COMPARISON OF ORGANOPHOSPHATE ESTER CONCENTRATIONS IN SURFACE/FLOOR DUST FROM UK AND GERMANY

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Introduction

Recent restrictions on the use of polybrominated diphenyl ethers (PBDEs) have not been accompanied by relaxations in flame retardancy regulations. It is thus important to monitor human exposure to potential "PBDE replacements" like organophosphate esters (OPEs). While it is known that the ingestion of indoor dust contributes substantially to human exposure to PBDEs [1] the situation for OPEs is still not fully characterised. The aim of this study was to provide the first data on the concentrations of OPEs in surface/floor dust from the UK. These concentrations are compared to those in similar samples from Germany for which - notwithstanding our preliminary report last year [2] - data is similarly lacking. Surface floor dust samples were taken in the West Midlands of the UK from six cars, 23 living rooms and 26 offices. Additionally six cars, ten living rooms and six office samples were taken throughout Germany. Samples were analysed for six OPEs and a preliminary assessment of human exposure to OPEs in those samples was conducted.

Materials and methods:

Sampling: Floor dust samples were collected according to a standardised protocol [1] from six cars, 26 offices and 23 homes in the West Midlands and six cars, six offices and ten homes at various locations in Germany between December 2010 and July 2011.

Target compounds: Samples were analysed for the following OPEs: Tris-2-chloroethyl phosphate (TCEP), Tri (1-chloro-2-propyl) phosphate (TCPP), Tris-1,3-dichloropropyl phosphate (TDCPP), Tri-n-butyl phosphate, (TnBP), Triphenyl phosphate (TPhP) and Tricresyl phosphate (TCP)

Sample preparation: Sample extraction and clean-up was achieved via an adaptation of the method of van den Eede et al. [3]. Internal standards (d_{27}-TBP and d_{15}-TPhP) were added to dust samples (typically 50 mg – accurately weighed) prior to extraction via ultrasonication and vortexing with hexane:acetone (3:1. v/v). The combined supernatant was concentrated and dissolved in 1 mL hexane prior to elution through a Florisil (1 g) microcolumn with n-hexane to isolate the PBDE fraction (not analysed in this study), followed by 10 mL of ethyl acetate to collect OPEs. The OPE-containing fraction was evaporated to incipient dryness and redissolved in 100 µL iso-octane.

Analysis: This was performed on a 30 m x 0.25 mm x 0.25 µm VF-5 column by GC-EI-MS operated in SIM mode. The ions monitored are given in van den Eede et al. [4] The GC program was 90°C for 1.25 min, 10°C/min to 170°C, 5°C/min to 240°C, hold for 10 min, 20°C/min to 310°C, hold for 10 min. One aliquot of SRM 2585 and one reagent blank were analysed with each batch of samples. In total 11 blanks, and 11 aliquots of SRM 2585 were analysed in this study.

Non-detect values were replaced by 1/2 LOQ for the purposes of calculating descriptive statistics.

Results and discussion:

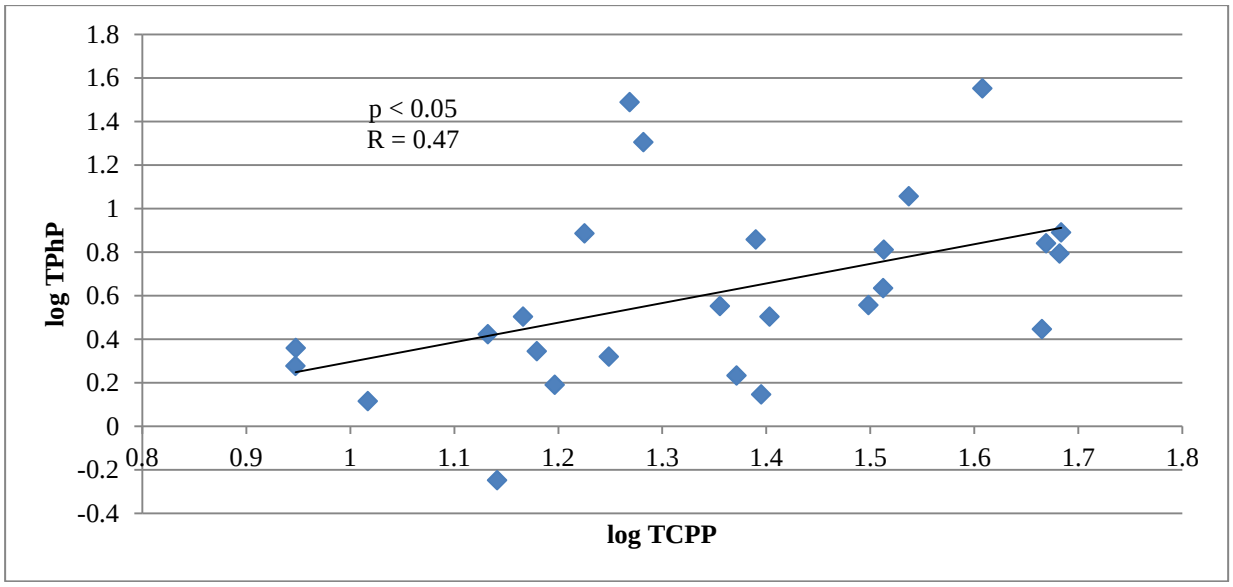
Levels of OPEs in UK and German indoor dust: Table 1 summarises the concentrations of target OPEs in the analysed dust samples. The concentrations detected in this study are broadly within the range of previously reported dust levels from Germany, Belgium and Japan [2,4,5]. However, concentrations of TCPP in UK samples are typically an order of magnitude higher than elsewhere in Europe. In UK dust log-transformed concentrations of TCPP were correlated significantly ($p<0.05$) with those of TPhP, indicating a common source of these two contaminants in the UK dust samples (see Figure 1, office dust data shown). Also of interest, ANOVA

comparison showed log-transformed concentrations of TDCPP in UK car dust to exceed significantly those in both office and house dust from the UK.

Table 1: Levels of OPEs µg g^{-1} in UK and German indoor dust compared to levels from other studies

	n=		*TnBP*	*TCEP*	*TCPP*	*TDCPP*	*TCP*	*TPhP*
House UK	23	Average	0.04	1.25	24	2.3	0.27	4.2
		Range	< 0.01-0.09	0.11-13	3.7-100	0.09-14	< 0.04-1.6	0.49-13
Office UK	26	Average	0.05	0.59	25	1.6	0.24	6.9
		Range	< 0.01 – 0.25	0.13-2.6	8.8-48	0.05-12	< 0.04-3.3	0.56-36
Car UK	6	Average	0.26	0.55	33	14	0.66	3.0
		Range	< 0.01-1.2	0.11-0.96	2.4-70	1.0-31	< 0.04-1.2	0.77-6.4
House Germany	10	Average	0.03	0.16	2.9	1.8	0.50	2.2
		Range	< 0.01-0.11	0.02-0.30	0.33-17	< 0.01-14	< 0.04-1.3	0.12-18
Office Germany	6	Average	0.06	0.27	1.8	0.86	0.60	1.7
		Range	0.04-0.09	0.14-0.63	0.36-4.8	<0.01-2.2	< 0.04-1.6	0.26-6.2
Car Germany	6	Average	0.04	0.29	4.0	3.0	2.4	1.5
		Range	< 0.01-0.07	0.16-0.62	0.09-15	< 0.01-12	< 0.04-9.0	0.33-2.5
Car Germany [2]	12	Average	0.11	0.95	3.1	130	24	3.0
Office Germany [2]	10	Average	0.22	0.12	3.0	0.15	0.37	2.5
House Germany [2]	6	Average	0.13	0.2	0.74	0.07	0.09	0.38
House Belgium [4]	33	Mean	0.25	0.49	4.8	0.57	0.44	2.0
House Japan [5]	41	Median	1.4	7.5	19.0	5.4	< 4.0	4.0

