“New” Brominated Flame Retardants (BFR) in the Nordic and Arctic Environments

Martin Schlabach

NILU, Norway

NILU Norsk institutt for luftforskning

Background

Flame retardants: Compounds used to reduce flammability of materials

Brominated flame retardants (BFR): PBDE, HBCD, TBBPA, and other ”new” BFRs

High focus on PBDE use, fate, and effects

Ban of PentaBDE and Octa BDE

Expect increase of other BFRs

NILU

Selection procedure

Review: ”Emerging ”New Brominated Flame Retardants in Flame Retardant Products and the Environment – Current State of Knowledge and Monitoring Requirements” SFT TA-2462/2008

Summarise/estimate: Properties, production volumes, effects

Special focus on persistency and long range transport potential (LRTP)

Priority list (14 compounds)based on production volume, LRTP, and Bioaccumulation

NILU

Several screening studies in 2009

Environmental screening of selected “new” brominated flame retardants and selected polyfluorinated compounds 2009”. KLIF, Oslo TA-2625/2010

Screening of decabromodiphenyl ethane (dbdpe) in lake sediment, marine sediment and peregrine falcon (Falco peregrinus) eggs. Ricklund, N., A. et al. (2009). ITM, Stockholm

New brominated flame retardants in Arctic biota. Sagerup et al. KLIF, Oslo TA-2630/2010

Results from the Swedish National Screening Programme 2009: Subreport 2. Dechlorane Plus. Kaj et al. IVL report in prep.

Arctic mammal screening on new brominated flame retardants, Bert van Bavel, Örebro university

Brominated Flame Retardants (BFR) in the Nordic Environment. Remberger et al. TemaNorden report 2011:528

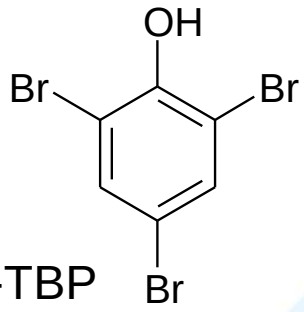
NILU

Compounds selected for NMR study

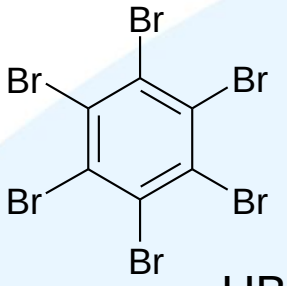
Compound name	Abbreviation	CAS #
Phenolic BFRs		
2,4-Dibromophenol	24DBP	615-58-7
2,4,6-Tribromophenol	246TBP	118-79-6
Pentabromophenol	PBP	608-71-9
Tetrabromobisphenol-A	TBBPA	79-94-7
BFR ethers and esters		
2,4,6-Tribromophenyl allyl ether	ATE	3278-89-5
2,3-Dibromopropyl- 2,4,6- tribromophenyl ether	DPTE	35109-60-5
1,2-Bis (2,4,6-tribromophenoxy) ethane	BTBPE	37853-59-1
2-Bromoallyl-2,4,6-tribromophenyl ether	BATE	-
2,4,6-Tribromoanisol	TBA	607-99-8
Bis (2-ethylhexyl) tetrabromophthalate	BEHTBP	26040-51-7
2-Ethylhexyl- 2,3,4,5-tetrabromobenzoate	EHTeBB	183658-27-7
Other flame retardants		
Dechlorane Plus	DP	13560-89-9
Hexabromobenzene	HBB	87-82-1
Pentabromotoluene	PBT	87-83-2
Pentabromoethylbenzene	PBEB	85-22-3
Decabromodiphenylethane	DBDPE	84852-53-9
1,2-Dibromo-4-(1,2-dibromoethyl)cyclohexane	TBECH	3322-93-8
Reference compounds		
Standard PBDEs		

NILU

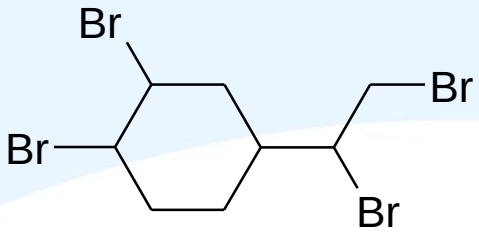
Typical chemical structures



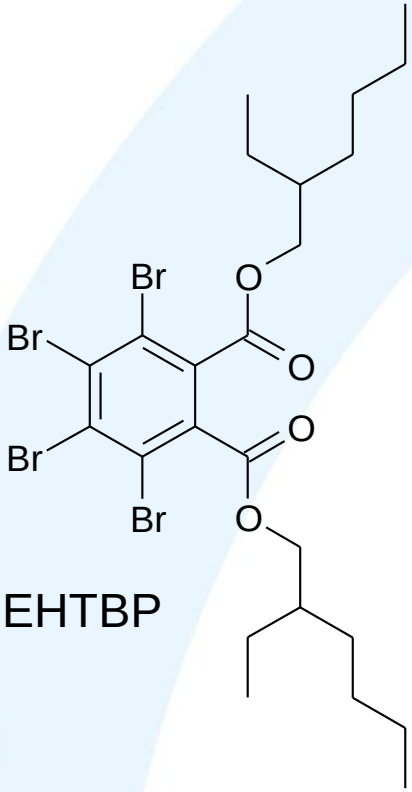
246-TBP



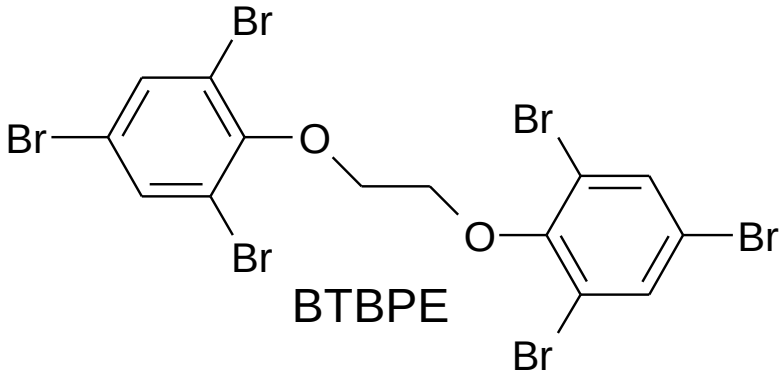
HBB



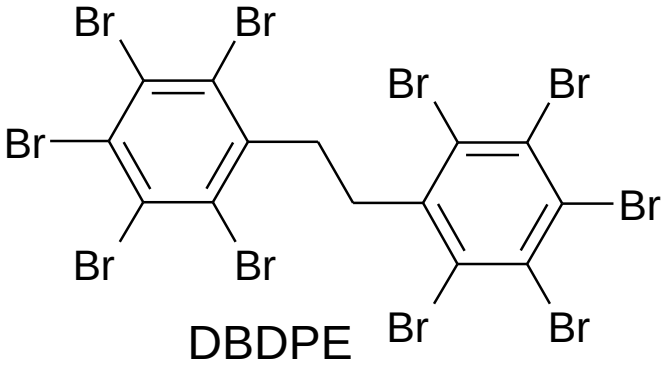
TBECH



BEHTBP



BTBPE



DBDPE

NILU

Sampling

National responsibility

Emission samples: Sludge, waste water

Environmental samples: Air, moss, needles, sediment, biota

Spatial distribution: Some sample types from all Nordic countries and the Arctic

NILU

Analysis

Different Nordic laboratories

Extraction

(Derivatisation of Phenolic compounds)

Dedicated clean-up

GC/LRMS, GC/HRMS, LC/MS

Different detection limits

NILU

Measurement uncertainties

Study design:

- Selection of compounds
- Selection of sample type, sites, time & frequency

Sampling

Transport & storage

Chemical analysis

Data treatment

Quantitation of uncertainty extremly difficult:

Estimated analytical uncertainty at least ± 20 - 40 %

NILU

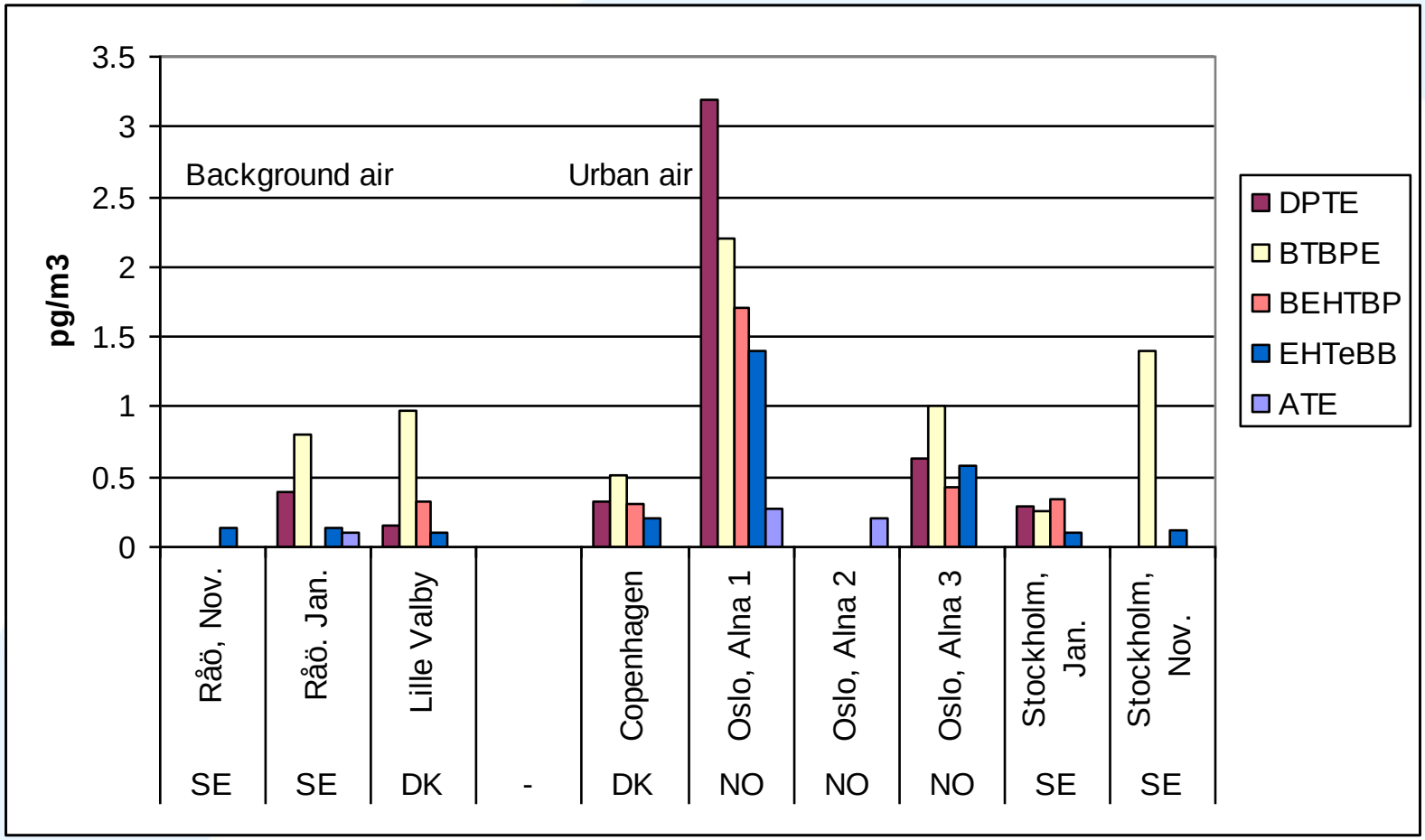
Results - Detection frequency

	NMR				Norway Main land						Arctic
Matrix	**Air**	**Sediment**	**Sludge**	**Biota**	**Air**	**Moss/ needles**	**Sediment**	**Sludge**	**Wastewater**	**Biota**	**Biota**
Number of samples	12	15	16	21	6	8	36	9	24	25	70
Phenolic BFRs	%	%	%	%	%	%	%	%	%	%	%
24DBP	58	78	8	39							
246TBP	50	92	23	91	0	0	3	0	0	40	20
PBP	8	8	15	17							
TBBPA	17	8	15	0							
BFR esters & ethers											
ATE	33	8	31	4	0	0	0	0	0	0	0
DPTE	67	8	31	17	0	0	0	0	0	0	0
BTBPE	92	50	100	91	0	0	19	67	25	0	6
BATE	25	0	31	4							
TBA	100	100	100	100							
BEHTBP	75	17	100	70	0	0	0	0	0	0	47
EHTeBB	92	25	77	57	0	0	0	0	0	0	94
TBBPA-AE					0	0	19	0	13	0	0
TBBPA-DPBPE					0	0	0	0	17	0	0
TBPA					0	0	0	0	0	0	0

