

THE DISTRIBUTION OF ORGANOPHOSPHORUS COMPOUNDS IN VARIOUS INDOOR ENVIRONMENTS

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Introduction

Organophosphorus compounds (OPs) are frequently utilized as flame retardants in plastics, textiles and building materials, however, they are also applied as plasticizers, anti-foaming agents and as additives in lubricants and hydraulic fluids, etc. In 1998, the consumption of chlorinated and non-chlorinated OPs in the West European market was estimated to amount to 29,500 and 28,500 tonnes, respectively¹. Since OPs are not generally chemically bound, leaching by volatilization or abrasion may occur from the products they are added to throughout their entire lifetime, and thus, OPs may end up in different environmental compartments. Physiological effects of exposure to OPs, such as haemolysis, contact dermatitis and inhibition of human carboxylesterase have been reported, and some OPs are documented carcinogenics and teratogenics²⁻⁶.

A screening project, aiming to investigate the occurrence as well as the sources of OPs in different environmental compartments, has been initiated by the Swedish Environmental Protection Agency. In this study, twelve OPs (Table 1) were analysed and their distribution pattern were investigated in air and settled dust from various types of buildings, representing occupational, public and domestic environments. Wipe tests from computer screens and covers were also analysed. Seven of the substances analysed (TCPP, TDCPP, TEHP, TPP, TBEP, TBP, and TCEP) dominated Swedish imports of OPs in 1999⁷, and six of these are also listed as EU High Production Volume Chemicals. Furthermore, TCEP is included in the European Commission second priority list⁸, while TCPP and TDCPP are included in the fourth priority list⁹. However, TCEP is currently being replaced (since the 1990's) by other flame retardants, primarily TCPP¹.

Table 1. Abbreviations and applications of organophosphorus compounds. For TPrP (Tripropyl phosphate), no application was listed in the literature or databases consulted.

Name	Abbreviation	Flame retardant	Plasticizer	Stabilizer	Hydraulic fluid	Floor finish, wax	Lacquer, paint	Anti-foam agent	Cosmetic prod.	Ind. processes	Fungus resist.
Tris(2-butoxyethyl)phosphate	TBEP	X	X			X	X	X			
Tris(2-chloroethyl)phosphate	TCEP	X	X				X			X	
Tris(2-chloroisopropyl)phosphate	TCPP	X	X								
Tris(1,3-dichloro-2-propyl)phosphate	TDCPP	X	X				X				
Triphenyl phosphate	TPP	X	X		X		X				
Tetraethyl ethylenediphosphonate	TEEdP								X	X	
Tris(2-ethylhexyl)phosphate	TEHP	X	X								X
Tributyl phosphate	TBP		X		X	X	X	X		X	
Di-n-octylphenyl phosphate	DOPP		X							X	
Tris(2-chloroethyl)phosphite	CLP1	X		X	X						
Trimethyl phosphate	TMP									X	

Methods and materials

Sampling

Dust samples were collected from used dust bags of conventional vacuum cleaners except for two samples which were handpicked (Table 2). The vacuum cleaner bags were made of paper and were used for one week in average. Wipe tests from computer screens and computer covers were performed using AYA antistatic cleaners. Duplicate air samples from each site were collected using Solid phase extraction (SPE) columns (Isolute NH₂, 25mg/1mL). Approximately 2.0 m³ air was pumped through the sampler using a laboratory vacuum pump. The airflow and sampled volume were measured with a mass flow meter connected to a totalizer.

Extraction and elution

One to two grams of each dust sample was extracted with 2 x 25 mL dichloromethane (DCM) for 20 min in an ultrasonic bath at room temperature, then filtered through two sandwiched Munktell filter papers (5.5 cm in diameter; coarseness 3 and 00H), using a vacuum filtration device. Screen cleaners from the wipe test samples were extracted in the same manner. Blanks were prepared in the same way and analysis by GC/NPD did not show any significant signals. Triphenyl phosphate was used as internal standard and added to SPE columns before elution with 10 mL DCM.

Analysis and Quantification

Quantitative analysis of OPs was performed using gas chromatography with a nitrogen phosphorus detector (GC/NPD). Separation was carried out on a J&W DB-5 column (30 m x 0.25 mm i.d, film 0.25 μm). The injector temperature was 250°C and the detector temperature was 310°C. Analysis was initiated by injecting 1 μL samples, 60 s splitless time. The GC oven was initially held at 40°C for 4 min, increased to 190°C at a rate of 15°C/min, then at 10°C/min to the final temperature, 310°C, which was maintained for 4 min. Since the GC-NPD system showed very good linearity for all OPs in the range between 10 and 1500 pg/μL, quantification was carried out using single-point calibration. OPs in the samples were identified by comparing their retention times and peak shapes with those of the reference standards. Triethyl phosphate was used as volumetric standard and was added to each sample prior to analysis. To verify the identity of the OPs, selected samples were reanalysed by GC-MS.

