Chlorinated ethyl and isopropyl phosphoric acid triesters in indoor environment – an inter-laboratory exposure study

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Abstract

The chlorinated organo-phosphate triesters, tris(2-chloroethyl)-phosphate (TCEP) and tris(monochloro-isopropyl)-phosphate (TCPP) are employed in consumer articles for indoor usage, such as flame retardants and plasticizers in foam material as well as in paints, varnishes and wall papers. As a result of this wide spread usage, both chemicals have been detected in the indoor environment employing domestic dust as a matrix. TCEP was present in 85 % of a total of 983 samples, whereas TCPPwas found in 60-90 % out of 436 cases, the levels ranging from 0.1 to 375 mg/kg. Since TCEP and TCPP residues in domestic dust are assumed to be condensates arising from primary sources, spot check analysis of various indoor materials was performed. The results show that soft foams, paints and wall papers contain mainly TCEP, whereas in insulation and sealant foams high contents of TCPP were found. Moreover, TCEP can also be detected in indoor air in concentrations up to 6,000 ng/m³. On the basis of this data, an estimate of the indoor exposure via oral and inhalative ingestion is given.

Key words: 1. Tris(2-chloroethyl)-phosphate (TCEP) 2. Tris(mono-chloroisopropyl)-phosphate (TCPP) 2. Domestic dust samples 3. Flame retardants 4. Plasticizers, 5. SVOC

Practical implications

The flame retardants tris(2-chloroethyl)-phosphate (TCEP) and tris(chloroiso-propyl)-phosphate (TCPP) are widely used in indoor housing materials and can be detected in household dust and indoor air. Human exposure to the two organo-phosphates may therefore be expected. In view of the uncertain toxilogical implications of these substances, efforts must be made to reduce the environmental burden, e.g. the use of lower emitting materials.

1 Introduction

A large variety of industrial chemical substances is regularly incorporated into consumer products in order to improve or otherwise enhance quality. In the past, public discussion has largely focused on the use and detection of biocide additives (e.g. for wood preservation) in the indoor environment. However, another class of substances, namely the phosphoric triesters, is less well known and is extensively added to consumer materials.

In 1996, the total European production of phosphorus based flame retardant additives reached about 100,000 metric tons, of which a major portion consisted of the chlorinated phosphoric acid derivatives (Frost & Sullivan,1997). These compounds serve as flame retardants and plasticizers in polyurethane foam, for example in soft foam for furniture, carpet backing, mattresses, acoustic and thermal insulation and in hard foam for building insulation materials. They are also added to textiles, felts and glass fiber wall papers as well as to paints and varnishes. As a result of such wide spread use, these substances may be expected to occur in the indoor environment.

2 Sampling Methods and Analysis

2.1 Study design

The present inter-laboratory exposure study investigates the distribution of tris(2-chloroethyl)-phosphate (TCEP) and tris(mono-chloroisopropyl)-phosphate (TCPP) employing house dust samples as a matrix. The data were independently collected and analysed by three participating laboratories specializing in indoor analysis. The comparability of the three sets of data was demonstrated by the congruent analytical results of a pooled sample. Most of the dust samples originated from clients who were referred to the laboratories because of health complaints. Attention was first directed to the presence of chlorinated organophosphates in the indoor environment because of a medical case report suggesting that TCEP in wood paneling might be responsible for a neurological disorder of a child (Ingerowski, 1997). Analytical screening programs of possible health hazard substances were subsequently carried out, including initially TCEP. Later, TCPP was also evaluated in the routine screening programs because of its increased utilization and detection in indoor materials.

The dust samples were obtained mainly from family homes in single or multiple housing facilities in the western part of Germany. In addition, a few samples from schools and business buildings were included. In most cases the samples were investigated because of problems ascribed to generalized indoor air pollutants and not especially to the possible presence of chlorinated organophosphates. There were no special criteria established to omit or include a sample for investigation, and all incoming samples were included in the study. After a significant TCEP or TCPP exposure had been detected in house dust, spot checks of suspicious materials were performed in individual cases to identify the primary source of the phosphate emission. In order to demonstrate the distribution of organophosphate concentrations in indoor air, data from earlier investigations on air contamination wood preservatives and PCB were retrospectively evaluated for chlorinated organophosphates.

