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Are atmospheric PBDE levels declining in Europe? Examination of seasonal variations, gas-particle partitioning and implications for long-range atmospheric transport

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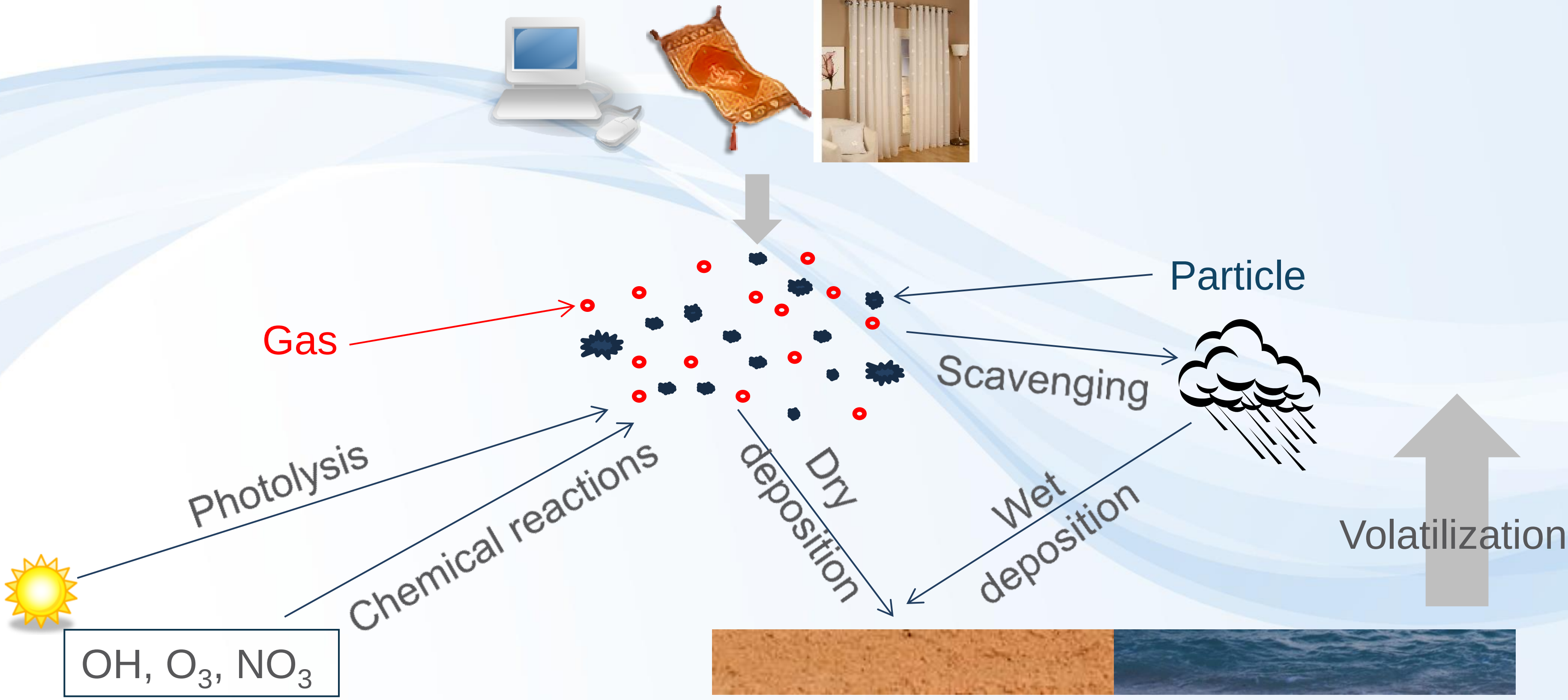
Introduction: PBDEs




- PBDEs are flame retardants used in plastics, textiles, computers, cars or synthetic materials
- 3 major commercial formulations: Penta-BDE, Octa-BDE and Deca-BDE
- All technical mixtures have been banned in Europe
- PBDEs are persistent, bioaccumulative, toxic and prone to LRAT

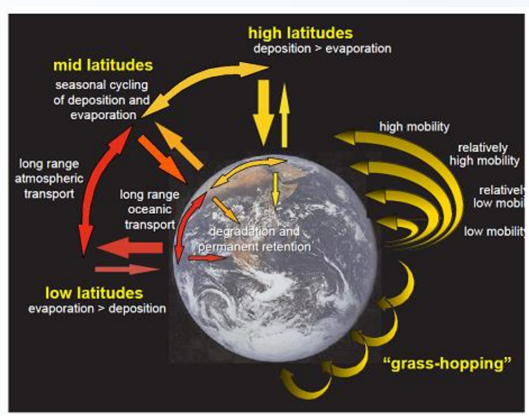


Transformations

Wet and dry deposition

Diffusive air-surface exchange

Long-range atmospheric transport



UNEP (2003)

