

BFRs IN MARINE MAMMALS FROM ARCTIC AND NORTH ATLANTIC REGIONS (1986-2009)



Pilot whale

FF1/3S09 – Photo: Paul Ensor

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Environment Agency and The Faroes museum of Natural History, The Faroe Islands

Biomonitoring of POPs

- Discover increases in background levels
- Support policy efforts
 - Stockholm Convention
- Evaluate the effectiveness of policy decisions
- Continuous monitoring
 - increase statistical power
 - delay in transport
 - replacement chemicals



Ringed seal



Guillemot

The Arctic – important indicator region for POPs



- Persistent
- Long-range transport

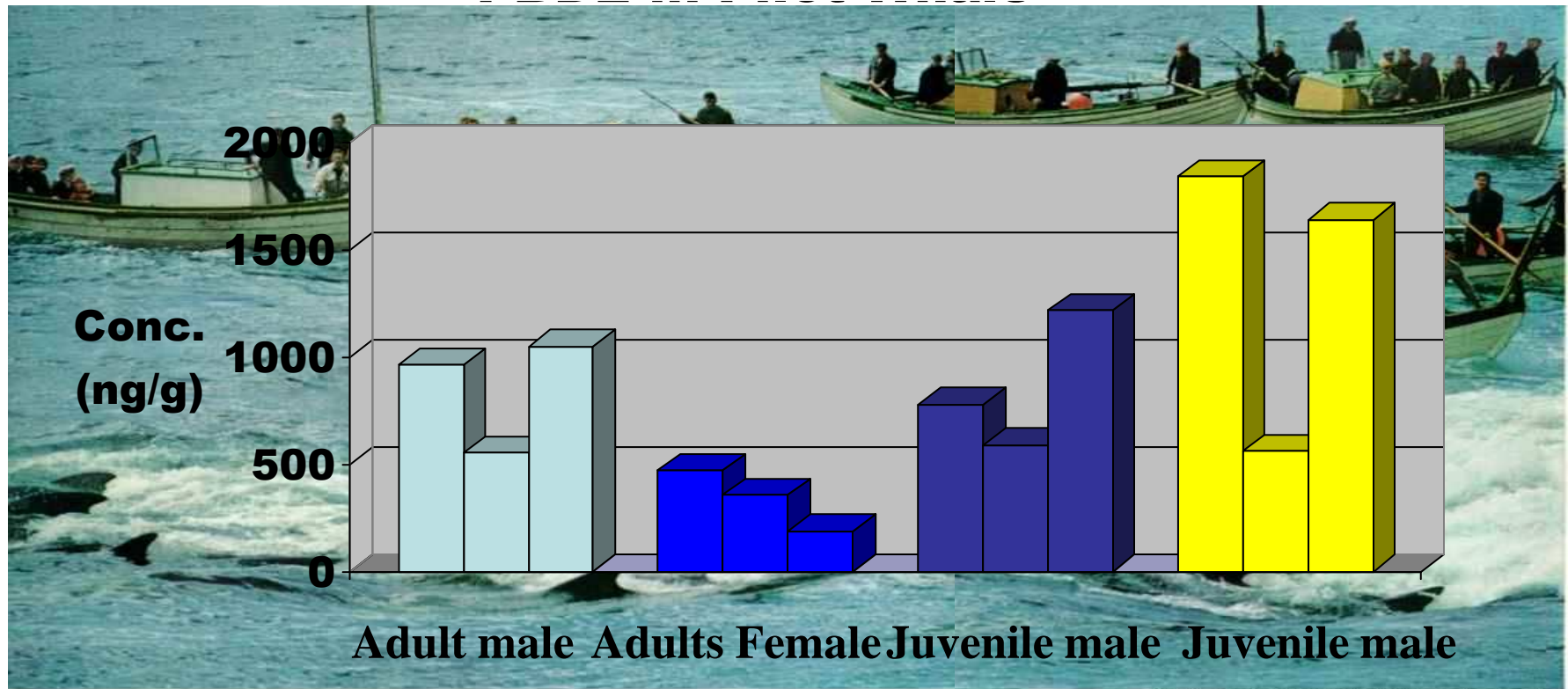


- Bioaccumulation
- Toxic



Stockholm Convention on persistent organic pollutants (POPs)

PBDEs in Pilot Whale 1995-96



At the same time

- PBDEs in Beluga or white whale
- Increasing levels in humans

Marine mammal species

- Arctic ringed seal (*Phoca hispida*)
- Hooded seal (*Cystophora cristata*)
- Long-finned pilot whale (*Globicephala melas*)
- Atlantic white-sided dolphin (*Lagenorhynchus acutus*)
- Harbour porpoise (*Phocoena phocoena*)
- Fin whale (*Balaenoptera physalus*)
- Minke whale (*Balaenoptera acutorostrata*)



