Trends in HBCD concentrations in the blubber of porpoises from the UK

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OSPAR hazardous substances strategy

- "*Concentrations of man-made chemicals in the environment should be zero or close to zero*"
- marine mammals are top predators in marine food chains and so accumulate lipophilic chemicals
- contaminants can have effects (PCBs)
- make good sentinel organisms for assessment

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Cetacean Strandings Investigation Programme

- Defra-funded since 1990
- meets UK obligations within ASCOBANS
- provides tissue samples from cetaceans UK-wide
- Cefas undertakes contaminant analysis
- Common (harbour) porpoise major species studied

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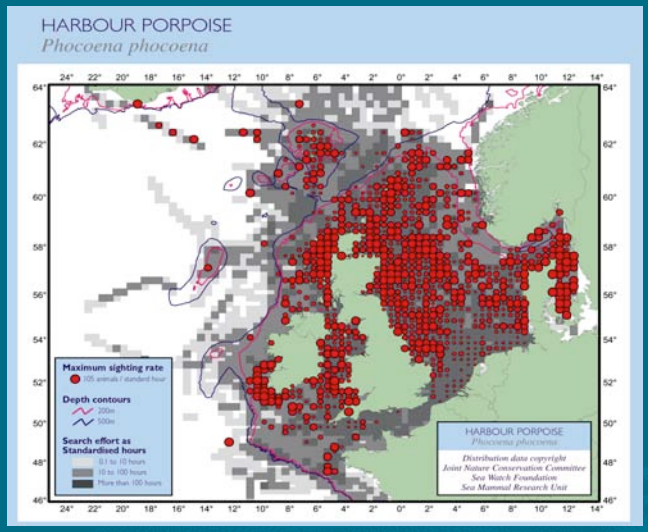
Common (Harbour) porpoise



- small cetacean, adults 1.4 – 1.7 m in length
- bottom feeder, eating small schooling fish (such as herring, anchovy, whiting, sandeels)
- mature at 3 – 4 years, few live beyond 9 years

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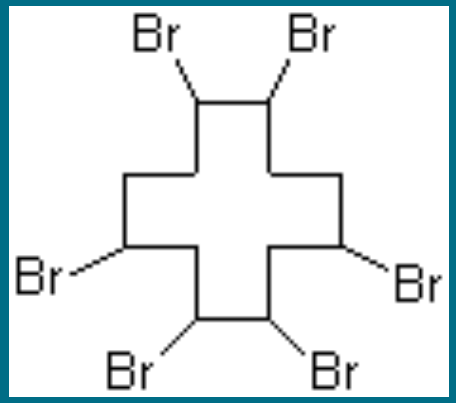
Hexabromocyclododecane



www.chemBlink.com

- HBCD is an additive flame retardant
- used in building insulation, textiles and electronics
- in 2001, World demand 16,700 tonnes with 9,500 tonnes used in Europe
- second highest volume BFR in Europe

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Properties

- molecular weight 641.7 Daltons
- log Kow 5.62, so bioaccumulative
- typical technical mixture mainly γ-HBCD (70-95%), β-HBCD and α-HBCD (5-30%)
- HBCD is not readily biodegradable
- diastereoisomers are chiral, exist as + & - enantiomers (16 theoretical stereoisomers)
- undergoes long-range atmospheric transport

