Dechlorane Plus (DP) and brominated flame retardants (BFR) in samples of coniferous and deciduous trees of the German Environment Specimen Bank

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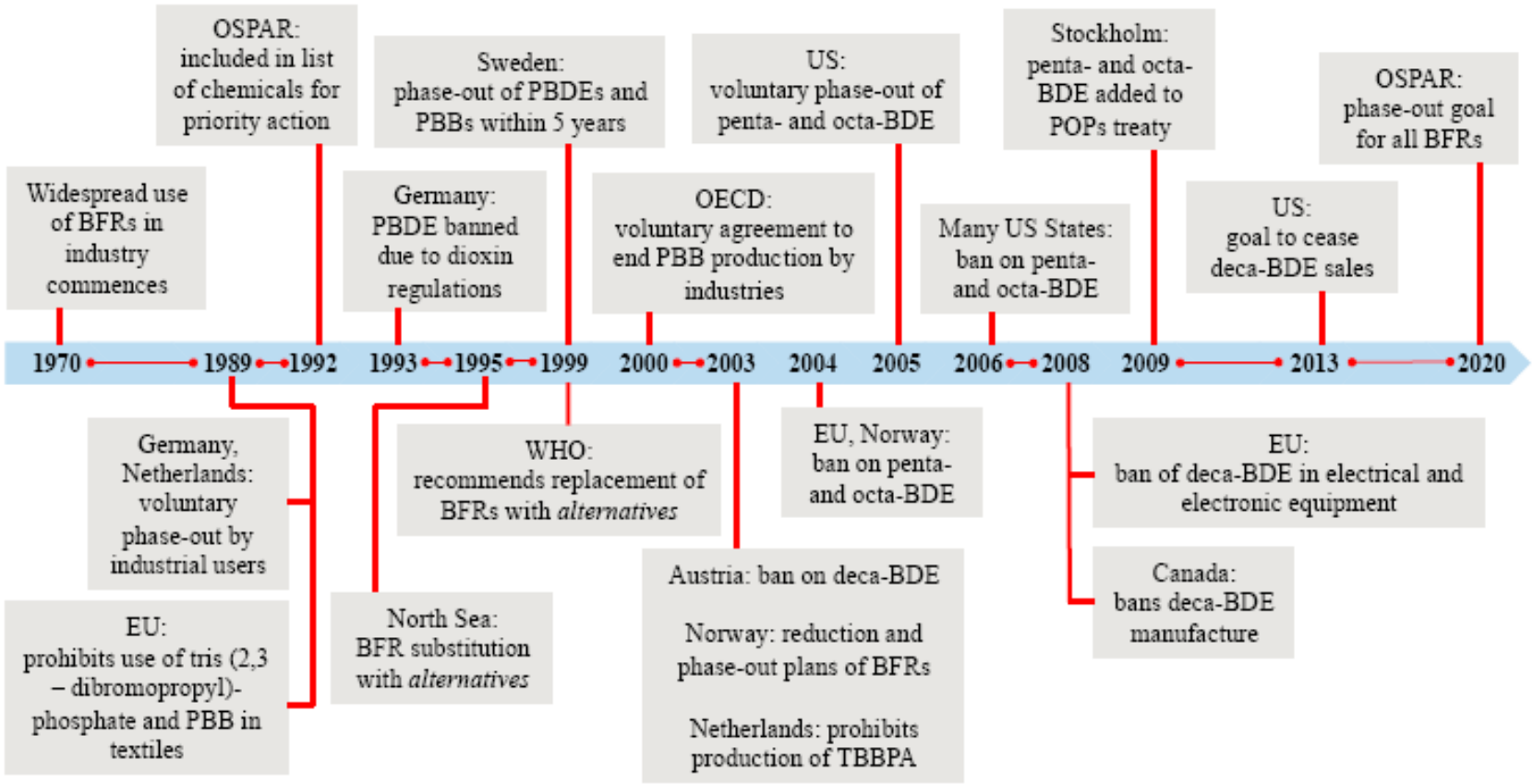
Legislative initiatives for BFR



Venkatesan & Halden. *Int. J. Environ. Res. Public Health.* 2015. *12.* 10549-10557.

German Environment Specimen Bank (ESB)

Environmental monitoring with human and environmental samples since 1980s

Managed by the Federal German Environment Agency (UBA)

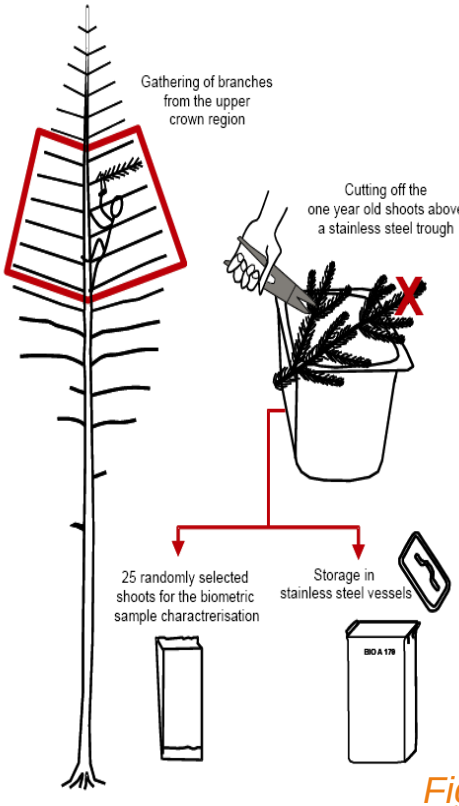
Contains different environmenal matrices representative for different types of ecosystems and trophic levels

→ Project on FRs in environmental matrices through time and space

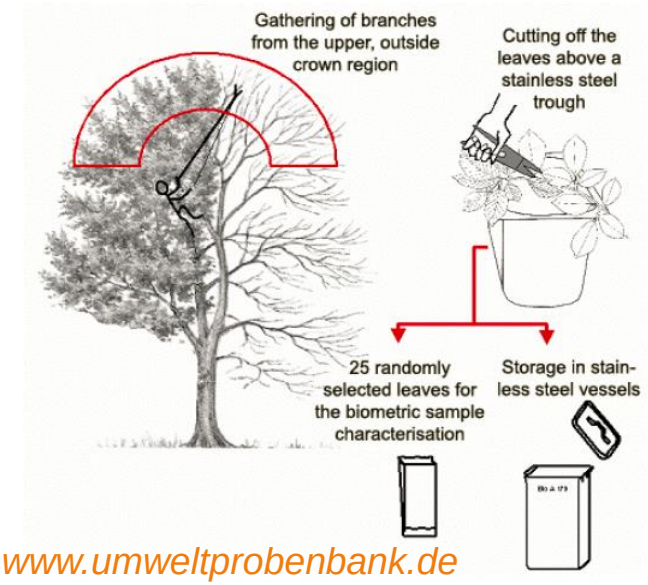
- Tree samples as bioindicator for atmospheric pollution
  - Do (A)FRs accumulate on tree leaf samples?
  - Spatial distribution
  - Temporal trends
  - (inter species differences)

Tree leaf sampling in the ESB

Coniferous: one year old shoots of pine (Pinus sylvestris) or spruce (Picea abies)
→sampling in spring



Deciduous: leaf samples of beech (Fagus sylvatica) or poplar (Populus nigra)
→sampling in late summer



