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Table S1: Additional information about the air sampling performed

Year	Sampled volume (min-max)	Number of samples	Number of samples excluded	Number of field blanks	Number of laboratory blanks	Time span covered
2011	4512 ; 5863	40	9	3	2	63%
2012	4015 ; 5864	26	1	3	2	42%
2013	3753 ; 5480	23	3	2	3	38%
2014	5236 ; 5597	25	0	3	4	41%

Table S2: Range of the limit of quantifications (LOQs) determined by the instrument (iLOQ) and by the field blank concentrations plus three times their standard deviations (LOQ_{blanks}). To calculate LOQs in pg m^{-3}, the average sample volume (V=5264 m^3) was used

	iLOQ (min-max)		LOQ_{blanks} (min-max)	
	pg/sample	pg/m^3	pg/sample	pg/m^3
BDE 28	0.26 - 5486	4.92E-05 - 1.04	0 - 4.84	0 - 9.19E-04
BDE 47	0.11 - 2089	2.09E-05 - 0.40	8.30 - 129.7	1.58E-03 - 2.46E-02
BDE 66	0.15 - 1001	2.87E-05 - 0.19	0 - 3.59	0 - 6.82E-04
BDE 100	0.18 - 281	3.50E-05 - 0.05	0 - 277	0 - 5.26E-02
BDE 99	0.27 - 1238	5.07E-05 - 0.24	12.5 - 107	2.37E-03 - 2.03E-02
BDE 85	0.25 - 310	4.75E-05 - 0.06	0 - 0	0 - 0
BDE 154	0.26 - 246	4.84E-05 - 0.05	0 - 6.26	0 - 1.19E-03
BDE 153	0.29 - 382	5.57E-05 - 0.07	0 - 0	0 - 0
BDE 183	0.84 - 593	1.59E-04 - 0.11	0 - 32.5	0 - 6.16E-03
BDE 209	3.10 - 5374	5.90E-04 - 1.02	0- 3031	0 - 5.76E-01

Table S3: Results of breakthrough experiments for PBDEs. Only samples for which analytes were detected in at least one of the PUF were considered. N/D indicates compounds that were detected neither in the lower or upper PUF

Compound	Frequency of detection on upper PUF	Frequency of detection on lower PUF	% of compound mass found on the lower PUF				
			Min	Max	Average	Standard deviation	Median
BDE 28	100%	50%	0.00	85.8	8.1	17.8	0.00
BDE 47	100%	100%	3.30	26.3	12.7	6.5	13.6
BDE 66	51.9%	7.7%	0.00	69.6	5.5	18.5	0.00
BDE 100	100%	96.2%	0.00	52.8	15.5	10.8	17.6
BDE 99	100%	100%	3.83	50.5	17.7	10.8	18.1
BDE 85	22.2%	0%	0.00	0.00	0.00		0.0
BDE 154	77.8%	34.6%	0.00	42.7	7.7	11.8	0.0
BDE 153	63%	11.5%	0.00	48.0	5.4	14.0	0.0
BDE 183	88.9%	73.1%	0.00	100.0	31.9	29.3	29.9
BDE 209	96.3%	84.6%	0.00	100.0	53.6	29.4	55.8

Table S4: Summary of the atmospheric concentrations (in pg m^{-3}) and detections (in %) of individual PBDEs found in this study

		BDE 28	BDE 47	BDE 66	BDE 100	BDE 99	BDE 85	BDE 154	BDE 153	BDE 183	BDE 209	Σ_9PBDEs
Gas phase	Detection	97	99	62	75	92	32	87	66	90	41	100
	Min	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.022
	Max	3.731	1.218	0.198	0.185	0.570	0.016	0.040	0.054	0.482	5.010	5.858
	Average	0.051	0.141	0.011	0.022	0.071	0.003	0.007	0.007	0.023	0.513	0.311
	SD	0.360	0.152	0.024	0.026	0.078	0.003	0.006	0.009	0.065	1.076	0.583
Particulate phase	Detection	51	82	43	89	99	25	90	82	96	79	99
	Min	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Max	0.036	0.312	0.104	0.111	0.424	0.039	0.152	0.142	0.367	0.685	1.380
	Average	0.004	0.043	0.017	0.017	0.071	0.006	0.023	0.028	0.059	0.257	0.232
	SD	0.006	0.054	0.021	0.020	0.082	0.008	0.029	0.030	0.069	0.142	0.285
Total	Detection	98	100	68	100	100	40	100	91	99	89	100
	Min	<LOQ	0.038	<LOQ	0.001	0.025	<LOQ	0.003	<LOQ	<LOQ	<LOQ	0.088
	Max	3.731	1.251	0.198	0.205	0.650	0.039	0.152	0.142	0.512	5.010	6.079
	Average	0.053	0.175	0.020	0.031	0.135	0.006	0.027	0.030	0.078	0.468	0.542
	SD	0.359	0.151	0.028	0.028	0.098	0.006	0.027	0.029	0.087	0.744	0.617

Table S5: Results of the Pearson correlation analysis (r) between the individual concentrations of PBDEs and different meteorological parameters. Numbers in bold indicates cases significant at the 99% confidence interval

