SUPPLEMENTARY INFORMATION

Particle size distribution of halogenated flame retardants and implications for atmospheric deposition and transport

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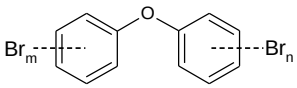
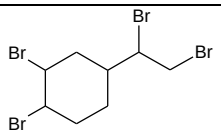
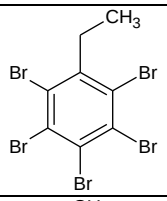
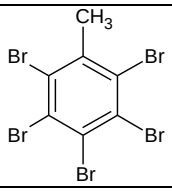
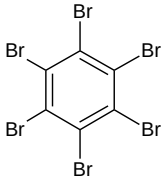
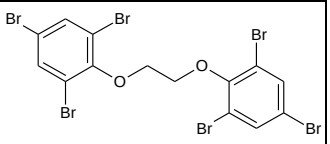
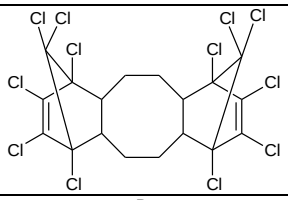
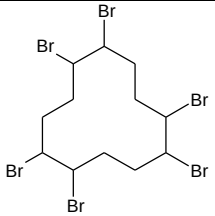
Table S1: Analyte information

Compound	CAS	Molecular mass	Vapor Pressure (Pa)*	Log K_{OA}*	Structure
PBDE Polybrominated diphenyl ether	PentaBDE 32534-81-9 OctaBDE 32536-52-0 DecaBDE 1163-19-5	BDE-28: 406.9 BDE-47: 485.8 BDE-66: 485.8 BDE-85: 564.7 BDE-99: 564.7 BDE-100: 564.7 BDE-153: 643.6 BDE-154: 643.6 BDE-183: 722.5 BDE-209: 959.2	BDE-28: 0.0016 BDE-47: 1.86×10^{-4} BDE-66: 2.38×10^{-4} BDE-85: 2.81×10^{-5} BDE-99: 6.82×10^{-5} BDE-100: 2.86×10^{-5} BDE-153: 8.43×10^{-6} BDE-154: 3.80×10^{-6} BDE-183: 4.68×10^{-7} BDE-209: 3.16×10^{-10}	BDE-28: 9.5 BDE-47: 10.53 BDE-66: 10.82 BDE-85: 11.66 BDE-99: 11.31 BDE-100: 11.13 BDE-153: 11.82 BDE-154: 11.92 BDE-183: 11.96 BDE-209: 14.98	
TBECH Tetrabromo-ethylcyclo-hexane	3322-93-8	427.8	0.014	8.01	
PBEB Pentabromo-ethylbenzene	85-22-2	500.7	3.2×10^{-4}	9.97	
PBT Pentabromo-toluene	87-83-2	486.6	1.22×10^{-3}	9.60	
HBB Hexabromo-benzene	87-82-1	551.5	3.17×10^{-4}	9.13	
BTBPE 1,2-bis(2,4,6 tribromo-phenoxy) ethane	37853-59-1	687.6	3.88×10^{-10}	15.7	
DP Dechlorane Plus	13560-89-9	653.7	9.47×10^{-8}	14.8	
HBCD Hexabromo-cyclododecane	3194-55-6	641.7	3.03×10^{-5}	10.46	

* Vapor pressure and logK_{OA} data are for a temperature of 25°C, and are obtained from the following references: Wong et al.[1], Tittlemier et al.[2], Harner and Shoeib[3], Cetin and Odabasi[4], Covaci et al.[5], Marvin et al.[6], and U.S. EPA EPI Suite[7].

Table S2: Duration and volume of samples collected for brominated compounds analysis

	Rural site			Urban site		
Season	**Sampling period (d/m/yyyy)**	**Duration of sampling (hrs:mins)**	**Volume sampled (m^3)**	**Sampling period (d/m/yyyy)**	**Duration of sampling (hrs:mins)**	**Volume sampled (m^3)**
Spring	9. - 16.4.2010	164:08	11162	9. - 16.4.2010	160:32	10915
	7. - 10.5.2010	35:15	2397	7. - 10.5.2010	63:08	4293
	7. - 14.6.2010	163:15	11103	14. - 21.6.2010	165:23	11245
Summer	5. - 11.7.2010	87:34	5957	12. - 19.7.2010	167:57	11420
	2. - 9.8.2010	168:00	11425	16. - 23.8.2010	158:28	10775
	9. - 15.9.2010	120:55	8313	15. - 18.9.2010	69:56	4755
Autumn	8. - 15.10.2010	107:18	7297	8. - 15.10.2010	159:49	10863
	30.10. - 3.11.2009	97:54	6659	30.10. - 2.11.2009	72:11	4909
	20. - 27.11.2009	168:00	11424	20. - 27.11.2009	161:14	10964
Winter	6. - 13.1.2010	161:57	11014	6. - 13.1.2010	163:50	11141
	3. - 9.2.2010	141:11	9604	3. - 10.2.2010	167:07	11364
	5. - 12.3.2010	168:00	11424	3. - 10.3.2010	166:25	11316

Sampling Instrument

Particulate matter (PM) was collected from October 2009 to October 2010 using a high volume air sampler equipped with a six-stage (<0.49 μm; 0.49-0.95; 0.95-1.5; 1.5-3.0; 3.0-7.2; 7.2-10 μm) cascade impactor (sampler: HV100-P, Baghirra Ltd; impactor: TE-6001 PM-10 Head, Tisch Environmental Inc.).

The impactor itself is a series of stacked slotted plates that are attached to a conventional high volume air sampler (Figure S1). The impactor used in this study consists of 5 slotted rectangular aluminium plates with dimensions of 15.2 x 17.8 cm and one larger base plate. The upper plates have parallel impaction slots calibrated to select particles according to their aerodynamic diameter. The sampler was equipped with a PM10 sampling head acting as a pre-selector, thus particles collected on the cascade impactor filters are all <10 μm. Slotted filter media (Figure S2) are place on each impactor plate to collect the particles. Particles passing through the slots in the impactor stages impact on the filters and are thereby collected. Collection of the particles by the filter fiber lattice improves particle retention compared with impaction on the metal surfaces alone. The collection substrates also act as the vacuum seal between impactor stages.

The particle size cut-offs are determined by the sampler geometry and the flow rate. The sampler is programmed to calibrate for temperature and pressure.

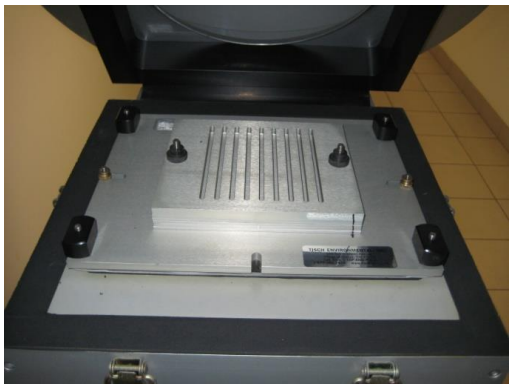


Figure S1: Cascade impactor filter unit

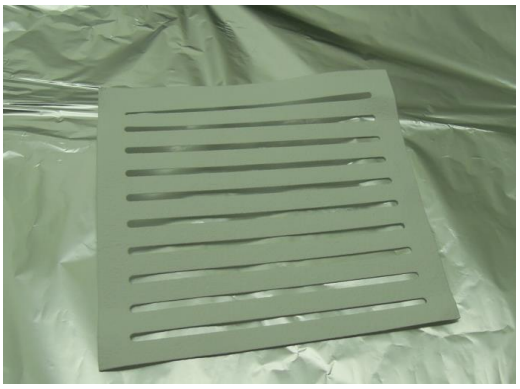


Figure S2: Cascade impactor filter

Sample Extraction and Analysis

Filters were extracted with toluene by means of a Büchi B-811 automated extraction system (3 cycles - 60 minutes warm Soxhlet followed by 30 minutes of solvent rinsing). Before extraction, internal standards were added (listed in QA/QC section). Samples were then solvent exchanged to dichloromethane. Clean-up was performed with H_2SO_4 modified silica gel column (30% w/w) eluted with dichloromethane:n-hexane (1:1, v/v). The extracts were reduced in volume by a gentle stream of nitrogen, and separated into planar and non-planar fractions by means of activated carbon column mixed with activated silica gel (1:40 w/w) eluted with DCM:cyclohexane (3:7 v/v) – first fraction, and toluene – second fraction. Both fractions were reduced in volume by a gentle stream of nitrogen and solvent exchanged to nonane. Recovery standards were added (^{13}C BDE-77 and ^{13}C BDE-138) to the first fraction which was subsequently used for PBDEs analysis. The second fraction was analyzed for PCDD/Fs and dioxin-like PCBs, results of which are presented elsewhere.[8] The final volume of the first fraction was 50 µl.

PBDEs were analyzed using an Agilent 7890A gas chromatograph (GC) equipped with a 15 m x 0.25 mm x 0.10 µm J&W DB5 column coupled to a Waters Micromass AutoSpec Premier mass spectrometer (HRMS) in positive electron ionization impact mode using selected ion monitoring at the resolution > 10 000. Injection was splitless 1 µL at 280°C, with He as a carrier gas at 1 mL·min^{-1}. The GC temperature program was 80°C with a 1 min hold, then 20°C·min^{-1} to 250°C, followed by 1.5°C·min^{-1} to 260°C with a 2 min hold and 25°C·min^{-1} to 320°C with a 4.5 min hold.

After PBDE analysis, the two fractions were recombined. Using the same instrument parameters, NFRs analysis was performed. Following the analysis of NFRs, samples were used for HBCDs analysis. Samples were evaporated to dryness, 5 µL of acetone was added, samples were vortexed, and acetonitrile was added to give a total volume of 250 µL. HBCDs were analyzed using an Agilent 1100 series liquid chromatography (HPLC) system. Chromatographic separation was accomplished using a Phenomenex LUNA C-18 end-capped analytical column (100 x 2mm, 3µm particles size) maintained at 30°C equipped with Phenomenex SecureGuard C18 pre-column. The mobile phases for the gradient separation of the HBCDs isomers were 1 mM water solution of ammonium acetate at pH 4 (solution A) and an acetonitrile solution with an addition of 1 mM ammonium acetate (solution B). The flow rate was 0.25 mL·min^{-1}, and the injection volume was 10 µL. A linear gradient began at an initial composition of (A/B) of 50:50 (v/v), ran to 10:90 over 6 min, where it was held for 8 min. The column was equilibrated for 5 min at the initial composition of the mobile phase. Analyte detection was performed by means of tandem mass spectrometer AB Sciex Qtrap 5500 operating in negative electrospray ionization mode at 450°C with N_2 as a nebulizer gas and an entrance potential of -4kV. Mode scheduled multiple reaction monitoring was used to follow signal from m/z 640.5 → 79.0 for quantification and 640.5 → 80.9 for qualification. HBCD isomers were identified using native α, β and γ-HBCD solutions and quantified using ^{13}C-labeled γ-HBCD.

Quality Assurance/Quality Control

Concentrations were quantified using a set of mass-labelled (C13) internal standards. For compounds with a corresponding C13 standard, this standard was used for quantification. Where a corresponding C13-labelled standard was not available, the C13 standard that was most structurally similar was used.