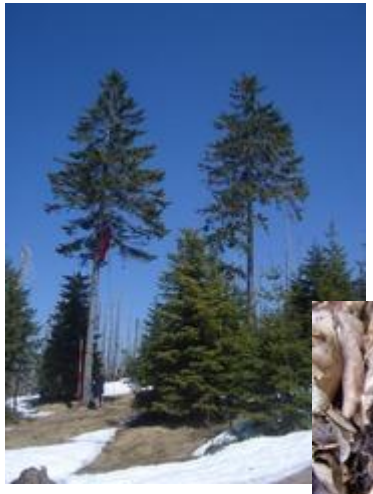
Figures: www.umweltprobenbank.de

Sampling sites

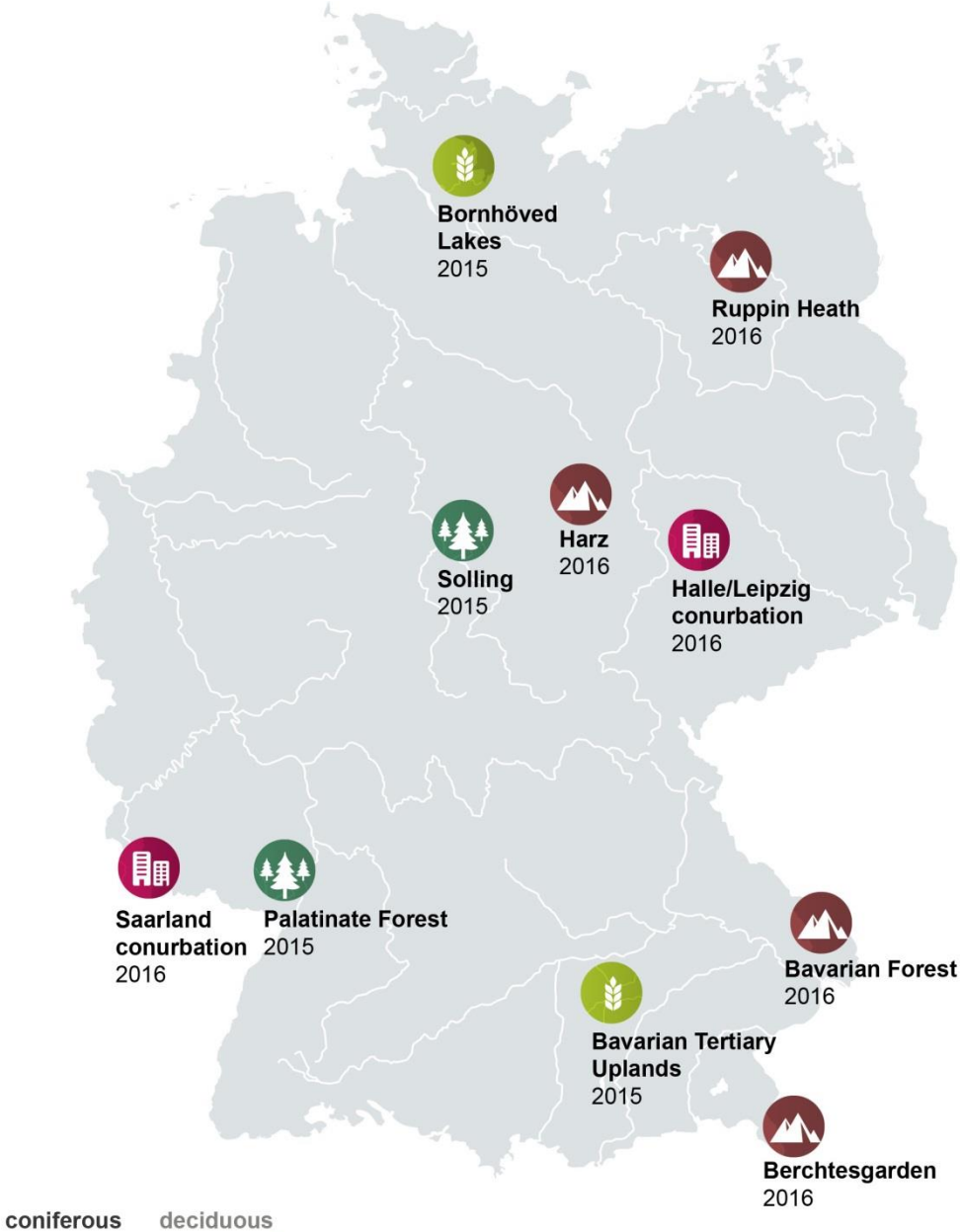
10 areas across Germany

- **10 coniferous**
- **9 deciduous**

4 ecosystem types



Figures: www.umweltprobenbank.de

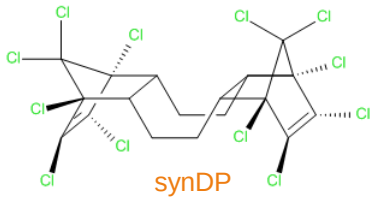


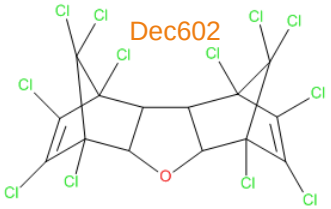
Analytical method – target compounds

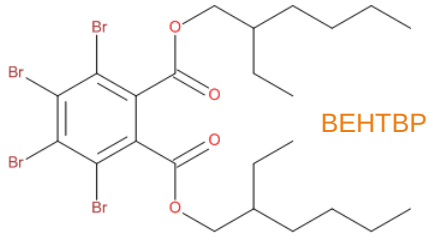
Multi-matrix multi-compound (38 substances) method with

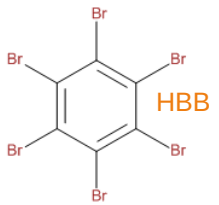
- **focus on Dechlorane Plus and dechlorane compounds**
- **Target AFR were chosen according to their observation in published reports (mainly *Schlabach et al. 2011. TemaNord. 528*; FOD > 50% in Nordic air samples)**
- **PBDE**

