Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting Information for

Stir Bar Sorptive Extraction and Thermal Desorption – Gas Chromatography/Mass Spectrometry for Determining Phosphorus Flame Retardants in Air Samples

Julius Matsiko,[a,b] Honghua Li,[a] Pu Wang,[a] Huizhong Sun,[a,b] Shucheng Zheng,[a,b] Dou Wang,[a,b] Weiwei Zhang,[a,b] Yanfen Hao,[a,b] Yingming Li,[a] Qinghua Zhang, [a,b,c,*] and Guibin Jiang [a,b]

[a]State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

[b]University of Chinese Academy of Sciences, Beijing 100049, China

[c]Institute of Environment and Health, Jianghan University, Wuhan 430056, China

Table of Contents

Section A

Chemical Standards

Chemical standards of the ten target PFRs, i.e., Triethyl phosphate (TEP), Tri-n-propyl phosphate (TPP), Tri-n-butyl phosphate (TNBP), Tris(2-chloroethyl) phosphate(TCEP), Tris(2-chloroisopropyl)phospahte(TCIPP), Tris(1,3-dichloro-2-propyl) phospahte (TDCIPP), Tris(2-butoxyethyl) phosphate (TBOEP), Triphenyl phospahte (TPHP), 2-Ethylhexyl diphenyl phosphate (EHDPP) and Tris(2-ethylhexyl) phospahte (TEHP), and the internal labelled standards, Tri-n-butyl phosphate-d_{27} (d_{27}-TNBP) and Triphenyl phospahte-d_{15} (d_{15}-TPHP) were purchased as 50 $\pm$ 2.5μg/mL solutions (chemical purity $>$ 98%) in Toluene from Wellington Laboratories (CANADA). The working solutions for the individual standards were prepared by appropriate dilution with toluene (>99.5%) which was purchased from Mallinckrodt Baker (Phillipsburg, USA). Nitrogen gas (99.999% pure) was used for thermal desorption of the stir bars, while helium gas (99.999%) was used as a carrier gas for chromatographic analysis.

Section B

High Volume – Active Air Sampling (HV–AAS) procedure

Before active air sampling, the PUF disks were prewashed by dichloromethane/hexane (1/1, v/v) using accelerated solvent extraction (ASE 300, Dionex Corporation). The glass fiber filters were baked at 450℃ for 6 hours to minimise their water and organic matter blanks [1] prior to weighing and then deployment. Thereafter, the high volume – active air sampler (SIBATA HV–1000R, ID 220135, Version 1.00) was equipped with two PUF disks (for gas phase) and a quartz fiber filter (QFF) (to remove the particulate phase compounds). The bottom PUF disc was to trap analytes that could break through the top PUF disc.[2] The active air sampling rate was 500 L/min. Four active air samples were collected on different days during the passive sampling campaign of 21 days. Active sample volume was 720 m^3. After sampling, the QFFs and PUF disks were stored at −20°C prior to extraction. Method blanks were controlled at various levels to gather information about any background and procedural contamination.

Section C

Chromatographic analysis

Analyte chromatographic separation was carried out using a DB-5MS column (30m × 0.25 mm i.d., 0.25μm film thickness, Agilent J&W GC Columns). The initial column temperature was kept at 90°C for 5 minutes, ramped at 10°C/min to 240°C and finally ramped at 8°C/min to 320°C. The carrier gas velocity was 1.00 mL/min. Analyte detection was carried out using the electron impact (EI) ionisation in selected ion mornitoring (SIM) mode. The ion source and interface temperatures were set at 230 and 300°C, respectively and the solvent cut time was 5 minutes. The total analytical time was 30 minutes.

