Non-PBDE halogenated and non-halogenated flame retardants as ***global*** emerging contaminants

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Sampling and Analysis of Emerging Contaminants in the Aquatic Environment: Current and Future Challenges

Oslo, 02.03.2012

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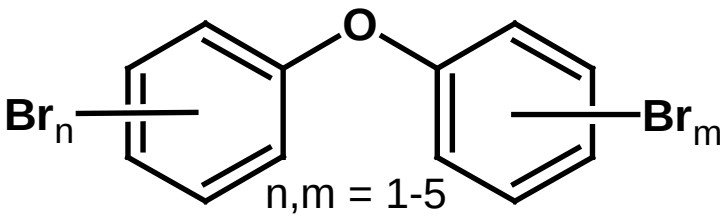
Zentrum für Material- und Küstenforschung

PBDEs…

Polybrominated diphenyl ethers (PBDEs)

- used for several decades as FRs
- harmful for the environment and humans
  - → Persistent, bioaccumulative, toxic (PBT)
  - → long-range atmospheric transport (LRAT)
- ubiquitous in various compartments



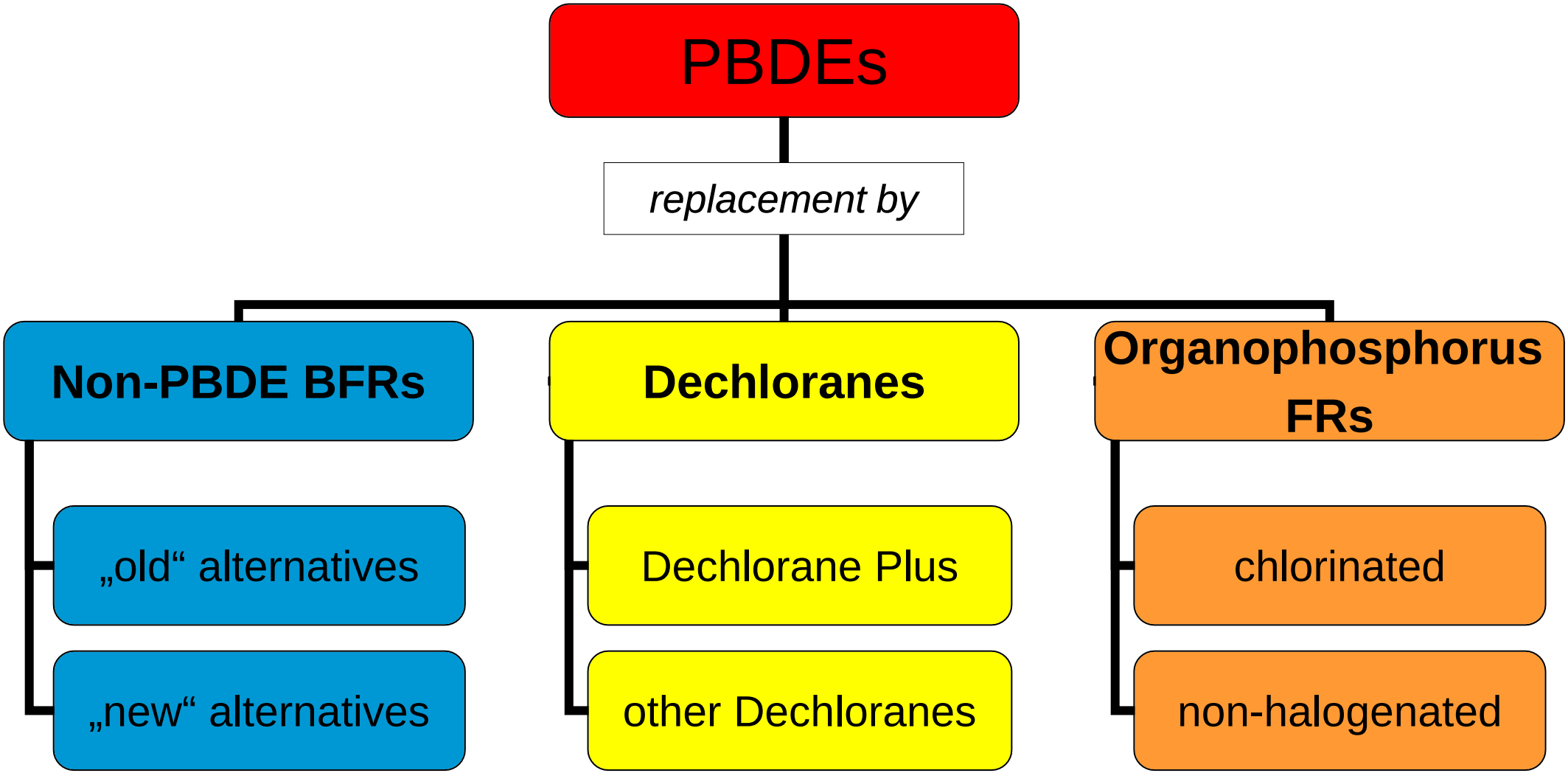
→ *Ongoing worldwide banishment since early 2000s*

2004/2006	PentaBDE, OctaBDE (>0.1 %)
2008:	*DecaBDE in E&E*
2009:	*Penta- and OctaBDE: POPs*

→ *DecaBDE in other products*

→ *no production, but import*

…what's next?


PBDEs
replacement by
Non-PBDE BFRs
Dechloranes
Organophosphorus FRs
„old“ alternatives
„new“ alternatives
Dechlorane Plus
other Dechloranes
chlorinated
non-halogenated

Alternative BFRs

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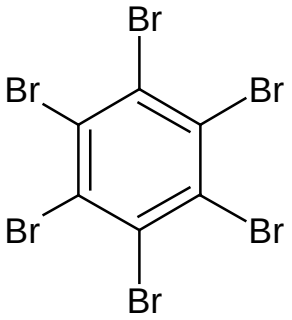
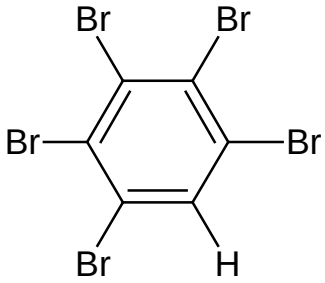
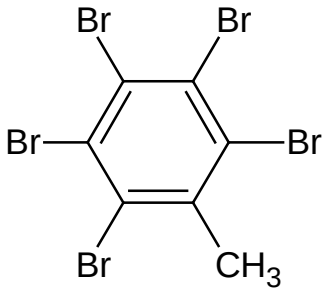


