FLAME RETARDANTS IN THE INDOOR ENVIRONMENT.PART IV: CLASSIFICATION OF EXPERIMENTAL DATA FROM HOUSE DUST, INDOOR AIR AND CHAMBER TESTS

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ABSTRACT
Organophosphate esters are frequently applied as flame retardants in building products and other materials for indoor use. Exposure of residents to flame retardants mainly results from accumulation in house dust and indoor air. Some agents of this compound class are suspected to cause adverse health effects. However, risk assessment for the indoor environment is difficult due to the lack of measured indoor air concentrations and toxicological data. In this paper, results of house dust analysis, indoor air measurements and chamber tests are summarised. The data provide an overview about distribution and range of concentrations in house dust and indoor air and enable estimation of daily rates for oral intake and air inhalation.

INDEX TERMS
Flame retardant, SVOC, Field measurement, Chamber study, Exposure assessment

INTRODUCTION
Flame retardant is the collective term for those compounds which give flame-proof properties to numerous materials. Many building products, furnishings, electronic devices and fittings used in the indoor environment are, for safety reasons, equipped with flame retardants. Results of test chamber studies and household dust examinations (part I – III of this series; see Pardemann et al., 2000; Salthammer et al., 2002, Pardemann and Wensing, 2002) show that these flame retardants and their decomposition products can be released under living conditions. This is of importance under an indoor air hygiene aspect as some of the chemical components are rated injurious to health. At present, there are no reference data for assessing the results of house dust examinations from a toxicological point of view. There is need for a pragmatic assessment approach until such values are available. Guidelines for indoor air measurements have recently been introduced (Sagunski and Roßkamp, 2002). The present work contains an extensive compilation of results of indoor air, test chamber and house dust examinations aiming at organophosphorous flame retardants. In addition to the data from parts I – III, further results are presented. Values taken from literature are also considered. All data are processed statistically and may be used for a better assessment of measurement results with regard to their significance for indoor air. The data may also serve for appraising which emission and exposure must be expected from flame retardant application.

METHODS
Most data presented here were taken from other publication. Details about investigated materials, methods, procedures for sampling and analysis can be obtained from cited references.

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RESULTS AND DISCUSSION

Organophosphorous flame retardants are preliminary halogenated and non-halogenated phosphate esters, which represent more than 20 % of the worldwide production (WHO, 1997; Umweltbundesamt, 2000). The most important compounds are listed in Table 1. For selected substances a number of publications are available, which physical, chemical and toxicological properties as well as their behaviour in the environment (WHO, 1991a; 1991b, 1997; 1998; Umweltbundesamt 2000). However, there is low information about the occurrence of flame retardants in house dust and indoor air.

Table 1. Organophosphate esters with general structure $O=P(O\text{-}R)_3$ applied as flame retardants and abbreviations used in the text and tables.

R	Chemical name	Abbreviation
$-(CH_2)_3-CH_3$	tris(n-butyl)phosphate	TBP
$-O-C_4H_9$	tris(2-butoxyethyl)phosphate	TBEP
$-CH_2-CH_2Cl$	tris(2-chloroethyl)phosphate	TCEP
$-CH_2-CHCl-CH_3$	tris(2-chloro-1-propyl)phosphate	TCPP (Isomer 1)
$-CH(CH_3)-CH_2Cl$	tris(1-chloro-2-propyl)phosphate	TCPP (Isomer 2)
$-CH_2-CHCl-CH_2Cl$	tris(2,3-dichloro-1-propyl)phosphate	TDCPP
$-CH_2-CH(C_2H_5)-(CH_2)_3-CH_3$	tris(2-ethylhexyl)phosphate	TEHP
$-C_2H_5$	triethyl-phospate	TEP
$-C_6H_4(CH_3)$	tricresyl-phosphate	TCP
$-C_6H_5$	triphenyl-phosphate	TPP

Analysis of House Dust

To estimate the intake of flame retardants by humans, the fraction which passes into the body via oral and dermal exposure is of interest. If house dust is used as a basis to assess the exposure, the heterogeneity of the matrix must be considered. The composition of house dust is dependent on the type of indoor fittings and the general behaviour, especially the standard of hygiene. A distinction has to be made between “old dust” and “fresh dust”. The first is of unknown age as may be found on surfaces of fittings. The latter is determined by the measurement planning and is known exactly (VDI, 2001). Dust analysis from vacuum cleaner bags is frequently performed. Sampling is usually carried out by residents. Moreover, the procedure bears the possibility of collecting large masses of dust and enables fractionation. The result will strongly depend on the sample preparation. It is advisable to analyse defined dust components like < 2 mm fraction or < 63 µm fraction. When interpreting concentrations in household dust, one must also take into account whether the measurement was triggered by a specific event or not.

