Long term trends in PBDE concentrations in gannet (*Morus bassanus*) eggs from two UK colonies

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Ailsa Craig

Bass Rock

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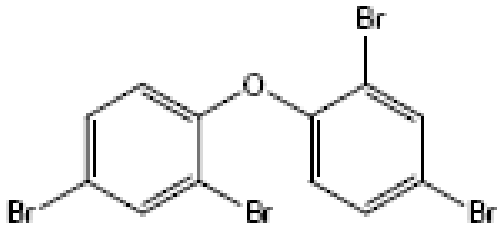
Overview

- What are PBDEs?
- Why should we study them?
- Pathways into the environment
- The gannet as a sentinel species
- Results
  - Spatial trends
  - Temporal trends
  - Toxicity



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

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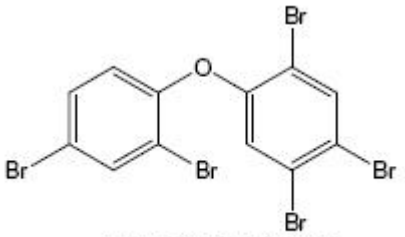
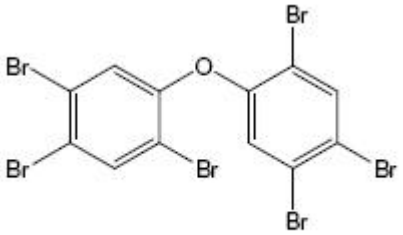
PBDEs



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

- Additive flame retardants
- Similar chemical structure to PCBs
- Used in high impact plastics, textiles, furniture foam
  - Not chemically bonded to the products they are incorporated into
  - Can dissociate out when exposed to light and heat
  - Releasing non-combustable gasses that dilute flammable gases and scavenge free radicals
- Release to environment from product manufacture, use, disposal

Congeners and formulations

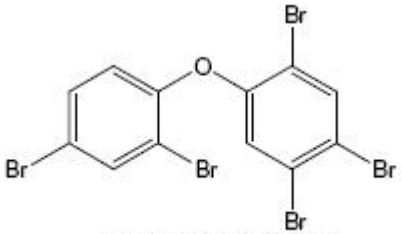


BDE153 (2,2',4,4',5,5'-)

- 209 theoretical congeners
  - Varying degrees of bromination
  - Different chemical properties
  - Environmentally relevant congeners: 28, 47, 99, 100, 153, 154, 183, 197, 209
- Technical products utilise a mixture of congeners
  - Often reported in the environment with reference to these formulations
  - PeBDE (BDEs 99, 47)
  - OBDE (BDE183)
  - DeBDE (BDE209)
- Naturally occurring methoxylated and hydroxylated PBDEs
  - OH/MePBDEs metabolytes

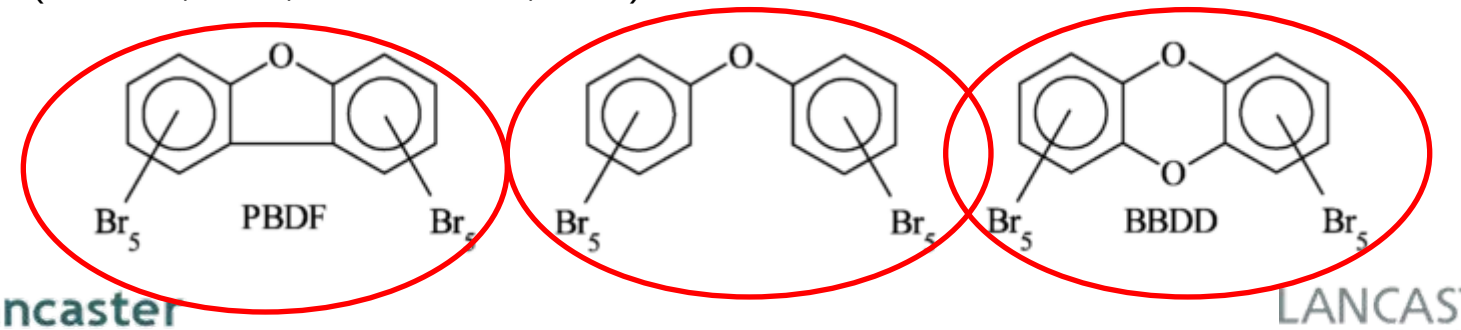
Why should we care?

- Ubiquitous and persistent organic pollutants
  - Lipophilic
  - Bioaccumulative
  - Low aqueous solubility
  - Long range transport



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

- Evidence of toxicity in wildlife
  - Rats, chickens, fish, birds of prey, humans
  - Hormone metabolism – T4, AhR, CYP450
- Formation of PBDDs and PBDFs
  - (US EPA, 2006,Rahman et al., 2001)



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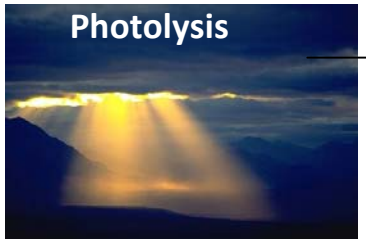
Legislation

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

- Penta and Octa BDE mixtures now ‘banned’
  - Germany 1986
  - Scandinavia 1990s
  - US and Europe 2004
- 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
  - Scheduled to be banned in US by 2013
- All formulations still in circulation in consumer goods

Cycling of PBDEs



Wet & dry Deposition

Agricultural Soils

Shipping / Drilling

Volatile/ particulate emissions/dust

Consumption & metabolism by plants & animals

Commercial products

Production /incorporation into consumables

Consumption and metabolism by humans

Water courses

Industrial effluents

Target organism for biomonitoring

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Gannets as Biomonitoring tools

