

# Arctic Screening of BFRs in Marine Mammals in the Nordic Arctic

**Bert van Bavel, Anna Rotander, Guðjón Atli Auðunsson,  
Frank Rigét, Anuschka Polder, Maria Dam**

MTM Research centre, Örebro University, Sweden

Innovation Center Iceland, Dep. Analytical Chem. And Marine Research Institute, Iceland

National Environmental Research Institute University of Aarhus, Denmark

Norwegian School of Veterinary Science and the Norwegian Polar Institute, Norway

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



Norwegian School of Veterinary Science

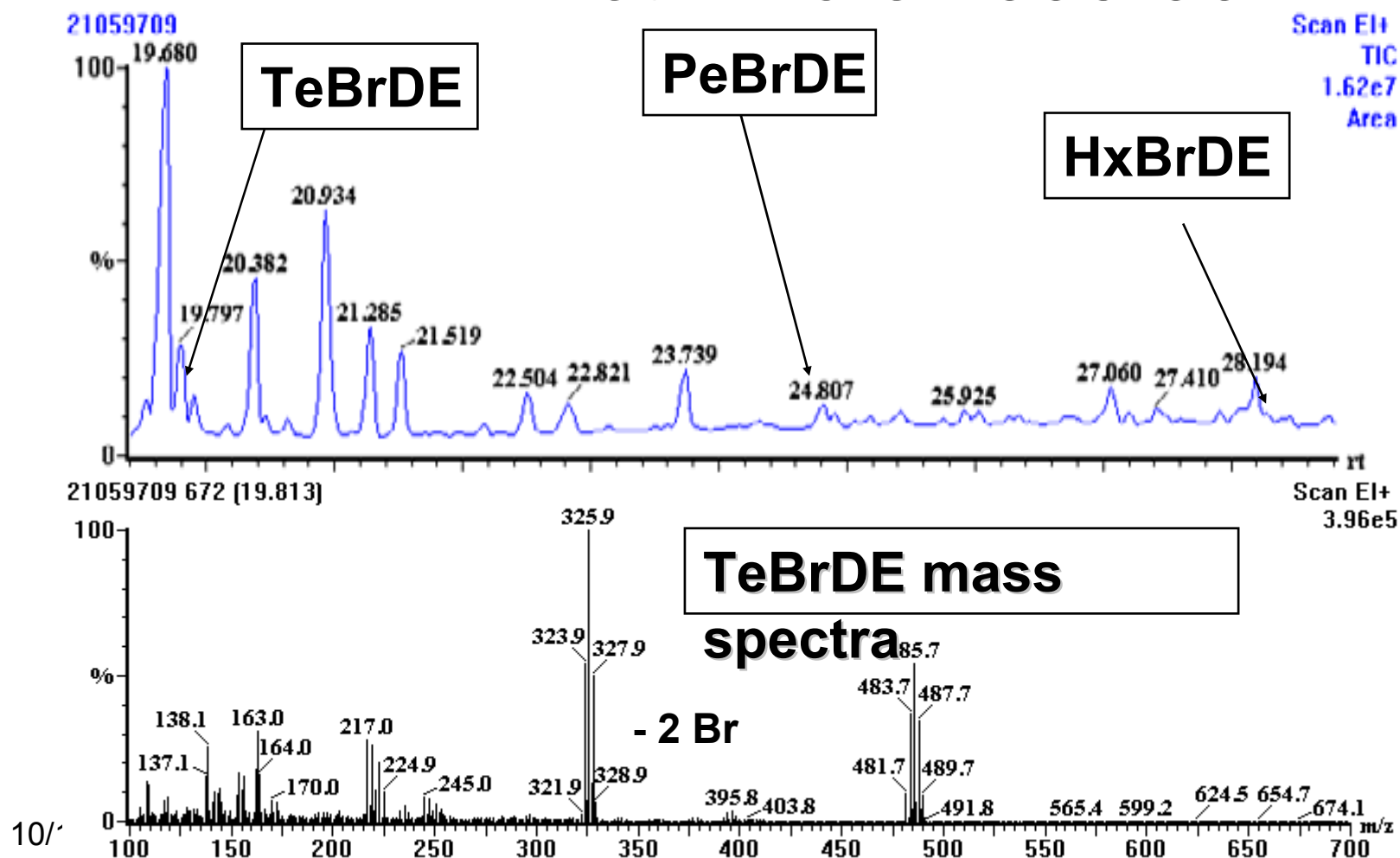


# BFRs in the Arctic

- Why (still) look for BFRs in Arctic Mammals?
    - Levels BDE well documented since 1990s
    - BDE since 2009 one of the POPs on the Stockholm Convention
    - Literature data suggests decreasing levels
1. Polybrominated diphenyl ethers (BDE)
  2. Natural organic bromo compounds
  3. New BFRs