Hooded seal



Ringed seal



White-sided dolphin



Harbour porpoise



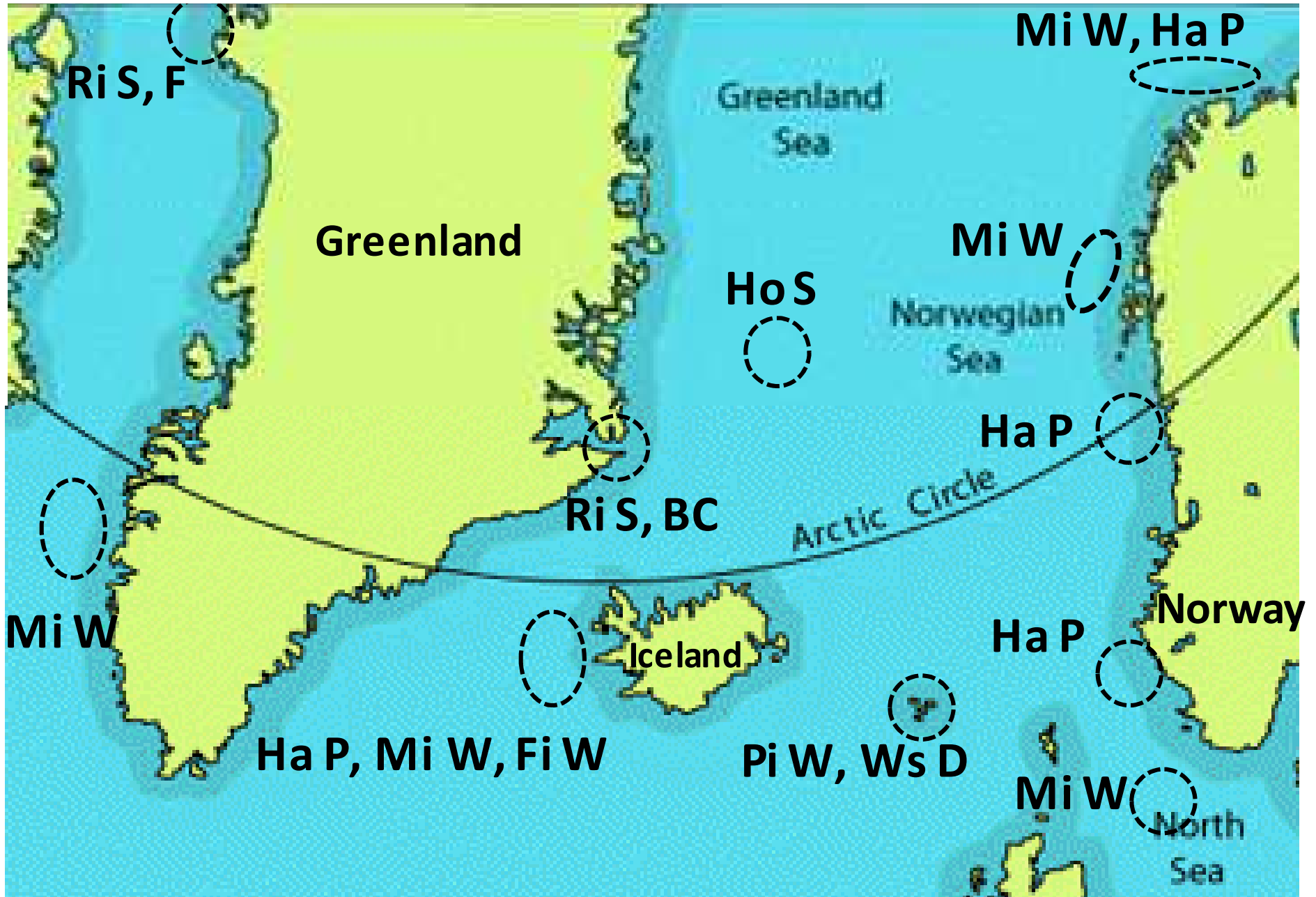
Minke whale



Fin whale



Pilot whale



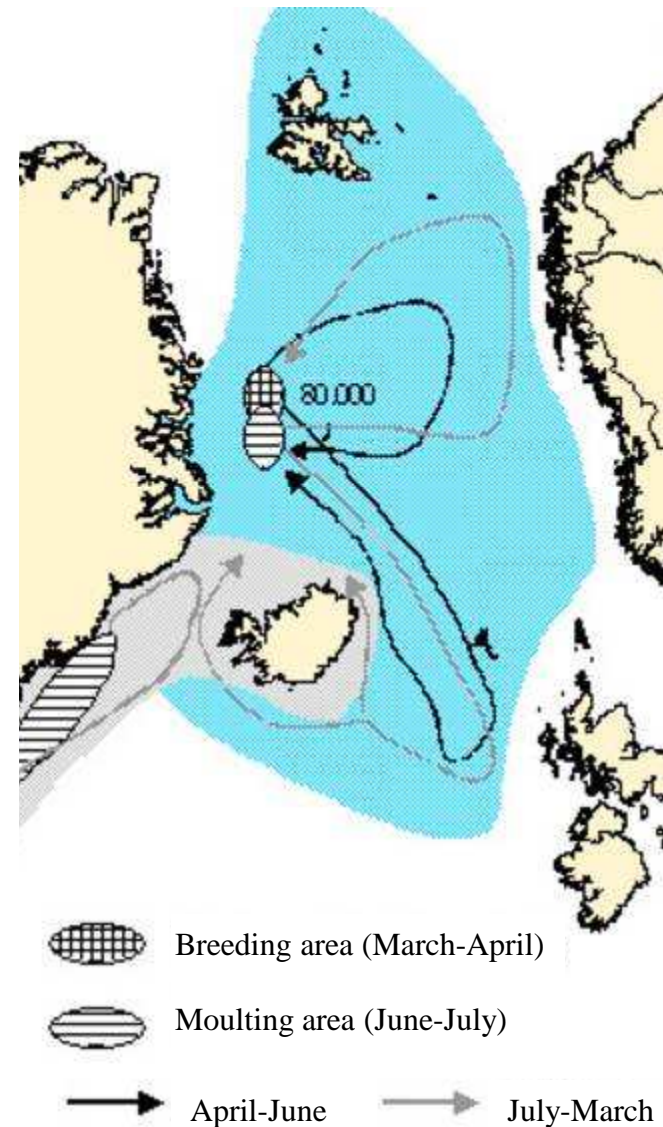
Sampling

- Sample collection
/Sample identification
 - Problematic location of samples
- Sample transport and import
 - Laborious CITES procedures for 1-5 g of fat
- Specimen banks
- Pooled samples (4-8, males in general)
- Local hunters or predefined routes
- Teeth (ringed seal), and length (pilot whales) for age determination



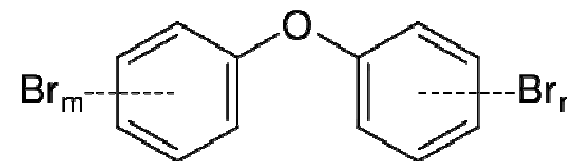
Hooded seal migration

- Use of migratory species in biomonitoring
 - Effect of feeding behaviour
- Data interpretation
 - 3 pooled samples



Target Compounds

BDEs



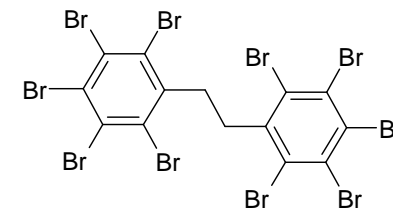
BDE28, 47, 66, 85, 99, 100, 138, 153, 154, 183, 209 (Deca BDE)

MeO-BDEs

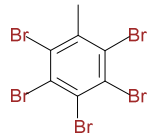
2'-MeO-BDE68, 5-MeO-BDE47, 6-MeO-BDE47, 4'-MeO-BDE49,
5'-MeO-BDE100, 4'-MeO-BDE103, 5'-MeO-BDE99, 4'-MeO-BDE101

"new" BFRs

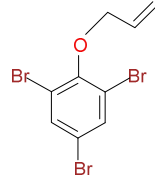
Allyl 2,4,6-tribromophenyl ether (**ATE**),
2-bromoallyl 2,4,6-tribromophenyl ether (**BATE**), pentabromotoluene (**PBT**), *DBDPE*,
hexabromobenzene (**HBB**), 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (**EHTBB**),
hexachlorocyclopentadienyldibromo-cyclooctane (**HCDBCO**), 1,2-*bis*(2,4,6-
tribromophenoxy)ethane (**BTBPE**), and *bis*(2-ethyl-1-hexyl)tetrabromophthalate
(**BEHTBP**), 1,2-dibromo-4-(1,2-dibromoethyl) cyclohexane (**TBECH**), 1,2-
bis(pentabromodiphenyl)ethane or decabromodiphenyl ethane (**DBDPE**)



