

## A PILOT STUDY OF THE DETERMINATION OF ORGANOPHOSPHATE FLAME RETARDANTS IN INDOOR AIR

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**Abstract:** In recent years, the production and use of organophosphate flame retardants (OPFRs) have been increased significantly due to their excellent fire resistance and the prohibition of the use of several brominated flame retardants. However, there is little knowledge of levels of OPFRs in the environment, including the indoor environment, especially in Viet Nam. Therefore, the aim of this study is to investigate the occurrence and distribution of 15 OPFRs in indoor air samples collected from 3 districts of Ha Noi city, Viet Nam. Nine out of fifteen OPFRs were detected in the indoor air with the mean concentration of total OPFRs ( $\Sigma$ OPFRs) of 151 ng/m<sup>3</sup> (ranged from 39.3 to 372 ng/m<sup>3</sup>). Congener profiles of OPFRs in dust indoor air samples showed that tris(1-chloro-2-propyl) phosphate (TCPP) was the most predominant compound in all indoor air samples with a mean concentration of 114 ng/m<sup>3</sup> (ranged from 21.1 to 329 ng/m<sup>3</sup>), accounting for 67.5 % (ranged 43.1 - 93.0 %) of the total OPFR levels. The following is tris(2-butoxyethyl) phosphate (TBEP), which was also detected in all samples with a mean concentration of 29.4 ng/m<sup>3</sup>, accounting for 23.9% of the total OPFRs. Whereas triphenyl phosphate (TPP), tris(1,3-dichloroisopropyl) phosphate (TDCPP), tributyl phosphate (TBP), and tri(2-chloroethyl) phosphate (TCEP) were found in some samples with lower concentrations (average value of 2.58; 2.48; 1.36 and 0.50 ng/m<sup>3</sup>, respectively). Concentrations of  $\Sigma$ OPFRs in the environmental apartments (ranged 166.4 - 372.0 ng/m<sup>3</sup>) were higher than those in the individual houses (ranged 39.3 - 134 ng/m<sup>3</sup>), probably attributed to strict requirements for the use of flame-retardant building materials and interior decorations of apartment buildings.

**Keywords:** organophosphate flame retardant; gas chromatograph-mass spectrometry; indoor air.

**Classification numbers:** 3.2.

### 1. INTRODUCTION

Flame retardants (FRs) are chemicals added to materials to prevent or delay the initial phase of a developing fire. They are widely used in building materials, textiles, chemicals, and electronic industries [1]. However, there is now increasing concern about their toxicity to

humans and the environment. Many flame retardants have been restricted or banned for use such as brominated flame retardants. This has led to the use of alternative flame retardant chemicals, such as organophosphate flame retardants (OPFRs) that typically have increased rapidly in recent years [2]. These compounds have been widely used as flame retardants additives in a large variety of products, including plastics, textiles, furniture, building materials, vehicle, electrical and electronic equipment. Additionally, they are also used as plasticizers, stabilizers, electrical and electronic equipment. Additionally, they are also used as plasticizers, stabilizers, antifoaming, and as additives in lubricants and hydraulic fluids, etc. [3]. The widespread use of these compounds has increased globally, specifically OPFRs consumption in 2011 was 500,000 tons and increased to 680,000 tons in 2015, which was accounted for about 30% of the total volume of flame retardants used in the worldwide [4].

Most of the OPFRs are semi-volatile organic compounds. They are mainly used as chemical additives that are not chemically bonded to the materials, so they easily get out of products and release into the surrounding environment by volatilization and abrasion. As a result, OPFRs has widely distributed in the environment. OPFRs have been detected in various environments, including indoor and outdoor air [5, 6], surface water, groundwater, seawater, and drinking water [7, 8], sediment [9], soil [10] and indoor dust [11], especially in aquatic biota, human adipose tissue and breast milk due to their high bioaccumulation potential [12, 13].