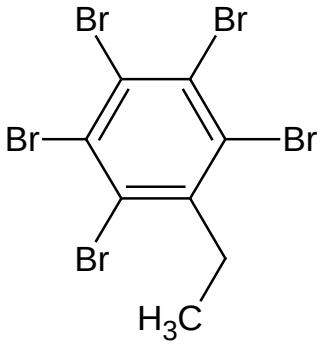
HBB



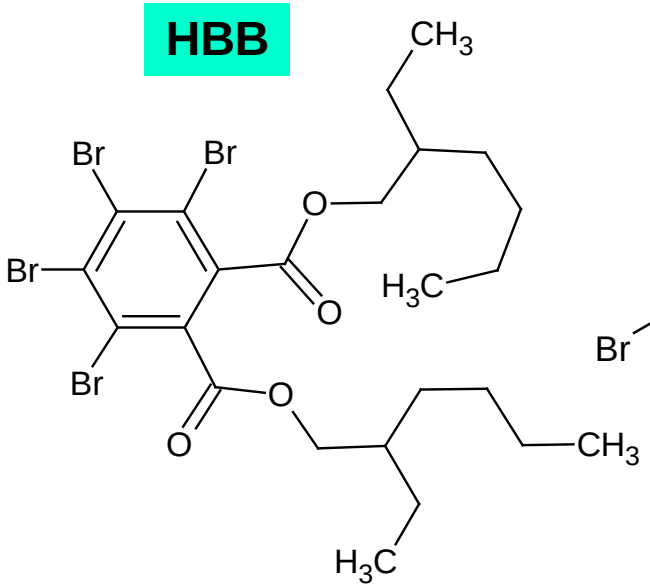
PBBz



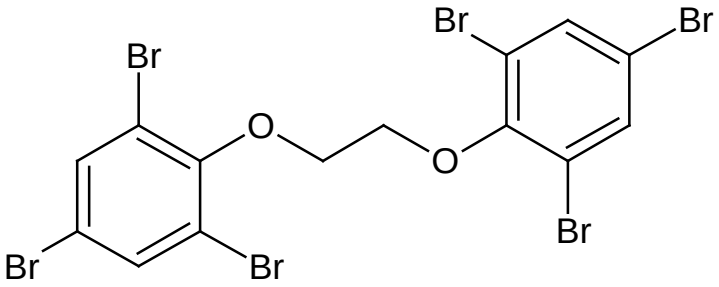
PBT



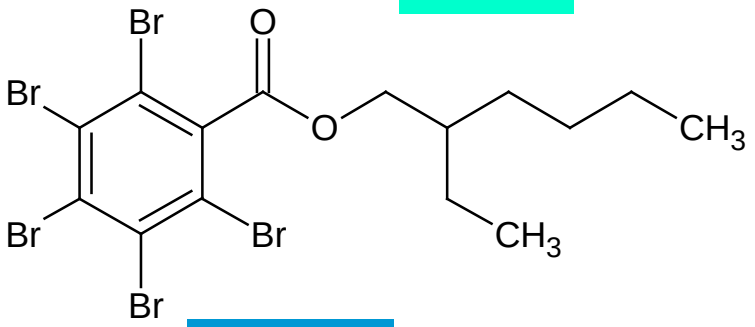
PBEB



TBPH, BEHTBP

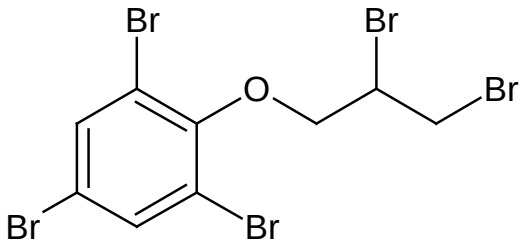


BTBPE



EHTBB

+ dozens of other new and old brominated FRs



DPTE

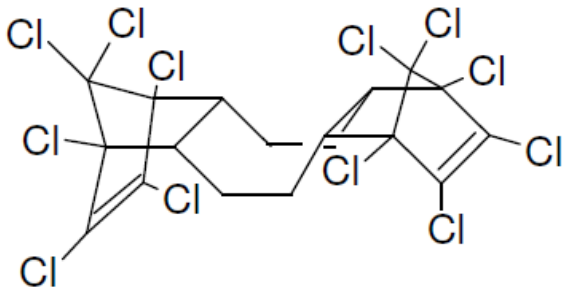
Dechloranes

Environ. Sci. Technol. 2006, 40, 1184–1189

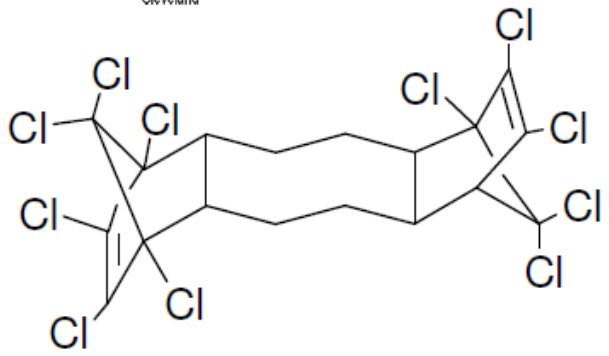
Dechlorane Plus, a Chlorinated Flame Retardant, in the Great Lakes

EUNHA HOH, LINGYAN ZHU, AND RONALD A. HITES*
School of Public and Environmental Affairs, Indiana University, Bloomington, Indiana 47405

A highly chlorinated flame retardant, Dechlorane Plus (DP), was detected and identified in ambient air, fish, and

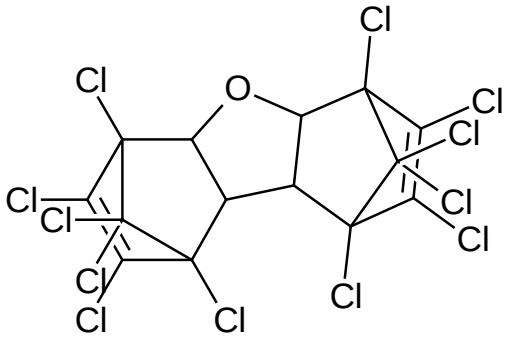


synDP

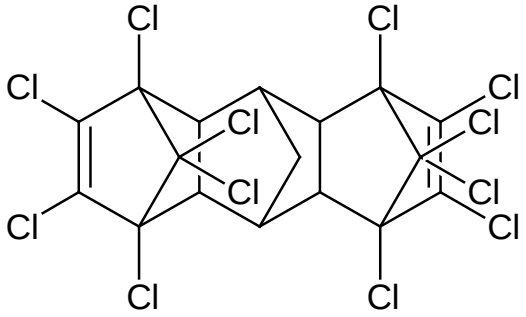


antiDP

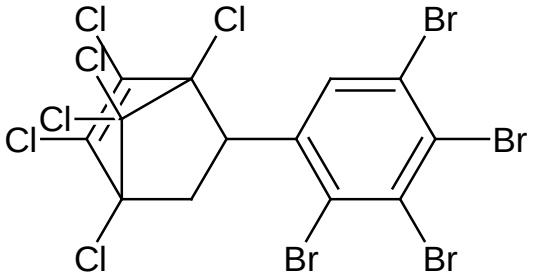
Dechlorane Plus (605)