- Why use gannets?
  - High trophic position
  - Discreet colonies
  - Lay one egg per year
  - Low capacity for xenobiotic metabolism (Walker & Knight 1981)

- Why use eggs?
  - Consistent media
  - Easy to collect
  - Long running archive 1977-present
  - Good accumulators of lipophilic contaminants
  - Integrated sentinel – more representative of the ecosystem as a whole

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Study aims

- Rationale
  - Few detailed temporal trends for PBDEs
  - No long term trends for UK wildlife

- Specific aims
  - Temporal trends
    - PBDE concentration
    - PBDE congener profile
  - Spatial trends

- Toxicity
  - Shell thickness
- Methodology
  - Egg extracts analysed by GC-MS
  - 5 eggs per year, per colony for 10 years (1977-2007)

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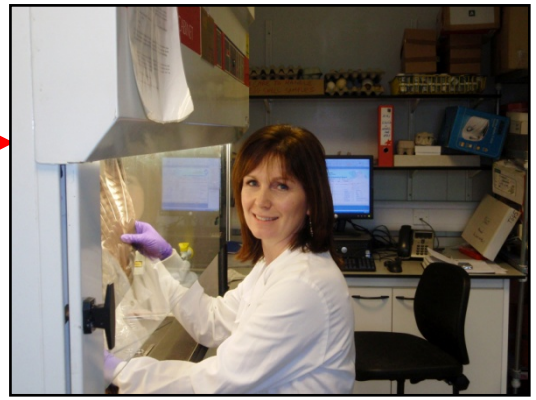
Predatory bird monitoring scheme

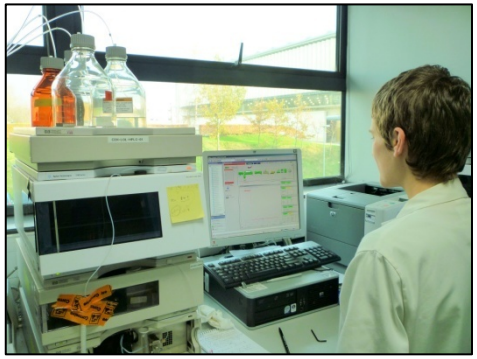


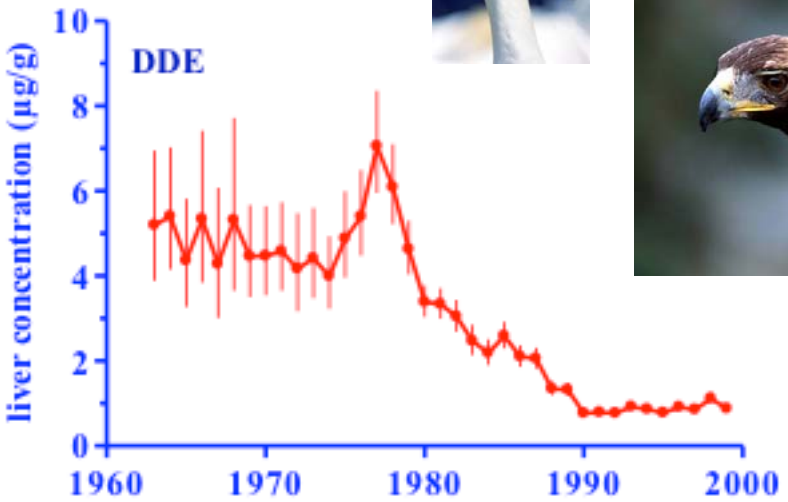
Volunteer

PM examination

Sample archive

Chemical analysis





Data analysis

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CEH Centre for Ecology & Hydrology
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Results

- Spatial trends
  - PBDE concentrations in eggs did not differ between colonies except in one year (1977)

- Congener profile
  - BDE 47 dominant congener
  - BDE 35, 47, 49, 99, 100, 153, 154 present in all eggs (major congeners)
  - All major congeners except BDE35 components of PeBDE technical formula
  - All major congener concentrations correlated with ΣPBDE concentrations ($p<0.000$) [BDE35, $p<0.05$]