Similar to brominated flame-retardant compounds, the increasing use of OPFRs has caused concerns about their adverse effects on the environment, particularly the health of animals and humans because many of them are toxic and persistent. Numerous studies have demonstrated that OPFRs caused adverse effects on aquatic organisms and the human body, including effects on the reproductive system, endocrine disorders, weakened immune system, neurological effects, and potentially carcinogenic. In particular, the chlorinated OPFRs which are highly toxic and persistent, have a low degradation potential and thus may be persistent and accumulate in the environment [14, 15]. Chlorinated OPFRs have been proved to be neurotoxic and carcinogenic [3, 4]. Tri(2-chloroethyl) phosphate (TCEP) and tri(1,3-dichloroisopropyl) phosphate (TDCPP), caused tumor growth in various organs in rodents after long-term exposure and thus are suspect carcinogens [16]. TCEP has been classified as a “potential human carcinogen” (carcinogen category 3) by the EU in 2008 [17]. TDCPP was added to California's Proposition 65 List of Potential Carcinogens in 2011 [18]. Moreover, TDCPP was also identified to have neurotoxic properties [19] and reduced thyroid hormone levels. Exposure to triphenyl phosphate (TPP) and TDCPP has been also associated with altered hormone levels and decreased semen quality in males. In addition, several studies have suggested that OPFRs may be associated with certain effects on human health, such as mucosal irritation and contact dermatitis [20].

Viet Nam does not directly produce OPFRs. However, these compounds can be released into the environment through volatilization and/or abrasion from OPFRs-containing products and materials during use and disposal. As reported by the US Department of Environmental Protection, in today's modern life, the majority of human activity takes place indoors (80-90% of the time) therefore they will be more exposed to indoor pollutants than outdoor pollutants. Various studies have also shown that the concentration of organic pollutants in the indoor environment is higher than those in the outdoor environment. Therefore, the determination of OPFRs in indoor air is needed. A simple, highly sensitive and selective analytical method using gas chromatography coupled with mass spectrometry (GC/MS) was used in this research for the simultaneous determination of fifteen OPFRs in indoor air samples collected from 3 districts of Ha Noi city. As a result, contamination levels and distribution of OPFRs in indoor air are

clarified. A health risk assessment of some detected OPFRs in indoor environment is implemented. To our knowledge, this is the first study to determine the occurrence and distribution of OPFRs in the indoor air in Viet Nam.

## **2. MATERIALS AND METHODS**

### **2.1. Chemicals and materials**

Fifteen organophosphates flame retardant standards (purity > 98 %) were purchased from Wellington Laboratories (Ontario, Canada): triethyl phosphate (TEP); tributyl phosphate (TBP); tri(2-chloroethyl) phosphate (TCEP); tris(1-chloro-2-propyl) phosphate (TCPP, mixture of 3 isomers); dibutyl phenyl phosphate (DBPP); tris(1,3-dichloroisopropyl) phosphate (TDCPP); triphenyl phosphate (TPP); tris(2-butoxyethyl) phosphate (TBEP); 2-ethylhexyl diphenyl phosphate (EHDP); tris(2-ethylhexyl) phosphate (TEHP); tris(2-methylphenyl) phosphate (TOCP); tris(3-methylphenyl) phosphate (TMCP); tris(4-methylphenyl) phosphate (TPCP).

The internal standard Hexamethyl benzene (HMB, 99.5 %) was purchased from the laboratories Ehrenstofer-Schäfer Bgm-Schlosser. Four surrogate standards: d15-TEP (99.1 %), d27-TNBP (98 %), d15-TPHP (98 %), and d12-TCEP (98 %) were purchased from Sigma-Aldrich Japan K.K. (Tokyo, Japan). The working standard solutions of OPFRs were prepared from the stock standard solutions with n-hexane. All solvents used in this study including n-hexane (Hex), acetone (Ace), and ethyl acetate (EtAc) were purchased from Kanto Chemical Co. (Tokyo, Japan) and they were of analytical grade. The polyurethane foam (PUF) plugs (CAS No: 21031 Supelco) were purchased from Supelco (Japan). Glass fiber filters (GFF) (CAS No: WHA1851032 Aldrich) were purchased from Advantec Toyo Kaisha, Ltd. (Tokyo, Japan).

