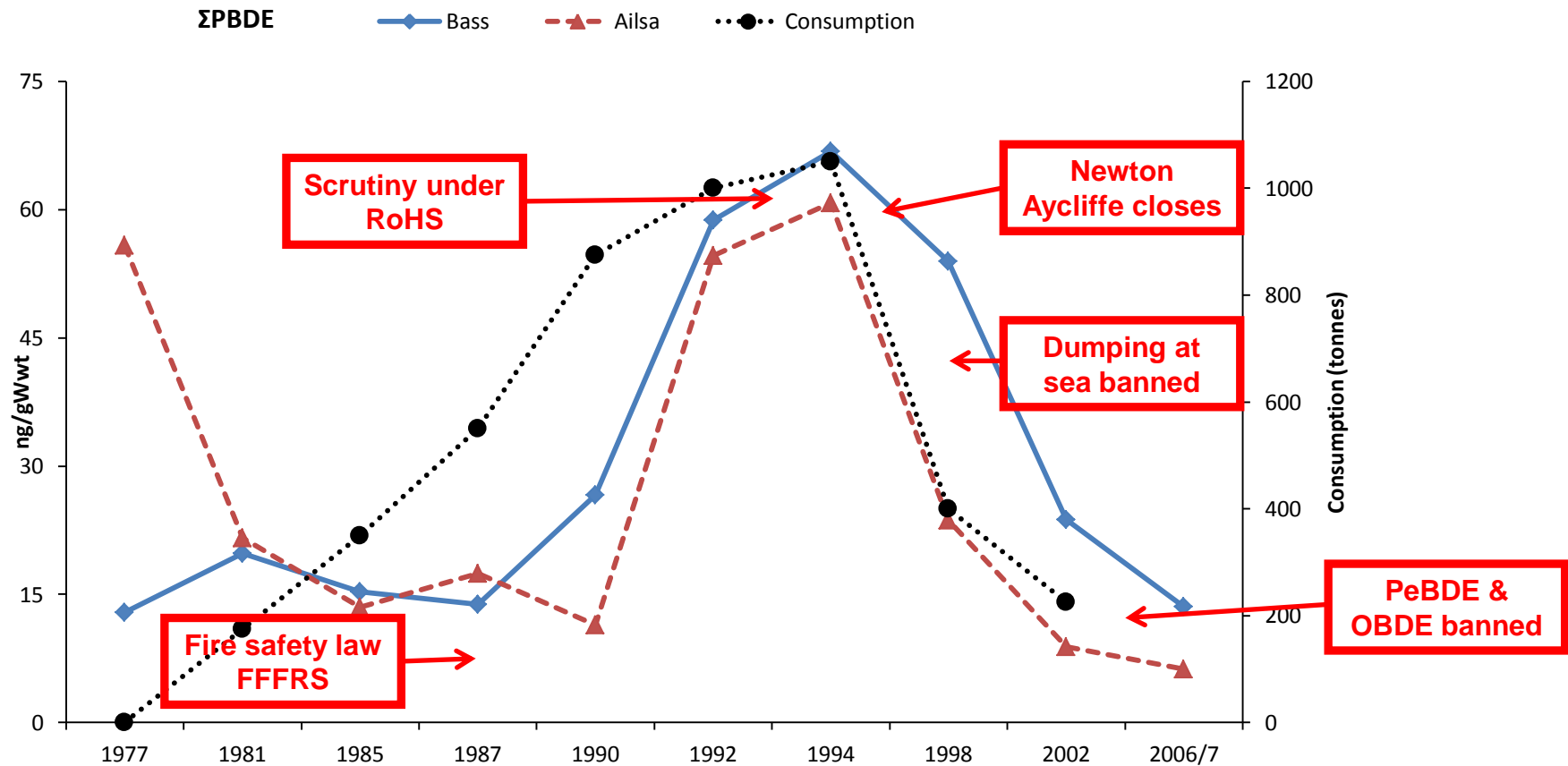


# Study 1 - Results



# Factors affecting consumption in the UK

- Legislative drivers
  - For and against



- Environmental concentrations respond rapidly

# Summary

- No spatial differences
  - North Sea and Irish Sea exhibit similar levels of contamination
- Congeners associated with PeBDE
  - BDE47 most dominant congener
- Temporal changes
  - Marine environmental concentrations respond rapidly to change
  - Increase in higher brominated congeners over time
- Toxicity
  - No significant effect on egg volume or shell thickness