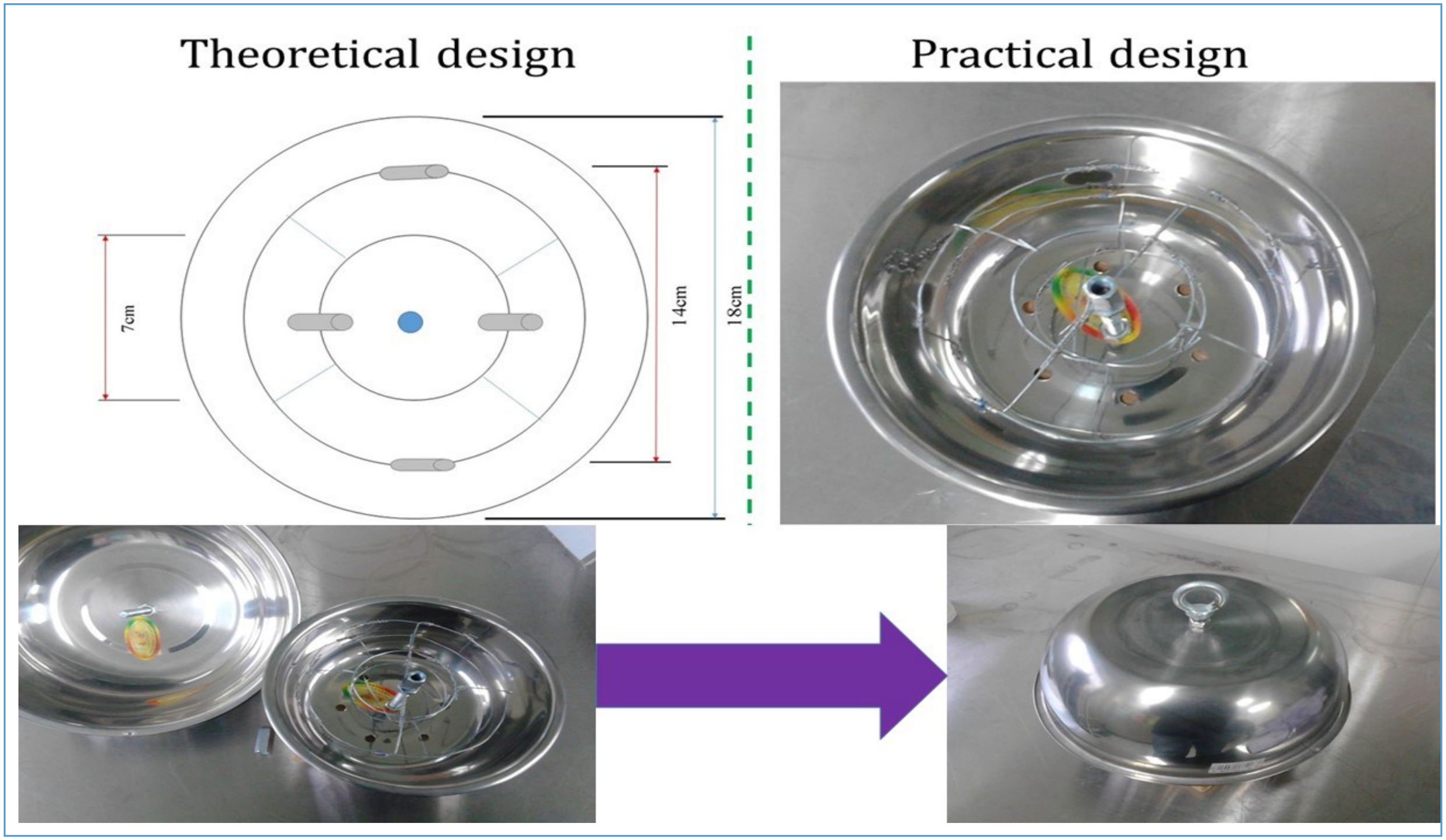


Figure S1. Our sampler design. Four PDMS-PASs were clumped inside the two stainless steel domes