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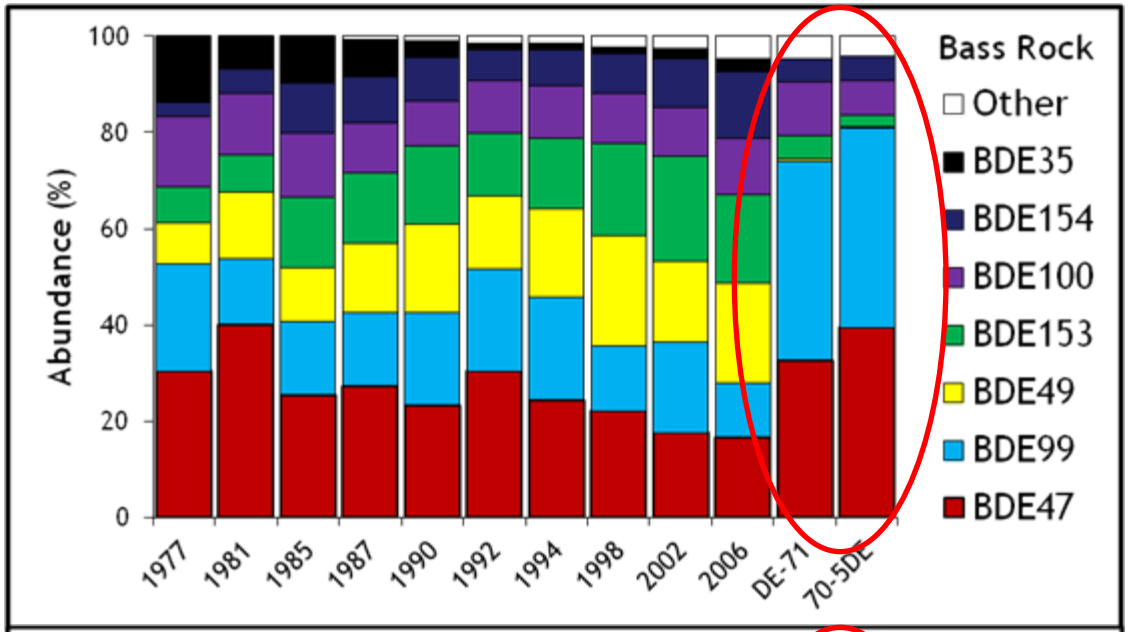
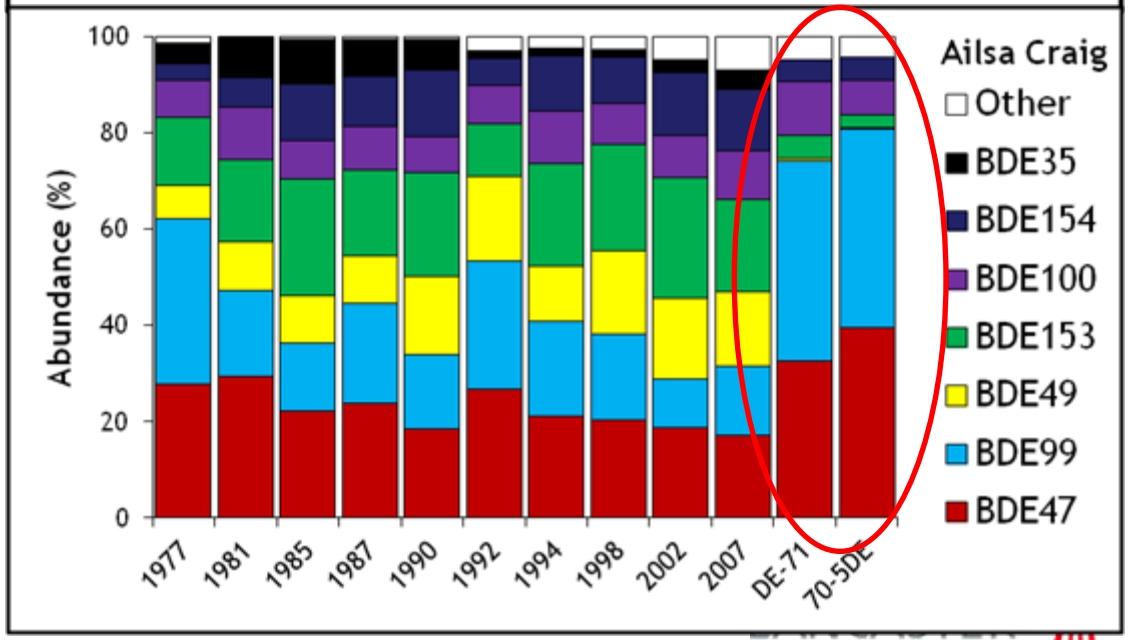
Congener profile

- Egg PBDE profile similar to technical mixture profile

- Elevated levels of BDE49 and depleted BDE99 are indicative of metablolism [by fish]





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Temporal trends

- Temporal trends did not differ significantly between colonies
- Total concentrations:
  - 12.9-66.8 ng/g (Bass)
  - 6.3-60.8 ng/g (Ailsa)
  - Levels within the range seen for other EU birds

- Concentrations of major congeners and Σ PBDE exhibited very similar trend
  - BDE35 exhibited a linear decline (R^2=0.855, $F_{2, 17}$=50.27, P<0.001)
- Significant increase in Σ PBDE between 1980s and 1994 (P<0.001)
  - 1994 peak year
- Significant decline between 1994 and 2006/7 (P<0.001)
  - Similar or less than 1970s levels