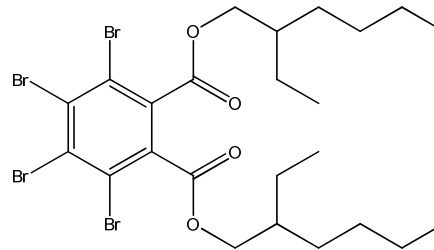
"new" BFRs



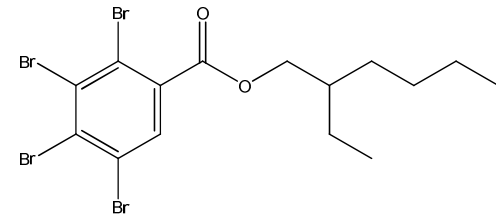
PBT



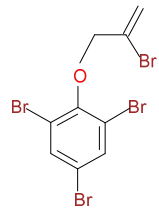
ATE



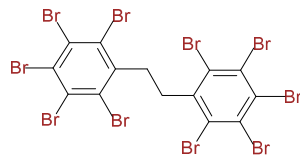
BEHTBP



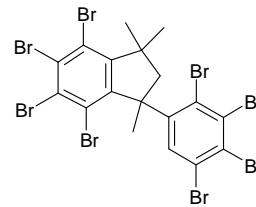
EHTBB



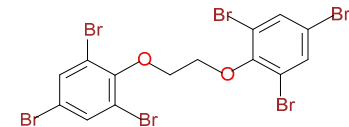
BATE



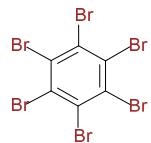
DBDPE



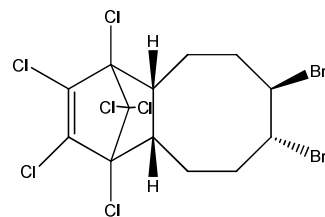
OBIND



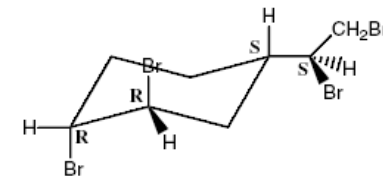