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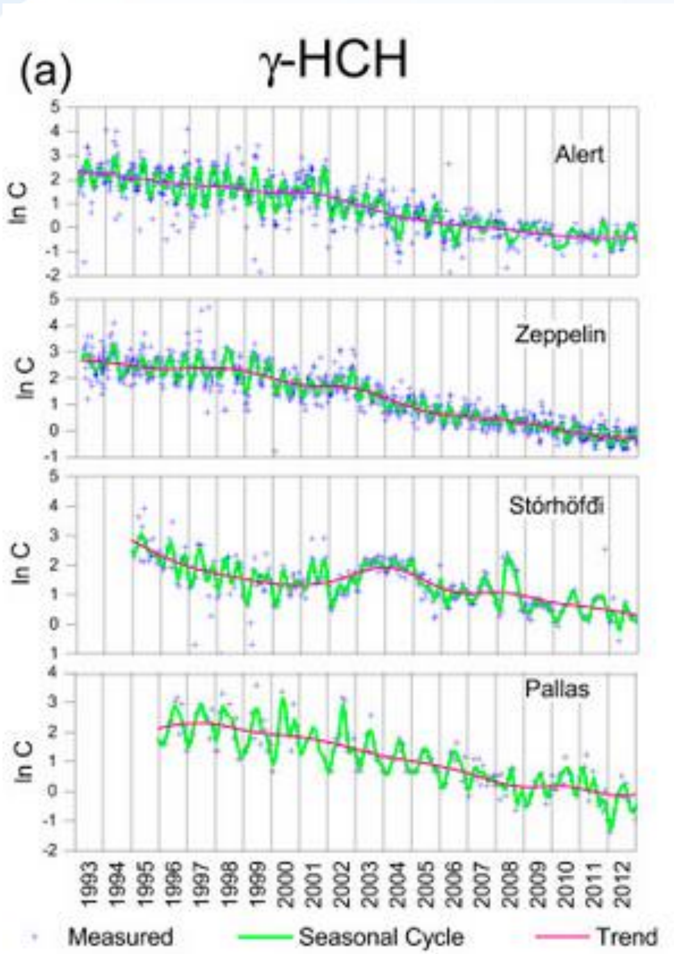
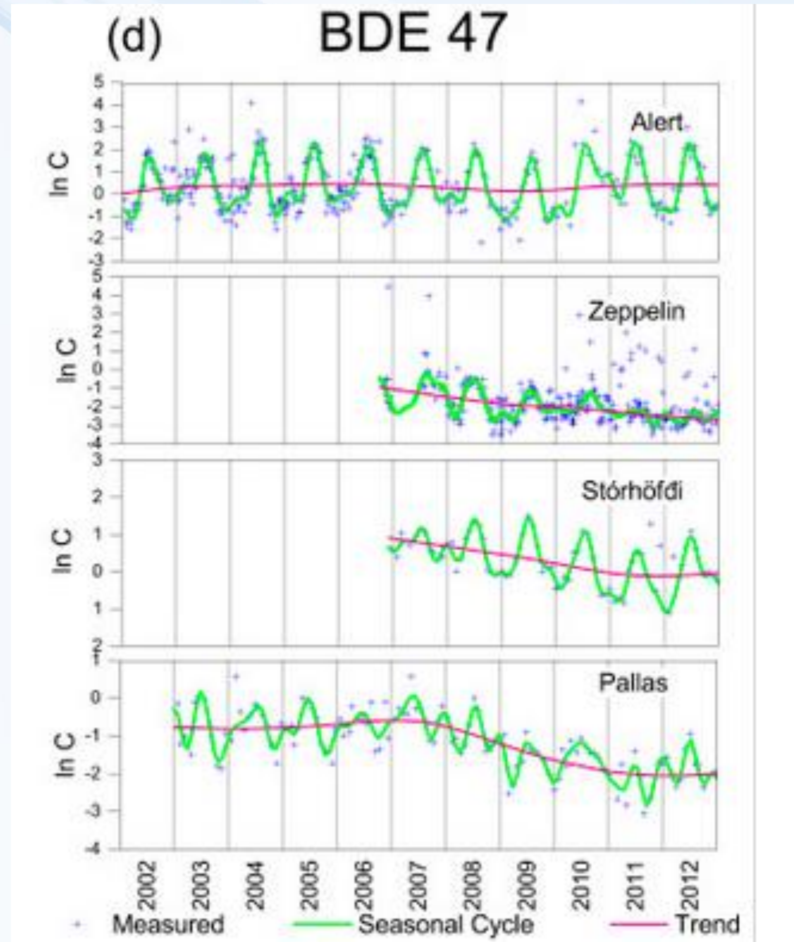
Long-term trends of POPs





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Hung et al; 2016

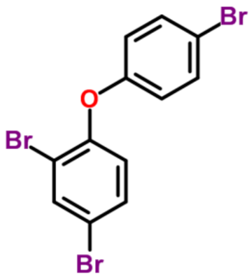
Aim of this study

- Provide novel semi-long-term (i.e. 4 years) data on atmospheric PBDEs at a Central European background site
- Assess the seasonal and long-term variations of PBDEs
- Assess the efficiency of different G/P models for PBDEs