2.2 Sampling procedures

2.2.1 House Dust Samples

Samples of house dust (1-5 g) were obtained either from individual case studies or as part of an explorative survey (Pöhner et. al., 1998). Samples were collected by the participants of the test using conventional vacuum cleaners with filter dust bags over representative areas of the living space surfaces. The dust collection was executed after a general cleaning was carried out one week before und no collection was allowed in the meantime. Thus, the average age of the collected dust samples was about one week. (VDI Guidelines 4300 Bl. 8, Draft 1999) To exclude theoretical contamination of samples by vacuum cleaners and filter bags, control analysis was carried out in several cases.

2.2.2 Other Materials

Samples of building materials and other inventory were obtained from the individual test locations after a significant dust concentration had been previously detected. For the analysis of building materials, carpets, foams and paints, 0.1-1g per sample was utilized. The wood panel shavings were obtained according to VDI-regulations (VDI-4300 Bl. 2, 1995) by combining randomly chosen samples taken up to the shaving depth of 2 mm.

2.2.3 Indoor Air

Air samples were drawn at standard temperature (VDI-Guideline 4300 Bl. 4, 1994) after sealing off the corresponding rooms for at least 8 hours in order to obtain atmospheric equilibration. Highly purified polyurethane foam cartridges served as the adsorptive matrix (Orbo 1000, Supelco, Deisenhofen). Control analysis of the cartridges showed no contamination with the two phosphate esters. For the sampling procedure a glass fiber filter was not inserted in front of the foam cartridges so that the analysis results include chemicals adsorbed onto air-borne particles as well as in the gaseous phase. The flow rate was adjusted to 5 liters/min and the total sampled volume was approximately 1000 liters. The cartridge extraction was performed in a Soxhlet apparatus (ASTM D 4861) after which the sample was analysed by GC-MS. The limit of determination was 1 ng/m³.

2.3 Analysis of TCEP and TCPP

The analytical procedures of the three participating laboratories varied to some extent. The internal quality control check showed that the results of each laboratory are comparable. Therefore, a representative procedure previously described in detail (Sagunski, 1997) is briefly given (Lab #3). Each dust sample was combined with a number of internal standards as a check for analytic reliability. After sample extraction with n-hexane-acetone (8+2) in a soxhlet apparatus for eight hours, a concentrated aliquot of the extract was analyzed directly by means of GC/MS under the following operational conditions:

- GC: HP 5890 with autosampling device · Injector: *Gerstel* KAS (cold insertion system) with temperature program
- Injection: 2 µl splitless
- Column: DB-5.625 (length: 30 m; inner diameter 0,25 µm; film thickness 0,5 µm)
- Temperature program: 85 °C (2 min); 10 °C/min up to 200 °C; 3 °C/ min up to 260 °C; 10 °C /min up to 310 °C (15 min)
- Transfer line: 310 °C
- Detector: HP MSD 5971
- Operational mode: SIM
- Quantification: SIM- mode

TCEP: m/z 249 (quantifier), m/z 251, 223, 205 (qualifier)
TCPP: m/z 277 (quantifier), m/z 279, 251 (qualifier)

The pure substance TCEP (97 % purity) was purchased from Sigma-Aldrich Chemie GmbH, Grünwalder Weg 30, 82041 Deisenhofen, Germany; TCPP was kindly donated by Bayer, Leverkusen, Germany.

2.4 Internal Quality Control

To check for systematic errors, all three laboratories carried out an analysis of TCEP and TCPP in a single pooled homogenized fine dust sample obtained from approximately 20 housing facilities.. A fraction was analyzed by each laboratory. The extraction procedure for the phosphate esters differed in the three laboratories as indicated in Table 1. The results demonstrate good correspondence.

Table 1: *Extraction procedures and results of an internal quality control experiment (mg/kg)*

Lab.	Extraction agent	Extraction method	TCEP	TCPP	LOD*
#1	acetone/ cyclohexane (1+1)	2 x 10 min. ultrasonic bath	4.7	1.7	0.4
#2	Water /acetone (1+1)	12 h cold extraction	4.9	2.0	0.1
#3	n-hexane /acetone (8+2)	8 h Soxhlet-extraction	4.6	1.8	0.1

** Limit of determination for TCEP and TCPP, respectively.*

3 Results

3.1 TCEP and TCPP in house dust samples

The percentual distributions of TCEP and TCPP in domestic dust samples for the three laboratories are shown in Figures 1 and 2. The data are depicted on a linear scale with class intervals of 0.5 mg/kg for TCEP and 0.2 mg/kg for TCPP.