BTBPE



HBB

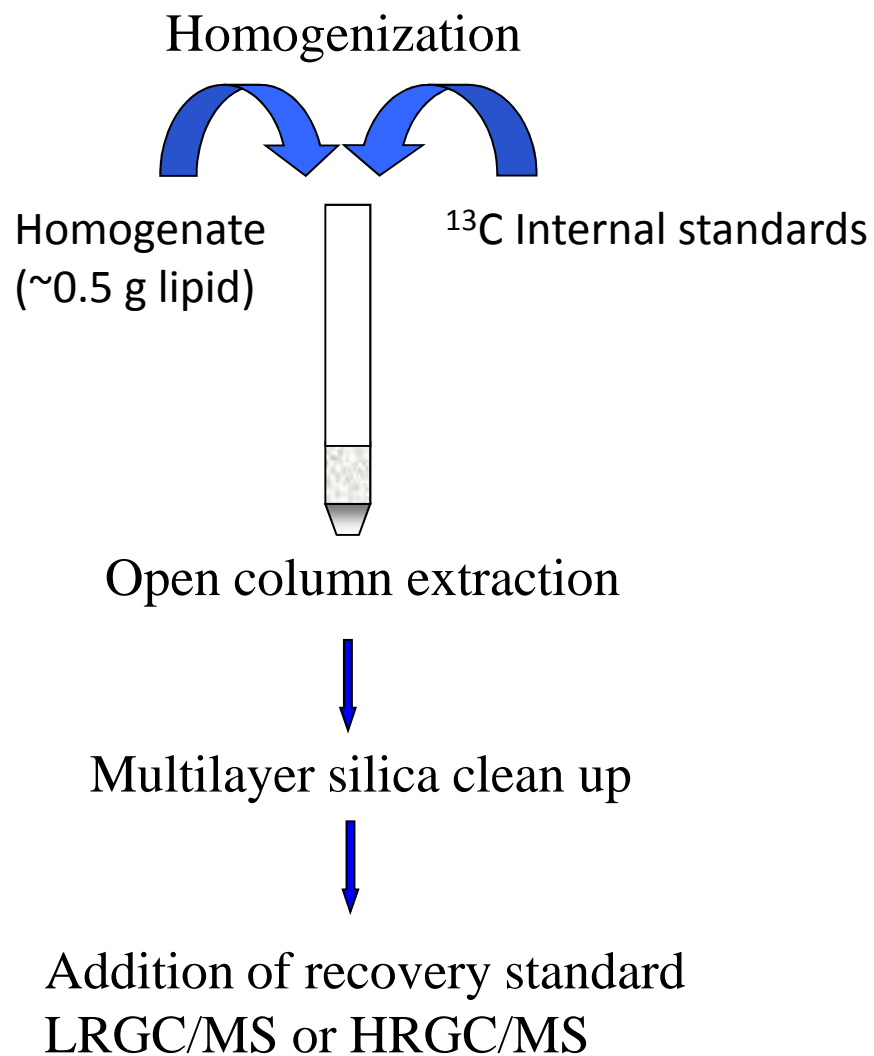


HCDBCO



β -TBECH

Analytical methodology



GC/MS

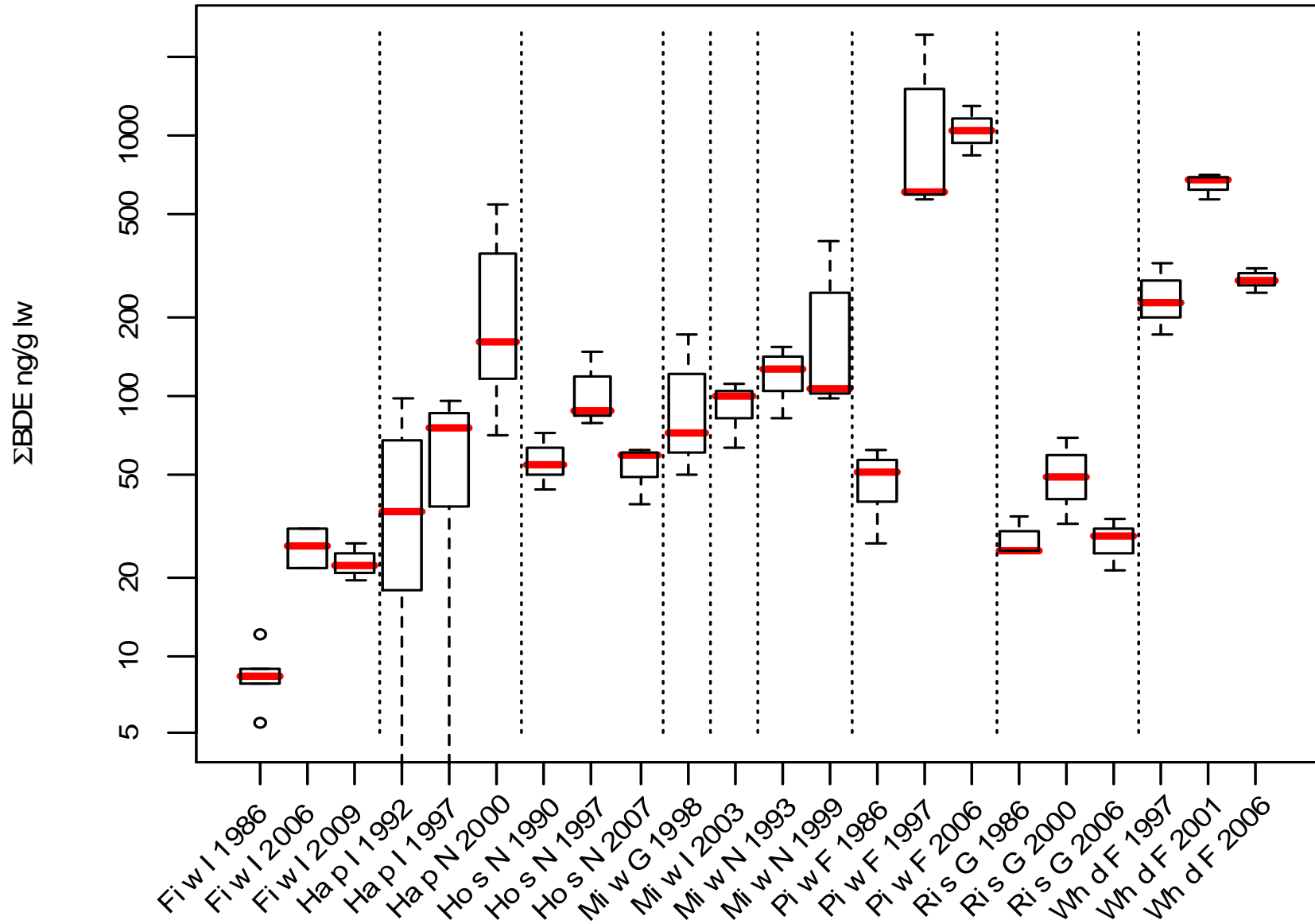


GC-MS/MS

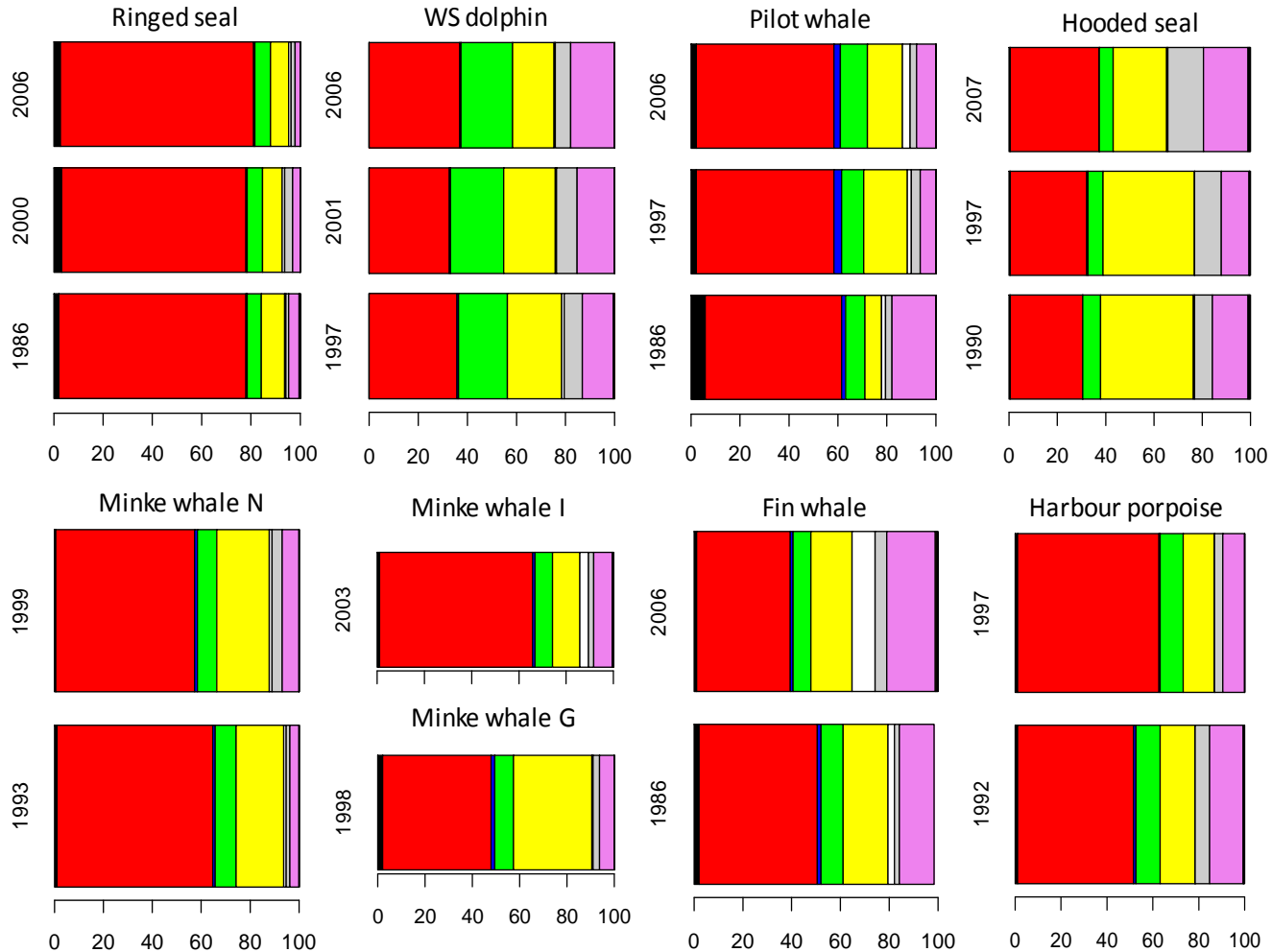


HRGC/HRMS

PBDE inter-species comparison

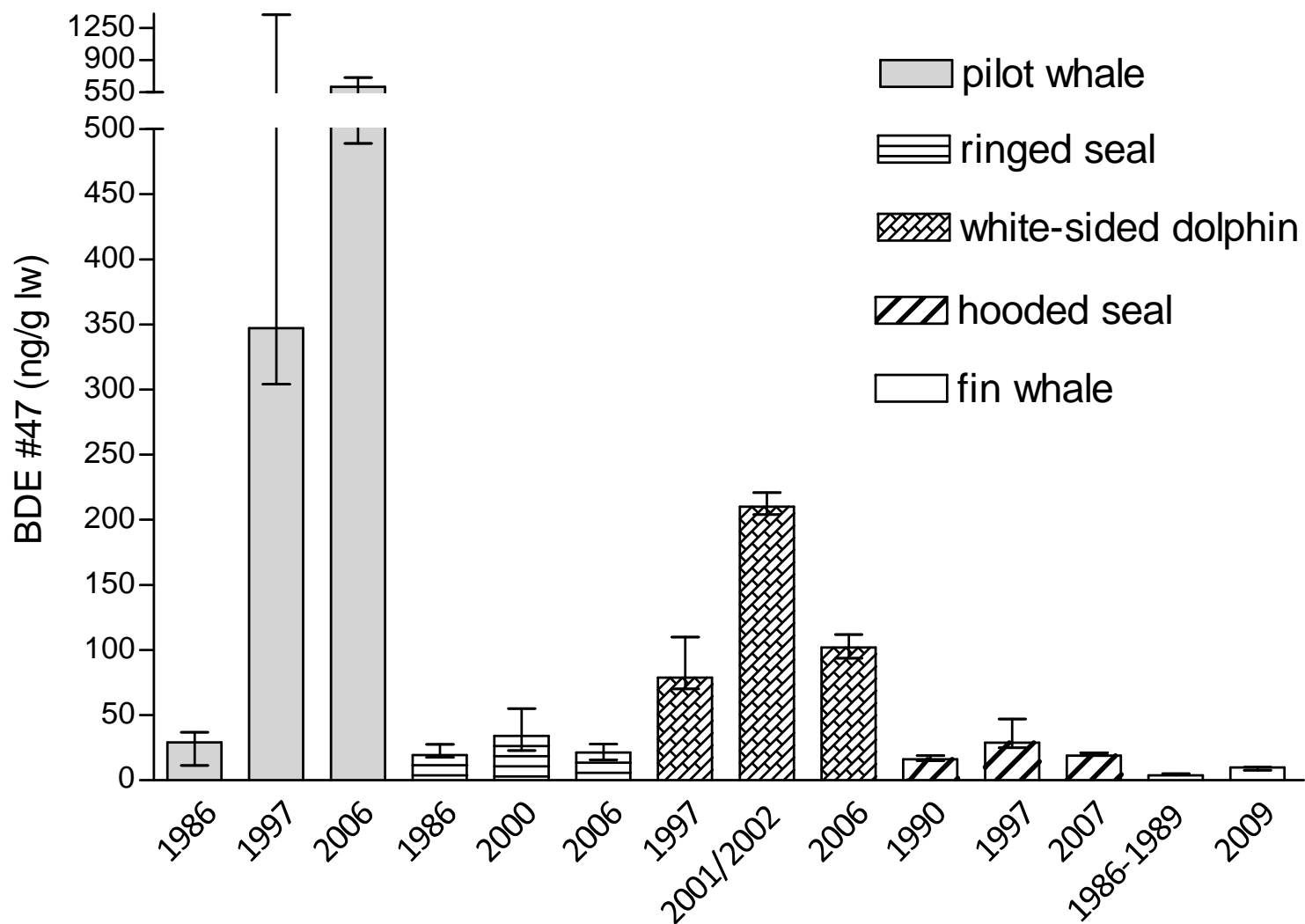


BDE congener composition

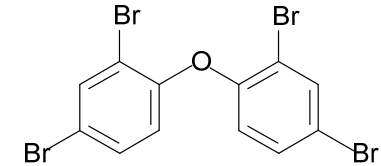


28 – Black, # 47 – Red, # 100 – Green, # 99 – Yellow, # 153 – Grey, # 154 – Violet