All glassware was firstly cleaned by soak detergent water, and washed with hot chromic acid (including 5 % potassium dichromate in sulfuric acid solution). After carefully rinsed the glassware with deionized water and acetone, the glassware was dried at 250 °C for 5 h prior to usage.

### **2.2. Sample collection**

Indoor air samples (n = 10) were collected from 4 apartments and 6 individual houses in Long Bien district, Cau Giay district, and Thanh Xuan districts of Ha Noi city in summer (June 2018). These are new, developing districts with high population densities and many new apartment buildings. During sampling, the presence of consumer products, furniture, carpets, curtains, polymers, and textile products as well as room area, wall/floor material in the sampling locations were recorded. Detailed information of the collected samples is listed in Supplementary Table 1.

The indoor air samples were all taken in the living room during the daytime by a low-volume air sampler (model MP-W5P, Shibata, Japan). During indoor air sampling, all adjacent doors and windows were closed. The air samples were collected on polyurethane foam (PUF) plugs and glass fiber filter (GFF) at a sampling rate of 5 L/min for 10 hours each. The samplers (pre-cleaned with ethyl acetate prior to use to avoid possible contamination) were installed at a height of ~ 0.5 m above the ground/floor at each sampling location. After sampling, the PUFs were immediately placed in brown glass vials, the GFFs were wrapped in ethyl acetate solvent-rinsed aluminum foil and sealed in polyethylene bags. All the samples are stored at -20 °C (Thermo Scientific UGL-2320V) until analysis (no more than 1 week).

Table 1. Detailed information on sampling sites.

No	Name	District	Type	Number of electrical equipment	Furniture
1	N1	Long Bien	House	6	tiled floor, curtains, sofa, plaster ceiling
2	N2	Long Bien	House	4	tiled floor, wooden sofa
3	N3	Cau Giay	apartment	6	wooden floor, curtains, sofa, plaster ceiling
4	N4	Cau Giay	House	6	tiled floor, wooden sofa
5	N5	Cau Giay	House	5	tiled floor, curtains, wooden sofa
6	N6	Cau Giay	House	5	tiled floor, sofa
7	N7	Thanh Xuan	apartment	8	wooden floor, curtains, sofa, wallpaper, plaster ceiling
8	N8	Thanh Xuan	apartment	7	wooden floor, curtains, sofa, wallpaper, plaster ceiling, carpet
9	N9	Thanh Xuan	apartment	7	wooden floor, curtains, wooden sofa plaster ceiling, carpet
10	N10	Thanh Xuan	House	5	tiled floor, wooden sofa

### 2.3. Sample extraction

Samples were extracted immediately after collection and were analyzed within a week. The extraction of samples was carried out according to the method described by Xiang *et al.* [21] with some modifications to optimize for the extraction of OPFRs in indoor air samples. Prior to extraction, 20  $\mu\text{L}$  mixture of the surrogate solution (500 ng/mL each) is spiked into each sample. Extraction was conducted by accelerated solvent extractor (ASE 350, Dionex, Thermo Fisher Scientific, Inc.) with mixture of n-hexane/acetone (1:1, v/v), cell pressure: 1500 psi; cell temperature: 100  $^{\circ}\text{C}$ ; preheat time: 1 mins; heat time: 5 mins; cycles: 2; static time: 10 mins; flush volume: 50 %; purge time: 100 secs. The extracts were transferred to new test tubes and concentrated to approximately 1 mL using a rotary evaporator. After that, 5 mL hexane was added into the extract and evaporated to 100  $\mu\text{L}$  by using a gentle nitrogen stream. Prior to analysis by GC/MS instrument, 10  $\mu\text{L}$  internal standard solution was added into the final extract.

