Measurement report: Seasonal, distribution and sources of organophosphate esters in $PM_{2.5}$ from an inland urban city in southwest China

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Abstract. Organophosphate esters (OPEs) are contaminants of emerging concern and studies concluded that urban areas were a significant source of OPEs. Samples were collected from six ground-based sites located in Chengdu, a typical fast developing metropolitan of southwest China and were analyzed for seven OPEs in atmospheric $PM_{2.5}$. The concentrations of Σ_7 OPEs in $PM_{2.5}$ ranged from 5.83 to 6.91 ng m^{-3}, with a mean of 6.6 ± 3.3 ng m^{-3}, and the primary pollutants were TBEP, TnBP, TCEP and TCPP which together made up more than 80% in the Σ_7 OPEs. The concentrations of Σ_7 OPEs were higher in autumn/winter than that in summer. Nonparametric test showed that there was no significant difference in Σ_7 OPEs concentrations among the six sampling sites, but the occurrence of unexpected high level of individual OPEs at different sites in autumn might indicate that there was a noteworthy emission. Very strong correlation ($R^2 = 0.98$, $p<0.01$) between the OPEs in soil and in $PM_{2.5}$ was observed. The backward trajectory analysis displayed that OPEs in $PM_{2.5}$ were mainly affected by local sources. The principal component analysis (PCA) identified the OPEs in $PM_{2.5}$ were largely sourced from the plastic industry / interior decoration / traffic emission (34.5%) and chemical, mechanical and electrical industry (27.8%), while PMF model found the main sources were the plastics industry / indoor source emissions, the food / cosmetics industry, and industrial emissions. Differed from the coastal cities, the sustained and stable high local emissions in the inland city were identified which were particularly noteworthy. The chlorinated phosphate, especially TCPP and TCEP have a high content, whose usage and source emissions should be controlled.

1. Introduction

With the prohibition of brominated flame retardants, the production and the demand of organophosphate esters (OPEs) have rapidly increased in recent years (Wang et al., 2013). To date, OPEs are widely distributed in the environment and have been detected in air (Guo et al., 2016; Li et al., 2017), water (Bacaloni et al., 2008; Wang et al., 2013; Li et al., 2014), soil (Yin et al., 2016), sediment (Cristale J. et al., 2013; Celano R, et al., 2014) and organisms (Kim et al., 2011). However, many scholars found that the residues of OPEs in the environment could cause toxic effects on organisms (WHO, 1991, 1998, 2000; Van der Veen and de Boer, 2012; Du et al., 2015). Some countries have legislated to restrict the usage of OPEs (Blum et al., 2019; Exponent, 2018; State of California, 2020). Nevertheless, the production and usage of OPEs in China is still on the rise.

As synthetic substances, the only source of OPEs in the environment is anthropogenic emissions. The detection of OPEs in Arctic and Antarctic snow samples and atmospheric particulate matter samples demonstrated that OPEs can be transported over long distances (Möller et al., 2012; Li et al., 2017). Studies on OPEs in oceans were carried out a lot, and the concentrations of particle-bound OPEs ranged from tens to thousands of ng m^{-3} (Möller et al., 2011; 2012; Li et al., 2017; McDonough et al., 2018). Researchers noted that the contribution of air flow originated from the mainland when high concentrations of OPEs (thousands of ng m^{-3}) appeared (Möller et al., 2012; Lai et al., 2015). In addition, studies proved the urban area was the highest pollution area of OPEs. However, until now, only a few papers reported the concentration and distribution of OPEs in urban atmospheric $PM_{2.5}$. Concentrations of atmospheric OPEs in most cities were lower than 10 ng m^{-3}, higher concentrations of 19.2 ng m^{-3} were observed at a suburban site in Shanghai, and 49.1 ng m^{-3} were observed in Hongkong (Ohura et al., 2006; Salamova et al., 2014b; Shoeib et al., 2014; Yin et al., 2015; Liu et al., 2016; Ren et al., 2016; Guo et al., 2016; Wong et al., 2018). To date, most of studies in China focus on the OPEs in the Yangtze River Delta and Pearl River Delta, especially eastern coastal cities while little attention was paid to the western inland cities.