# Where it all started

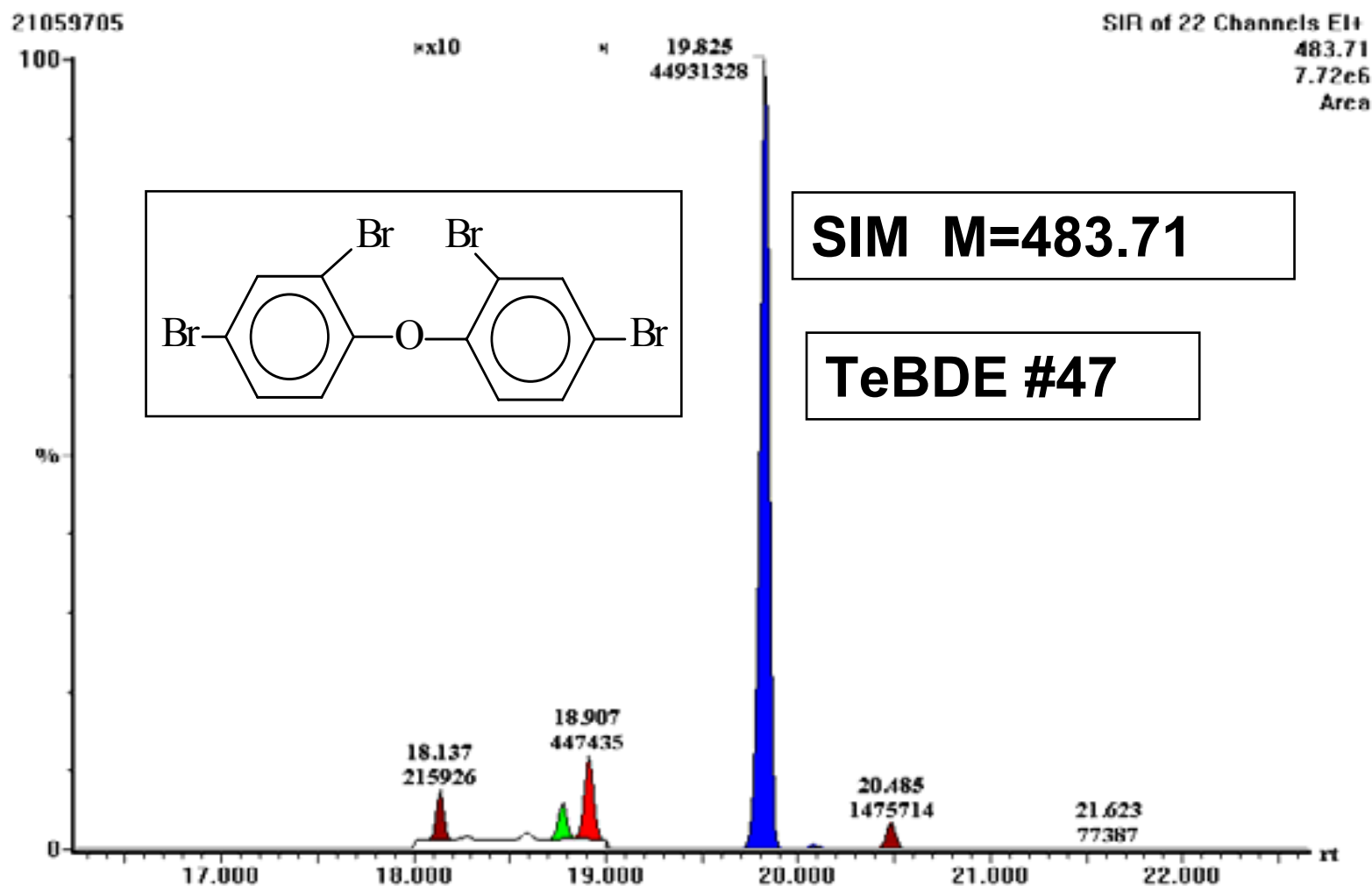
## BDE in Pilot Whale 1995-96



Low Resolution GC/MS  
Full Scan

# Selective ion monitoring

## 17 Tetra-Hexa BDEs in whale



10/14/2010

4

\* de Boer et al (Science) , Haglund et al ES&T

# Beluga or White Whale BDE in the Arctic 1997



10/14/2010

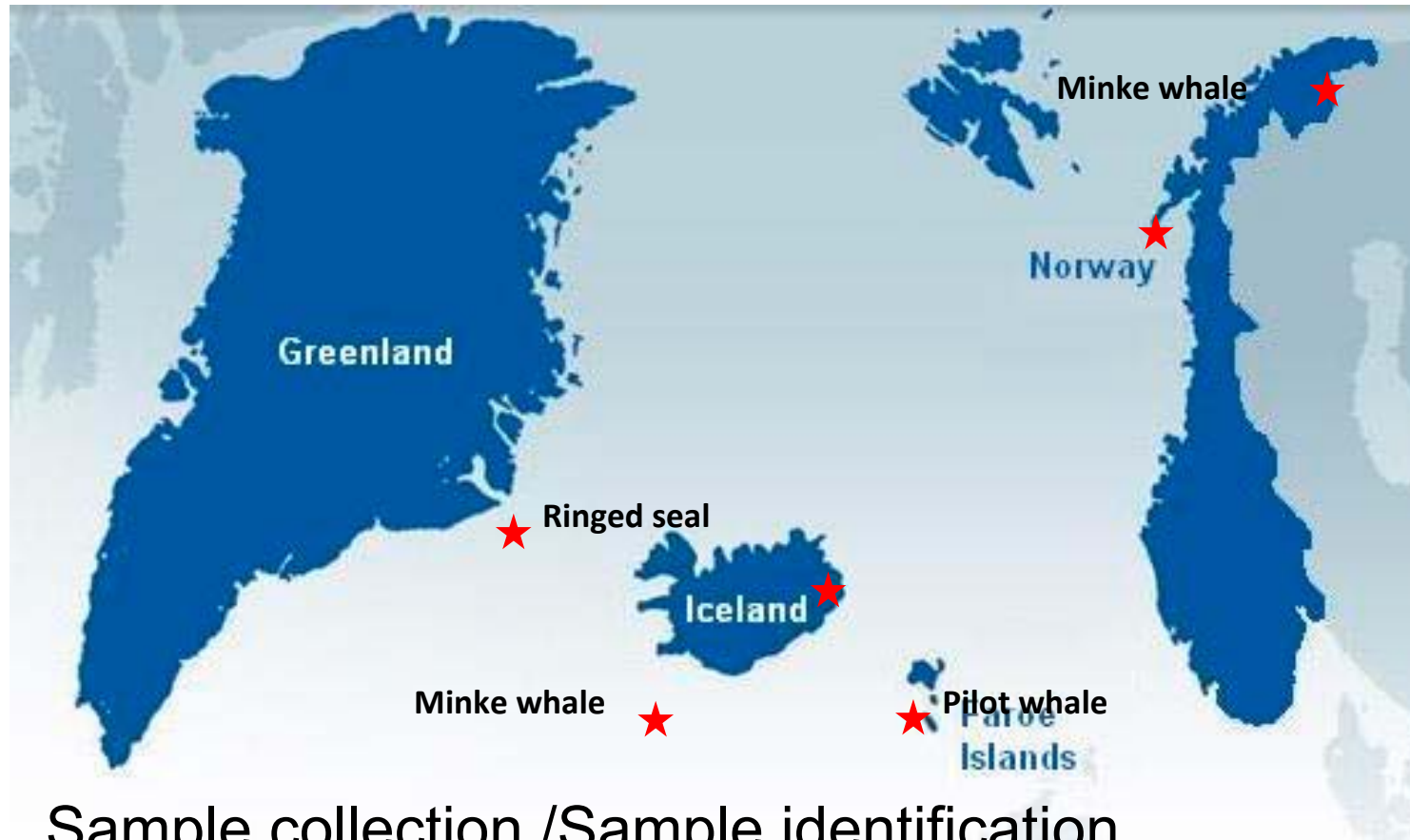
	Juv. Male	Juv. Female	Ad. Female	Ad. Male
TeBDE (d)	1.16	1.00	ND	1.60
TeBDE #47	137.43	106.21	17.53	78.39
PeBDE (d)	12.91	10.35	ND	7.52
PeBDE #99	9.11	7.77	ND	3.34
HxBDE (b)	3.48	5.15	ND	ND
TeBDE-O-Me (a)	1.84	1.76	ND	ND
TeBDE-O-Me (b)	19.48	15.70	ND	ND
TeBDE-O-Me (c )	143.02	125.56	23.55	84.19

Simultaneously  
Increasing levels in humans Noren, Bergman<sup>5</sup>et al  
EHP