Dechlorane 602



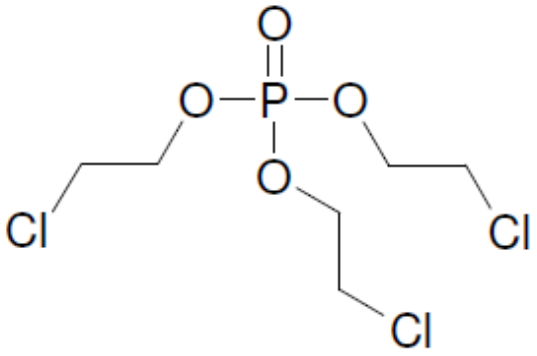
Dechlorane 603



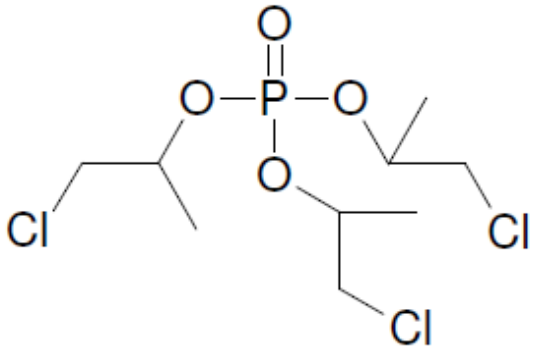
Dechlorane 604

Organophosphorus FRs

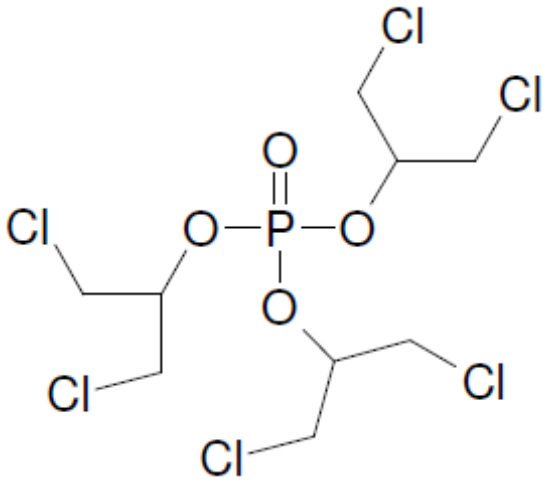
Chlorinated OPs – Flame retardants



TCEP



TCPP



TDCP

Alkylated OPs

- TnBP, TiBP – plasticizer, hydraulic fluids, …
- TEHP – plasticizer, …
- TBEP – Flame retardant, plasticizer, …

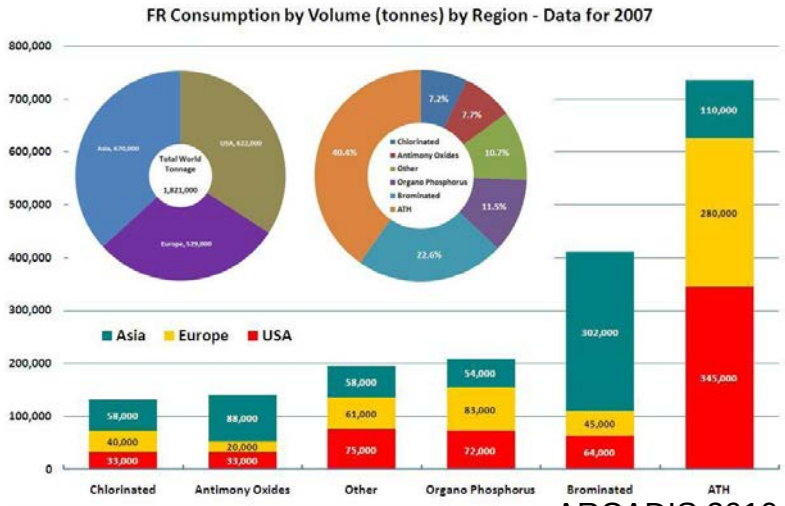
+ dozens of other (non)-halogenated OPFRs

Arylated OP

- TPhP – Flame retardant, plasticizers, …

Production and properties

1. **Production**
   - → Little data on alternative BFRs and DP
   - → BFRs and DP in U.S. and Asia
   - → OPFRs worldwide incl. Western Europe
   - → Production since ***several decades***



ARCADIS 2010

2. **PBT properties**
   - → BFRs and DP: modelled **P** and **B** + bioaccumulation studies
     T mostly unknown, some effects observed
   - → OPFRs: **P** high for chlorinated OPs, **B** ? - but observed in biota
     T – various known effects (carcinogenic, skin irritation,…)
3. **LRAT**
   - → BFRs and DP: modelled LRAT potential, occurence in Arctic biota
   - → OPFRs: Atmospheric half life <1d, but occurence in snow, Antarctic aerosols…

Global distribution of alternative FRs

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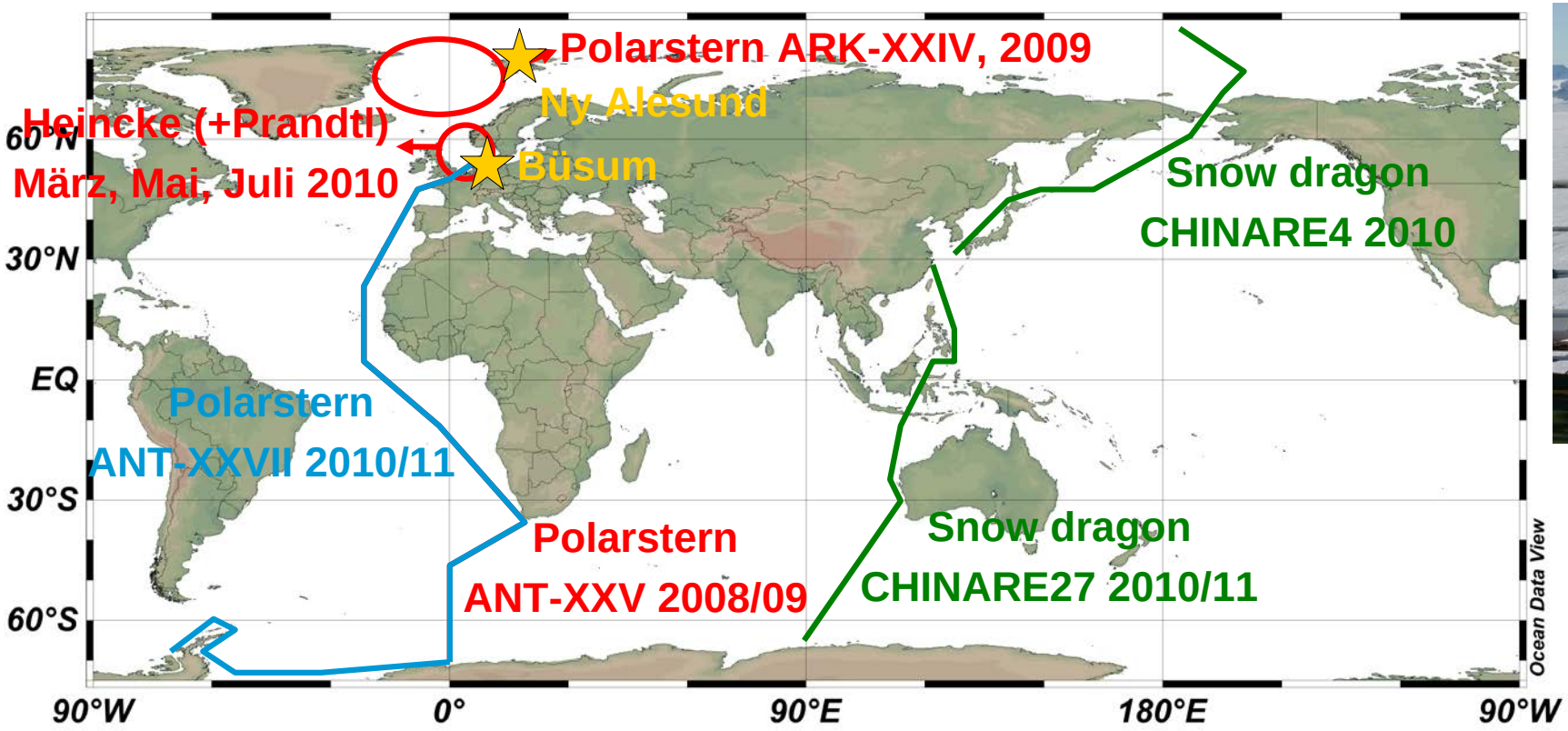

