

Characteristics of Organophosphate Ester Formation during Smoking

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Abstract

This study examines the occurrence of organophosphate esters (OPEs) in cigarettes and sidestream cigarette smoke and to see the OPE formation characteristics during smoking. All seven OPEs in both gas and particulate phases were measured in sidestream cigarette smoke for four brands of cigarettes. Tributyl phosphate (TBP), tris(2-butoxyethyl) phosphate (TBEP), tris(2-chloroethyl) phosphate (TCEP), and triphenyl phosphate (TPP) were found frequently. Median total OPE increases in the air samples during smoking were 56.2 ng per cigarette for gas-phase OPEs and 2360 ng per cigarette for particulate-phase OPEs. TBP and TCEP could be absorbed to particles in air more readily than alkanes as seen from the correlation line between gas-particle partition coefficients (K_p) and the subcooled liquid vapor pressures (P_L°) for alkanes. Furthermore, TBP was determined in the cigarettes. Median total OPE decreases in the cigarette samples during smoking were 1200 ng per cigarette. The combustion reaction increased TBP and TBEP levels in cigarettes, and particulate-phase TBEP in air appeared to influence the production of TBP, TCEP, and TPP. TBP and TBEP in cigarettes likely affect the production of TBP, TBEP, TCEP, and TPP in air during smoking.

Keywords: cigarette, sidestream cigarette smoke, organophosphate esters, gas-particle partitioning coefficient, formation characteristics

1. Introduction

Organophosphate esters (OPEs) are a group of chemicals widely used as organic plasticizers, flame retardants, hydraulic fluids, and other industrial products. The use of OPEs as replacements for polybrominated diphenyl ethers and other brominated flame retardants has recently increased (Brommer et al., 2012; Van der Veen et al., 2012). Global consumption of OPEs was 186 000 tons in 2001 and increased to 292 000 tons in 2011 (Marklund et al., 2005; Townsend Solutions, 2012). In this situation, OPEs have been detected in a variety of environments (Kawagoshi et al., 1999; Andresen et al., 2004; Chung et al., 2009; Fries et al., 2011; Shimazu et al., 2013; Salamova et al., 2014; Lai et al., 2015).

Some of the OPEs show carcinogenic and/or neurotoxic properties. The World Health Organization has listed tris(2-chloroethyl) phosphate (TCEP) and tris(1,3-dichloro-2-propyl) phosphate (TDCPP) as carcinogenic compounds (WHO, 1998). Tris(2-butoxyethyl) phosphate (TBEP) and tris(2-chloroisopropylethyl) phosphate are also suspected to be carcinogenic (WHO, 1998; WHO, 2000). TBEP, tributyl phosphate (TBP), TCEP, and triphenyl phosphate (TPP) are considered neurotoxins (WHO, 1991a; WHO, 1991b; WHO, 1998; WHO, 2000). Triethyl phosphate (TEP) is considered a weak enzyme inhibitor (Gosselin et al., 1984). The use of OPEs has therefore been restricted in multiple countries. TCEP is shown in the Candidate List of primary concern substances issued by the European Union (European Chemicals Agency, 2009). The use of TCEP, TDCPP, and tris(1-chloro-2-propyl) phosphate as flame retardants in toys and children's products is prohibited by the US (TÜV Rheinland Group, 2013).

Shimazu (2016) has reported particulate-phase OPEs in cigarette smoke. Little information, however, is available on OPEs in sidestream cigarette smoke, which mainly affects passive smokers. To evaluate the health effects of OPEs in cigarette smoke, OPE partition between the gas and particulate phases should be elucidated. This study examined the occurrence of OPEs in gas and particulate phases and their gas/particulate partitioning in sidestream cigarette smoke.

In addition, Shimazu (2016) has reported OPEs in the cigarette body prior to smoking. To assess OPE emissions from cigarettes and their formation characteristics during smoking, this study also examined the occurrence of

OPEs in cigarettes and cigarette butts.

2. Materials and Methods

2.1 Samples

Four brands of cigarettes were investigated in this study. Tar and nicotine contents were 6–19 mg and 0.5–1.4 mg per cigarette, respectively. OPE concentrations in air and cigarette samples before and after cigarettes had been smoked were measured.