BDE47

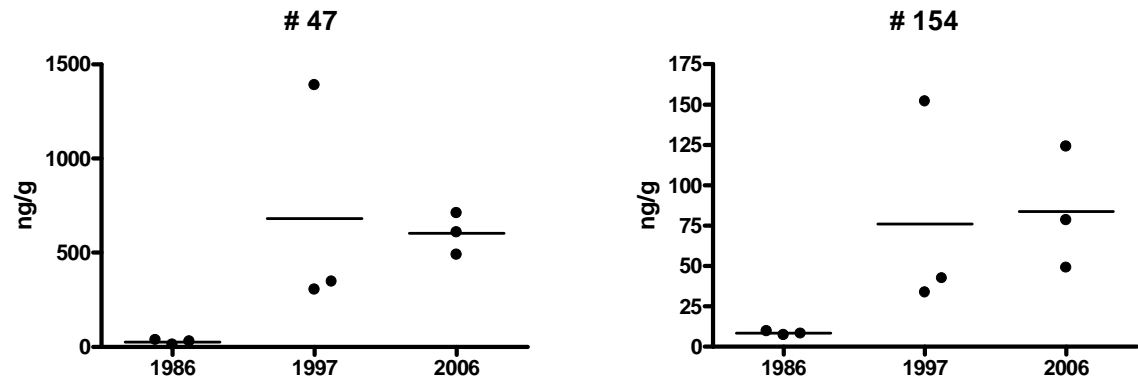


PBDEs

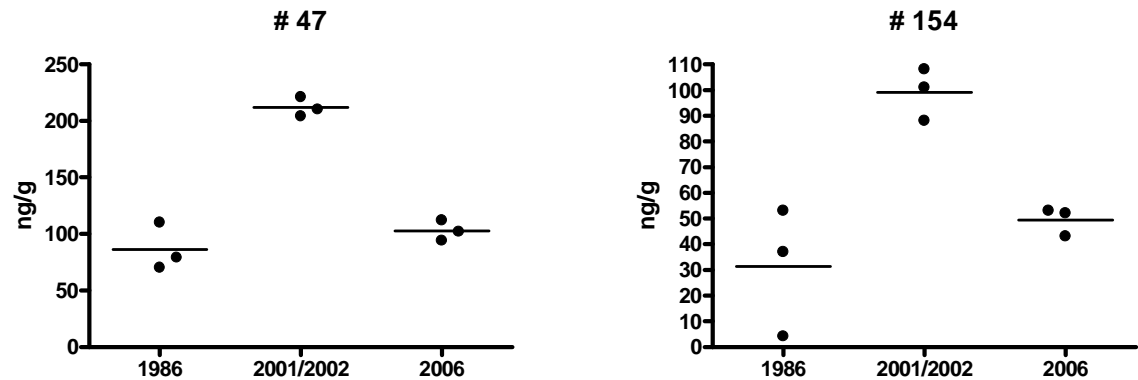


- Increase in PBDE levels since the mid-80s.
- Levels seem to level out/decrease after the end of the 90s.
- Increased relative exposure to higher brominated BDEs was indicated in some species.

