

SUPPORTING INFORMATION FOR ABDALLAH ET AL, 2013

**ORGANOPHOSPHATE FLAME RETARDANTS IN INDOOR DUST
FROM EGYPT; IMPLICATIONS FOR HUMAN EXPOSURE**

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8 pages, 4 tables.

Table SI-1: Characteristics of the sampled microenvironments.

House no.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Ventilation	AC	N	AC	N	N	AC	AC	AC	N	AC	N	N	N	AC	AC	N	AC	N	N	AC
No. of electronics	5	3	4	2	3	4	6	4	4	5	3	3	5	7	5	4	5	5	4	6
No. of Foam furniture	7	14	10	12	8	10	15	11	8	10	7	12	14	9	10	8	12	10	9	11
Carpeted	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Year of Construction	1987	1992	1983	1986	2002	2004	1985	1982	1994	1997	1985	1985	1985	2001	1997	1986	1983	1994	1986	2001
Office no.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Ventilation	AC	AC	AC	N	AC	AC	N	N	AC	AC	AC	AC	N	AC	N	AC	AC	N	AC	AC
No. of electronics	7	5	5	8	6	5	3	5	9	7	11	6	5	7	4	14	8	6	9	8
No. of Foam furniture	14	11	6	8	8	12	9	11	6	15	10	11	8	6	9	11	4	8	7	10
Carpeted	Yes	Yes	No	No	Yes	No	Yes	Yes	No	No	Yes	Yes	Yes	No	No	No	Yes	Yes	Yes	No
Year of Construction	1991	1995	1991	1987	1982	1984	1986	1984	1991	1993	1986	1988	1993	1991	1988	1992	1991	1986	1984	1992
Car no.	1		2		3		4		5		6		7		8		9		10	
Manufacturer	Toyota		Hyundai		Hyundai		Mitsubishi		KIA		Hyundai		Renault		Mitsubishi		Nisan		FIAT	
Year	2006		2008		2009		2005		2008		2010		2012		2005		2009		1988	
Ventilation	AC		AC		AC		AC		AC		AC		AC		AC		AC		N	
Seat cover	Fabric		Fabric		Leather		Fabric		Fabric		Fabric		Fabric		Leather		Fabric		Fabric	
Car no.	11		12		13		14		15		16		17		18		19		20	
Manufacturer	OPEL		FIAT		FIAT		KIA		Hyundai		OPEL		Renault		Mitsubishi		Lada		Chevrolet	
Year	1998		1986		2009		2010		1999		2006		2011		2008		1998		2006	
Ventilation	AC		N		AC		AC		N		AC		AC		AC		N		AC	
Seat cover	Leather		Fabric		Fabric		Fabric		Fabric		Fabric		Fabric		Leather		Fabric		Fabric	

Table SI-1 (continued): Characteristics of the sampled microenvironments.

PMEs	Coffee Shop1	Coffee Shop2	Coffee Shop3	Coffee Shop4	Rest-aurant1	Rest-aurant2	Rest-aurant3	Res-aurant4	Super-market1	Super-market2	Super-market3
Ventilation	AC	N	N	N	AC	AC	AC	N	AC	N	AC
No. of electronics	9	14	19	12	12	9	9	6	18	16	14
No. of Foam furniture	24	6	18	16	22	32	26	4	4	1	2
Carpeted	Yes	No	No	Yes	No	No	No	No	No	No	No
Year of Construction	2008	2012	2006	2010	2004	2000	2002	2011	2006	2000	1996

Sample Extraction:

The method is largely based on the recent method described by Van den Eede et al¹. In detail, a sample aliquot (~50 mg) was accurately weighed and spiked with 50 ng IS (TCEP-d₁₂, TBOEP-d₆, TDCPP-d₁₅, TPHP-d₁₅ and TAP). Samples were extracted using 2 mL Hex-Ac (3:1 v/v) by a combination of vortexing and ultrasonic extraction (2 × 1 min vortex and 5 min ultrasonic extraction) which was repeated three times. After each extraction cycle, dust extracts were centrifuged at 3500 rpm for 2 min and supernatants were collected and transferred into clean glass tubes. The pooled supernatants were evaporated until dryness under a gentle nitrogen flow and redissolved in 1 mL Hex.

Prior to fractionation, Florisil[®] cartridges were conditioned with 6 mL of Hex. The extracts were quantitatively transferred and fractionation was achieved by eluting with 8 mL of Hex (F1) followed by 10 mL of EA (F2). The EA eluate (F2) was evaporated until dryness and resolubilized in 80 µl of isooctane containing 200 pg µl⁻¹ of BDE-77 used as a recovery determination standard (RDS).