Four air samples were collected before and after cigarettes of brands A–D had been smoked. The air sampling room was 2.5 m high, 5.3 m long, and 5.0 m wide, with a volume of approximately 66 m³. Each air sample was collected prior to smoking using a high-volume air sampler (HV-500R; Sibata Scientific Technology Ltd., Souka, Japan) over a period of 1 h at a flow rate of 400 L/min, giving a sampling volume of 24 m³. Particulate matter was collected on a quartz fiber filter (QR-100; Advantec, Tokyo, Japan). Particles with diameters of 0.3 µm were taken by the filter with a minimum particle collection efficiency of 99.99% when the air was passed through the sampler at a velocity of 5 cm/s. Gas-phase OPEs were collected on two polyurethane foam plugs (080130-0941A; Sibata Scientific Technology Ltd.) After the initial air samples had been collected, the door and windows of the sampling room were left open for approximately 1 h. The door and windows were then closed, and two cigarettes were smoked in the room. Sidestream smoke samples were collected using the high-volume air sampler over a period of 2.75 h at a flow rate of 400 L/min, giving a sampling volume of 66 m³. Particulate-phase OPEs were collected on a quartz fiber filter, and gas-phase OPEs were collected on two polyurethane foam plugs. The filters and polyurethane foam plugs were then analyzed as described below.

OPE levels in cigarettes before and after smoking were also determined. Cigarette samples (before smoking) and butt samples (after smoking) were analyzed. The arithmetic means of the weights of the four brands of cigarettes before smoking (n = 4) were 0.107–0.181 g for the filters and 0.525–0.586 g for the leaves. Cigarette weights after smoking (n = 4) were 0.158–0.285 g for the filters and 0.075–0.078 g for the leaves. Whole filters and leaves of cigarette samples were analyzed as described below. After each brand was smoked, whole filters and leaves of the butt samples were also analyzed.

2.2 OPEs

The target compounds were the seven OPEs listed in Table 1. These OPEs have been frequently detected in multiple environmental media and are known to exert toxic effects. The standard of OPEs were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) and diluted with acetone and hexane to produce calibration standards.

Table 1. OPEs measured in this study

OPEs	Abbreviations	CAS No.
Tris(2-butoxyethyl) phosphate	TBEP	78-51-3
Tributyl phosphate	TBP	126-73-8
Tris(2-chloroethyl) phosphate	TCEP	115-96-8
Tris(1,3-dichloro-2-propyl) phosphate	TDCPP	13674-78-8
Tris(2-ethylhexyl) phosphate	TEHP	78-42-2
Triethyl phosphate	TEP	78-40-0
Triphenyl phosphate	TPP	115-86-6

Note. The abbreviations are used in this study.

2.3 Analytical Methods and Instruments

Each quartz fiber filter was weighed with an electronic balance before and after smoking. Each filter that had been used to sample air after smoking was cut into 16 sections. All sections of the filter were set in 260-mL bottles and extracted with 100 mL of hexane for pesticide residue and polychlorinated biphenyl analysis by Wako Pure Chemical Industries, Ltd. (Tokyo, Japan) for 15 min in an ultrasonic bath. The extract was concentrated to 3 mL with a rotary evaporator, and passed through a disposable filter (Whatman Puradisc 25 TF; GE Healthcare Life Sciences, Maidstone, UK). The extract was then concentrated to 1.5 mL under nitrogen flow.

Finally, 200 μL of internal standard mixture and hexane were added to bring the volume to 2 mL.

Two polyurethane foam plugs were used in each experiment. Each polyurethane foam plug that had been used to sample air after smoking was cut into 16 sections. All sections were set in 260-mL bottles and extracted with 220 mL of hexane for 15 min in an ultrasonic bath. The separate extracts of the two foam plugs were each concentrated to 3 mL with a rotary evaporator and then mixed. Next, the extract was passed through a disposable filter and concentrated to 1.5 mL under nitrogen flow. Finally, 200 μL of internal standard mixture and hexane were added to bring the volume to 2 mL.

Cigarette filters and leaves before and after smoking were analyzed. Each sample was weighed, placed into a cellulose extraction thimble (Whatman high-performance cellulose extraction thimbles; GE Healthcare Life Sciences), and extracted with 100 mL of hexane for 15 min in an ultrasonic bath. The extract was concentrated to 3 mL using a rotary evaporator and passed through a disposable filter device. Next, the extract was concentrated to 1.5 mL under nitrogen flow. Finally, 200 μL of internal standard mixture and hexane were added to bring the volume to 2 mL.