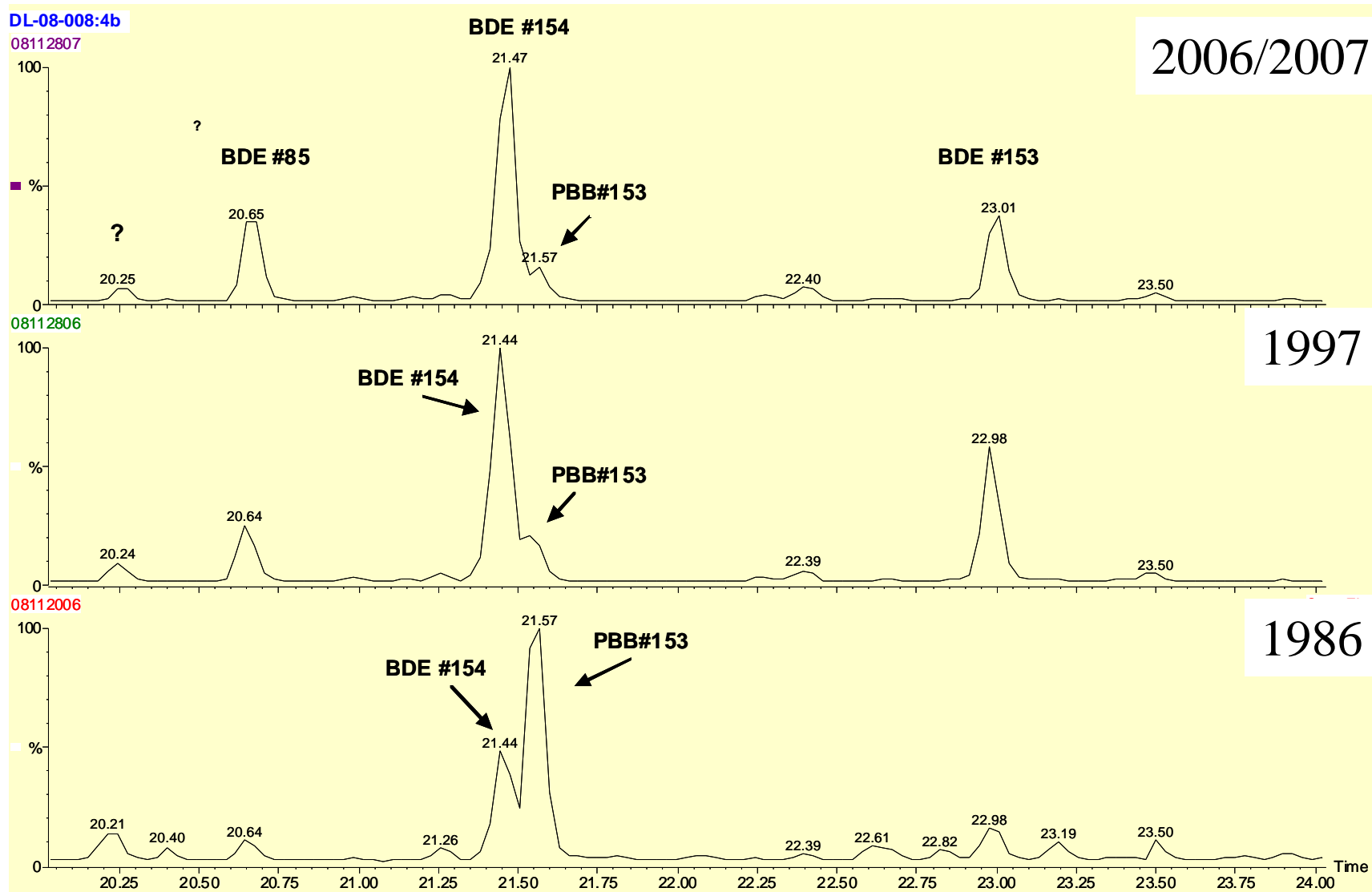
Pilot whale



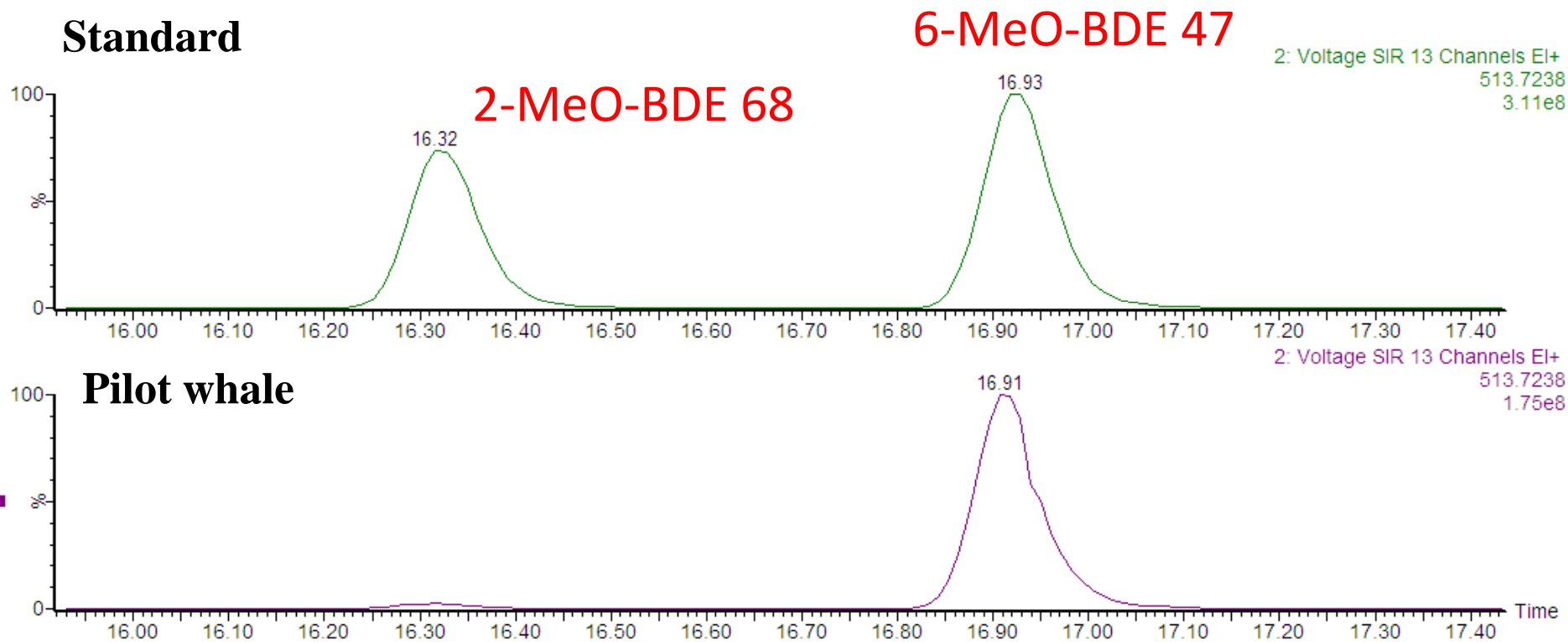
White sided dolphin



BDE154 and PBB153 in pilot whale



MeO-PBDE



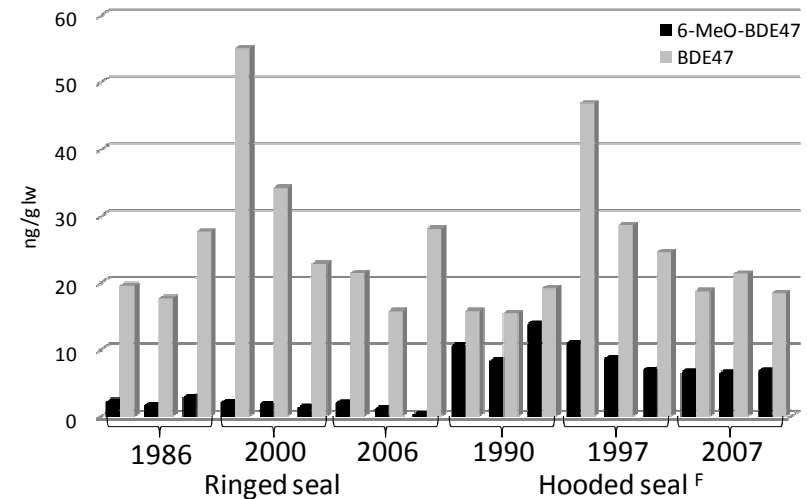
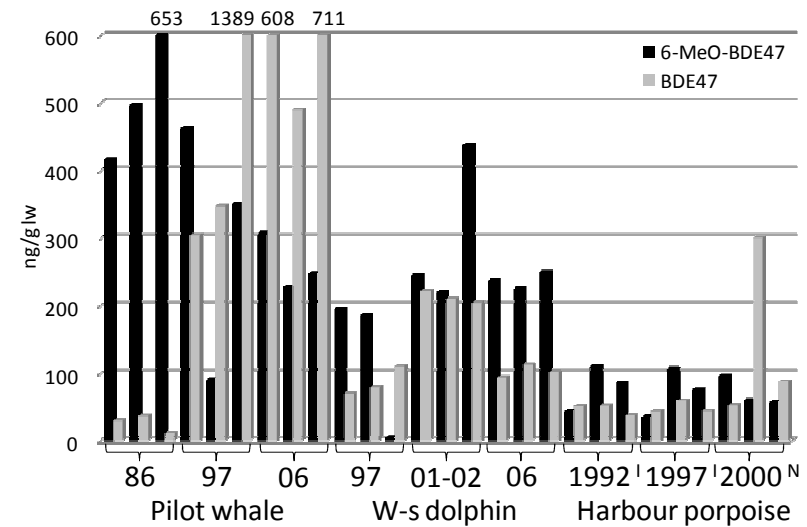
Pilot whale: 150-650 ng/g l.w. (n=3) (6-MeO-BDE 47)

Ringed seal: 0.3-3 ng/g l.w. (n=7)

Minke whale: 3-18 ng/g l.w. (n=6)

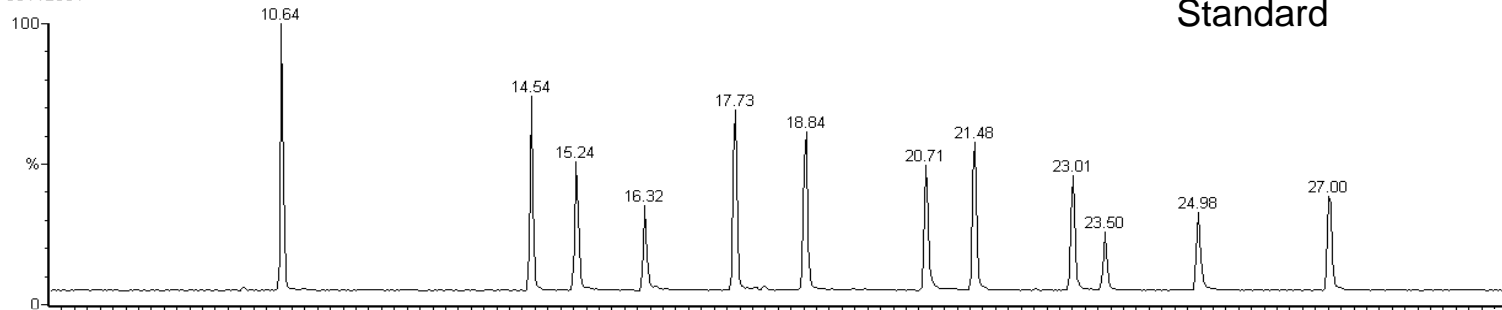
MeO-PBDE

- MeO-PBDE levels highest in most whale species.
- Weak correlation between PBDEs and MeO-PBDEs.
- Support for a natural formation of MeO-PBDEs.
 - Metabolization cannot be ruled out.