		BDE 28	BDE 47	BDE 66	BDE 100	BDE 99	BDE 85	BDE 154	BDE 153	BDE 183	BDE 209
Ctot	precipitation	-0.03	0.04	-0.07	-0.10	-0.16	0.05	**-0.32**	**-0.33**	**-0.26**	-0.08
	wind direction	0.04	-0.07	-0.07	-0.20	**-0.27**	-0.08	**-0.36**	**-0.39**	**-0.31**	0.03
	wind speed	-0.01	**-0.30**	-0.24	-0.23	**-0.28**	-0.16	-0.21	-0.18	-0.11	0.06
	RH	0.00	-0.18	0.14	0.06	0.07	0.14	**0.34**	**0.45**	**0.26**	0.03
	1/T	-0.12	**-0.25**	**0.29**	0.08	0.15	0.13	**0.58**	**0.53**	**0.27**	-0.04
	hmix	0.03	-0.08	-0.21	**-0.31**	**-0.37**	-0.15	**-0.53**	**-0.56**	**-0.39**	-0.03
Cg	precipitation	-0.02	0.10	0.08	0.13	0.15	0.20	0.12	0.09	0.02	0.00
	wind direction	0.04	0.01	0.12	0.03	-0.01	0.04	-0.01	0.03	0.01	0.09
	wind speed	-0.01	-0.23	-0.17	-0.15	-0.20	**-0.26**	**-0.24**	-0.12	0.02	0.11
	RH	-0.01	**-0.31**	-0.14	**-0.28**	**-0.38**	**-0.28**	**-0.38**	-0.17	-0.09	0.02
	1/T	-0.13	**-0.46**	-0.13	**-0.47**	**-0.58**	**-0.43**	**-0.59**	**-0.51**	**-0.28**	-0.13
	hmix	0.04	0.08	0.06	0.07	0.11	0.09	0.14	0.09	0.06	0.05
Cp	precipitation	-0.06	-0.20	-0.20	**-0.31**	**-0.34**	-0.06	**-0.34**	**-0.35**	**-0.35**	**-0.34**
	wind direction	-0.18	**-0.26**	**-0.25**	**-0.33**	**-0.31**	-0.11	**-0.35**	**-0.39**	**-0.40**	**-0.27**
	wind speed	-0.17	-0.19	-0.16	-0.13	-0.15	-0.03	-0.15	-0.14	-0.16	-0.22
	RH	0.29	**0.40**	**0.39**	**0.44**	**0.44**	**0.31**	**0.42**	**0.48**	**0.41**	0.04
	1/T	**0.42**	**0.61**	**0.61**	**0.71**	**0.72**	**0.37**	**0.69**	**0.66**	**0.60**	**0.41**
	hmix	**-0.30**	**-0.48**	**-0.41**	**-0.52**	**-0.55**	-0.22	**-0.54**	**-0.57**	**-0.55**	**-0.33**

Table S6: Results of correlation analysis between $\theta_{measured}$ and the inverse of temperature (K^{-1}) for individual congeners. Numbers in bold indicate cases for which correlation were statistically significant ($p<0.05$)

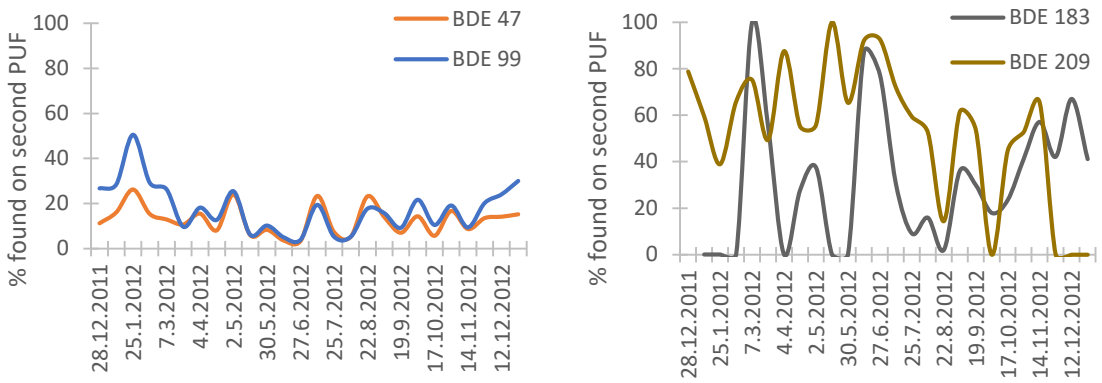
	BDE 28	BDE 47	BDE 66	BDE 100	BDE 99	BDE 85	BDE 154	BDE 153	BDE 183	BDE 209
r2	**0.31**	**0.74**	**0.57**	**0.54**	**0.84**	**0.51**	**0.76**	**0.61**	**0.49**	**0.06**
slope	1125.97	2296.02	3144.01	3137.97	3391.30	2919.25	3342.59	2927.09	2033.25	925.10
intercept	-3.89	-7.92	-10.81	-10.63	-11.55	-9.92	-11.25	-9.72	-6.51	-2.55

Table S7: Results of correlation analysis between $\theta_{measured}$ and the precipitation rate for individual PBDEs. Numbers in bold indicate cases for which the correlations were statistically significant ($p<0.05$)

	BDE 28	BDE 47	BDE 66	BDE 100	BDE 99	BDE 85	BDE 154	BDE 153	BDE 183	BDE 209
precipitation rate	**0.05**	**0.11**	**0.11**	**0.08**	**0.15**	0.06	**0.18**	**0.14**	**0.10**	0.03
RH	**0.13**	**0.31**	**0.32**	**0.25**	**0.38**	**0.30**	**0.31**	**0.27**	**0.14**	0.02

Table S8: Half lives of individual PBDEs observed in this study and elsewhere. Compounds in bold represent the cases which were statistically significant at the 95% confidence interval.

Reference	This study				Schuster et al; 2010	Birgul et al; 2012			Ma et al; 2013				
Location, type of site	Kosetice, CZ, background site				UK and Norwegian background sites	London, UK	Manchester, UK	HAZ, UK	Chicago, USA	Cleveland, USA	St. Point, USA	S.B.D., USA	Eagle Harbor, USA
Years	2011-2014				2000-2008	2002-2010	2003-2010	2000-2010	2005-2011				
	N	Half-life	r2	p	Half-life ± SD	Half-lives (min-max)			Half-lives (gas/particle)				
BDE 28	112	-7.37	0.01	0.22									
BDE 47	114	22.77	0	0.38	2.4 ± 0.2				5.2/5.3	8.9/9.2	-9.4/ns	-7/ns	-7.4/ns
BDE 66	77	-4.89	0.03	0.15									
BDE 100	**114**	**2.83 (1.87 ; 6.82)**	**0.1**	**<0.01**	4.0 ± 0.4								
BDE 99	**114**	**3.61 (2.44 ; 7.33)**	**0.12**	**<0.01**	3.3 ± 0.3				-9.5/10.1	ns/9.1	-4.6/ns	-4.3/ns	-4.7/ns
BDE 85	46	2.81	0.07	0.08									
BDE 154	114	7.91	0.01	0.21	3.3 ± 0.1								
BDE 153	**104**	**4.52 (2.33 ; 71.74)**	**0.04**	**0.04**	1.4 ± 0.3								
BDE 183	113	10.05	0.01	0.36									
BDE 209	**101**	**2.58 (1.79 ; 4.58)**	**0.17**	**<0.01**						2.6/5.3	ns/8.5		
Σ_9PBDEs	114	9.16	0.02	0.12									
ΣPBDEs						3.4 (2.2-6.9)	2.0 (1.3-4.6)	2.2-9.0					



a) b)