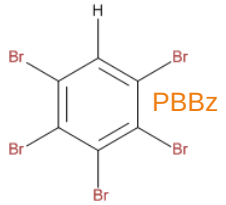
Analytical method – target compounds

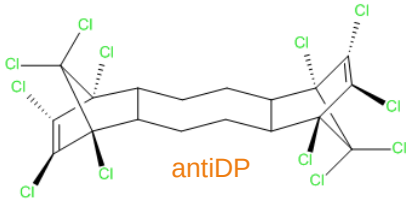


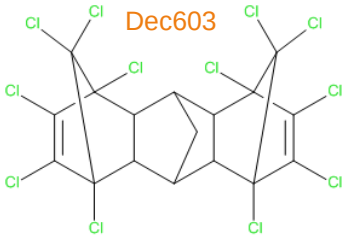


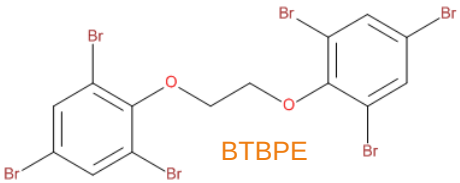


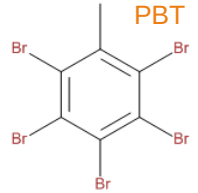


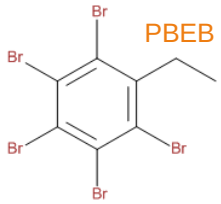


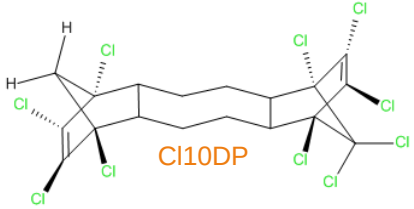


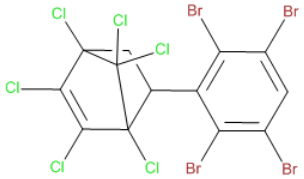


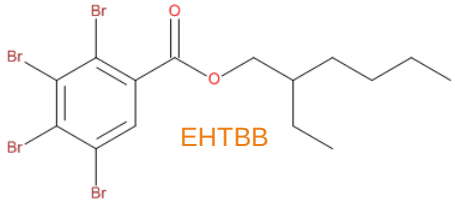


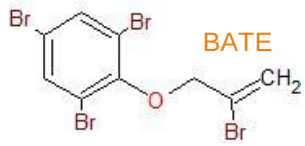


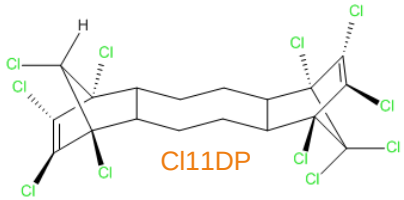


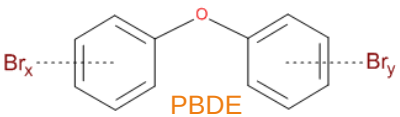


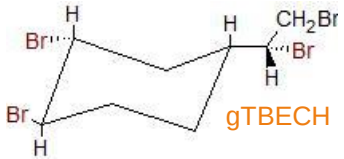


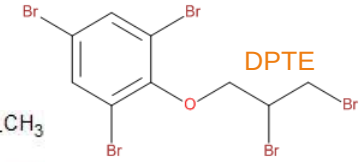


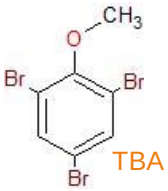


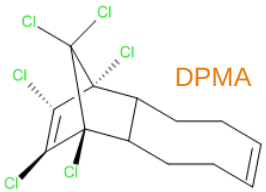


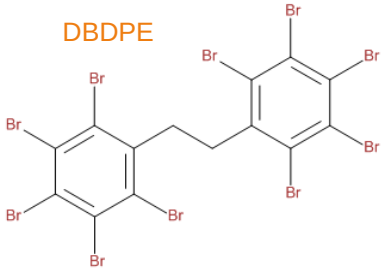


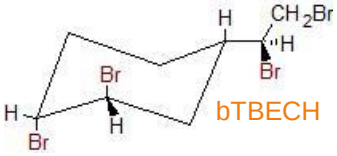


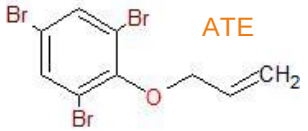












Analytical method - analysis

preparation (homogenisation, freeze-drying)

Addition of ^{13}C-/^{2}H-quantification standards

ASE Extraction
(DCM/Hx 1:1 v/v)

Clean-up 1: Silica + Na_2SO_4 (Tol/Hex 1:1)

Clean-up 2: GPC BioBeads SX-3 (CHx/EtAc 1:1)

Clean-up 3: Florisil/5% H_2O (Hex, Hex:Tol 1:1)

Fraction 1: 19 HFRs

+ rec. std. $^{13}C_{12}$-HxBDE #138

Fraction 2: EHTBB; BEHTBP

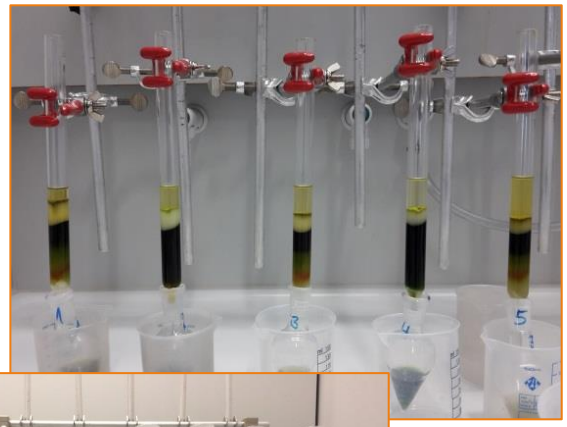
+ rec. std. $^{13}C_{12}$-HxBDE #138

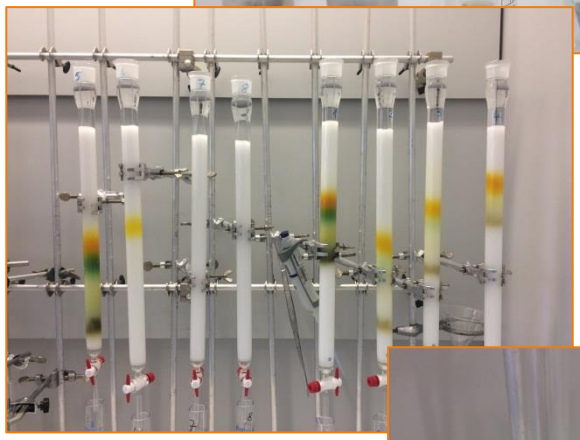
GC: Agilent 7890 + 15m DB5HT; 1 µL SSL/inert liner
MS: Waters XEVO-TQ S API MS-MS

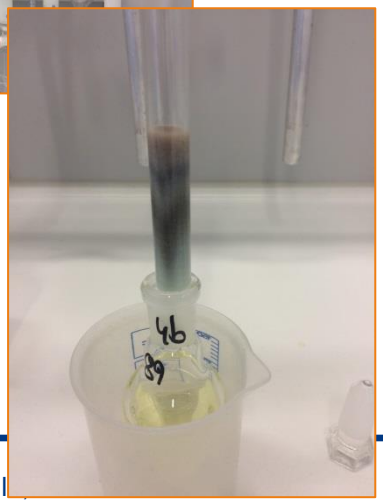
GC-MS/MS
measurement #1
(DP, most HFR)

GC-MS/MS
measurement #2
(BEHTBP, EHTBB)

GC-MS measurement #3
(PBDE)