### 2.4. Instrumentation and analysis

The analysis of OPFRs was performed by gas chromatography coupled with a mass spectrometer (GC/MS; QP-2010 Plus, Shimadzu, Japan). One  $\mu\text{L}$  of the final extract was injected into a DB-5ms column (30 m  $\times$  250  $\mu\text{m}$   $\times$  0.25  $\mu\text{m}$ , Agilent) using the splitless mode. Ultra-high purity helium was used as the carrier gas with a constant flow rate of 1 mL/min. The injection temperature was set at 250  $^{\circ}\text{C}$ . The column temperature program started at an initial temperature of 40  $^{\circ}\text{C}$  and held for 2 min, then increased to 310  $^{\circ}\text{C}$  at a rate of 8  $^{\circ}\text{C}/\text{min}$  and held at 310  $^{\circ}\text{C}$  for 4 min. The mass spectrometer was run in selected ion monitoring (SIM) mode with a dwell time of 30 ms. Ionization at a source temperature and electron energy of

250 °C and 70 eV, respectively. The quadrupole and interface temperatures were set at 150 °C and 310 °C, respectively. Analysis conditions on GC/MS were referred according to Hartmann *et al.* [22].

## **2.5. Quality assurance and quality control**

Quality assurance and quality control were carried out by analyzing procedural blanks (n = 5), spiked blanks (n = 5, spiked OPFRs standards into PUF), using the same extraction and analytical method like the analysis of environmental samples. The internal standard method was used for the quantification of each target compound.

Ten concentration points that ranged from 0.1 to 500 ng/mL of individual OPEs were used for creating calibration curves. The calibration curves were generated across a wide range of concentrations with good linearity (the regression coefficients of the calibration curves,  $R^2 > 0.997$ ). To avoid potential degradation of OPFRs during storage, all samples were placed in brown glass vials or covered with aluminum foil, sealed in airtight polyethylene bags, kept at -20 °C until analysis.

The limit of detection (LOD) was determined as the average value of the individual OPFRs plus three times the standard deviation of the procedural blanks. LOD for the different OPFRs ranged from 0.076 to 0.43 ng/m<sup>3</sup>. The limit of quantification (LOQ) was determined as the average value of the individual OPFRs plus ten times the standard deviation of the procedural blanks, ranged from 0.25 to 1.45 ng/m<sup>3</sup> depending on the compound. Recoveries of fifteen OPFRs spiked into indoor air samples (n = 5) were calculated to assess the accuracy of the method.

During these analyses, concentrations of OPFRs below the LODs were assigned a value of zero for data analysis. In this study, the total concentration of OPFRs was the total amount of detected target compounds.

## **3. RESULTS AND DISCUSSION**

### **3.1. Laboratory contamination control and method validation**

Background contamination is a major problem in the analysis of OPFRs. Therefore, in order to effectively reduce background contamination in the process of sample treatment, it is necessary to identify the potential sources of pollution in the laboratory. Analyzing the level of OPFRs in air samples requires a careful examination of the sources of background contamination. Because OPFRs were widely used in many applications such as flame retardants and plasticizers, the usage of any plastic and rubber materials should be avoided to minimize possible contamination of the samples during sampling, storage, and extraction. Some tools and equipment used in the sample collection and handling processes such as PUF, GFF, parts of low-volume air sampler (e.g. PP tubes, pipet tips, the internal part of the sampling and analysis device) may contain OPE, so pre-cleaning with a solvent strong enough to extract the OPE is required. We found that EtAc is powerful enough to clean all target OPEs [23]. Another prominent source of OPFRs contamination may be indoor dust. To reduce the contamination, all glassware must be pre-cleaned with Acetone and EtAc, covered with aluminum foil to avoid dust contamination and pre-cleaned SPE columns.

The average recoveries of 15 OPFRs in 5 indoor air samples spiked standards ranged from 82.3 to 109 %. Recoveries of the surrogate standards generally ranged from 78.3 – 95.6 %.

Concentrations of most OPFRs were below detection limits in all blank samples analyzed, and thus, contamination during extraction and analysis can be excluded. Only TCPP and TBEP were detected in some of the blank samples, on average at 0.41 ng/m<sup>3</sup> and 0.12 ng/m<sup>3</sup>, respectively. However, all measured concentrations of OPFRs in blank samples were subtracted from the sample values. The relative standard deviations (RSD) of OPFRs were low, ranged between 3.86 % and 4.78 %. These results demonstrated that this method had good accuracy and repeatability and suitable for the determination of OPFRs in indoor air samples.