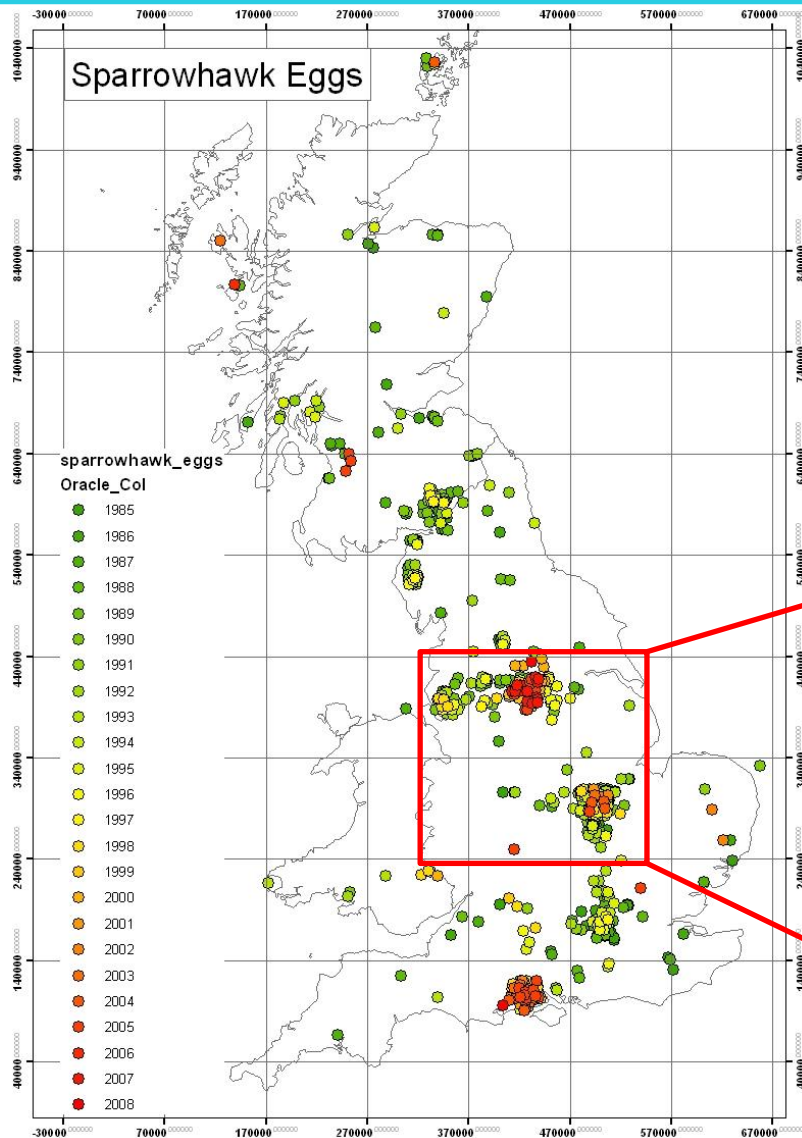


# Study 2 - sparrowhawks

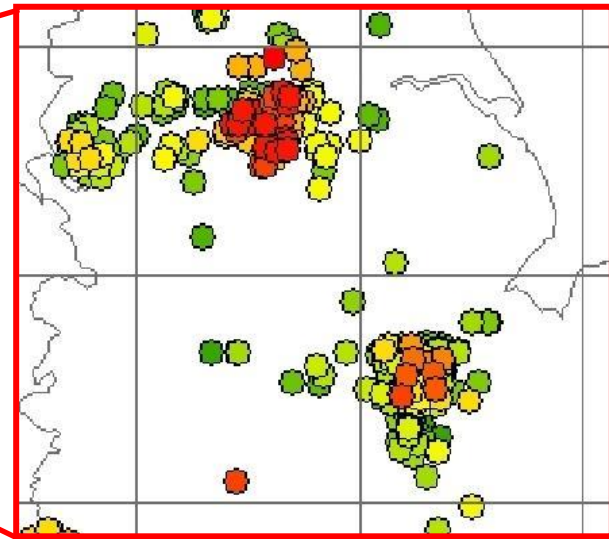
- Terrestrial raptor
- Wide geographic distribution
- Long running archive
  - 1985 - 2007
- Specific aims
  - Temporal trends
    - PBDE concentration
    - PBDE congeners
    - BDE209 was not analysed for as this analysis was being conducted by Jacob de Boer's group (Leslie et al., 2011)
- Toxicity
  - Shell thickness