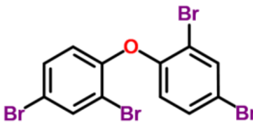
Methodology



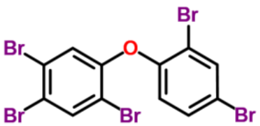

- Weekly air samples were taken from January 2011 to December 2014 (N= 114) at Košetice (background site) using a HVAS (Digitel DH77, 31.3 m^3 h^{-1}), collecting gas and particles
- Air samples were extracted with DCM using an automatic Soxhlet extractor
- Clean up using a sulfuric modified silica column (2011-2012) or a multi-layer silica column (2013-2014)
- Ten PBDEs (i.e. BDE-28, -47, -66, -100, -99, -85, -154, -153, -183 and -209) were quantified using isotope dilution method on a GC-HRMS (Agilent 7890A GC, Waters AutoSpec Premier MS)



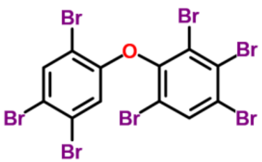
BDE-28



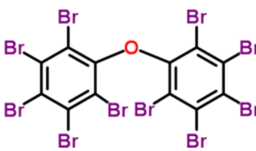
BDE-47



BDE-99



BDE-183



BDE-209

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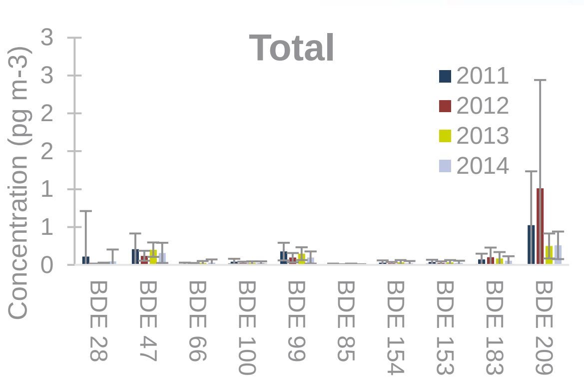
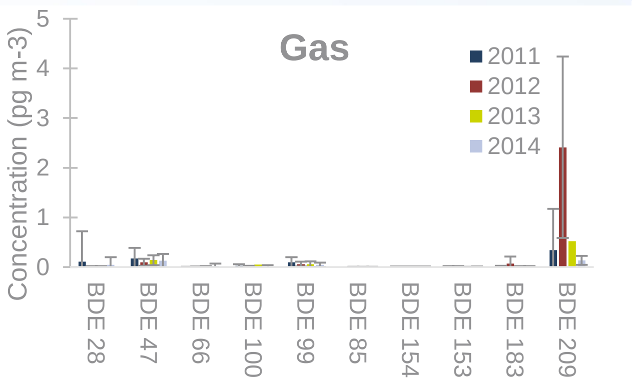
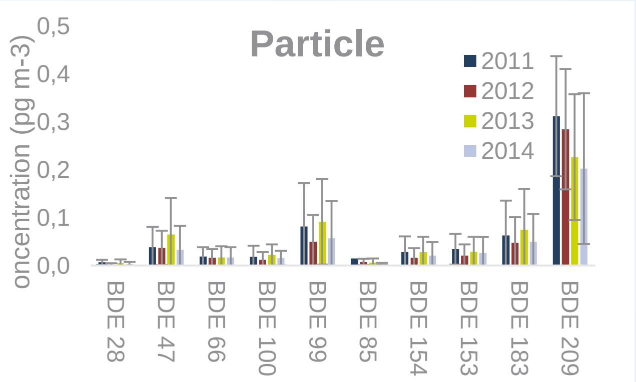
PBDEs air concentrations

- Σ_9PBDEs total concentrations = 0.0882 - 6.08 pg m^{-3} (0.542)
- BDE-209 = 0.0499 to 5.01 pg m^{-3} (0.468)
- BDE-47, -99 and -183 accounted for 36.0, 27.1 and 14.4% of Σ_9PBDEs