### 3.2. Concentration of OPFRs in indoor air

A fast and accurate analytical method with good recovery has been used for the analysis of OPFRs in indoor air samples collected from three districts of Ha Noi City. Concentrations and detection frequency of fifteen OPFRs in 10 indoor air samples are summarized in Table 2.

Table 2. Concentrations of OPFRs in indoor air samples in Ha Noi (ng/m<sup>3</sup>).

Compound	Long Bien. D		Cau Giay. D				Thanh Xuan. D				DF (%)
	N1	N2	N3	N4	N5	N6	N7	N8	N9	N10	
TEP	0	0	0	0	0	0	0	0	0	0	0
TBP	1.81	0.18	1.08	0.10	1.0	0	5.30	3.21	0.86	0	80
DBPP	0	0	0	0	0	0	0	0	0	0	0
TPP	3.74	2.43	2.78	4.63	5.36	0.56	2.35	1.98	1.06	0.88	100
TBEP	22.7	21.3	125	10.7	10.9	5.87	14.7	35.4	21.7	25.4	100
EHDP	0.49	0	1.53	0	0.34	0	0.53	0.87	0.26	0	60
TEHP	0	0	0	0	0	0	0	0	0	0	0
TOCP	0	0	0	0	0	0	0	0	0	0	0
TMCP	0	0	0	0	0	0	0	0	0	0	0
TPCP	0	0	0	0	0	0	0	0	0	0	0
TCEP	1.20	0.25	0.46	0.32	0.46	0	0.99	1.29	0	0	70
TCPP	98.0	31.4	116	23.2	35.2	32.8	316	329	141	21.1	100
TDCPP	5.98	3.94	0	6.73	6.62	0	0	0	0	1.52	50
ΣCl-OPs	105	35.6	116	30.3	42.3	32.8	317	331	141	22.6	
ΣNon-Cl-	28.7	23.9	131	15.4	17.7	6.44	22.9	41.5	25.6	26.3	
ΣOPFRs	134	59.5	248	45.7	60.0	39.3	340	372	166	48.9	

TCPP = Σ mixture of 3 isomers of TCPP , ΣCl-OPs = ΣChlorinated organophosphate;

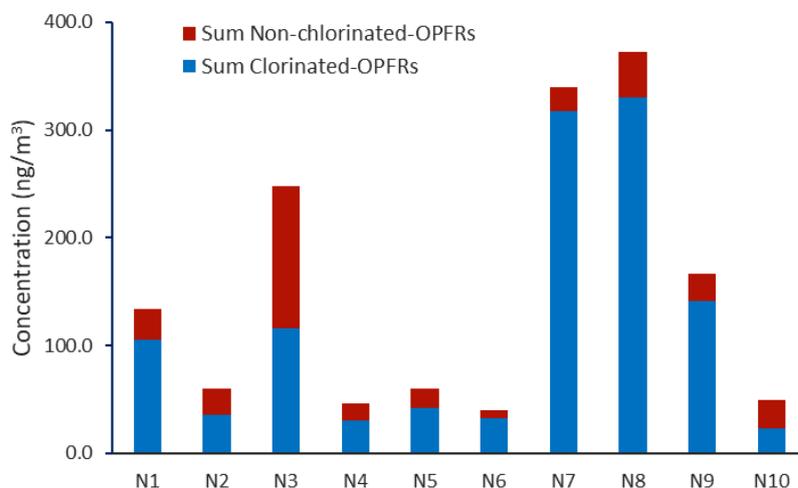
ΣNon-Cl- = ΣNon-chlorinated organophosphate, ΣOPFRs = total concentration of all compounds;

N3, N7, N8, N9: samples were collected in apartments; N1, N2, N4, N5, N6, N10: samples were collected in individual houses.