## Screening for new POPs in the Nordic Arctic for three decades 1986-1995/96-2006

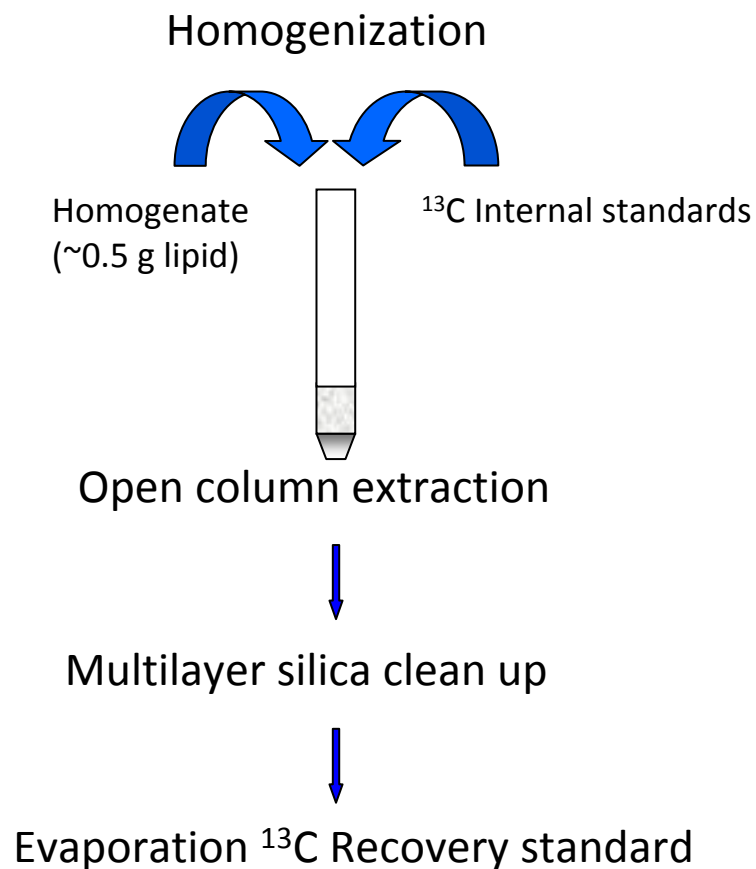
- Ringed Seal (*Phoca hispida*)
- Minke Whale (*Balaenoptera acutorstrata*)
- Long-finned pilot whale (*Globicephala melas*)
- In addition
  - Fin whale
  - White sided dolphins
  - Hooded seals
  - Harbour porpoise
- Pooled samples (4-8 males)
- Local hunters or predefined routes
- Teeth (Ringed seal), and length (Pilot whales)  
for age determination

## Screening for new POPs in the Nordic Arctic for three decades 1986-1995/96-2006



- Sample collection /Sample identification
  - Problematic location of samples
- Sample transport and import
  - Laborous CITES procedures for 1-5 g of fat

# Analytical methodology



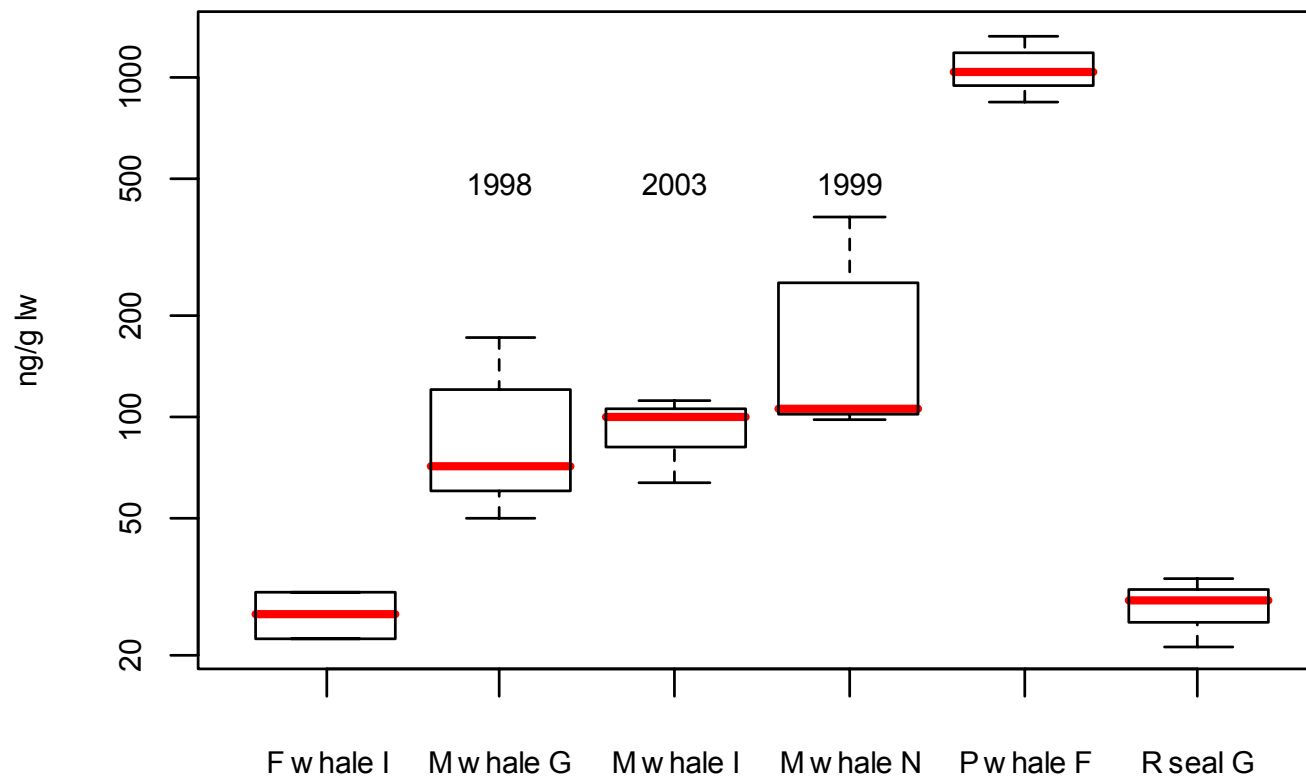
- GC/MS analysis
  - Low Res NCI
    - Routine BDEs
    - $m/z$  79 and 81
  - Low Res EI
    - Interferences
    - Molecular mass
  - High res EI
    - Accurate mass
    - New BFRs
    - Confirmation