Figure 1: Correlation between Log-transformed Concentrations of TCPP and TCP in UK Office Dust



Exposure assessment via dust ingestion for UK samples: Preliminary estimates of human exposure to OPFRs

arising from dust ingestion under three exposure scenarios are provided in Table 2. The scenarios are: (a) low exposure, where the human receptor is assumed to ingest dust contaminated at the 5th percentile concentration at the average rate (20 mg and 50 mg day^{-1} for adults and toddlers respectively); (b) "typical" exposure, where dust contaminated at the median concentration is ingested at the average rate; and (c) high exposure in which dust contaminated at the 95th percentile concentration is ingested at the high rate (50 mg and 200 mg day^{-1} for adults and toddlers respectively). In the absence of definitive data to the contrary, 100% absorption of intake was assumed for the purposes of exposure assessment. To express intakes normalised to body weight, values of 12.3 kg and 70 kg were assumed for toddlers and adults respectively. With respect to time-activity patterns; adults were assumed to spend 4.2 % in cars, 23.8 % in offices and the rest of the day at home. By comparison, toddlers were assumed to spend 4.2 % time in cars and the rest of their time at home. Dust ingestion was assumed to be pro-rata to the time spent in a microenvironment category.

Table 2: Estimation of human exposure to OPEs via dust ingestion (ng/kg bw/day)

	RfD [4]	**Toddler low**	**Toddler typical**	**Toddler high**	**Adult low**	**Adult typical**	**Adult high**
TnBP	2400	0.02	0.12	2.0	0.001	0.010	0.10
TCEP	2200	0.50	1.6	58	0.04	0.11	2.2
TCPP	8000	23	81	1100	1.9	6.0	44
TDCPP	1500	0.55	5.3	180	0.04	0.39	6.7
TCP	1300	0.10	0.63	15	0.01	0.04	0.68
TPhP	7000	2.8	12	180	0.24	0.84	11

While exposure to most OPEs under even the high-end exposure scenario for toddlers was at least 30 times lower than the proposed reference dose (RfD)[4]; high-end exposure of toddlers to TCPP was only eight times lower than the corresponding RfD.

Conclusions: Although caution is required because of the relatively small database reported here; this study suggests that OPE levels in UK are in general comparable to other recent studies in Europe. However, concentrations of TCPP in UK car and office dust are an order of magnitude higher than elsewhere in Europe. The reduced margin of safety for TCPP under a high-end exposure scenario for young children means that although the current picture is generally reassuring, more detailed examination of the exposure of toddlers via dust ingestion appears prudent. Further work in this project will focus on a greater number of dust samples from domestic environments and will include samples from children's bedrooms and mattresses. In addition, other exposure pathways for the UK population that may further erode the margin of safety between exposure and the RfD, such as inhalation, diet and infant consumption of human milk will be monitored [6–8].

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References:

1. S. Harrad, C. Ibarra, M. A.-E. Abdallah, R. Boon, H. Neels, and A. Covaci, *Environment International*, 2008, **34**, 1170-1175.

2. S. Brommer, S. Harrad, N. Van den Eede, and A. Covaci, Poster presentation at Dioxin 2011.

3. N. Van den Eede, A. C. Dirtu, N. Ali, H. Neels, and A. Covaci, *Talanta*, 2011, **89**, 292-300.

4. N. Van den Eede, A. C. Dirtu, H. Neels, and A. Covaci, *Environment International*, 2011, **37**, 454-61.

5. A. Kanazawa, I. Saito, A. Araki, M. Takeda, M. Ma, Y. Saijo, and R. Kishi, *Indoor Air*, 2010, **20**, 72-84.

6. A. M. Sundkvist, U. Olofsson, and P. Haglund, *Journal of Environmental Monitoring : JEM*, 2010, **12**, 943-51.

7. I. Saito, A. Onuki, and H. Seto, *Indoor Air*, 2007, **17**, 28-36.

8. C. Bergh, R. Torgrip, G. Emenius, and C. Ostman, *Indoor Air*, 2011, **21**, 67-76.