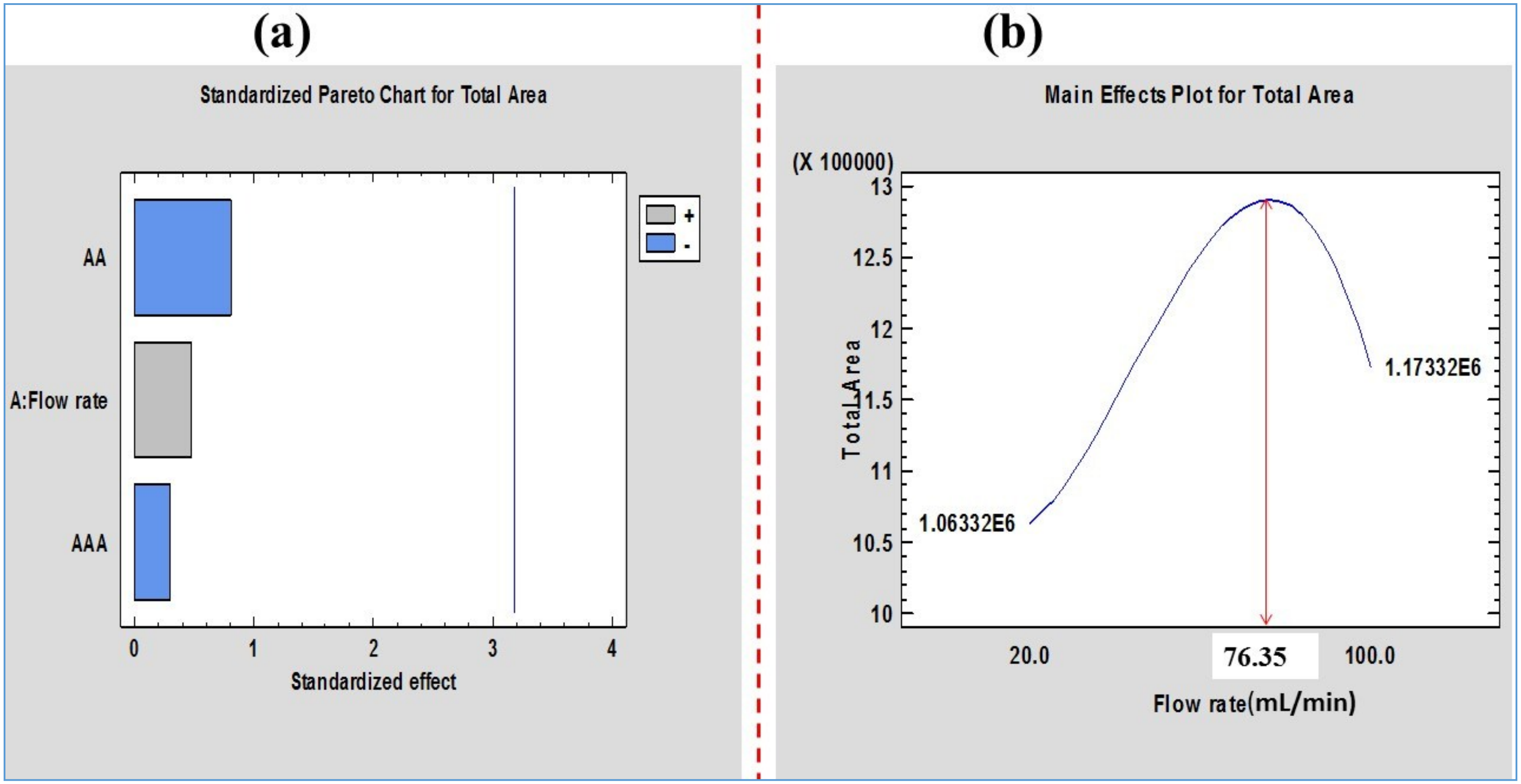


Figure S2. Standardized Pareto chart for the effect of desorption flow rate and the corresponding interactions on the total area (a) (Vertical line in the chart defines 95% confidence level) and a plot of total peak area against desorption flow rate (b).