Results and Discussion

Among the substances analysed, eleven OPs were detected, and eight of them were found in all dust samples and in most of the air samples. TMP was not detected in any of the samples. The average limit of detection was 0.4 ng/m³ in air samples and 0.03 mg/kg in dust samples. The distribution patterns, illustrated in Fig. 1, show TBEP as the most abundant in nearly all dust samples (levels ranging from 0.014- 4.9 g/kg) followed by TCEP, TCPP and TDCPP, while the chlorinated OPs, TCEP and TCPP, occurred more frequently than the non-chlorinated in the air samples. The dust from the *library* was vacuumed from books and shelves. The fact that TBEP did not dominate in this dust sample implies floors as the primary source of TBEP, either from PVC coverings or from the use of floor polishes and waxes. A remarkably high level of TBEP, 4.9 g/kg, was found in the *prison*. Other sites with high levels of TBEP were the *office*, the *hospital* and the *public dance hall* (120-270 mg/kg). The floors in these buildings were of linoleum or PVC, except for the *public dance hall*, which had a wooden floor. The high levels of TBEP are almost certainly associated with the regular use of floor polishes and waxes on these floors. In the air samples containing TBEP, the levels ranged between 0.6-1.8 ng/m³ except for the *prison* which showed a

concentration of 55 ng/m³. In wipe test samples from computers, TPP proved to be the main component of the OPs analysed.

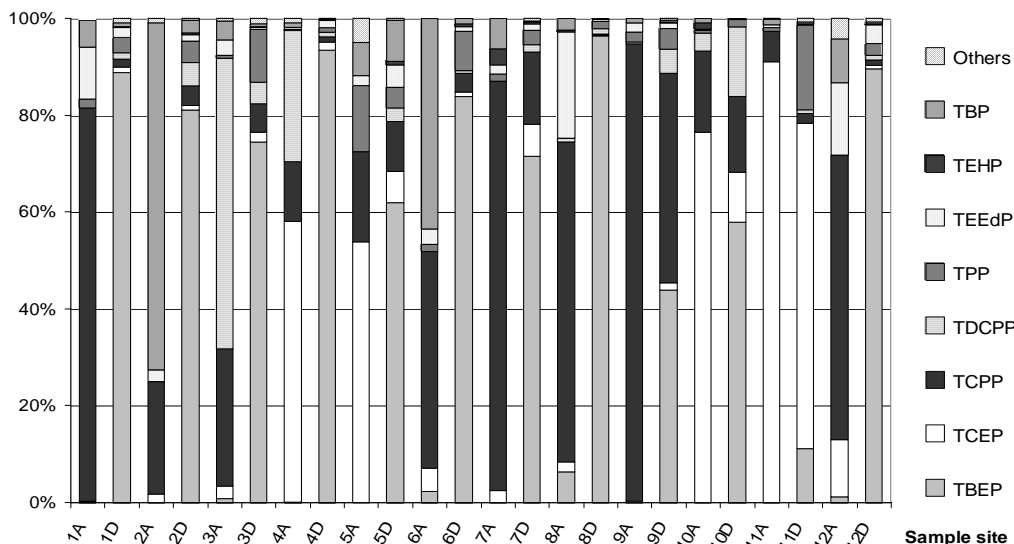


Figure 1. Distribution patterns of OPs in air (A) and dust (D) samples from twelve indoor environments. (Identification of the sample sites in table 2.)

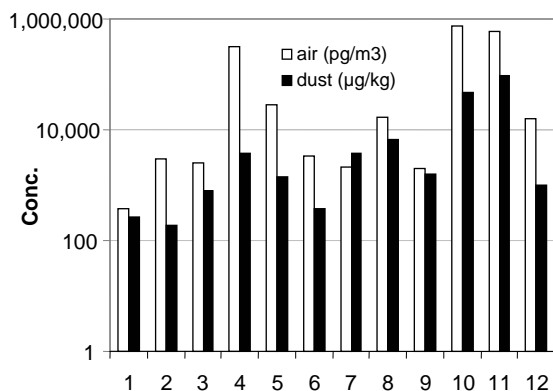


Figure 2. Concentrations of TCEP in air and dust samples. (Identification of sample sites in table 2.)

The correlation between concentrations of OPs in dust and air was more pronounced for the lighter and more volatile OPs, such as TCEP, vapour pressure (V_p); 8 Pa (Fig. 2), compared to TBEP which is heavier and has a V_p of 3×10^{-6}

Table 2. Total conc. of OPs in dust and air samples at 12 sample sites.

N	Sample site	Σ OPs in dust (mg/kg)	Σ OPs in air (ng/m ³)
1	Home 1	28	260
2	Home 2	22	170
3	Day care centre	42	99
4	Hospital wards ^a	230	550
5	Radio shop	22	53
6	Textile shop ^a	37	71
7	Hotel	59	82
8	Prison	5040	860
9	University lobby	110	470
10	Office dust handpicked	470	950
11	Library	140	650
12	Public dance hall	130	130

Pa. The highest level of TCEP, 94 mg/kg dust was found in the *library*, which also had a high concentration in air, 590 ng/m³ (11A and D in Fig 1). A possible source is the acoustic ceiling, which may contain TCEP. TCPP was also detected in all samples. In dust, the highest levels were found in the *office* and in the *University lobby* (73 and 50 mg/kg). These sample sites and the *prison* and *home 1*, showed the highest concentration of TCPP in air 160-570 ng/m³. Since TCPP is used to flame retard upholstery, the main source in these premises was probably furniture. TPP in the plastic material of computers is most likely the source of TPP found in the samples from computer covers and screens, in which it was the most abundant of the analysed compounds.

In summary, there are great differences in the individual and total concentrations of OPs among the sampled sites, but generally, the samples appear to reflect the materials and products used in the indoor environments. Dust from public buildings tends to have approximately 10 times higher levels of TBEP than domestic buildings. For TBEP, TCEP and TCPP, the results in this study are quite comparable to previously published data regarding OPs in dust and air¹⁰⁻¹². These substances may eventually reach the outer environment through various processes, such as ventilation, flushing of dust particles collected during wet cleaning and disposal of dust bags on dumpsites.

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