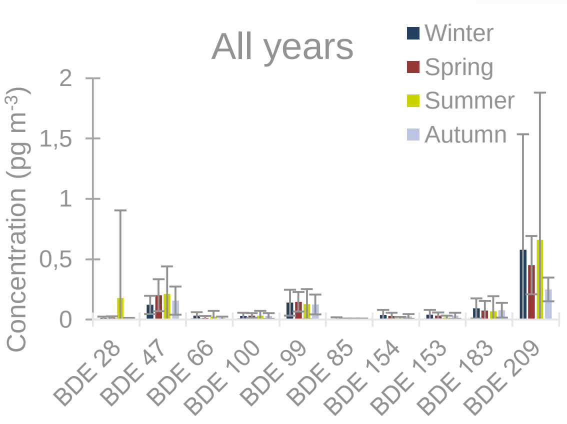


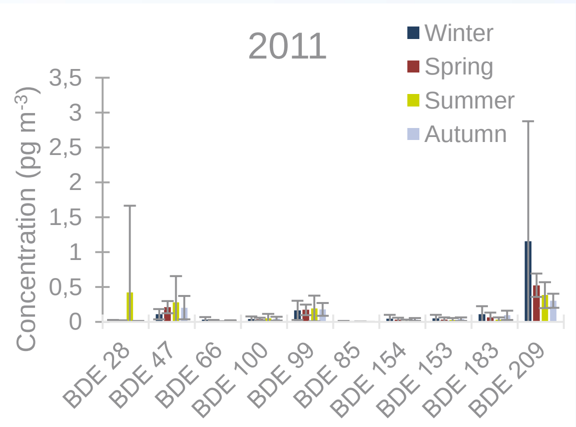
Seasonal variations

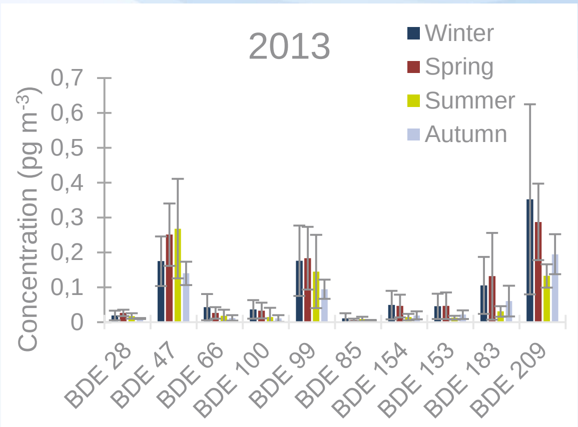
- What seasonal variations can we expect?

Winter
Combustion (domestic heating)

Summer
Re-volatilization from surfaces
Higher photolysis
Faster degradation







PBDE atmospheric levels are still influenced by primary sources (release during intended usage of goods)

Gas-particle partitioning: Results

- Huge seasonality of G/P!
- e.g. for BDE99, in summer θ=0.18 and in winter, θ = 0.88. Similar strong seasonal variations for all congeners, except for BDE-28 and BDE-209
- This may explain contradictory results in some studies, the time of the year (i.e. T) is an extremely important parameter that will highly affect G/P of PBDEs

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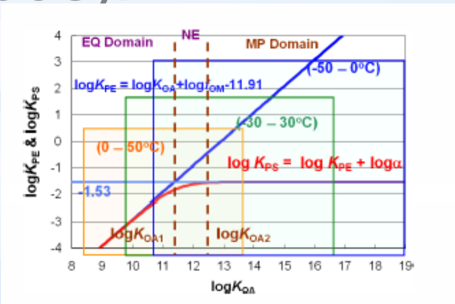
Gas-particle partitioning: Modelling

- K_{OA} equilibrium model (Harner and Bidleman, 1998):

  $$\log K_{pe} = \log K_{OA} + \log f_{OM} - 11.91$$

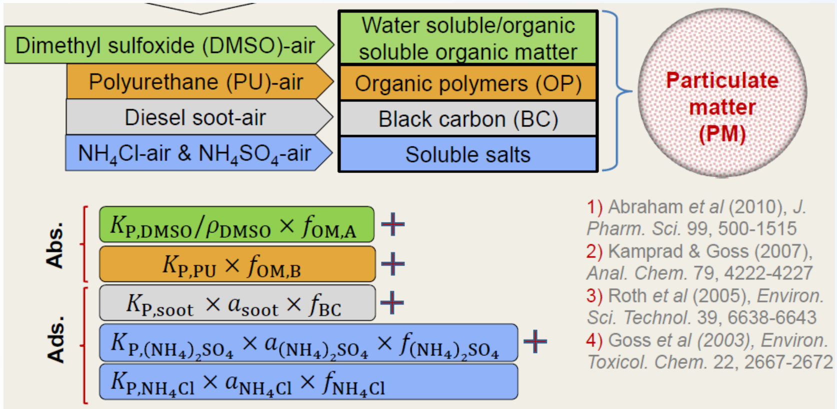


- K_{OA} steady state model (Li and al; 2015):