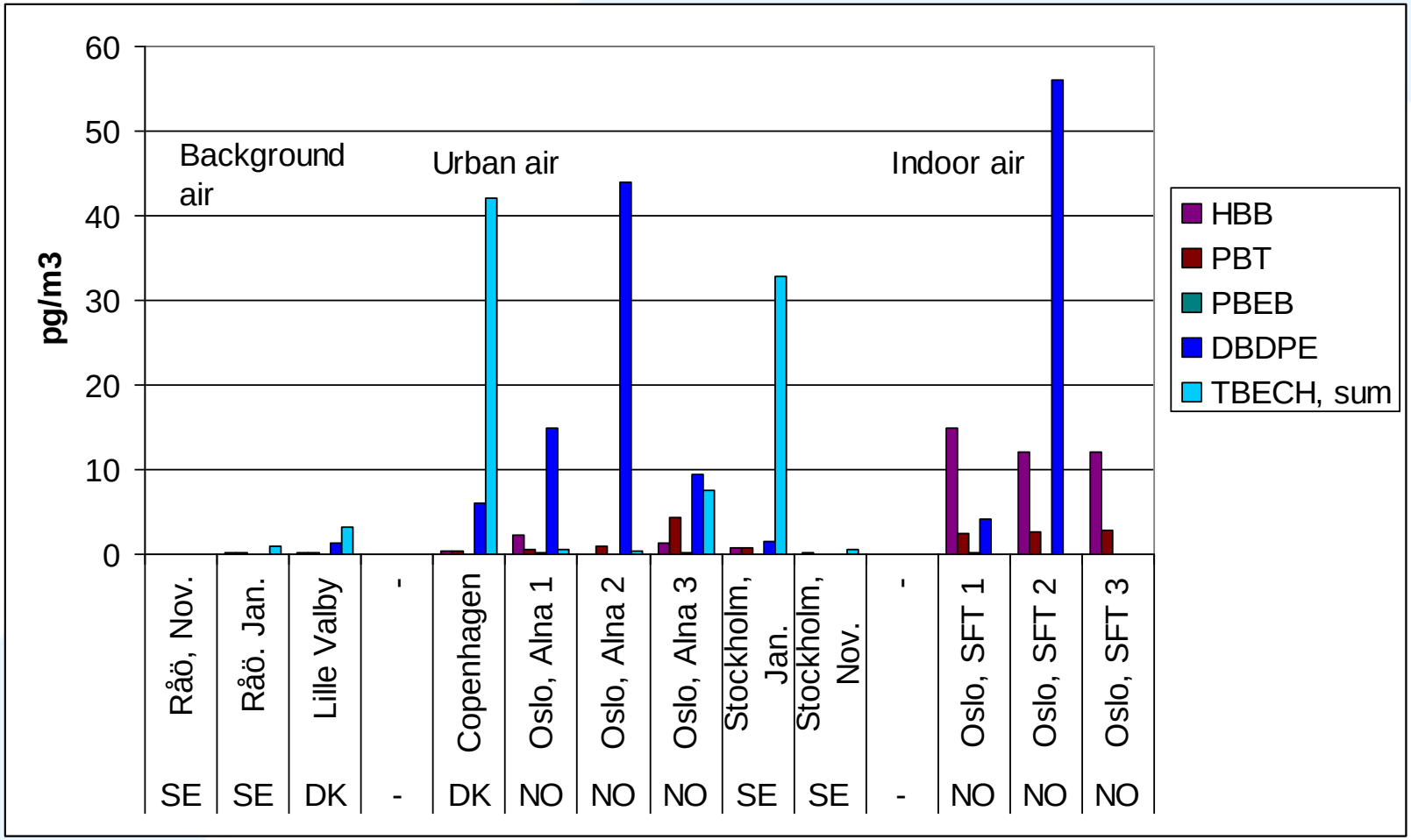
Results - Detection frequency

	NMR				Norway Main land						Arctic
Matrix	**Air**	**Sediment**	**Sludge**	**Biota**	**Air**	**Moss/ needles**	**Sediment**	**Sludge**	**Wastewater**	**Biota**	**Biota**
Number of samples	12	15	16	21	6	8	36	9	24	25	70
	%	%	%	%	%	%	%	%	%	%	%
Others flame retardants											
DP	75	100	100	52							
HBB	92	50	31	100	50	63	25	100	100	0	0
PBT	92	92	100	100	0	0	19	0	25	0	0
PBEB	67	58	69	43	0	0	17	0	13	0	0
DBDPE	100	50	100	70	0	25	8	89	21	0	1
TBECH, sum	92	50	46	81							
BTBPI					0	0	0	0	0	0	0
Reference BFR											
BDE-28	100	94	75	100							
BDE-47	100	100	83	100							
BDE-71/49	50	89	83	100							
BDE-66	33	44	25	70							
BDE-77	17	6	0	10							
BDE-99	100	100	75	100							
BDE-100	67	100	75	100							
BDE-85	33	22	17	25							
BDE-119	0	0	0	35							
BDE-138	33	22	25	5							
BDE-153	50	50	75	80							
BDE-154	50	67	75	100							
BDE-183	67	50	75	40							
BDE-196	33	17	50	10							
BDE-206	50	39	83	30							
BDE-209	100	78	92	95							