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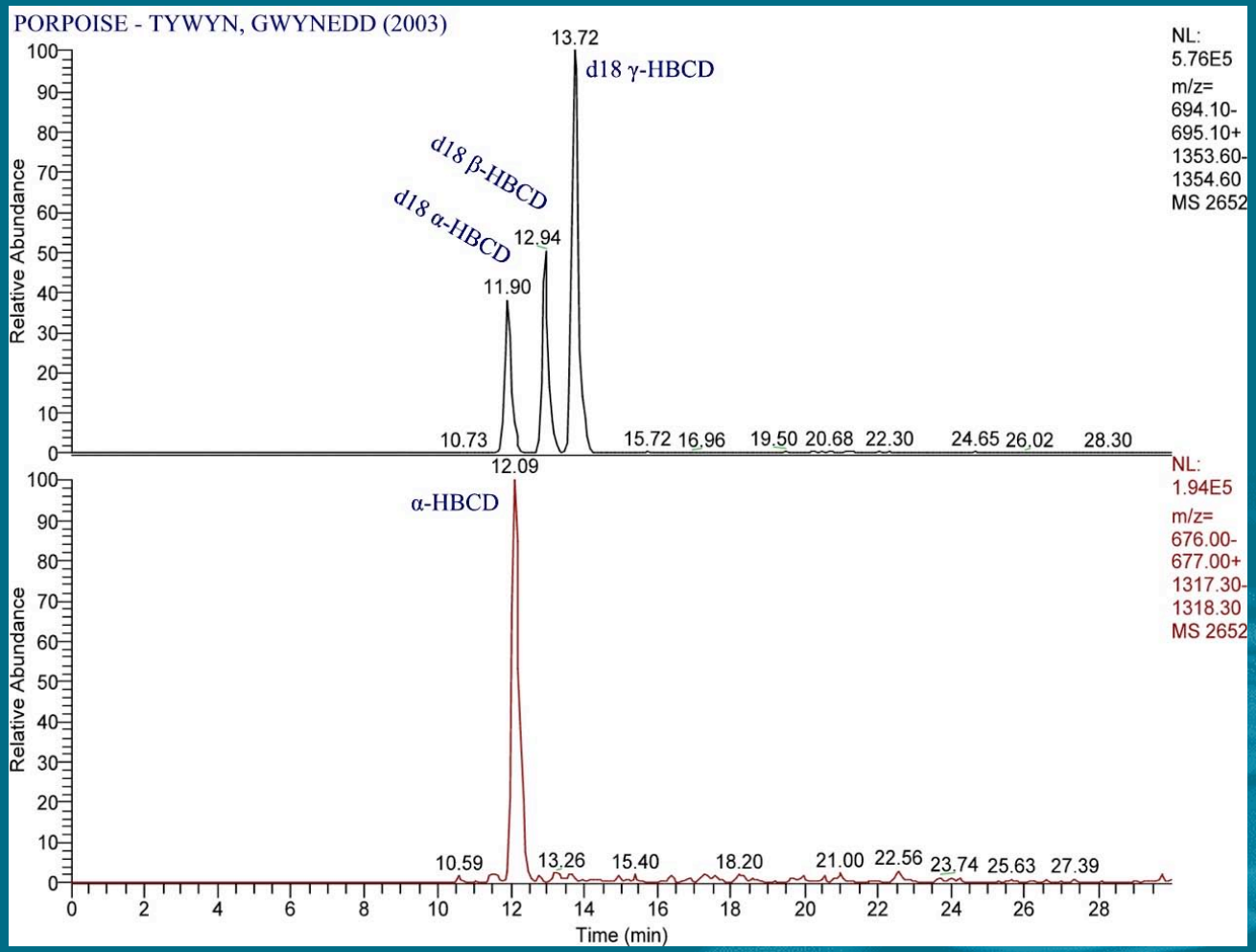
LC-MS analysis



LC-MS/MS analysis

- LC-MS used quantitatively
- Soxhlet extraction acetone/n-hexane, GPC clean-up followed by sulphuric acid treatment
- final extract transferred to methanol
- LC-MS in electrospray negative ionisation mode, quantification using deuterated ISs
- LC-MS/MS used qualitatively for confirmation
- two transitions 676.7 → 640.7, 1318.2 → 676.7

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Analytical Quality Control

- procedural blanks and reference materials within each batch – accept/reject
- no CRMs – spiked cod muscle LRM used
- quality control charts plotted
- successful participation in QUASIMEME and NIST interlaboratory proficiency tests
- need for more CRMs, and for more interlaboratory exercises & Laboratory Proficiency Schemes to include HBCD

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Initial time trend assessment

- porpoises stranded or bycaught 1994 – 2003 (n = 85) – HBCD on a lipid basis
- assessed using nonparametric statistics
- null hypothesis of no trend
- also investigated possible confounding factors (age, sex, area, death from trauma or infectious disease, nutritional status)