# Sum BDE different species

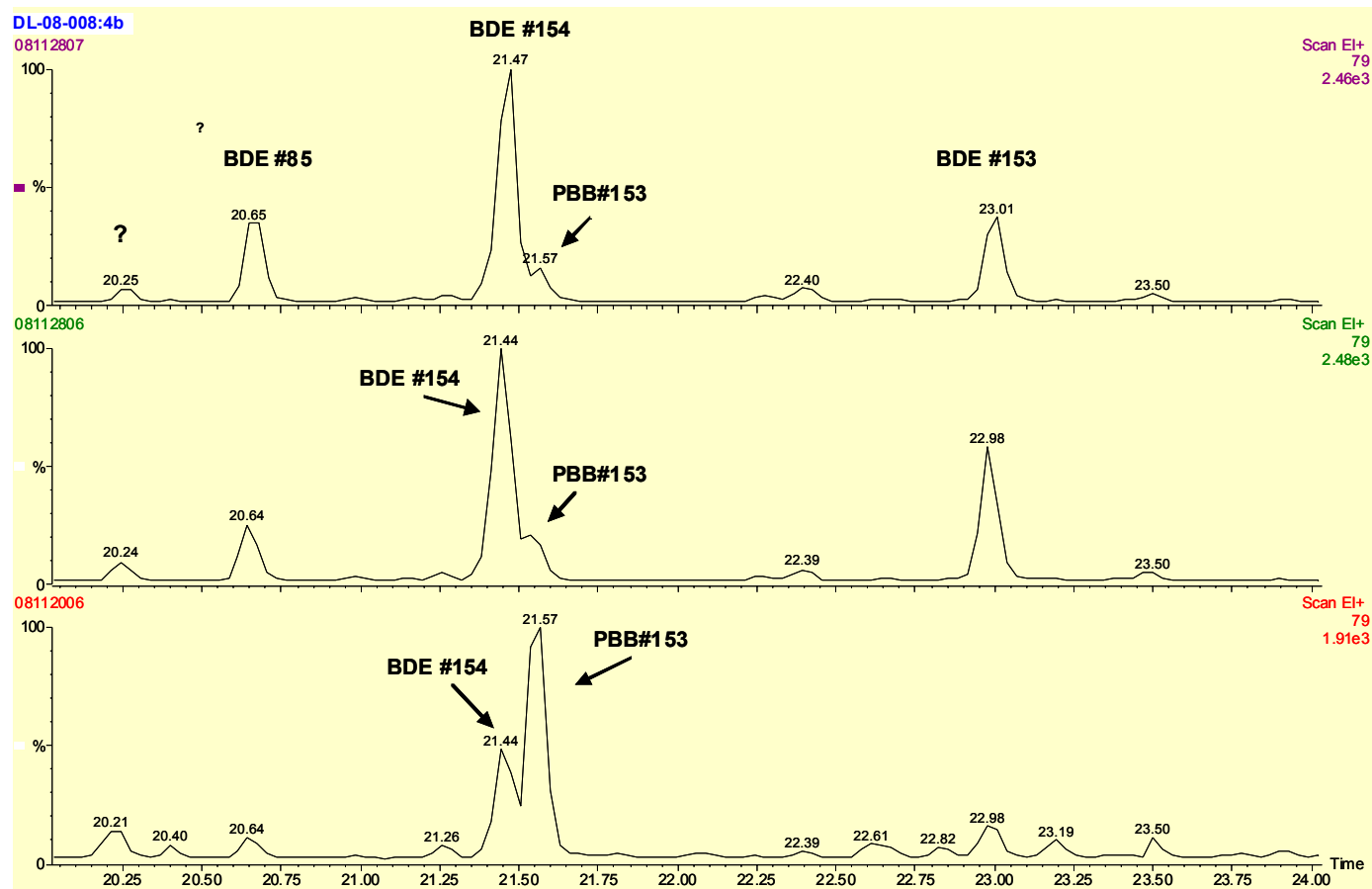
## 2006

$\Sigma$ PBDE

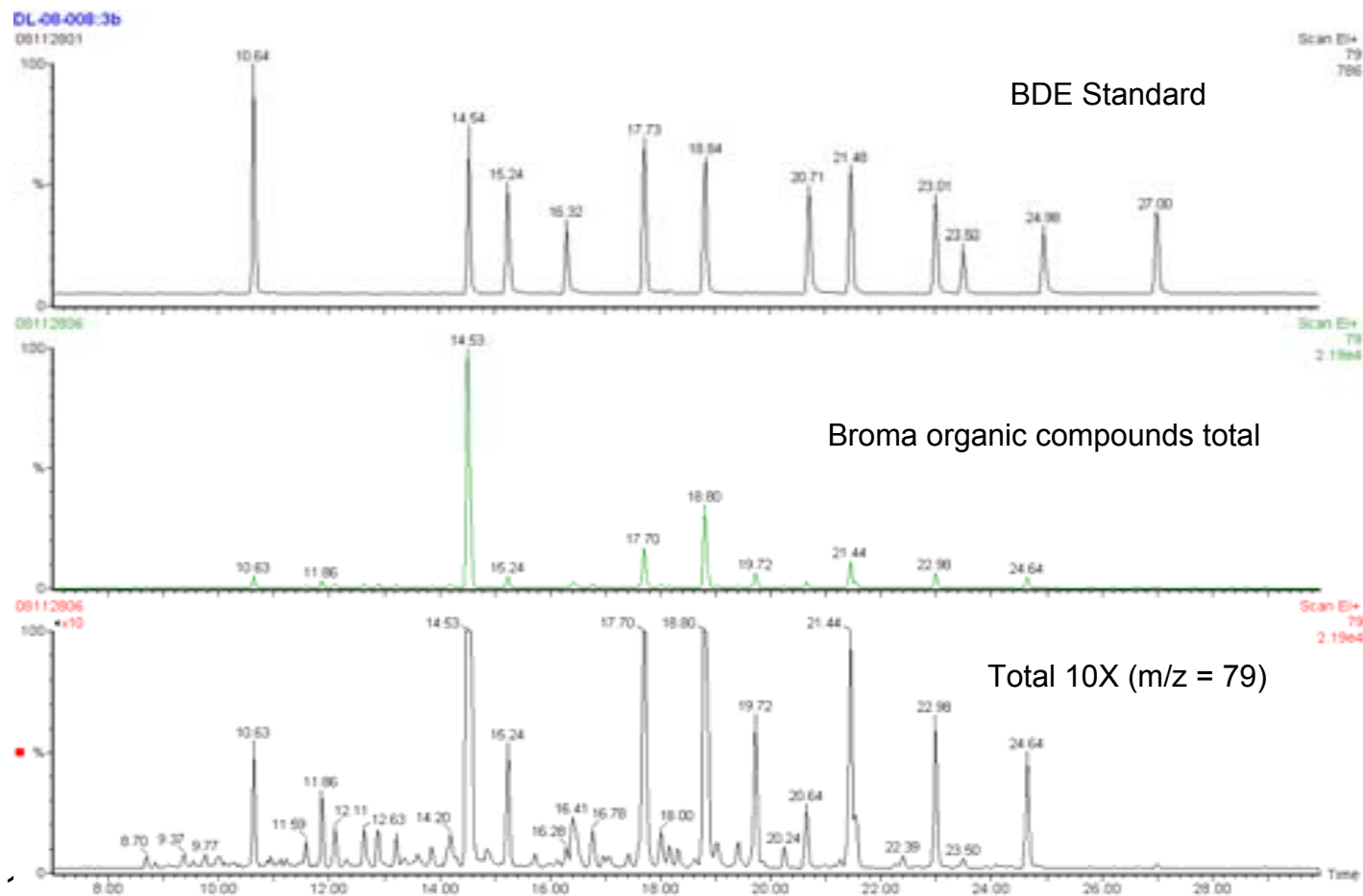


\*All data 2006 except Minke Whale

# BDE #154 and PBB #153 1986-1997-2006/07

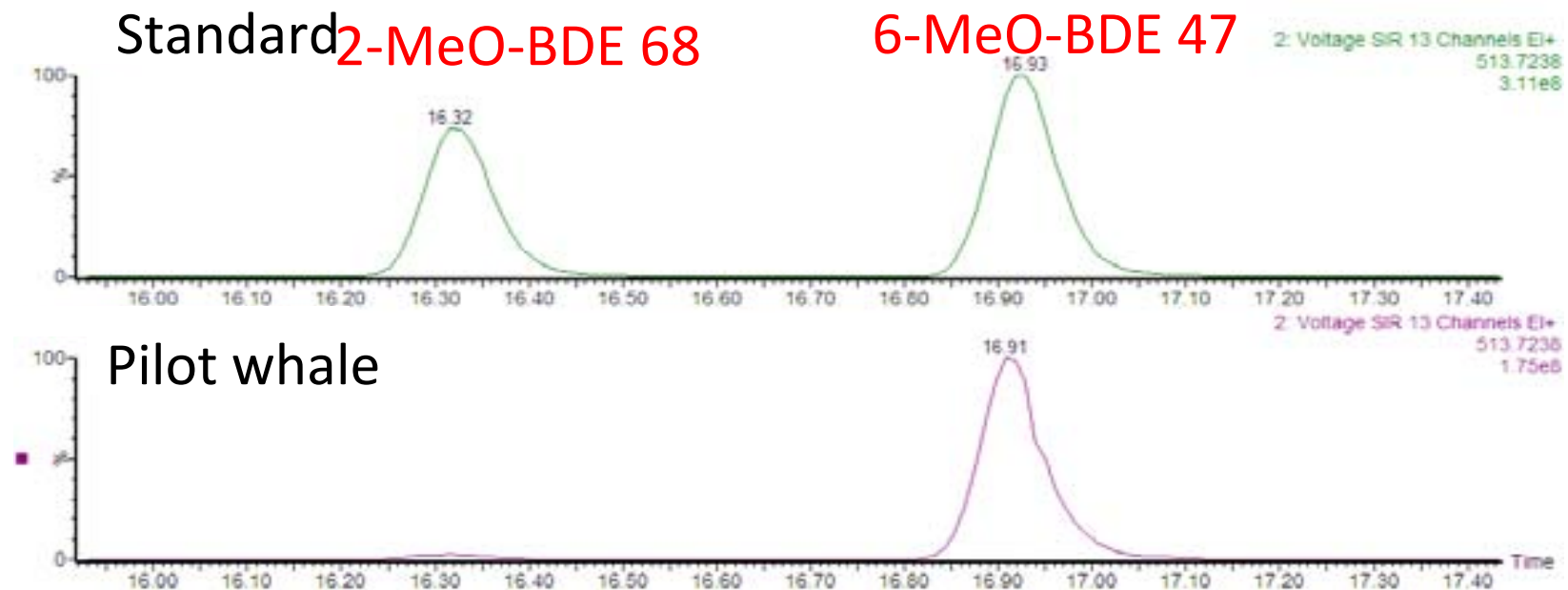


# Other BFRs Pilot Whales 1986-1997-2006/07



# Natural BFRs? MeO-PBDEs

2-MeO-BDE 68, 5-MeO-BDE 47, 6-MeO-BDE 47, 4-MeO-BDE 49,  