Internal standards:^{13}C BDE-28,^{13}C BDE-47,^{13}C BDE-66,^{13}C BDE-85,^{13}C BDE-99,^{13}C BDE-100,^{13}C BDE-153,^{13}C BDE-154,^{13}C BDE-183,^{13}C BDE-209, ^{13}C PBBZ, ^{13}C HBB, ^{13}C BTBPE, ^{13}C a-DP, ^{13}C s-DP, ^{13}C DBDPE, ^{13}C γ-HBCD

Analytical results for NFRs were validated through participation in an interlaboratory comparison study for NFRs (REF report).The analytical methods/laboratory performance of the RECETOX laboratories (where sample analysis took place) demonstrated good accuracy for the compounds included in this study (Table S3).

Table S3: Percentage difference between measured value from RECETOX laboratories and reference (actual) value from participation in an inter-laboratory comparison for NFRs.

Compound	Percent difference from reference value
TBECH	15%
PBEB	7.1%
PBT	7.8%
HBB	9.1%
BTBPE	11%
s-DP	14%
a-DP	14%
α-HBCD	1.0%
β-HBCD	2.1%
γ-HBCD	6.7%

Table S4: Field and laboratory blank averages, standard deviations and ranges. Samples were blank subtracted, and were reported as <LOD if concentration was less than the avg. blank + 3 standard deviations.

	Avg. ± standard deviation (pg)	Range (pg)
TBECH	203±190	<LOD-480
PBEB	4.82±4.38	<LOD-10.7
PBT	6.82±6.49	1.65-17.0
HBB	2.95±6.60	<LOD-17.8
s-DP	190±113	59.4-322
a-DP	<LOD	<LOD
TBCO	8.31±18.6	<LOD-41.6
α-HBCD	3970±3060	167-8410
β-HBCD	660±520	20-1150
γ-HBCD	1330±660	490-2370

Table S5: Mass median diameters (MMDs) and corresponding geometric standard deviations (σ_g) of atmospheric aerosols measured in the experiment

	Rural site				**Urban site**			
	Spring	**Summer**	**Autumn**	**Winter**	**Spring**	**Summer**	**Autumn**	**Winter**
MMD	0.741	0.769	0.808	0.802	0.990	0.772	0.932	0.802
σ_g	3.64	3.73	3.31	2.59	5.70	6.33	4.66	2.59

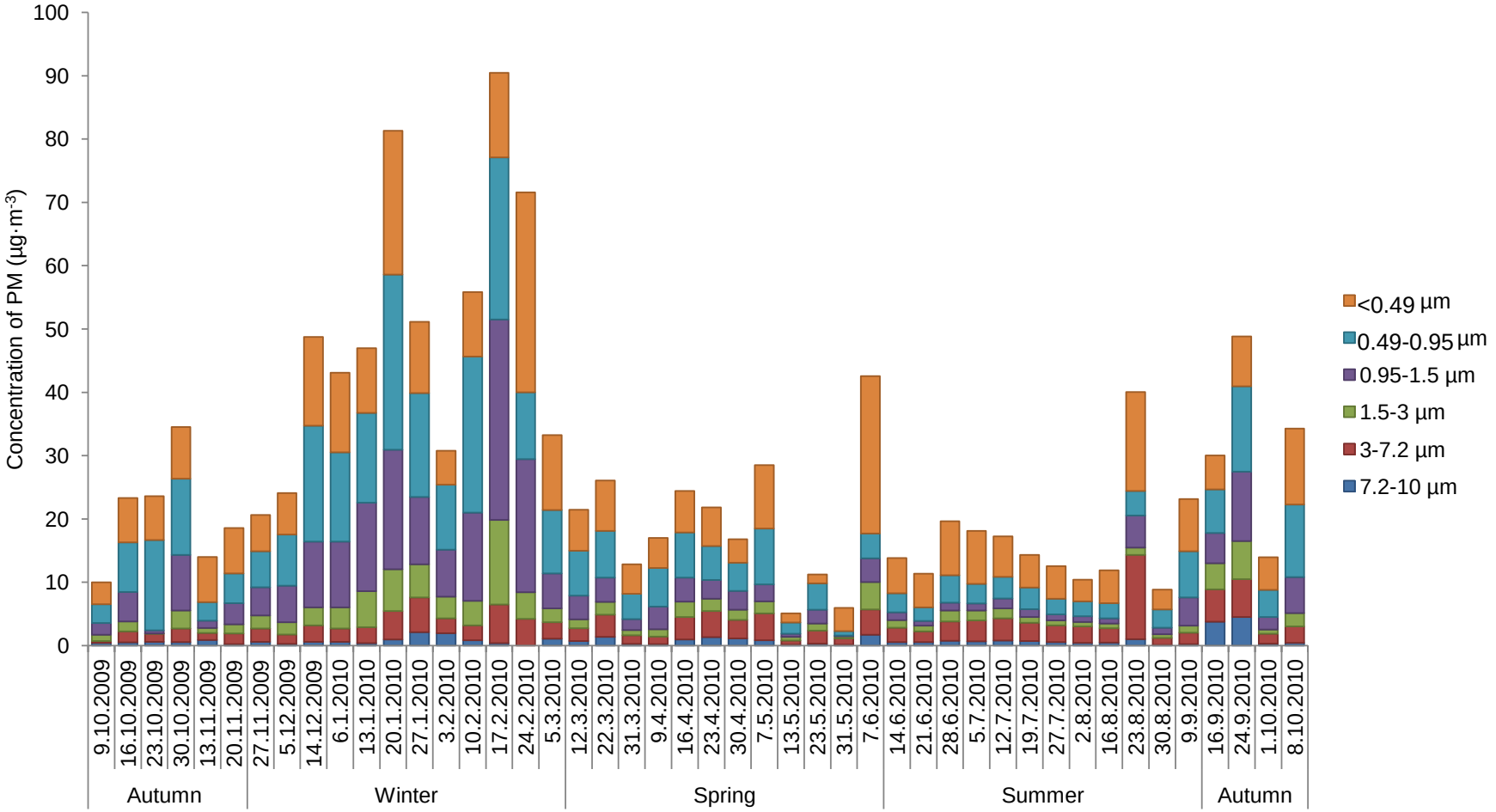


Figure S3: Concentration of particulate matter (PM) during sampling period at rural site.

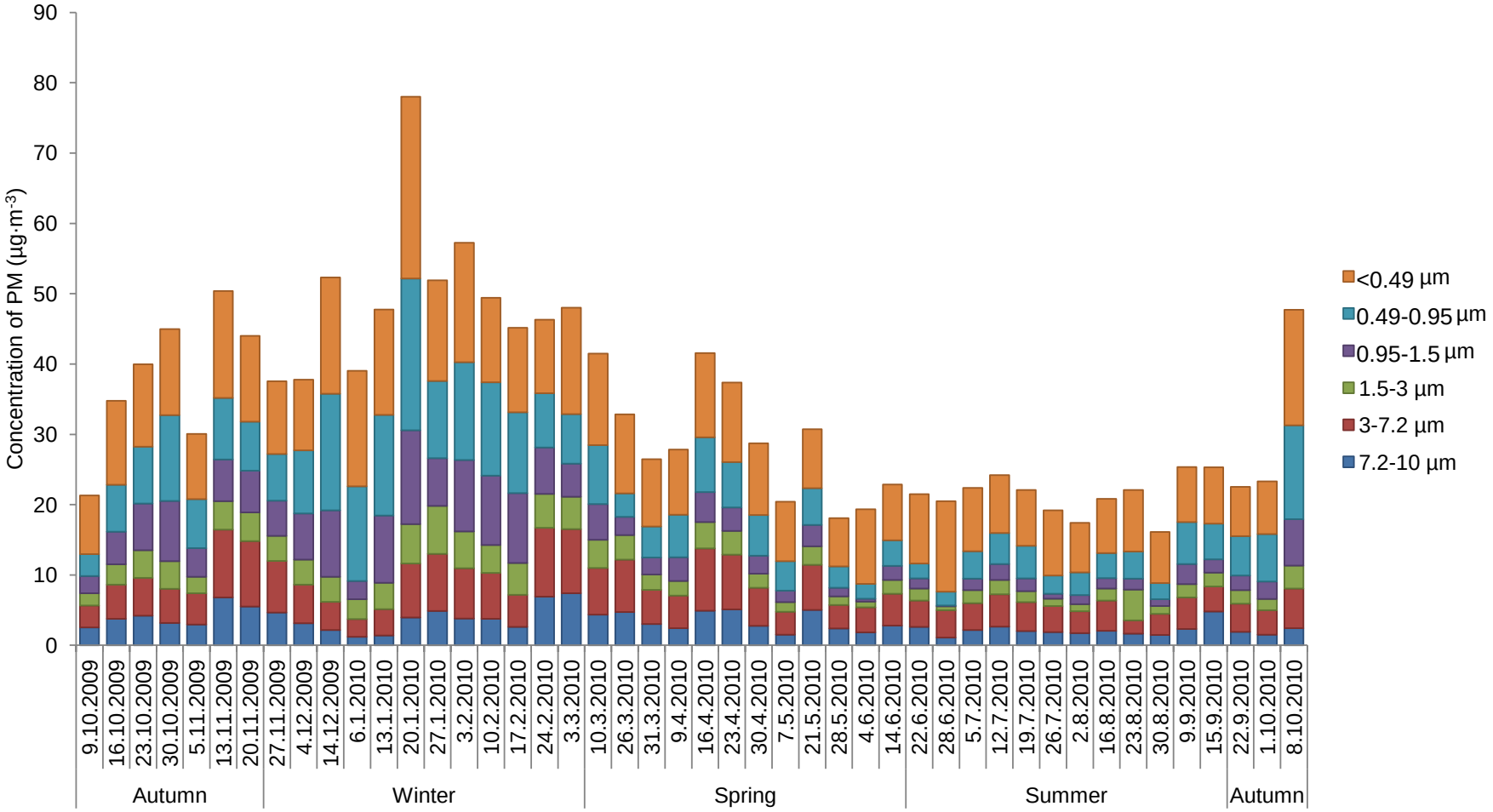


Figure S3: Concentration of PM during sampling period at urban site.

Table S6: Concentrations of PBDEs (in $fg \cdot m^{-3}$) at rural site. Results below LOD (limit of detection, equal average value of the blank + 3 standard deviations) for the purpose of statistical analysis are assigned values equal to 0.5 LOD and are noted in italics.