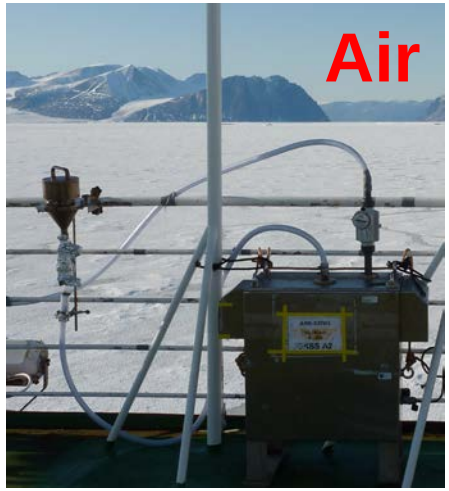

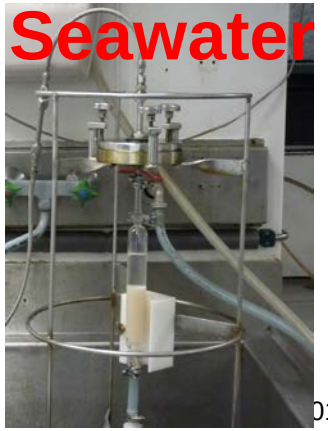

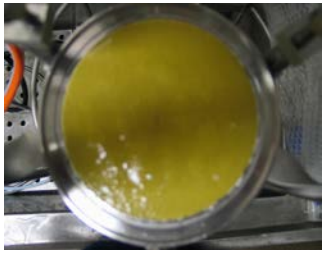

BFRs – Atlantic Ocean air and seawater

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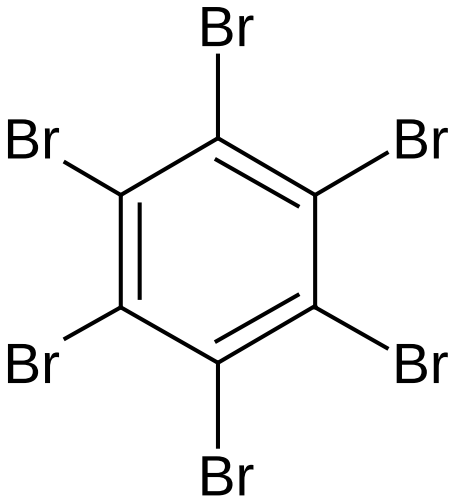
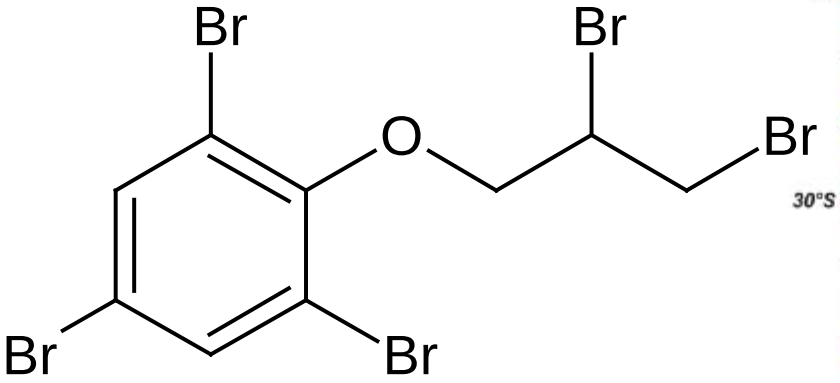
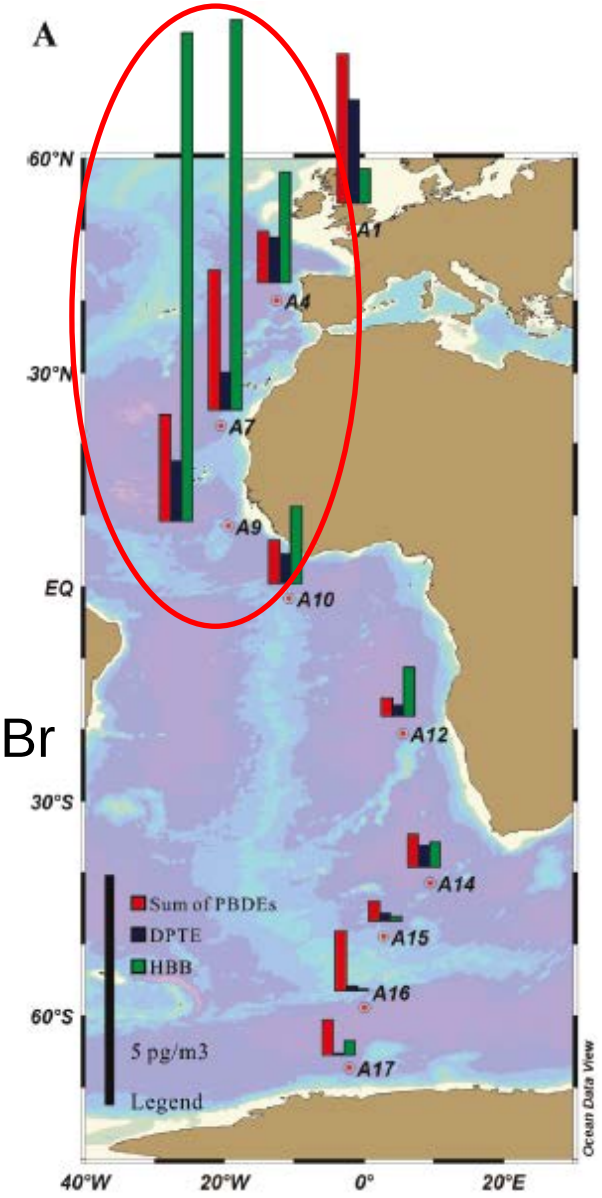