OPEs in the extracts were injected in splitless mode in an HP-5MS capillary column (30-m long, 0.25-mm i.d., 0.25- μm film thickness; Agilent Technologies, Santa Clara, CA, USA) with a gas chromatograph-mass spectrometer (5975B inert XL E/CI MSD; Agilent Technologies). The gas chromatograph was used with a sample volume of 2 μL and an injection port temperature of 250°C. The oven temperature program started at 70°C (held for 1.5 min), and was then increased by 20°C/min to 180°C, followed by an increase of 5°C/min to 280°C (held for 1 min). Helium was used as the carrier gas. The mass spectrometer was operated in electron impact ionization mode and an electron energy of 70 eV. After each analyte was identified using two representative fragment ions, it was quantified using the largest fragment ion. Quantification was performed with an internal standard calibration method using standards containing the seven OPEs shown in Table 1 and three deuterated polycyclic aromatic hydrocarbons (525 Fortification Solution, 48230-U; Supelco, Bellefonte, PA, USA).

Total suspended particulate concentration ($\mu\text{g}/\text{m}^3$) was defined as the difference between the weight of the quartz fiber filters before and after air sampling divided by 24 m^3 for a sample collected before cigarettes had been smoked or 66 m^3 for a sample collected after cigarettes had been smoked.

3. Results and Discussion

3.1 Gas-phase and Particulate OPEs in Air Samples

Three gas-phase OPEs were detected in the air samples before cigarettes had been smoked (Table 2). Gas-phase TBP was detected in seven of the 16 samples; the highest concentration detected was 3.10 ng/m^3 . The total gas-phase OPE concentrations before smoking peaked at 9.72 ng/m^3 .

All seven gas-phase OPEs were detected in the air samples after cigarettes had been smoked (Table 2). TBP and TCEP were detected in 11 of the 16 samples. TPP was detected in nine samples. The median concentration of TCEP, which was the most abundant gas-phase OPE measured after smoking, was 2.10 ng/m^3 (range: Not detected to 3.67 ng/m^3). The median of the total gas-phase OPE concentrations after smoking was 4.77 ng/m^3 (range: Not detected to 16.6 ng/m^3). The concentrations of gas-phase OPEs in the air samples were higher after smoking. The medians of these concentration differences before and after smoking were 0.01 ng/m^3 for TBP, 2.10 ng/m^3 for TCEP, and 0.11 ng/m^3 for TPP.

Three particulate-phase OPEs were detected in the air samples before cigarettes had been smoked (Table 3). TCEP was detected in 11 of the 16 samples. TBP was detected in seven samples, and tris(2-ethylhexyl) phosphate (TEHP) was detected in one sample. The median concentration of TCEP, which was the largest particulate-phase OPE measured before smoking, was 2.35 ng/m^3 (range: Not detected to 6.57 ng/m^3). The highest particulate-phase OPE concentration before smoking was 10.8 ng/m^3 .

All seven particulate-phase OPEs were detected in the air samples after cigarettes had been smoked (Table 3). TBP was detected in all 16 samples. Other OPEs were detected in 15 samples (TBEP and TCEP), 13 samples (TPP), seven samples (TEHP), and one sample (TDCPP and TEP). The median concentration of TBEP, which was the largest particulate-phase OPE measured after smoking, was 64.7 ng/m^3 (range: Not detected to 103 ng/m^3). The median of the total particulate-phase OPE concentrations after smoking was 74.2 ng/m^3 (range: 7.50–115 ng/m^3). The concentrations of particulate-phase OPEs in the air samples were higher after smoking. The medians of these concentration differences before and after smoking were 64.7 ng/m^3 for TBEP, 4.48 ng/m^3 for TBP, 0.68 ng/m^3 for TCEP, and 0.97 ng/m^3 for TPP.

The median concentration of suspended particulate matter before smoking was 21 $\mu\text{g}/\text{m}^3$ (range: 8–33 $\mu\text{g}/\text{m}^3$).

After smoking, the median was $104 \mu\text{g}/\text{m}^3$ (range: $73\text{--}152 \mu\text{g}/\text{m}^3$).

