Long term trends of PBDEs in sparrowhawk (*Accipiter nisus*) eggs, an apex terrestrial predator in the UK

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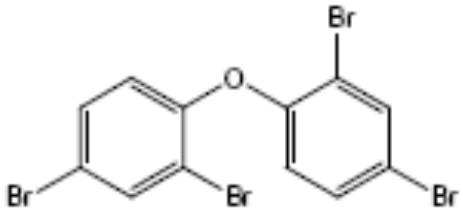
Overview

- PBMS and POPs
- PBDEs
  - What are they?
  - Why should we care?
  - Trends in the environment
- Study aims and sample selection
- Results
  - Spatial trends
  - Temporal trends
  - Toxicity



BDE47 (2,2',4,4'-)

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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

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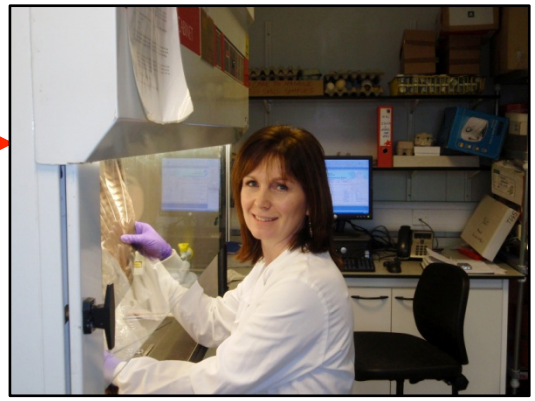
How it works

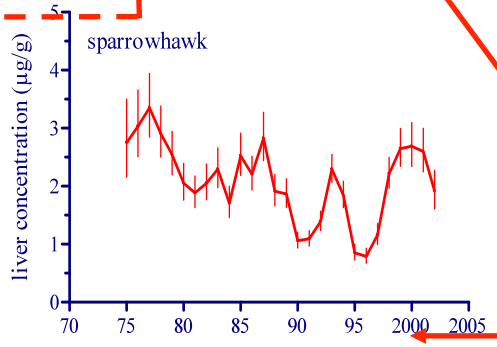


Volunteer submission

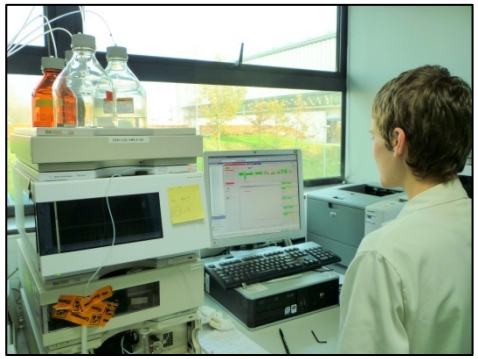
PM examination

Sample archive

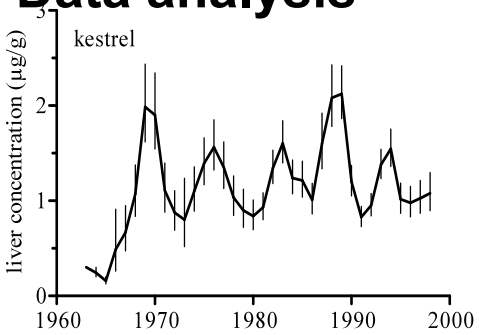
Publication



Chemical analysis

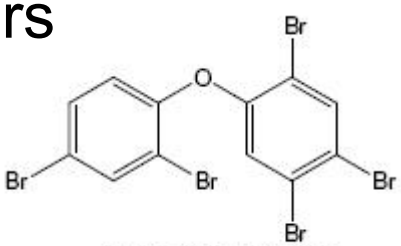


Data analysis



PBDEs

- Additive flame retardants
- Used in high impact plastics, textiles, furniture foam
- Release to environment from product manufacture, use, disposal
- 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)
- Persistent, lipophilic, evidence of toxicity
  - Hormone metabolism – T4, AhR, CYP450



BDE99 (2,2',4,4',5-)

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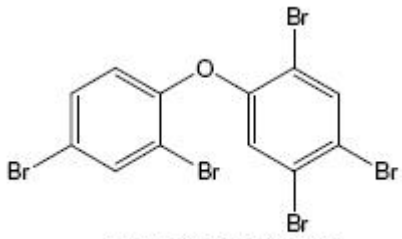
Specific examples in predatory birds

- Henny et al., (2009)
  - Osprey
  - Reduced productivity (concs >1ug/g wwt)

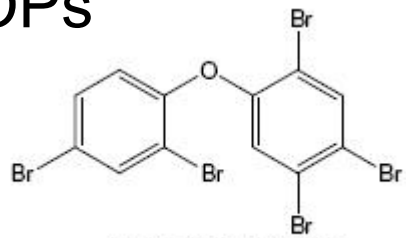


BDE99 (2,2',4,4',5-)