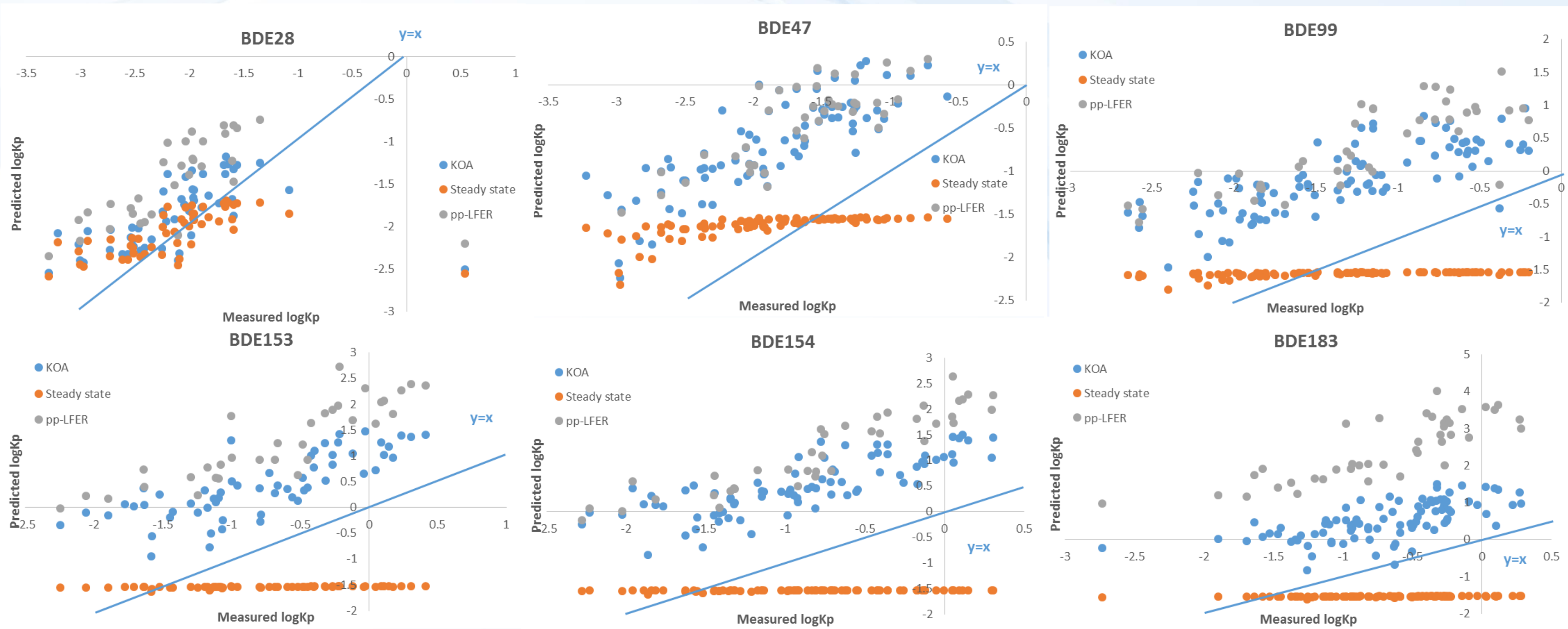
  $$\log K_{ps} = \log K_{pe} + \log \alpha$$

With $\alpha = 1/(1 + G/C)$, with $G = 2.09 \times 10^{-10} \times f_{OM} \times K_{OA}(T)$ and C = 5 (not clearly defined in their paper)

- pp-LFER equilibrium model accounting for all significant molecular interactions between solute and sorbent (Shahpoury et al; 2016)



Gas-particle partitioning: Modelling results (absorption and steady state), logKp



- Model predictions indicate that model assumptions are ok for BDE28
- For other congeners, K_{OA} and pp-LFER equilibrium model tends to clearly overestimate K_p while K_{OA} steady state model tends to underestimate K_p

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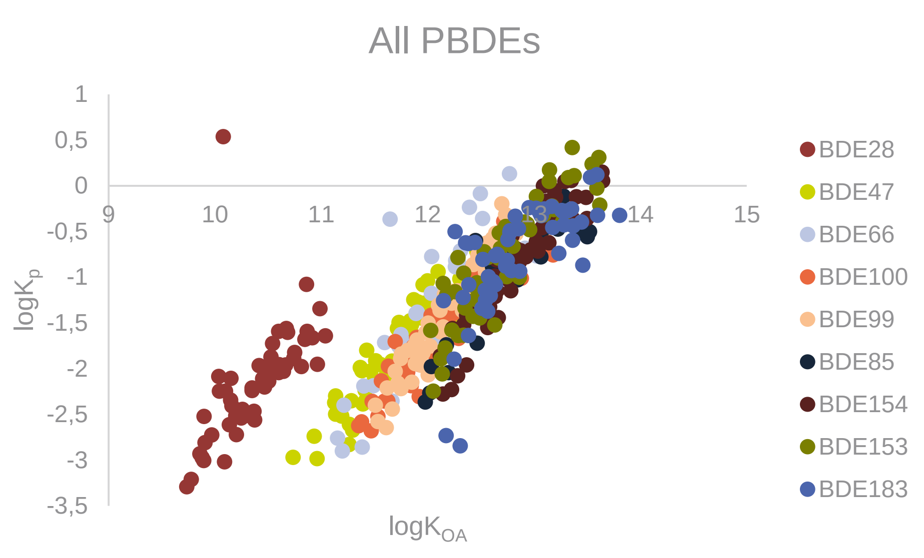
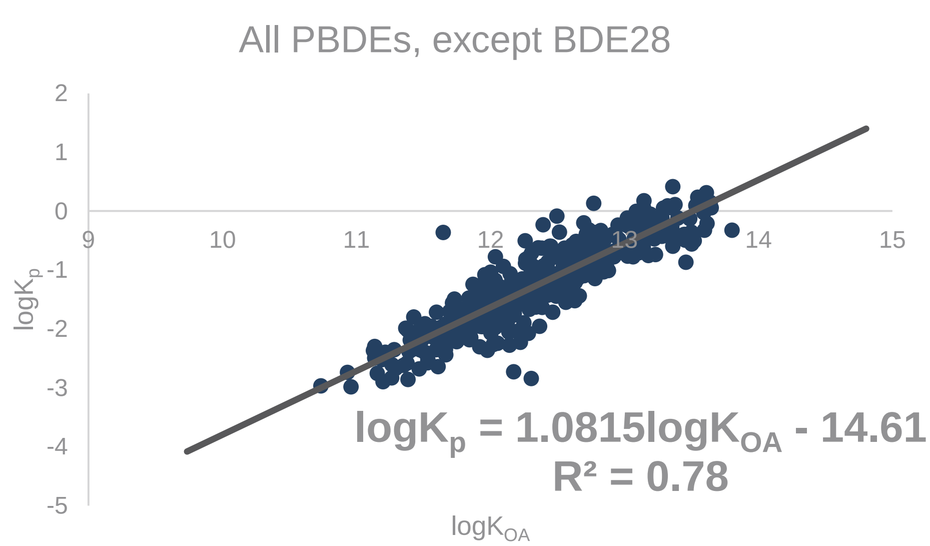
Gas-particle partitioning: Regression approach