Results of house dust analysis on various organophosphorous flame retardants are summarized in Table 2. Due to the non-symmetric data distribution, median (= 50-Percentile), 90-P, 95-P and measured maximum values are presented. All samples represented fresh dust, collected over 1 - 2 weeks in private residences. Pardemann and Wensing (1999) have analyzed < 63 µm fractions. Other references give no information about sample preparation. Analysis of total collected dust is therefore assumed. Maximum rates for oral intake can be estimated assuming a daily dust intake of 10.3 mg/kg body weight per day (calculated for a child of 1 - 3 years) (Stubenrauch et al., 1999).

Table 2. Occurrence of organophosphorous flame retardants in house dust (P = Percentile).

compound	n	50-P	90-P	95-P	max.	reference
		mg/kg				
TBP	50	0.4	-	1.7	5.7	Pardemann and Wensing (1999) 1)
TBEP	50	5.2	-	37.8	59.4	Pardemann and Wensing (1999) 1)
TCEP	59	0.9	-	8.4	94	Sagunski et al. (1997) 2)
	356	0.60	4.0	8.8	64	Ingerowski et al. (2001) 2)
	541	0.60	4.0	7.5	121	Ingerowski et al. (2001) 2)
	86	0.77	5.8	12	94	Ingerowski et al. (2001) 2)
	50	1.5	-	5.4	6.9	Pardemann and Wensing (1999) 1)
TCPP	216	0.40	2.0	3.4	33	Ingerowski et al. (2001) 2)
	147	0.60	4.7	8.8	36	Ingerowski et al. (2001) 2)
	73	0.70	4.1	5.6	375	Ingerowski et al. (2001) 2)
	47	1.4	-	7.5	27.3	Pardemann and Wensing (1999) 1)
TDCPP	37	1.3	-	5.1	6.8	Pardemann and Wensing (1999) 1)
TEHP	50	0.2	-	0.8	1.8	Pardemann and Wensing (1999) 1)
TCP	50	2.3	-	18.0	35.8	Pardemann and Wensing (1999) 1)
TPP	50	3.1	-	13.8	15.7	Pardemann and Wensing (1999) 1)

1) Analysis of vacuum cleaner bag (< 63 µm fraction)
2) Analysis of vacuum cleaner bag (total dust)

Table 3. Occurrence of organophosphorous flame retardants in indoor air.

compound	n	50-P	range	reference
		µg/m³		
TBP	5	-	0.01 - 0.064	Carlsson et al. (1997)
TBEP	13	-	< 0.01 - 0.03	Hansen et al. (2001)
	5	-	0.001 - 0.006	Carlsson et al. (1997)
TCEP	50	0.10	< 0.005 - 6	Ingerowski et al. (2001)
	14	0.38	< 0.01 - 3.9	Hansen et al. (2001)
	5	-	0.011 - 0.250	Carlsson et al. (1997)
TCPP	5	-	0.019 - 0.058	Carlsson et al. (1997)
TEHP	5	-	< 0.001 - 0.010	Carlsson et al. (1997)
TCP	7	-	< 0.01	Hansen et al. (2001)
TPP	5	-	< 0.001	Carlsson et al. (1997)
	13	-	< 0.01	Hansen et al. (2001)

Analysis of Indoor Air

In most cases indoor air measurements are carried out to determine the inhalative exposure of residents to certain substances. The result is strongly dependent on the boundary conditions chosen for the measurement (VDI, 2002). For estimation of intake rates the mean indoor concentrations are of interest. Assuming a daily air intake of 0.53 m^3/kg body weight per day (calculated for a child with breath of 5.3 m^3/d over 21 h per day) (Stubenrauch et al., 1999) and taking the maximum values from Table 3, maximum rates for inhalation can be derived.

A German commission has developed a scheme for the calculation of indoor air guideline values on the basis of toxicological data (Ad-hoc Working Group, 1996). Here, guideline II (RW II) defines a value that requires immediate action. Guideline I (RW I = RW II/10) is the concentration not be exceeded for lifelong exposure. For TCEP Sagunski and Roßkamp (2002) have derived values of RW II = 50 µg/m^3 and RW I = 5 µg/m^3. Under consideration of insufficient toxicological data for other organophosphorous compounds the authors suggest RW I/II as sum values for TCEP-, TCPP-, TBP-, TBEP- TEHP- and TPP-concentrations.