5-MeO-BDE 100, 4-MeO-BDE 103, 5-MeO-BDE 99, 4-MeO-BDE 101

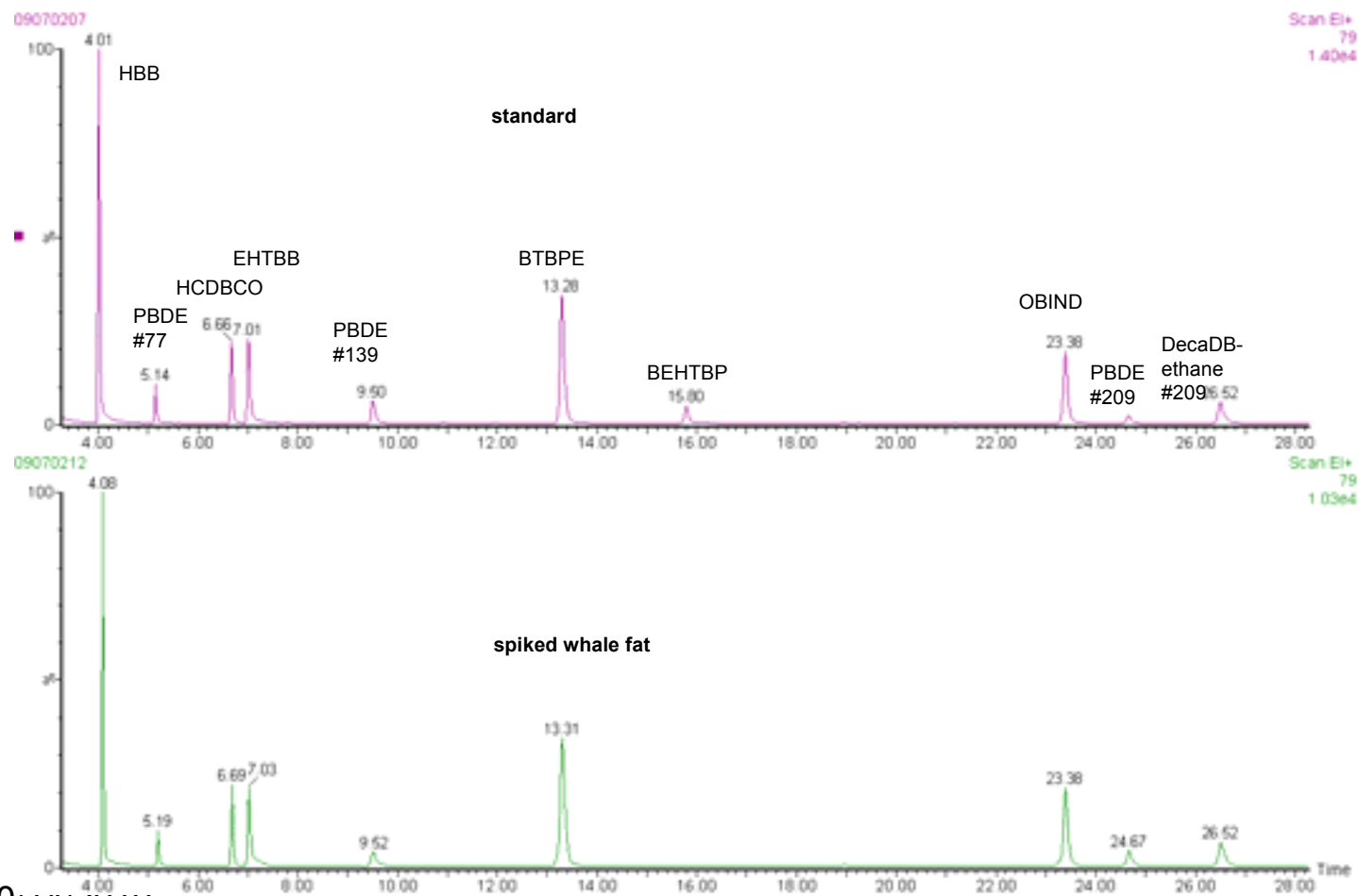


**Pilot whale: 150-650 ng/g l.w. (n=3) (6-MeO-BDE 47)**

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

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

# 'New' BFRs



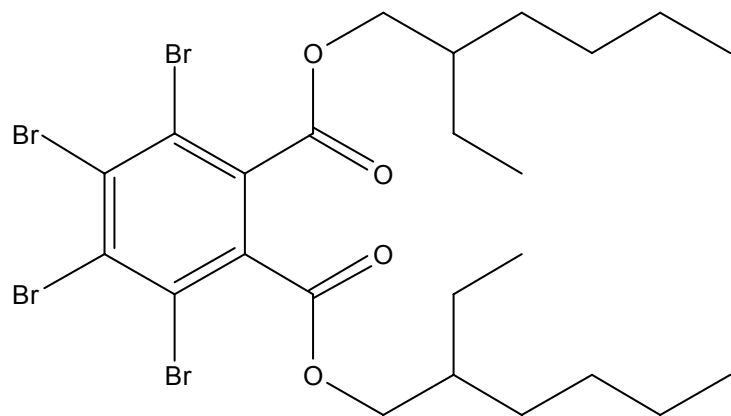
10/14/2010

# DLs new BFRs

Substance	Detection limit [pg/g]
ATE	6.0
BATE	3.0
PBT	3.0
HBB	39
EHTBB	13
HCDBCO	30
BTBPE	20