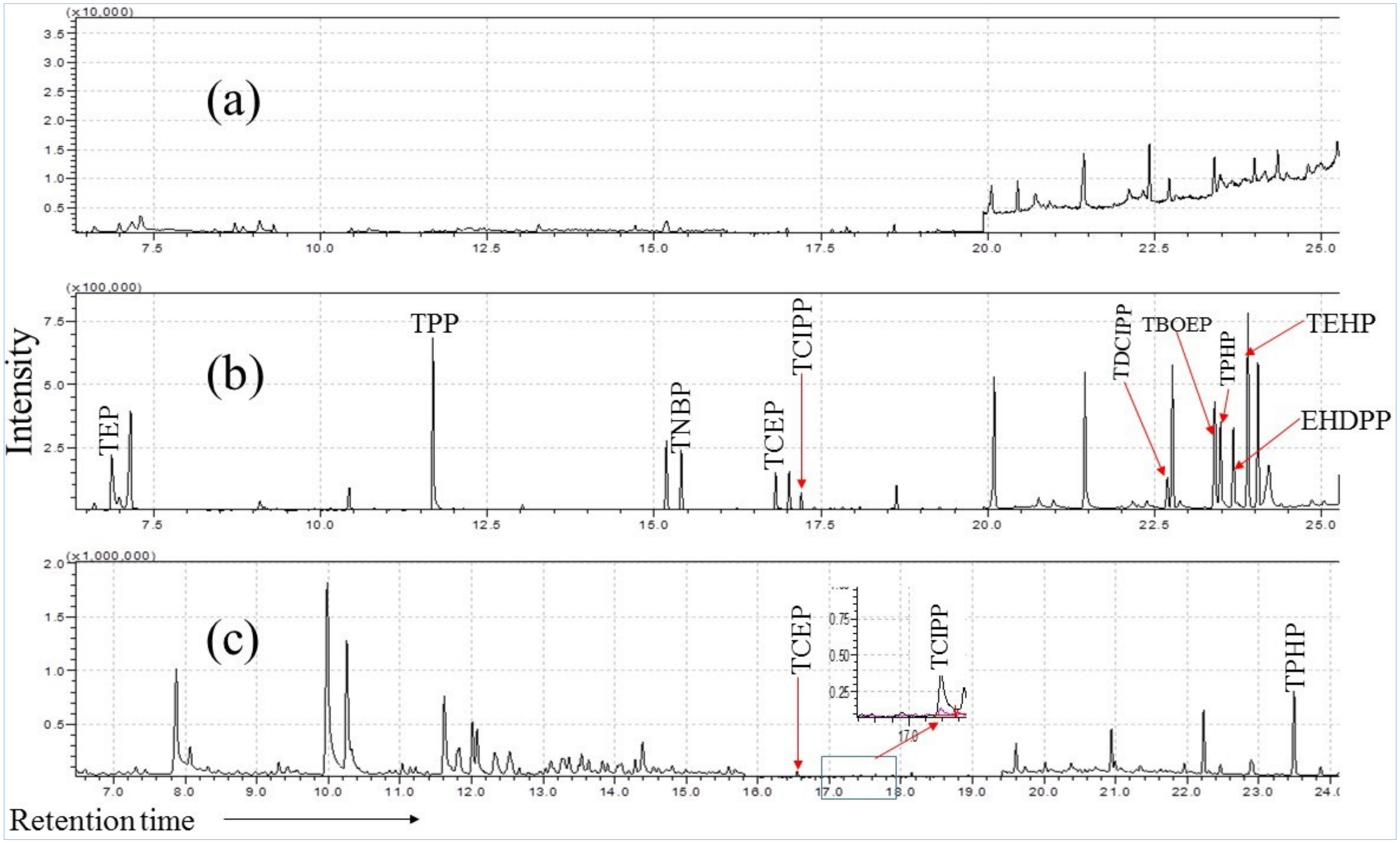
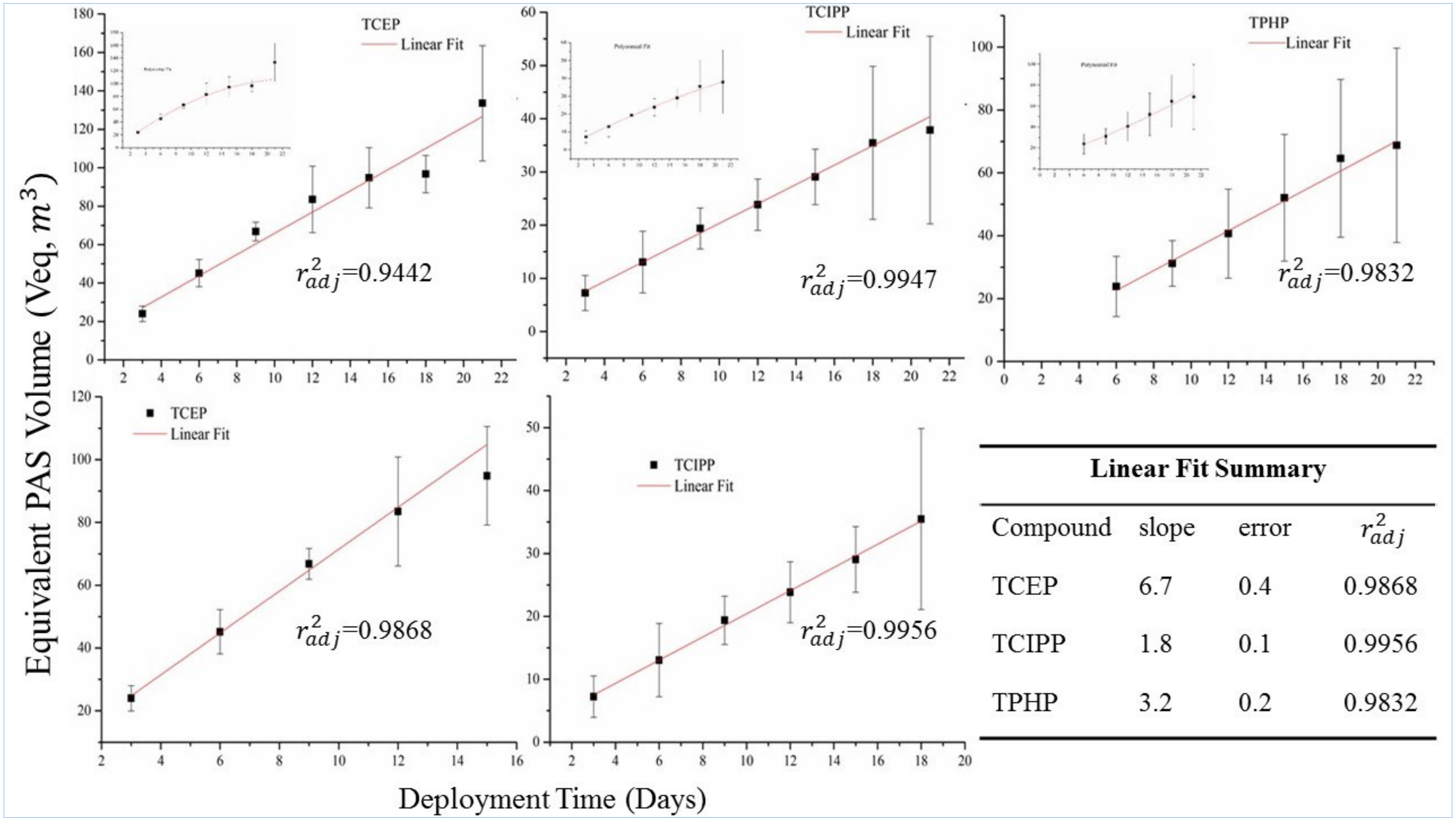