Season	Size fraction	BDE-28	BDE-47	BDE-66	BDE-85	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209
Spring	7.2-10 µm	1.53	20.9	*0.02*	*0.03*	6.23	1.64	0.62	0.52	*0.82*	49.5
	3.0-7.2 µm	0.54	5.32	0.14	*0.02*	3.28	0.61	0.43	0.54	*0.82*	107.0
	1.5-3.0 µm	0.60	5.69	0.22	0.14	5.06	0.83	1.64	1.64	1.71	44.7
	0.95-1.5 µm	0.69	11.3	0.71	1.08	17.1	3.38	7.36	5.23	12.9	339.1
	0.49-0.95 µm	0.82	16.2	1.05	*0.02*	31.4	5.88	11.6	8.40	19.2	27.0
	<0.49 µm	0.67	13.3	1.36	3.68	50.0	84.7	11.3	10.4	*0.82*	25.3
Summer	7.2-10 µm	*0.03*	19.8	*0.58*	*0.09*	0.19	*0.04*	3.92	1.28	*0.79*	33.4
	3.0-7.2 µm	*0.03*	7.73	1.45	*1.29*	7.20	*0.04*	1.92	0.85	*0.79*	*0.58*
	1.5-3.0 µm	*0.03*	2.96	1.30	*1.31*	5.02	*0.04*	*0.16*	*0.03*	*0.79*	96.6
	0.95-1.5 µm	0.18	3.17	0.41	*0.64*	4.70	0.79	1.84	0.89	2.47	33.4
	0.49-0.95 µm	0.32	11.0	0.38	0.24	9.90	1.95	3.88	1.58	4.54	23.8
	<0.49 µm	0.38	8.01	0.41	0.92	17.2	3.10	10.7	5.50	22.0	168.1
Autumn	7.2-10 µm	0.15	1.38	0.06	*0.02*	1.90	0.39	0.43	0.32	0.80	33.8
	3.0-7.2 µm	0.28	3.85	0.24	*0.02*	6.67	1.42	1.47	1.51	1.26	202.7
	1.5-3.0 µm	0.44	8.39	0.60	*0.04*	15.7	3.32	5.89	4.68	7.20	95.1
	0.95-1.5 µm	1.86	25.7	1.87	2.99	55.6	12.8	19.5	16.2	40.5	90.6
	0.49-0.95 µm	2.38	36.8	3.31	3.11	79.0	18.9	29.2	23.1	54.5	112.2
	<0.49 µm	1.63	43.9	7.12	5.84	118.4	22.3	31.7	31.3	95.3	108.1
Winter	7.2-10 µm	0.68	6.9	*0.22*	0.58	6.03	1.08	1.19	1.25	1.96	65.5
	3.0-7.2 µm	1.37	10.9	0.84	1.58	15.9	3.74	4.16	5.05	9.78	245.3
	1.5-3.0 µm	4.59	24.5	2.33	5.34	38.3	8.50	9.76	12.2	29.3	152.4
	0.95-1.5 µm	10.8	67.2	9.61	13.3	102.2	25.5	37.1	37.9	72.5	98.8
	0.49-0.95 µm	19.4	107.9	18.4	19.2	198.3	71.0	46.6	64.9	*0.63*	148.2
	<0.49 µm	12.1	92.7	9.87	11.5	150.4	37.0	39.4	39.2	71.6	234.4

Table S7: Concentrations of PBDEs (in $fg \cdot m^{-3}$) at urban site. Results below LOD (limit of detection, equal average value of the blank + 3 standard deviations) for the purpose of statistical analysis are assigned values equal to 0.5 LOD and are noted in italics.

Season	Size fraction	BDE-28	BDE-47	BDE-66	BDE-85	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209
Spring	7.2-10 µm	0.68	13.3	0.46	*0.17*	11.8	2.95	1.83	1.30	5.86	100.3
	3.0-7.2 µm	0.86	15.3	0.58	*0.15*	16.1	3.41	6.67	2.99	18.6	133.7
	1.5-3.0 µm	0.60	12.2	0.74	*0.11*	12.5	3.50	8.98	3.87	26.1	*2.65*
	0.95-1.5 µm	0.72	16.6	1.67	0.92	24.6	5.81	23.6	10.1	74.1	32.4
	0.49-0.95 µm	0.97	31.0	2.92	*0.88*	60.6	11.5	34.3	16.6	102.1	32.4
	<0.49 µm	1.68	125.4	4.65	*2.50*	211.6	38.9	47.6	28.1	142.8	95.2
Summer	7.2-10 µm	0.56	12.5	0.61	*0.12*	13.6	2.58	2.39	1.34	4.97	95.4
	3.0-7.2 µm	0.98	42.9	4.82	5.22	96.5	14.6	19.8	10.3	18.5	23.8
	1.5-3.0 µm	0.45	14.5	1.44	1.23	20.6	3.48	3.78	2.08	7.84	*13.6*
	0.95-1.5 µm	0.60	17.3	2.54	2.94	36.0	7.44	8.15	3.79	5.21	*12.6*
	0.49-0.95 µm	0.72	17.0	1.47	*0.12*	22.5	4.42	3.95	2.16	9.53	159.7
	<0.49 µm	1.96	87.2	5.26	*2.15*	214.2	35.2	56.2	17.4	37.8	72.1
Autumn	7.2-10 µm	0.60	11.4	0.31	*0.10*	13.9	2.55	2.86	1.92	11.2	135.2
	3.0-7.2 µm	1.13	20.8	1.64	0.86	25.1	6.50	7.87	5.29	33.2	455.6
	1.5-3.0 µm	0.89	24.5	1.93	1.82	37.7	7.77	8.44	7.66	19.6	208.0
	0.95-1.5 µm	2.35	56.4	6.14	*1.87*	95.3	20.2	22.6	20.6	41.2	101.8
	0.49-0.95 µm	4.69	149.6	9.27	*1.57*	289.0	65.9	50.9	41.9	106.4	127.0
	<0.49 µm	5.74	347.4	14.8	6.52	534.0	102.4	67.7	61.4	125.5	198.8
Winter	7.2-10 µm	0.57	9.26	0.65	*0.18*	12.5	2.21	2.33	1.72	6.61	118.4
	3.0-7.2 µm	1.24	19.0	*0.91*	1.82	28.9	6.49	7.20	5.03	14.0	187.9
	1.5-3.0 µm	2.65	25.8	1.17	2.78	43.0	7.38	11.1	10.6	19.6	55.9
	0.95-1.5 µm	11.1	137.4	16.3	16.3	205.2	*0.03*	38.9	52.2	83.6	200.3
	0.49-0.95 µm	11.5	169.1	12.6	16.0	209.8	47.1	52.5	48.6	87.6	101.2
	<0.49 µm	16.2	440.9	42.0	*5.23*	387.2	121.4	57.0	76.6	98.2	187.7

Table S8: Concentrations of PBDEs (in $ng \cdot g^{-1}$) at rural site. Results below LOD (limit of detection, equal average value of the blank + 3 standard deviations) for the purpose of statistical analysis are assigned values equal to 0.5 LOD and are noted in italics.

Season	Size fraction	BDE-28	BDE-47	BDE-66	BDE-85	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209
Spring	7.2-10 µm	1.61	21.98	*0.02*	*0.03*	6.57	1.73	0.65	0.55	*0.86*	52.13
	3.0-7.2 µm	0.19	1.92	0.05	*0.01*	1.19	0.22	0.16	0.20	*0.30*	38.63
	1.5-3.0 µm	0.23	2.15	0.08	0.05	1.92	0.31	0.62	0.62	0.65	16.91
	0.95-1.5 µm	0.19	3.15	0.20	0.30	4.79	0.94	2.06	1.46	3.61	94.83
	0.49-0.95 µm	0.15	3.00	0.20	*0.00*	5.83	1.09	2.15	1.56	3.57	5.01
	<0.49 µm	0.05	0.93	0.09	0.26	3.50	5.92	0.79	0.73	*0.06*	1.77
Summer	7.2-10 µm	*0.06*	46.17	*1.36*	*0.21*	0.43	*0.09*	9.16	3.00	*1.84*	78.03
	3.0-7.2 µm	*0.01*	3.09	0.58	*0.51*	2.87	*0.02*	0.77	0.34	*0.31*	*0.23*
	1.5-3.0 µm	*0.03*	2.90	1.28	*1.28*	4.93	*0.04*	*0.15*	*0.03*	*0.77*	94.74
	0.95-1.5 µm	0.09	1.50	0.20	*0.30*	2.22	0.37	0.87	0.42	1.17	15.81
	0.49-0.95 µm	0.08	2.67	0.09	0.06	2.41	0.47	0.95	0.38	1.10	5.79
	<0.49 µm	0.06	1.31	0.07	0.15	2.80	0.50	1.74	0.90	3.59	27.39
Autumn	7.2-10 µm	0.39	3.68	0.17	*0.07*	5.07	1.04	1.14	0.87	2.13	90.35
	3.0-7.2 µm	0.13	1.87	0.12	*0.01*	3.24	0.69	0.71	0.73	0.61	98.36
	1.5-3.0 µm	0.22	4.18	0.30	*0.02*	7.81	1.65	2.93	2.33	3.58	47.34
	0.95-1.5 µm	0.34	4.72	0.34	0.55	10.19	2.34	3.58	2.97	7.43	16.63
	0.49-0.95 µm	0.28	4.30	0.39	0.36	9.23	2.21	3.41	2.70	6.37	13.11
	<0.49 µm	0.18	4.97	0.81	0.66	13.41	2.53	3.59	3.55	10.80	12.25
Winter	7.2-10 µm	0.58	5.89	*0.19*	0.50	5.13	0.91	1.01	1.06	1.66	55.67
	3.0-7.2 µm	0.58	4.62	0.35	0.67	6.72	1.58	1.76	2.14	4.14	103.84
	1.5-3.0 µm	1.56	8.32	0.79	1.81	12.99	2.88	3.31	4.14	9.93	51.73
	0.95-1.5 µm	1.39	8.66	1.24	1.72	13.17	3.29	4.79	4.89	9.34	12.73
	0.49-0.95 µm	1.69	9.39	1.60	1.67	17.25	6.18	4.05	5.65	*0.05*	12.89
	<0.49 µm	1.19	8.06	0.86	1.13	14.83	3.65	3.42	3.86	6.23	20.39

Table S9: Concentrations of PBDEs (in $ng \cdot g^{-1}$) at urban site. Results below LOD (limit of detection, equal average value of the blank + 3 standard deviations) for purpose of statistical analysis are assigned values equal to 0.5 LOD and are noted in italics.

Season	Size fraction	BDE-28	BDE-47	BDE-66	BDE-85	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209
Spring	7.2-10 µm	0.28	5.45	0.19	*0.07*	4.86	1.21	0.75	0.54	2.41	41.18
	3.0-7.2 µm	0.20	3.49	0.13	*0.03*	3.67	0.78	1.53	0.68	4.26	30.57
	1.5-3.0 µm	0.31	6.39	0.39	*0.06*	6.55	1.83	4.70	2.03	13.68	*1.39*
	0.95-1.5 µm	0.29	6.63	0.67	0.37	9.85	2.32	9.41	4.02	29.62	12.97
	0.49-0.95 µm	0.20	6.55	0.62	*0.19*	12.82	2.43	7.26	3.52	21.59	6.86
	<0.49 µm	0.20	14.64	0.54	*0.29*	24.71	4.54	5.56	3.29	16.67	11.11
Summer	7.2-10 µm	0.20	4.46	0.22	*0.04*	4.84	0.92	0.85	0.48	1.78	34.06
	3.0-7.2 µm	0.23	10.00	1.12	1.22	22.50	3.41	4.62	2.41	4.30	5.55
	1.5-3.0 µm	0.23	7.62	0.76	0.64	10.83	1.83	1.99	1.09	4.12	*7.13*
	0.95-1.5 µm	0.32	9.22	1.36	1.57	19.20	3.97	4.35	2.02	2.78	*6.70*
	0.49-0.95 µm	0.17	4.06	0.35	*0.03*	5.37	1.05	0.94	0.51	2.27	38.06
	<0.49 µm	0.25	10.93	0.66	*0.27*	26.85	4.41	7.05	2.18	4.74	9.04
Autumn	7.2-10 µm	0.16	2.97	0.08	*0.03*	3.62	0.67	0.74	0.50	2.91	35.28
	3.0-7.2 µm	0.16	2.98	0.23	0.12	3.58	0.93	1.12	0.76	4.74	65.11
	1.5-3.0 µm	0.24	6.58	0.52	0.49	10.12	2.09	2.27	2.06	5.28	55.88
	0.95-1.5 µm	0.11	2.71	0.29	*0.09*	4.58	0.97	1.09	0.99	1.98	4.89
	0.49-0.95 µm	0.45	14.24	0.88	*0.15*	27.50	6.27	4.84	3.99	10.12	12.08
	<0.49 µm	0.41	24.94	1.06	0.47	38.34	7.35	4.86	4.41	9.01	14.27
Winter	7.2-10 µm	0.14	2.23	0.16	*0.04*	3.01	0.53	0.56	0.41	1.59	28.48
	3.0-7.2 µm	0.20	3.02	*0.14*	0.29	4.59	1.03	1.14	0.80	2.22	29.87
	1.5-3.0 µm	0.63	6.10	0.28	0.66	10.17	1.74	2.62	2.49	4.64	13.21
	0.95-1.5 µm	1.91	23.60	2.79	2.81	35.25	*0.01*	6.69	8.97	14.36	34.40
	0.49-0.95 µm	1.00	14.75	1.10	1.40	18.30	4.10	4.58	4.24	7.64	8.83
	<0.49 µm	1.00	27.25	2.60	*0.32*	23.92	7.50	3.53	4.73	6.07	11.60