Table 2. Gas-phase OPEs in air samples

	Brand A		Brand B		Brand C		Brand D	
	Before	After	Before	After	Before	After	Before	After
TBEP	ND (0/4)	0.84 (2/4)	ND (0/4)	0.71 (2/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)
	[ND]	[ND-2.69]	[ND]	[ND-5.27]	[ND]	[ND]	[ND]	[ND]
TBP	ND (0/4)	7.37 (4/4)	0.98 (3/4)	ND (0/4)	ND (1/4)	2.07 (3/4)	1.63 (3/4)	1.67 (4/4)
	[ND]	[2.34-7.83]	[ND-2.61]	[ND]	[ND-3.10]	[ND-4.35]	[ND-2.32]	[1.42-2.22]
TCEP	ND (0/4)	2.19 (4/4)	ND (1/4)	2.55 (4/4)	ND (0/4)	ND (0/4)	ND (0/4)	2.26 (3/4)
	[ND]	[1.15-2.76]	[ND-0.48]	[1.92-3.67]	[ND]	[ND]	[ND]	[ND-2.83]
TDCPP	ND (0/4)	ND (1/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)
	[ND]	[ND-3.70]	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]
TEHP	ND (0/4)	0.80 (2/4)	ND (0/4)	2.23 (4/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)
	[ND]	[ND-1.92]	[ND]	[0.43-2.23]	[ND]	[ND]	[ND]	[ND]
TEP	ND (0/4)	ND (1/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)
	[ND]	[ND-0.56]	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]
TPP	ND (0/4)	1.59 (4/4)	ND (1/4)	2.30 (4/4)	ND (0/4)	ND (1/4)	ND (0/4)	ND (0/4)
	[ND]	[0.23-2.15]	[ND-6.63]	[2.11-2.49]	[ND]	[ND-0.53]	[ND]	[ND]

Note. The upper values show median concentration (detection rate) and the lower values show [concentration range]. All units are ng/m^3 . ND means Not detected.

Table 3. Particulate-phase OPEs in air samples

	Brand A		Brand B		Brand C		Brand D	
	Before	After	Before	After	Before	After	Before	After
TBEP	ND (0/4)	59.2 (4/4)	ND (0/4)	78.8 (4/4)	ND (0/4)	64.1 (4/4)	ND (0/4)	34.8 (3/4)
	[ND]	[41.4-83.7]	[ND]	[67.9-103]	[ND]	[34.5-78.4]	[ND]	[ND-62.9]
TBP	1.55 (3/4)	6.72 (4/4)	0.32 (2/4)	6.69 (4/4)	ND (1/4)	3.71 (4/4)	ND (1/4)	3.87 (4/4)
	[ND-7.71]	[5.12-7.16]	[ND-4.09]	[5.91-8.53]	[ND-0.86]	[3.02-5.20]	[ND-0.82]	[1.86-5.37]
TCEP	4.57 (4/4)	4.09 (4/4)	2.62 (4/4)	3.55 (4/4)	1.91 (3/4)	3.27 (4/4)	ND (0/4)	2.70 (3/4)
	[3.12-6.57]	[3.79-4.92]	[0.97-3.07]	[2.96-3.76]	[ND-3.03]	[2.66-3.62]	[ND]	[ND-2.94]
TDCPP	ND (0/4)	ND (1/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)
	[ND]	[ND-3.91]	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]
TEHP	ND (0/4)	1.45 (4/4)	ND (0/4)	0.74 (2/4)	ND (1/4)	ND (1/4)	ND (0/4)	ND (0/4)
	[ND]	[0.47-1.99]	[ND]	[ND-2.19]	[ND-1.88]	[ND-0.59]	[ND]	[ND]
TEP	ND (0/4)	ND (1/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)
	[ND]	[ND-0.15]	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]
TPP	ND (0/4)	1.08 (4/4)	ND (0/4)	0.79 (4/4)	ND (0/4)	0.55 (2/4)	ND (0/4)	0.99 (3/4)
	[ND]	[0.96-1.95]	[ND]	[0.64-1.18]	[ND]	[ND-1.71]	[ND]	[ND-1.42]

Note. The upper values show median concentration (detection rate) and the lower values show [concentration range]. All units are ng/m^3 . ND means Not detected.

3.2 OPEs in Cigarettes

Table 4 lists OPE concentrations in cigarette filters before and after smoking. TBP and TBEP were detected in all 16 samples before smoking. TBP was detected in two samples after smoking. Other OPEs were not detected either before or after smoking. The median concentration of TBEP, which was the largest OPE measured before smoking, was 344 ng/g (range: 190–1620 ng/g). The median total OPE concentrations ranged from 356 to 2320 ng/g before smoking, and from non-detectable levels to 448 ng/g after smoking.