Instrumental Analysis:

GC-EI/MS analysis of PFRs in F2 was performed using a FOCUS GC coupled to a DSQII mass spectrometer (Thermo Fisher Scientific, Austin, TX, USA) operated in electron ionization (EI) mode according to the method previously described¹. Separation of target analytes was performed on Agilent DB-5 capillary column (30m x 0.25mm; 0.25µm) using helium as the carrier gas. One µL of purified extract was injected using cold splitless injection. The injection temperature was set at 90 °C, hold 0.03 min, ramp 700 °C/min to 290 °C. Injection was performed using a pressure of 1 bar until 1.25 min and purge flow to split vent of 50 mL/min after 1.25 min. The GC temperature program was 90 °C, hold 1.25 min, ramp 10 °C/min to 240 °C, ramp 20 °C/min to 310 °C, hold 16 min. Helium was used as a carrier gas with a flow rate of 1.0 mL/min. The mass spectrometer was run in selected ion monitoring (SIM) mode. Dwell times ranged between 20 and 30 ms in different acquisition windows. The ion source, quadrupole and interface temperatures were set at 230, 150 and 300 °C, respectively, and the electron multiplier voltage was at 2200 V.

Table SI-2: Selected analytical characteristics of the applied method.

PFR	Chemical name	Identification/ Quantification Ions	Internal Standard	Blank levels (ng)		LOQ (ng)
				Median	Range	
TPHP	Triphenyl phosphate	325/ 326	TPHP-d ₁₅	1	0 - 4	9
EHDPP	2-Ethyl hexyl diphenyl phosphate	250/ 251	TPHP-d ₁₅	0	0	2
TCEP	Tris-(2-chloroethyl)-phosphate	251/249	TCEP-d ₁₂	3	0 - 6	8
TCIPP	Tris-(2-chloroisopropyl) phosphate	279/277	TCEP-d ₁₂	5	3 - 8	15
TDCPP	Tris-(2,3-dichloropropyl)-phosphate	379/381	TDCPP-d ₁₅	3	0 - 6	9
TBOEP	Tri-(2-butoxyethyl)-phosphate	199/299	TBOEP-d ₆	0	0 - 1	3
TnBP	Tri-n-butyl-phosphate	155/211	TAP	4	3 - 7	10
TiBP	Tri-iso-butyl-phosphate	155/211	TAP	7	5 - 11	17

Table SI-3: Concentration (ng/g) of target PFRs in NIST SRM 2585 from this and other studies.

	This study (n=5)	Bergh et al ² (n=5)	Van den Eede et al ³ (n=11)	Brandsma et al ⁴ (interlab study)
TPHP	970 ± 50	1100 ± 100	990 ± 70	1104
EHDPP	880 ± 20	1000 ± 120	nm ± nm	963
TCEP	720 ± 50	730 ± 60	700 ± 170	792
TCIPP	750 ± 120	880 ± 140	820 ± 100	844
TDCPP	1900 ± 110	2300 ± 280	2020 ± 260	1556
TBOEP	75000 ± 4200	73000 ± 6500	79000 ± 9600	73464
TnBP	170 ± 20	190 ± 20	180 ± 20	269
TiBP	<LOQ	<LOQ	<LOQ	<LOQ

Table SI-4: International comparison of concentrations ($\mu\text{g g}^{-1}$) of target PFRs in indoor dust from different types of microenvironments.

Microenvironment	Country	TPHP	EHDPP	TCEP	TCIPP	TDCPP	TBOEP	TnBP	TiBP
Houses	Egypt (n=20)	0.10	0.05	0.05	0.05	0.15	0.09	0.02	0.03
	Belgium (n=33) ³	2.02	nm*	0.49	4.82	0.57	6.58	0.25	4.2
	Spain (n=8) ⁵	2.6	nm	1.7	3.9	0.35	9.9	0.25	0.21
	Boston, USA (n=50) ⁶	7.36	nm	nm	0.57	1.89	nm	nm	nm
	California, USA (n=16) ⁷	2.8	0.56	2.7	2.2	2.1	11	<0.08	<0.08
	Germany (n=6) ⁸	0.38	nm	0.2	0.74	<0.08	0.73	0.13	nm
	Sweden (n=10) ⁹	1.6	0.6	7.6	3.1	12	8.5	0.6	1.4
	Japan (n=41) ¹⁰	5.4	nm	7.5	18.7	4	1570	1.4	nm
	NewZealand (n=34) ¹¹	0.6	nm	0.11	0.35	0.23	4.02	0.08	nm
	Kuwait (n=15) ¹²	1.1	0.93	0.76	1.9	0.53	10.7	0.01	0.11
	Pakistan (n=15) ¹²	0.15	0.09	0.04	0.02	0.033	0.028	0.01	0.02
	Phillipines (n=34) ¹³	0.08	0.07	0.02	nm	nm	nm	0.02	nm
Offices	Egypt (n=20)	0.09	0.04	0.05	0.12	0.10	0.49	0.03	0.03
	Belgium (n=15) ³	4.7	nm	1.17	5.16	4.61	11.8	0.63	1.45
	Germany (n=10) ⁸	2.5	nm	0.12	3	0.15	7	0.22	nm
	Sweden (n=10) ⁹	8.8	15	36	32	30	250	0.7	2.4
Cars	Egypt (n=20)	0.39	0.07	0.20	0.51	0.09	0.28	0.07	0.05
	Spain (n=2) ¹⁴	1.3	nm	20.1	9.3	10	25.8	0.07	0.36
	Germany (n=12) ⁸	3	nm	0.95	3.1	130	21	0.11	nm
	Kuwait (n=15) ¹²	2.2	0.87	3.5	35.9	35.8	5.3	0.08	0.79
	Pakistan (n=15) ¹²	0.67	0.07	0.26	0.59	0.13	0.13	<0.08	0.04
PMEs	Egypt (n=11)	0.96	0.05	0.28	0.23	0.60	0.31	0.11	0.14

