Electronic Supplementary Material (ESI) for Environmental Science: Processes .

SUPPLEMENTARY INFORMATION

Outdoor passive air monitoring of semivolatile organic compounds (SVOCs): a critical evaluation of performance and limitations of polyurethane foam (PUF) disks.

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Materials and Methods

Sample preparation

Briefly, prior to deployment, the PUF-PAS were pre-extracted for 8 hours in acetone and 8 hours in dichloromethane, dried under vacuum and stored in multiple layers of solvent-rinsed aluminum foil inside air tight polyethylene zip bags.

After exposure, PUF disks were wrapped in two layers of aluminum foil, labelled, placed into zip-lock polyethylene bags, and transported in a cooler at 5 °C to the laboratory where they were stored at -20°C until analysis.

Sample Cleanup and Analysis

PCBs, OCPs, PBDEs, PCDDs, PCDFs, and NBFRs

Extraction and clean-up of the chlorinated and brominated SVOCs followed the same procedure for PUF-PAS disks, active PUFs and QMFs. Samples were extracted with toluene using automated warm Soxhlet extraction (Büchi B-811, Switzerland). ^{13}C labelled BDE 28, 47, 99, 100, 153, 154, 183 and 209 congeners, ^{13}C dl-PCBs congeners and ^{13}C US EPA PCDDs/Fs congeners (Wellington, Canada) were added prior to the extraction. Extracts were cleaned-up using glass column (1 cm i.d.) filled with 5 g of H_2SO_4 modified silica (Merck, Germany), and eluted with 40 mL DCM:*n*-hexane mixture (1:1). Cleaned extracts were evaporated using nitrogen (TurboVap II, Caliper LifeSciences, USA) and further fractionated on a charcoal column (6 mm i.d.), filled with 50 mg silica, 70 mg charcoal (Sigma Aldrich, Czech Republic) /silica (1:40) and 50 mg of silica. The column was prewashed with 5 mL of toluene, followed by 5 mL of DCM:cyclohexane mixture (30%), then the sample was applied and eluted with 9 mL DCM:cyclohexane mixture (30%) for fraction 1 (mono-ortho dl-PCBs, PBDEs, NBFRs) and 40 mL of toluene for fraction 2 (PCDDs/Fs, non-ortho dl-PCBs). Each fraction was concentrated under nitrogen, solvent exchanged to nonane and transferred into a vial insert. ^{13}C labelled syringe standards were added (final volume 50 μL).

PCBs and OCPs were analyzed on GC-MS/MS system consisting of a 6890N GC (Agilent, USA), equipped with a 60 m x 0.25 mm x 0.25 μm DB5-MS column (Agilent J&W, USA) coupled to Quattro MicroGC MS (Waters, Micromass, UK). The MS was operated in positive electron ionisation impact mode (EI+) using multiple reaction monitoring (MRM). Injection was splitless 1 µL at 280°C, with He as carrier gas at 1.5 mL min^{-1}. The GC temperature programme was 80°C (1 min hold), then 15°C min^{-1} to 180°C, and finally 5°C min^{-1} to 300°C (5 min hold).

Analysis of PBDEs and nBFRs (Table S3) were performed using GC/HRMS consisting of a 7890A GC (Agilent, USA) equipped with a 15 m x 0.25 mm x 0.10 µm DB5 column (Agilent J&W, USA) coupled to AutoSpec Premier MS (Waters, Micromass, UK). The MS was operated in EI+ SIM mode at the resolution of >10 000. For BDE 209, the MS resolution was set to >5 000. Injection was splitless 1 µL at 280°C, with He as carrier gas at 1 mL min^{-1}. The GC temperature programme was 80°C (1 min hold), then 20°C min^{-1} to 250°C, followed by 1.5°C min^{-1} to 260°C (2 min hold) and 25°C min^{-1} to 320°C (4.5 min hold).