Table 5 lists OPE concentrations in cigarette leaves. TBP and TBEP were detected in all 16 samples before smoking. TBP was detected in four samples after smoking. Other OPEs were not detected either before or after smoking. The median concentration of TBEP, which was the largest OPE measured before smoking, was 1870 ng/g (range: 329–2810 ng/g). The median total OPE concentrations ranged from 516 to 2950 ng/g before smoking and from non-detectable levels to 1100 ng/g after smoking. OPE concentrations in cigarettes were higher in leaves than in filters.

Table 4. OPEs in cigarette filters

	Brand A		Brand B		Brand C		Brand D	
	Before	After	Before	After	Before	After	Before	After
TBEP	451 (4/4)	ND (0/4)	438 (4/4)	ND (0/4)	301 (4/4)	ND (0/4)	503 (4/4)	ND (0/4)
	[296-1620]	[ND]	[275-807]	[ND]	[190-485]	[ND]	[286-1440]	[ND]
TBP	710 (4/4)	ND (1/4)	308 (4/4)	ND (0/4)	259 (4/4)	ND (0/4)	363 (4/4)	ND (1/4)
	[49.3-728]	[ND-126]	[114-393]	[ND]	[166-596]	[ND]	[118-390]	[ND-448]
TCEP	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)
	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]
TDCPP	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)
	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]
TEHP	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)
	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]
TEP	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)
	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]
TPP	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)
	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]

Note. The upper values show median concentration (detection rate) and the lower values show [concentration range]. All units are ng/g. ND means Not detected.

Table 5. OPEs in cigarette leaves

	Brand A		Brand B		Brand C		Brand D	
	Before	After	Before	After	Before	After	Before	After
TBEP	1970 (4/4)	ND (0/4)	1800 (4/4)	ND (0/4)	2620 (4/4)	ND (0/4)	707 (4/4)	ND (0/4)
	[1730-2560]	[ND]	[1310-2810]	[ND]	[2110-2720]	[ND]	[329-1130]	[ND]
TBP	52.4 (4/4)	ND (1/4)	45.6 (4/4)	ND (1/4)	62.4 (4/4)	ND (1/4)	122 (4/4)	ND (1/4)
	[20.5-60.5]	[ND-676]	[32.9-138]	[ND-440]	[30.1-185]	[ND-1100]	[22.0-186]	[ND-1010]
TCEP	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)
	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]
TDCPP	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)
	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]
TEHP	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)
	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]
TEP	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)
	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]
TPP	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)	ND (0/4)
	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]	[ND]

Note. The upper values show median concentration (detection rate) and the lower values show [concentration range]. All units are ng/g. ND means Not detected.

3.3 Gas-Particle Partitioning of OPEs

Gas-particle partitioning is one of the important factors that affect the fate of semi-volatile organic compounds in environments (Yamasaki, et al., 1982; Pankow, 1987; Lohman et al., 2000). Gas-particle partitioning of OPEs in air is presented here using the gas-particle partition coefficient (K_p , $m^3/\mu g$) calculated for OPEs determined simultaneously in the gas and particulate phases:

$$K_p = (F / TSP) / A$$

Where F is the particulate-phase concentration of OPEs (ng/m^3), A is the gas-phase concentration (ng/m^3), and TSP is the total suspended particulate concentration ($\mu g/m^3$). The mean values of $\log K_p$ for the OPEs detected in both the gas and particulate phases ($n \geq 5$) ranged from -1.79 (TCEP) to -2.24 (TPP) after smoking.

The partition coefficient K_p for a given compound was correlated with its subcooled liquid vapor pressure (PL° , Torr) using the following equation (Liang et al, 1996; Tsapakis et al., 2005; Akyüz, 2010):

$$\log K_p = mr \times \log PL^\circ + br$$

Where mr and br are the slope and the intercept of the regression line, respectively. The relationships between $\log K_p$ and $\log PL^\circ$ before and after smoking are shown in Figure 1. Median values of the measured data summarized by Sühring et al. (2016) were used as the PL° of OPEs. The dotted line represents the relationship between $\log K_p$ and $\log PL^\circ$ for alkanes by Liang et al. (1996). The points for low- $\log PL^\circ$ OPEs such as TPP lie near the correlation line for alkanes, but the points for high- $\log PL^\circ$ OPEs such as TBP and TCEP lie far from the correlation line. High- $\log PL^\circ$ OPEs were adsorbed to particles in air more readily than alkanes. These findings show that the low- $\log PL^\circ$ OPEs tend to exist in the gas phase, and the high- $\log PL^\circ$ OPEs tend to exist in the particulate phase.