- 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

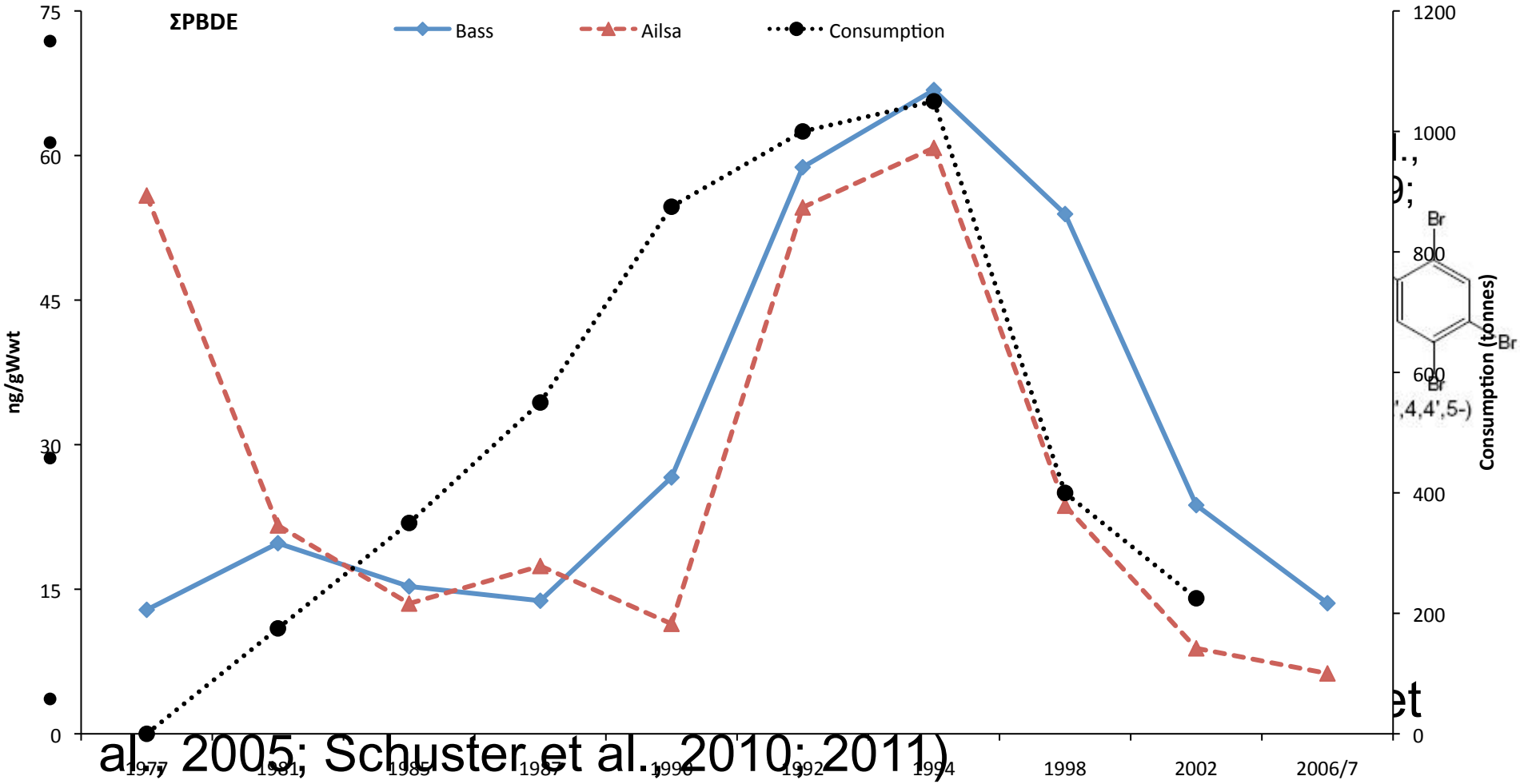
- Penta and Octa BDE mixtures now ‘banned’
- Inclusion into the Stockholm Convention on POPs
  - Tetra, Penta, Hexa, Hepta BDEs
  - Annex A (Elimination)
    - OC pesticides and PCBs



BDE99 (2,2',4,4',5-)

- Deca BDE now prohibited in EU in electrical goods
  - ~80% of usage
  - Scheduled to be banned in US by 2013
- All formulations still in circulation in consumer goods

Changes in environmental concentrations



al., 2005; Schuster et al., 2010; 2011)