# Sample selection



- Criteria 1
  - 1985-2007 (encompassing major legislation)
  - ~5 eggs per year
- Criteria 2
  - Smallest geographical area possible



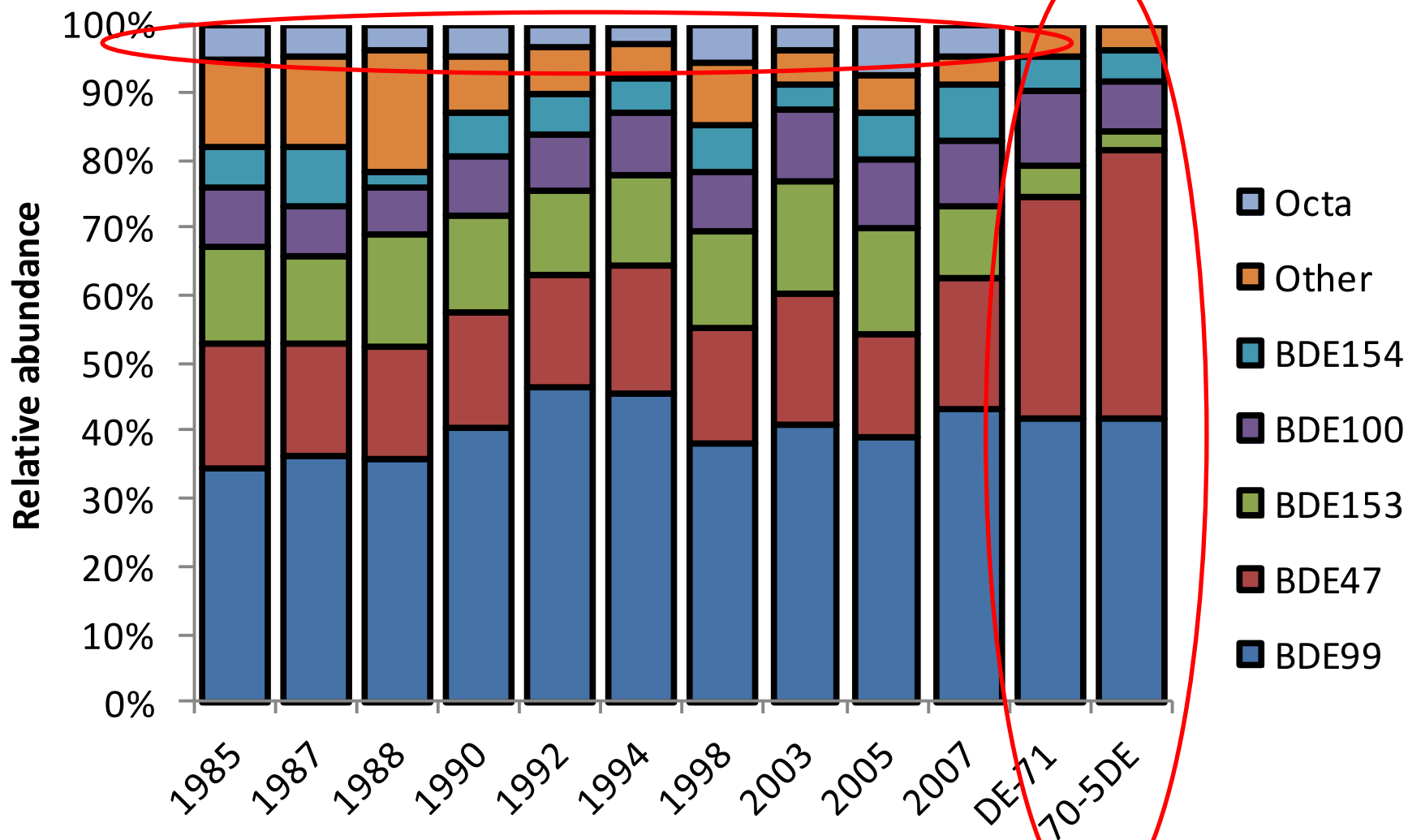


# Results

- Concentrations
  - 34 – 2281 ng/g ww
  - Several orders of magnitude higher than the gannets
- Congener profile
  - BDE 99 dominant congener
  - BDEs 99>47>153>100>154 dominated the PBDE profile
    - Smaller contributions of BDEs 28, 85, 138
  - All congeners co-correlated with each other and with  $\Sigma$ PBDE concentrations ( $p < 0.001$ )
  - Very similar to PeBDE mixture
  - Similar profile to that found in prey sp (Van den Steen et al., 2009)