3.4 OPE Emission Characteristics during Smoking

The emission characteristics for TBP, TBEP, TCEP, and TPP are described here because these OPEs were detected frequently in this study. Figure 2 presents the median contents of these OPEs in air and cigarettes before and after smoking. Levels in air were calculated as the median concentrations multiplied by $24 m^3$ for a sample collected before smoking and by $66 m^3$ for a sample collected after smoking. Levels in cigarettes were calculated as the median of the cigarette filter concentrations multiplied by the weights times two, plus the median of the cigarette leaf concentrations multiplied by the weights times two. The reason for multiplying by two was that

two cigarettes of each brand were smoked during the experiments. Non-detectable levels were treated as zero. The median contents of OPEs before smoking were 223 ng/room per cigarette (TBP), 2130 ng/room per cigarette (TBEP), and 56.2 ng/room for particulate-phase TCEP. Median contents after smoking, however, were much higher (e.g., 348 ng/room for particulate-phase TBP and 4260 ng/room for particulate-phase TBEP). Table 6 lists the correlation coefficients for the relationships between the particulate-phase OPEs after smoking. TBP and TCEP concentrations tended to increase as TBEP concentrations increased. TPP concentrations tended to increase as TCEP concentrations increased. These findings imply that TBP and TBEP concentrations in cigarettes increased with the combustion reaction, and some were transformed to other OPEs and then emitted into air. TBP and TBEP in cigarettes probably affect the production of the OPEs during smoking.

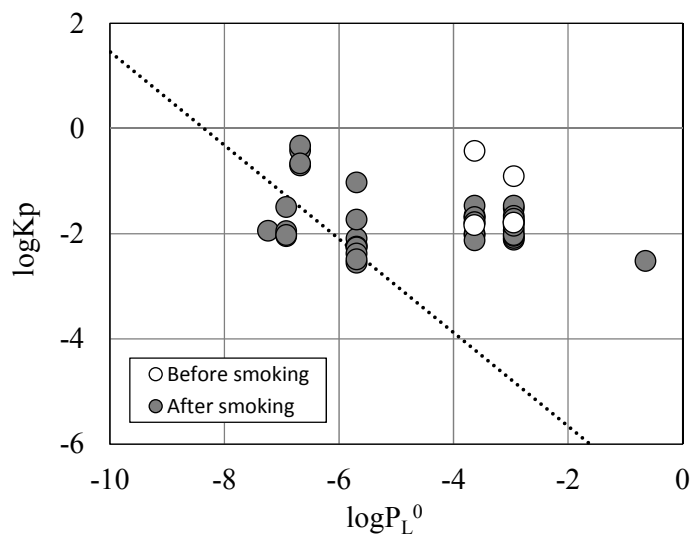


Figure 1. Relationships between logKp and log PL° before and after smoking

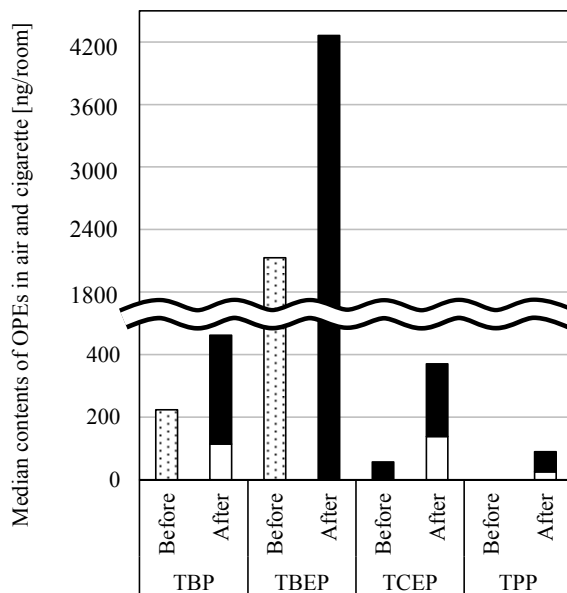


Figure 2. Median contents of OPEs in air and cigarettes before and after smoking

Note. Before indicates before smoking, and After indicates after smoking. Stippled bars, open bars, and solid bars show contents for OPEs in cigarettes, gas-phase OPEs in airs, and particulate-phase OPEs in airs, respectively.

Table 6. Pearson Coefficients for Correlations among the detected particulate-phase OPEs in airs after smoking

	TBEP	TBP	TCEP
TBP	0.421		
TCEP	0.251	0.531*	
TPP	-0.096	0.010	0.365

Note. *:p < 0.05.