HBB

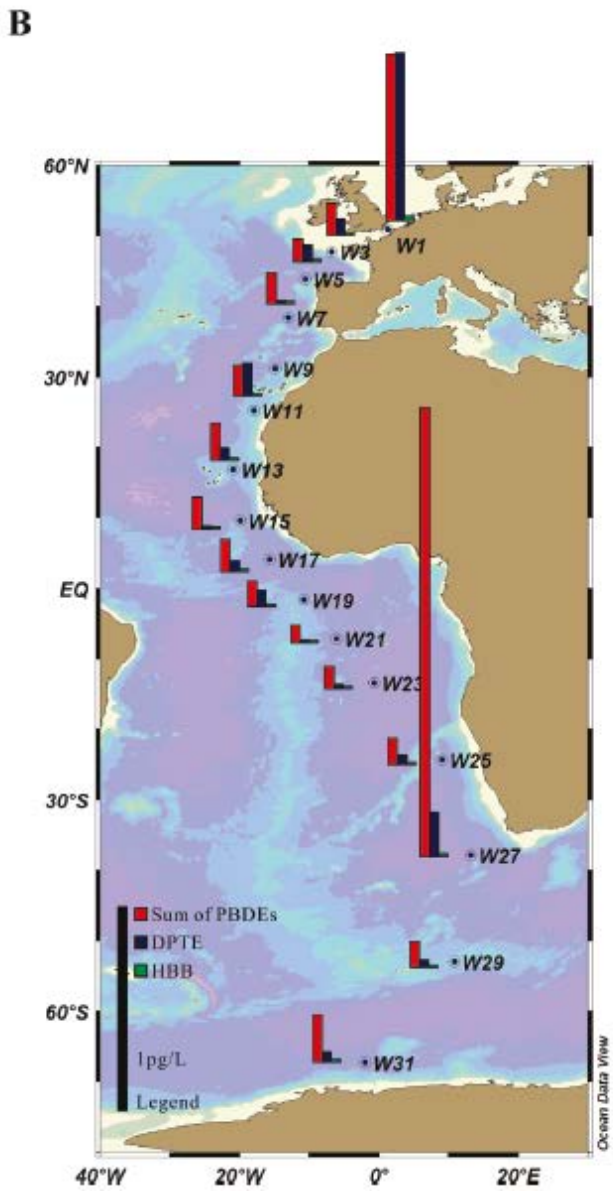


DPTE

Atmosphere



Seawater



Xie et al., ES&T 2011

BFRs and DP – Pacific Ocean air

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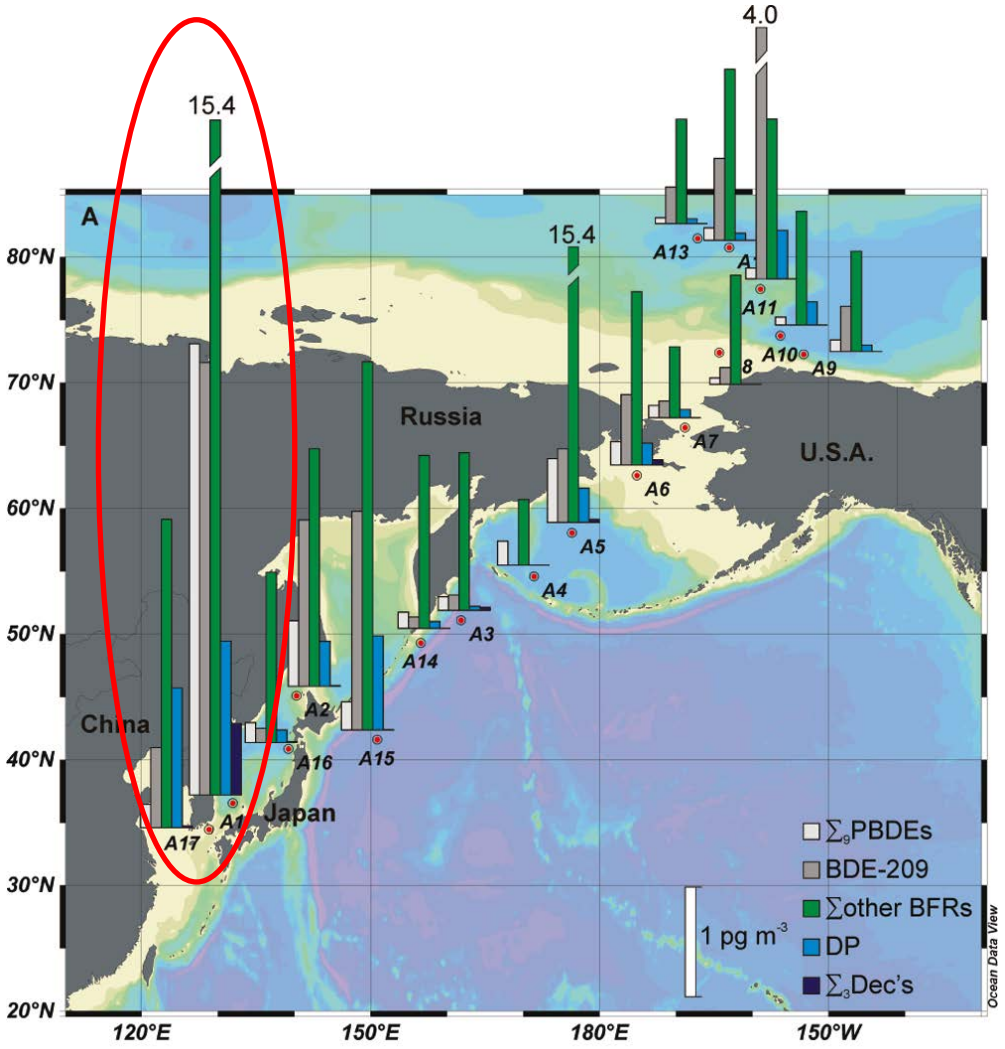