Results samples 2015/2016

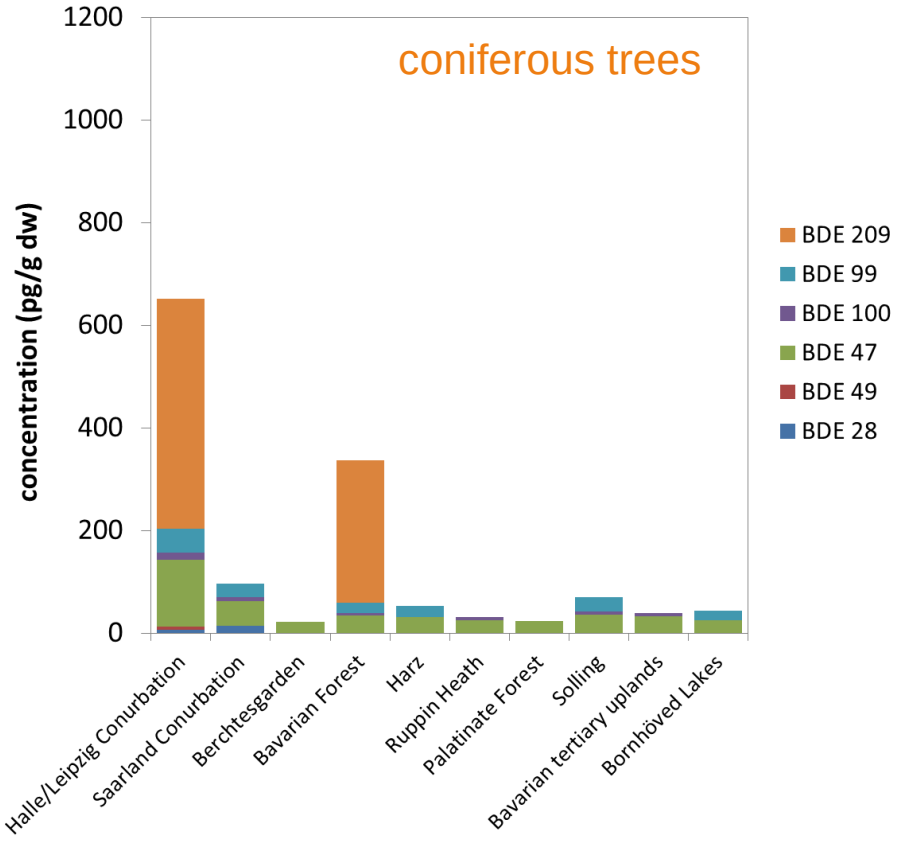
Frequency of quantification (FOQ)

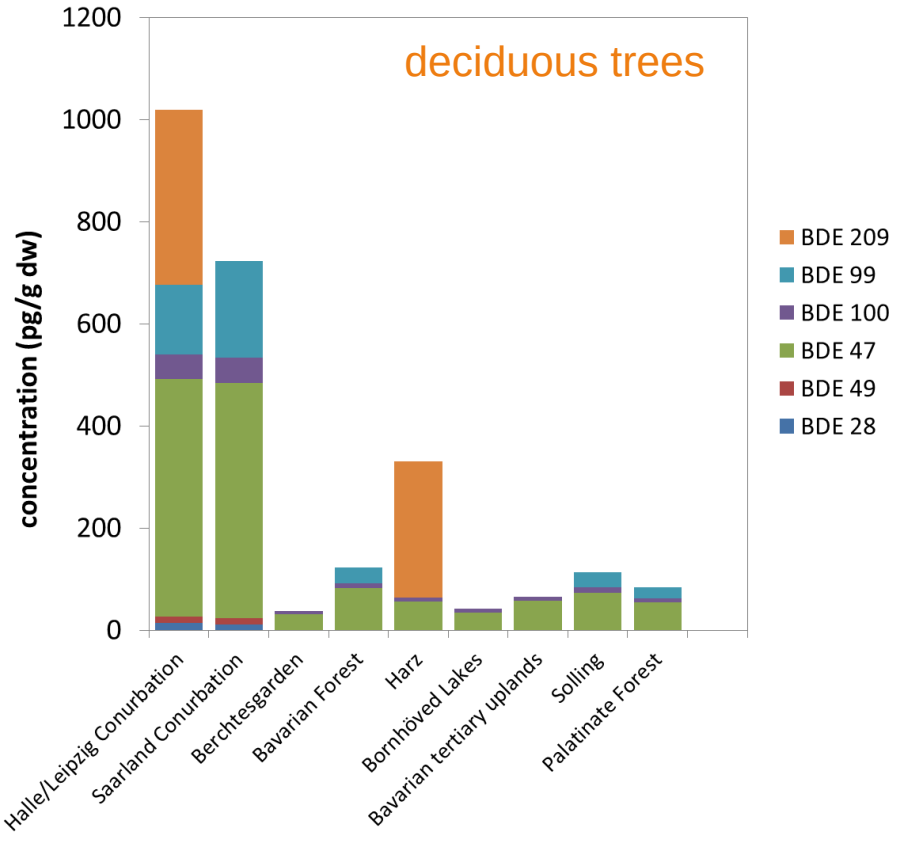
	FOQ tot	FOQ (conif.)	FOQ (decid.)
PBDE			
BDE 28	21%	20%	22%
BDE 49	16%	10%	22%
BDE 71	0%	0%	0%
BDE 47	100%	100%	100%
BDE 66	5%	0%	11%
BDE 77	0%	0%	0%
BDE 100	79%	60%	100%
BDE 119	0%	0%	0%
BDE 99	58%	60%	56%
BDE 85	0%	0%	0%
BDE 154	0%	0%	0%
BDE 153	0%	0%	0%
BDE 138	0%	0%	0%
BDE 183	0%	0%	0%
BDE 196	0%	0%	0%
BDE 206	0%	0%	0%
BDE 209	21%	20%	22%

	FOQ tot	FOQ (conif.)	FOQ (decid.)
AFR			
b-TBECH	5%	10%	0%
g-TBECH	5%	10%	0%
TBA	16%	30%	0%
ATE	58%	50%	67%
BATE	37%	20%	56%
DPTE	100%	100%	100%
BTBPE	42%	40%	44%
EHTeBB	11%	10%	11%
BEHTBP	21%	10%	33%
PBT	32%	30%	33%
HBBz	58%	70%	44%
PBEB	11%	10%	11%
DBDPE	100%	100%	100%
Dec602	100%	100%	100%
Dec603	0%	0%	0%
Dec604	0%	0%	0%
DPMA	5%	0%	11%
Cl10-AntiDP	0%	0%	0%
Cl11-AntiDP	84%	70%	100%
Syn-DP	100%	100%	100%
Anti-DP	100%	100%	100%

Results samples 2015/2016 : PBDE only

[PBDE]: conif. < decid.