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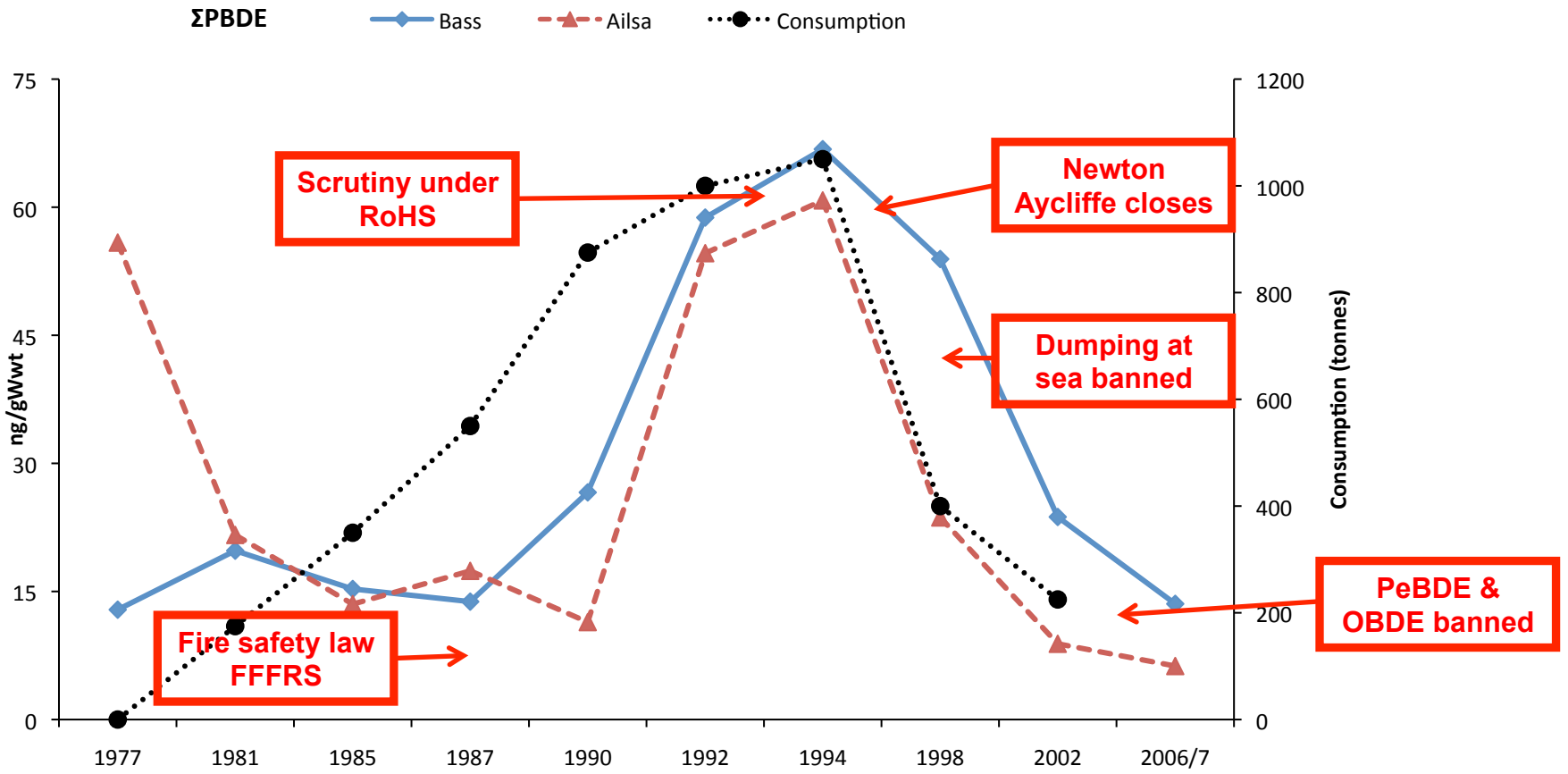
Factors affecting consumption in the UK

- Legislative drivers
  - For and against



- Environmental concentrations respond rapidly

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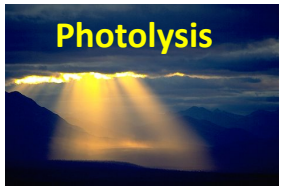
Cycling of PBDEs



Wet & dry Deposition

Agricultural Soils

Shipping / Drilling

Volatile/ particulate emissions/dust

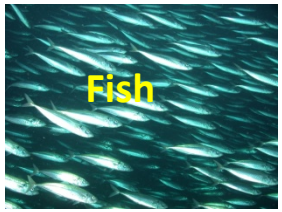
Commercial products

Production / incorporation into consumables

Consumption and metabolism by humans

Water courses

Industrial effluents



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Sparrowhawks as Biomonitoring tools

- Why use sparrowhawks?
  - High trophic position
  - Wide geographical distribution
  - Integrated terrestrial sentinel – more representative of the ecosystem as a whole

- Why use eggs?
  - Consistent media
  - Easy to collect
  - Long running archive ~1970-present
  - Good accumulators of lipophilic contaminants

Study aims

- Rationale
  - Few detailed temporal trends for PBDEs
  - Fewer temporal trends for terrestrial species globally
  - No long term trends for UK terrestrial wildlife
- Specific aims
  - Egg extracts analysed by GC-MS
  - Temporal trends
    - PBDE concentration
    - PBDE congener profile
- Toxicity
  - Shell thickness