# BEHTBP

- Only 'new' BFR at levels > LOD
- BEHTBP



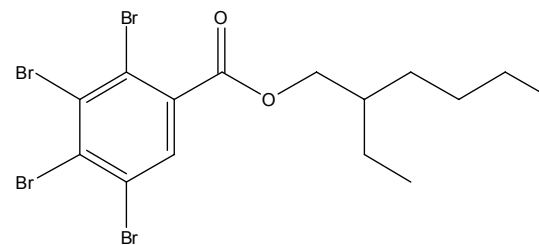
10/14/2010

Firemaster 550:

bis(2-ethyl-1-hexyl) tetrabromophthalate  
(BEHTBP)

2-ethyl-1-hexyl 2,3,4,5-tetrabromobenzoate  
(EHTBB)

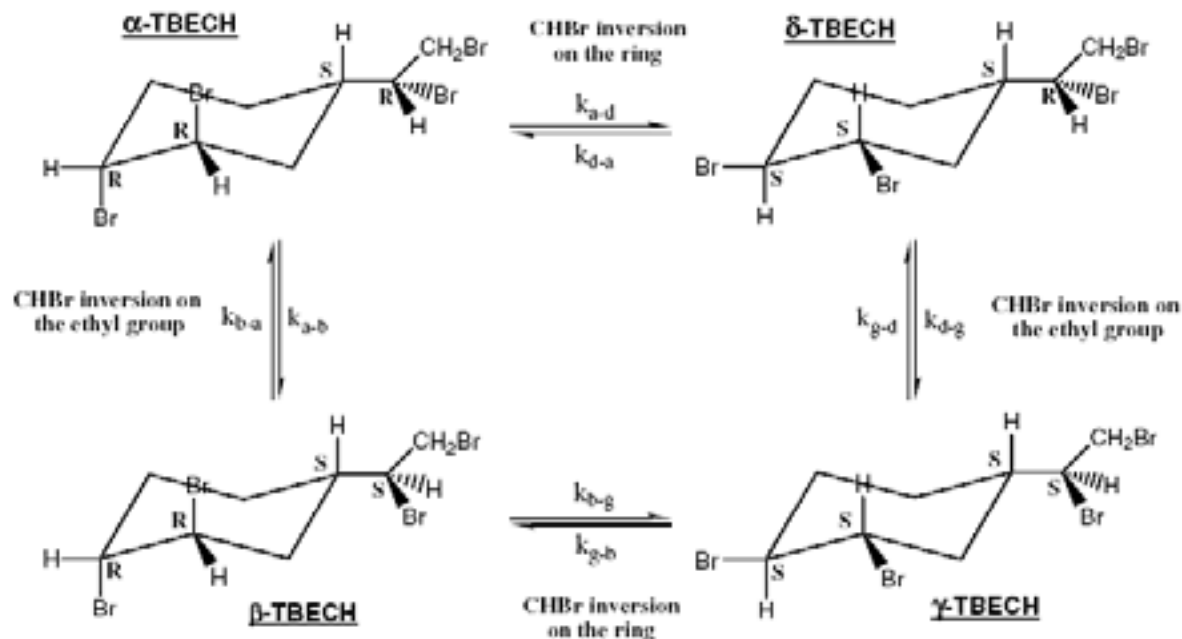
BEHTBP is also used as a plasticizer in neoprene and polyvinyl chloride both substances were detected in household dust by Stapleton et al.



EHTBB lost in clean up

# Is confirmation by high resolution GC/MS necessary?

- Tetrabromoethylcyclohexane (TBECH)
- High biological activity (Larsson, Olsson et al.)
- Found in Beluga Whale (Tomy et al.)