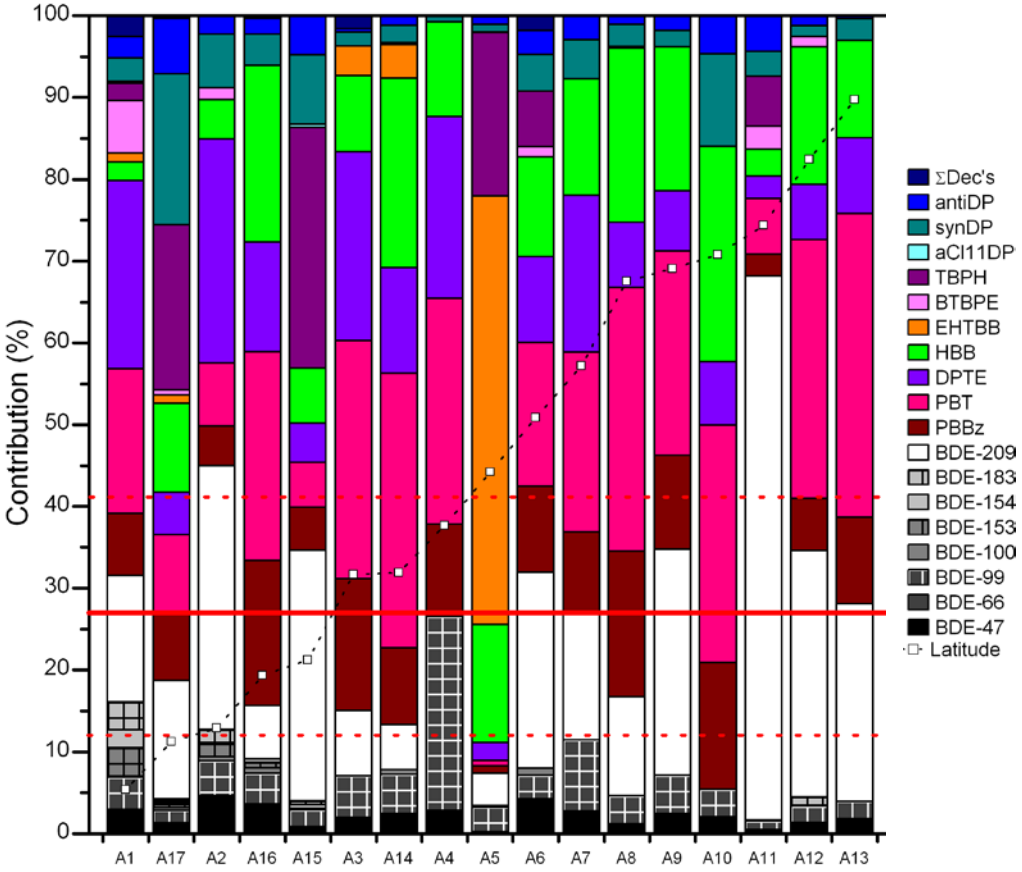

PBT > BDE-209 > HBB = PBBz = DPTE > BDE-47

Möller et al., ES&T 2011

BFRs and DP – Indian Ocean air

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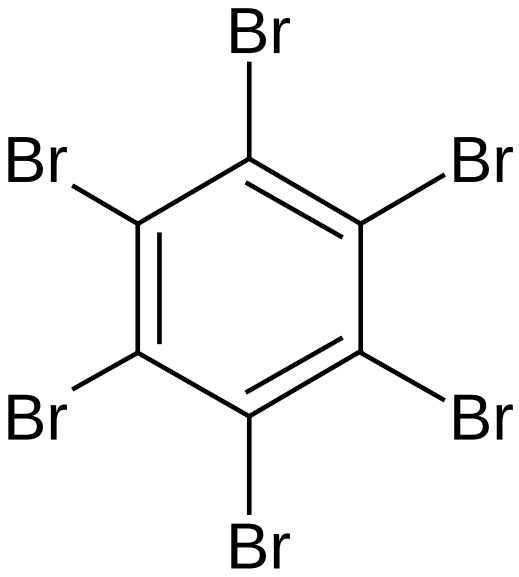
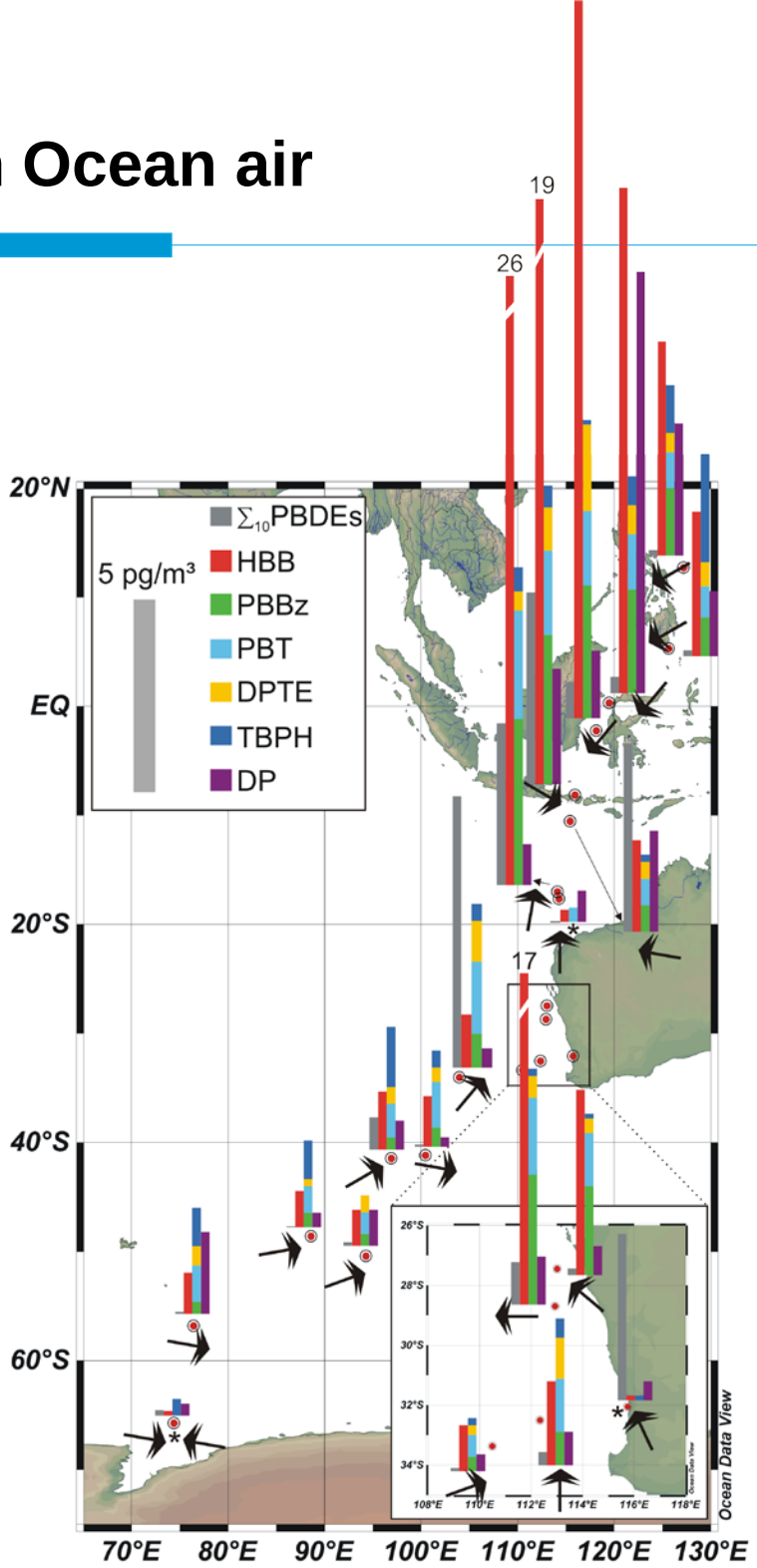
…again



HBB



Möller et al., ES&T 2012

OPFRs – Pacific and Indian Ocean air

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→ global occurence, particle-bound