dl-PCBs and PCDDs/Fs were analyzed on the same GC/HRMS but on a 60m x 0.25mm x 0.25µm DB5-MS column. The MS was operated in EI+ SIM mode at the resolution of >10 000. Injection was splitless 1 µL at 280°C, with He as carrier gas at 1.7 mL min^{-1}, and 1.9 mL min^{-1} for dlPCBs and PCDD/Fs respectively. The GC temperature programme for dl-PCBs was 130°C (1 min hold), then 40°C min^{-1} to 190°C, followed by 1.5°C min^{-1} to 240°C and 8°C min^{-1} to 310°C (3.42 min hold). The temperature programme for PCDDs/Fs was 135°C (1 min hold), then 15°C min^{-1} to 220°C, followed by 1°C min^{-1} to 240°C, 3.5°C min^{-1} to 260 °C and 6°C min^{-1} to 320°C (5 min hold).

PAHs

Samples for PAHs analysis were extracted using automated warm Soxhlet extraction with dichloromethane (DCM). The extract was fractionated on a silica column (5 g of activated silica 0.063 – 0.200 mm). The first fraction (10 mL *n*-hexane), containing aliphatic hydrocarbons, was discarded. The second fraction (20 mL DCM), containing PAHs, was collected and then reduced by stream of nitrogen and transferred into an insert in a vial. Terphenyl was added as syringe standard (final volume 200 µL).

PAHs were analyzed on GC-MS, 6890N GC (Agilent, USA), equipped with a 60m x 0.25mm x 0.25um DB5-MS column (Agilent, J&W, USA) coupled to 5973N MS (Agilent, USA). Injection was 1 µL splitless at 280°C, with He as carrier gas at constant flow 1.5 mL min^{-1}. The GC programme was 80°C (1 min hold), then 15°C min^{-1} to 180°C, followed 5°C min^{-1} to 310°C (20 min hold). The MS was operated in EI+ SIM mode.

QA/QC

Method performance for was tested prior to sample preparation by analyzing a reference material (soil). Recovery of native analytes measured in a reference material varied from 88 to 100% for PCBs, from 75 to 98% for OCPs, from 72 to 102% for PAHs. The results for PBDEs, dl-PCBs, and PCDDs/Fs samples were recovery corrected. The remaining analytes were not recovery corrected. Recoveries were higher than 75% and 70% for PCBs+OCPs and PAHs, respectively. 3 PUF-PAS, 2 active PUFs and 2 QMFs field blanks were analyzed within each set of PUF-PAS and high volume samples.

Table S1. Information from the reference active sampler during the 12 weeks sampling period: average air concentrations, gas/particle distribution (expressed as % in gas phase), and detection frequency (%).

	C_{act} (pg m^{-3})/(ng m^{-3})*		Gas phase distribution (%)	Detection frequency (%)
	Average	Std	Average	
PCB 28	5.28	1.11	100	100
PCB 52	1.84	0.48	99	100
PCB 101	1.99	0.46	91	100
PCB 118	0.72	0.15	77	100
PCB 153	3.02	0.68	80	100
PCB 138	2.16	0.46	73	100
PCB 180	1.94	0.58	51	100
Sum PCB-7	17.00		85	
PCB77	0.215	0.120	78	100
PCB81	0.016	0.008	84	100
PCB126	0.028	0.012	54	100
PCB169	-	-	-	58
PCB105	0.310	0.112	73	100
PCB114	0.019	0.008	85	100
PCB123	0.023	0.007	85	100
PCB156	0.272	0.078	55	100
PCB157	0.030	0.011	54	100
PCB167	0.131	0.040	62	100
PCB189	0.046	0.020	30	100
Sum dlPCB	1.10		72	