4. Conclusions

The OPE concentrations in four brands of cigarettes and their sidestream smoke were examined, and the characteristics of OPE formation during smoking were investigated from the OPE mass balance in the cigarettes and smoke. The results are summarized as follows.

(1) OPE levels in sidestream cigarette smoke before and after smoking were determined in an air sampling room with an approximate volume of 66 m³. The medians of total gas-phase and particulate-phase OPE concentrations after two cigarettes were smoked were 4.77 ng/m³ and 74.2 ng/m³, respectively, and the concentrations were higher after smoking. Median total OPE increases in the air samples during smoking were 56.2 ng/cigarette for gas-phase OPEs and 2360 ng/cigarette for particulate-phase OPEs.

(2) The points for high-log PL^o OPEs such as TBP and TCEP lie far from the correlation line between gas-particle partition coefficients (K_p) and the subcooled liquid vapor pressures (PL^o) for alkanes. High-log PL^o OPEs were adsorbed to particles in air more readily than alkanes.

(3) OPE levels in cigarettes before and after smoking were determined. Only TBP and TBEP were detected. The medians of total OPE concentrations before smoking in cigarette filters were 780 ng/g and 1900 ng/g, respectively; concentrations were lower after smoking. Median total OPE decreases in cigarettes during smoking were 1200 ng per cigarette.

(4) The combustion reaction increased TBP and TBEP levels in cigarettes, and particulate-phase TBEP in air appeared to influence the production of TBP, TCEP, and TPP. TBP and TBEP in cigarettes likely affect the production of TBP, TBEP, TCEP and TPP in air during smoking.

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References

- Akyüz, M., & Çabuk, H. (2010). Gas–particle partitioning and seasonal variation of polycyclic aromatic hydrocarbons in the atmosphere of Zonguldak, Turkey, *Science of the Total Environment*, 408, 5550–5558. <https://doi.org/10.1016/j.scitotenv.2010.07.063>
- Andresen J. A., Grundmann A., & Bester K. (2004). Organophosphorus flame retardants and plasticisers in surface waters. *Science of the Total Environment*, 332, 155–166. Retrieved from https://ac.els-cdn.com/S0048969704003316/1-s2.0-S0048969704003316-main.pdf?_tid=21edd8b9-cd84-4472-a251-9f5f11621e90&acdnat=1527648076_86b0c1464194cd8023e42eb8e1712703
- Brommer, S., Harrad, S., Van den Eede, N., & Covaci, A. (2012) Concentrations of organophosphate esters and brominated flame retardants in German indoor dust samples. *Journal of Environmental Monitoring*, 14, 2482–2487. Retrieved from <http://pubs.rsc.org/en/content/articlepdf/2012/EM/C2EM30303E>
- Chung, H. W., & Ding, W. H. (2009). Determination of organophosphate flame retardants in sediments by microwave-assisted extraction and gas chromatography–mass spectrometry with electron impact and chemical ionization. *Analytical and Bioanalytical Chemistry*, 395, 2325–2334. Retrieved from <https://link.springer.com/article/10.1007/s00216-009-3139-4>
- European Chemicals Agency. (2009). *Inclusion of substances of very concern in the candidate list*.
- Fries, E., & Mihajlovic, I. (2011). Pollution of soils with organophosphorus flame retardants and plasticizers. *Journal of Environmental Monitoring*, 13, 2692–2694. Retrieved from <http://pubs.rsc.org/en/content/articlepdf/2011/EM/C1EM10538H>