Figure S3. GC-MS Chromatograms of the field blank (a), intermediate calibration point (b) and real sample (c). TCEP, TCIPP and TPHP were quantified. The rest of the compounds were detected but not quantified (c).



Linear Fit Summary

Compound	slope	error	r^2_{adj}
TCEP	6.7	0.4	0.9868
TCIPP	1.8	0.1	0.9956
TPHP	3.2	0.2	0.9832

Figure S4. Uptake profiles of equivalent air volumes (ratio of accumulated PAS mass to gas phase AAS concentration) plotted against the deployment time (2017.12.21 to 2018.01.11). The error bar represents the standard deviation of the analytical results obtained from the four PDMS-PASs. The insets represent the polynomial fits that were used to determine when the uptake goes into the curvilinear region.

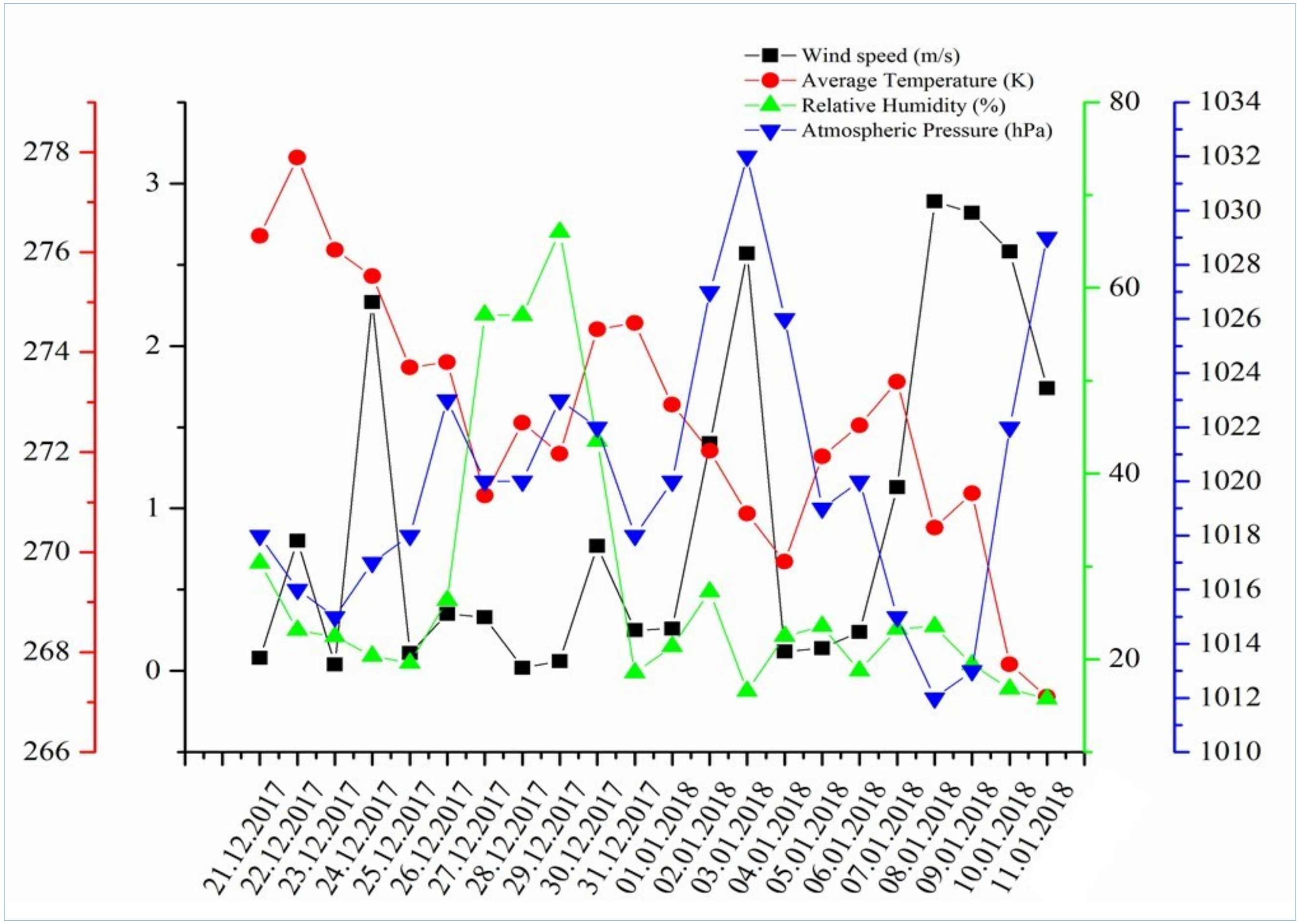
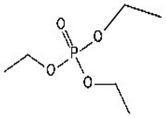
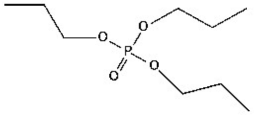
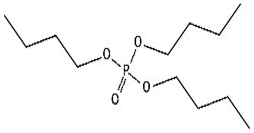
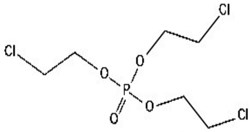
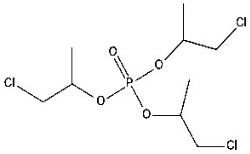
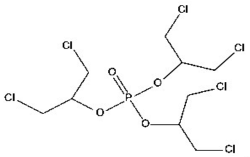
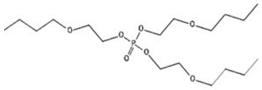