# TBECH in Beluga Whale

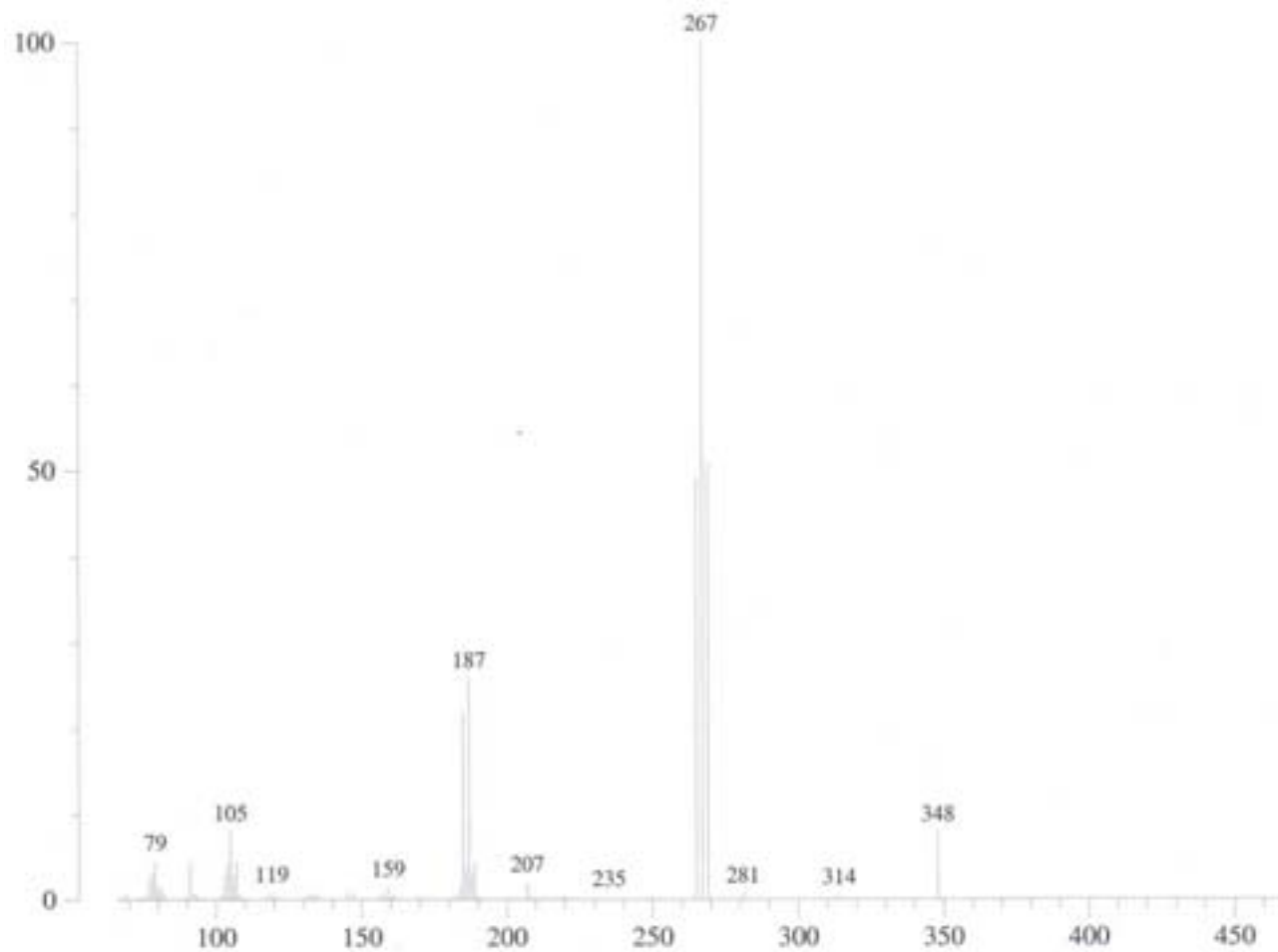
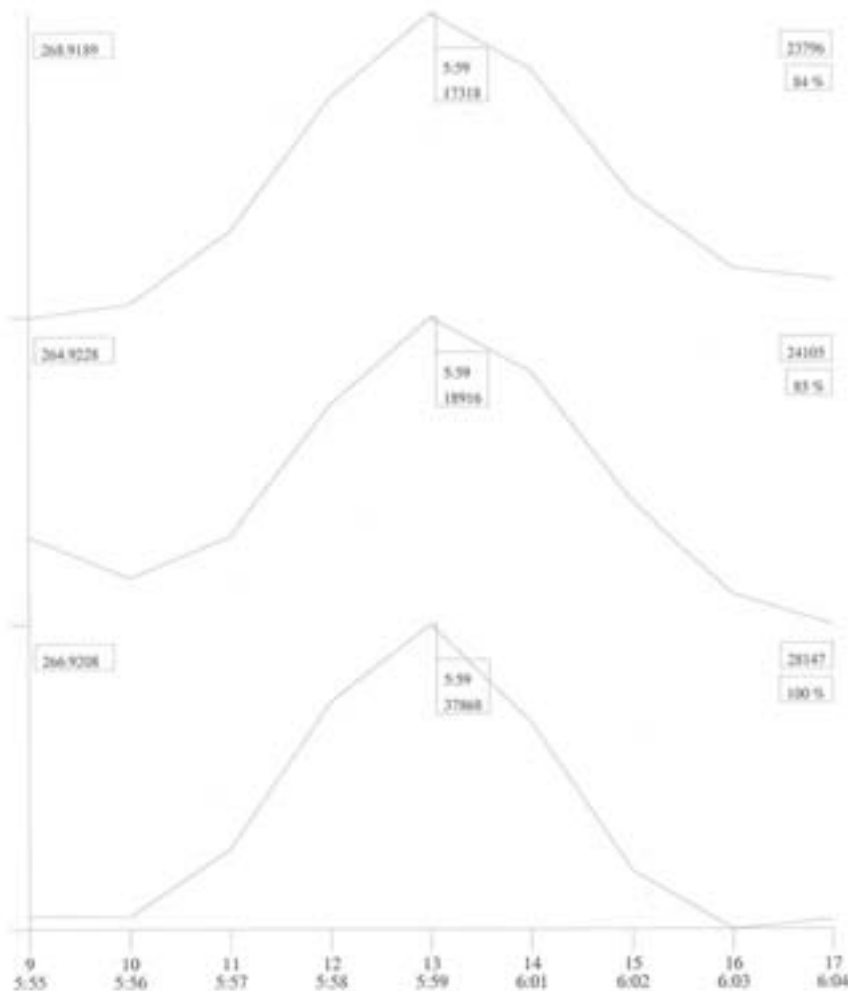


Figure SI1. EI full-scan ( $m/z$  50-450) mass spectrum of  $\beta$ -isomer (1ng/ $\mu$ L, 1 $\mu$ L injection). Tomy et al ES&T

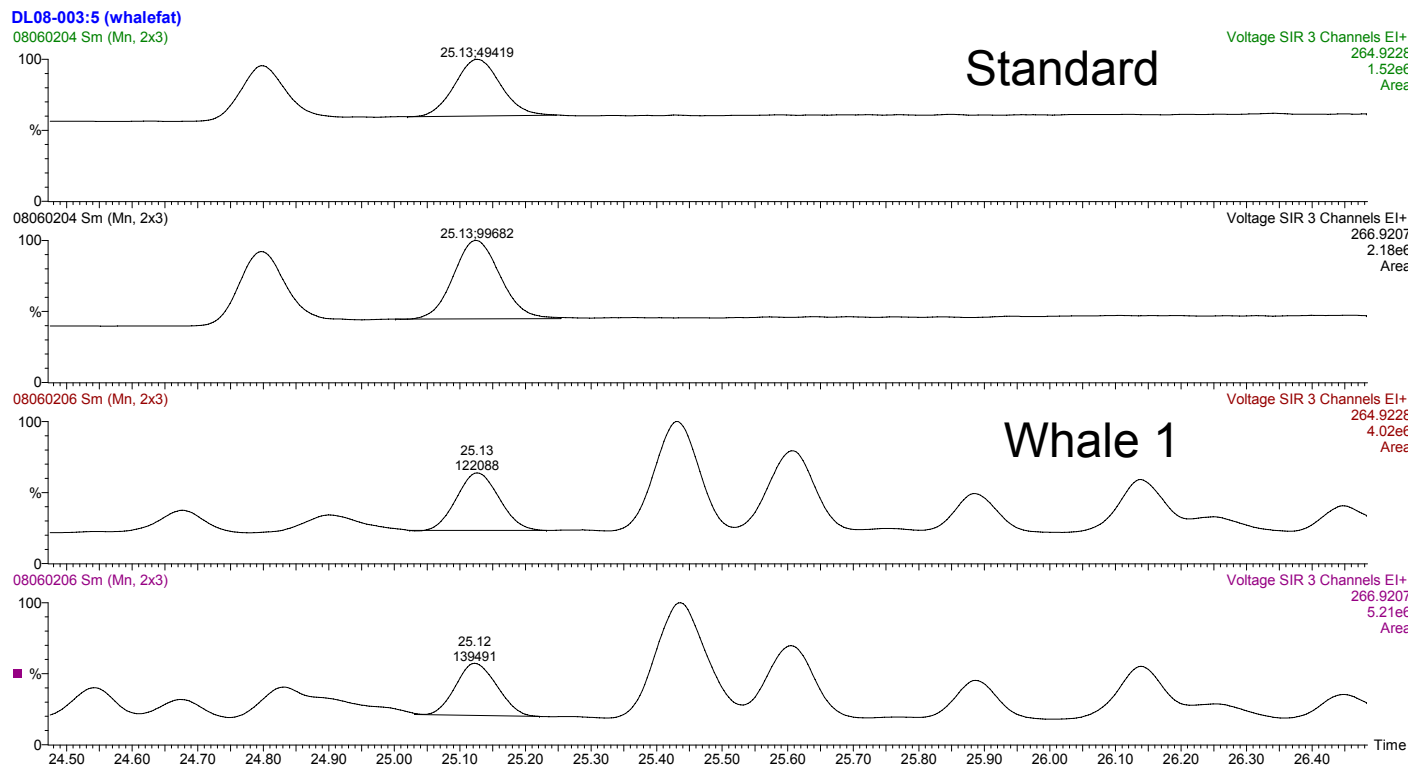
# TBECH in Beluga Whale



**Figure 4SI.** HRGC/EI-HRMS selected ion chromatograms of  $m/z$  268.9189 (top panel)  $m/z$  264.9228 (middle panel) and  $m/z$  266.9208 (bottom panel) of the  $\beta$ -isomer in a beluga blubber extract (Pangnirtung Island).