PeCB	3.67	1.73	100	100
HCB	29.56	7.40	100	100
α-HCH**	-	-	-	-
β-HCH**	-	-	-	-
γ-HCH**	-	-	-	-
δ-HCH**	-	-	-	-
Sum HCHs	-		-	
***o,p′*-DDE**	0.90	0.57	93	100
***p,p′*-DDE**	19.6	11.33	92	100
***o,p′*-DDD**	0.88	0.41	75	100
***p,p′*-DDD**	2.14	2.04	64	100
***o,p′*-DDT**	1.55	0.71	83	100
***p,p′*-DDT**	2.42	1.54	68	100
Sum DDTs	25.70		85	
Naphthalene	8.10*	10.15	88	100
Acenaphtylene	3.37*	3.79	91	100
Acenapthene	1.50*	1.03	98	100
Fluorene	10.59*	5.73	96	100
Phenanthrene	23.07*	10.10	89	100
Anthracene	1.21*	0.69	84	100
Fluoranthene	10.87*	5.18	66	100
Pyrene	7.62*	3.65	61	100
Benz(a)anthracene	2.24*	1.63	18	100
Chrysene	3.38*	1.88	22	100
Benzo(b)fluoranthene	4.13*	2.26	2	100
Benzo(k)fluoranthene	1.59*	0.81	2	100
Benzo(a)pyrene	2.20*	1.37	1	100
Indeno(123cd)pyrene	2.58*	1.42	0	100
Dibenz(ah)anthracene	0.16*	0.11	0	100
Benzo(ghi)perylene	1.95*	0.98	0	100
Sum EPA PAHs	84.56*		67	
2378-TCDD	-	-	13	67
12378-PeCDD	-	-	14	63
123478-HxCDD	0.013	0.007	12	92
123678-HxCDD	0.024	0.012	9	92
123789-HxCDD	0.020	0.009	13	92

1234678-HpCDD	0.210	0.117	14	100
OCDD	0.470	0.274	12	100
Sum PCDD	0.740		13	
2378-TCDF	0.035	0.019	49	83
12378-PeCDF	0.026	0.014	33	83
23478-PeCDF	0.049	0.029	24	100
123478-HxCDF	0.036	0.021	16	100
123678-HxCDF	0.033	0.020	16	100
234678-HxCDF	0.044	0.027	13	100
123789-HxCDF	0.018	0.011	21	83
1234678-HpCDF	0.115	0.073	17	100
1234789-HpCDF	0.022	0.015	21	92
OCDF	0.080	0.057	16	92
Sum PCDF	0.458		19	
BDE 28	0.00	0.000	-	0
BDE 47	0.93	0.60	49	100
BDE 66	0.00	0	-	0
BDE 100	0.20	0.17	17	100
BDE 99	0.91	0.89	12	100
BDE 85	0.00	0	-	0
BDE 154	0.17	0.26	0	67
BDE 153	0.77	2.26	0	25
BDE 183	4.65	15.20	4	75
BDE 209**	-	-	-	-
Sum BDE w/o 209	7.65		28	
ATE	0.100	0.07	45	100
α,β,γ,δ-TBECH	2.76	1.10	97	100
BATE	0.02	0.03	100	100
TBCO	0.28	0.11	95	100
p-TBX	0.03	0.006	91	100
DPMA	0.002	0.003	67	50
PBEB	0.01	0.009	81	92
PBT	0.13	0.047	86	100
DPTE	0.38	0.365	31	100
HBB	0.07	0.041	65	83
HCDBCO	-	-	-	0

EHTBB	0.20	0.064	39	100
BTBPE	0.29	0.146	0	100
s-DP**	-	-	-	-
a-DP**	-	-	-	-
BEHTBP	0.09	0.171	59	33
DBDPE	0.24	0.171	25	100
Sum nBFR	15.0		45	

*Air concentrations presented in ng m^{-3}.

**Excluded due to laboratory problems with field blanks and analysis (i.e. high MDLs)

Table S2. Exposure time specific R_S (m^3 day^{-1}) obtained by *Method 2*. Average of triplicates.