Root mean square error (rmse)

	Absorption	Steady state	pp-LFER	Regression
All PBDEs	1.27	0.83	2.21	0.56
BDE28	0.61	0.55	0.91	1.31
BDE47	1.24	0.58	1.27	0.28
BDE66	1.20	0.81	2.51	0.50
BDE100	1.30	0.58	3.80	0.24
BDE99	1.30	0.66	1.64	0.28
BDE85	1.67	0.81	1.21	0.43
BDE154	1.44	0.90	2.09	0.32
BDE153	1.28	1.00	1.87	0.30
BDE183	1.28	0.99	3.18	0.43
All except BDE28	1.32	0.85	2.32	0.34

rmse<0.5

0.5<rmse<1

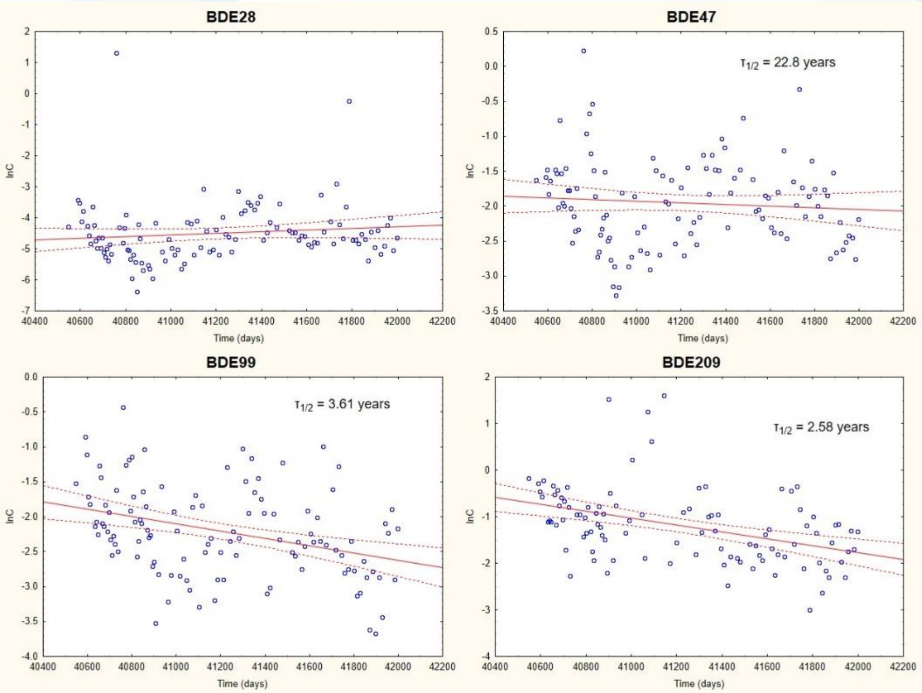
1<rmse

Recommendations:

- For BDE28: K_{OA} steady state model or K_{OA} equilibrium model
- For other congeners, regression . They may be in steady state but considerations within the steady state is not significant for predictability

Semi-long-term trends

Using all individual concentrations



	Half-life (years)	r2	p
BDE 28	-7.37 ± 4.61	0.01	0.22
BDE 47	22.77 ± 6.37	0.00	0.38
BDE 66	-4.89 ± 3.61	0.03	0.15
BDE 100	**2.83 ± 5.53**	**0.10**	**<0.01**
BDE 99	**3.61 ± 7.51**	**0.12**	**<0.01**
BDE 85	2.81 ± 2.49	0.07	0.08
BDE 154	7.91 ± 5.37	0.01	0.21
BDE 153	**4.52 ± 4.82**	**0.04**	**0.04**
BDE 183	10.05 ± 5.28	0.01	0.36
BDE 209	**2.58 ± 5.9**	**0.17**	**<0.01**
Σ9PBDEs	9.16 ± 6.45	0.02	0.12

Significant decrease of BDE100, 99, 153 and 209 in 2011-2014, with apparent half-lives of 2.6-4.5 years. No significant trends for other congeners.
BDE-28 and BDE-66 showed a generally increasing trend -> photolytic conversion of higher brominated congeners?
Increasing trend of light BDEs in Europe in the coming years?