Figure S1: Results of the breakthrough experiments for BDE47, BDE99 (a), BDE183 and BDE209 (b)

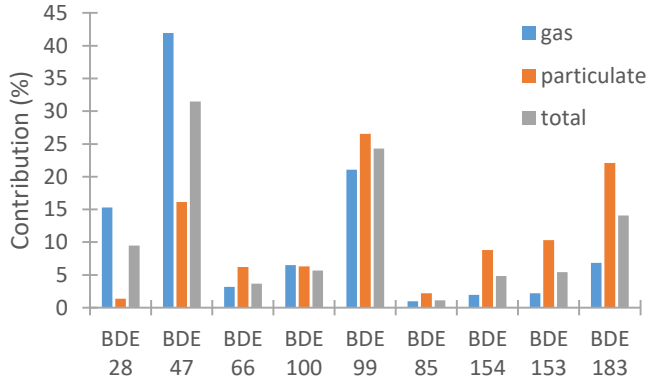
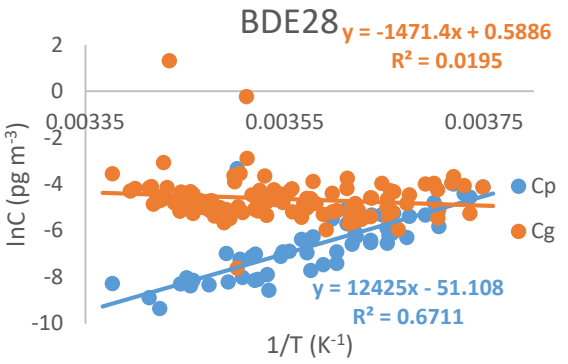
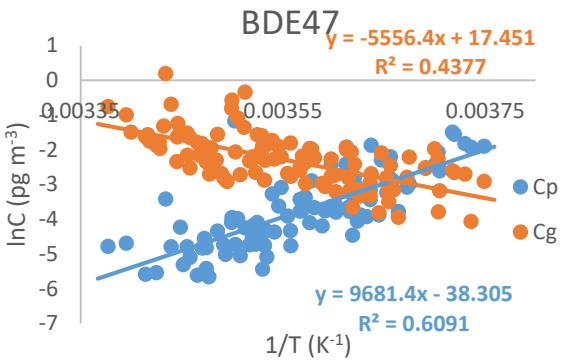
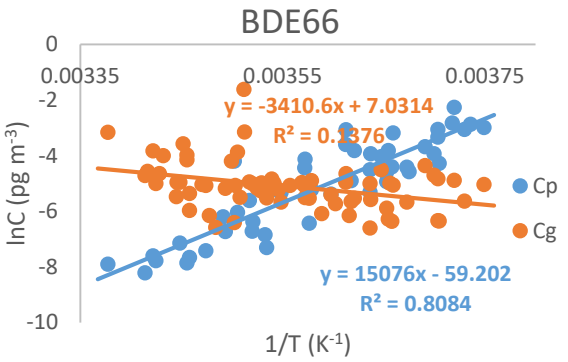
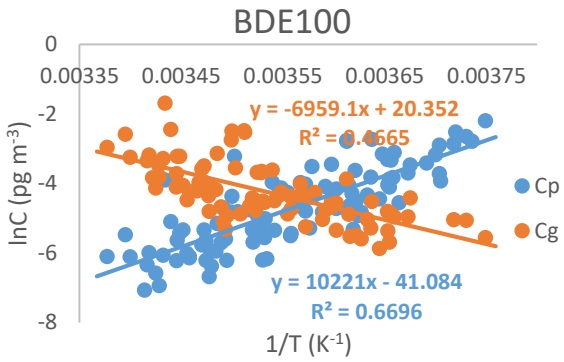


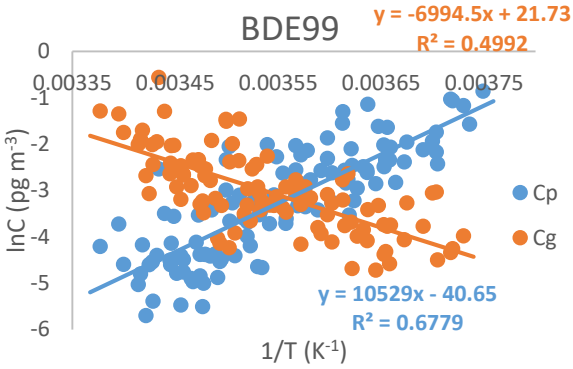
Figure S2: Contribution of individual BDEs to Σ_9PBDEs

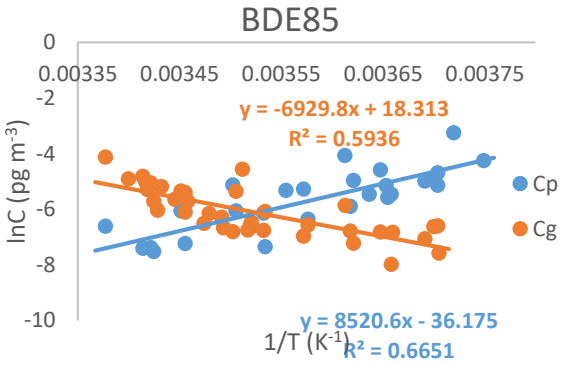

BDE28
y = -1471.4x + 0.5886
R² = 0.0195
y = 12425x - 51.108
R² = 0.6711
lnC (pg m-3)
1/T (K-1)
Cp
Cg


BDE47
y = -5556.4x + 17.451
R² = 0.4377
y = 9681.4x - 38.305
R² = 0.6091
lnC (pg m-3)
1/T (K-1)
Cp
Cg


BDE66
y = -3410.6x + 7.0314
R² = 0.1376
y = 15076x - 59.202
R² = 0.8084
lnC (pg m-3)
1/T (K-1)
Cp
Cg


BDE100
y = -6959.1x + 20.352
R² = 0.4665
y = 10221x - 41.084
R² = 0.6696
lnC (pg m-3)
1/T (K-1)
Cp
Cg