Figure S5. Variation of the relevant meteorological conditions during the sampling period.

Table S1. The Physical – Chemical Properties of the Target PFRs [3,4]

No.	Compound	Practical Abbreviation (PRAB)	B.p (°C)	Structure	CAS Number	MW	Log K_{ow}	Koc	Vapour Pressure (Pa)
1	Triethyl phosphate	TEP	216		78-40-0	182.16	0.80	36	5.25E+01
2	Tri-n-propyl phosphate	TPP	254		513-08-6	224.24	1.87	676	5.77E-01
3	Tri-n-butyl phosphate	TNBP	289		126-73-8	266.32	3.60	977	1.71E00
4	Tris(2-chloroethyl) phosphate	TCEP	351		115-96-8	285.49	1.47	150	1.44E-02
5	Tris(2-chloroisopropyl)phosphate	TCIPP	342		13674-84-5	327.56	2.59	275	2.69E-03
6	Tris(1,3-dichloro-2-propyl) phosphate	TDCIPP	457		13674-87-8	430.90	3.27	1440	5.43E-06
7	Tris(2-butoxyethyl) phosphate	TBOEP	414		78-51-3	398.48	3.75	1020	3.33E-06

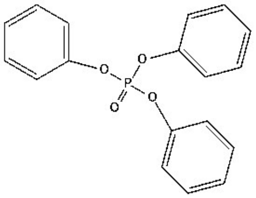
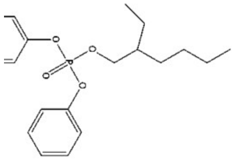
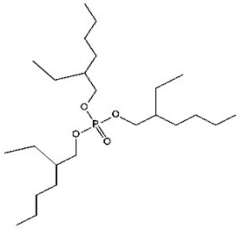
8	Triphenyl phosphate	TPHP	370		115-86-6	326.29	4.59	2630	8.37E-03
9	2-Ethylhexyl diphenyl phosphate	**EHDPP**	**375**		1241-94-7	362.40	5.73	9499	6.20E-04
10	Tris(2-ethylhexyl) phosphate	TEHP	220		78-42-2	434.64	9.49	617000	1.10E-05

Table S2. Experimental results for desorption flow optimization

run	*Flow rate*	*Average Total Peak Area* ± *CV (n=3)*
	mL/min	
1	100	1220400 ± 6
2	40	996996 ± 9
3	20	1082460 ± 11
4	20	1082514 ± 10
5	60	1482934 ± 5
6	80	1134740 ± 4
7	100	1164580 ± 9