Law *et al*. Environmental Science and Technology 40, 2177-2183, 2006

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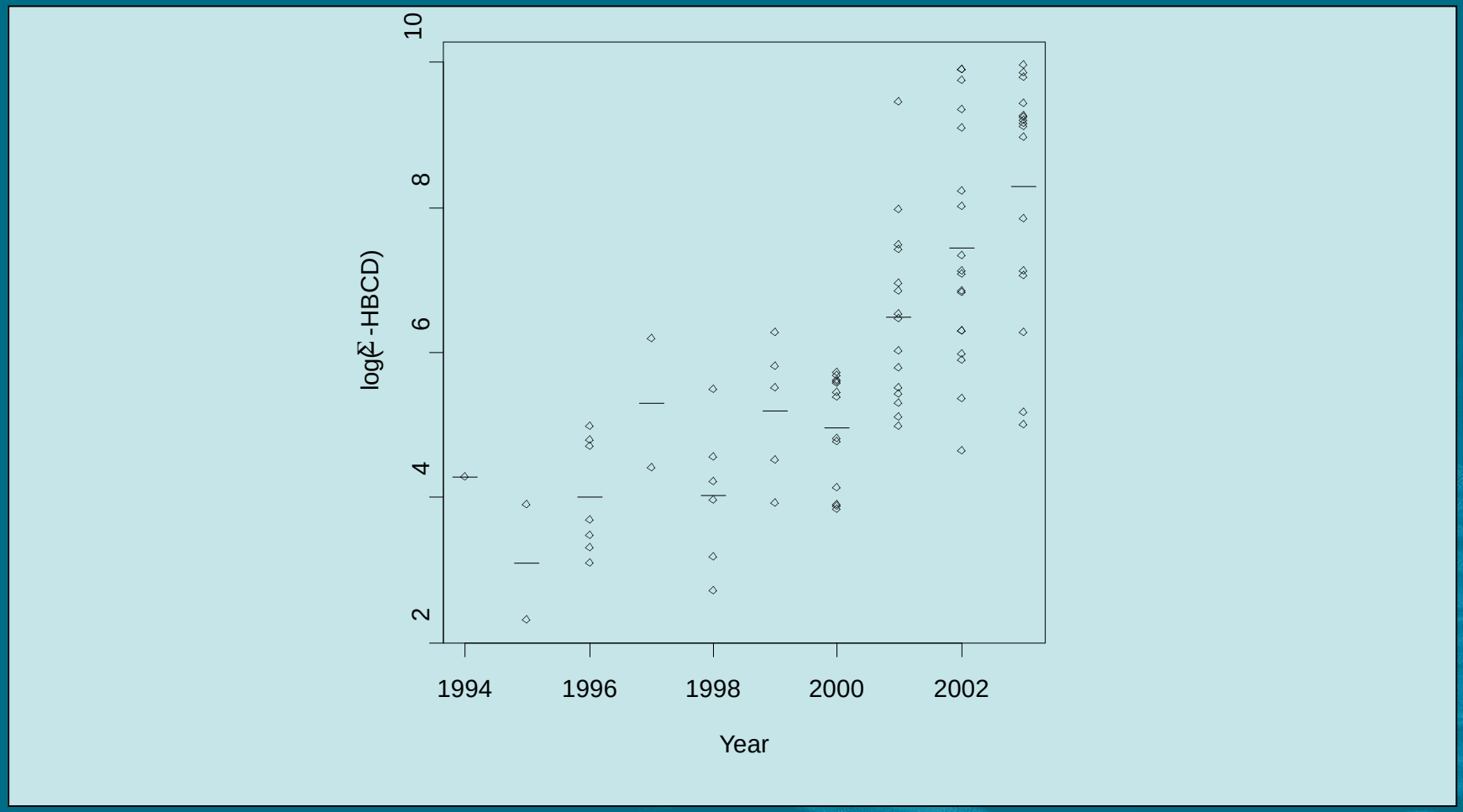