Chengdu is a typical inland city located in the southwest of China. It is the capital and megacity of Sichuan Province, which covers an area of 14,335 square kilometers and has a permanent population of 16.33 million. As the important national high-tech industrial base, commercial logistics centre and comprehensive transportation hub determined by the State Council, Chengdu is the important central city in the western region (https://en.wikipedia.org/wiki/Chengdu). Liu et al. (2016) reported an investigation of three chlorinated OPEs in the atmosphere at 10 urban sites in China during 2013–2014 and found that the highest annual mean concentrations were observed in Chengdu (1,300 ± 2,800 ng m^{-3}). However, there is still a lack of information regarding the levels, sources, and fate of OPEs in the southwest China which may obviously differed from the coastal cities or over the sea. Our previous study has investigated the OPEs concentrations in $PM_{2.5}$ at two sites (urban and suburban sites) in Chengdu (an economically fast growing city in southwest of China), and found that OPEs concentrations and profile were similar at two sites (Yin et al., 2015). But the influence factors and potential sources of OPEs in $PM_{2.5}$ in Chengdu are still unclear. Therefore, in this study, $PM_{2.5}$ was collected over one year (October 2014 to September 2015) at six sites in Chengdu to: a) report the levels and composition profiles of OPEs in urban air in the typical inland city; (b) obtain the seasonal and spatial variation of OPEs in $PM_{2.5}$; (c) investigate the relationships and correlations among the target compounds or with influence factors; (d) illustrate the potential sources of OPEs in $PM_{2.5}$.

2. Materials and Methods

2.1. Chemicals

The main reagents, such as ethyl acetate, acetone, hexane and acetonitrile, were High Performance Liquid Chromatography (HPLC) grade (Kelon Chemical Corp., China). The standard solutionsincluding tri-n-butyl phosphate (TnBP), tris-(2-ethylhexyl)phosphate (TEHP), tris-(2-butoxyethyl) phosphate (TBEP), triphenyl phosphate (TPhP), tris-(2-chloroethyl)-phosphate (TCEP), tris-(2-chloroisopropyl)phosphate (TCPP), and tris-(2.3-dichloropropyl)-phosphate (TDCIPP) and internal standard (TDCPP-d_{15} and TPhP-d_{15}) were all purchased from Sigma-aldrich Corp., USA. Copper, aluminium oxide, silica gel, Na_2SO_4 and other chemicals were purchased from Kelon Chemical Corp., China. Deionized water was supplied from a Milli-Q equipment.

2.2. Sample collection

The atmospheric sampling sites were located in the main city area (site B: downtown; site C: south; site D: east; site E: north; site F: west) and suburban area (site A) of Chengdu, as shown in Fig. S1. The atmospheric samples were collected by KC - 6120 medium flow atmospheric comprehensive sampler with quartz film. The speed was set at 100 L min^{-1}, and each collection campaign lasted 23 h. The sampling campaign was carried out between October 2014 and September 2015. In each season, continuous sampling was carried out for about one week, except for rainy days. In autumn, the sampling duration was from October 23 to October 29, 2014 (no sample was obtained due to the rain on October 26 and 27); in winter, the sampling duration was from December 22 to December 30, 2014 (no sample was obtained due to the rain on October 25 and 26); in spring, the sampling duration was from March 25 to March 30, 2015; in summer, the sampling duration was from July 16 to July 24, 2015 (no sample was obtained due to the rain on July 21). A total of 149 samples were obtained. Most of the weather conditions were cloudy days, with south / north wind whose speed was lower than 5.5

m / s. Temperature ranged from 0 to 35 ℃. Weather conditions could represent typical weather conditions of the season.

2.3. Sample preparation and analysis

The shredded $PM_{2.5}$ sample film was placed in a test tube and incubated in 20 mL ethyl acetate/acetone (v: v, 3: 2) for 12 hours. After ultrasonic extraction for 30 minutes, the liquid was separated, and the residue was further extracted with 10 mL ethyl acetate/acetone (v: v, 3: 2) by ultrasonic extraction for 15 minutes. The extracts were combined and concentrated by vacuum-condensing equipment (Buchi Syncore Q-101, Switzerland) to approximately 1 mL, then loaded onto an activated aluminium oxide / silica gel (v: v, 3: 1) column. The column was first eluted with 20 mL hexane to remove impurities, then with 20 mL ethyl acetate/acetone (v: v, 3: 2) and the latter eluate (ethyl acetate / acetone) was collected. The eluate was concentrated to near dryness by vacuum-condensing equipment and then fixed volume to 200 μL with hexane for gas chromatography - mass spectrometry (GC - MS) (Shimadzu 2010 plus, Japan) analysis.