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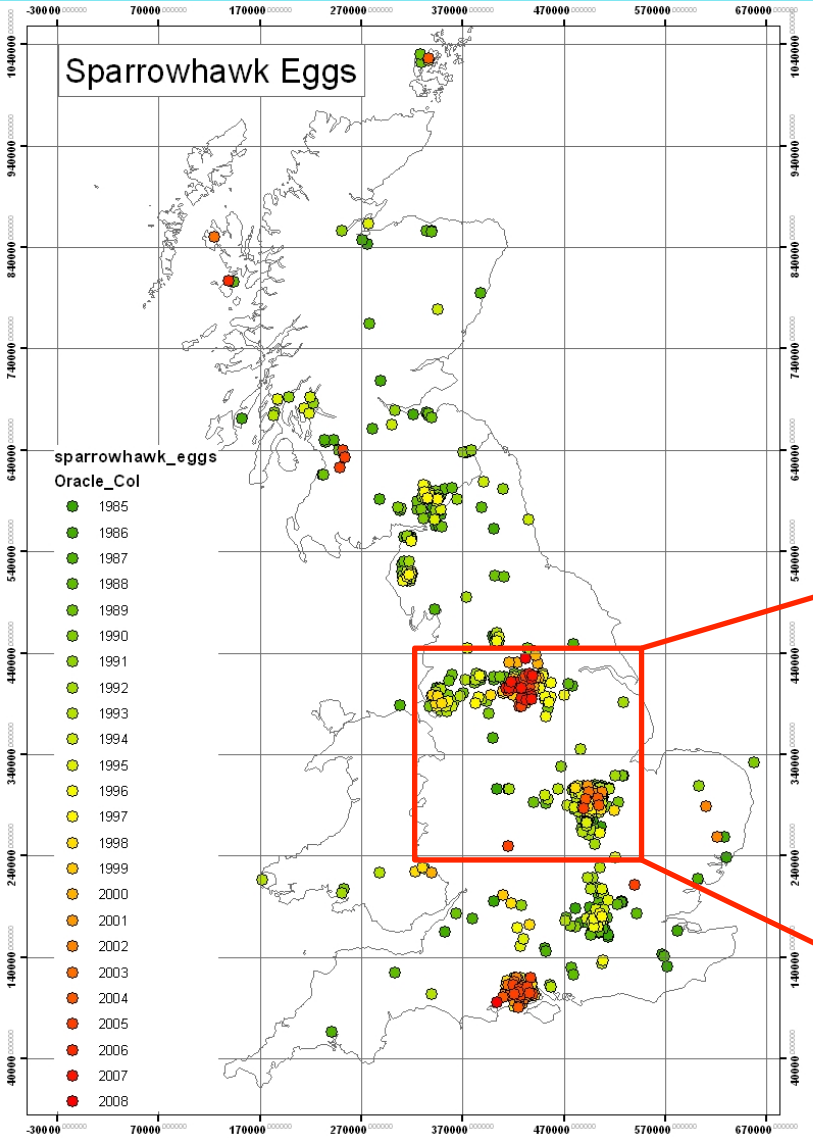
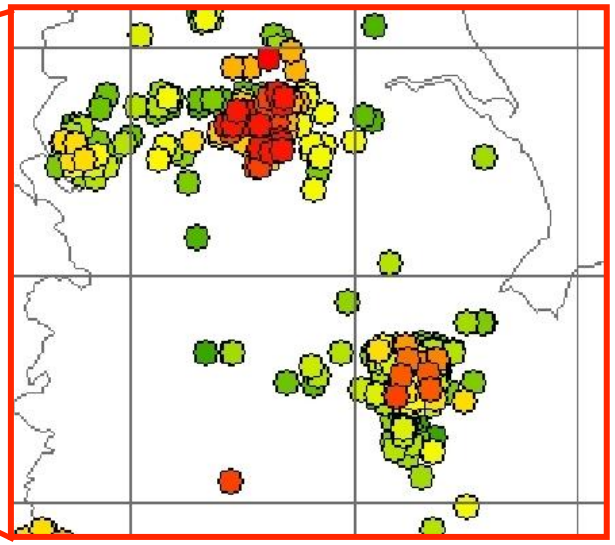
Sample selection