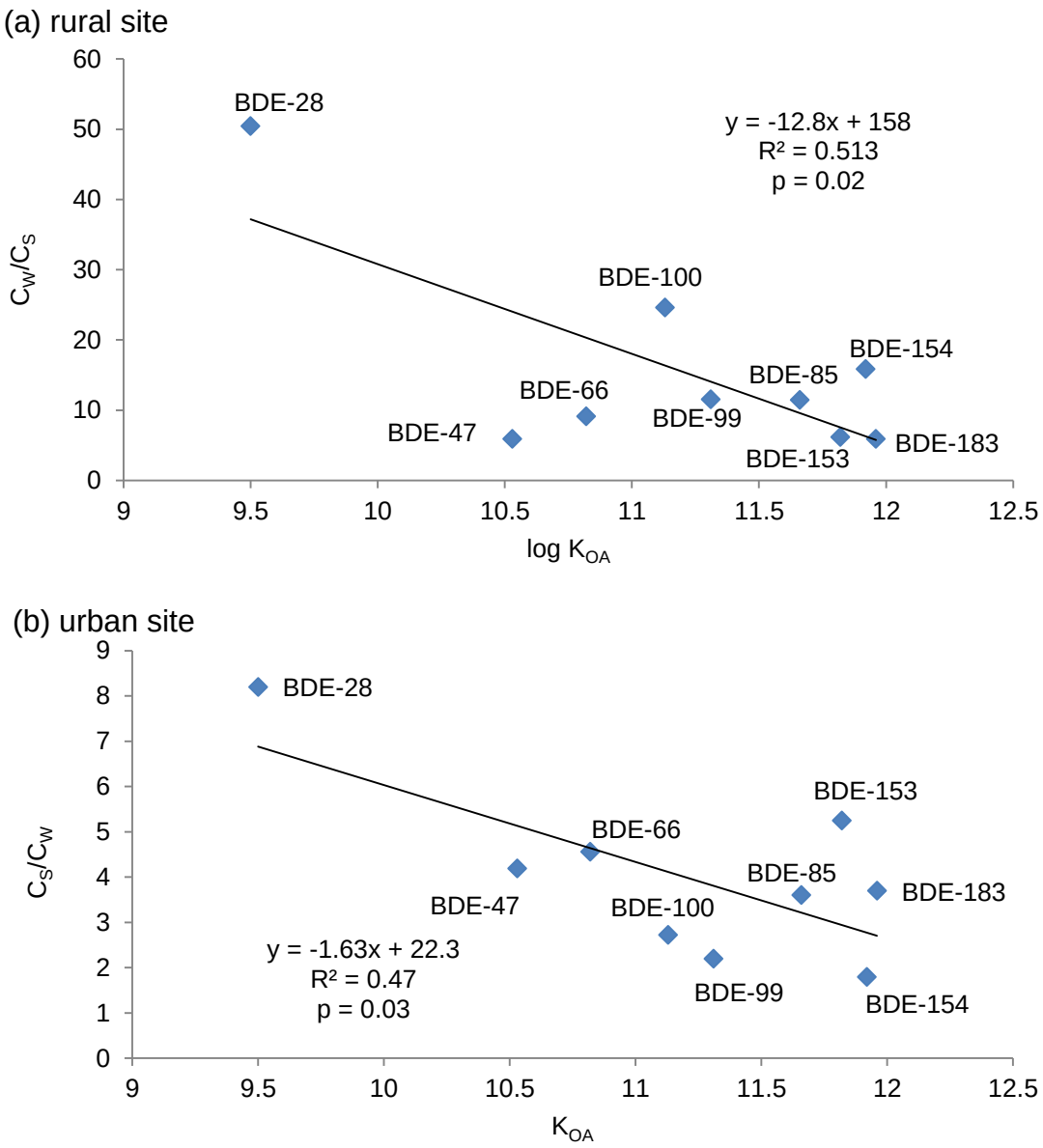


Figure S4: Relation between octanol-air partition coefficient (K_{OA}) and winter/summer concentration ratio (C_w/C_s) for PBDEs at (a) rural and (b) urban sites.

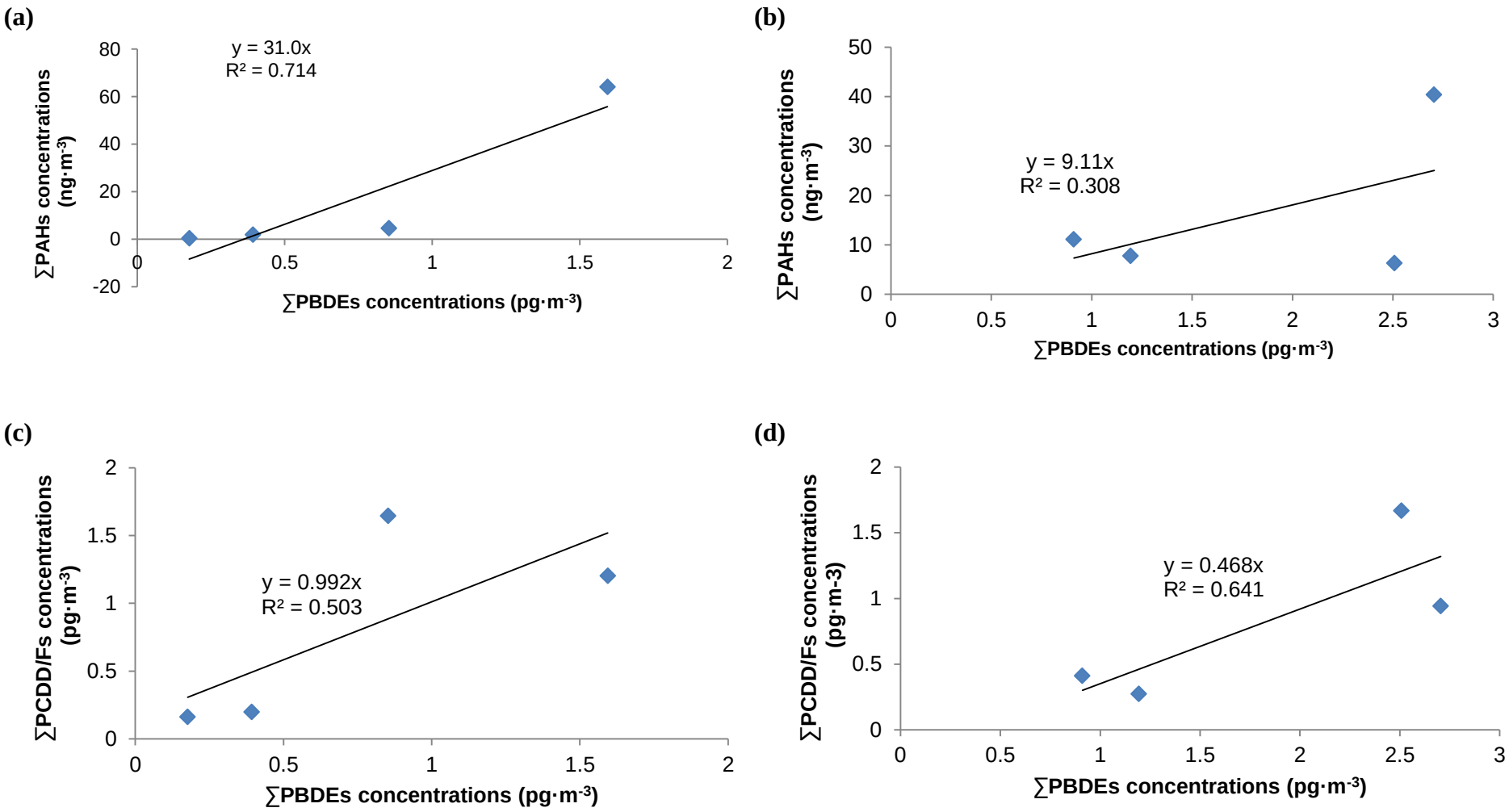


Figure S5: Correlations between PBDEs and PAHs at (a) urban site and (b) rural sites and PCDD/Fs at (c) urban site and (d) rural site from Degrendele et al.[8]

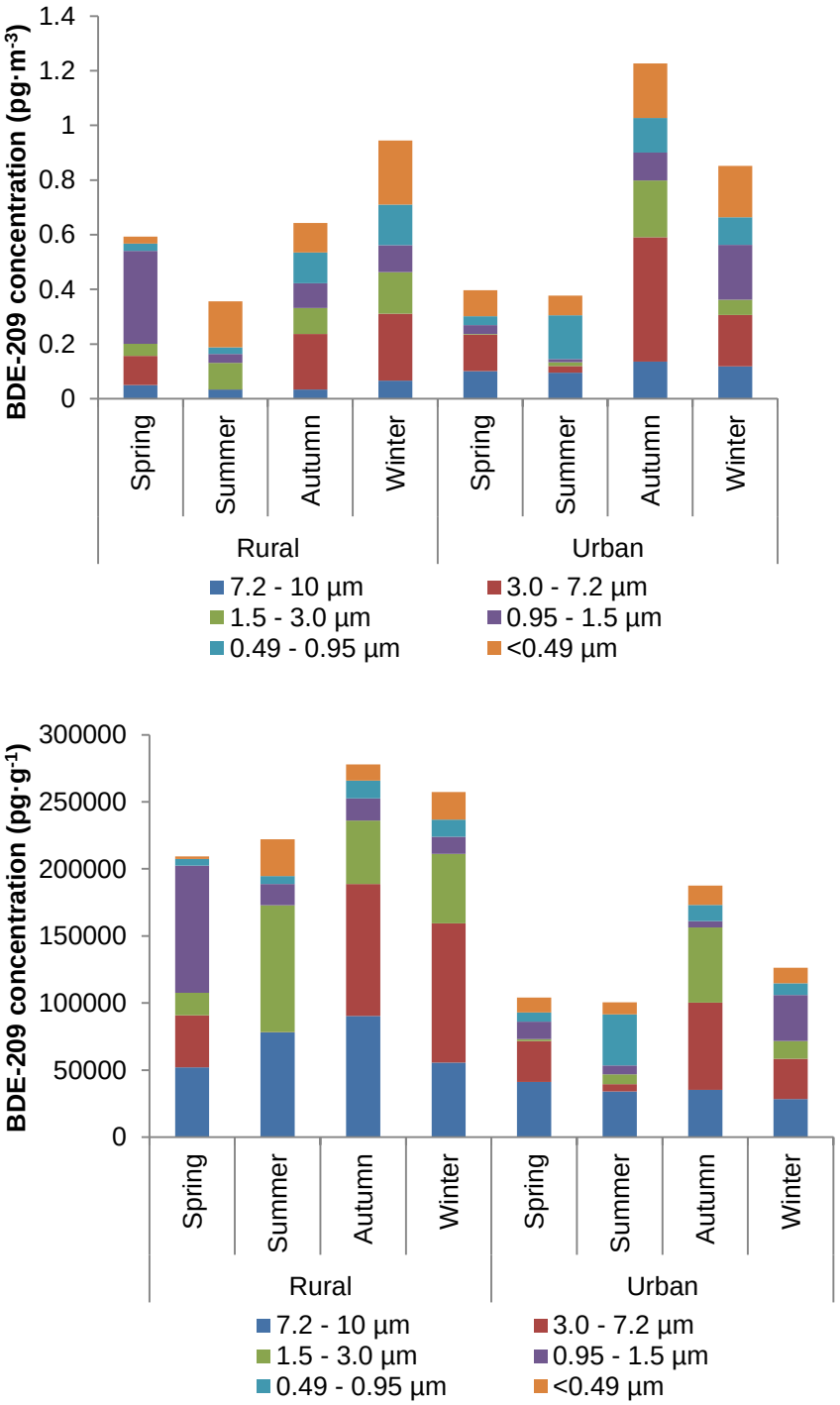


Figure S6: Concentrations of BDE-209 (in pg·m^{-3} and pg·g^{-1}).