The GC is equipped with a capillary column SH-Rxi-5Sil MS (30 m × 0.25 μm × 0.25 mm, Shimadzu, Japan). Splitless injection was applied and the inlet temperature was 280 ℃. The MS source was electron impact (EI) and the MS was operated in selected ion monitoring (SIM) mode. Helium was used as carrier gas with a flow rate of 1.00 mL min^{-1}. The GC oven temperature was held at 50 ℃ for 1 minute, increased to 200 ℃ at 15 ℃ min^{-1} and held for 1 minute,then to 250 ℃ at 4.00 ℃ min^{-1}, and to 300 ℃ at 20 ℃ min^{-1}, held for 4 minutes. The interface temperature was 280 ℃, and the ion source temperature was 200 ℃. The respective characteristic ion and reference ions (m / z) of the 7 target compounds were: 155 / 99, 211, 125 (TnBP), 249 / 63, 143, 251 (TCEP), 125 / 99, 201, 277, 157 (TCPP), 75 / 99, 191, 209, 381 (TDCPP), 326 / 325, 77, 215 (TPhP), 85 / 100, 199, 299 (TBEP), 99 / 113 and 211 (TEHP).

2.4. QA / QC

Thorough QA / QC procedures for OPEs analysis were conducted to ensure data quality. To evaluate the recovery efficiencies of analytical procedures, all samples were added with internal standard (TDCPP-d_{15} and TPhP-d_{15}), and the accuracy was evaluated by their recoveries. The concentrations of the 7 OPEs were determined by an external standard method. The correlation coefficients of the standard curves of the seven OPE monomers were all greater than 0.990. The recoveries of the 7 OPEs and the internal standard were between 78.9% and 122.5%. A matrix blank was analysed with each batch of samples. Only TnBP was detected in the blanks, and the level of TnBP found in the blanks was <5% of the concentrations measured in all samples, which meant it was negligible. Field blanks were done at each site to evaluate the background contamination in the field. TBEP, TnBP and TEHP were detected in it. The level of them found in the blank were <15% of the concentrations measured in all samples. The instrument precision was in the range of 1.9%-8.3%.

2.5 Statistical analysis

Data analysis was done through IBM SPSS 22.0. Parameter test and nonparametric test were used to analyze the difference between data. Pearson's correlation coefficients were used to evaluate the linear relationship between the two variables, while Spearman’s rank correlation coefficients were used to evaluate the monotonic relationship between the two variables.

3. Results and Discussion

3.1. Levels of OPEs in $PM_{2.5}$

OPEs were present in $PM_{2.5}$ samples collected across the study area (Fig. S1). Seven OPEs were detected in 96.7% - 100% of the samples (n=149). The high detection frequencies of most OPEs indicated OPE contamination was ubiquitous in the air of Chengdu city.

Concentrations of Σ_7 OPEs in $PM_{2.5}$ across the six sites were in the range of 3.5 - 11.5 ng m^{-3}, and the annual median concentration of Σ_7 OPEs was 6.5 ± 3.3 ng m^{-3} (Fig. 1). The seasonal average value of OPEs in $PM_{2.5}$ at each site was almost at the same level (5.8 ± 1.3 ng m^{-3} - 6.9 ± 2.5 ng m^{-3}). Nonparametric test showed that there was no significant difference in Σ_7 OPEs concentrations among the six sampling sites, indicating that the atmosphere mixed evenly, and there was no particularly heavy or light polluted area in Chengdu city. These data were quite consistent with our previous study which reported the annual median concentration of OPEs in $PM_{2.5}$ from December 2013 to October 2014 (Yin et al., 2015). Interestingly, the concentration of Σ_7 OPEs at the suburban site was similar to, or even higher than some urban sites, which indicated more local sources of these compounds in the suburban area.