Figure 1: *Distribution of tris(2-chloroethyl)-phosphate (TCEP) in house dust samples*

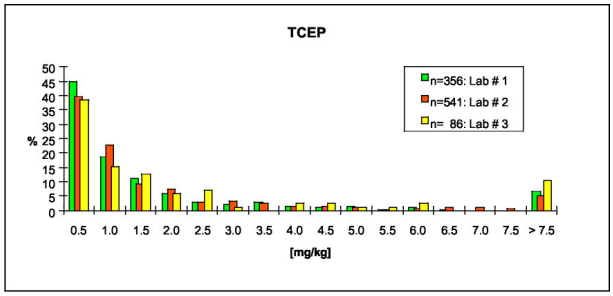
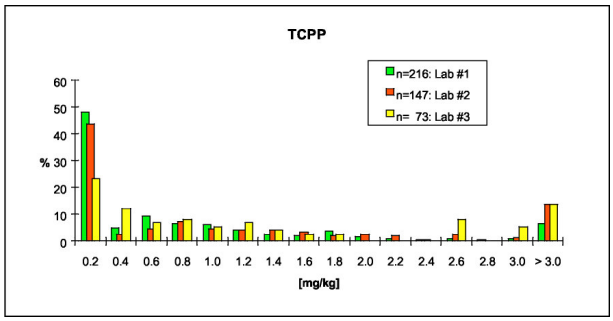


Figure 2: *Distribution of tris(monochloroisopropyl)-phosphate in house dust samples*



The statistical evaluation of the distribution of the concentration of the two phosphate triesters in house dust is shown in tables 2 and 3. For calculation purposes each value under the lowest limit of determination was defined as ½ of this limit.

Table 2: *Percentiles (50th, 90th, 95th, 98th), maximum, arithmetic, and geometric means of tris(2-chloroethyl)-phosphate in house dust (in mg/kg)*

Lab.	n	50-P	90-P	95-P	98-P	Max		MAGM
#1	356	0.60	4,0	8,8	20	64	2.23	0.67
#2	541	0.60	4,0	7,5	16	121	2.24	0.64
#3	86	0.77	5,8	12	18	94	3.75	0.89

Table 3: *Percentiles (50th, 90th, 95th, 98th), maximum, arithmetic and geometric means of tris(monochloroisopropyl)-phosphate in house dust samples (in mg/kg)*

Lab.	n	50-P	90-P	95-P	98-P	Max		MAGM
#1	216	0.40	2,0	3,4	8,7	33	1.16	0.50
#2	147	0.60	4,7	8,8	17	36	2.03	0.38
#3	73	0.70	4,1	5,6	69	375	2.35	0.68

3.2 TCEP and TCPP in various indoor materials

Table 4 presents an overview of the potential sources for TCEP and TCPP showing the magnitude of concentrations found in the various materials. Because of the lack of representative data for each type of material, the highest TCEP/TCPP concentration found by one of the three laboratories in a given specimen is shown.

Table 4: *Primary sources of TCEP and TCPP*

Materials	TCEP (mg/kg)	TCPP (mg/kg)
wood preservation coatings	10,000	150
mattresses (polyurethane)	890	1,500
wall paper (glass fiber)	2,400	1,100
carpet backing (polyurethane)	n.a.*	13,100
polyurethane soft foam	19,800	n.a.
foam fillers (polyurethane)	32,000	180,000
Floor sealing material	n.a.	220
acoustic ceiling (coating)	68,000	n.a.*

*n.a. = no analysis

3.3 Indoor air

A limited number of air samples (n=50) showed the following distribution pattern for the ethyl ester.

Table 5: *Percentiles (10th, 50th, 90th, 95th, 98th), maximum, arithmetic and geometric means of tris(2-chloroethyl)-phosphate in indoor air samples (in ng/m³)*

Lab.	n	10-P	50-P	90-P	95-P	98-P	Max		MAGM
#2	50	5	10	40	250	600	6,000	52	14

The highest indoor air concentration of TCEP was found in the case of a very large primary source, an acoustic ceiling in a school building, which contained 68,000 mg/kg TCEP.

4 Evaluation of house dust concentrations of TCEP/TCPP.

On the basis of the above statistical data (Tables 2 and 3) an assessment of the distribution of TCEP/TCPP residues in domestic dust samples can be derived. In the case of a ubiquitously distributed substance, the 50 th and the 95 th percentiles are generally used to describe the typical prevalence of a substance in the environment. Therefore, concentrations of less than 1 mg/kg TCEP or TCPP in house dust may be regarded as background values. Quantities above 10 mg/kg indicate definitively that additional sources are prevalent.