Table S10: Concentrations of NFRs (in fg·m^{-3}) at rural site. For the purpose of statistical analysis, results below LOD (limit of detection, equal to the average blank + 3 standard deviations) are assigned a value equal to 0.5 of the LOD and are noted in italics.

Season	Size fraction	TBECH	PBEB	PBT	HBB	BTBPE	syn-DP	anti-DP
Spring	7.2-10 µm	91.6	0.92	*0.28*	*0.38*	*0.44*	25.6	15.1
	3.0-7.2 µm	79.7	*0.12*	*0.28*	*0.38*	*0.44*	36.0	33.0
	1.5-3.0 µm	46.8	*0.12*	*0.28*	*0.38*	*0.44*	98.2	59.3
	0.95-1.5 µm	35.3	*0.12*	*0.28*	*0.38*	3.86	55.3	51.3
	0.49-0.95 µm	51.4	*0.12*	*0.28*	*0.38*	4.82	53.2	44.0
	<0.49 µm	28.7	*0.12*	0.76	0.90	5.48	97.6	64.6
Summer	7.2-10 µm	41.5	0.49	*0.27*	*0.37*	*0.42*	*8.80*	*2.92*
	3.0-7.2 µm	46.2	0.31	0.71	*0.37*	1.41	68.9	32.5
	1.5-3.0 µm	51.7	0.48	1.21	*0.37*	2.23	*8.80*	9.3
	0.95-1.5 µm	66.3	0.72	3.71	1.29	9.23	*8.80*	12.6
	0.49-0.95 µm	88.1	2.60	4.71	2.87	14.9	*8.80*	8.7
	<0.49 µm	103.7	1.74	6.31	2.69	5.41	*8.80*	*2.92*
Autumn	7.2-10 µm	25.5	0.27	*0.28*	*0.37*	*0.43*	*8.91*	*2.96*
	3.0-7.2 µm	17.7	0.30	*0.28*	*0.37*	*0.43*	35.5	41.3
	1.5-3.0 µm	16.3	*0.12*	*0.28*	1.13	0.95	21.5	29.0
	0.95-1.5 µm	12.9	*0.12*	*0.28*	*0.37*	0.93	18.0	18.6
	0.49-0.95 µm	23.4	*0.12*	0.59	*0.37*	1.41	29.8	24.8
	<0.49 µm	18.7	1.05	1.65	15.1	4.76	99.2	80.0
Winter	7.2-10 µm	34.3	*0.09*	*0.22*	*0.29*	*0.34*	*7.06*	*2.34*
	3.0-7.2 µm	21.5	*0.09*	*0.22*	*0.29*	*0.34*	19.6	15.3
	1.5-3.0 µm	30.7	*0.09*	0.45	*0.29*	1.26	15.0	16.9
	0.95-1.5 µm	55.0	0.23	1.24	0.95	8.58	26.6	24.2
	0.49-0.95 µm	40.5	0.22	2.10	1.33	6.68	56.7	57.4
	<0.49 µm	34.6	*0.09*	1.77	1.12	4.48	32.1	23.4

Table S11: Concentrations of NFRs (in fg·m^{-3}) at urban site. For the purpose of statistical analysis, results below LOD are assigned a value equal to 0.5 of the LOD and are noted in italics.

Season	Size fraction	TBECH	PBEB	PBT	HBB	BTBPE	syn-DP	anti-DP
Spring	7.2-10 µm	14.3	0.35	*0.26*	*0.36*	*0.41*	59.6	20.2
	3.0-7.2 µm	15.7	0.31	*0.26*	0.78	2.39	39.8	33.6
	1.5-3.0 µm	11.6	*0.11*	*0.26*	*0.36*	5.53	22.7	27.7
	0.95-1.5 µm	15.1	*0.11*	*0.26*	*0.36*	*0.41*	25.8	32.4
	0.49-0.95 µm	12.4	*0.11*	0.99	1.83	18.8	96.5	48.2
	<0.49 µm	68.0	0.41	8.49	16.5	7.23	34.7	11.4
Summer	7.2-10 µm	63.2	0.34	0.82	*0.35*	1.44	*8.39*	6.40
	3.0-7.2 µm	39.9	*0.11*	1.08	0.88	1.47	*8.39*	19.2
	1.5-3.0 µm	54.3	0.28	2.27	1.93	2.69	*8.39*	17.8
	0.95-1.5 µm	81.2	0.83	5.46	6.18	7.23	*8.39*	11.7
	0.49-0.95 µm	129.7	1.63	9.10	8.49	4.24	*8.39*	11.7
	<0.49 µm	362.7	3.41	23.6	10.8	1.79	*8.39*	*2.78*
Autumn	7.2-10 µm	11.5	*0.11*	*0.26*	*0.35*	*0.40*	*8.46*	13.7
	3.0-7.2 µm	9.0	0.26	0.66	0.96	1.39	52.6	43.4
	1.5-3.0 µm	13.6	0.53	0.72	*0.35*	*0.40*	51.3	49.2
	0.95-1.5 µm	14.0	0.26	0.67	0.88	1.08	49.5	57.9
	0.49-0.95 µm	43.1	0.24	0.92	0.91	6.00	51.2	54.2
	<0.49 µm	41.2	0.48	7.89	11.0	*0.40*	29.2	13.6
Winter	7.2-10 µm	13.0	*0.09*	0.71	1.25	3.72	14.0	8.59
	3.0-7.2 µm	20.9	*0.09*	0.78	0.76	0.73	29.3	40.6
	1.5-3.0 µm	19.4	*0.09*	0.76	0.92	1.70	26.0	35.2
	0.95-1.5 µm	25.2	0.22	1.77	1.22	4.48	58.4	46.4
	0.49-0.95 µm	42.2	0.50	4.48	3.65	4.80	30.6	22.5
	<0.49 µm	133.4	0.98	15.7	9.85	*0.32*	27.2	7.78

Table S12: Concentrations of NFRs (in ng·g^{-1}) at rural site. For the purpose of statistical analysis, results below LOD are assigned a value equal to 0.5 of the LOD and are noted in italics.

Season	Size fraction	TBECH	PBEB	PBT	HBB	BTBPE	syn-DP	anti-DP
Spring	7.2-10 µm	96.51	0.97	*0.30*	*0.40*	*0.46*	27.03	15.90
	3.0-7.2 µm	28.79	*0.04*	*0.10*	*0.14*	*0.16*	12.99	11.90
	1.5-3.0 µm	17.72	*0.05*	*0.11*	*0.14*	*0.17*	37.13	22.45
	0.95-1.5 µm	9.88	*0.03*	*0.08*	*0.11*	1.08	15.45	14.35
	0.49-0.95 µm	9.55	*0.02*	*0.05*	*0.07*	0.89	9.87	8.17
	<0.49 µm	2.01	*0.01*	0.05	0.06	0.38	6.82	4.52
Summer	7.2-10 µm	96.98	1.13	*0.64*	*0.86*	*0.98*	*20.55*	*6.82*
	3.0-7.2 µm	18.42	0.12	0.28	*0.15*	0.56	27.49	12.97
	1.5-3.0 µm	50.71	0.47	1.19	*0.36*	2.18	*8.63*	9.10
	0.95-1.5 µm	31.39	0.34	1.75	0.61	4.37	*4.16*	5.95
	0.49-0.95 µm	21.43	0.63	1.15	0.70	3.62	*2.14*	2.12
	<0.49 µm	16.90	0.28	1.03	0.44	0.88	*1.43*	*0.48*
Autumn	7.2-10 µm	68.17	0.71	*0.74*	*0.99*	*1.14*	*23.80*	*7.90*
	3.0-7.2 µm	8.58	0.15	*0.13*	*0.18*	*0.21*	17.23	20.02
	1.5-3.0 µm	8.13	*0.06*	*0.14*	0.56	0.47	10.70	14.43
	0.95-1.5 µm	2.38	*0.02*	*0.05*	*0.07*	0.17	3.31	3.42
	0.49-0.95 µm	2.73	*0.01*	0.07	*0.04*	0.17	3.49	2.90
	<0.49 µm	2.11	0.12	0.19	1.71	0.54	11.24	9.07
Winter	7.2-10 µm	29.17	*0.08*	*0.19*	*0.25*	*0.29*	*6.00*	*1.99*
	3.0-7.2 µm	9.12	*0.04*	*0.09*	*0.12*	*0.14*	8.29	6.47
	1.5-3.0 µm	10.42	*0.03*	0.15	*0.10*	0.43	5.10	5.75
	0.95-1.5 µm	7.10	0.03	0.16	0.12	1.11	3.43	3.12
	0.49-0.95 µm	3.53	0.02	0.18	0.12	0.58	4.94	5.00
	<0.49 µm	3.41	*0.01*	0.17	0.11	0.44	3.16	2.31

Table S13: Concentrations of NFRs (in ng·g^{-1}) at urban site. For the purpose of statistical analysis, results below LOD are assigned a value equal to 0.5 of the LOD and are noted in italics.