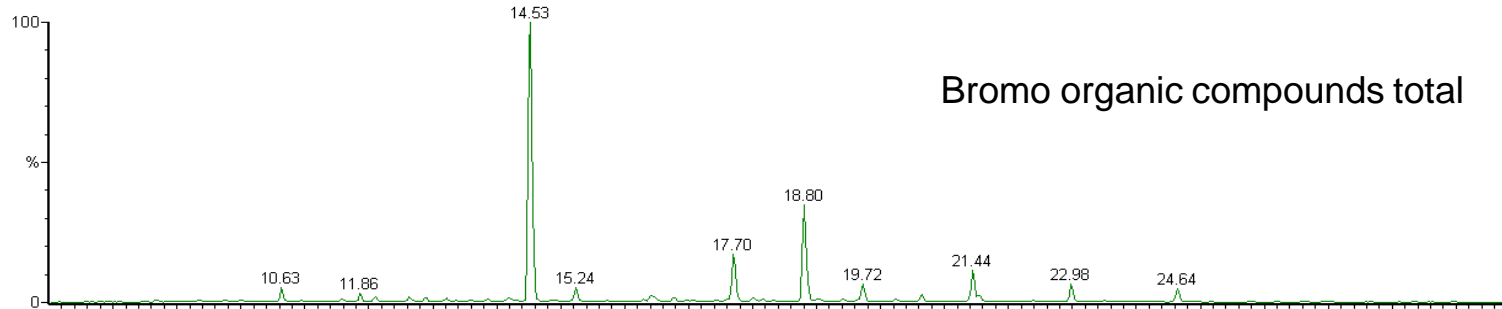


Other BFRs Pilot Whales 1986-1997-2006/07

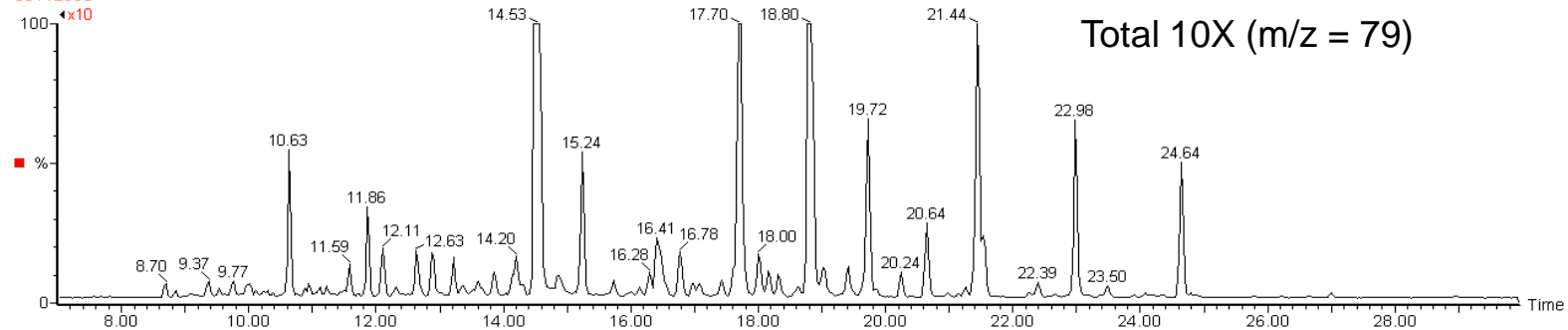
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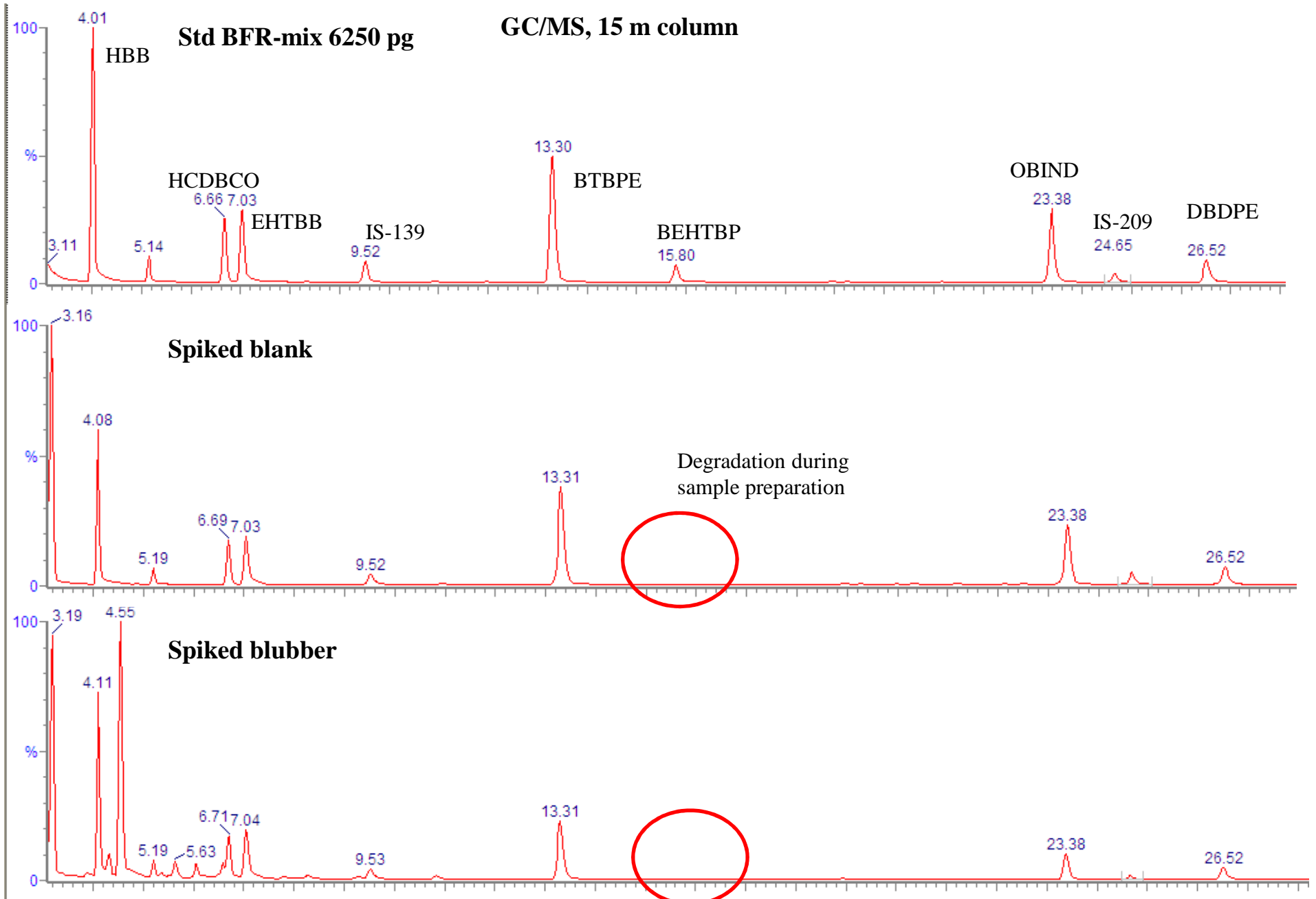
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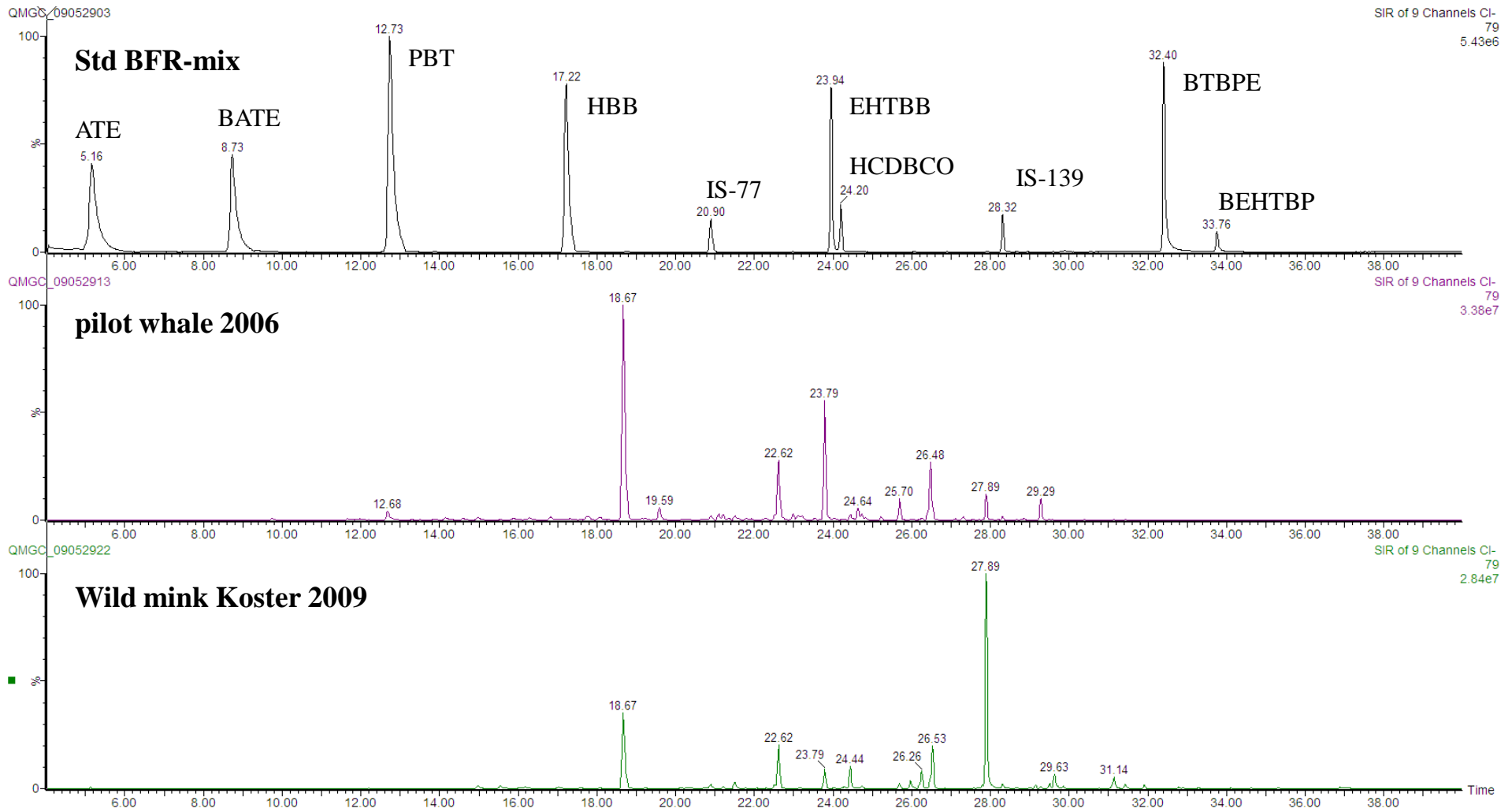
Screening for “new” BFRs

- Pilot whales, minke whales and ringed seals
- HBB found in whale samples (1-10 ng/g), others below LOD
- TBECH not confirmed on HRGC/HRMS
- Analysis alongside PBDEs, no sample prep or instrumental optimizations
 - Difference in solubility and extraction efficiency
- Relatively high LODs for the larger compounds
- Small sample size
- Spiking experiments showed breakdown during sample prep

- BTBPE found in a few Canadian Belugas (0.1-2.5 ng/g lw) and ringed seals (<0.01-0.29 ng/g lw) Tomy et al.
- DBDPE not found in ringed seals
- β -TBECH found in Beluga blubber (1.1-9.3 ng/g)



GC-MS/MS, 30 m column



PBDD/PBDF in selected samples

Tab. 9: Recoveries and detection limits for the PBDD/Fs

	Fin whale 1	Fin whale 2	Fin whale 3	Fin whale 4	Minke whale 1	Detection-limit
Standard	Rec [%]	Rec [%]	Rec [%]	Rec [%]	Rec [%]	pg/g