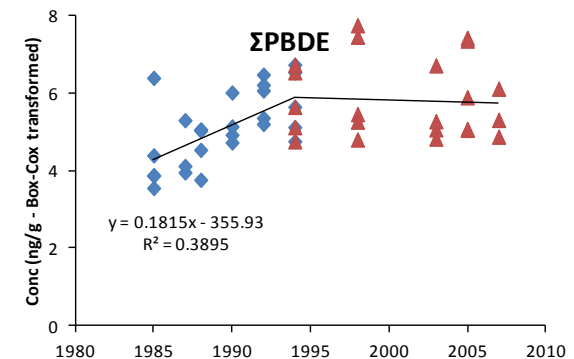
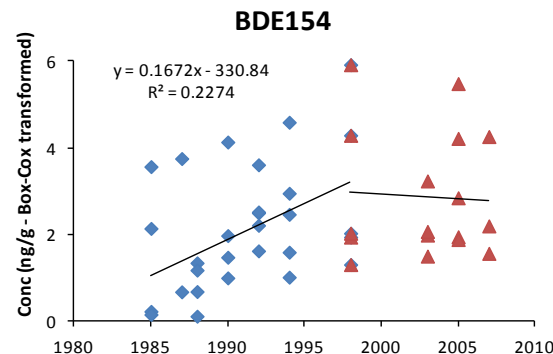
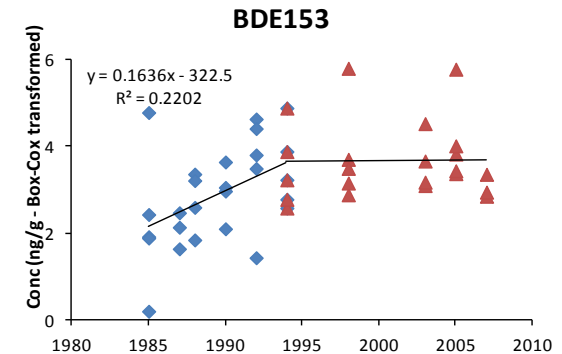
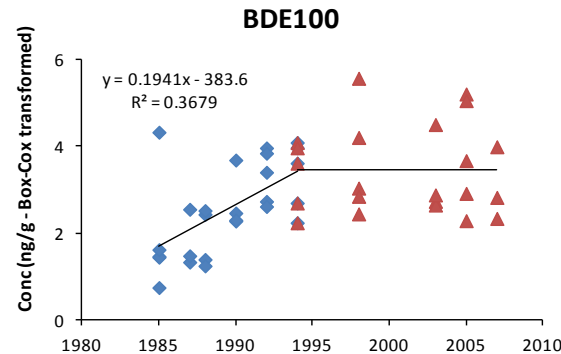
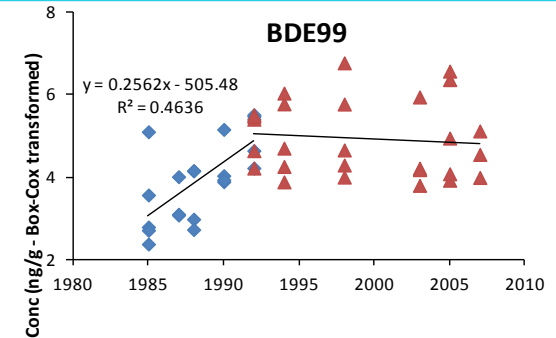
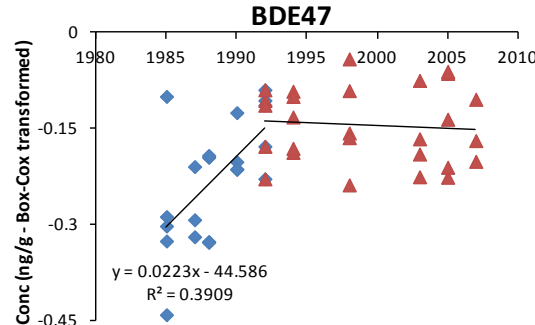
# Results: Congener profile