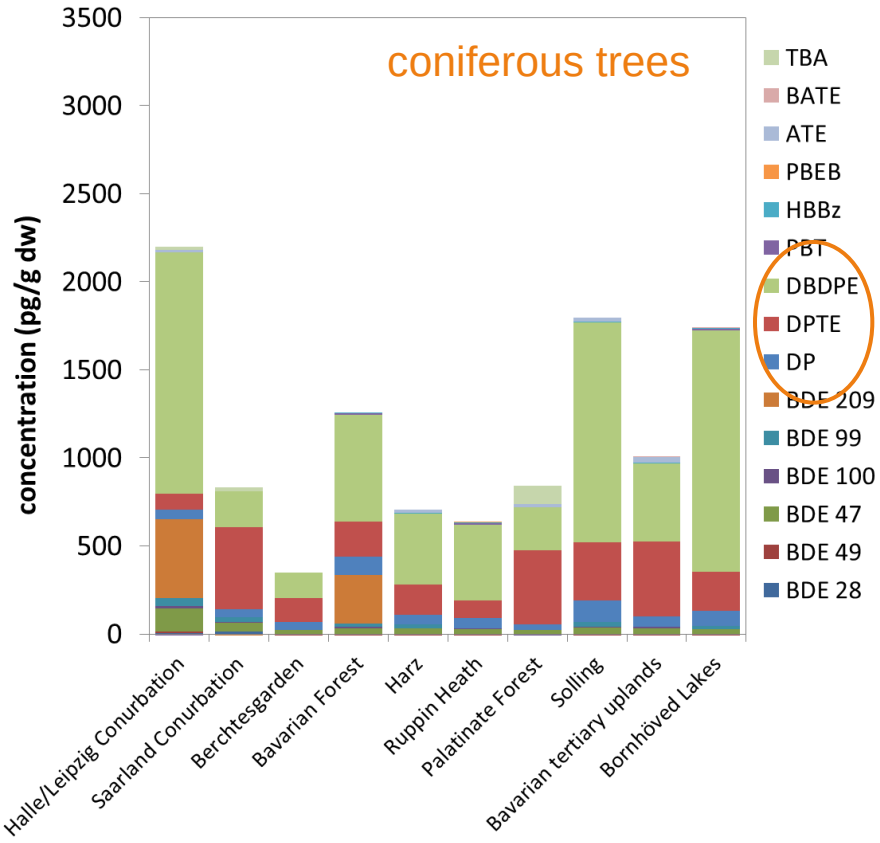


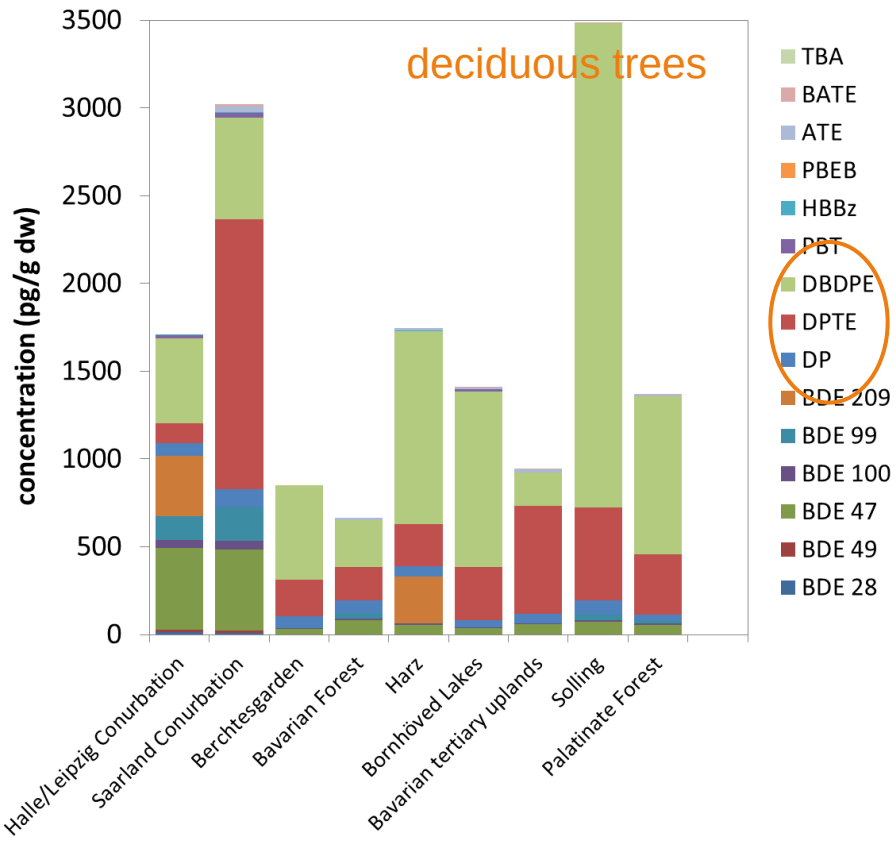


Results samples 2015/2016: all HFR

[DPTE, DBDPE, (BATE, PBT, Dec602)]: conif. < decid.

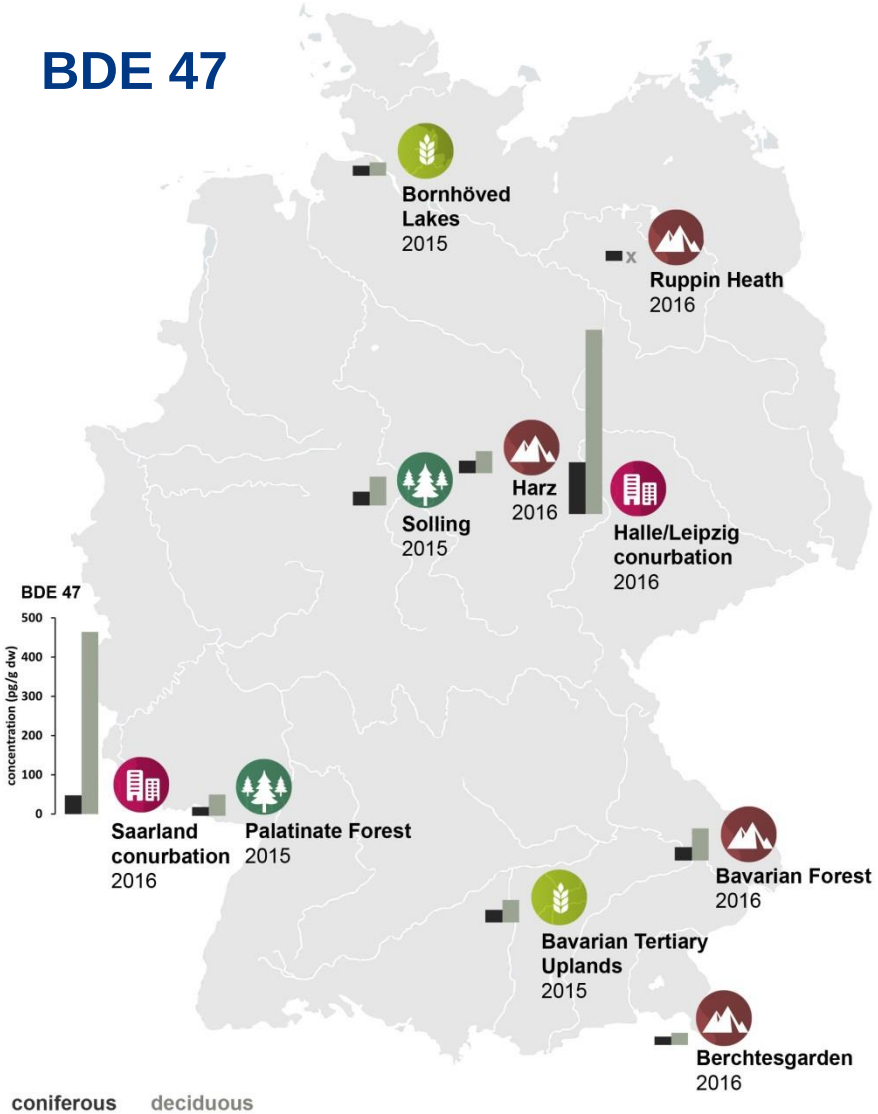
[DP, (ATE, HBBz)]: conif. = decid.