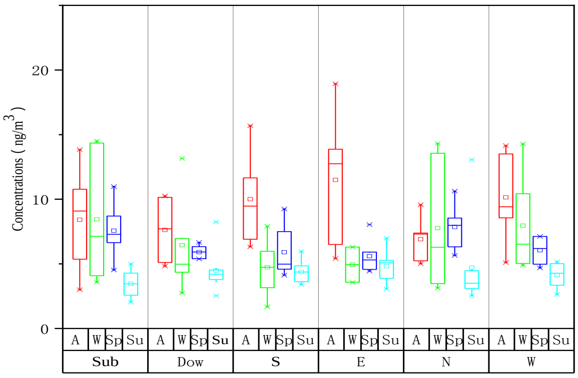


Figure 1. Levels and seasonal variation of Σ_7 OPEs in $PM_{2.5}$ at six sampling sites. A: autumn, W: winter, Sp: spring, Su: summer, Sub: suburbs, Dow: dowtown, S: south, E: east, N: north, W: west.

The concentrations of OPEs in the particles of Chengdu were comparable to that reported from Beijing (Σ_9 OPEs: 1.4 ng m^{-3}) (Wang et al., 2019), 6.6 ng m^{-3} (Σ_6 OPEs) for Shanghai urban site (Ren et al., 2016), 6.5 ng m^{-3} (Σ_6 OPEs) for Bursa, but higher than that in Houston, US (Σ_{12} OPEs, 0.16 - 2.4 ng m^{-3}) (Clark et al., 2017), Dalian (Σ_9 OPEs, 0.32-3.46 ng m^{-3},1.21 ± 0.67 ng m^{-3}) (Wang et al., 2019), European Arctic (0.033 - 1.45 ng m^{-3}) (Salamova et al., 2014b), Northern Pacific and Indian Ocean (0.23 - 2.9 ng m^{-3}) (Möller et al., 2012), the Yellow Sea and Bohai Sea (0.044 - 0.52 ng m^{-3}) (Li et al., 2018), South China Sea (0.047 - 0.161 ng m^{-3}) (Lai et al., 2015), North Atlantic and Arctic Oceans (0.035 - 0.343 ng m^{-3}) (Li et al., 2017). And they were lower than that in Guangzhou and Taiyuan (Σ_{11} OPEs, 3.10 - 544ng m^{-3}) (Chen et al., 2020), in Bursa, Turkey (Σ_6 OPEs, 0.53 - 19.14 ng m^{-3}) (Kurtkarakus et al., 2017), 20 industrial sites in an urban region (Σ_{12} OPEs, 0.52 - 62.75 ng m^{-3}) in Guangzhou, China (Wang et al., 2018).

3.2. The composition profiles of OPEs in $PM_{2.5}$

Non-chlorinated OPEs were the predominant OPEs across Chengdu city (Fig. 2). The annual median concentrations of total OPEs were fairly uniform at six sites and influenced mainly by the alkylated OPEs. As listed in Table 1, the general trend was found that TBEP was the most abundant OPE (annual media concentration: 2.3 ng m^{-3}, 35.3% of Σ_7 OPEs), followed by TCEP (1.1 ng m^{-3}, 16.3%) ≈ TnBP (1.0 ng m^{-3}, 15.6%) ≈ TCPP (1.0 ng m^{-3}, 15.0%) > TPhP (0.5 ng m^{-3}, 8.4%) > TEHP (0.3 ng m^{-3}, 5.1%) > TDCPP (0.3 ng m^{-3}, 4.3%), with the concentrations of TBEP being approximately 7 - 10 times higher than those of TDCPP and TEHP. The composition profile of OPEs was similar at all sites except for that the east site which has a higher contribution of TnBP. But TBEP, TCEP, TCPP and TnBP were dominant OPEs across the city who contributed more than 80% to Σ_7 OPEs. This profile was similar to that in Longyearbyen, Norway, with primary pollutants being TnBP and TBEP (Möller et al., 2012), as well as the OPEs in outdoor urban air being TBEP > TCPP > TCEP > TnBP > TPhP in Stockholm, Sweden (Wong et al., 2018) and TBEP > TCPP > TPhP > TEHP > TCEP in Turkey (Kurtkarakus et al., 2018). However, these results substantially differed from the report of an urban site in Shanghai that showed TCEP (0.1 - 10.1 ng m^{-3}, 1.8 ng m^{-3}) > TCPP (0.1 - 9.7 ng m^{-3}, 1.0 ng m^{-3}) > TPhP (0.06 - 14.0 ng m^{-3}, 0.5 ng m^{-3}) > TBP (0.06 - 2.1 ng m^{-3}, 0.4 ng m^{-3}) > TDCPP (Nd. - 23.9 ng m^{-3}, 0.3 ng m^{-3}), whereas TBEP was only detected in 3 out of 116 samples (Nd. - 0.7 ng m^{-3}, Nd.) (Ren et al., 2016), and the reported data over the Bohai and Yellow Seas showed TCPP (43 - 530 ng m^{-3}; 100 ng m^{-3}, 50 ± 11%)> TCEP (27 - 150 ng m^{-3}; 71 ng m^{-3}, 25 ± 7%) > TiBP (19 - 210 ng m^{-3}; 57 ng m^{-3}, 14 ± 12%) > TnBP (3.0 - 37 ng m^{-3}; 13 ng m^{-3}). Li et al. (2014) determined the primary pollutant of outdoor air in Nanjing was TCEP, and TBEP was not detected. These differences reflected that there were significant differences in OPE production and usage in different regions, even in the same country. It should be noted that concentrations of TCPP and TCEP were in the same level in this study, suggesting the industrial replacement of TCEP by TCPP wasn't identified in the southwest China which differed from that the higher concentration of TCPP in comparison with TCEP was observed due to the industrial replacement of TCEP by TCPP in Europe (Quednow and Püttmann, 2009). This was confirmed by the fact that there are manufacturers and sellers of TCEP and TCPP in Chengdu (https://show.guidechem.com/hainuowei, http://www.sinostandards.net/index.php), indicating that there is production and demand both for TCPP and TCEP in this region.