Conclusions

- No clear seasonality in the PBDE atmospheric levels
- But clear seasonality in PBDE G/P

-> consequences for interpretation of seasonal variations from passive sampling and for CC-plots

- G/P investigation suggest that none of the studied model is adequate for G/P modeling of PBDEs (except BDE28)
- Potential for LRAT -> higher transfer from mid latitudes towards extreme latitudes of light PBDEs (from "global distillation hypothesis" and from photolytic debromination of higher congeners)?

Acknowledgements

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Thank you for your attention

ANY QUESTIONS???

Breakthrough

- Breakthrough = loss of compounds downstream of the gas-phase sampling medium

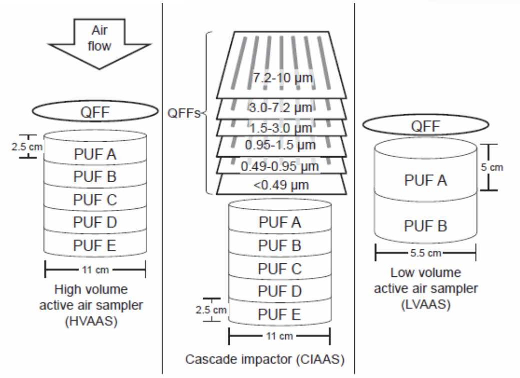

Fig. 1. Schematic representation of sampling trains.

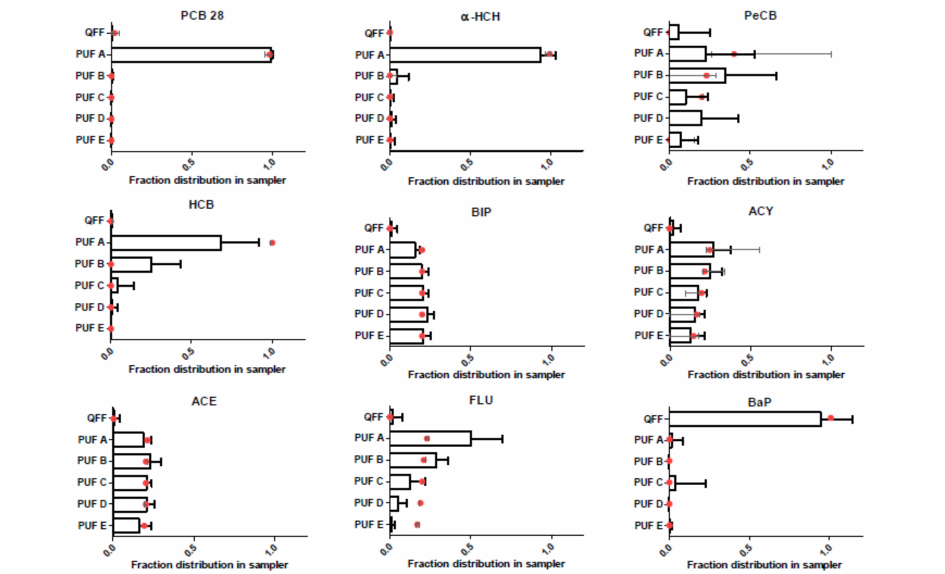

Fig. 3. Average measured and estimated distributions of selected SVOCs within the baseline HVAAS (24 h, ~700 m^3 sample volume) relative to the total mass captured by the sampler. Horizontal bars show the average distribution of 28 daily samples, and the black error bars show the standard deviation. Red points represent the theoretically-estimated distribution (described in SI) and grey error bars represent the uncertainty in the estimates due to the range of temperatures during sampling. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

- Source: Melymuk et al; 2016

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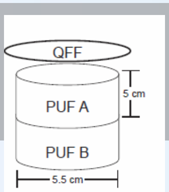
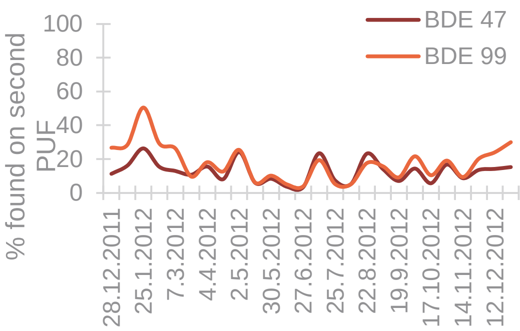
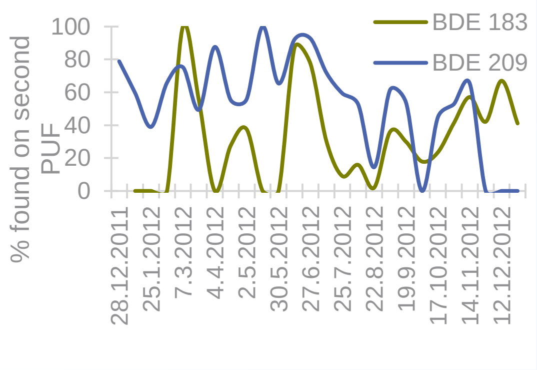
Breakthrough/sampling artefacts