BDE99
y = -6994.5x + 21.73
R² = 0.4992
y = 10529x - 40.65
R² = 0.6779
lnC (pg m-3)
1/T (K-1)
Cp
Cg


BDE85
y = -6929.8x + 18.313
R² = 0.5936
y = 8520.6x - 36.175
R² = 0.6651
lnC (pg m-3)
1/T (K-1)
Cp
Cg

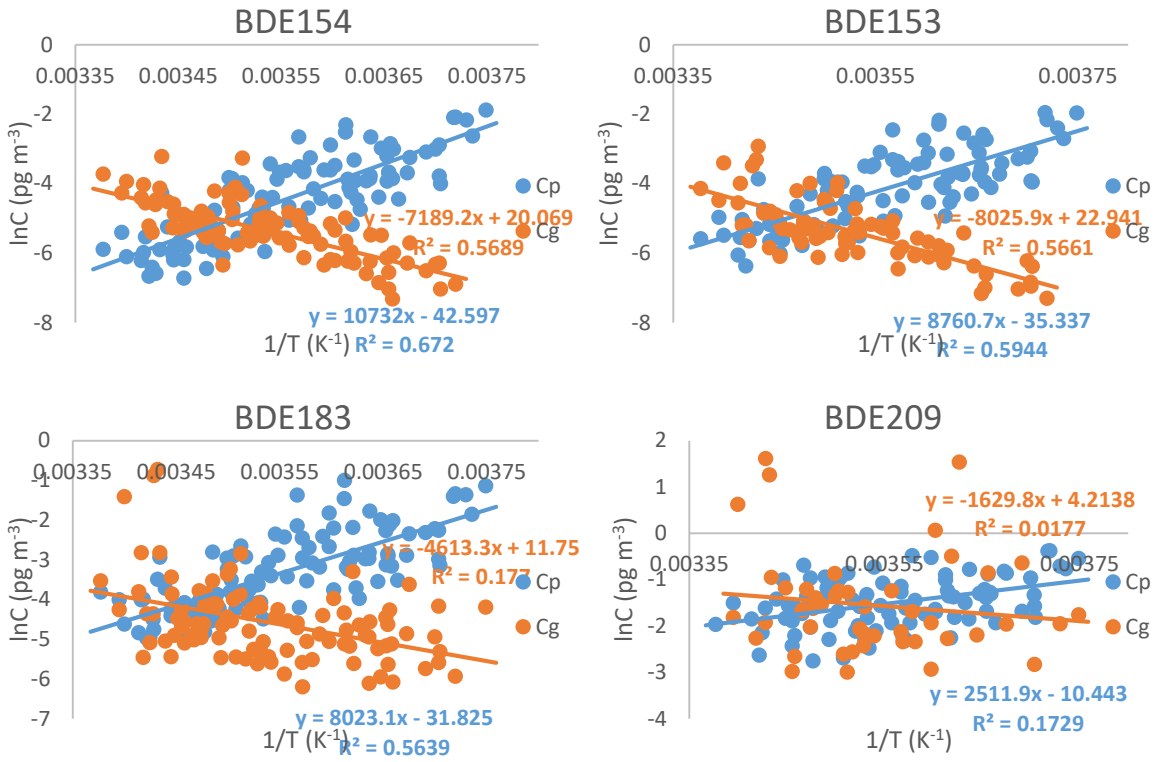


Figure S3: Correlation between the concentration of individual PBDEs (ln transformed) with the inverse of temperature

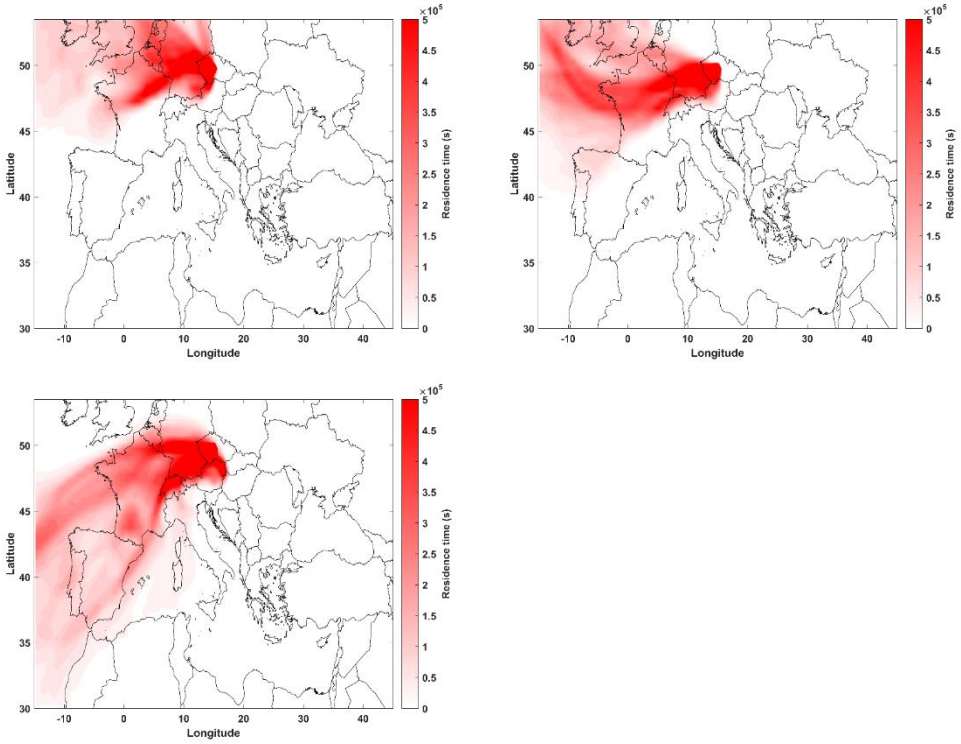


Figure S4: Selected examples of 5 days backward trajectories of samples associated with the lowest PBDE concentrations