Season	Size fraction	TBECH	PBEB	PBT	HBB	BTBPE	syn-DP	anti-DP
Spring	7.2-10 µm	5.89	0.14	*0.11*	*0.15*	*0.17*	24.49	8.31
	3.0-7.2 µm	3.59	0.07	*0.06*	0.18	0.55	9.09	7.69
	1.5-3.0 µm	6.07	*0.06*	*0.14*	*0.19*	2.90	11.87	14.52
	0.95-1.5 µm	6.02	*0.05*	*0.11*	*0.14*	*0.16*	10.33	12.95
	0.49-0.95 µm	2.61	*0.02*	0.21	0.39	3.97	20.40	10.19
	<0.49 µm	7.93	0.05	0.99	1.92	0.84	4.05	1.33
Summer	7.2-10 µm	22.55	0.12	0.29	*0.13*	0.51	*2.99*	2.29
	3.0-7.2 µm	9.31	*0.03*	0.25	0.21	0.34	*1.96*	4.47
	1.5-3.0 µm	28.52	0.15	1.19	1.01	1.41	*4.41*	9.35
	0.95-1.5 µm	43.36	0.44	2.91	3.30	3.85	*4.48*	6.25
	0.49-0.95 µm	30.90	0.39	2.17	2.02	1.01	*2.00*	2.79
	<0.49 µm	45.47	0.43	2.96	1.36	0.22	*1.05*	*0.35*
Autumn	7.2-10 µm	2.99	*0.03*	*0.07*	*0.09*	*0.11*	*2.21*	3.58
	3.0-7.2 µm	1.29	0.04	0.09	0.14	0.20	7.51	6.20
	1.5-3.0 µm	3.65	0.14	0.19	*0.09*	*0.11*	13.77	13.21
	0.95-1.5 µm	2.28	0.04	0.11	0.14	0.18	8.04	9.40
	0.49-0.95 µm	4.11	0.02	0.09	0.09	0.57	4.87	5.16
	<0.49 µm	2.96	0.03	0.57	0.79	*0.03*	2.10	0.97
Winter	7.2-10 µm	3.12	*0.02*	0.17	0.30	0.89	3.36	2.07
	3.0-7.2 µm	3.32	*0.01*	0.12	0.12	0.12	4.66	6.46
	1.5-3.0 µm	4.59	*0.02*	0.18	0.22	0.40	6.15	8.31
	0.95-1.5 µm	4.32	0.04	0.30	0.21	0.77	10.03	7.97
	0.49-0.95 µm	3.68	0.04	0.39	0.32	0.42	2.67	1.96
	<0.49 µm	8.24	0.06	0.97	0.61	*0.02*	1.68	0.48

Table S14: Concentrations of HBCDs (in pg·m^{-3}). For the purpose of statistical analysis, results below LOD are assigned a value equal to 0.5 of the LOD and are noted in italics.

Season	Size fraction	α-HBCD (rural)	β-HBCD (rural)	γ-HBCD (rural)	α-HBCD (urban)	β-HBCD (urban)	γ-HBCD (urban)
Spring	7.2-10 µm	*0.19*	*0.03*	0.04	0.41	0.09	0.17
	3.0-7.2 µm	0.35	*0.03*	0.29	0.58	0.14	0.54
	1.5-3.0 µm	*0.19*	*0.03*	0.10	*0.17*	*0.03*	0.20
	0.95-1.5 µm	0.27	0.38	0.34	0.28	0.06	0.13
	0.49-0.95 µm	0.39	0.09	0.17	0.61	0.18	0.28
	<0.49 µm	6.29	1.30	0.59	1.31	0.36	0.70
Summer	7.2-10 µm	*0.18*	*0.03*	0.31	*0.17*	*0.03*	0.22
	3.0-7.2 µm	0.35	0.11	1.46	*0.17*	0.11	0.29
	1.5-3.0 µm	*0.18*	*0.03*	0.44	0.34	0.09	0.48
	0.95-1.5 µm	0.34	0.08	0.19	0.47	0.11	0.29
	0.49-0.95 µm	1.02	0.28	0.61	0.42	0.12	1.00
	<0.49 µm	34.40	9.55	3.72	3.71	0.72	0.71
Autumn	7.2-10 µm	*0.18*	*0.03*	0.05	0.35	0.10	0.53
	3.0-7.2 µm	*0.18*	*0.03*	0.30	1.75	0.41	1.37
	1.5-3.0 µm	*0.18*	*0.03*	*0.04*	0.71	0.19	0.68
	0.95-1.5 µm	0.72	0.29	0.44	0.75	0.15	0.47
	0.49-0.95 µm	1.26	0.48	0.63	1.46	0.45	1.13
	<0.49 µm	7.76	2.74	1.00	3.17	1.09	2.82
Winter	7.2-10 µm	0.18	0.05	*0.04*	*0.14*	0.05	0.11
	3.0-7.2 µm	0.77	0.25	0.51	0.63	0.17	0.41
	1.5-3.0 µm	0.28	0.09	0.21	0.49	0.13	0.22
	0.95-1.5 µm	0.33	0.07	0.15	0.48	0.18	1.22
	0.49-0.95 µm	1.05	0.28	0.64	0.67	0.22	1.40
	<0.49 µm	3.12	0.74	0.95	1.75	0.48	0.80

Table S15: Concentrations of HBCDs (in ng·g^{-1}). For the purpose of statistical analysis, results below LOD are assigned a value equal to 0.5 of the LOD and are noted in italics.

Season	Size fraction	α-HBCD (rural)	β-HBCD (rural)	γ-HBCD (rural)	α-HBCD (urban)	β-HBCD (urban)	γ-HBCD (urban)
Spring	7.2-10 µm	*196.2*	*32.9*	45.7	166.6	35.2	69.9
	3.0-7.2 µm	127.8	*11.3*	104.2	132.5	31.1	122.5
	1.5-3.0 µm	*70.4*	*11.8*	38.8	*90.9*	*15.2*	103.8
	0.95-1.5 µm	75.2	105.9	93.8	110.7	24.5	50.6
	0.49-0.95 µm	71.8	16.5	32.3	129.7	37.7	58.4
	<0.49 µm	439.6	90.6	41.3	152.4	41.7	82.0
Summer	7.2-10 µm	*417.3*	*70.0*	733.6	*60.8*	*10.2*	77.1
	3.0-7.2 µm	138.7	45.7	581.8	*39.7*	26.6	67.6
	1.5-3.0 µm	*175.2*	*29.4*	430.2	176.0	48.5	252.8
	0.95-1.5 µm	158.9	35.9	89.5	250.1	58.2	152.3
	0.49-0.95 µm	247.4	67.9	148.4	101.1	29.4	238.5
	<0.49 µm	5605.8	1555.7	606.0	465.3	90.4	88.7
Autumn	7.2-10 µm	*483.2*	*81.1*	131.6	92.0	26.0	139.2
	3.0-7.2 µm	*87.8*	*14.7*	143.8	250.3	57.9	195.5
	1.5-3.0 µm	*90.0*	*15.1*	*19.4*	191.3	51.1	183.6
	0.95-1.5 µm	131.8	52.9	80.0	121.5	24.2	76.3
	0.49-0.95 µm	147.0	56.4	73.5	138.9	42.5	107.4
	<0.49 µm	879.6	310.0	112.8	227.5	78.2	202.1
Winter	7.2-10 µm	152.3	40.6	35.3	*32.6*	12.5	25.9
	3.0-7.2 µm	328.0	105.8	214.9	99.8	27.7	64.7
	1.5-3.0 µm	93.5	28.9	71.0	116.2	31.3	53.0
	0.95-1.5 µm	42.4	8.6	18.7	82.4	30.6	209.6
	0.49-0.95 µm	91.3	24.8	55.9	58.1	19.3	121.9
	<0.49 µm	307.8	72.7	93.4	108.2	29.5	49.3

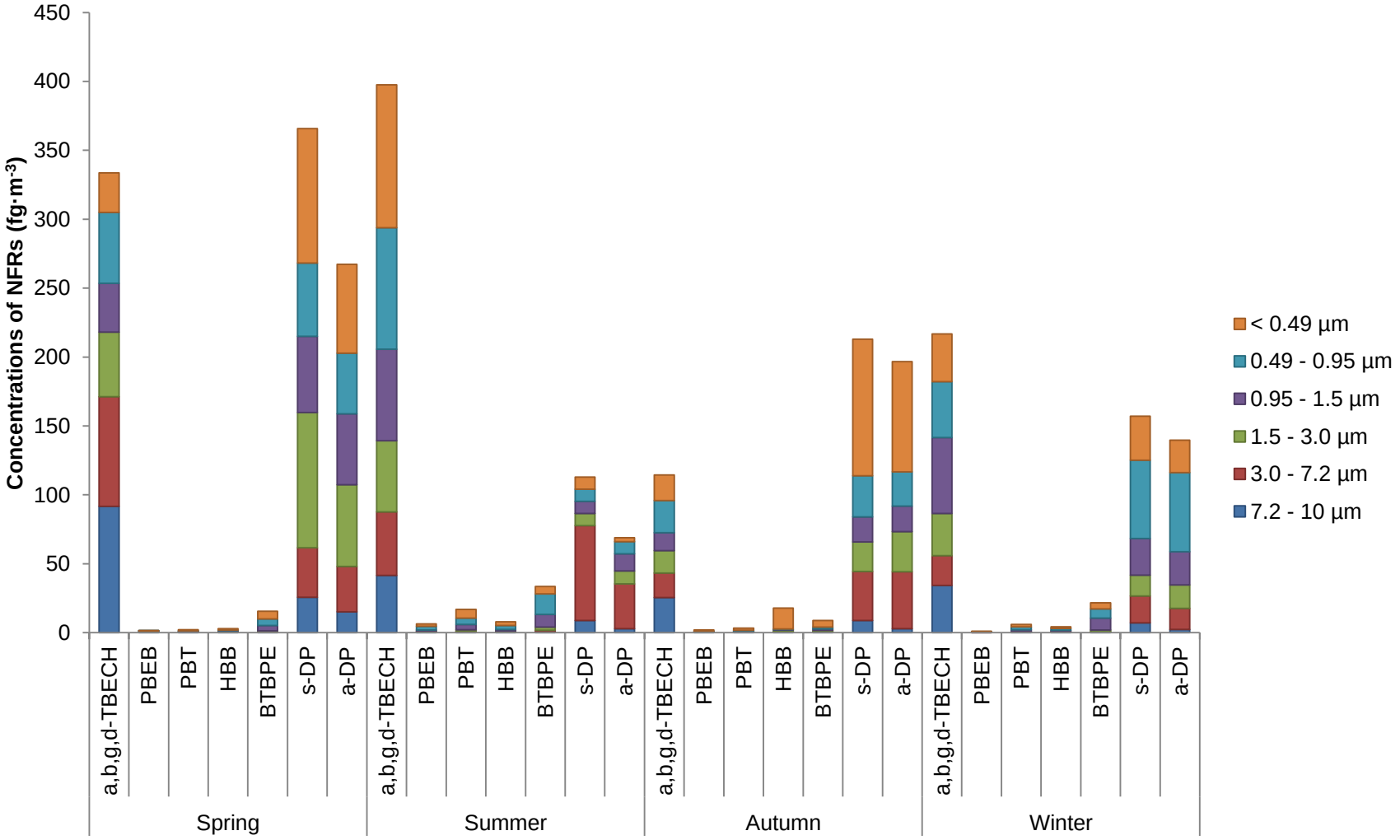


Figure S7: Concentrations of NFRs on size-specific particles at the rural site.