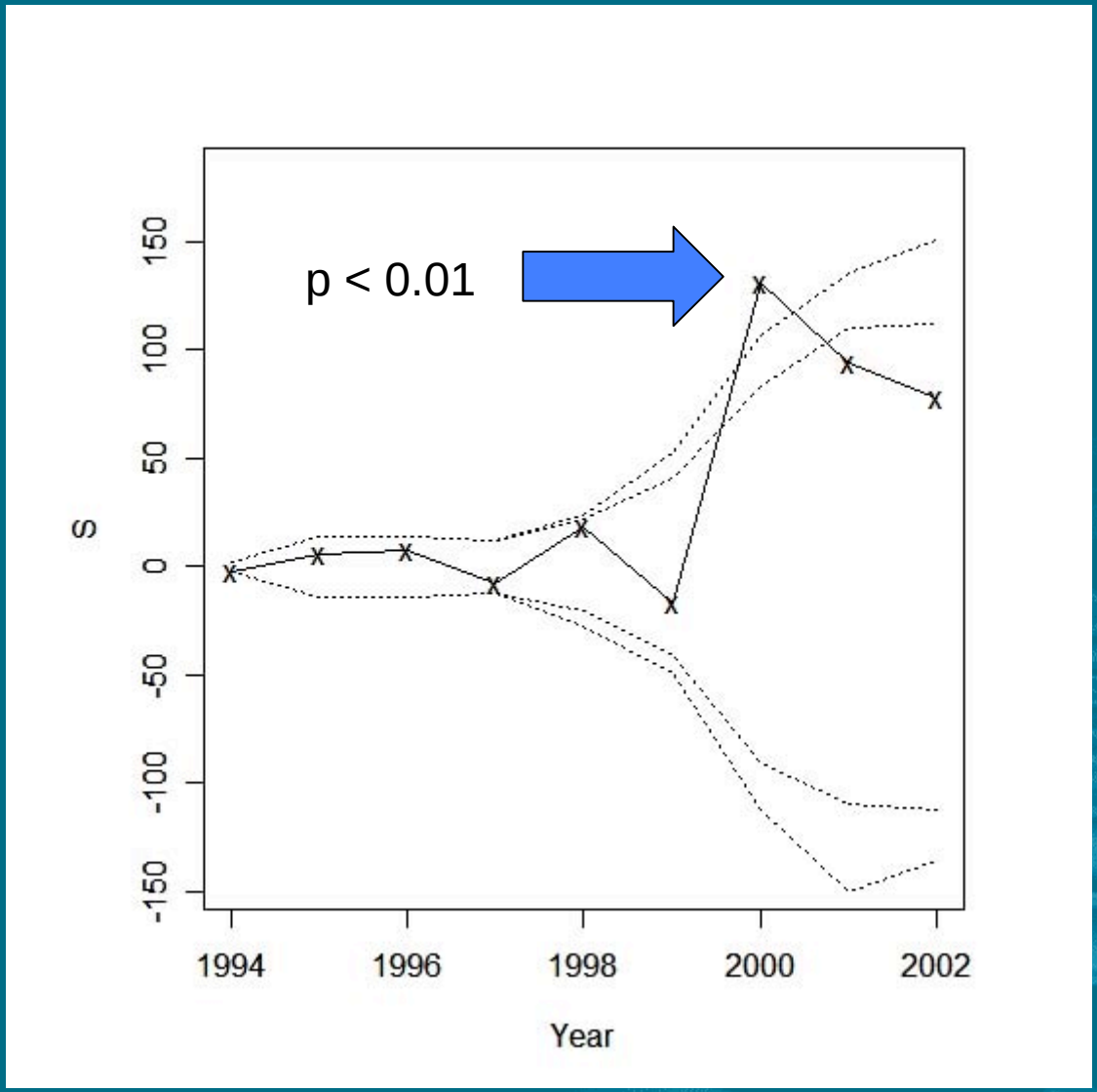
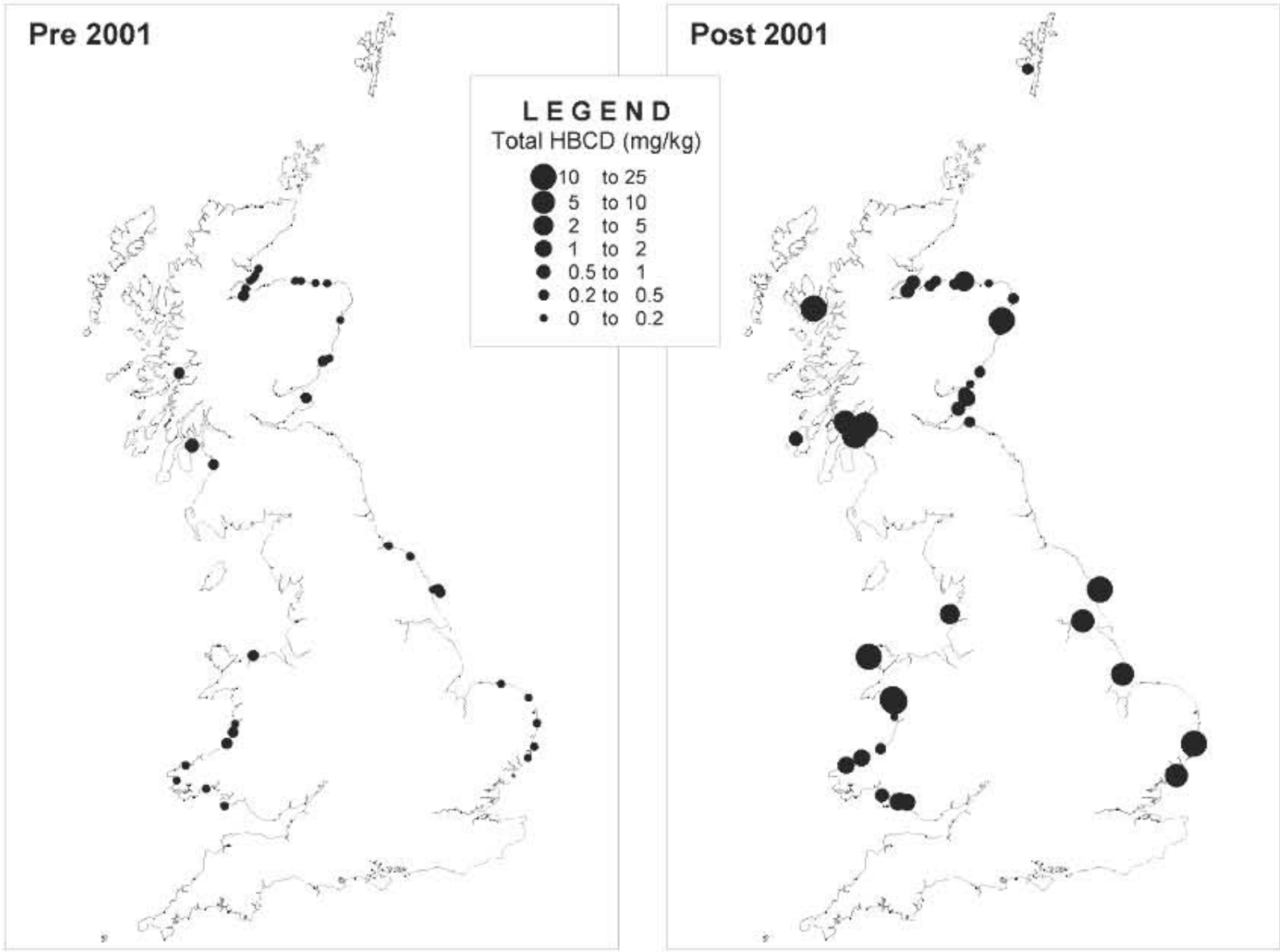
log(Σ-HBCD) vs Year