Analysis results showed that nine out of 15 OPFRs were detected in almost all of indoor air samples, including TCEP, TCPP (mixture of 3 isomers), TDCPP, TBP, TPP, TBEP, EHDP and the detection frequency of each OPFR compound varied among houses and apartments. The

total concentrations of OPFRs in indoor air samples (sum concentrations in vapor and particulate phases) varied widely among various homes, ranged from 39.3 to 372 ng/m<sup>3</sup> (mean 151 ng/m<sup>3</sup>). Among the detected OPFRs, TCPP was the prominent congeners detected in all indoor air samples with the highest level. Its occurrence and concentration varied among the apartments and houses, ranged from 31.4 to 98.0 ng/m<sup>3</sup> (mean 64.7 ng/m<sup>3</sup>) in Long Bien district and 23.2 to 116 ng/m<sup>3</sup> (mean 51.8 ng/m<sup>3</sup>) in Cau Giay district and 21.1 to 329 ng/m<sup>3</sup> (mean 202 ng/m<sup>3</sup>) in Thanh Xuan district. TBEP and TPP were also found with a detection frequency of 100 % indoor air samples with concentrations ranged from 5.87 to 125 ng/m<sup>3</sup> (mean 29.4 ng/m<sup>3</sup>) and 0.56 to 5.36 ng/m<sup>3</sup> (mean 2.58 ng/m<sup>3</sup>), respectively. TDCPP, TBP, TCEP, and EHDP were detected in some of the samples with low concentrations.

The total concentrations of chlorinated OPFRs (including TCEP, TCPP, TDCPP) and the total concentrations of non-chlorinated OPFRs (including TEP, TBP, TPP, TBEP, EHDP, TEHP, TOCP, TMCP, and TPCP) ranged from 22.6 to 331 ng/m<sup>3</sup> (mean 117 ng/m<sup>3</sup>), and ranged from 6.44 to 131 ng/m<sup>3</sup> (mean 34.0 ng/m<sup>3</sup>), respectively. Composition distribution of chlorinated OPFRs and non-chlorinated OPFRs in different indoor air samples were illustrated in Figure 1.



*Figure 1.* The concentration of chlorinated OPFRs and non-chlorinated OPFRs in indoor air at different locations in Ha Noi.

In general, chlorinated OPFRs were the predominant compounds in indoor air samples (accounting for an average of 71.9 % of the total median of OPFRs detected), while non-chlorinated OPFRs only accounted for a minor contribution to the sum concentrations (mean 28.1 %). Among chlorinated OPFRs, TCPP was the main compound with the mean concentration of 114 ng/m<sup>3</sup> (21.1 – 329 ng/m<sup>3</sup>), followed by TDCPP and TCEP with mean concentrations of 2.48 ng/m<sup>3</sup> (< LOD – 6.73 ng/m<sup>3</sup>) and 0.50 ng/m<sup>3</sup> (< LOD – 1.29 ng/m<sup>3</sup>), respectively. Relatively high levels of chlorinated OPFRs were observed in indoor air samples indicating that chlorinated OPFRs might be used widely in a variety of consumer products and materials in Viet Nam. For the non-chlorine OPFRs, TBEP and TPP were detected in all samples with mean concentrations of 29.4 ng/m<sup>3</sup> (5.87 – 125 ng/m<sup>3</sup>) and 2.58 ng/m<sup>3</sup> (0.56 – 5.36 ng/m<sup>3</sup>), respectively. TBP and EHDB were detected at low levels in some samples with mean concentrations of 1.36 ng/m<sup>3</sup> (< LOD – 5.30 ng/m<sup>3</sup>) and 0.41 ng/m<sup>3</sup> (< LOD – 1.53

ng/m<sup>3</sup>), respectively. TEP, DBPP, TEHP, TOCP, TMCP, and TPCP were almost not detected in any samples.