	Exposure time (weeks)											
	1	2	3	4	5	6	7	8	9	10	11	12
PCBs												
PCB 28	15.2	9.6	7.2	6.6	6.5	5.4	4.4	4.8	4.7	4.3	4.4	4.6
PCB 52	14.2	9.0	7.9	8.5	7.1	5.6	5.2	5.4	5.1	5.1	4.9	5.4
PCB 101	13.4	8.4	7.3	8.0	7.3	6.0	5.8	6.3	5.8	5.4	5.3	5.7
PCB 118	11.0	7.9	6.1	7.2	8.0	7.1	5.8	5.9	5.8	4.4	3.8	4.5
PCB 153	14.5	8.8	7.3	8.3	7.9	6.2	6.4	6.8	6.3	5.3	5.1	5.5
PCB 138	12.9	7.4	7.3	7.3	7.7	6.0	6.5	6.7	6.0	5.2	4.9	5.3
PCB 180	14.5	5.8	5.8	4.8	5.8	4.5	5.0	5.2	4.5	3.6	3.4	3.7
PCB 77	10.8	7.6	7.6	6.7	7.1	6.2	8.1	6.1	5.6	5.7	6.5	5.5
PCB 81			7.5	8.4	7.2	6.7	7.4	6.6	5.8	5.8	6.5	5.7
PCB 126			4.5	3.8	3.7	4.0	4.1	4.0	3.5	3.3	3.2	2.6
PCB 169												
PCB 105	6.9	6.0	6.1	5.5	6.0	5.7	6.7	5.8	5.1	5.1	5.3	4.7
PCB 114		2.7	7.4	6.5	6.6	5.9	6.5	6.0	5.9	6.0	6.4	5.4
PCB 123	6.7	8.0	6.9	6.5	5.6	7.0	7.0	6.0	5.0	6.0	5.3	4.4
PCB 156	27.1	5.3	6.1	4.2	5.3	5.4	5.5	5.5	4.8	4.5	4.4	3.6
PCB 157	3.3	5.3	6.5	4.0	5.0	4.9	5.1	5.1	3.9	3.8	4.1	3.2
PCB 167	9.2	5.8	6.4	4.5	5.5	5.5	5.8	5.6	5.0	4.6	4.8	3.9
PCB 189	12.4	3.5	4.4	2.5	3.3	3.0	3.5	3.3	2.8	2.4	2.5	2.1
OCPs												
PeCB	23.8	13.0	9.4	9.3	9.5	8.2	6.1	5.7	4.9	5.5	4.7	4.9
HCB	10.9	6.1	4.3	4.0	4.3	4.2	3.0	3.1	2.6	2.9	2.6	3.0
o,p'-DDE	10.2	7.0	5.5	6.1	6.4	5.6	5.3	5.4	5.4	4.9	4.7	5.3
p,p'-DDE	12.6	8.9	7.3	8.5	8.6	7.1	6.9	7.2	6.8	6.2	6.0	6.8
o,p'-DDD	10.4	5.7	4.2	4.1	5.2	4.2	4.3	4.7	4.5	3.9	4.2	4.4
p,p'-DDD	10.7	3.2	2.5	2.7	3.4	3.0	3.0	3.3	3.3	2.7	2.7	3.2