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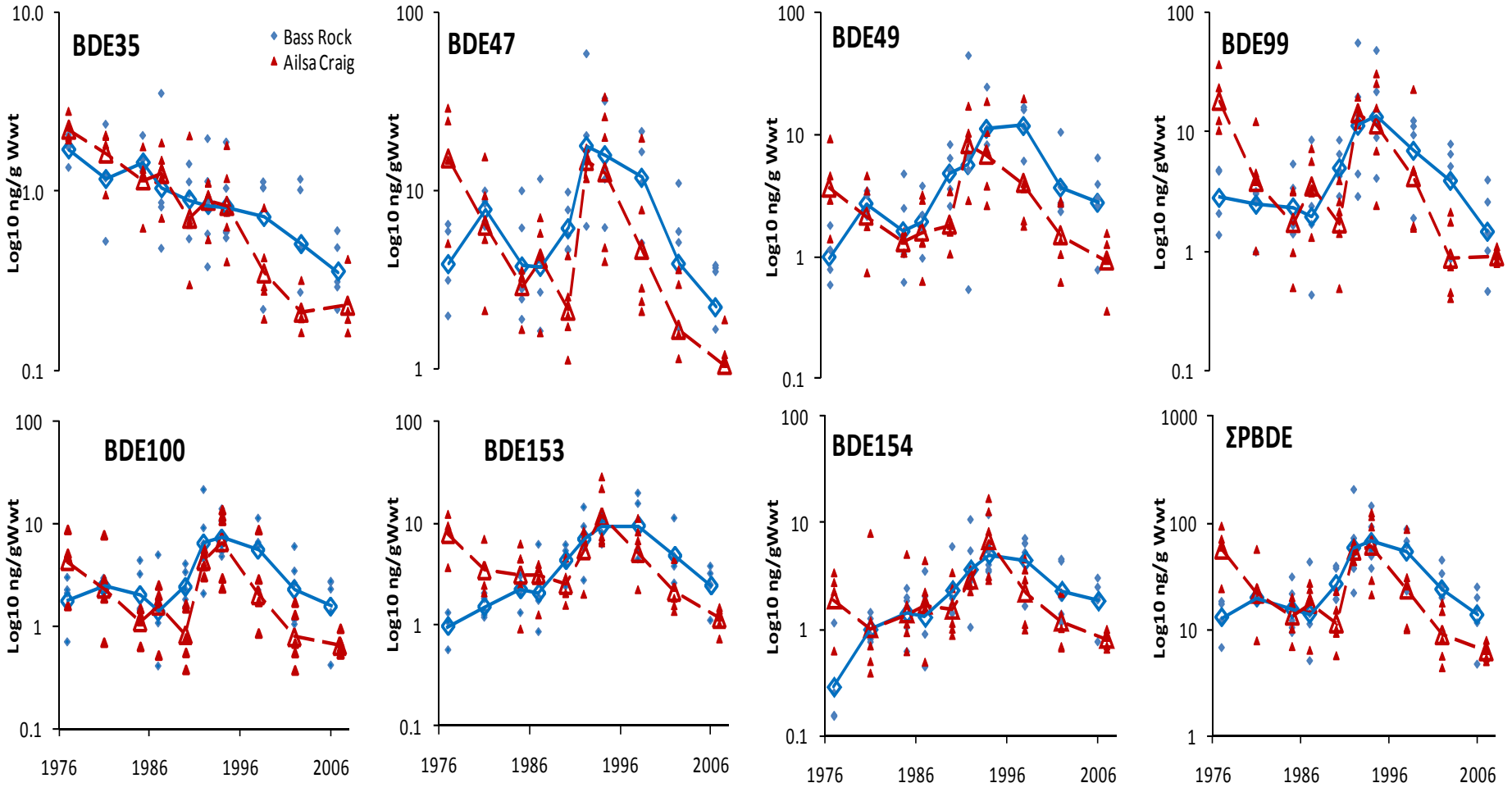
Temporal trends



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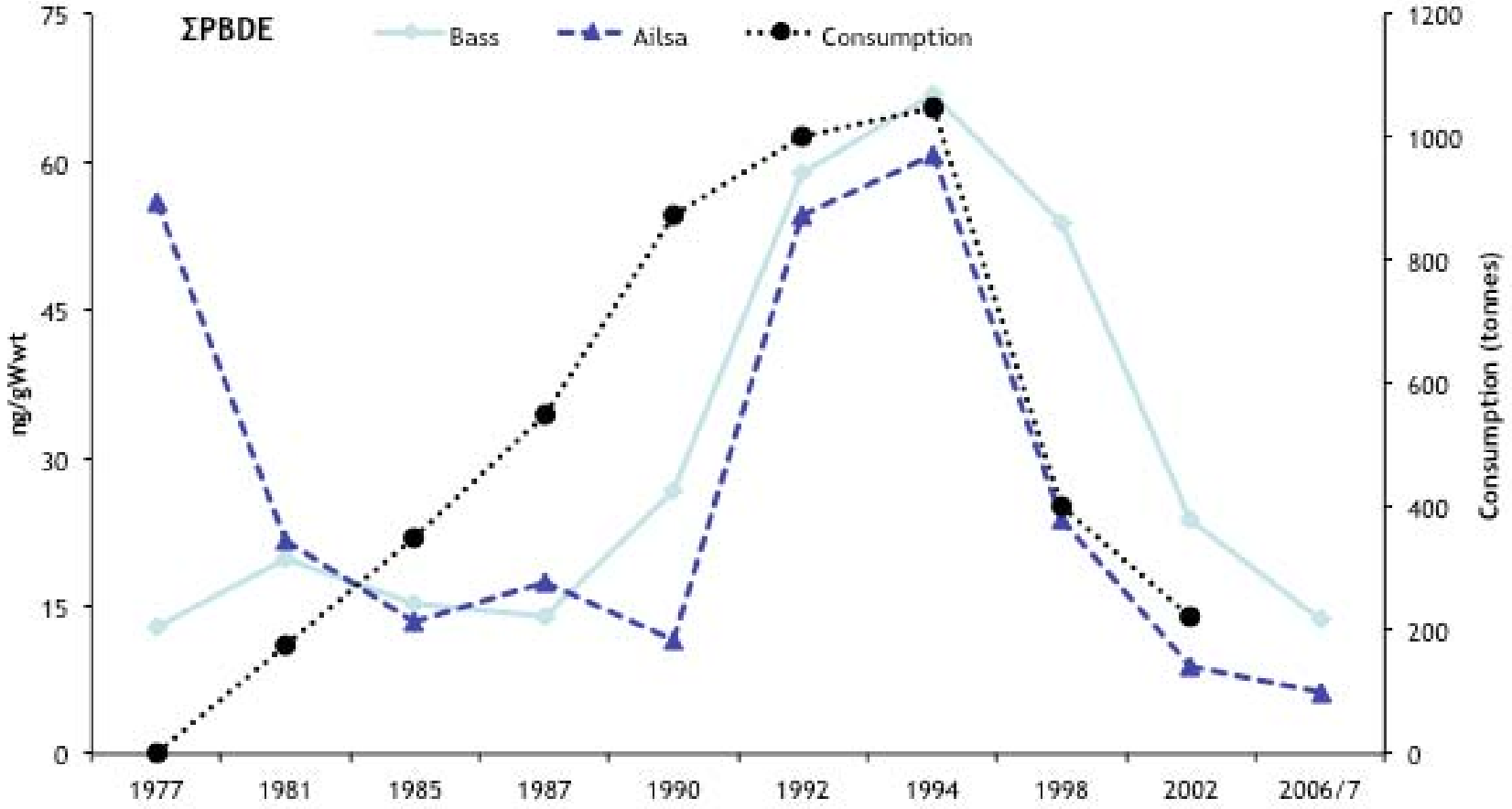
Temporal Trend in European PBDE consumption