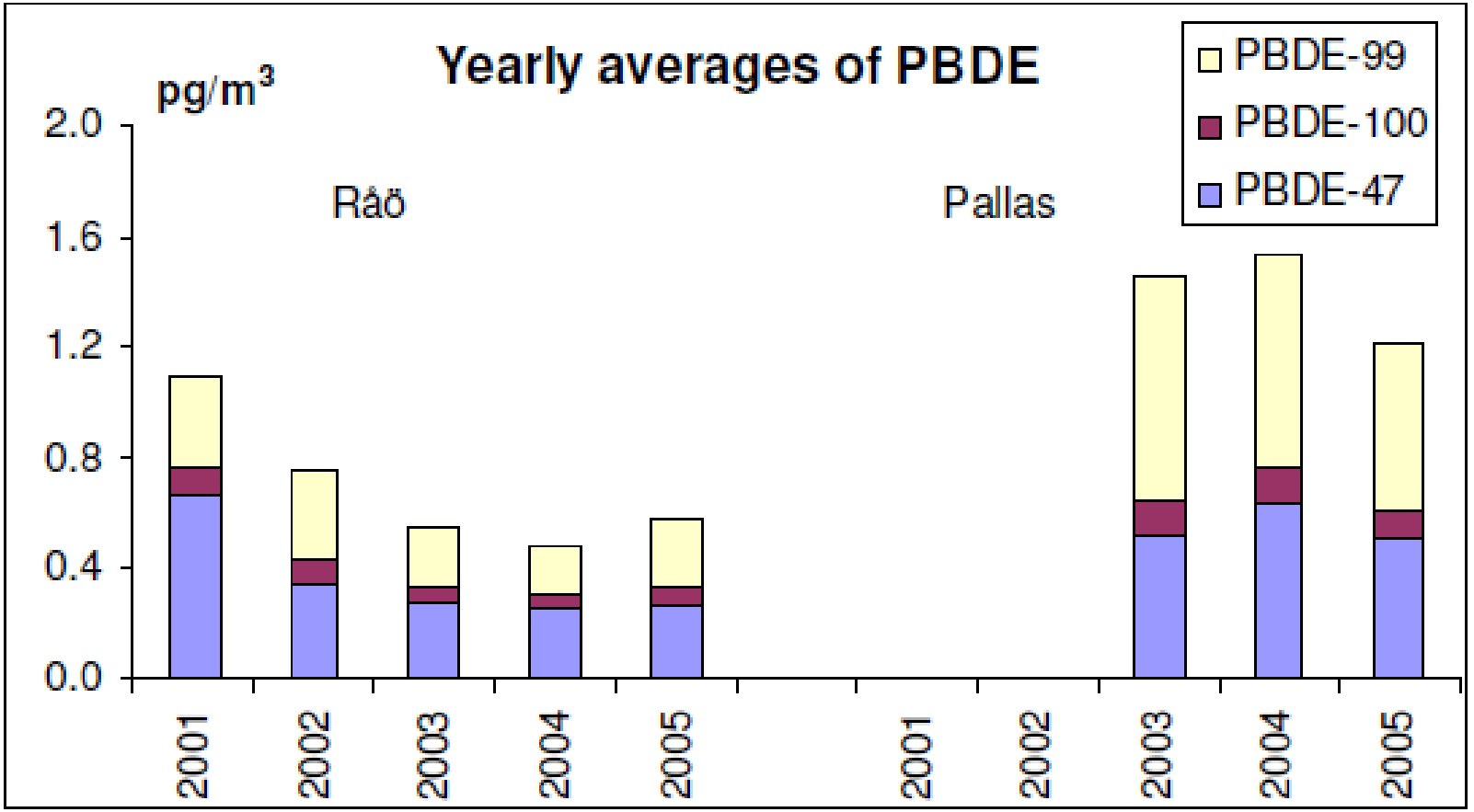
Air NMR BFR ethers/esters



Air NMR Other FRs

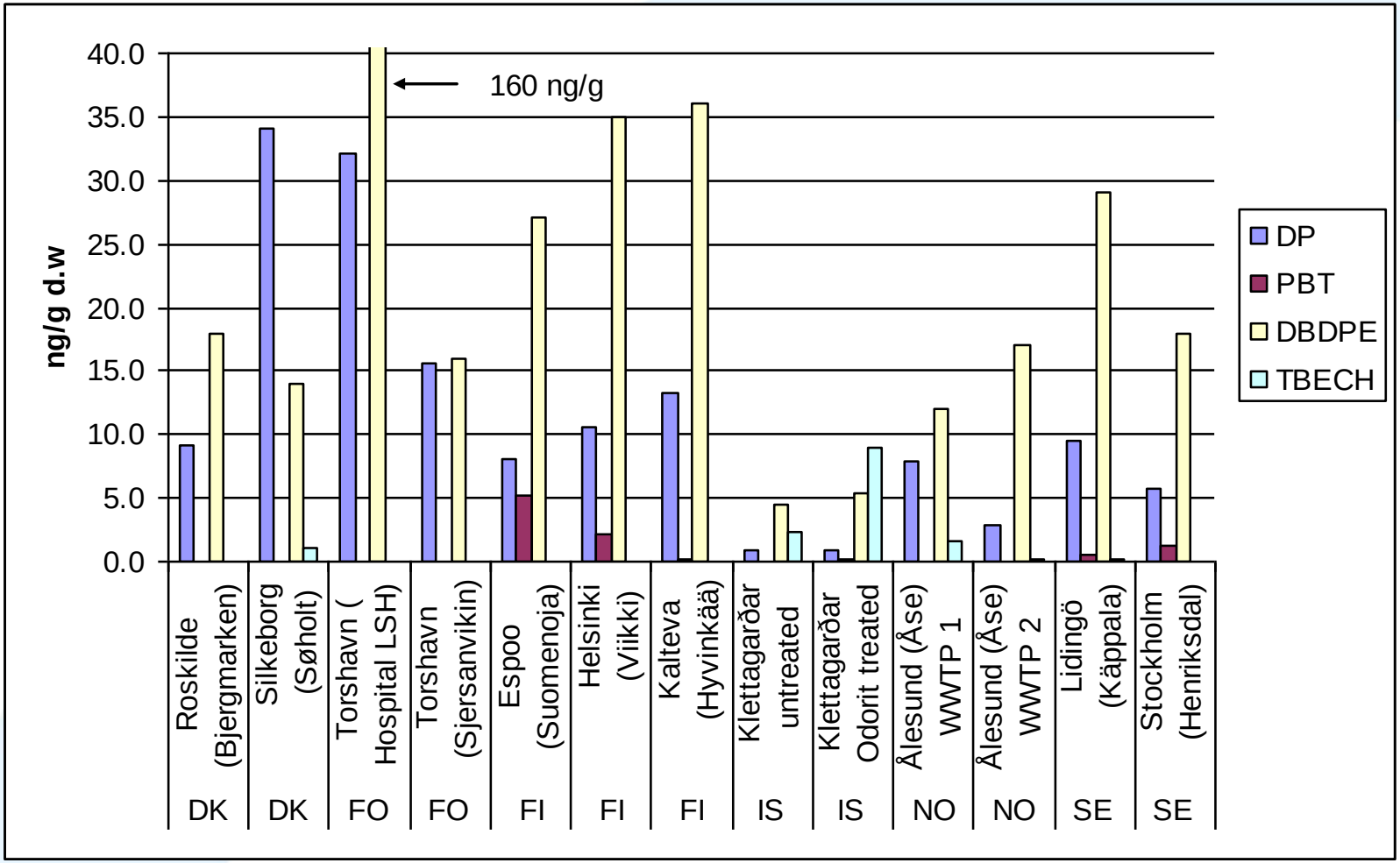


Air Råö/Pallas PBDE

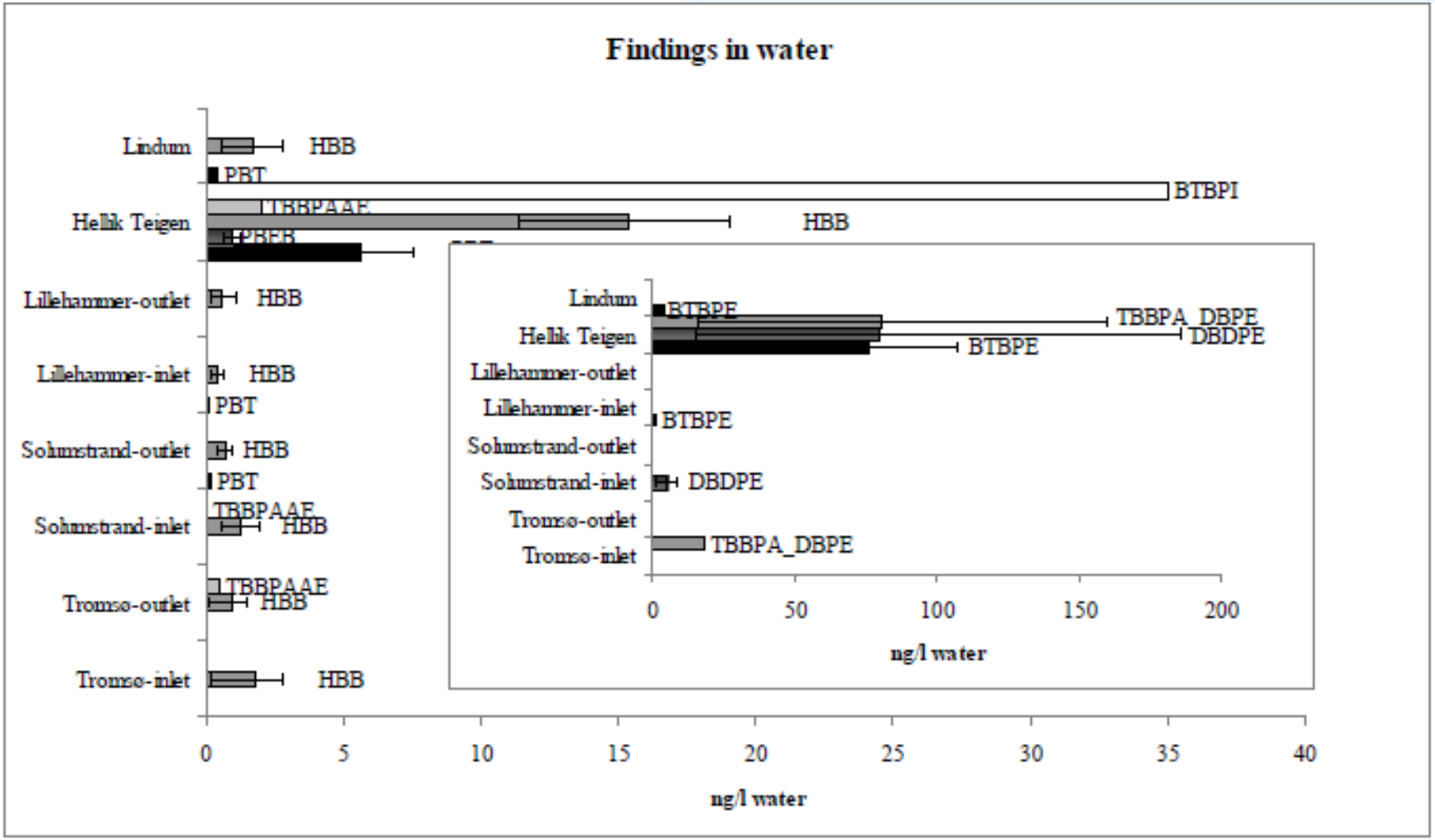


Hansson K. et al. (2006), IVL U1967

Sludge NMR Other FRs

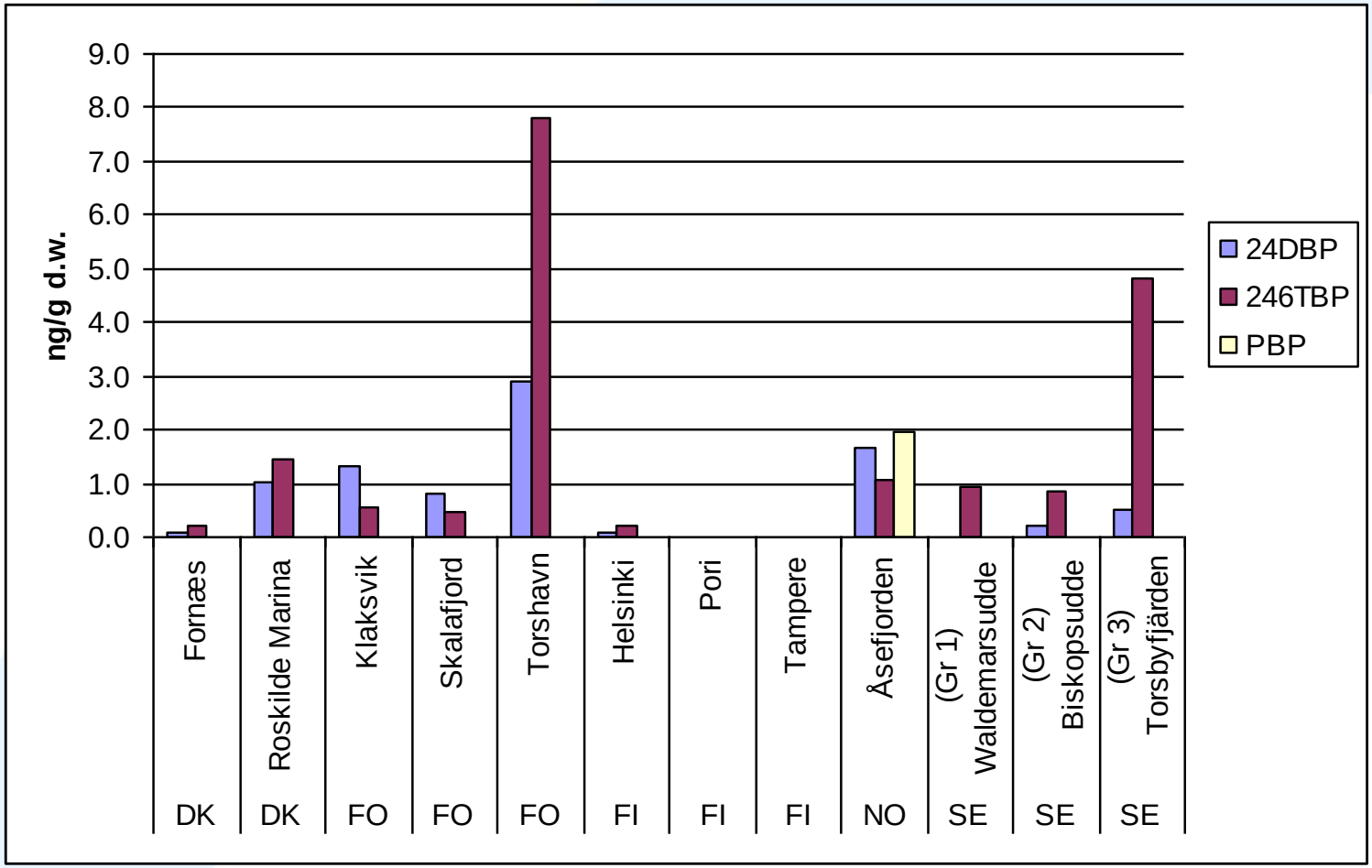


Sewage/seepage water Norway



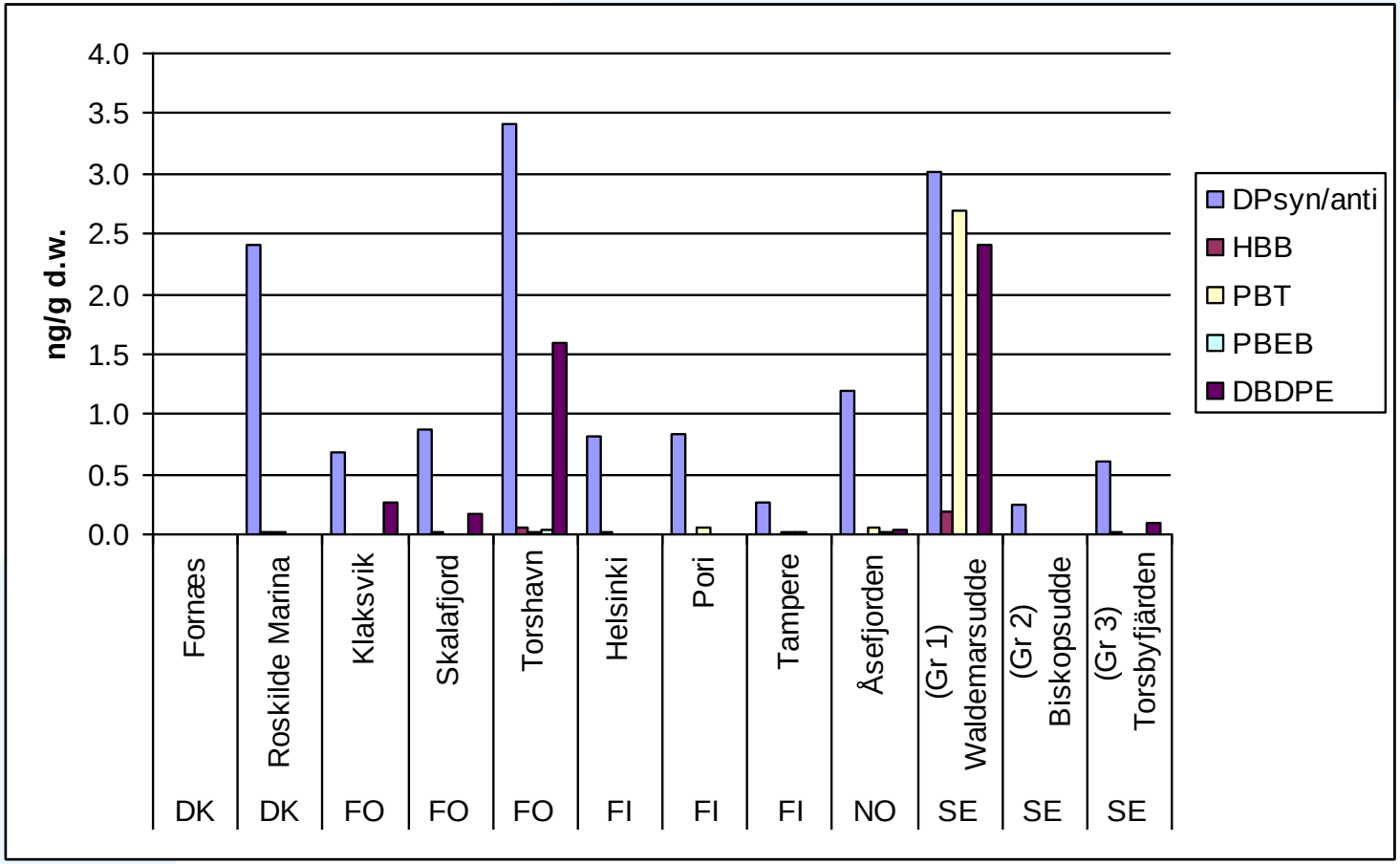
NILU

Sediment NMR Phenolic BFRs

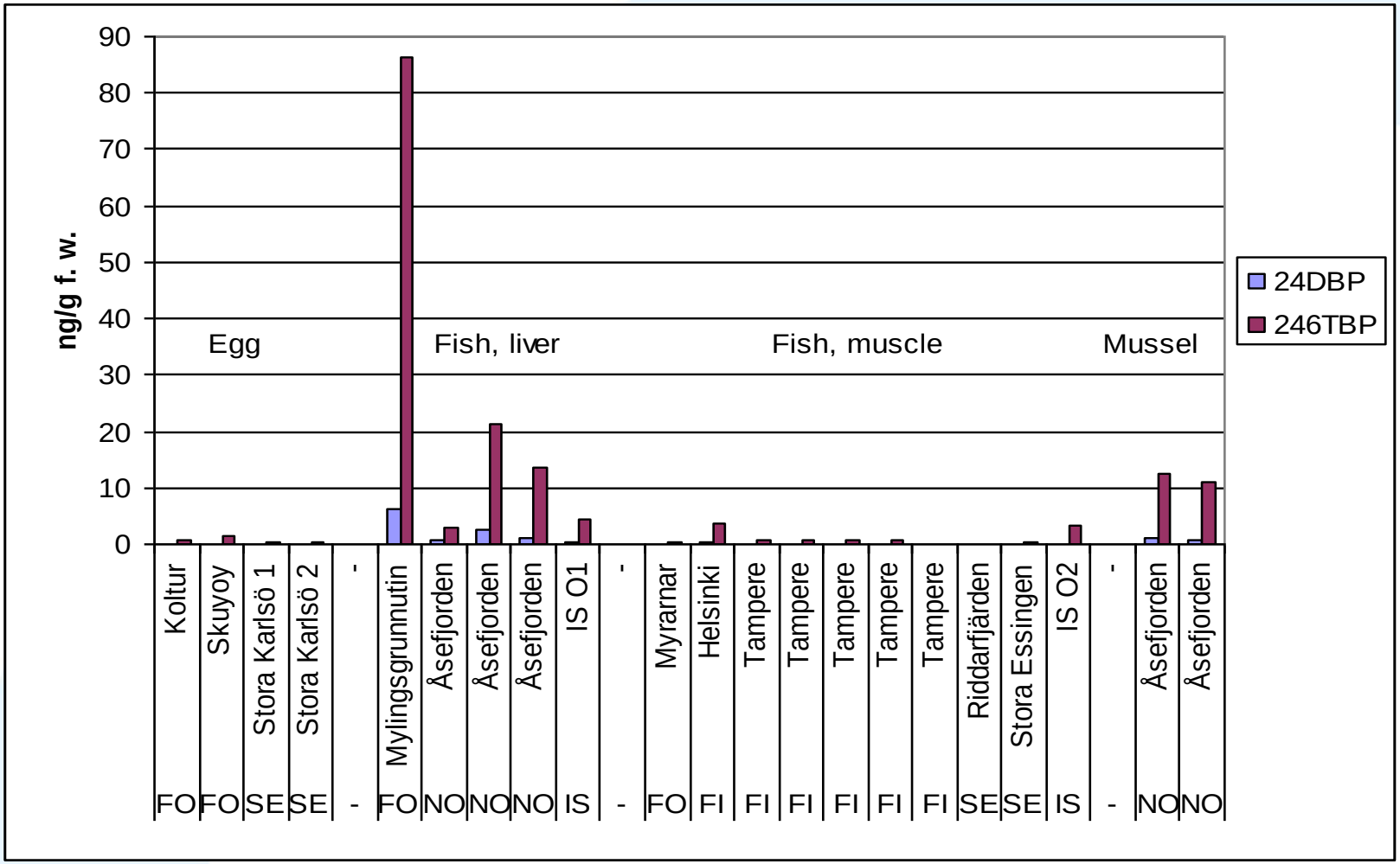


NILU

Sediment NMR Other FRs