### 3.3. Comparison with studies from other countries

The comparison of median concentrations for  $\Sigma$ OPFRs in indoor air in Viet Nam and various countries were shown in Figure 2. The mean concentration of  $\Sigma$ OPFRs in this study (151 ng/m<sup>3</sup>) was higher than those reported in Norway (mean 98.8 ng/m<sup>3</sup>) [24] and much higher than those in studies from Australia (mean 44.0 ng/m<sup>3</sup>) [25]. In particular, the mean levels of OPFRs in this study was approximately 30 times higher than that from the study of Nepal (mean 5.2 ng/m<sup>3</sup>) [26]. According to Yadav *et al.*, the lower levels of OPFRs in indoor air in Nepal are attributed to the lower use of OPFRs in Nepal compared to other countries. However, the mean concentration of  $\Sigma$ OPFRs in this study was comparable and slightly lower than those reported in Sweden (mean 154 ng/m<sup>3</sup>) [27], Germany (mean 164.3 ng/m<sup>3</sup>) [28] and much lower than those observed in Japan (mean 217.1 ng/m<sup>3</sup>) [29], the US (mean 426 ng/m<sup>3</sup>) [30]. As discussed in the Introduction, OPFRs are found ubiquitously in indoor dust and air worldwide because their consumption has increased as PBDEs have been gradually phased out [2, 4, 5, 6]. This increase has attracted concern about indoor pollution by OPFRs and potential risks on human health, especially with regard to their occurrence in indoor air. High concentrations of OPFRs in indoor air in Japan and in the United States is probably due to the strict fire safety regulations applied in those countries as well as being at the forefront of using OPFRs as alternatives for PBDEs [18, 31, 32].

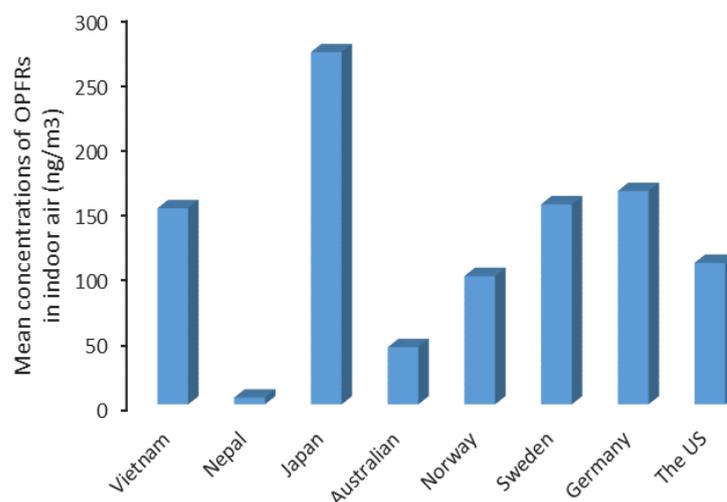


Figure 2. Comparison of mean concentrations (ng/m<sup>3</sup>) of  $\Sigma$ OPFRs in indoor air from studies in other countries.

### 3.4. Composition profile and emission sources of OPFRs in indoor air

The composition of OPFRs in indoor air samples in three districts of Ha Noi city is shown in Figure 3. TCPP and TBEP were detected in 100 % samples, which contributed to 67.5 % and 23.9 % of  $\Sigma$ OPFRs. While, other OPFRs such as TDCPP, TCEP, TPP, TBP, and EHDP were detected in some samples with small levels and only accounted for an average from 0.5 % to

1.6 % of the total of OPFRs. The high level of TCPP in indoor air samples of this study probably indicates the high usage of TCPP-containing products and materials indoors. Since TCPP and TCEP are mainly used as flame retardants in plastic products, polyurethane foams, textiles, insulation and furniture upholstery [16], therefore furniture, sofas, mattress, curtains, baby products, spray foam insulation, etc. are may be the main sources of these compounds to the indoor environment. However, TCEP has not been used because of its carcinogenic potential and it has been gradually replaced by other flame retardants, primarily TCPP [2]. That may be the reason why TCPP accounted for high levels in indoor air samples. In many studies in other countries, TCPP was also the most predominant OPFR in the indoor air [22, 25, 27, 30]. TBEP is an important additive. It was used in materials and furniture such as floors, furniture, toys, construction materials, curtains, etc. and in this study, a few samples with high levels were also found in modern apartments with wooden floors. TPP was used in the plastic material of computers is most likely the source of TPP found in the samples from computer covers and screens, T.V screens, sound systems. TEP, DBPP, TOCP, TMCP, and TPCP were not detected in any of the samples, which is consistent with expectations since these substances are mainly used in industrial processes.