Analysis of Variance for Total Area

Source	*Sum of Squares*	*Df*	*Mean Square*	*F-Ratio*	*P-Value*
A:Flow rate	7.62762E9	1	7.62762E9	0.22	0.6696
AA	2.23101E10	1	2.23101E10	0.65	0.4792
AAA	3.04281E9	1	3.04281E9	0.09	0.7854
Total error	1.02998E11	3	3.43328E10		
Total (corr.)	1.46896E11	6			

Table S3. Extrapolation of the model to establish the best operating conditions

Step	*Desirability*	*Total Area*	*Flow rate (mL/min)*
0	0.361255	1.25288E6	60.0
1	0.372564	1.26079E6	62.0
2	0.382793	1.26796E6	64.0
3	0.393477	1.27543E6	66.4
4	0.40349	1.28244E6	69.2
5	0.413612	1.28953E6	74.0
6	0.414912	1.29044E6	76.4

Table S4. Control of blanks and transit spikes (compared with laboratory spikes).

Targets	Lab blanks (pg), n= 9	Transit blanks (pg), n= 5	Field blanks (pg), n= 8	PDs[a] (pg), n=8	PDs[b] (pg), n=9	Spikes[a] , n= 5		Spikes[b] ,n= 5	
						100pg	1000pg	100pg	1000pg
TEP	< 29.0	< 29.0	< 29.0	< 29.0	< 29.0	87 ± 14	110 ± 14	99 ± 15	118 ± 18
TPP	<31.0	< 31.0	<31.0	< 31.0	<31.0	80 ± 3	112 ± 5	94 ± 12	129 ± 6
TNBP	<42.0	<42.0	< 42.0	< 42.0	<42.0	78 ± 3	107 ± 1	82 ± 12	106 ± 4
TCEP	<40.0	<40.0	<40.0	< 40.0	<40.0	85 ± 4	127 ± 12	107 ± 18	110 ± 12
TCIPP	<42.0	<42.0	< 42.0	< 42.0	<42.0	100 ± 17	109 ± 9	94 ± 20	97 ± 12
TDCIPP	< 46.0	< 46.0	< 46.0	< 46.0	< 46.0	95 ± 20	146 ± 19	81 ± 17	118 ± 4
TBOEP	< 48.0	< 48.0	< 48.0	< 48.	< 48.	100 ± 9	143 ± 5	88 ± 17	129 ± 14

				0	0				
TPHP	< 42.0	< 42.0	< 42.0	< 42.0	< 42.0	98 ± 13	95 ± 12	77 ± 7	129 ± 19
EHDPP	<40.0	< 40.0	<40.0	< 40.0	<40.0	94 ± 18	115 ± 16	101 ± 13	120 ± 16
TEHP	< 38.0	< 38.0	< 38.0	< 38.0	< 38.0	89 ± 13	115 ± 14	97 ± 17	129 ± 18

PDs^{a} and PDs^{b} refer to post conditioning detections without and with the internal standard solution, respectively.

Spikes^{a} refers to laboratory spikes while Spikes^{b} refers to transit spikes.

Table S5. Accuracy (Recovery) and storage stability results.

Target compounds	Accuracy (Recovery (%) ± CV (n=5))			Storage stability;Recovery (%) ± CV (n=3)				
	50pg	500pg	2000pg	0 days	3 days	7 days	10 days	14 days
TEP	120 ± 13	97 ± 11	100 ± 17	100 ± 13	101 ± 4	100 ± 13	86 ± 13	96 ± 10
TPP	100 ± 11	103 ± 5	101 ± 14	103 ± 7	95 ± 6	102 ± 1	87 ± 10	96 ± 8
TNBP	107 ± 6	102 ± 3	100 ± 12	101 ± 2	103 ± 4	100 ± 2	93 ± 8	96 ± 5

TCEP	124 ± 19	101 ± 6	113 ± 14	101 ± 9	104 ± 10	85 ± 17	75 ± 2	74 ± 6
TCIPP	103 ± 19	100 ± 10	108 ± 17	96 ± 9	88 ± 11	94 ± 9	108 ± 14	99 ± 5
TDCIPP	77 ± 7	102 ± 5	93 ± 19	99 ± 4	85 ± 10	81 ± 15	98 ± 12	96 ± 8
TBOEP	110 ± 9	111 ± 5	95 ± 17	111 ± 3	84 ± 11	89 ± 20	91 ± 18	95 ± 7
TPHP	85 ± 13	98 ± 13	94 ± 20	90 ± 6	90 ± 4	99 ± 12	109 ± 5	114 ± 1
EHDPP	101 ± 12	94 ± 13	98 ± 13	96 ± 9	81 ± 8	88 ± 20	92 ± 13	95 ± 7
TEHP	95 ± 11	91 ± 9	107 ± 20	91 ± 10	90 ± 9	103 ± 11	101 ± 3	118 ± 7

Table S6. Compounds retention times, monitoring ions and recoveries at the second and fourth calibration levels.