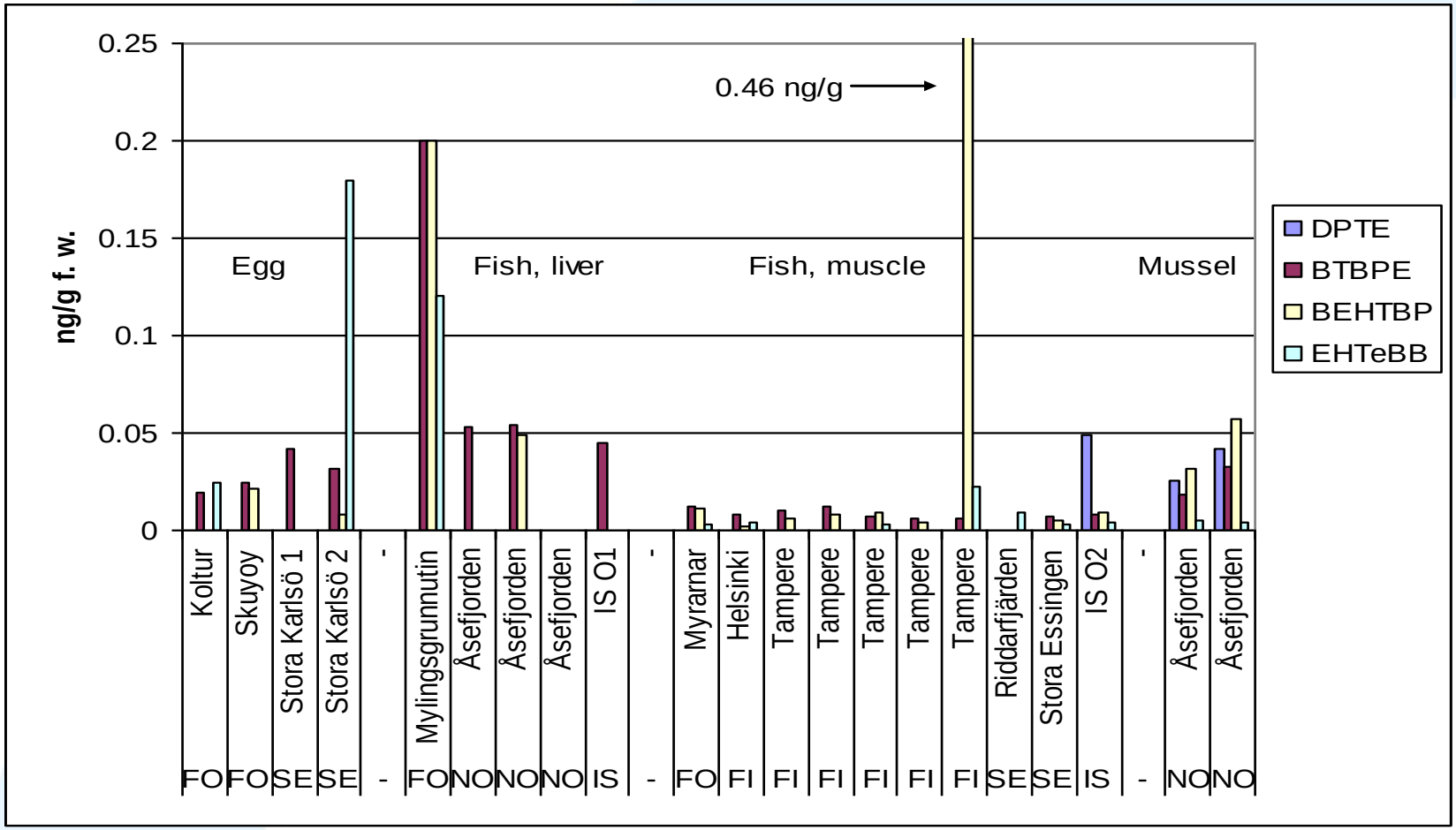


Biota NMR Phenolic BFRs

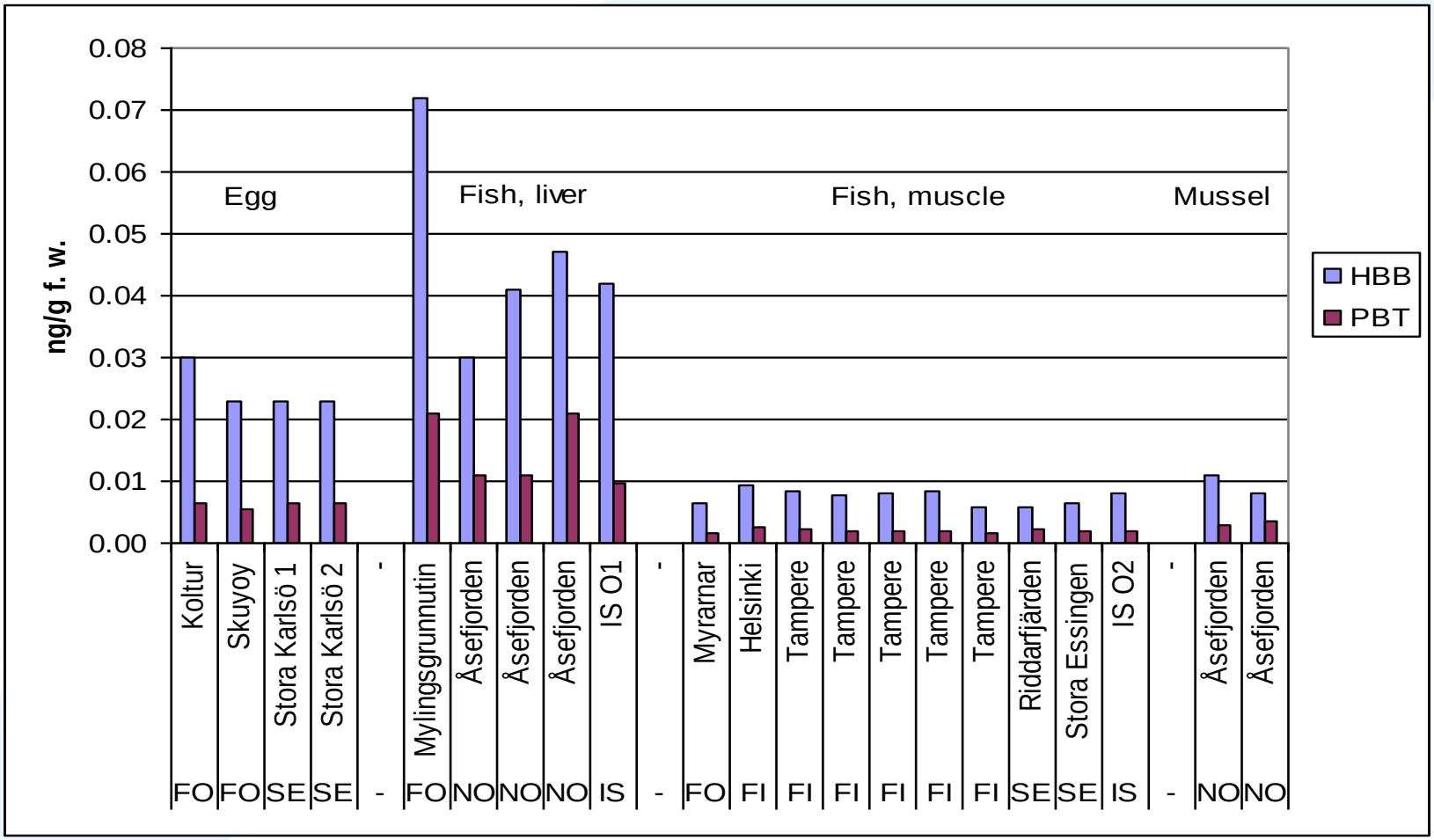


NILU

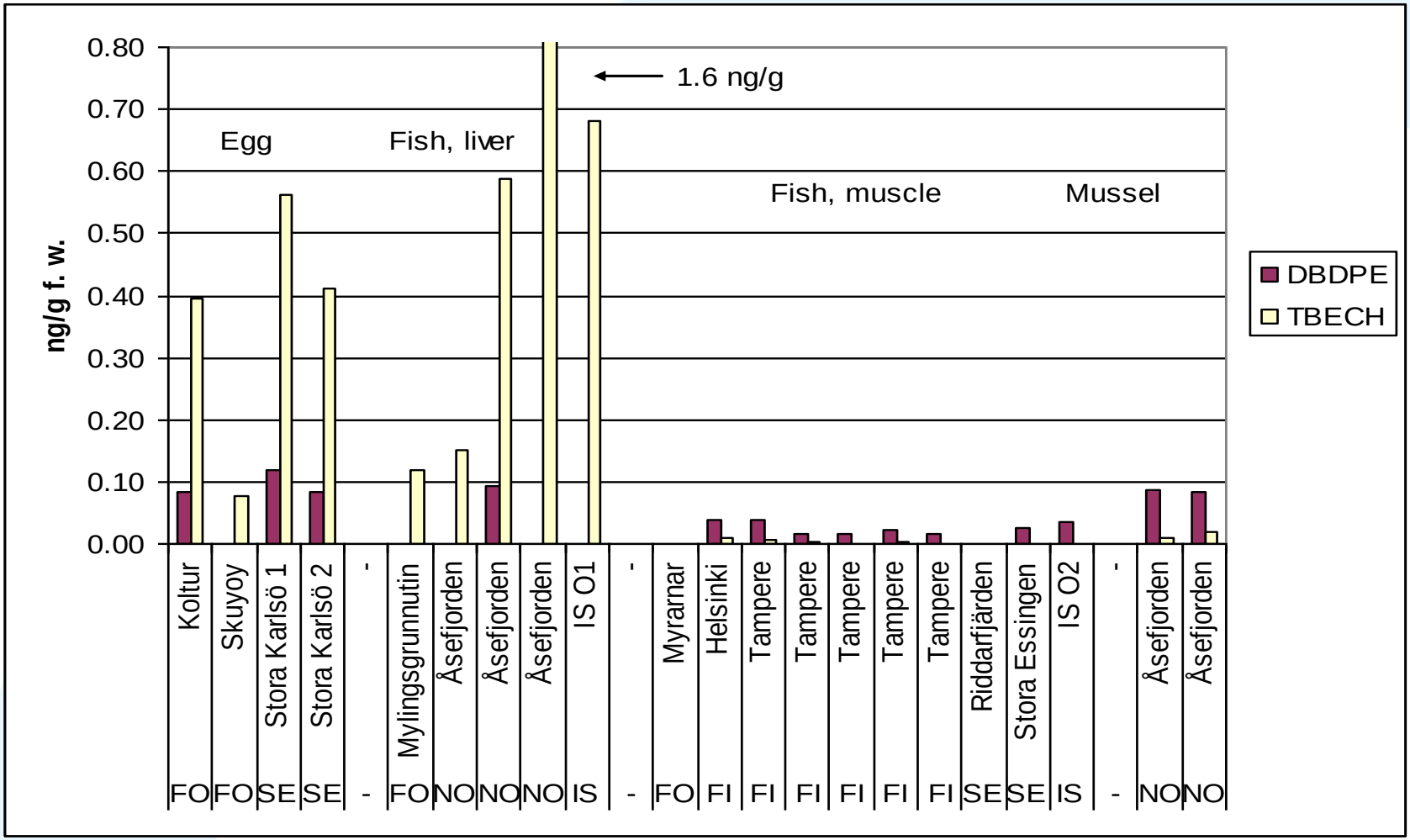
Biota NMR BFR ethers/esters



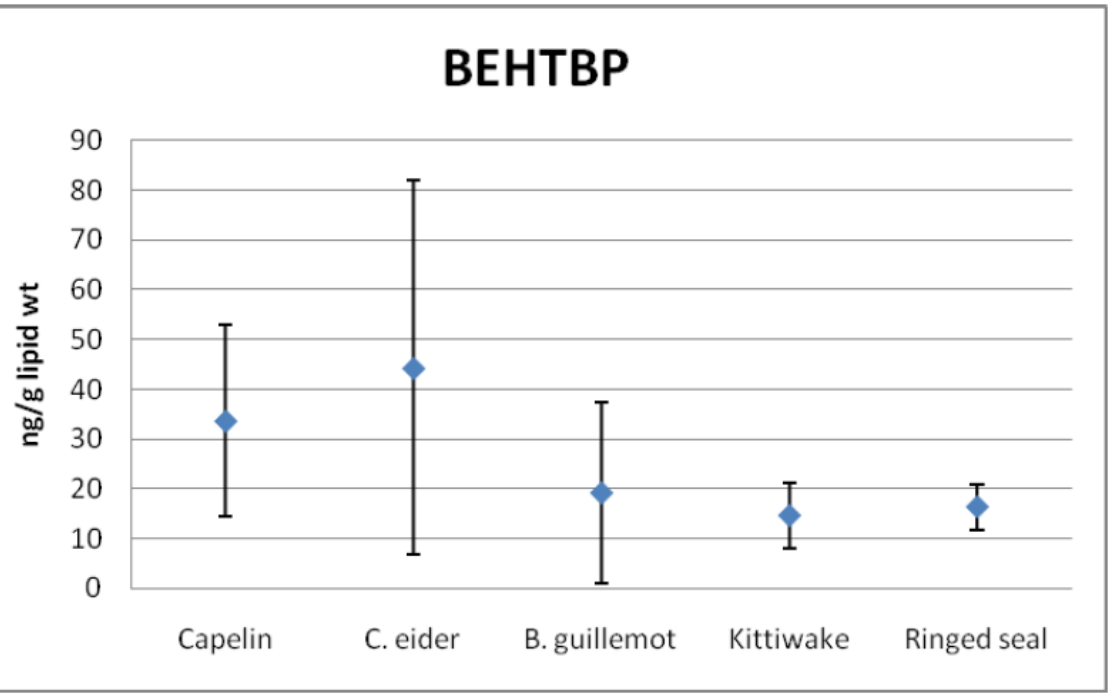
Biota NMR HBB/PBT

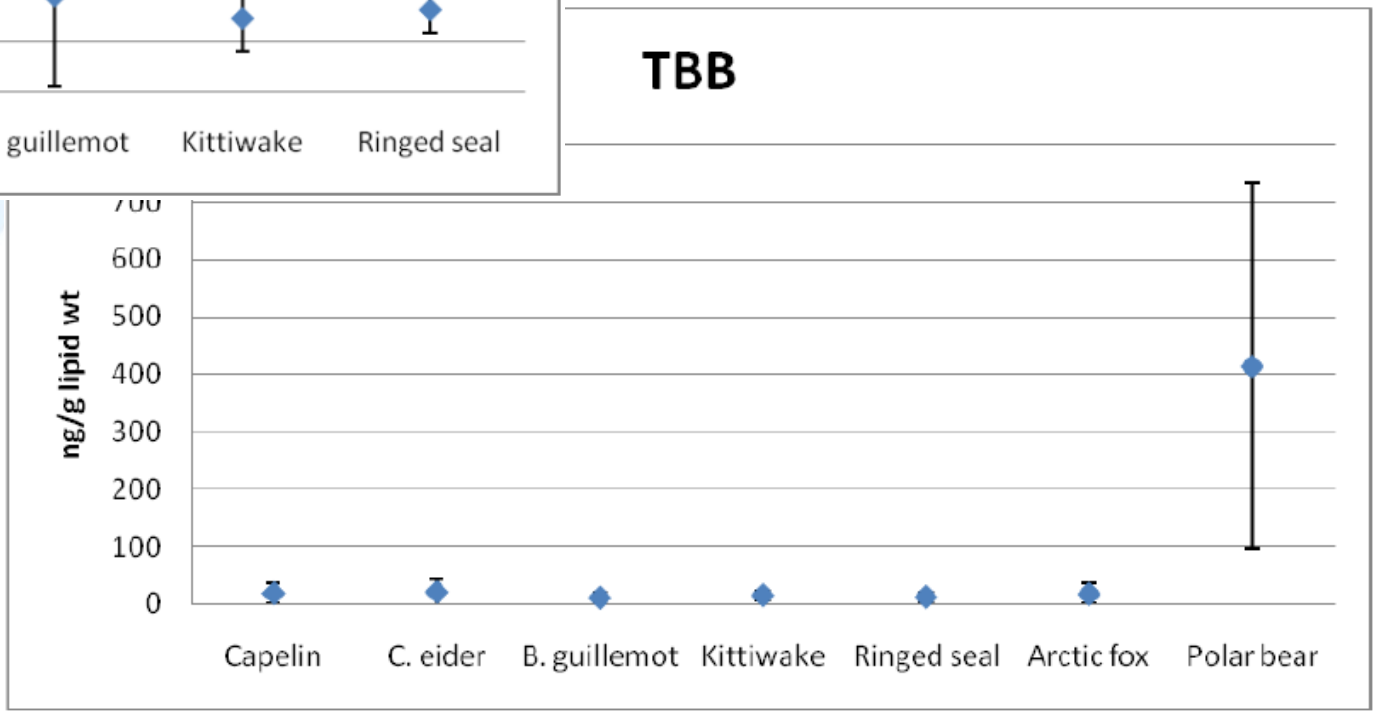


Biota NMR DBDPE/TBECH



Biota Arctic EHTeBB/BEHTBP





NILU

Summary results

Selected compounds regularly found in environmental and emission samples:

Phenolic BFRs	BFR esters & ethers	Others flame retardants