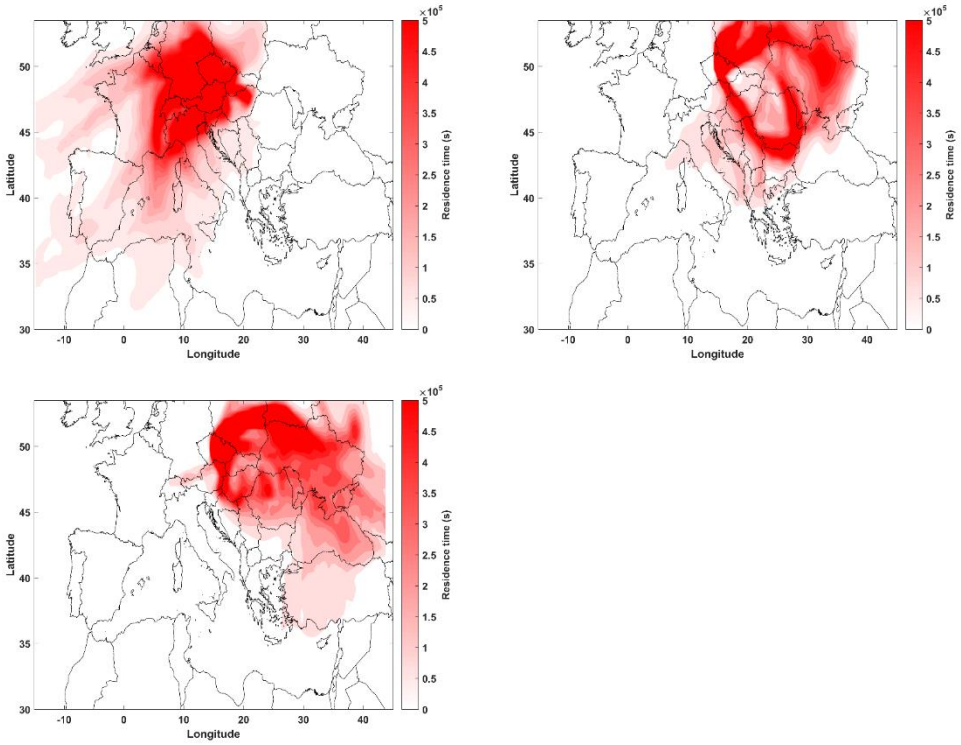


Figure S5: Selected examples of 5 days backward trajectories of samples associated with the highest PBDE concentrations

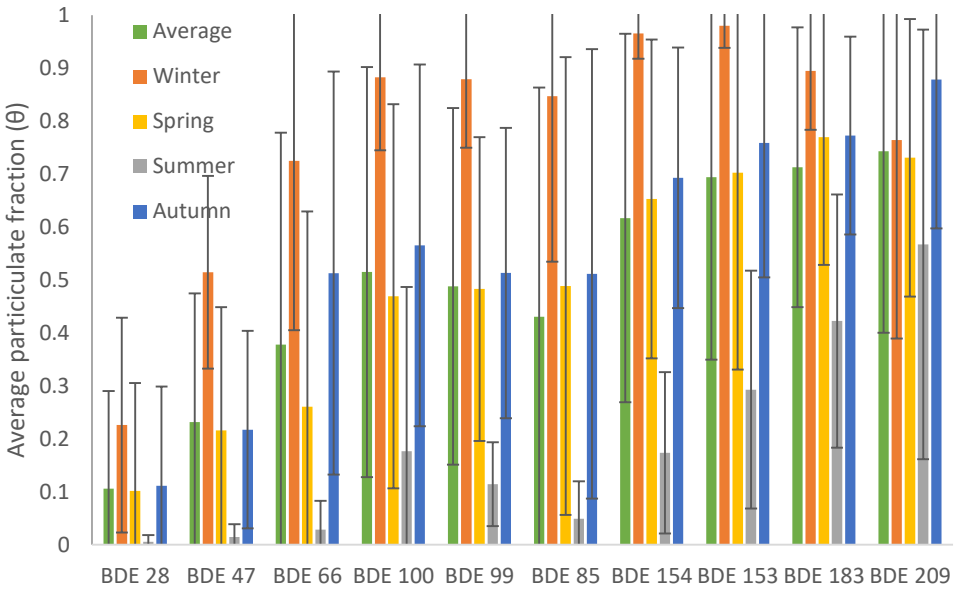
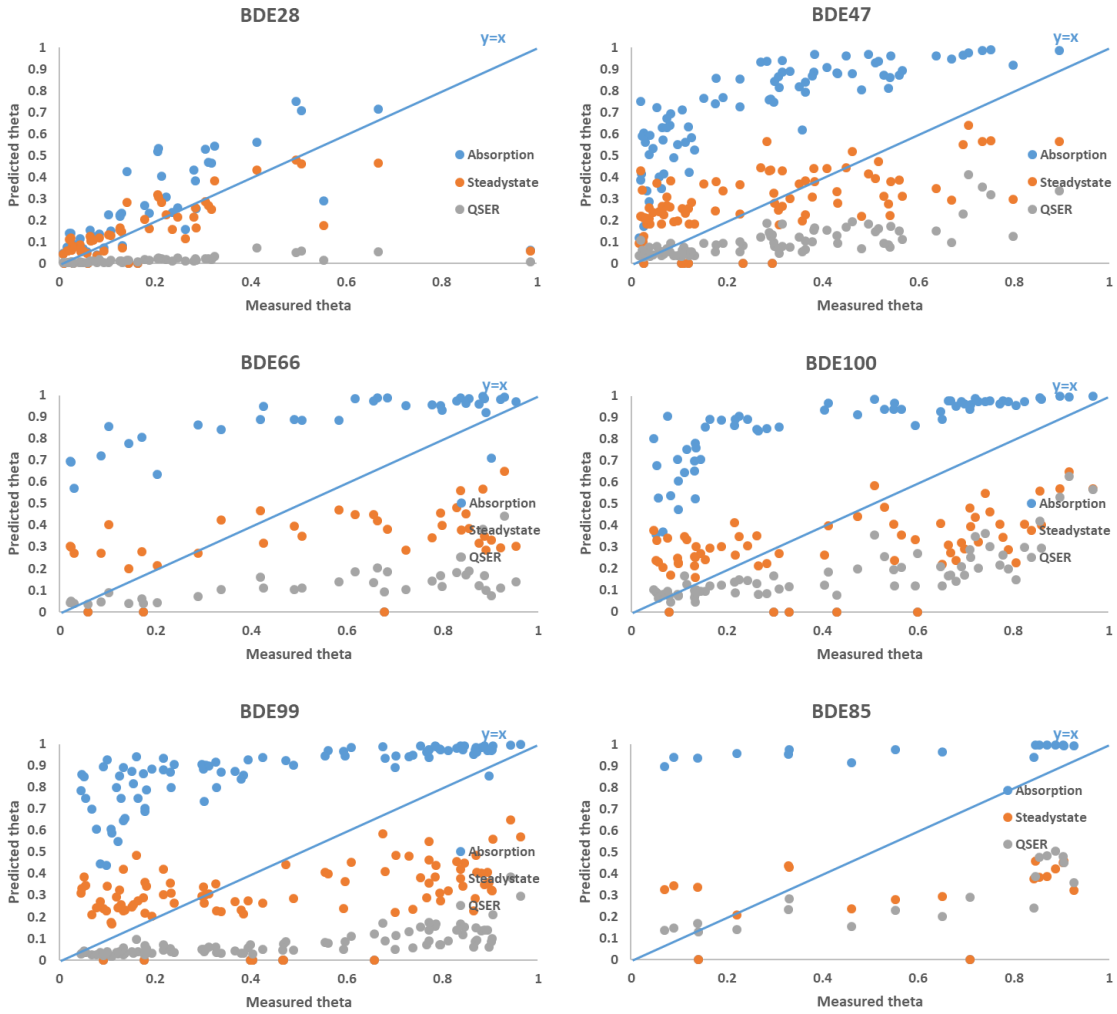