Egg concentrations correspond well with consumption estimates

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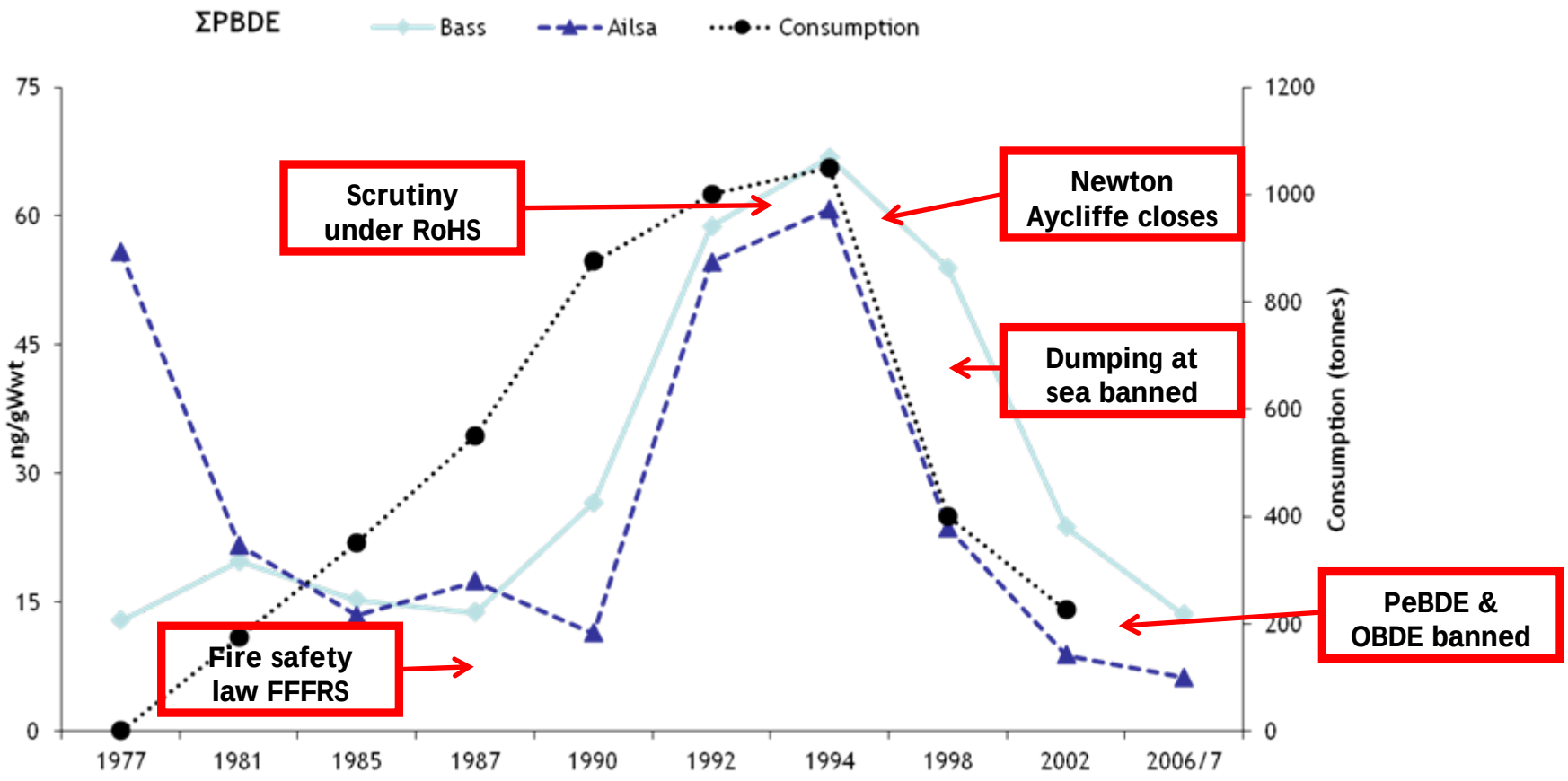
Factors affecting consumption in the UK



Environmental concentrations respond rapidly to legislative drivers

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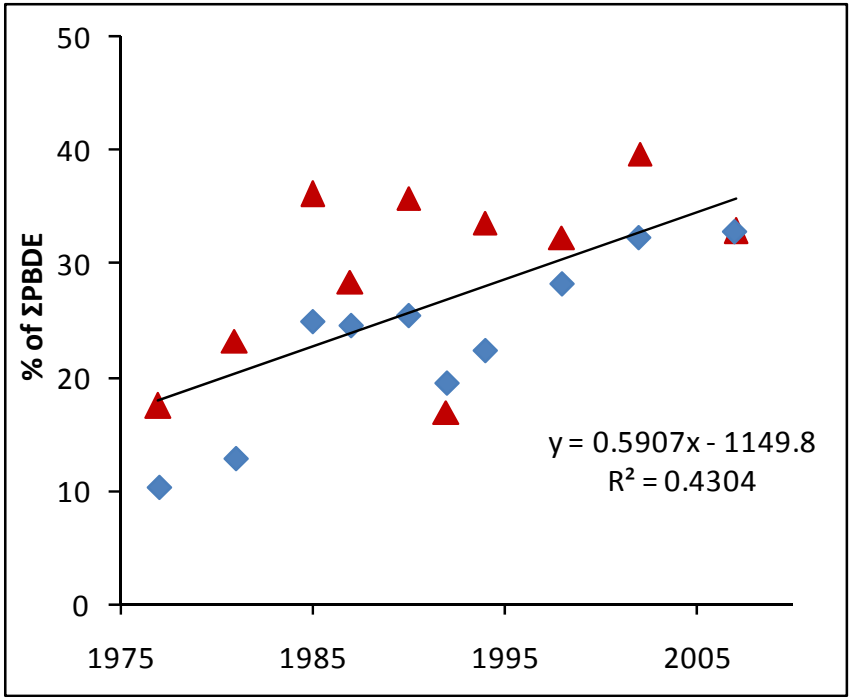
Congener patterns and temporal trends