Targets	Retention Time (min)	**Monitoring Ions**		Recovery (%) ± CV (n=5)	
		Quantifier ion	Qualifier ions	100pg	1000pg
TEP	6.89	99	155, 127	91 ± 10	89 ± 9
TPP	11.69	99	141, 183	89 ± 18	115 ± 4

TNBP	15.41	155	211, 125	78 ± 4	108 ± 2
TCEP	16.82	249	251	87 ± 3	127 ± 12
TCIPP	17.20	277	279	107 ± 15	107 ± 19
TDCIPP	22.69	381	379	102 ± 15	129 ± 7
TBOEP	23.40	299	199	96 ± 14	119 ± 11
TPHP	23.48	326	325	73 ± 12	96 ± 18
EHDPP	23.67	251	250	103 ± 13	104 ± 18
TEHP	23.89	99	113, 211	89 ± 11	111 ± 20

Table S7. PUF Active air samples concentrations.

	Concentration (pg/m^3)				Mean (pg/m^3)	CV (n = 4)
Sampling Date	2017.12.21	2017.12.28	2018.01.03	2018.01.10		
TEP	< 5.2	< 5.2	< 5.2	< 5.2	< 5.2	
TPP	7.1	8.2	7.3	2.9	6.4 ± 2.3	36.7

TNBP	< 41.7	< 41.7	< 41.7	< 41.7	< 41.7	
TCEP	6.3	6.2	6.2	6.9	6.4 ± 0.32	5.0
TCIPP	10.2	10.6	5.8	4.5	7.8 ± 3.1	39.9
TDCIPP	< 4.2	< 4.2	< 4.2	< 4.2	< 4.2	
TBOEP	< 30.1	< 30.1	< 30.1	< 30.1	< 30.1	
TPHP	2.6	2.7	2.5	1.3	2.3 ± 0.68	29.8
EHDPP	< 4.1	< 4.1	< 4.1	< 4.1	< 4.1	
TEHP	*nd*	*nd*	*nd*	*nd*	*nd*	

For the compounds that were not quantified, <MLOQ is recorded based on the real sample data. *nd* represents not detected.

Table S8. Analyte masses accumulated by the stir bars after a given time interval

	Accumulated mass (pg) from 2017.12.21 to 2018.01.11						
	3 days	6 days	9 days	12 days	15 days	18 days	21 days
TEP	< 522.6	< 522.6	< 522.6	< 522.6	< 522.6	< 522.6	< 522.6
TPP	< 238.8	< 238.8	< 238.8	< 238.8	< 238.8	< 238.8	< 238.8

TNBP	< 602.2	< 602.2	< 602.2	< 602.2	< 602.2	< 602.2	< 602.2
TCEP	154 ± 27	289 ± 45	427 ± 31	534 ± 111	607 ± 87	619 ± 72	855 ± 192
TCIPP	56 ± 4	102 ± 45	151 ± 30	186 ± 38	227 ± 33	277 ± 112	295 ± 138
TDCIPP	< 13.5	< 13.5	< 13.5	< 13.5	< 13.5	< 13.5	< 13.5
TBOEP	< 57.8	< 57.8	< 57.8	< 57.8	< 57.8	< 57.8	< 57.8
TPHP	< 33.0	55 ± 22	72 ± 17	94 ± 33	120 ± 40	149 ± 58	158 ± 71
EHDPP	< 6.0	< 6.0	< 6.0	< 6.0	< 6.0	< 6.0	< 6.0
TEHP	< 28.2	< 28.2	< 28.2	< 28.2	< 28.2	< 28.2	< 28.2

References

1 F. Mercier, P. Glorennec, O. Blanchard and B. Le Bot, *J. Chromatogr. A*, 2012, **1254**, 107-114.

2 R. Liu, Y. Lin, R. Liu, F. Hu, T. Ruan and G. Jiang, *Talanta*, 2016, **147**, 69-75.

3 I. van der Veen and J. de Boer, *Chemosphere*, 2012, **88**, 1119-1153.

4 Å. Bergman, A. Rydén, R. J. Law, J. de Boer, A. Covaci, M. Alaee, L. Birnbaum, M. Petreas, M. Rose, S. Sakai, N. Van den Eede and I. van der Veen, *Environ. Int.*, 2012, **49**, 57-82.