# Temporal trends

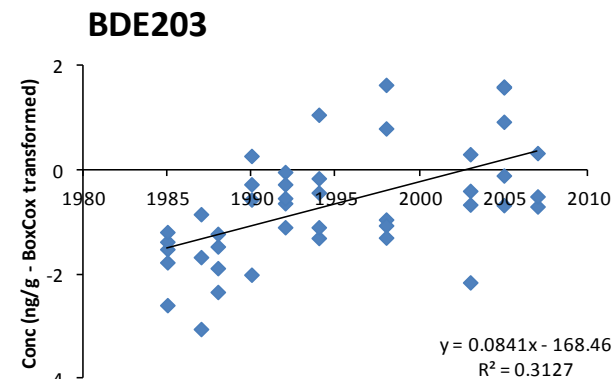
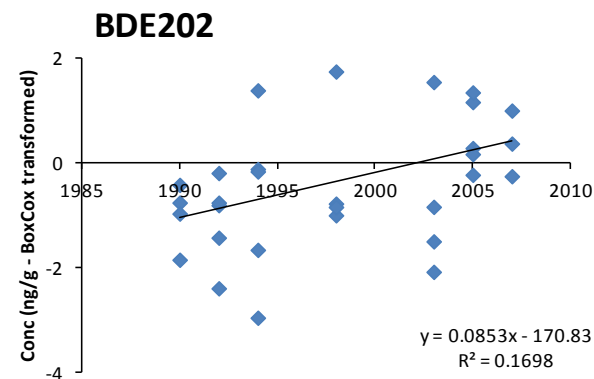
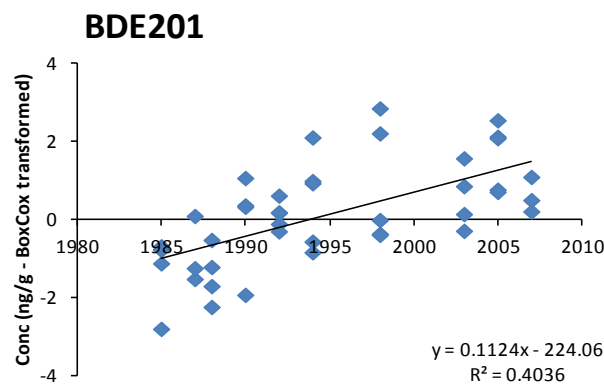
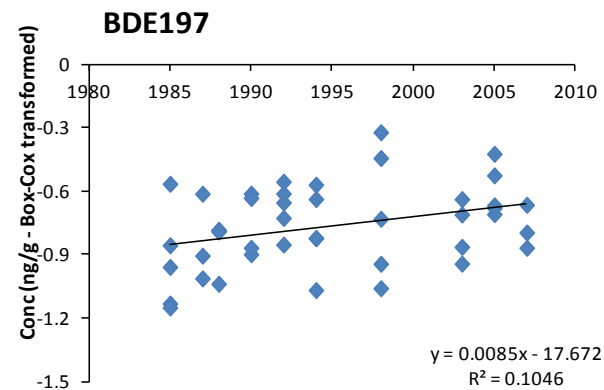
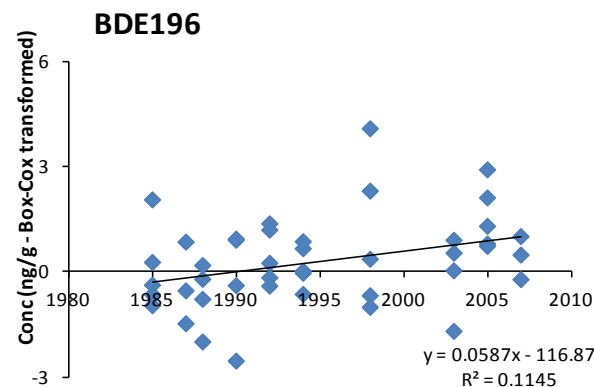
- Linear increase of  $\Sigma$ PBDE concentrations until mid 1990s ( $R^2=0.39$ ,  $F_{1,42}=17.5$ ,  $P<0.001$ )

- Similar pattern for BDEs 47, 99, 100, 153, 154
- BDE concentrations remained high from mid 1990s onwards
- No significant decline



# Temporal trends

- OBDE-associated BDEs 196, 197, 201, 202, 203 increased linearly over time ( $R^2 \leq 0.40$ ,  $F_{1,42} \leq 27.75$ ,  $P < 0.05$ )