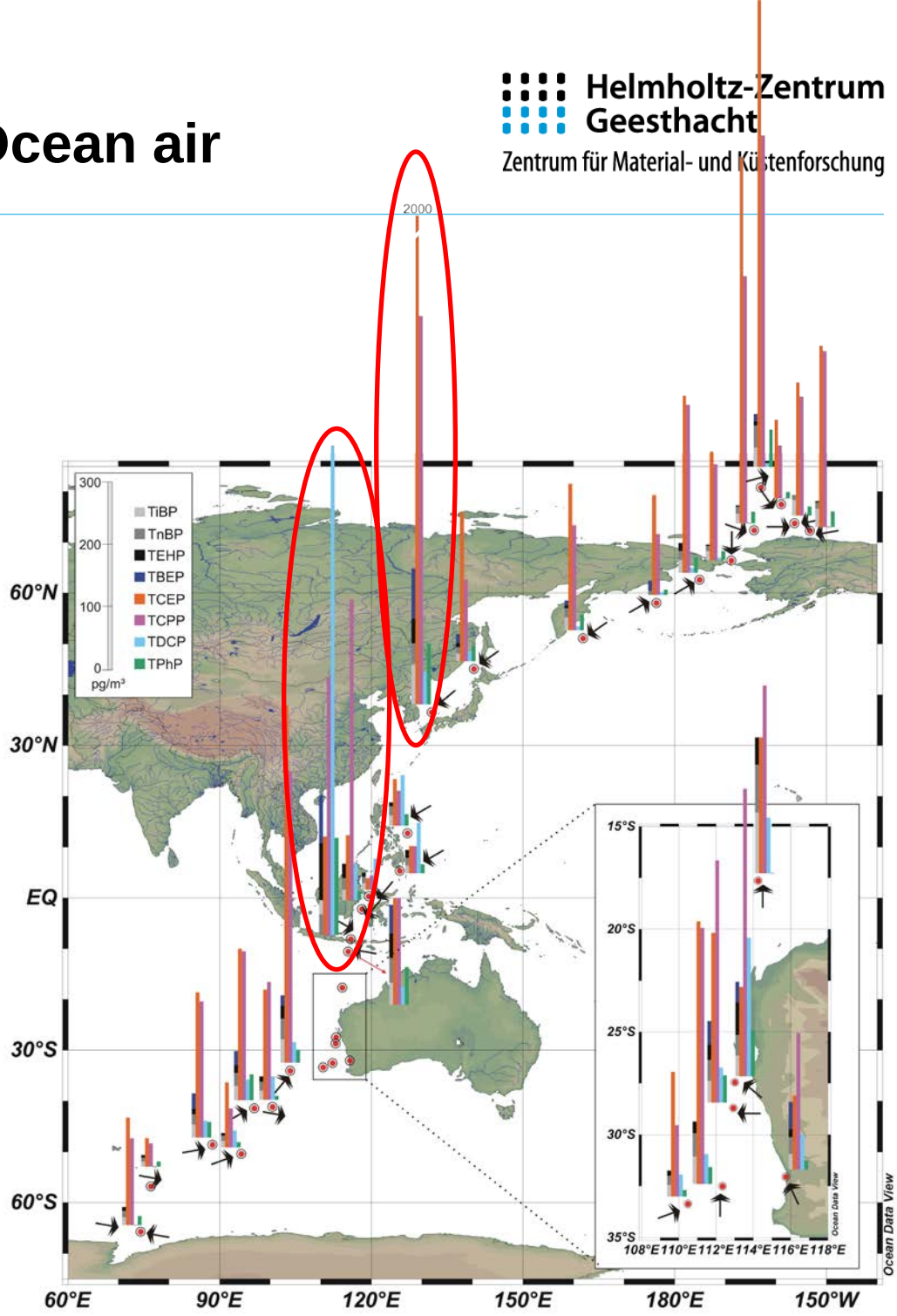
→ concentrations up to **2 ng/m³**

→ dominated by TCPP and TCEP

→ but also non-halogentated OPFRs!

→ concentrations **1-3 magnitudes higher than typical PBDE** concentrations

→ marginal seas, open oceans and polar regions



Möller et al., ES&T 2012

OPFRs - North Sea + estuaries surface water

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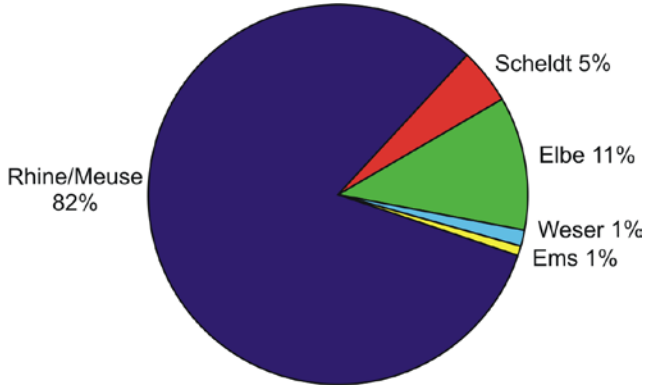
River	Station	ΣOP in ng/L	TCPP in ng/L	TCEP in ng/L	TDCP in ng/L	TEP in ng/L	TiBP in ng/L	TBEP in ng/L	TPhP in ng/L	TPPO in ng/L
Elbe	E1	**435**	134	35.5	30.8	22.3	19.2	94.3	10.3	80.7
	E2	**249**	84.3	9.25	10.9	33.9	15.4	24.2	2.31	65.2
	E3	**96.9**	44.0	4.93	6.4	6.99	4.31	n.d.	3.82	25.2
Rhine	R1	**360**	79.2	12.6	14.3	55.1	84.0	30.3	1.51	73.7
	R2	**326**	74.8	12.4	13.2	37.2	78.6	32.6	1.65	65.6
	R3	**466**	139	22.0	30.6	52.2	80.6	53.9	2.02	64.8
	R4	**375**	159	25.8	20.5	29.7	16.8	38.7	1.42	43.6
	R5	**586**	115	18.4	18.6	82.7	78.2	51.7	1.21	183
	R6	**485**	122	14.9	15.7	55.0	68.7	28.5	1.72	133
Scheldt	S1	**1092**	570	69.9	67.0	84.5	5.27	72.0	2.30	185
North Sea		**5-50**	3-28							



Overall OP discharge into the North Sea:

~50 tons/year

Bollmann et al., Water Research 2012

Conclusions

- **several alternative BFRs, DP, and OPFRs are present in the global marine atmosphere (and seawater)**
- "traditional" alternative BFRs – **HBB, PBT, and DPTE** – in concentrations similar to or higher than PBDEs
- OPFRs, especially **TCPP and TCEP**, 1-3 magnitudes higher than PBDEs
- BFRs and OPFRs undergo gaseous (e.g., HBB, DPTE, PBT) and/or particle-bound (OPFRs, DP) long-range atmospheric transport from source regions (Asia!) over the oceans toward the Polar Regions
- OPFRs are heaviliy emitted into surface waters and the (coastal) marine environment (sources: WWTPs…)

…there will be several more (non)-halogenated non PBDEs!