- Proportion of more highly brominated congeners increased linearly (R^2=0.43, $F_{2,17}$=4.09, P<0.05)
  - An increase of 10-20%
  - BDEs 153, 154, 183



- May be due to debromination of current use DeBDE

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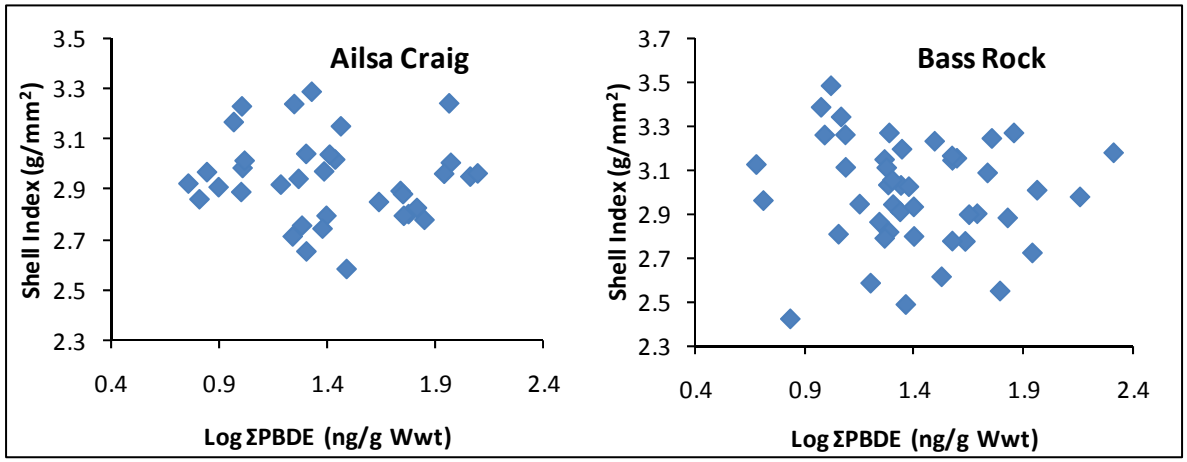
Toxicity

- Gannets have be shown to be susceptible to shell thinning caused by DDE (Elliot et al., 1988; Cooke et al., 1979)
- PBDEs reported to be associated with shell thinning and impaired reproductive success in other birds of prey (Fernie et al., 2009: Henny et al., 2009)



- No evidence of shell thinning in gannet eggs related to PBDEs ($R^2 \leq 2.41$, $F \leq 0.96$, $P > 0.05$)
  - Levels generally lower than other studies

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Summary

- Concentrations in gannet eggs represent environmental concentrations during the breeding season
  - Can infer magnitudinal changes
- Dominated by PeBDE mix congeners
  - BDE47
  - Evidence of environmental degradation
- Proportion of heavy BDEs increasing
  - Possible debromination of DeBDE

- Temporal trends may be directly related to consumption
  - Rapid environmental response
- No obvious effect on gannet reproduction or numbers

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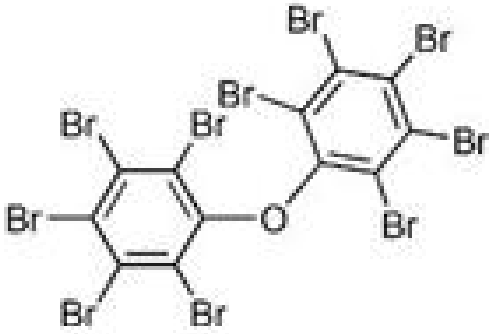
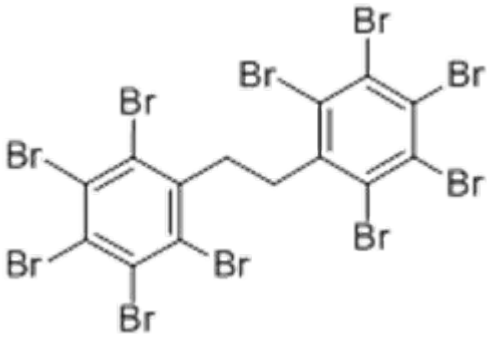
What's next?

- DeBDE will eventually be banned
  - New flame retardants already on the market
  - DecaBromoDiphenyl*Ethane*
  - Replacement for DecaBromoDiphenyl*Ether* (DeBDE)



DeBDE (209)