2,3,7,8-TeBDF	82	74	83	78	78	1.6
2,3,4,7,8-PeBDF	49	49	61	59	52	9.3
1,2,3,4,7,8-HxBDF	76	65	74	76	64	1.4
1,2,3,4,6,7,8-HpBDF	25	26	20	25	26	9.9
OBDF	n.d.	n.d.	n.d.	n.d.	n.d.	-
2,3,7,8-TeBDD	88	79	80	82	77	1.9
1,2,3,7,8-PeBDD	64	59	66	63	57	17
1,2,3,4,7,8-HxBDD	72	60	67	68	63	2.1
1,2,3,6,7,8-HxBDD	71	61	72	75	58	5.3
1,2,3,4,6,7,8-HpBDD	n.d.	n.d.	n.d.	n.d.	n.d.	-
OBDD	n.d.	n.d.	n.d.	n.d.	n.d.	-

Conclusion

- PBDEs generally decreasing/levelling out
 - Large data variations for some pools/species
 - BDE #154 different behaviour
- MeO-PBDEs
 - In all samples
 - Relatively high levels in pilot whales and minke whales
 - Weak correlation between MeO-PBDEs and PBDEs
 - Support for natural formation
 - Metabolization cannot be ruled out
- “New” BFRs
 - HBB found in pilot whales and minke whales
 - Others below LOD
 - Many unknown brominated organic compounds
 - Optimized sample prep and larger sample volumes for future analysis
 - Method development
 - Use of labelled standards
 - Inter-laboratory comparisons



Thank you for your attention!

Acknowledgements

➤ The Nordic Council of Ministers

Pilot whales
FF1/3S09 – Photo: Paul Ensor