# Toxicity

- ΣPBDE in sparrowhawk eggs ranged from 0.34-2.28 ug/g wet weight (wwt)
  - 0.27-27.4 ug/g (lipid weight)
- Exceed the threshold for shell thinning and reproductive impairment found in other raptors (Fernie et al., 2009; Henny et al., 2009; Marteinson et al., 2010)
- No relationship between ΣPBDE nor individual congeners on sparrowhawk eggshell thickness ( $p > 0.05$ )
  - Shell thickness increasing over time ( $R^2 = 11.4$ ,  $F_{1,37} = 5$ ,  $P < 0.05$ )
- Eggs collected represent failed or abandoned eggs
  - May not be associated with PBDEs

# Summary

- Concentrations in sparrowhawk eggs represent environmental concentrations during the breeding season
- PBDE concentrations are not declining in sparrowhawk eggs
  - Slow clearance from the terrestrial system
  - Stark contrast to the marine system and other studies
- Dominated by PeBDE mix congeners
  - BDE99
  - Input from OBDE congeners
  - Slower clearance of these congeners
- Concentration of heavy BDEs increasing
  - BDE209 detected in a subsample of eggs
  - Debromination of labile BDE209



# Summary (continued)

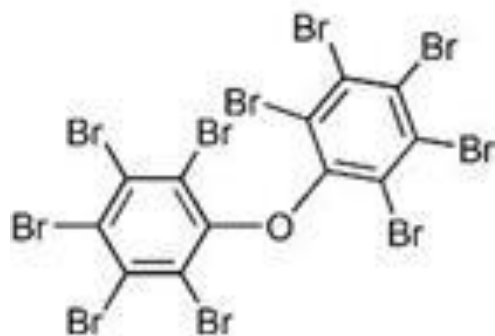
- Concentrations amongst the highest ever reported in bird eggs
  - Exceed threshold for shell thinning and impaired reproductive output
  - We did not find any effect of PBDEs on shell thinning
  - Difficult to relate cause and effect of PBDE concentrations on egg failures



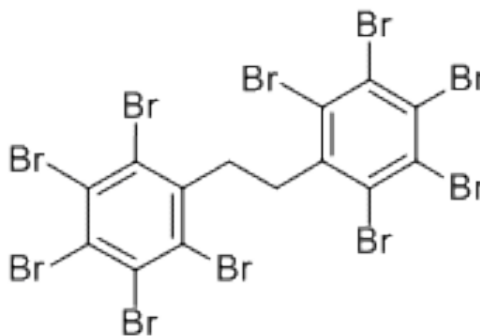


# What's next?

- DeBDE being phased out in US
  - UK following
  - New flame retardants already on the market
    - PBT, PBEB, HBB, DP, BTBPE, OBIND, TBPAE, TBECH, BATE, DBDPE
  - DecaBromoDiphenylEthane
  - Replacement for DecaBromoDiphenylEther (DeBDE)



DeBDE (209)



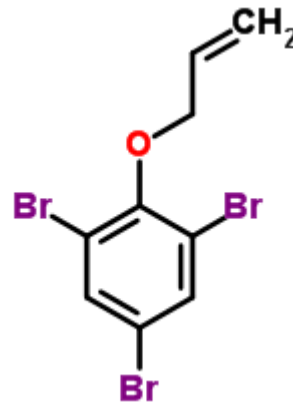
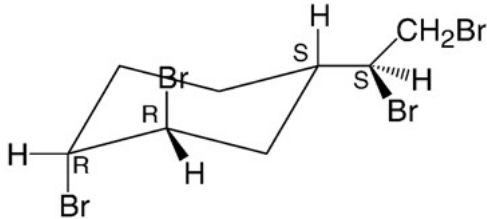
DBDPE



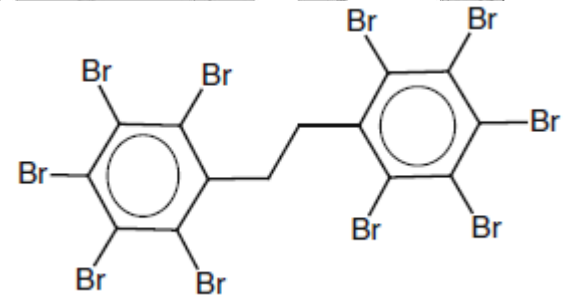
# A long way from home...