Figure S6: Average measured particulate fraction ($\theta_{measured}$) found in this study



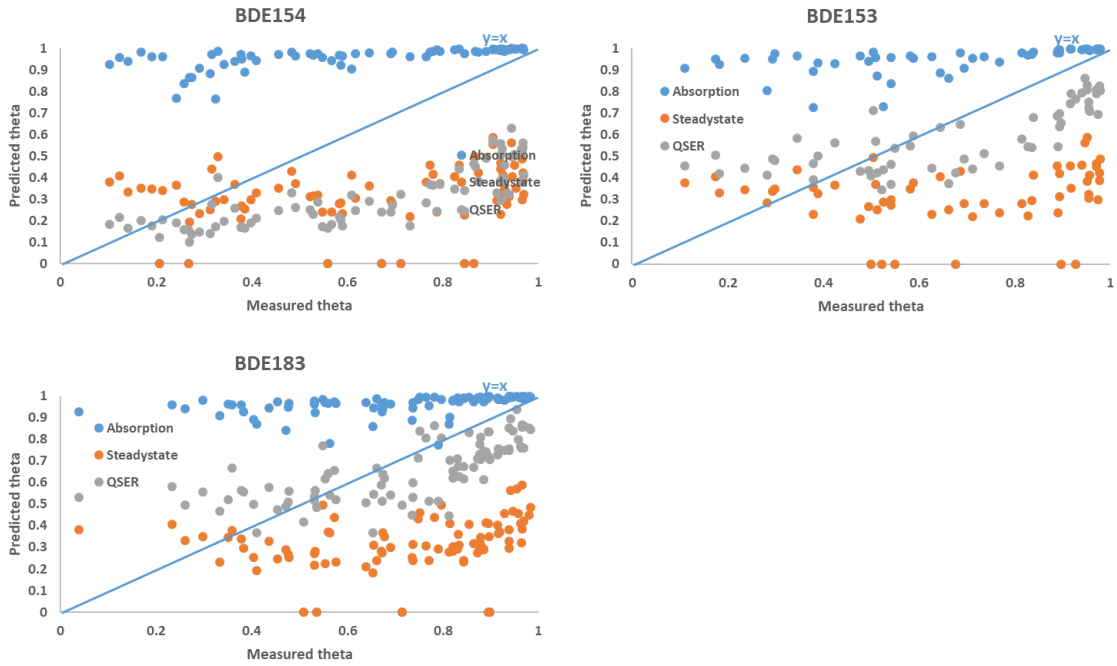
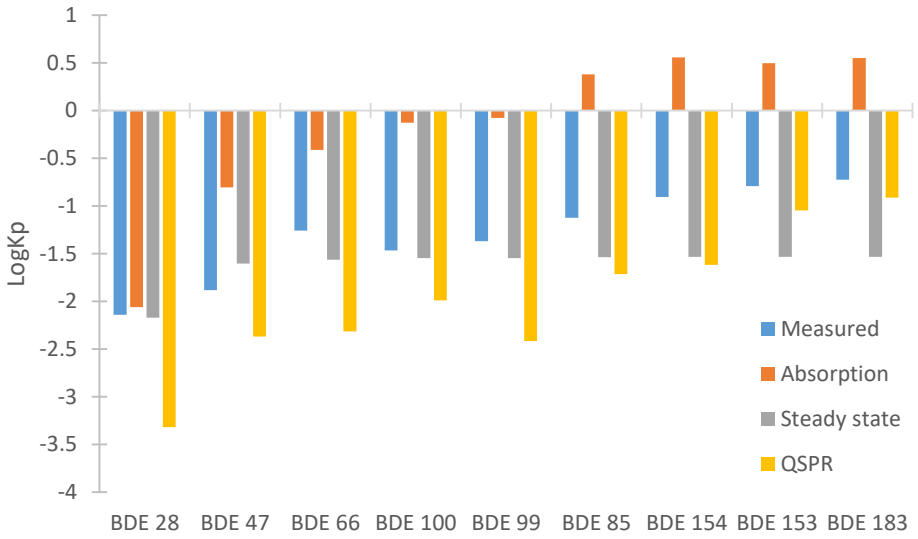
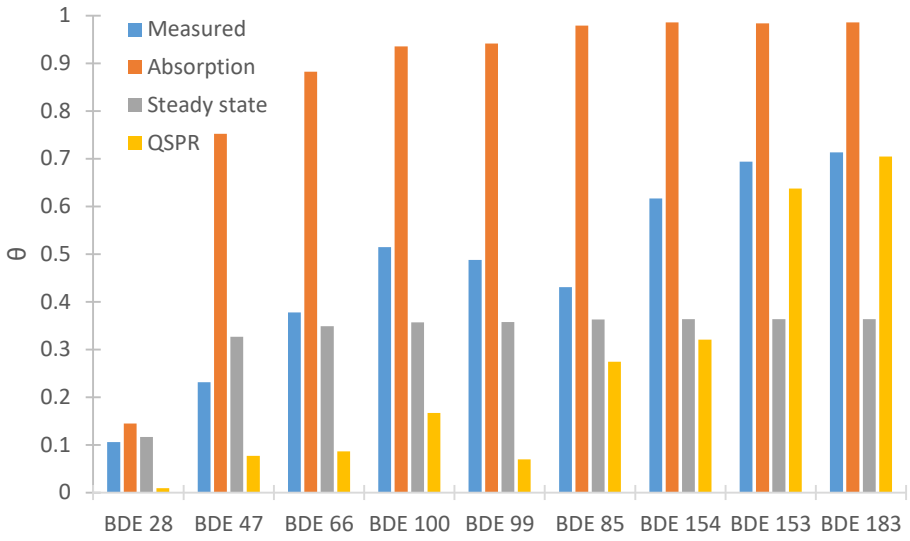