Is the time trend significant ?




Pre 2001
Post 2001
LEGEND
Total HBCD (mg/kg)
10 to 25
5 to 10
2 to 5
1 to 2
0.5 to 1
0.2 to 0.5
0 to 0.2

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Trends elsewhere

- almost exponential increase in HBCD concentrations in male US sea lions 1993 – 2003 (n = 25)
- doubling time = ~ 2 years

Stapleton *et al*. Marine Pollution Bulletin 52, 522–531, 2006

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Second time trend study

- porpoises stranded or bycaught 1994 – 2006 (n = 223) – HBCD on a lipid basis
- assessed using nonparametric statistics
- null hypothesis of no trend
- also investigated possible confounding factors (age, sex, area, death from trauma or infectious disease, nutritional status)

Law *et al*. Environmental Science and Technology 42, 9104-9109, 2008

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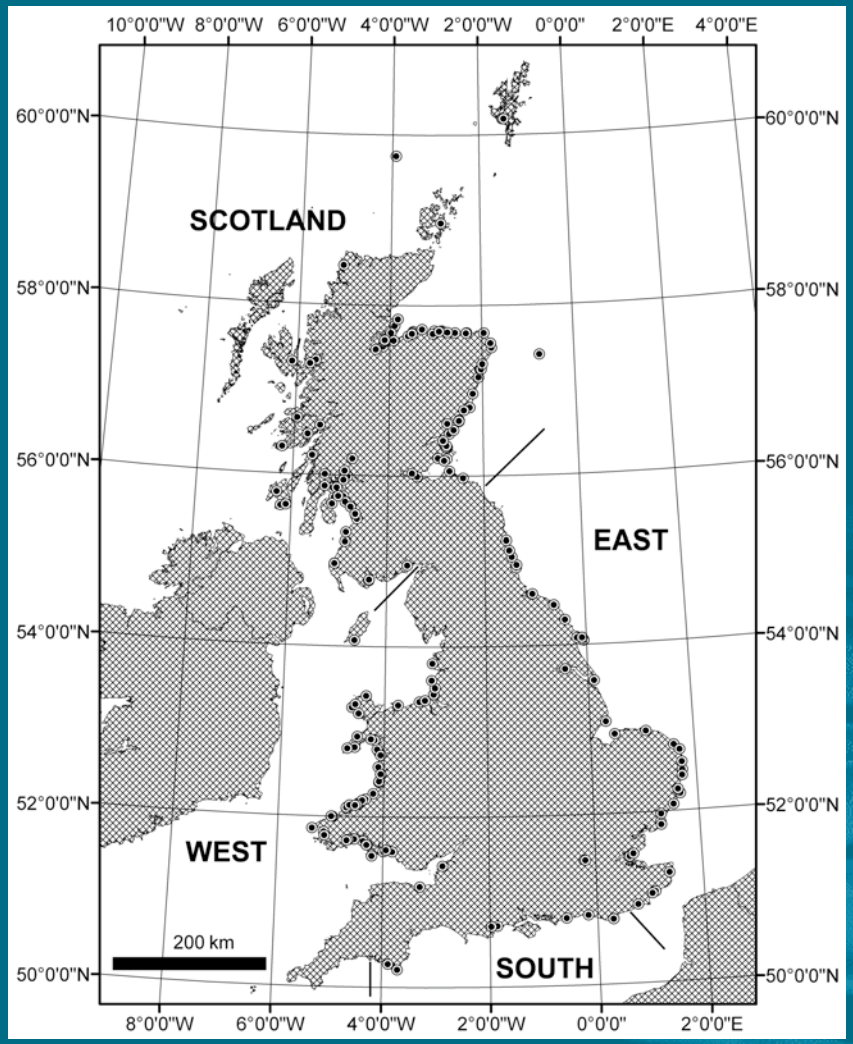
Sampling locations