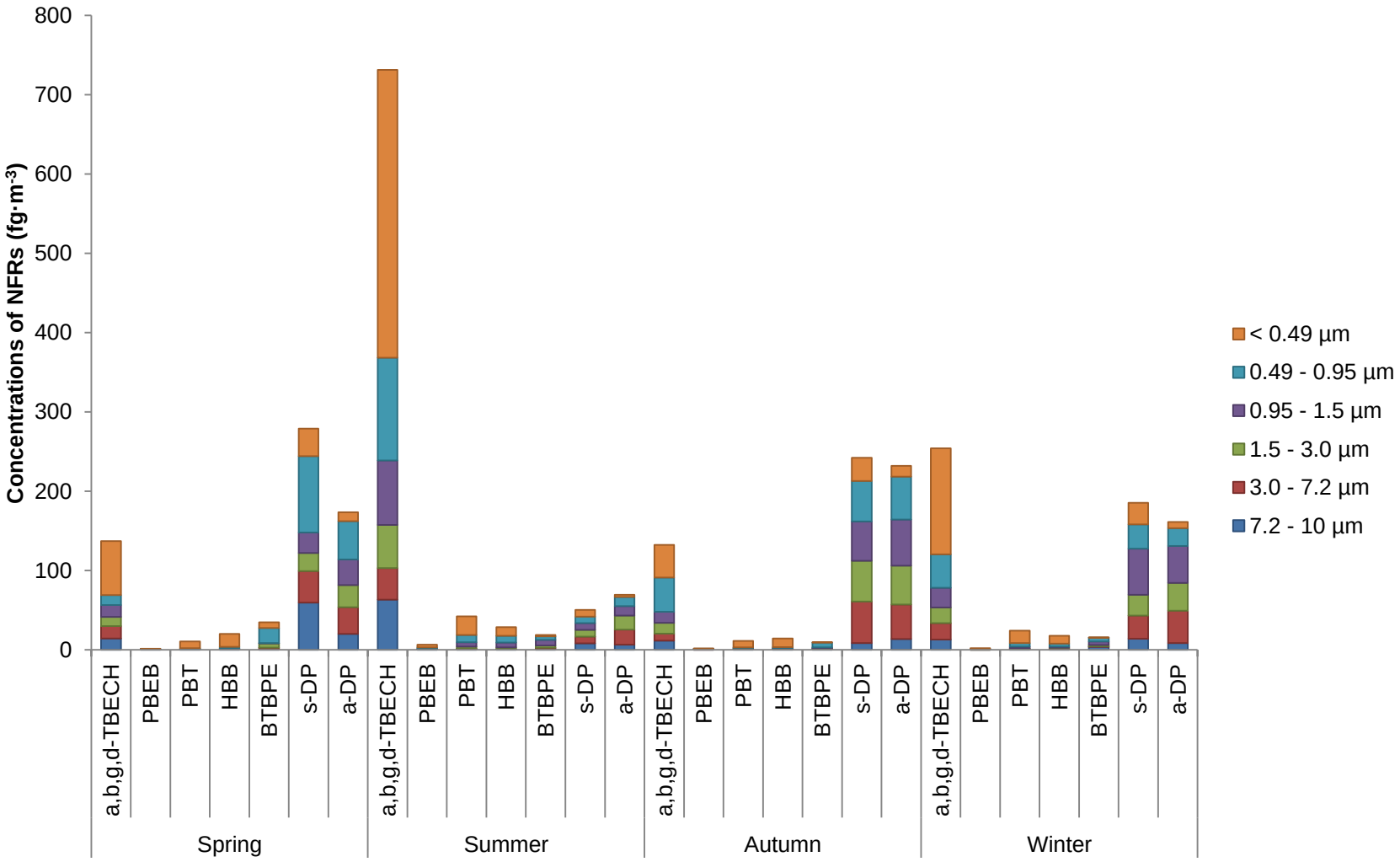


Figure S8: Concentrations of NFRs on size-specific particles at the urban site.

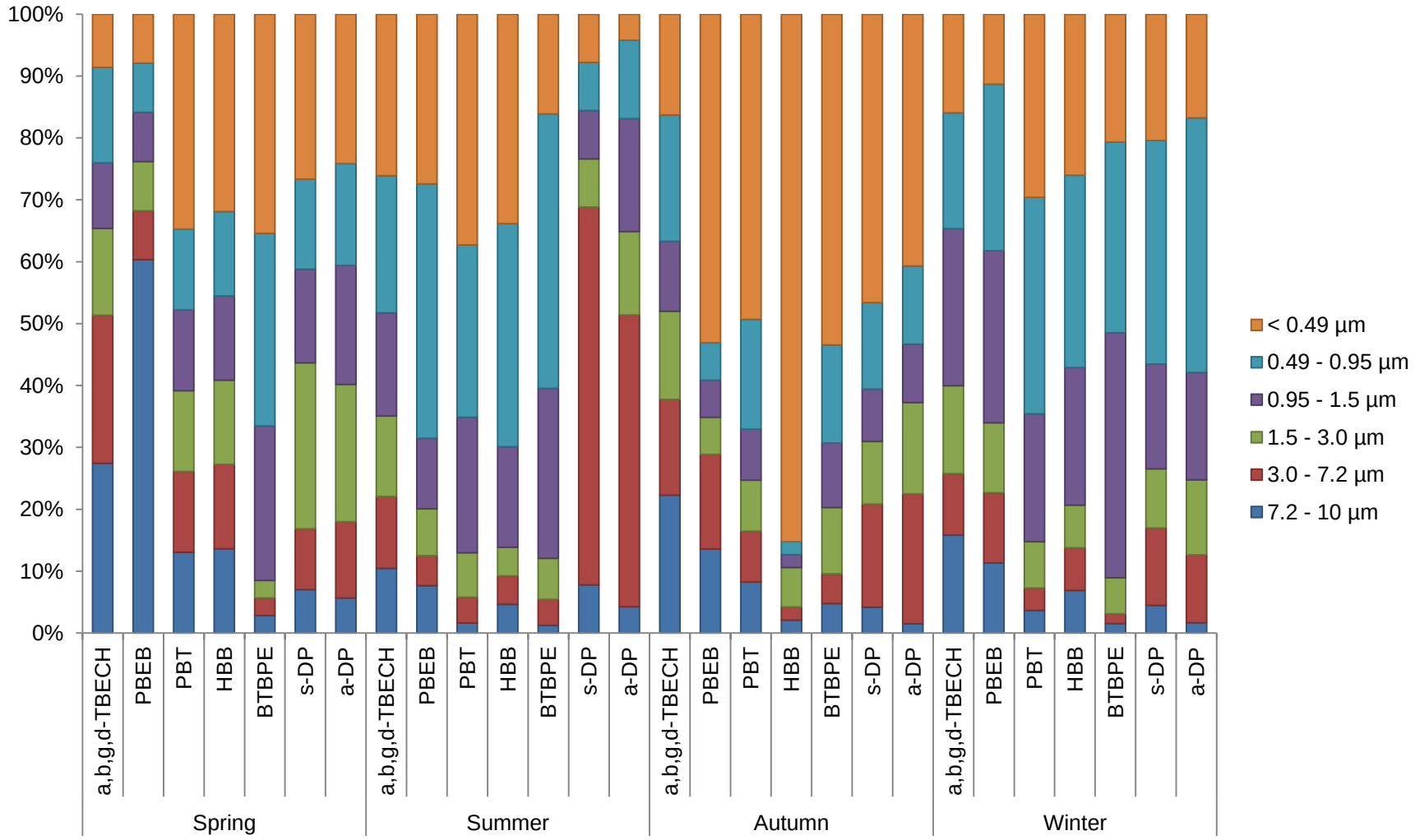


Figure S9: Distribution of NFRs on size-specific particles at the rural site.

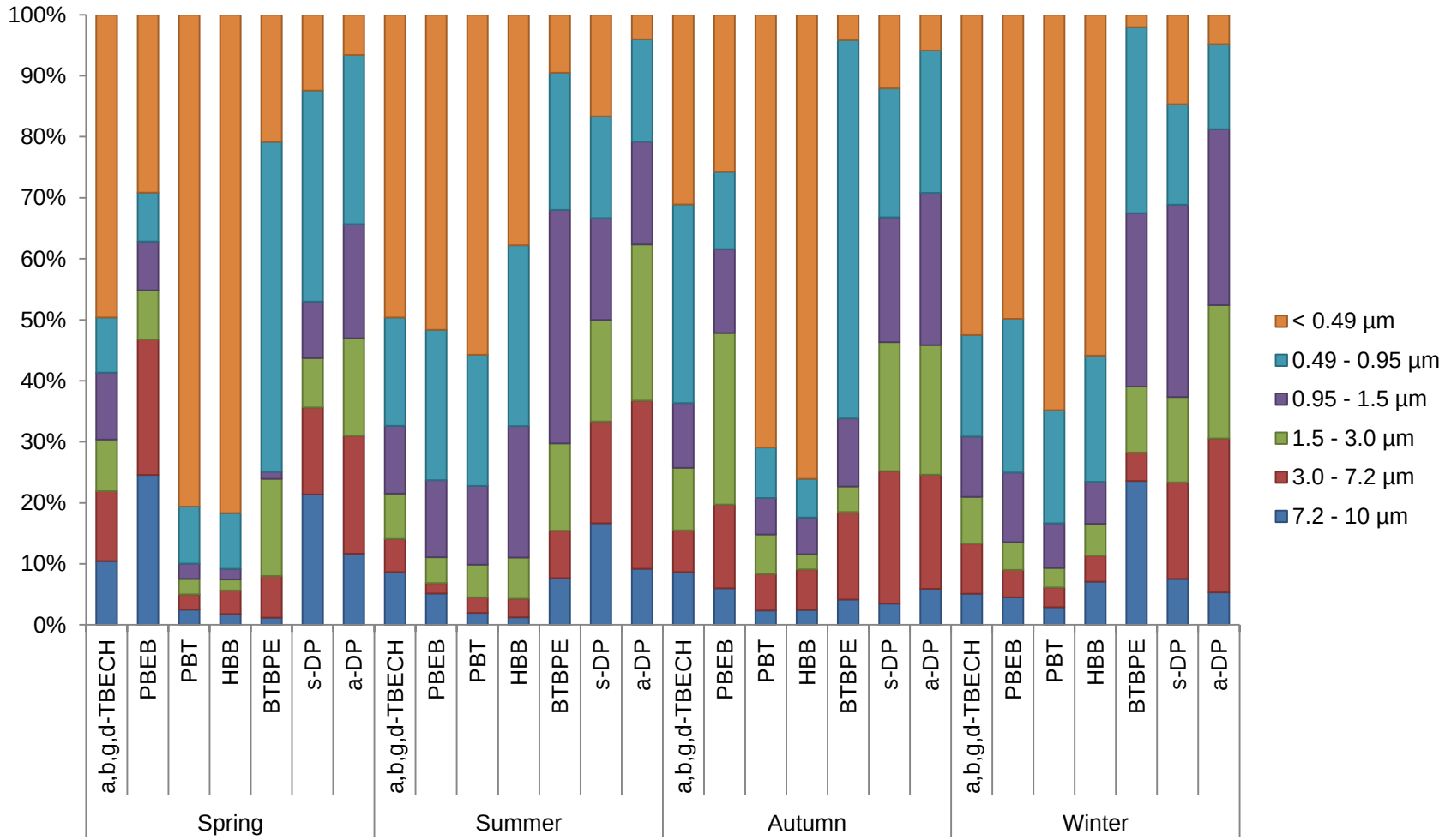


Figure S10: Distribution of NFRs on size-specific particles at the urban site.