Figure S7: Comparison of measured and predicted θ



a)



b)

Figure S8: Comparison of the predicted and measured logK_p (a) and θ (b) using the average conditions at the sampling site (i.e. T=281.8 K, PM_{10}=19.6 µg.m^{-3})

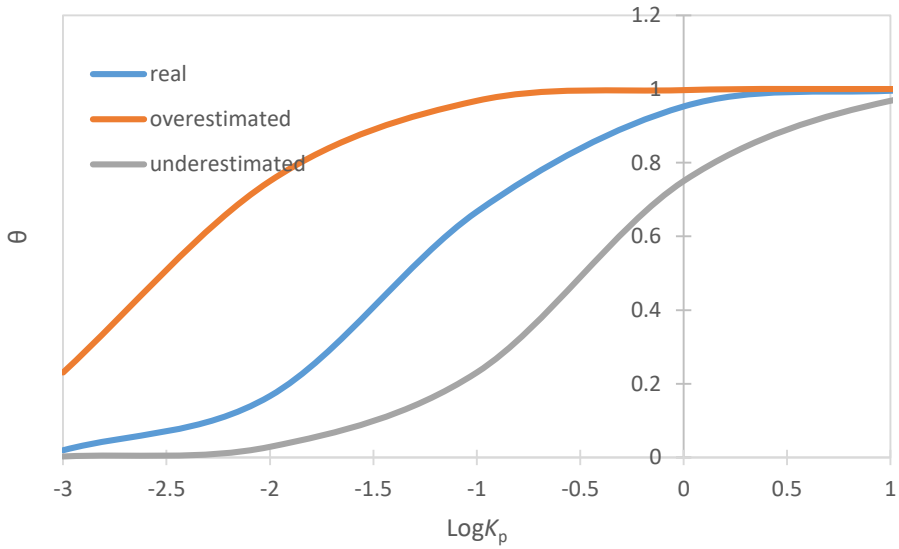


Figure S9: Schematic of the effect of an over- or under-estimation of K_p by one order of magnitude in terms of θ. The average PM_{10} concentrations (19.6 µg.m^{-3}) at the sampling site during this study was used.

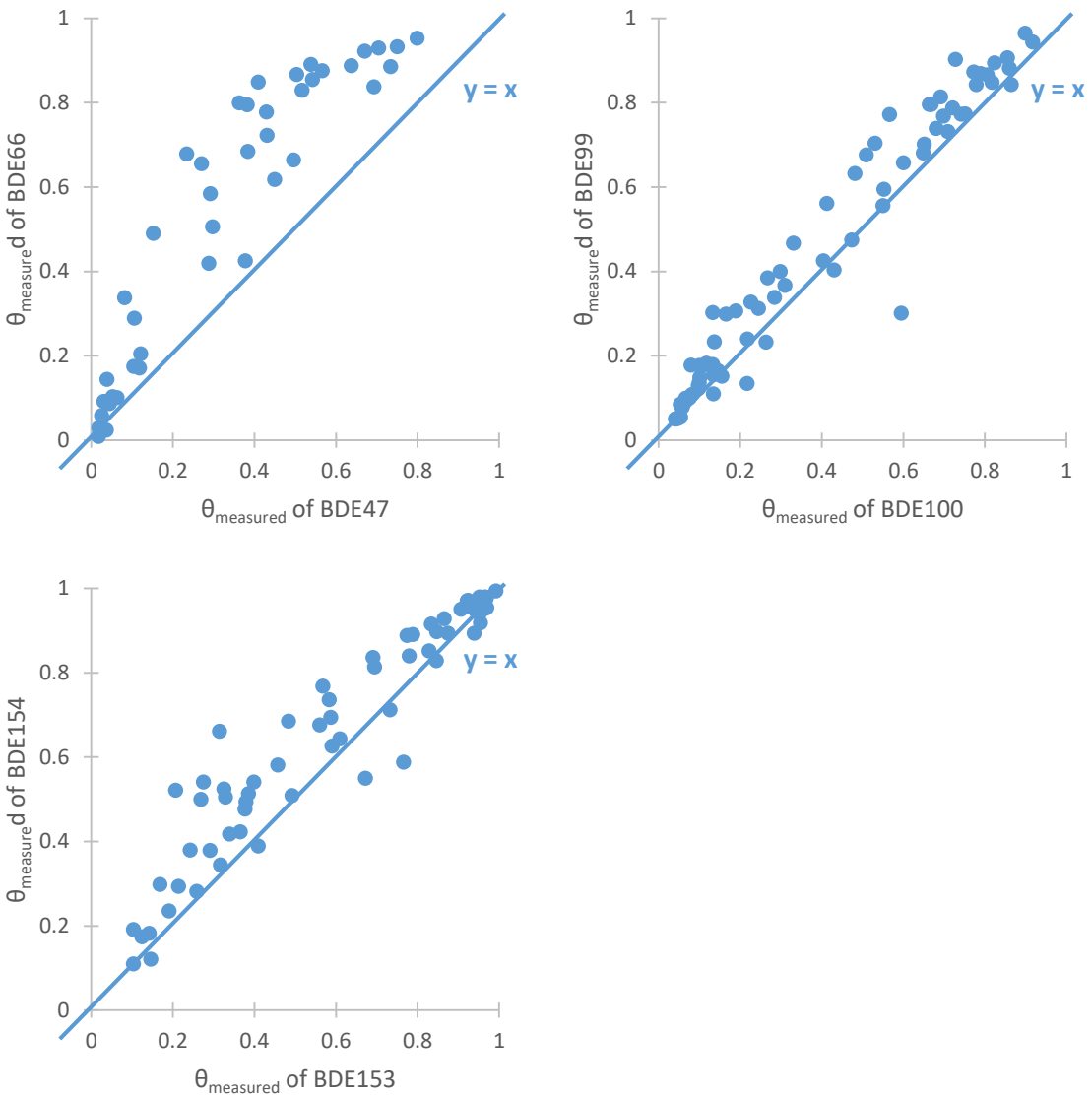


Figure S10: Comparison of the measured particulate fractions ($\theta_{measured}$) of three sets of isomers. Cases when each isomers were detected in both the gaseous and particulate phases were considered