Plotted on each ion chromatogram are the retention times and integrated areas. Tomy et al ES&T

# TBECH in Pilot Whale

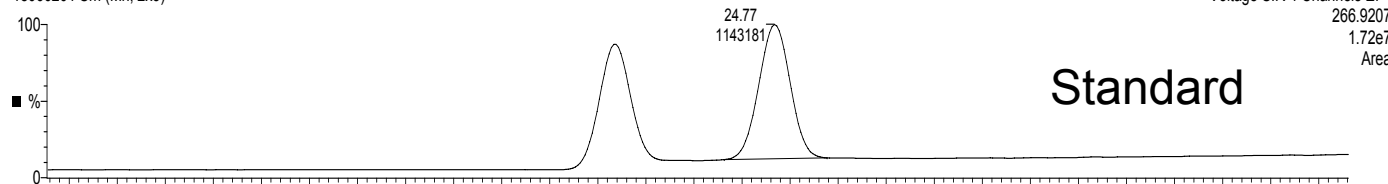


**Figure 2.** GC – EI/HRMS selected ion chromatograms ( $m/z$  264.9228 ; 266.9207) of standard  $\beta$ - TBECH isomer (50pg/ $\mu$ L) (the 2 top panels) and whale sample 1 (the 2 bottom panels). Plotted on each chromatogram are the retention times and the integrated areas.

# TBECH in Minke Whale

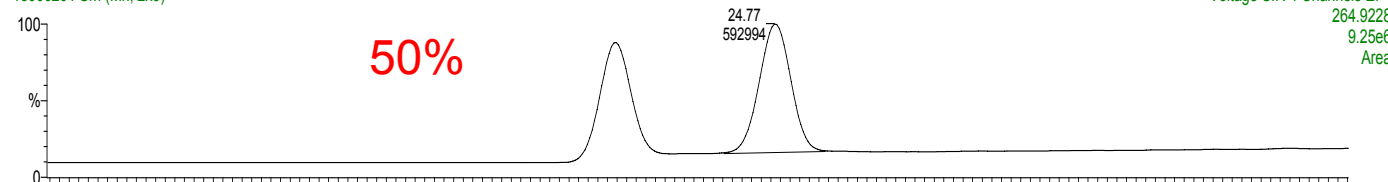
DL08-003:std TBECH 19 a,b,c,d 500 pg

18060201 Sm (Mn, 2x3)



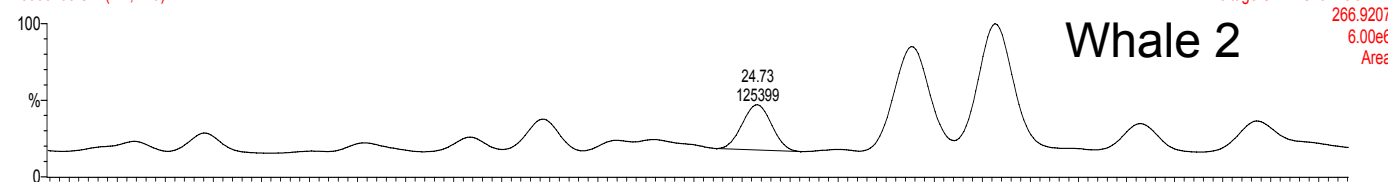
Voltage SIR 4 Channels EI+  
266.9207  
1.72e7  
Area

18060201 Sm (Mn, 2x3)



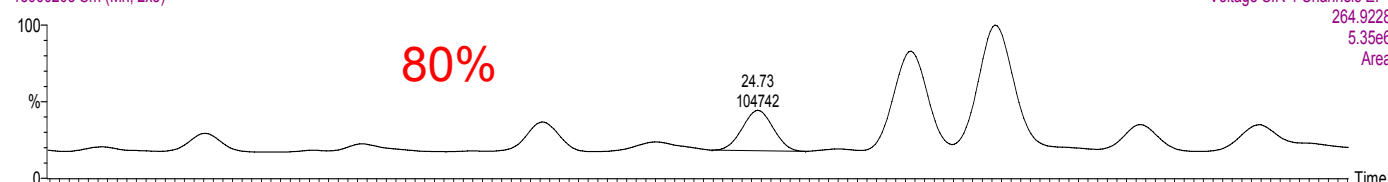
Voltage SIR 4 Channels EI+  
264.9228  
9.25e6  
Area

18060203 Sm (Mn, 2x3)



Voltage SIR 4 Channels EI+  
266.9207  
6.00e6  
Area

18060203 Sm (Mn, 2x3)



Voltage SIR 4 Channels EI+  
264.9228  
5.35e6  
Area

		[M]	[M+2]	[M+4]
TBECH	C <sub>8</sub> H <sub>12</sub> Br <sub>4</sub>	423.7673	425.7652	427.7632
- Br	C <sub>8</sub> H <sub>12</sub> Br <sub>3</sub>	344.8489	346.8469	348.8448
- 2Br	C <sub>8</sub> H <sub>12</sub> Br <sub>2</sub>	265.9306	267.9285	
- 3Br	C <sub>8</sub> H <sub>12</sub> Br	187.0122	189.0102	
- HBr	C <sub>8</sub> H <sub>11</sub> Br <sub>3</sub>	343.8411	345.8390	347.8370
- HBr <sub>2</sub>	C <sub>8</sub> H <sub>11</sub> Br <sub>2</sub>	264.9228	266.9207	268.9187
- H <sub>2</sub> Br <sub>2</sub>	C <sub>8</sub> H <sub>10</sub> Br <sub>2</sub>	263.9149	265.9129	
- HBr <sub>3</sub>	C <sub>8</sub> H <sub>11</sub> Br	186.0044	188.0024	
- H <sub>2</sub> Br <sub>3</sub>	C <sub>8</sub> H <sub>10</sub> Br	184.9966	186.9945	

# 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

- BDEs generally decreasing
    - Pilot Whale data not conclusive
    - BDE #154 different behaviour
  - Me-O-BDE
    - In all samples
    - Relatively high in Pilot Whale and Minke Whale
    - No correlation 1996 Pilot Whale data
    - Maybe weak correlation taken all data into account
  - New BFRs
    - HxBB
    - BEHTBP (Firemaster 550)
    - HBCD (confirmation analysis on going)
    - Many unknown Brominated organic compounds
- No new BFRs?
- TEBCH
  - PBDD/DFs
  - Others at low levels