DBDPE

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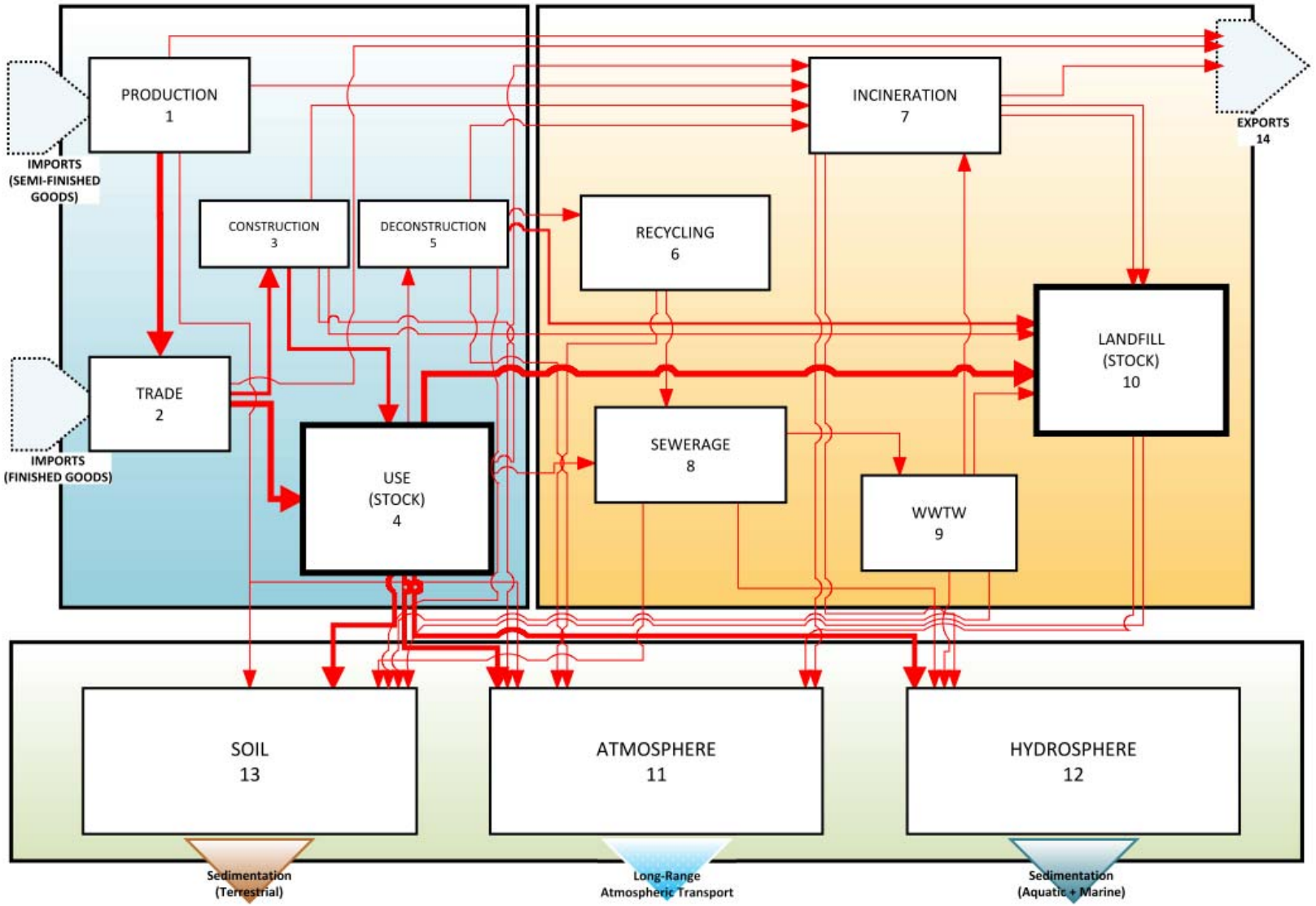
Substance Flow Analysis model for Deca



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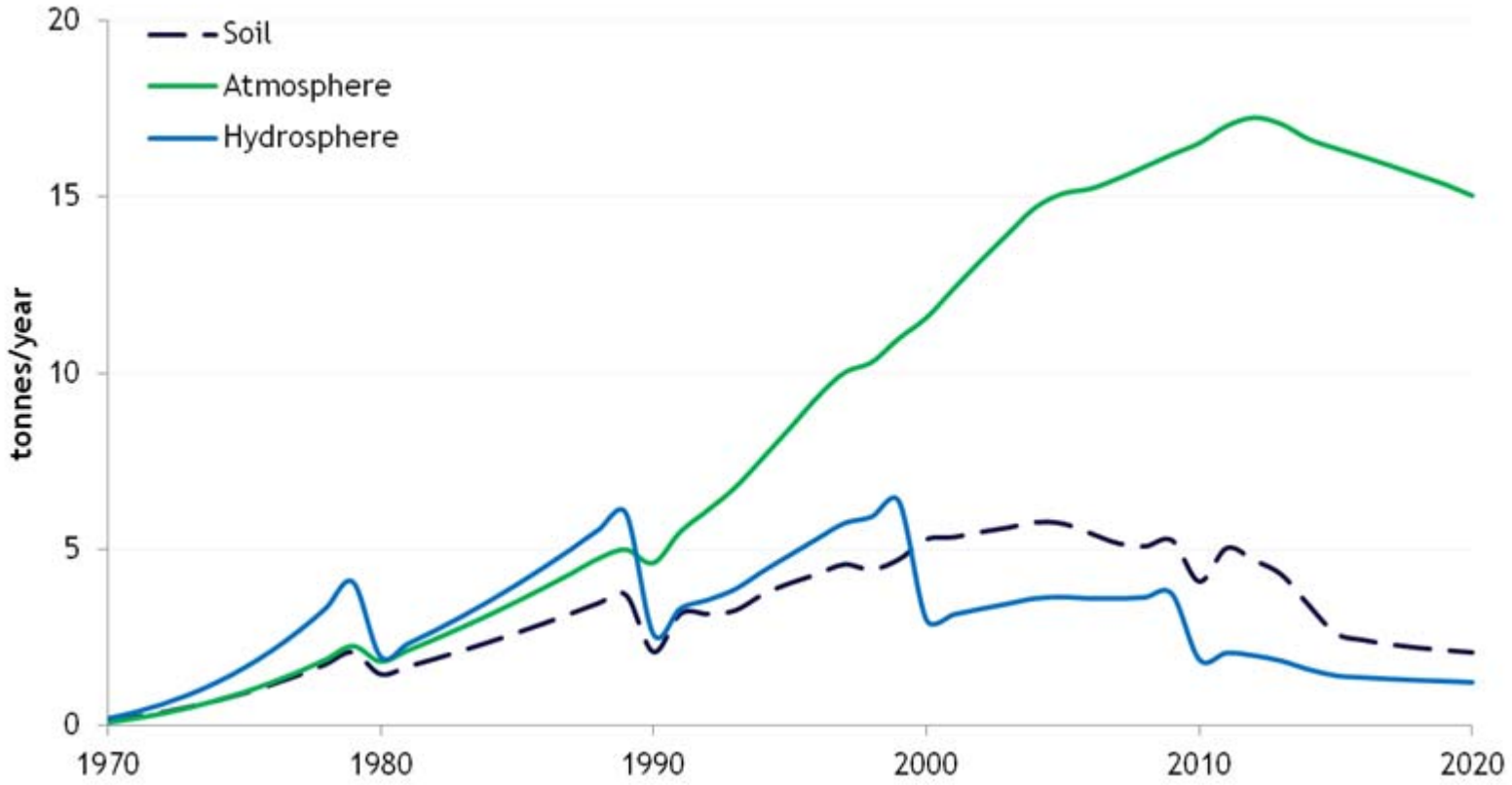
Estimated Environmental Emissions