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



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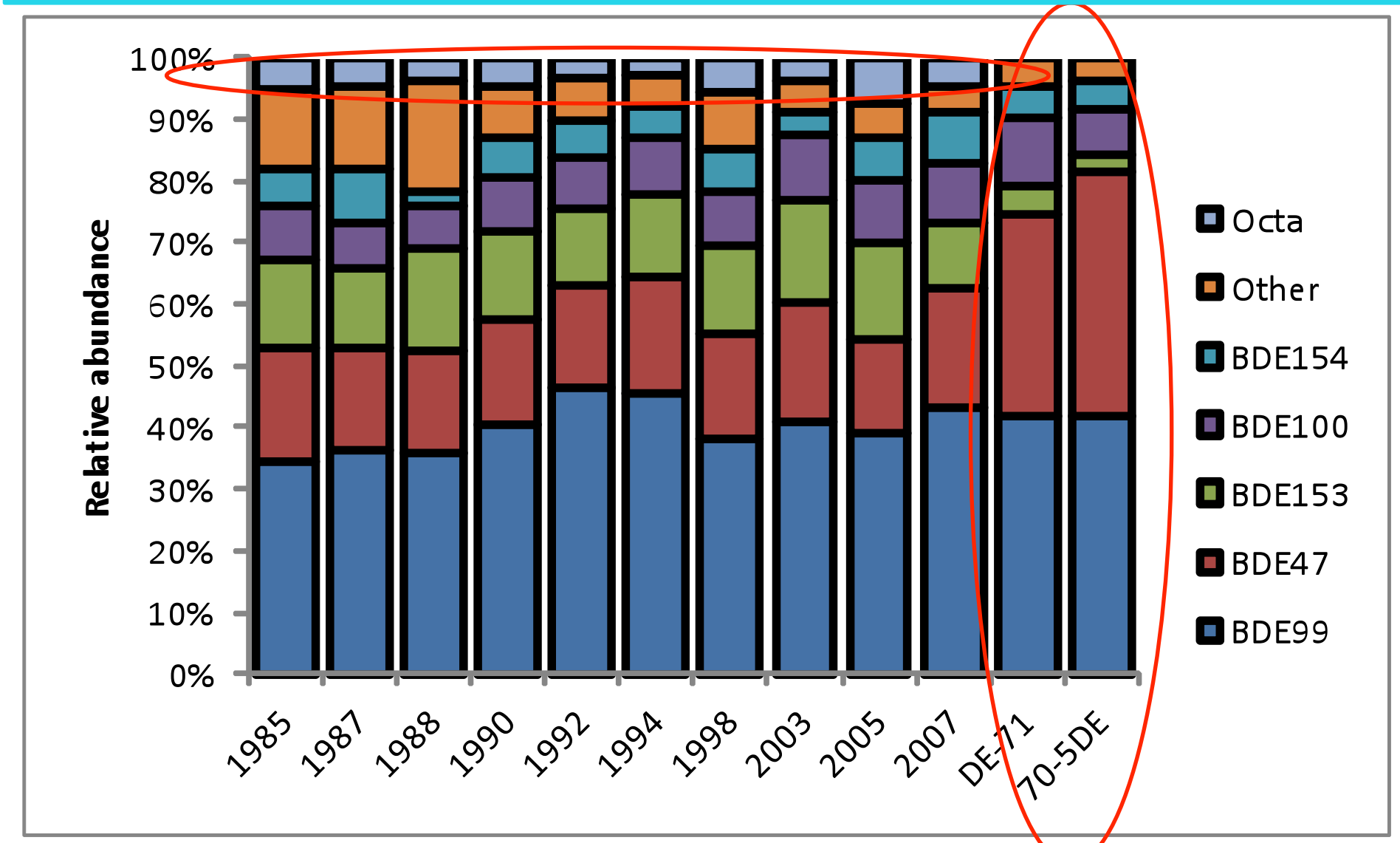
Results: Congener profile



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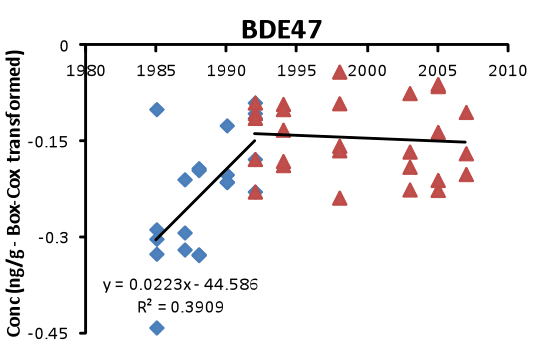
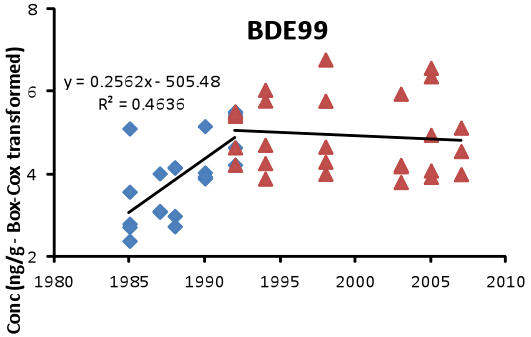
Congeners