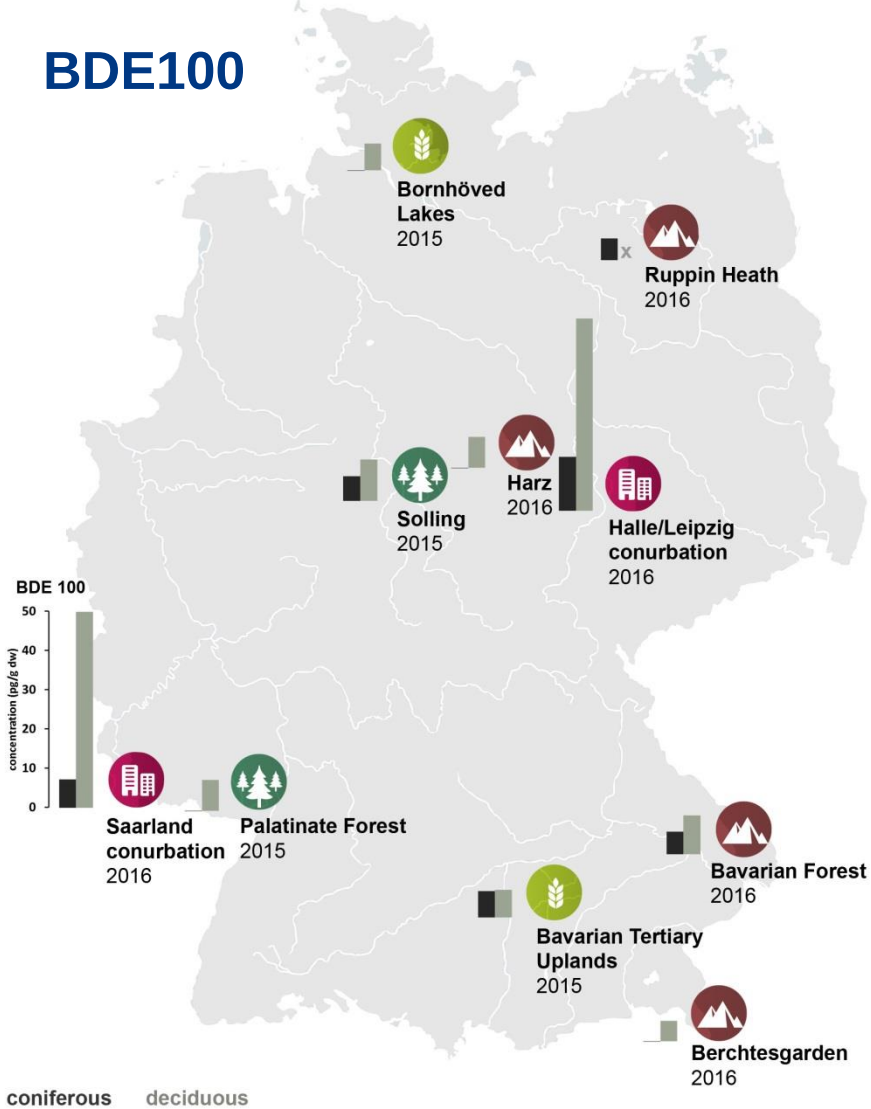


Spatial distribution samples 2015/2016

BDE 47

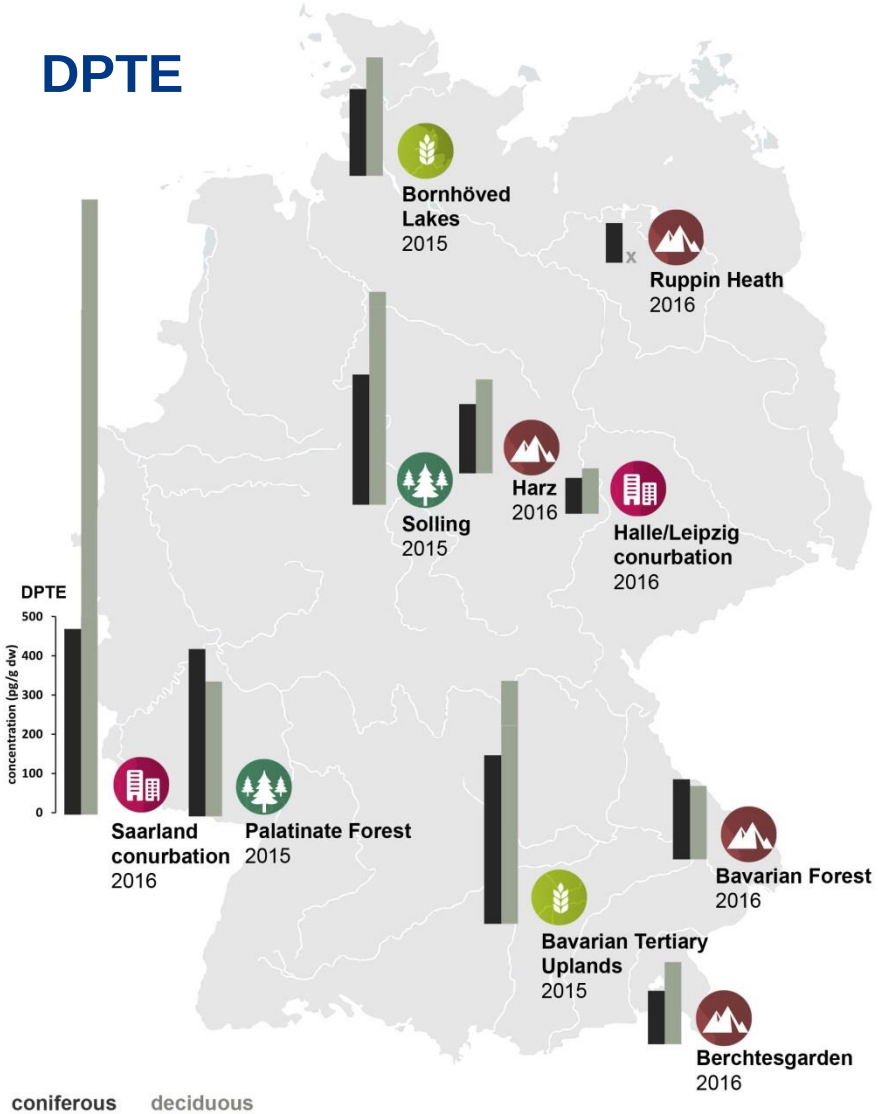


BDE100



Spatial distribution samples 2015/2016