o,p′-DDT	9.0	5.7	5.0	12.1	6.8	7.6	5.9	6.2	6.8	6.2	5.0	7.8
p,p′-DDT	13.6	4.6	3.1	9.5	4.9	6.2	4.2	4.8	5.3	4.6	3.6	6.0
PAHs												
Naphthalene	35.8	34.6	13.6	6.4		2.9	9.6	6.4	13.0	8.0	6.3	3.5
Acenaphtylene	5.5	5.8	3.2	1.3		0.5	3.2	1.1	3.6	0.7	0.9	0.8
Acenapthene	11.7	10.6	9.4	3.9	2.9	2.6	5.1	4.5	5.2	5.0	4.2	3.6
Fluorene	6.8	5.7	4.5	2.2	1.8	1.7	3.3	3.1	4.4	4.2	3.9	3.7
Phenanthrene	6.1	5.9	5.2	2.8	2.5	2.3	4.5	4.5	5.3	5.3	5.0	5.0
Anthracene	4.3	4.8	3.9	1.9	1.6	1.4	3.2	2.9	3.6	3.7	2.9	3.1
Fluoranthene	5.1	4.0	3.7	2.2	2.2	2.1	4.5	4.2	4.2	3.9	3.9	3.9
Pyrene	4.7	3.5	3.1	1.8	1.9	1.8	3.8	3.6	3.5	3.3	3.1	3.1
Benz(a)anthracene	1.0	0.6	0.6	0.3	0.4	0.4	0.8	0.6	0.6	0.5	0.5	0.4
Chrysene	1.5	0.9	0.8	0.5	0.5	0.5	1.1	1.0	0.9	0.8	0.7	0.6
Benzo(b)fluoranthene	0.5	0.3	0.3	0.2	0.2	0.2	0.4	0.3	0.3	0.3	0.2	0.2
Benzo(k)fluoranthene	0.6	0.4	0.3	0.2	0.2	0.2	0.4	0.3	0.3	0.3	0.3	0.2
Benzo(a)pyrene	0.4	0.3	0.2	0.1	0.1	0.1	0.2	0.1	0.2	0.2	0.2	0.1
Indeno(123cd)pyrene	0.2		0.2	0.1	0.1	0.1	0.2	0.1	0.2	0.2	0.2	0.2
Dibenz(ah)anthracene												
Benzo(ghi)perylene	0.4		0.2	0.1	0.2	0.1	0.3	0.2	0.2	0.2	0.2	0.2
PCDDs												
2378-TCDD							5.7		4.7			
12378-PeCDD							2.7	1.0	2.6	0.7		
123478-HxCDD							1.9	0.7	2.3	0.4		0.6
123678-HxCDD				0.7	1.6		1.5	0.5	1.4	0.8		0.5
123789-HxCDD	17.0	1.6		1.7	2.4		3.5	1.3	1.8	0.4		0.5
1234678-HpCDD	6.2	1.0	0.8	0.6	1.0	0.4	0.9	0.5	0.7	0.4	0.4	0.3
OCDD	4.0	0.9	0.6	0.5	0.7	0.3	0.7	0.4	0.6	0.3	0.3	0.3
PCDFs												
2378-TCDF	6.3	3.9	3.4	3.1	3.4	3.3	3.3	3.1	2.6	2.3	2.2	1.7
12378-PeCDF	8.3	2.3	2.3	2.0	2.7	1.8	2.1	1.9	2.3	1.2	1.3	1.1
23478-PeCDF	5.0	1.8	1.1	1.3	1.4	1.3	1.5	1.4	1.2	0.9	0.9	0.7
123478-HxCDF	5.6	0.9	0.8	1.1	1.3	0.5	1.5	0.8	0.8	0.8	0.6	0.5
123678-HxCDF	6.8	1.8	1.1	1.5	1.7	0.9	1.7	1.0	1.4	0.8	0.8	0.6
234678-HxCDF	7.4	1.3	1.0	1.0	1.2	0.6	1.0	0.7	1.0	0.5	0.6	0.5
123789-HxCDF	24.3			0.8	2.0		2.7		2.5	0.3	0.7	0.2
1234678-HpCDF	9.4	1.2	0.9	0.8	1.2	0.5	1.3	0.6	1.0	0.5	0.5	0.4
1234789-HpCDF	17.8	3.6	2.0	1.9	3.8	0.7	3.1	1.2	2.6	1.0	1.0	0.9
OCDF	17.3	2.5	1.7	1.6	2.6	0.4	2.3	1.0	2.2	0.7	0.8	0.5
PBDEs												
BDE 28												
BDE 47	7.3	4.9	3.9	3.6	3.6	3.3	3.1	3.4	3.4	2.7	2.6	2.4
BDE 66												
BDE 100					4.9	2.5		2.2	1.7	1.6		1.3