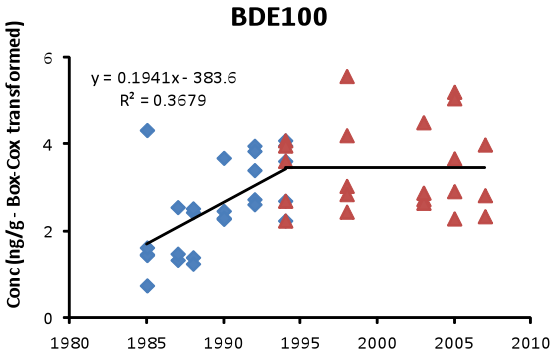
- Congener profile
  - BDE 99 dominant congener
  - BDEs 99>47>153>100>154 dominated the PBDE profile
    - Smaller contributions of BDEs 28, 85, 138
  - All congeners co-correlated with each other and with ΣPBDE concentrations ($p<0.001$)
  - Very similar to PeBDE mixture
  - Similar profile to that found in prey sp (Van den Steen et al., 2009)
  - OBDE associated congeners detected in >80% of eggs
    - BDEs 183, 196, 197, 201, 203
    - Correlation with ΣPBDE concentrations ($p<0.01$)
    - BDE 202 detected – not part of any technical mix
    - No correlation between BDE202 and ΣPBDE ($p>0.05$)

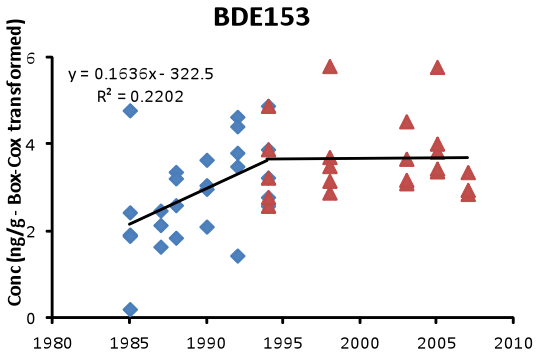
Temporal trends

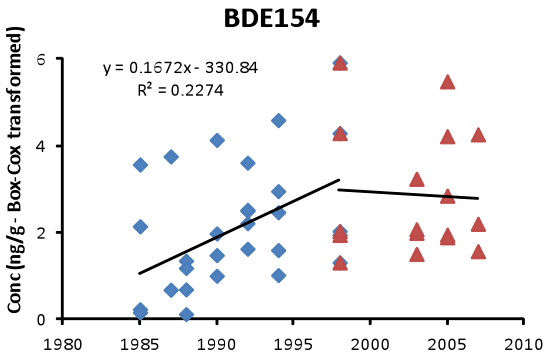
- Linear increase of ΣPBDE concentrations until mid 1990s (R^2=0.39, $F_{1,42}$=17.5, P<0.001)
  - Similar pattern for BDEs 47, 99, 100, 153, 154
  - BDE concentrations remained high from mid 1990s onwards
  - No significant decline

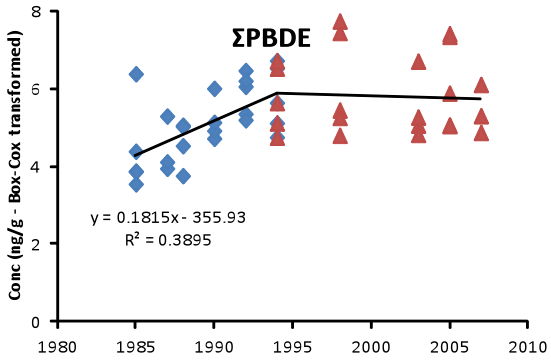












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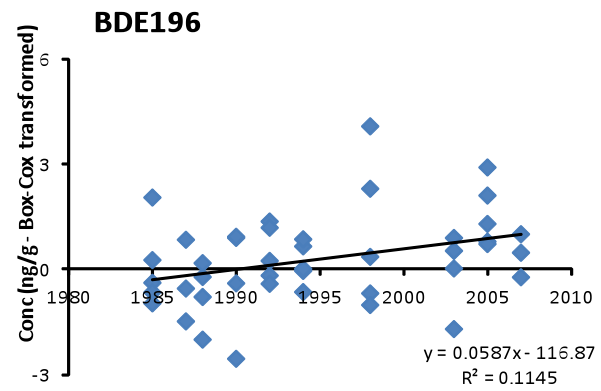
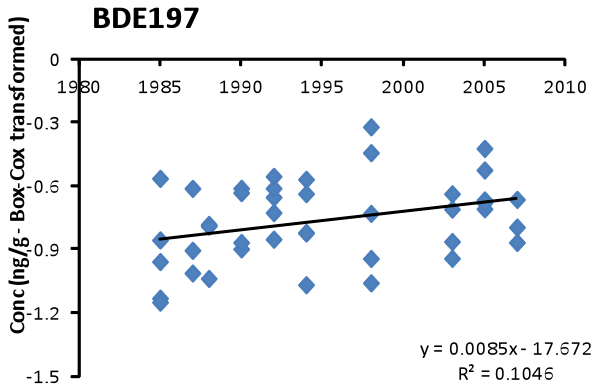
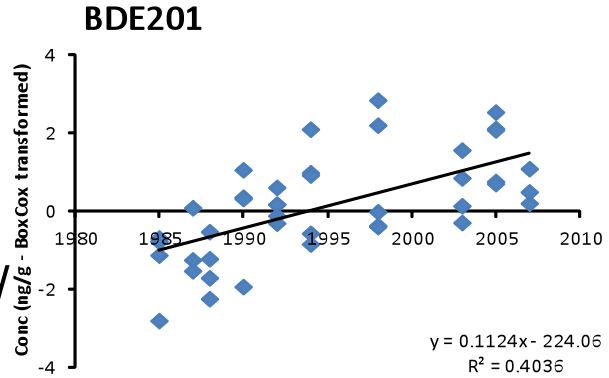
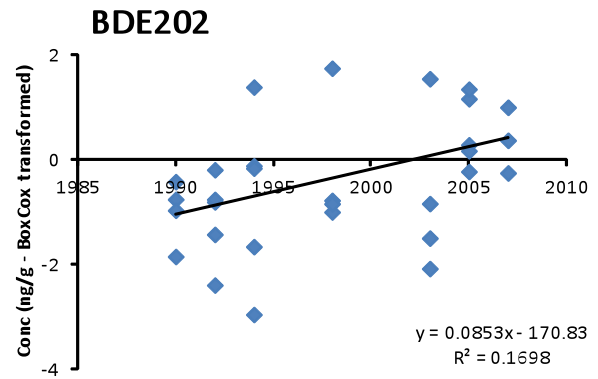
Temporal trends