DPTE



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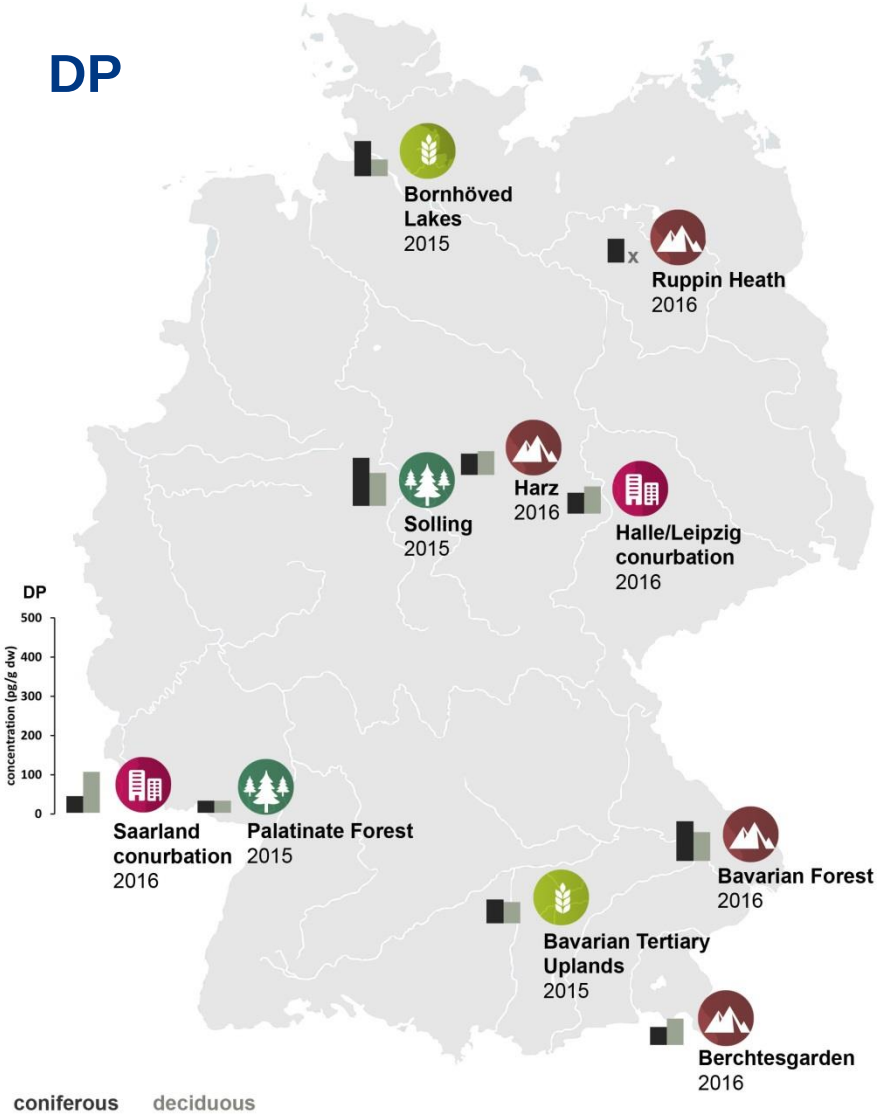
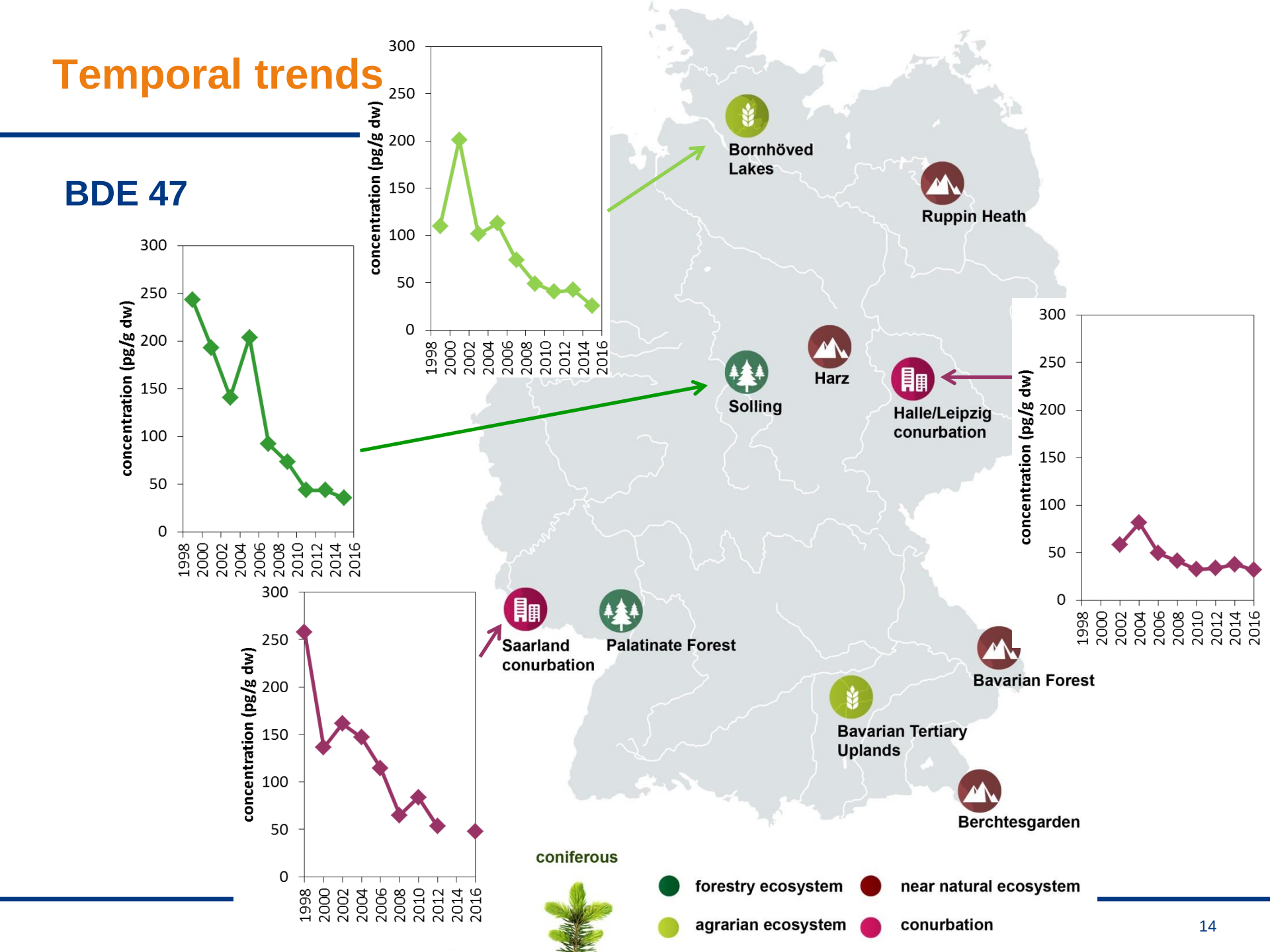