5 Indoor Exposure Assessment

Potential human exposure to an indoor burden caused by these substances can be roughly assessed on the basis of the results of this house dust pilot study. Oral exposure to house dust containing TCEP or TCPP may be estimated as follows: A typical daily uptake of dust is approximately 10 mg, the 95 th percentile ranging up to 50 mg/day. TCEP/TCPP-concentrations in dust in the order of 1-100 mg/kg could therefore lead to an oral exposure of 0,01-5 µg/day, assuming complete resorption.

Despite of the limited data on indoor air concentrations in this study, the respiratory uptake for TCEP can be estimated as follows. Assuming an indoor air concentration of TCEP from 10 to 100 ng/m³ and a respiratory volume of 20 m³/day, a total daily intake would then range from 0.2 to 2 mg. Compared with the oral intake data, indoor air inhalation uptake of TCEP may well turn out to be a major source of human exposure.

6 Discussion

Studies on the sick building syndrome in Denmark have revealed the presence of TCEP in dust samples from public buildings under 5 mg/kg (Wilkens, 1993). Carlsson et al. investigated the exposure to flame retardant chemicals in more detail (Carlsson, 1997). Evidence of ubiquitous contamination of the indoor environment by TCEP was presented by Sagunski et al. and preliminary assessments were made to establish guide line values for TCEP indoor exposure

(Sagunski,1997). In contamination studies on semi- and non-volatile pollutants in indoor environment, Pöhner et al. demonstrated the presence of TCEP/TCPP in most of the analyzed house dust samples (Pöhner, 1997, Summary in Pöhner,1998).

Recently, Pardemann et al. demonstrated in emission chamber experiments that TCEP and TCPP were capable of diffusing from a matrix to yield measureable air concentrations (Pardemann, 2000). The current study documents that the two chlorinated organic phosphates are ubiquitously distributed in the indoor environment over a large area of the western part of Germany and the distribution pattern is similar in each geographic region, although slightly differing analytical methods were employed.

In every case where dust samples yielded TCEP/TCPP burdens in excess of the 95th percentile, a primary source of organophosphates was subsequently found. Hence, an individual exposure impact from dust samples containing 10 mg/kg or greater indicates the general presence of these flame retardants in the corresponding building material or inventory items. In cases of primary sources with large surface areas, high concentrations were found in both dust and air samples. Due to the small case numbers however, it was not attempted to demonstrate a correlation between the content of the phosphates in materials, dust and indoor air. Experience from studies of biocide prevalence in buildings implicate that such correlations are not reproducible under real conditions. In view of the widespread distribution of these chlorinated substances, the question arises as to wether there is a potential health hazard for building inhabitants.

In the past, organic phosphate triesters have gained notoriety in the environmental medical literature because of their neurotoxic potential. The best documented case is that of tris(o-cresyl)-phosphate, which causes degeneration of the distale axon with the subsequent clinical syndrome of muscular weakness and atrophy combined with sensory neuropathy. (Andreas, 1994) The most important halogenated organic phospho-triester is tris(dibromopropyl)-phosphate (TRIS), which was employed as a flame retardant in textiles until 1975. After animal studies had indicated carcinogenic properties and the metabolite dibromopropanol was found in the urine of test persons wearing garments impregnated with TRIS, the use of the substance was prohibited in the late seventies (IPCS, 1995).

Until 1989 no information existed about the carcinogenic risk for humans for the chlorinated ethyl phosphate (WHO,1990). Meanwhile TCEP has been classified in Germany as carcinogenic and embryotoxic for animals (TRGS 905, 2000). In addition to carcinogenicity, neurotoxic effects in animals have also been demonstrated (Matthews, 1993). For TCPP no data are available.

Efforts to establish guideline values for TCEP have been undertaken (Sagunski, 1997), but the weak toxicological database allows only a very rough and insufficient estimation of the toxicological relevance. For TCPP, a corresponding assessment has not yet been published. In view of the ubiquitous distribution of these esters in the indoor environment and the possible detrimental effects to the health of exposed persons in contaminated surroundings, there is urgent need for more profound toxicological data in order to establish reliable guideline values for TCEP and TCPP in indoor air and household dust.

7 References

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