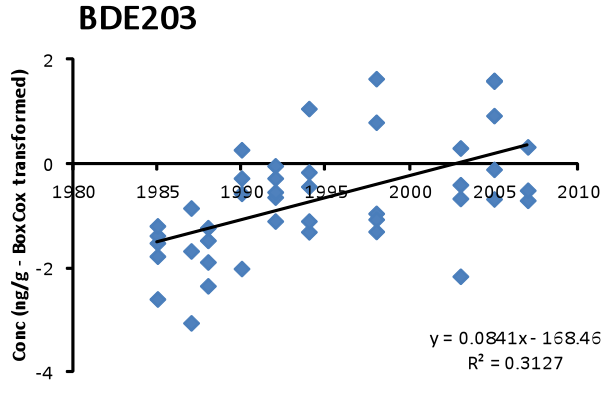
- OBDE-associated BDEs196, 197, 201, 202, 203 increased linearly over time ($R^2 \leq 0.40$, $F_{1,42} \leq 27.75$, $P<0.05$)
- Slow environmental clearance?
- Breakdown of nona/deca?
- BDE202 not a part of any technical mix
- Breakdown of DeBDE?
- BDE209 detected in sparrowhawk eggs (Leslie et al., 2011)











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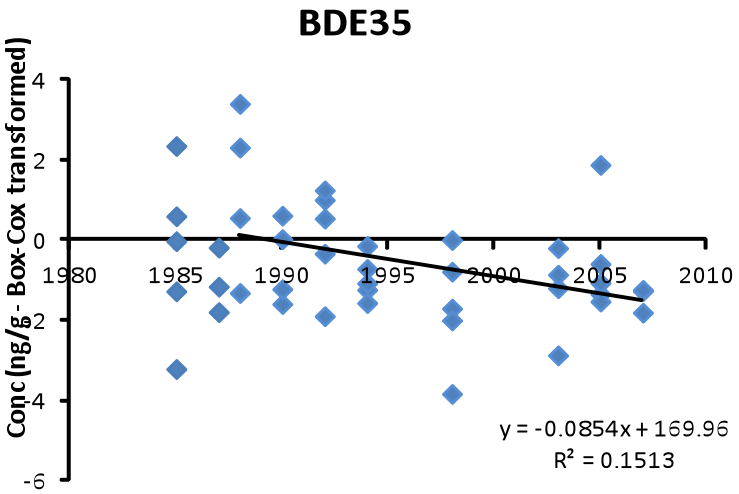
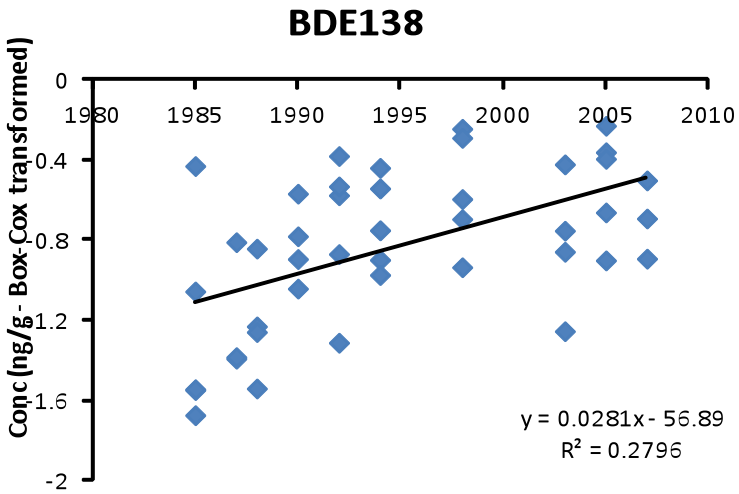
Temporal trends





- Linear decrease of BDE35
- Linear increase of BDE138.
  - Enrichment over PeBDE profile
  - Breakdown of higher brominated BDEs?