* not measured.

References

1. Van den Eede, N.; Dirtu, A. C.; Ali, N.; Neels, H.; Covaci, A., Multi-residue method for the determination of brominated and organophosphate flame retardants in indoor dust. *Talanta* **2012**, *89*, 292-300.
2. Bergh, C.; Luongo, G.; Wise, S.; Oestman, C., Organophosphate and phthalate esters in standard reference material 2585 organic contaminants in house dust. *Analytical and Bioanalytical Chemistry* **2012**, *402*, (1), 51-59.
3. van den Eede, N.; Dirtu, A. C.; Neels, H.; Covaci, A., Analytical developments and preliminary assessment of human exposure to organophosphate flame retardants from indoor dust. *Environment International* **2011**, *37*, (2), 454-461.
4. Brandsma, S. H.; de Boer, J.; Cofino, W. P.; Covaci, A.; Leonards, P. E. G., Organophosphorus flame-retardant and plasticizer analysis, including recommendations from the first worldwide interlaboratory study. *Trac-Trends in Analytical Chemistry* **2013**, *43*, 217-228.
5. Garcia, M.; Rodriguez, I.; Cela, R., Microwave-assisted extraction of organophosphate flame retardants and plasticizers from indoor dust samples. *J Chromatogr A* **2007**, *1152*, (1-2), 280-286.
6. Stapleton, H. M.; Klosterhaus, S.; Eagle, S.; Fuh, J.; Meeker, J. D.; Blum, A.; Webster, T. F., Detection of Organophosphate Flame Retardants in Furniture Foam and US House Dust. *Environmental Science & Technology* **2009**, *43*, (19), 7490-7495.
7. Dodson, R. E.; Perovich, L. J.; Covaci, A.; Van den Eede, N.; Ionas, A. C.; Dirtu, A. C.; Brody, J. G.; Rudel, R. A., After the PBDE Phase-Out: A Broad Suite of Flame Retardants in Repeat House Dust Samples from California. *Environmental Science & Technology* **2012**, *46*, (24), 13056-13066.
8. Brommer, S.; Harrad, S.; Van den Eede, N.; Covaci, A., Concentrations of organophosphate esters and brominated flame retardants in German indoor dust samples. *Journal of Environmental Monitoring* **2012**, *14*, (9), 2482-2487.
9. Bergh, C.; Torgrip, R.; Emenius, G.; Ostman, C., Organophosphate and phthalate esters in air and settled dust - a multi-location indoor study. *Indoor Air* **2011**, *21*, (1), 67-76.
10. Martinez-Carballo, E.; Gonzalez-Barreiro, C.; Sitka, A.; Scharf, S.; Gans, O., Determination of selected organophosphate esters in the aquatic environment of Austria. *Sci Total Environ* **2007**, *388*, (1-3), 290-299.
11. Ali, N.; Dirtu, A. C.; Van den Eede, N.; Goosey, E.; Harrad, S.; Neels, H.; t Mannetje, A.; Coakley, J.; Douwes, J.; Covaci, A., Occurrence of alternative flame retardants in indoor dust from New Zealand: Indoor sources and human exposure assessment. *Chemosphere* **2012**, *88*, (11), 1276-1282.
12. Ali, N.; Ali, L.; Mehdi, T.; Dirtu, A. C.; Al-Shammari, F.; Neels, H.; Covaci, A., Levels and profiles of organochlorines and flame retardants in car and house dust from Kuwait and Pakistan: Implication for human exposure via dust ingestion. *Environment International* **2013**, *55*, 62-70.
13. Chung, H. W.; Ding, W. H., Determination of organophosphate flame retardants in sediments by microwave-assisted extraction and gas chromatography-mass spectrometry with electron impact and chemical ionization. *Analytical and Bioanalytical Chemistry* **2009**, *395*, (7), 2325-2334.
14. Garcia, A.; Rodriguez, I.; Cela, R., Optimisation of a matrix solid-phase dispersion method for the determination of organophosphate compounds in dust samples. *Anal Chim Acta* **2007**, *590*, (1), 17-25.