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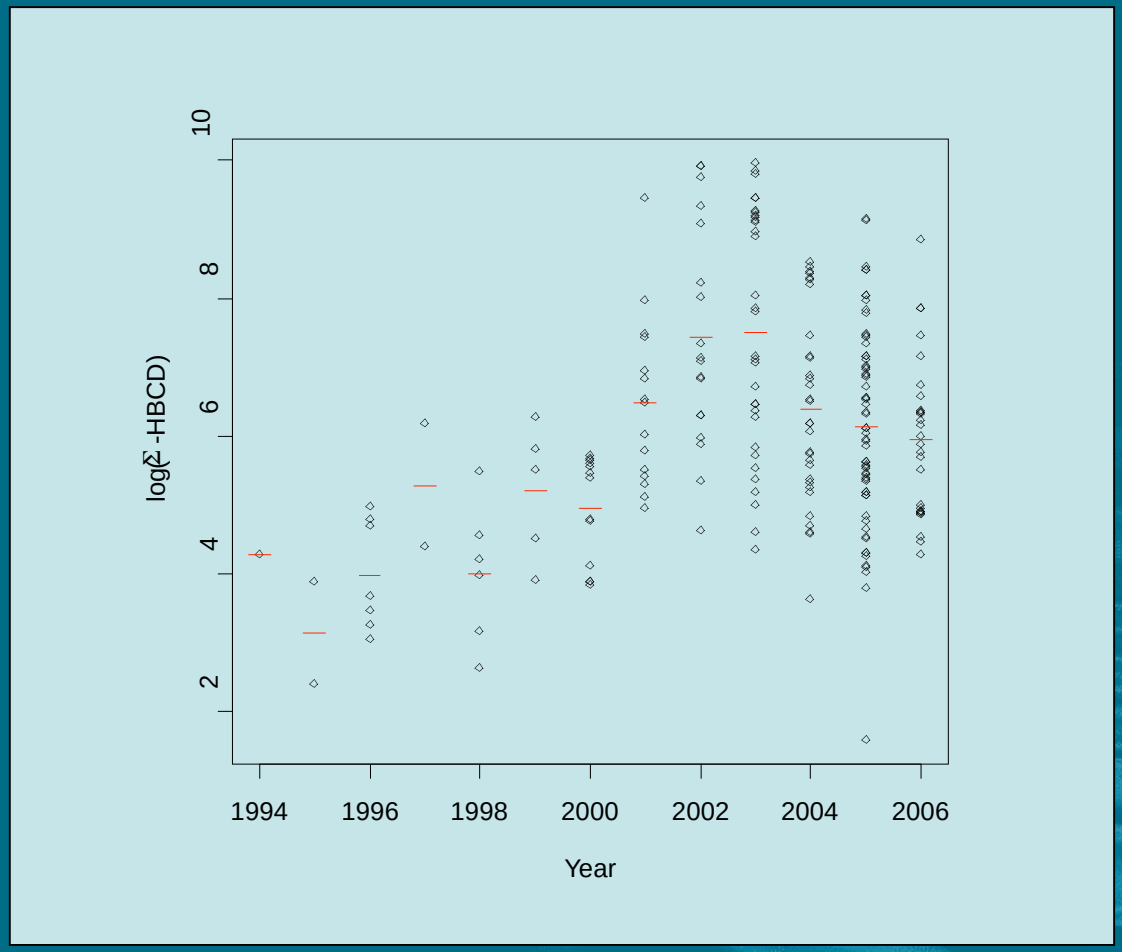
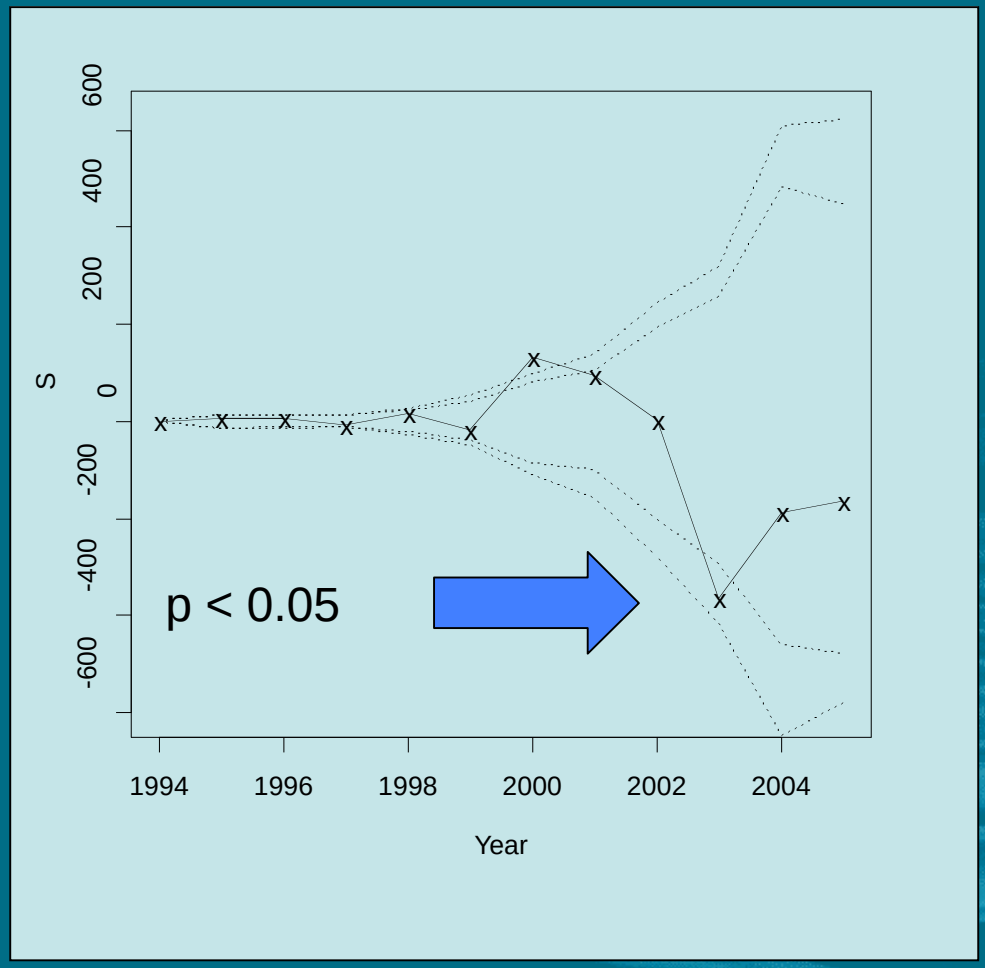
log(Σ-HBCD) vs Year