Oral and inhalative intake

The results of house dust analysis (Table 2) and indoor air concentrations (Table 3) can be used for estimation of oral and inhalative intake rates (in µg/kg body weight per day) of organophosphorous compounds (see Table 4). For the calculation, the maximum 95-Percentile values were used. The data for inhalation are based on maximum concentrations measured in indoor air. Ingerowski et al. (2001) have estimated an oral exposure of 0.01 - 5 µg/day and air inhalation of 0.2 - 2 µg/day for TCEP/TCPP from their data.

Table 4. Calculated oral and inhalative intake for selected halogenated and non-halogenated phosphate esters.

compound	**oral intake 1)** [µg/(kg d)]	**inhalative intake 2)** [µg/(kg d)]
TBP	0.018	0.034
TBEP	0.389	0.016
TCEP	0.124	3.180
TCPP	0.091	0.031
TDCPP	0.053	n.d.
TEHP	0.008	0.005
TCP	0.185	< 0.005
TPP	0.142	< 0.005

1) calculated from max. of 95-P values in Table 2 with dust intake of 10.3 mg/(kg d) (Stubenrauch et al., 1999)
2) calculated from max. values in Table 3 with air intake of 0.53 m^3/(kg d) (Stubenrauch et al., 1999)

Chamber Testing

For assessing the risk of exposure it is desired to study the release of flame retardants from building materials and products for indoor use under living conditions. This can be achieved in test chambers by measuring organophosphate concentrations in the chamber air and performance of fogging experiments (Wensing, 1999, Pardemann and Wensing, 2002). Some halogenated hydrocarbons are typical degradation products of phosphate esters and can be used as tracer compounds (Salthammer et al., 2002). In case of a polyurethane soft foam (see Table 5) 1-chloro-2-propanol and 1,2-dichloropropane indicated TCPP and TDCPP.

Table 5. Results of test chamber studies on organophosphorous flame retardants.

compound	product	SER		
TEP	PU hard foam (new)	3	µg/(m² h)	(14 d) 1)
TCPP	PU soft foam (new)	< 0.10	µg/(m² h)	(2 d) 2)
TCEP	television sets (new)	< 0.01	µg/h	(0 - 7 d) 3)
	television sets (aged)	< 0.01 – 0.30	µg/h	(0 – 7 d) 3)
TCEP	video recorders (new)	< 0.01	µg/h	(0 – 7 d) 3)
	video recorders (aged)	< 0.01 – 0.08	µg/h	(0 – 7 d) 3)
TPP	computer monitor	0.10	µg/h	(14 d) 4)
TCEP		0.06	µg/h	(14 d) 4)
TCPP		0.02	µg/h	(14 d) 4)

1) SER was calculated from chamber air sampling
2) 1-Chloro-2-propanol and 1,2-dichloropropane were detected in the chamber air
3) SER was calculated from fogging analysis (7 d sampling)
4) SER was calculated from chamber air sampling, operation time 8 h/d

CONCLUSIONS

Halogenated and non-halogenated phosphate esters are widely applied as flame retardants in building products. In the indoor environment they can be found in house dust and indoor air. The big number of investigated house dust samples provides a satisfactory statistical distribution. With regard to the quantity of oral intake of human residents via house dust, the compounds TBEP, TCEP, TCP and TPP are of highest relevance. In comparison, only little information is available about concentrations in indoor air. However, the data indicate that TCEP is by far the most important compound concerning inhalative exposure. TCP and TPP seem to have no meaning for indoor air. Both compounds are accumulated in house dust, which acts as an effective sink. Toxicological evaluation of intake rates lacks from missing ADI-values (ADI = acceptable daily intake). For a limited number of substances NOAEL-values are available. The evaluation of indoor air concentrations can be achieved by comparison with guidelines I and II (RW I/II), which have been derived for TCEP by Sagunski and Roßkamp (2002). Only for one measurement RWI (5 µg/m³) was exceeded with 6 µg/m³. All other concentrations were significantly lower, in most cases more than an order of magnitude.

To estimate the impact of single materials on indoor air quality, theoretical indoor air concentrations can be calculated from test chamber experiments assuming a model room with V = 17,4 m^3 and ACH = 0.5 h^{-1} according to ENV 13419-1 (1999). In the case of electronic equipment the resulting concentrations are well below RWI. For the measured maximum emission rate of SER = 0.3 µg/h (television set, see Table 5) a concentration of 0.03 µg/m³ results for the model room. However, for evaluation of test chamber experiments, the release of hazardous degradation products of flame retardants has also to be considered (Salthammer et al., 2002).

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