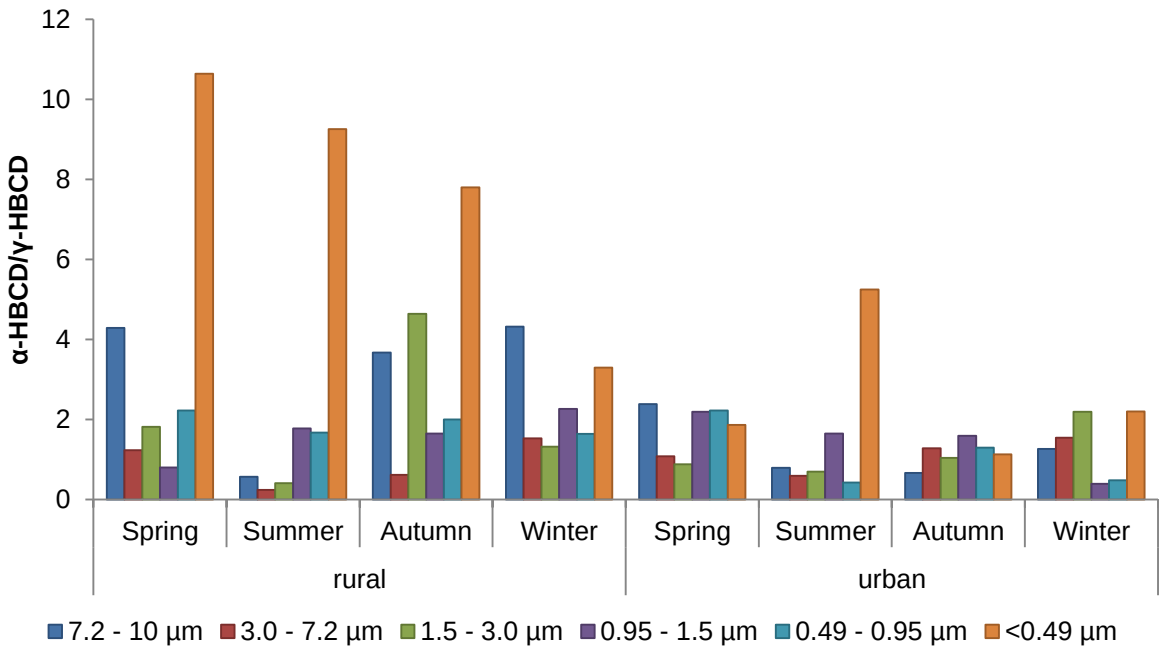


Figure S11: Ratio of normalized concentrations ($ng \cdot g^{-1}$) of HBCDs congeners (α and γ).

Table S16: Overestimation of wet and dry deposition. Values indicate how much deposition would be overestimated when using bulk aerosol instead of size-segregated particulates data (on average). Particle size specific deposition velocities are from Zhang et al.,[9] bulk deposition velocity is taken from Hillery et al.[10] Particle size specific scavenging coefficients are from Ebert et al.[11] and bulk scavenging coefficient is an average of the size fraction-specific wet deposition coefficients.[11]

	Particle size (µm)	Particle size specific deposition velocity ($m \cdot s^{-1}$) /scavenging coefficient (s^{-1})*	Bulk deposition velocity ($m \cdot s^{-1}$)/ scavenging coefficient (s^{-1})*	Overestimation of bulk deposition			
				BDE-47	BDE-209	Dechlorane Plus	HBCD
Dry	<0.49	1.46×10^{-3}	$2.00 \cdot 10^{-3}$	2.2×	2.2×	2.5×	2.1×
	0.49 – 0.95	0.420×10^{-3}					
	0.95 – 1.5	0.333×10^{-3}					
	1.5 – 3.0	0.373×10^{-3}					
	3.0 – 7.2	0.698×10^{-3}					
	7.2 – 10	1.80×10^{-3}					
Wet*	<0.49	1.95×10^{-8}	$9.59 \cdot 10^{-8}$	2.9×	1.2×	1.7×	2.6×
	0.49 – 0.95	3.43×10^{-9}					
	0.95 – 1.5	1.43×10^{-9}					
	1.5 – 3.0	5.50×10^{-9}					
	3.0 – 7.2	1.16×10^{-7}					
	7.2 – 10	4.30×10^{-7}					

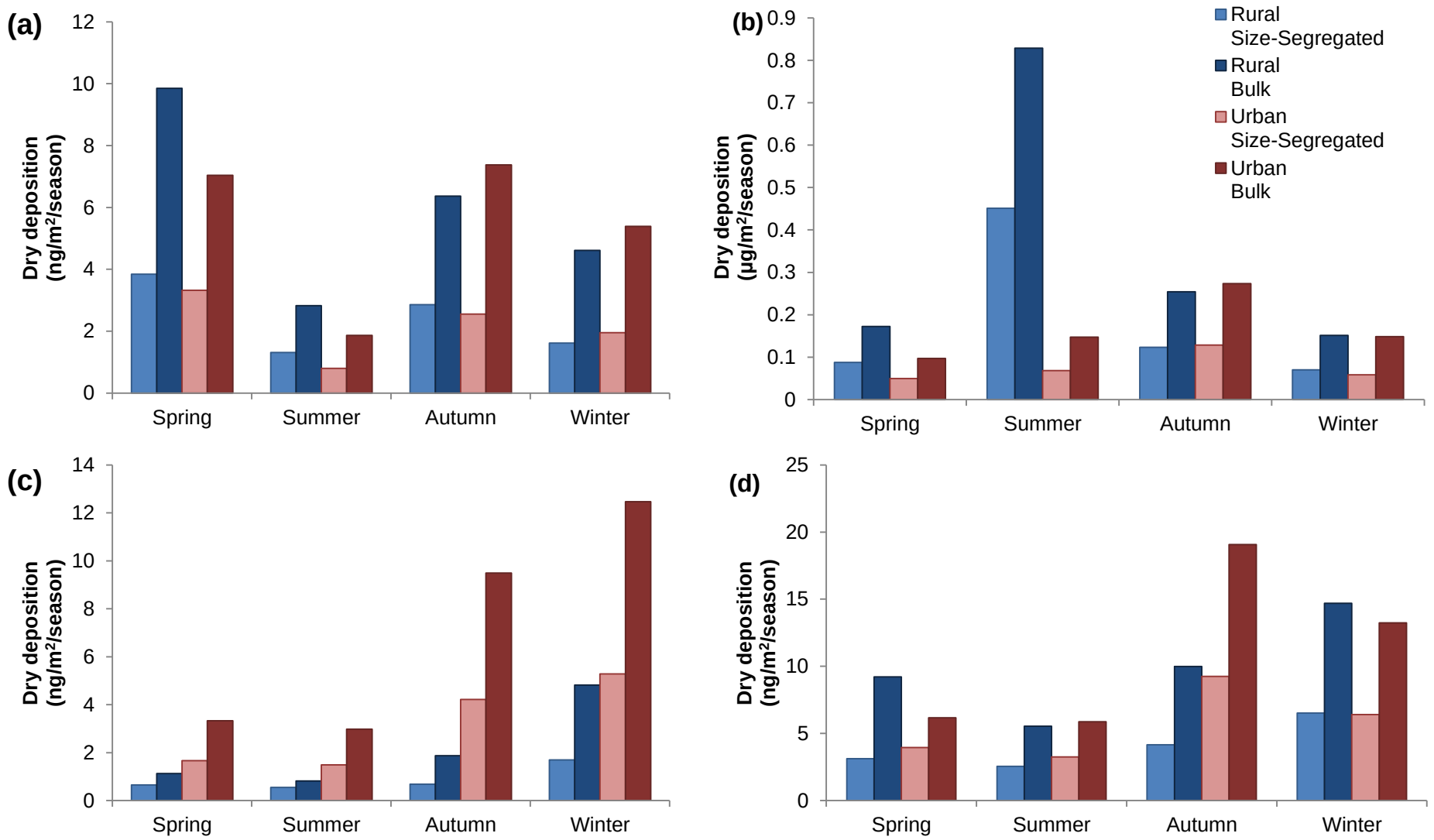


Figure S12: Dry deposition estimates for (a) Dechlorane Plus, (b) HBCD, (c) BDE-47 and (d) BDE-209.

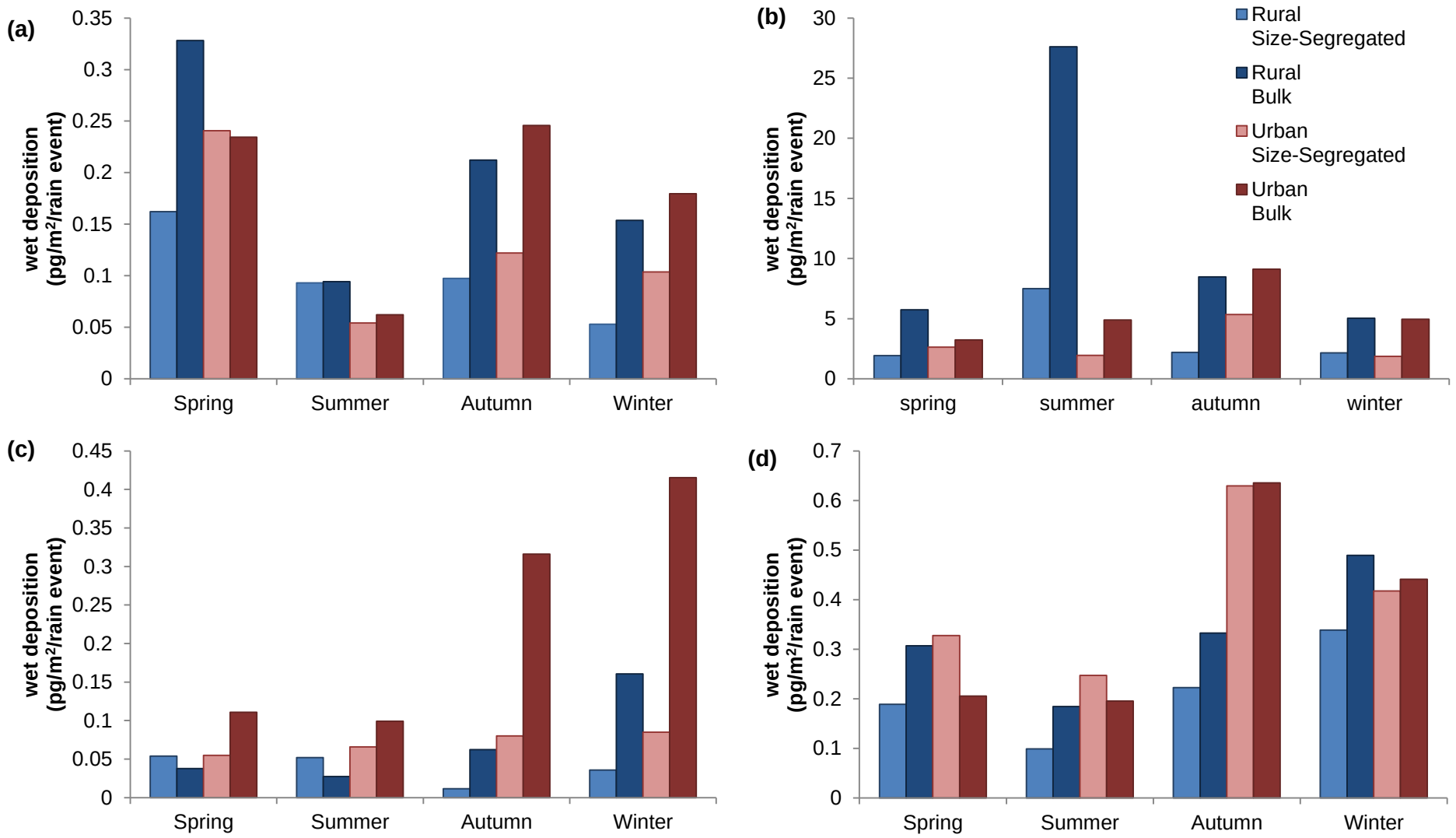


Figure S13: Wet deposition estimates for (a) Dechlorane Plus, (b) HBCD, (c) BDE-47 and (d) BDE-209.

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