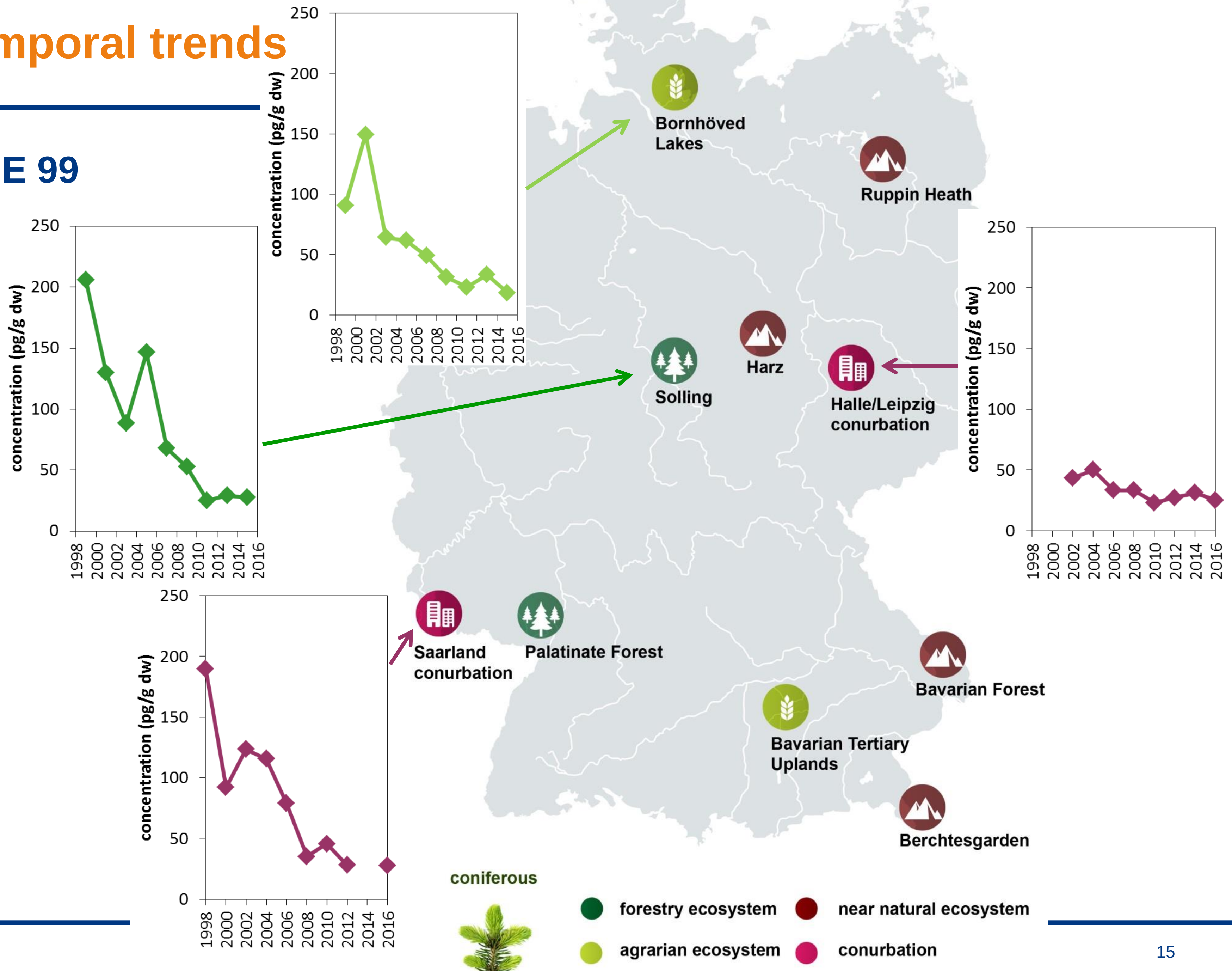
Temporal trends

BDE 47



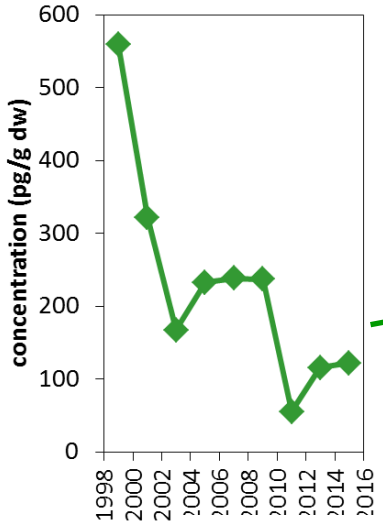
Temporal trends

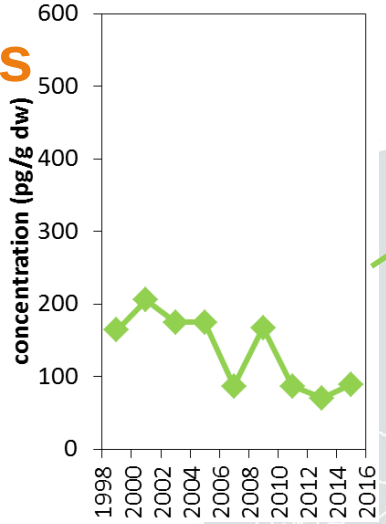
BDE 99

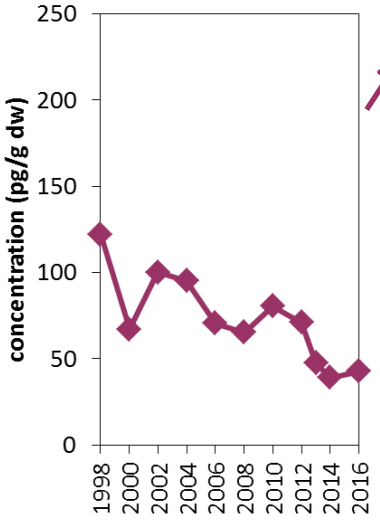


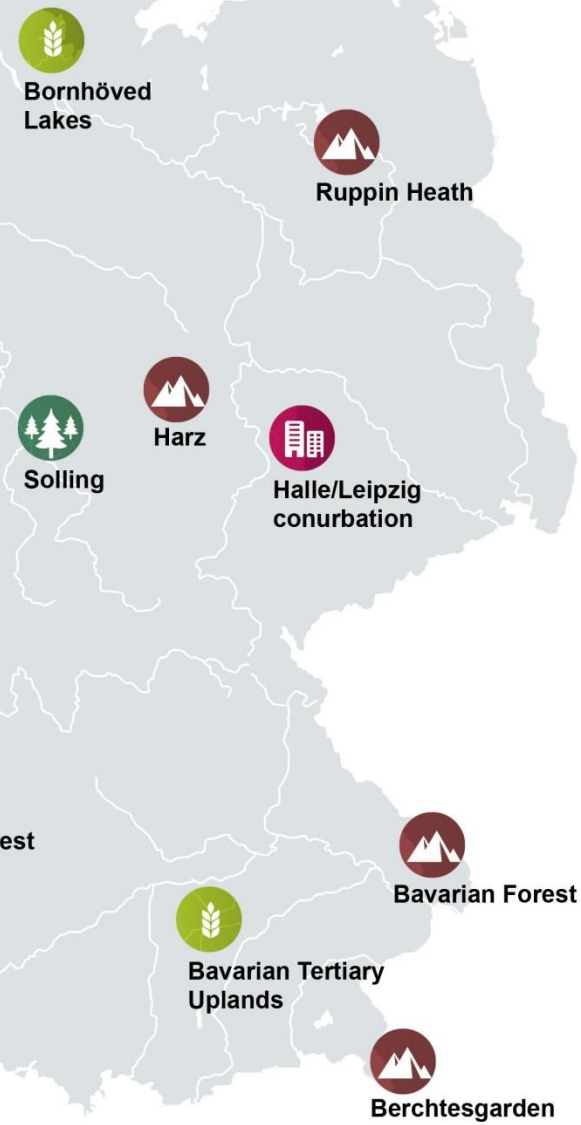
Temporal trends

DP









Summary

Broad distribution of FR of atmospheric origin in Germany

Spatial distribution differs

- **PBDE max. conc. in urban areas**
- **DP rel. uniform distribution**
- **DPTE concentrations higher at sites in the west than in the east**

FR in different species at the „same“ site mostly differed within a factor of 2-3 indicating that conif. as well as decid. tree leaf samples are suited as bioindicators for atm. pollution

First results indicate decreasing trends for PBDEs & DP in conif. trees in Germany within the past 20 years

Thank you for your attention !