Acknowledgements

Helmholtz-Zentrum Geesthacht
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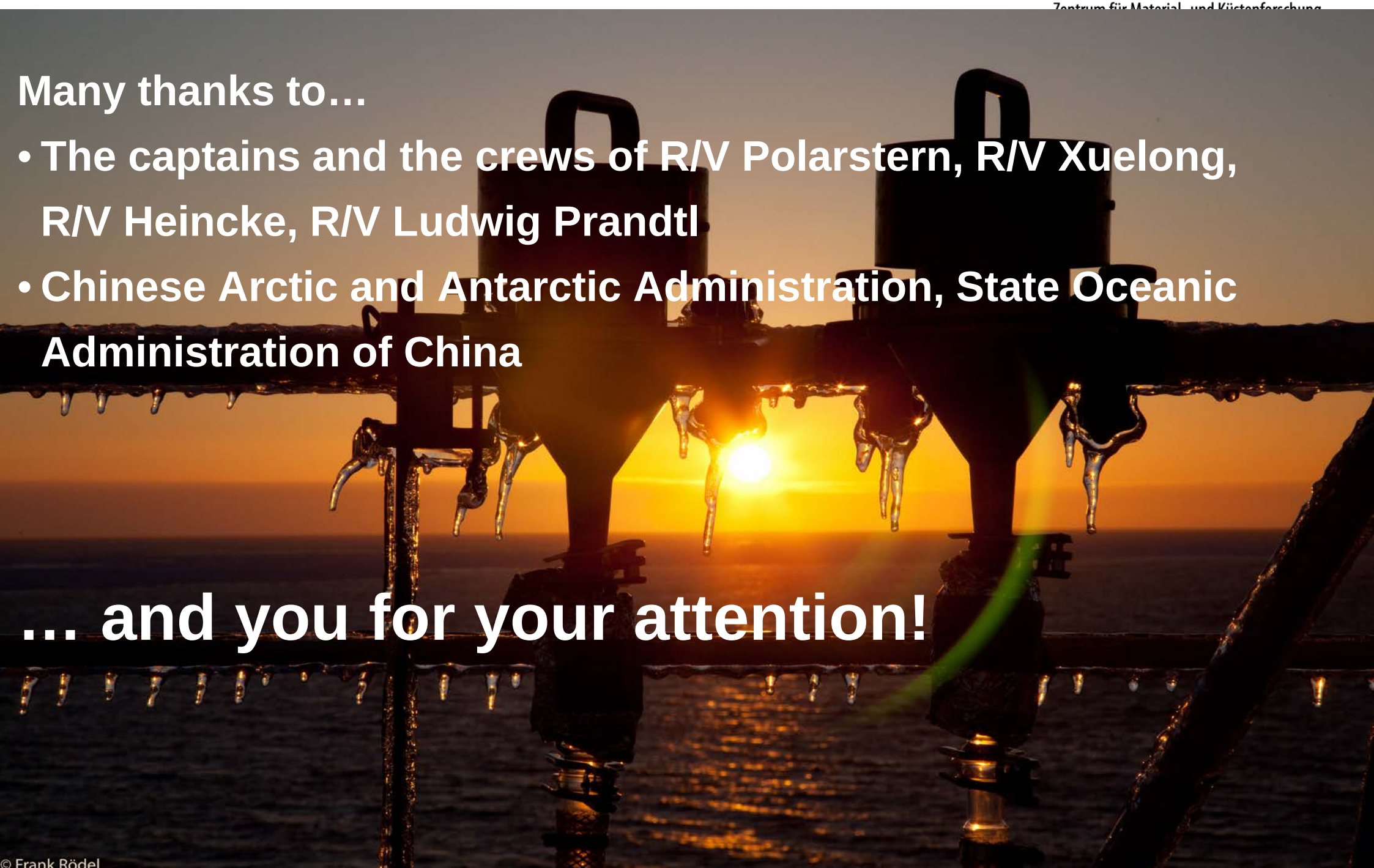

Many thanks to…

- The captains and the crews of R/V Polarstern, R/V Xuelong, R/V Heincke, R/V Ludwig Prandtl
- Chinese Arctic and Antarctic Administration, State Oceanic Administration of China

… and you for your attention!

Sampling and analysis – air and water

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…when sampling and analyzing **PBDEs,** (most) alternative ***BFRs and Dechloranes*** come for free!

Air-sampling: High-vol (GFF + PUF/XAD-2) or PAS

Water sampling: High-Vol (GFF + PAD-2/3)

Extraction: Soxhlet, ASE,…

Analysis: GC-MS techniques, mostly ECNCI
→ only bromine!
→ HR or MS/MS techniques for comprehensive studies on BFRs

…various methods for sampling and analysis of **OPFRs** have been reported since decades!

Air-sampling: High-vol (**GFF** + PUF/XAD-2) or PAS

Water sampling: Low volumes

Extraction: SPE, LLE, Soxhlet, ASE,…

Analysis: GC-MS, GC-NPD, LC-MS/MS

BFRs and DP over the global oceans

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	Year	BDE-47	BDE-209	ΣPBDEs	HBB	PBT	DPTE	DP
Atlantic Ocean[1]	2008	0.57-8.3	n.a.	0.86-6.4	n.a.	n.a.	n.a.	n.a.
Atlantic Ocean[2, 3]	2008	0.18-2.3	n.a.	0.43-3.3	0.10-11	0.01-0.05	0.10-2.3	0.05-1.6
Atlantic Ocean (North Sea)[4]	2010	0.10-0.79	n.d.-9.4	0.31-10.7	0.09-6.3	n.d.-0.24	n.d.-2.5	0.13-22
Pacific Ocean[5]	2010	0.04-0.11	n.d.-2.0	0.22-2.3	0.10-2.5	0.12-0.64	0.18-0.41	0.01-0.86
Pacific Ocean[6]	2003	0.88-17	<0.5-27	1.4-37	n.a.	n.a.	n.a.	n.a.
Pacific Ocean (East Asian Seas)[5]	2010	0.07-0.76	0.13-3.9	0.31-8.1	0.26-5.9	0.36-4.53	0.26-5.9	0.52-0.75
Pacific Ocean (East Asian Seas)[6]	2003	<0.16-112	<0.50-29	2.3-199	n.a.	n.a.	n.a.	n.a.
Pacific Ocean (East and South China Seas)[1]	2008	0.41-13	n.a.	2.9-29	n.a.	n.a.	n.a.	n.a.
Pacific Ocean (East Indian Archipelago and Philippine Sea)[7]	2010/11	0.14-0.32	n.d.-4.0	0.14-4.6	3.7-19	0.71-2.2	0.44-2.3	1.7-11
Indian Ocean[1]	2008	0.57-8.3	n.a.	1.15-13	n.a.	n.a.	n.a.	n.a.
Indian Ocean[8]	2004/05	<3.4-13	<0.6	1.5-16	n.a.	n.a.	n.a.	n.a.
Indian Ocean[5]	2010/11	n.d.-0.49	n.d.-6.5	n.d.-6.6	0.15-26	n.d.-2.8	n.d.-1.1	0.26-2.1
Arctic Ocean[5]	2010	0.03-0.04	n.d.-4.0	0.07-4.1	0.16-0.42	0.22-0.79	0.10-0.19	0.05-0.44
Arctic Ocean[6]	2003	<0.16-31	<0.50-41	<2.58-61	n.a.	n.a.	n.a.	n.a.
Arctic Ocean (Greenland Sea)[3, 9]	2009	0.06-0.95	n.d.-0.07	0.09-1.8	0.08-0.66	n.d.-0.02	0.01-1.7	0.02-4.2
Southern Ocean[2, 3]	2008	0.58	n.a.	0.78	0.32	0.02	0.04	0.07
Southern Ocean[7]	2010/11	0.08	n.d.	0.13	0.12	n.d.	n.d.	0.31

[1] Li et al., AE 2012 [2] Xie et al., ES&T 2011 [3] Möller et al., ES&T 2010 [4] Möller et al., AE 2011 [5] Möller et al., ES&T 2011 [6] Wang et al., ES&T 2005 [7] Möller et al., ES&T under revision [8] Wurl et al., AE 2006 [9] Möller et al., EP 2011