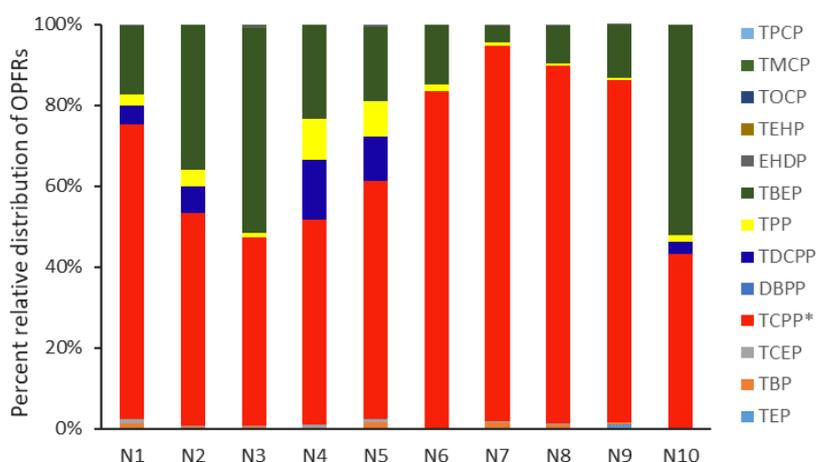


Figure 3. Relative distribution of OPFRs concentrations in indoor air samples in three districts of Ha Noi city.

In general, the concentration of OPFRs, especially TCPP in indoor air samples collected in apartments (including N3, N7, N8, and N9, ranged from 116 to 329 ng/m<sup>3</sup>) were higher than those in individual houses (including N1, N2, N4, N5, N6, and N10, ranged from 21.1 to 98.0 ng/m<sup>3</sup>). The total concentrations of OPFRs in indoor air samples collected in apartments ranged from 140 to 372 ng/m<sup>3</sup> (mean 273 ng/m<sup>3</sup>). Meanwhile, the total concentration of OPFRs in indoor air samples collected in individual houses ranged from 39.3 to 166 ng/m<sup>3</sup> (mean 70.0 ng/m<sup>3</sup>). The concentration of TCPP in indoor air samples collected in apartments was on average 3-4 times higher than those in individual houses. This phenomenon can be explained by strict requirements about fire resistance of building materials and interior decorations of apartment buildings such as upholstered furniture, acoustic ceilings, wooden flooring [33, 34]. Specifically, samples (N3, N7, N8, and N9) were collected in apartments with plaster ceiling and wooden floor while samples (N1, N2, N4, N5, N6, and N10) were collected in individual houses with tiled floor and no plaster ceiling. Besides that, the apartments in this study are apartments of young families that have small areas, enclosed space, living rooms directly connected to the

kitchens, modern design style with lots of curtains, carpets, large sofas, and a lot of electrical and electronic equipment. This suggests that the different levels of individual OPFR components in apartments and individual houses may have resulted from the use of building materials and interior decoration, furniture, consumer products, electrical and electronic equipment as well as ventilation in each home.

#### 4. CONCLUSION

In this study, the occurrence and distribution of 15 OPFRs in indoor air environments in three districts of Ha Noi city were investigated. The results indicated that nine out of fifteen OPFRs were detected in the indoor air samples with the median concentrations of  $\Sigma$ OPFRs was 151 ng/m<sup>3</sup>. TCPP, TBEP, and TPP were detected in all samples. In particular, TCPP (chlorinated-OPFR) was the predominant compound, accounting for 67.5 % of  $\Sigma$ OPFRs on average, followed by TBEP (average 23.9 %) and TPP (average 3.2 %). While other OPFRs were only found in some samples with small levels. The relatively high concentrations of OPFRs in indoor air samples from mainly in apartments indicated that the significant usage of these compounds in building materials, interior decorations, and consumer products. However, to give an overall picture of the distribution of OPFRs in the air environment as well as their effects on human health, more comprehensive and in-depth studies on OPFRs are needed in the future.

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