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Toxicity

- ΣPBDE in sparrowhawk eggs ranged from 0.34-2.26 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
  - Occurrence of BDE 202

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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

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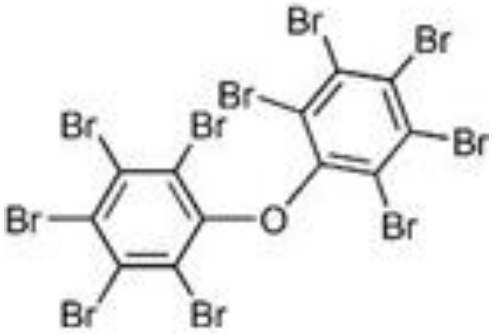
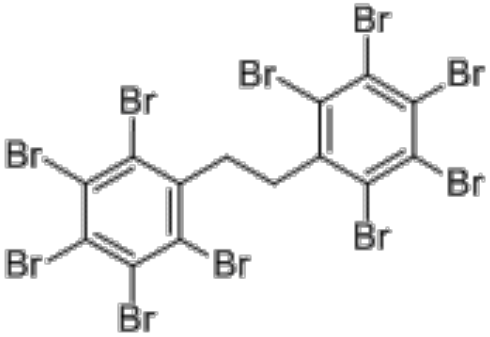
What's next?

- DeBDE will be banned in USA in 2013
  - UK likely to follow
  - New flame retardants already on the market
    - PBT, PBEB, HBB, DP, BTBPE, OBIND, TBPAE, BATE, DBDPE
  - DecaBromoDiphenyl*Ethane*
  - Replacement for DecaBromoDiphenyl*Ether* (DeBDE)



DeBDE (209)



DBDPE

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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

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RSPB
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Environment Agency

THINK WILDLIFE
Campaign for Responsible Rodenticide Use

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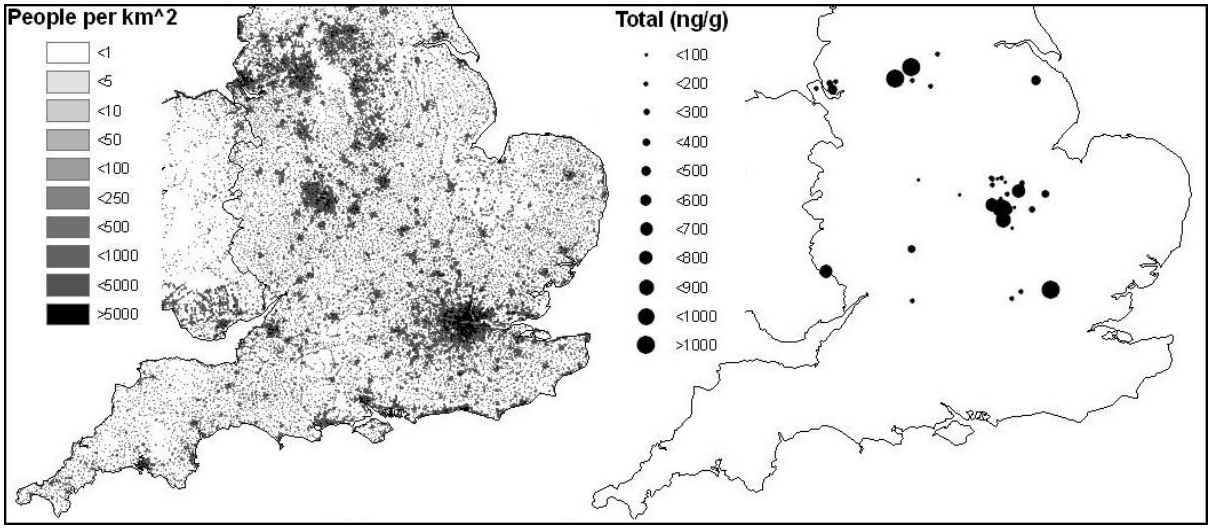
Spatial analysis

- Population density
  - Data from Office for National Statistics 2001
  - 200m resolution
  - Locally weighted approach
  - $\mathbf{A=\Sigma(pop_i/r_i^2)}$
  - Schuster et al., (2010)

- Landuse
  - UK Landcover map 2000
  - 10km^2 around nest site
  - Arable, Urban, Grassland, Woodland, Semi-natural
  - 1km resolution

Spatial trends



- No correlation between population density and ΣPBDE nor any BDE congeners ($R^2 \leq 20.2$, $F_{1, 24} \leq 4.12$, $P>0.05$)
- Neither ΣPBDE nor any BDE congeners correlated with urban landcover ($p>0.05$)
- Population density has no clear influence on the PBDE burden in sparrowhawk eggs
- Contrast to what other studies have reported for other matrices (Moeckel et al 2010; Ricklund et al., 2010; Van den Steen et al 2009, Gouin et al 2005, Butt et al., 2004)

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