24DBP	DPTE	DP
246TBP	BTBPE	HBB
	(TBA)	PBT
	BEHTBP	PBEB
	EHTeBB	DBDPE
		TBECH, sum

NILU

Summary results NMR

Matrix	Biota (ng/g f.w.)[a]	Sediment (ng/g d.w.)[b]	Sludge (ng/g d.w.)[c]
Phenolic BFRs			
24DBP	<0.02-6.4	<0.03-2.9	<0.04-40
246TBP	<0.03-86	<0.03-7.8	<0.01-100
BFR esters & ethers			
BTBPE	<0.0052-0.2	<0.0081-1.7	<0.075-3.9
TBA	0.013-14	0.0009-0.66	0.00034-2
BEHTBP	<0.026-0.46	<0.013-3.3	<0.13-42
EHTeBB	<0.006-0.18	<0.0082-0.21	<0.25-2.6
Other BFRs			
DP syn+anti	0.002-0.083	0.0084-3.4	0.051-34
HBB	0.0058-0.072	<0.022-0.19	<0.14-0.72
PBT	0.0015-0.021	<0.011-2.7	<0.027-5.2
PBEB	<0.00034-0.0044	<0.0098-0.046	<0.00095-0.13
DBDPE	<0.082-0.12	<0.00001-2.4	<2.5-160
TBECH, sum	0.0032-1.6	0.010-350	0.018-9.0
Reference compounds			
pentaBDE[d]	0.062-36	0.096-13	0.18-76

NILU

Conclusion

Waste reclamation	→	Important point source
Present in air samples	→	Long range atmospheric transport
Widespread in biota	→	Bioaccumulation
Real effect data are scarce	→	Ecotox. relevance unclear

NILU

Conclusion

Bioaccumulation → Negative effects on higher organisms cannot be excluded

Some compounds in same concentration as PBDE

Broader monitoring and more effect studies are recommended

Selection based on production volume and fate modelling is working

NILU

Acknowledgement

Thanks to

Audience for attention

NORMAN for arranging this workshop

NMR for this project

My colleagues for good collaboration