Is the time trend significant ?



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Summary

- HBCD concentrations showed a steep rise from 2000/2001, then a decrease from 2003
- highest concentration 21.3 mg/kg lipid weight in a porpoise bycaught in 2003 off Bridlington in NE England

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HBCD concentrations

porpoise	Ireland 2001-2003	9.6 mg/kg lw
white-sided dolphin	MA, USA 1993-2004	0.38 mg/kg lw
finless porpoise	China 1990	0.037 mg/kg lw
finless porpoise	Hong Kong 2000-2001	0.055 mg/kg lw
striped dolphin	Japan 2003	0.94 mg/kg lw
porpoise	This study 2003	21.3 mg/kg lw

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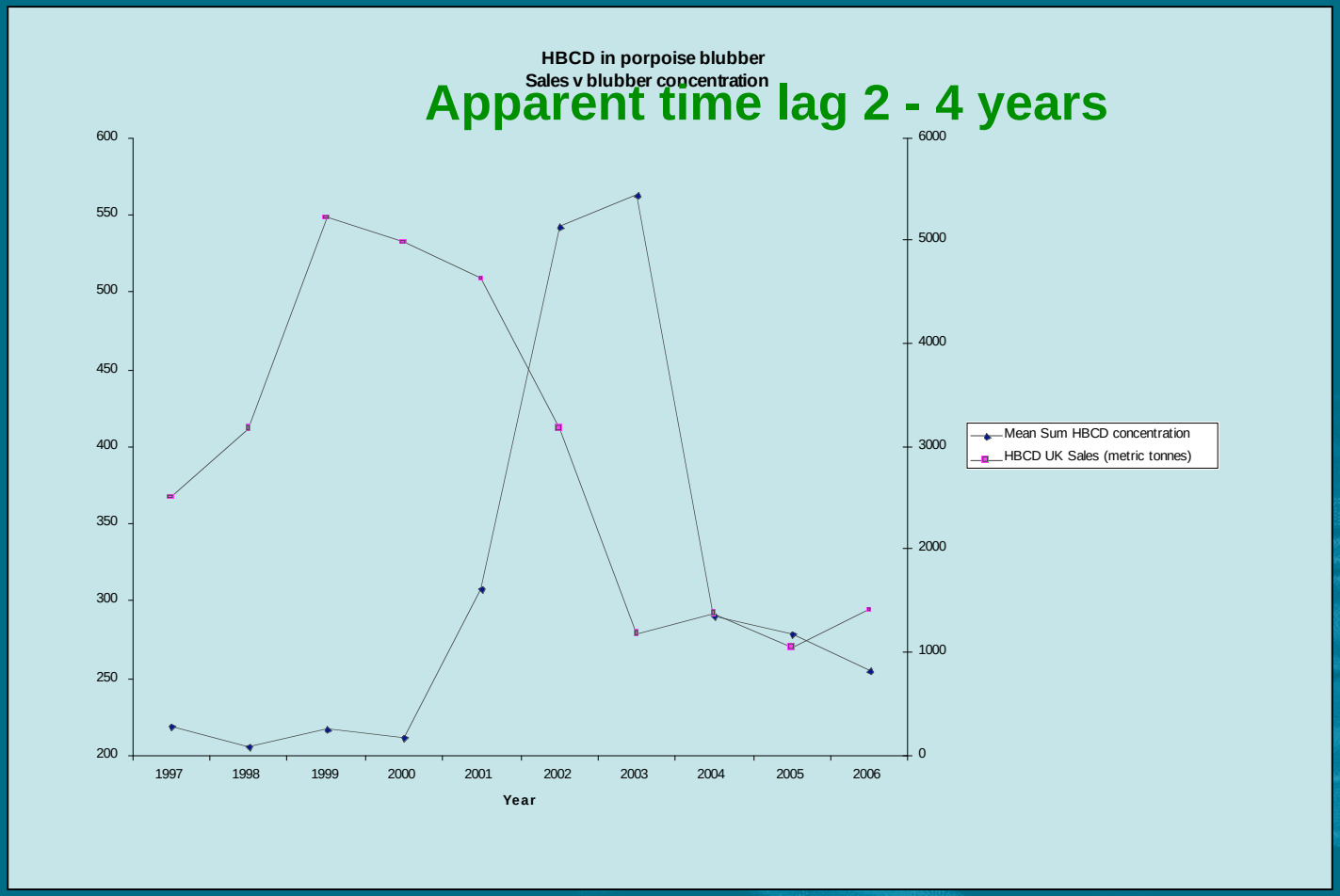
HBCD sales data



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Why the decline ?

Possible contributory factors:

- closure of HBCD manufacturing site in NE England in 2003 (largest single source of environmental HBCD – EU HBCD risk assessment)
- closure of expanded polystyrene manufacturing site in NW England in 2002
- bromine industry initiatives intended to reduce emissions ?

Bromine industry initiatives

- VECAP – Voluntary Emissions Control Action Programme for BFRs
- SECURE – Self Enforced Control of Use to Reduce Emissions
- VECAP has reduced emissions of deca-mix PBDE formulation from UK textile industry by 97% during 2002 – 2006
- no data for HBCD, but only began formally in the UK in 2006

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Further work

- apparent time lag of 2 – 4 years suggests food chain response is rapid
- HBCD is persistent and bioaccumulative, so rapidly eliminated or metabolised ?
- further monitoring work needed to confirm and to follow future trends
- expect concentrations to decline, and then plateau to reflect primarily diffuse inputs

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Future work on other BFRs

- investigate time trends in concentrations of BDEs in UK porpoises 1992 – 2008 (n = 415)
- from BFR2007 and Dioxin 2008, identified 13 “novel” BFRs for which no UK data exist
- using current GC-MS and LC-MS methods, can determine 10 of these
- undertake initial UK survey in porpoises and estuarine sediments – evaluate need for further work

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Thanks for your attention !

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