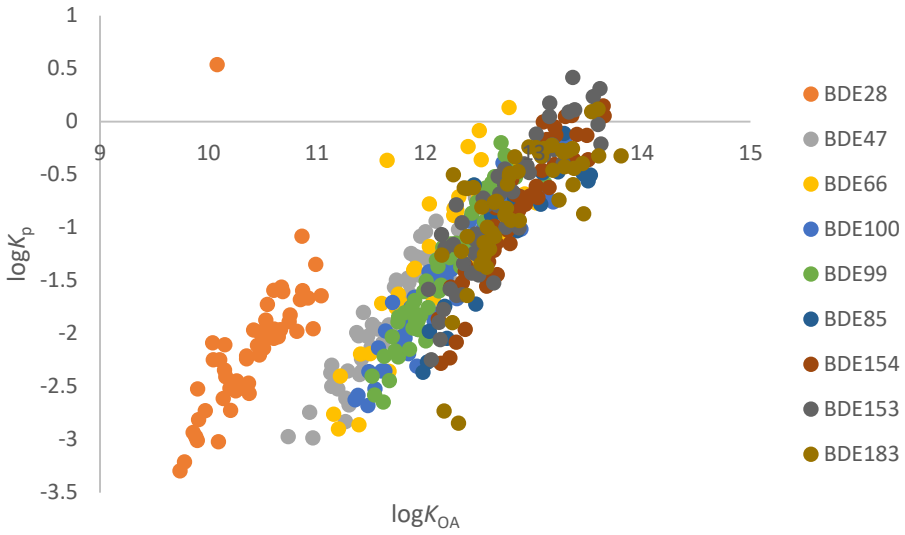


Figure S11: Influence of logK_{OA} on measured logK_p for individual PBDEs

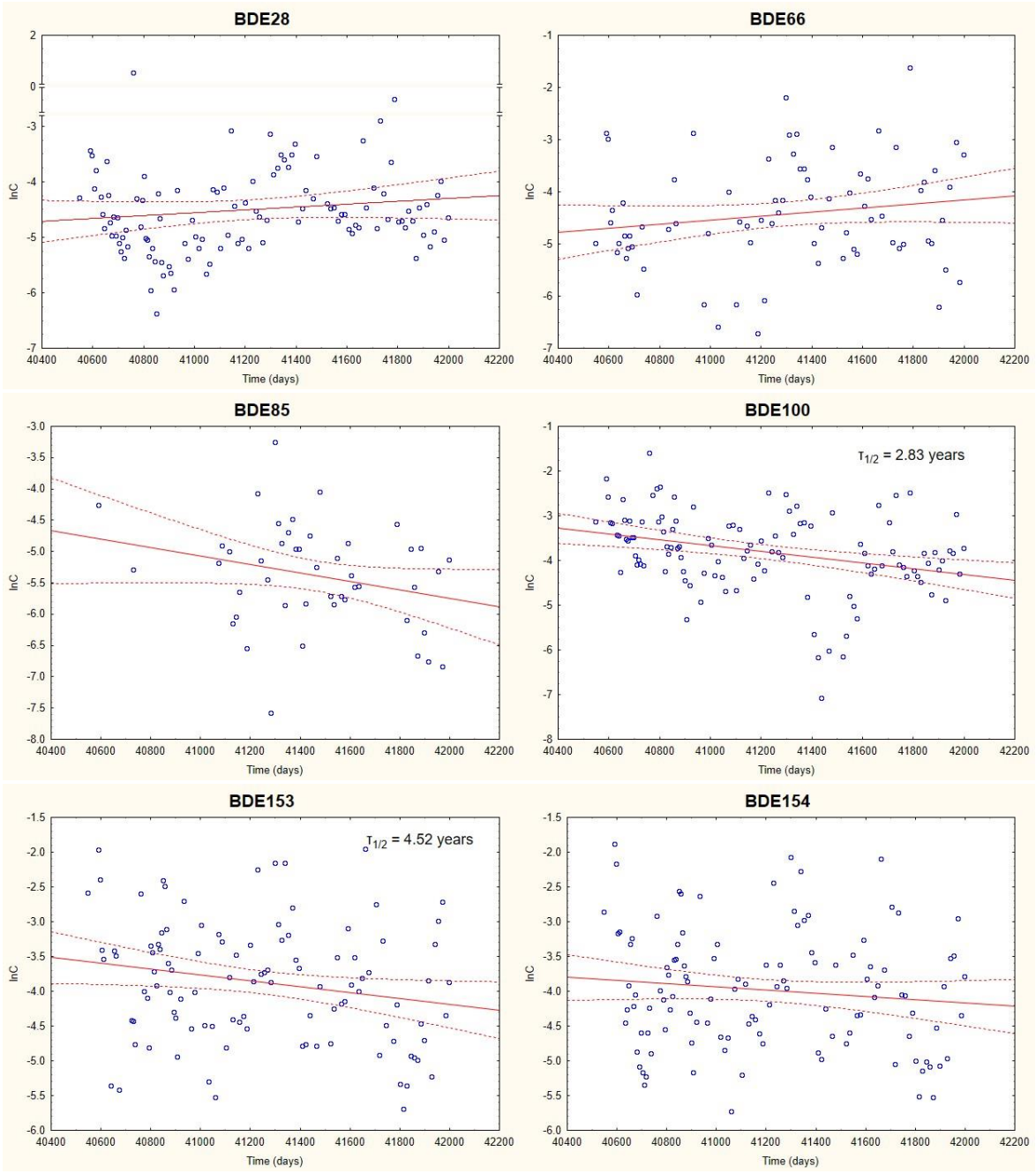


Figure S12: Multi-years trend of some PBDEs