- Atmospheric emissions of BDE-209 will peak sometime in the current decade and decline thereafter as the “stock” in use declines
- Emissions to Soil and the Hydrosphere have remained relatively stable due to advances in waste management technology

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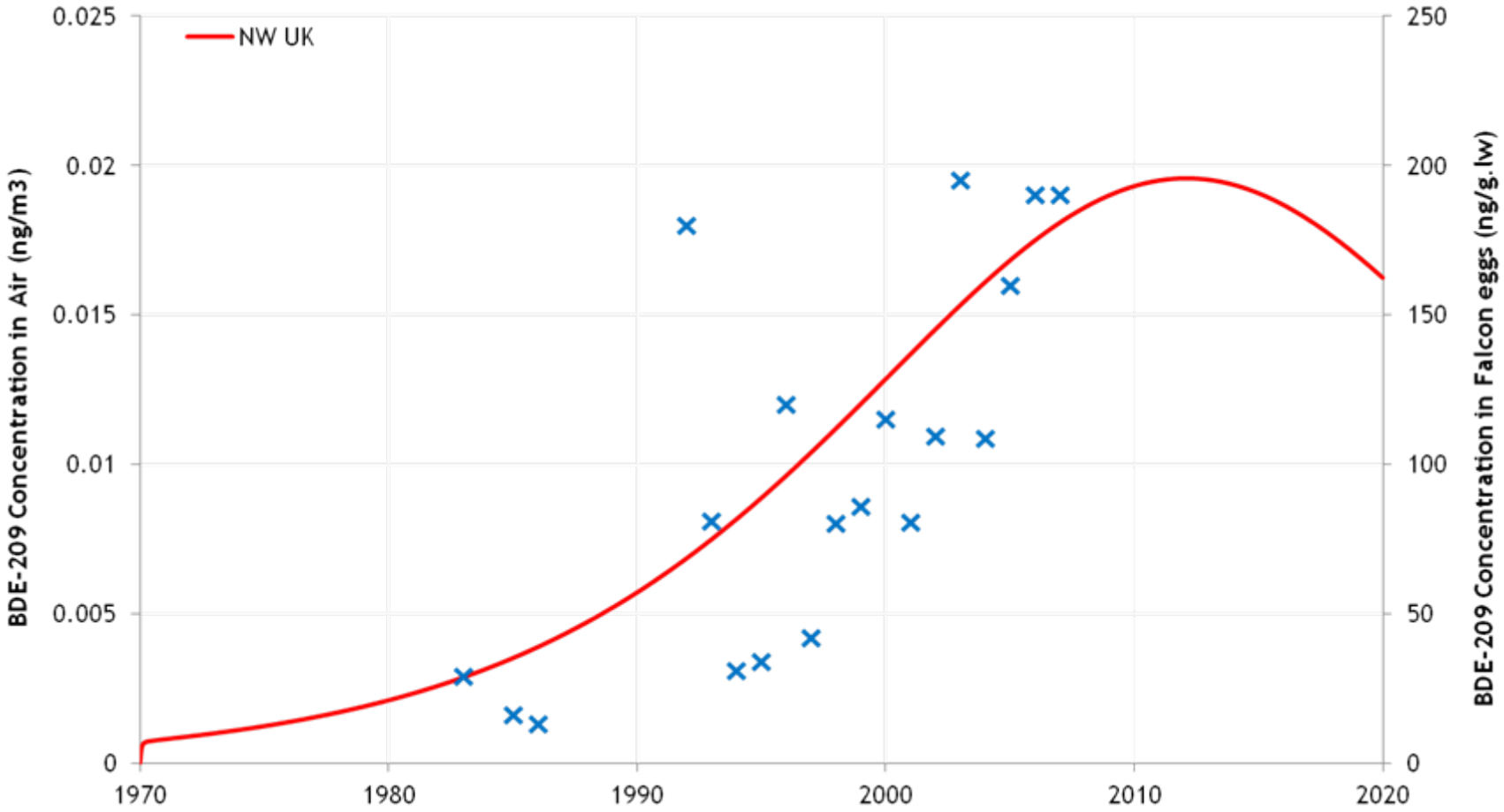
Predicted BDE-209 Atmospheric Concentrations (ng/m^3) compared with Measured Concentrations in Swedish Peregrine Falcon Eggs (ng/g.lw)



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Acknowledgements

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  - CEH
  - Natural England
  - RSPB
  - EA
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  - Dave Hughes and Lee Walker

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