- Breakthrough was evaluated by quantifying separately each of the two PUFs placed in series in 2012 (N=25)
- For PBDEs, no breakthrough is expected as these compounds are not volatile (low Vp, high Koa)

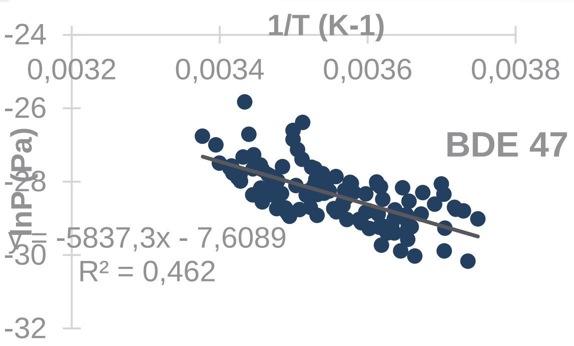
BUT…

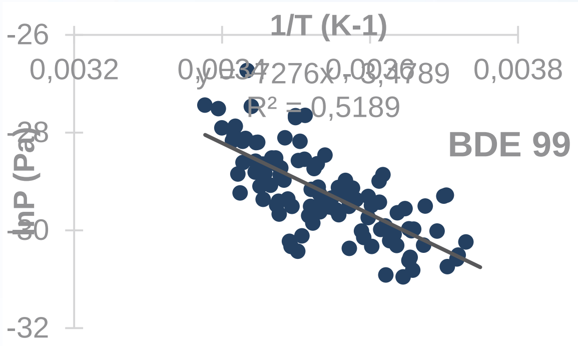


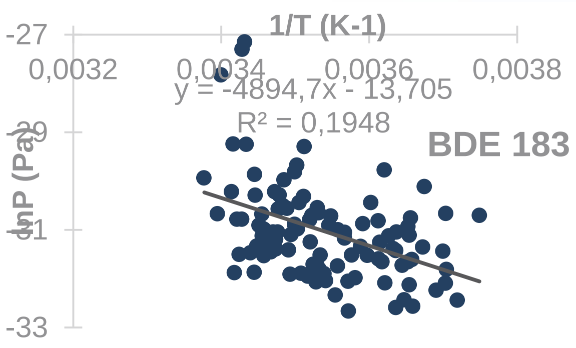


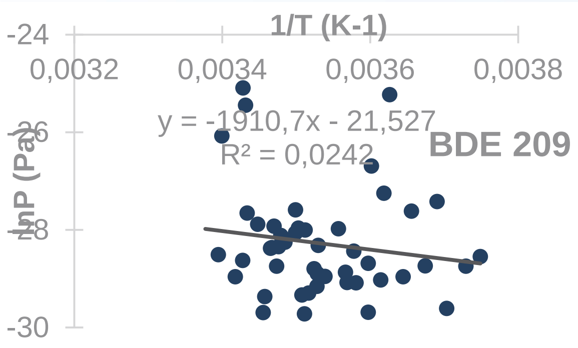
- 31.9% and 53.5% of BDE183 and BDE209 were found on the lower PUF
- For PBDEs, no breakthrough is expected as these compounds are not volatile (low Vp, high Koa)
- Likely not from breakthrough… Maybe from:
  - Uncertainties and limits with the analytical quantification (true for BDE209 but not for BDE183)
  - Blow-off = volatilization loss of PBDEs from the filter (but why they would end up in the 2nd PUF?

Seasonal variations – CC plots









	r2	p	N	m	b
BDE 28	0.03	0.08	111.00	-1752.40	-24.30
BDE 47	**0.46**	**<0.01**	**113.00**	**-5837.30**	**-7.61**
BDE 66	**0.16**	**<0.01**	**71.00**	**-3691.30**	**-18.03**
BDE 100	**0.49**	**<0.01**	**86.00**	**-7241.00**	**-4.86**
BDE 99	**0.52**	**<0.01**	**105.00**	**-7276.00**	**-3.48**
BDE 85	**0.61**	**<0.01**	**37.00**	**-7211.80**	**-6.89**
BDE 154	**0.59**	**<0.01**	**99.00**	**-7471.20**	**-5.27**
BDE 153	**0.58**	**<0.01**	**75.00**	**-8307.70**	**-2.40**
BDE 183	**0.19**	**<0.01**	**103.00**	**-4894.70**	**-13.71**
BDE 209	0.02	0.30	47.00	-1910.70	-21.53

- CC plots suggest that gaseous PBDEs (except BDE28 and BDE209) are influenced by temperature dependent sources (e.g. air-surface exchange)
- Cannot it be just by seasonality of G/P? (LRT vs. volatilization is it only that?)