- Gosselin, R. E., Smith, R. P., & Hodge, H. C. (1984). *Clinical Toxicology of Commercial Products* (5th ed.). Baltimore, II-302.
- Kawagoshi, Y., Fukunaga, I., & Itoh, H. (1999). Distribution of organophosphoric acid triesters between water and sediment at a sea-based solid waste disposal site. *Journal of Material Cycles and Waste Management*, *1*, 53–61.
- Lai, S., Xie, Z., Song, T., Tang, J., Zhang, Y., Mi, W., ... Ebinghaus R. (2015). Occurrence and dry deposition of organophosphate esters in atmospheric particles over the northern South China Sea. *Chemosphere*, *127*, 195–200. Retrieved from https://ac.els-cdn.com/S0045653515001174/1-s2.0-S0045653515001174-main.pdf?_tid=171c4284-0dfd-4185-9a5e-ec300d8181a7&acdnat=1527647019_a940c25f89809ab81c2526fb0164e790
- Liang, C., & Pankow, J. F. (1996). Gas/particle partitioning of organic compounds to environmental tobacco smoke: partition coefficient measurements by desorption and comparison to urban particulate material. *Environmental Science and Technology*, *30*, 2800-2805. Retrieved from <https://pubs.acs.org/doi/pdf/10.1021/es960050x>
- Lohmann, R., Harner, T., Thomas, G. O., & Jones, K. C. (2000). A comparative study of the gas-particle partitioning of PCDD/Fs, PCBs, and PAHs. *Environmental Science and Technology*, *34*, 4943-4951. Retrieved from <https://pubs.acs.org/doi/pdf/10.1021/es9913232>
- Marklund, A., Andersson, B., & Haglund, P. (2005). Organophosphorus flame retardants and plasticizers in Swedish sewage treatment plants. *Environmental Science and Technology*, *39*, 7423–7429. Retrieved from <https://pubs.acs.org/doi/pdf/10.1021/es0510131>
- Pankow, J. F. (1987). Review and comparative analysis of the theories on partitioning between the gas and aerosol particulate phases in the atmosphere. *Atmospheric Environment*, *21*, 2275-2283. [https://doi.org/10.1016/0004-6981\(87\)90363-5](https://doi.org/10.1016/0004-6981(87)90363-5)
- Salamova, A., Hermanson, M. H., & Hites, R. A. (2014). Organophosphate and halogenated flame retardants in atmospheric particles from a European arctic sites. *Environmental Science and Technology*, *48*, 6133–6140. Retrieved from <https://pubs.acs.org/doi/pdf/10.1021/es500911d>
- Shimazu, H., Shibata, T., & Horie, T. (2013). Bioaccumulation characteristics of organophosphoric acid triesters and polycyclic aromatic hydrocarbons in *Phragmites*. *Journal of Water and Environment Technology*, *11*, 287–297. <https://doi.org/10.2965/jwet.2013.287>
- Shimazu, H. (2016). Determination of Organophosphate Esters in Cigarettes and Cigarette Smoke. *Modern Environmental Science and Engineering*, *2(12)*, 792-799. Retrieved from <http://www.academicstar.us/UploadFile/Picture/2017-9/201792232818615.pdf>
- Sühring, R., Wolschke, H., Diamond, M. L., Jantunen, L. M., & Scheringer, M. (2016). Distribution of organophosphate esters between the gas and particle phase—model predictions vs measured data. *Environmental Science and Technology*, *50*, 6644-6651. <https://pubs.acs.org/doi/pdf/10.1021/acs.est.6b00199>
- Tsapakis, M., & Stephanou, E. G. (2005). Polycyclic aromatic hydrocarbons in the atmosphere of the Eastern Mediterranean. *Environmental Science and Technology*, *39*, 6584-6590. Retrieved from <https://pubs.acs.org/doi/pdf/10.1021/es0505321>
- Townsend Solutions. (2012). *Plastic Additives 8 Global Market Study*.
- TÜV Rheinland Group. (2013). *US Tighens Requirements On Flame Retardants For Children Products*.
- Van der Veen, I., & de Boer, J. (2012). Phosphorus flame retardants: properties, production, environmental occurrence, toxicity and analysis. *Chemosphere*, *88*, 1119–1153. Retrieved from https://ac.els-cdn.com/S0045653512004353/1-s2.0-S0045653512004353-main.pdf?_tid=7915f8c0-4f21-40fa-b04a-95b706e6ef77&acdnat=1527645888_1f1a608b462d44e3330186bd578a3ed0
- WHO. (1991a). Tributyl phosphate, *Environmental Health Criteria 112*.
- WHO. (1991b). Triphenyl phosphate, *Environmental Health Criteria 111*.
- WHO. (1998). Flame Retardants: Tris(chloropropyl) phosphate and tris(2-chloroethyl) phosphate. *Environmental Health Criteria 209*.
- WHO. (2000). Flame Retardants: Tris(2-butoxyethyl) phosphate, tris(2-ethylhexyl) Phosphate and tetrakis

(hydroxymethyl) phosphonium salts. *Environmental Health Criteria*, 218.

Yamasaki, H., Kuwata, K., & Miyamoto, H. (1982). Effects of ambient temperature on aspects of airborne polycyclic aromatic hydrocarbons. *Environmental Science and Technology*, 16, 189-194. <https://doi.org/10.1021/es00098a003>

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