BDE 99	6.0	2.7	2.8	2.2	2.5	2.2	1.6	2.2	1.8	1.4	1.3	1.1
BDE 85												
BDE 154												
BDE 153												
BDE 183												
BDE 209*												
nBFRs												
ATE	2.7	3.3	2.1	1.7	1.9	2.1	2.0	2.0	1.5	1.6	1.5	1.4
a,b,g,d-TBECH	8.5	8.2	7.8	5.9	5.9	5.6	5.6	6.1	4.1	4.5	4.0	4.8
BATE												
TBCO	15.2	13.4	12.6	8.4	7.8	7.4	6.5	7.5	5.9	5.4	5.3	7.1
p-TBX	18.0	10.1	8.7	7.4	8.7	7.3	6.2	6.7	5.4	4.7	5.4	5.0
DPMA												
PBEB	33.7	18.3	12.4	15.6	13.4	8.3	9.0	8.3	5.5	4.9	4.6	4.8
PBT	26.0	17.4	12.7	9.1	10.6	8.8	8.3	9.5	6.4	7.1	5.9	5.8
DPTE	1.7	1.9	1.1	0.9	1.0	1.7	1.3	1.6	1.8	1.5	1.3	1.5
HBB	39.8	30.6	20.2	12.3	12.7	8.1	6.6	8.3	6.0	11.8	7.1	6.2
HCDBCO												
EHTBB	14.6	5.9	3.0	3.0	3.1	3.4	3.3	3.4	2.6	3.0	2.5	2.9
BTBPE	88.3				5.5	2.4		2.1	2.0	2.0	3.1	1.6
s-DP*												
a-DP*												
BEHTBP												
DBDPE		9.0	6.8	2.4	2.5			1.4	6.9	2.9	2.5	3.4

*Excluded due to laboratory problems with field blanks and analysis (i.e. high MDLs)

Table S3. Monitored ions by MS analysis for nBFRs.

compound	m/z quan	m/z qual
ATE	369.8027	371.8027
a,b,g,d-TBECH	266.9207	268.9187
BATE	331.7693	329.7714
TBCO	266.9207	268.9187
p-TBX	340.7999	342.7979
DPMA	344.9353	379.9041
PBEB	499.6266	501.6247
PBT	485.6111	487.609
DPTE	529.6372	531.6353
HBB	551.5038	549.5059
HCDBCO	267.9285	269.9265
EHTBB	420.672	418.674
BTBPE	358.7928	356.7984
s-DP	271.8102	273.8072
a-DP	271.8102	273.8072
BEHTBP	464.6618	462.6638

DBDPE	484.6032	486.6012

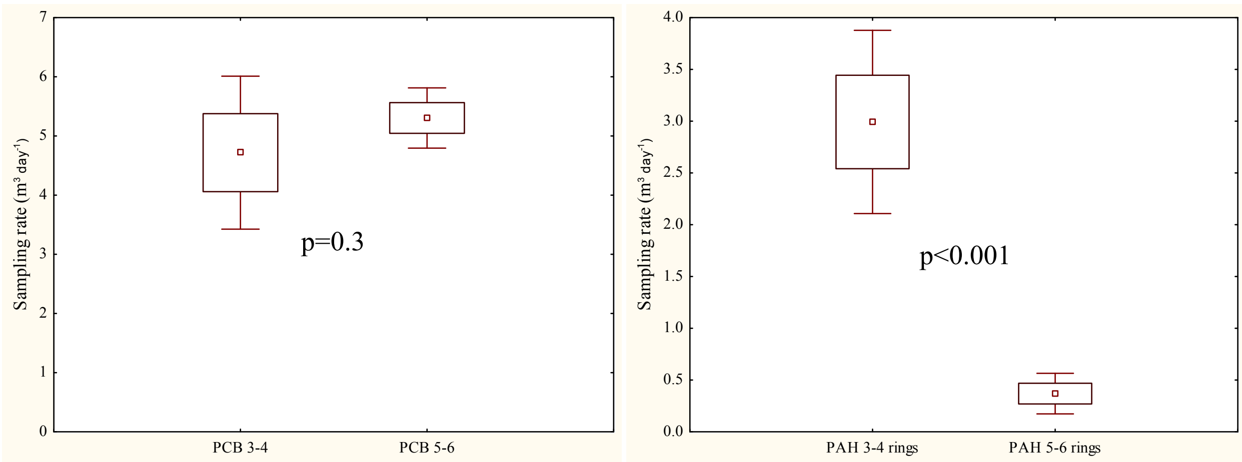

Figure S1. Homologue grouped sampling rates for a) 3-4 and 5-6 PCBs, and b) 3-4 and 5-6 ring PAHs