TBECH

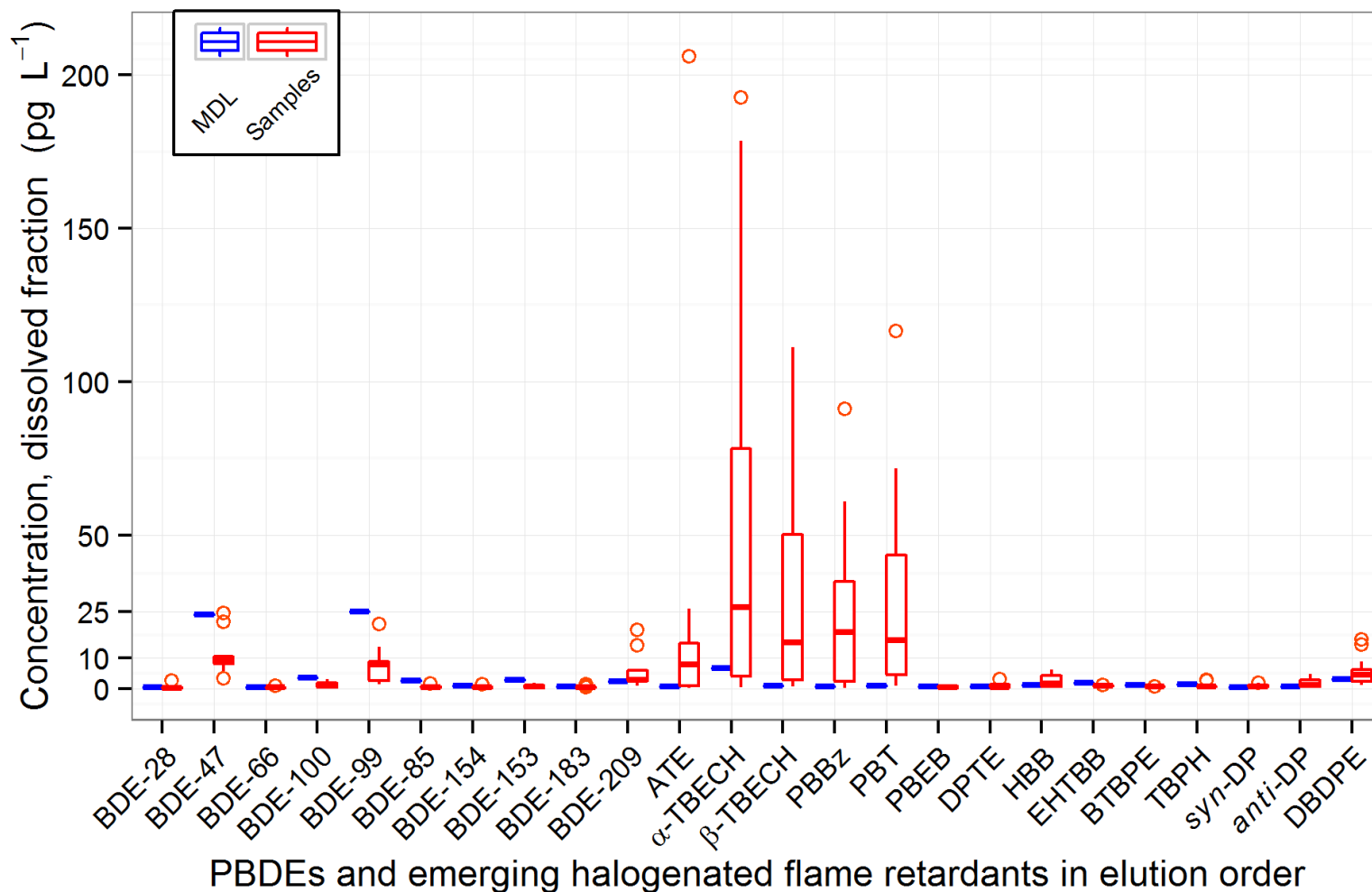


ATE



DBDPE

# A long way from home...



# Acknowledgements

- NERC & PBMS
  - CEH
  - Natural England
  - RSPB
  - EA
  - CRRU
- Lancaster University (CCM)
- Volunteers who collected the eggs
- Everyone else who helped out
  - Dave Hughes and Lee Walker
  - Dr Sabino Del Vento
  - Dr Jasmin Schuster
  - Dr Gareth Thomas



a million voices for nature