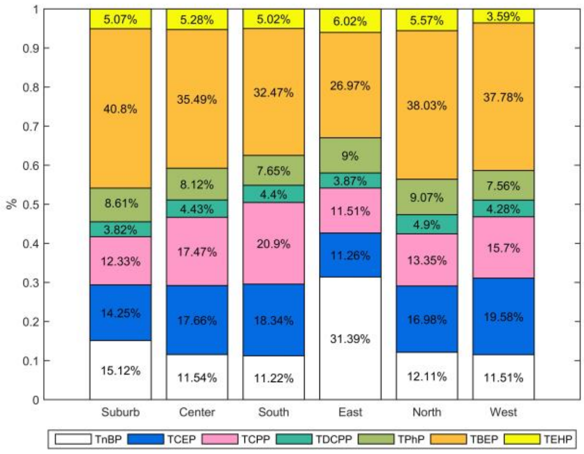


Figure 2. Percentages of individual OPEs contributing to the Σ_7 OPEs at each sampling site.

Table 1. The annual median concentrations of OPEs in $PM_{2.5}$ from Chengdu (ng m^{-3}).

Sampling sites	TnBP	TCEP	TCPP	TDCPP	TPhP	TBEP	TEHP	Σ_7 OPEs
suburb	1.0	1.0	0.8	0.3	0.6	2.7	0.3	6.7
downtown	0.7	1.0	1.0	0.3	0.5	2.1	0.3	5.8
south	0.7	1.1	1.2	0.3	0.5	1.9	0.3	5.9
east	2.1	0.8	0.8	0.3	0.6	1.8	0.4	6.6
north	0.8	1.1	0.9	0.3	0.6	2.5	0.4	6.7
west	0.8	1.4	1.1	0.3	0.5	2.6	0.3	6.9
median	1.0	1.1	1.0	0.3	0.5	2.3	0.3	6.4

Combined with the data of 2013 - 2014 year (Yin et al., 2015), TBEP was always the dominant OPEs during the two sampling periods (2013 - 2014 and 2014 - 2015). Kruskal Wallis test was used and found that TnBP and TCPP had no significant difference between the two sampling periods, but there were significant differences in other kinds of OPEs between the two sampling periods. This indicated that the production and usage of individual OPEs have certain change suggesting that OPEs should be better investigated and governed for individual compounds.

OPEs can be categorized by whether they are halogenated, alkylated or aryl OPEs. Of the OPEs measured in this study, TCEP, TCPP and TDCPP are halogenated, TBEP, TnBP and TEHP are alkylated, and TPhP is aryl OPEs. The OPEs in $PM_{2.5}$ at all sites were dominated by the alkylated compounds (55.9 ± 10.1%), followed by halogenated OPEs (35.8 ± 9.9%) and aryl OPEs (8.3 ± 4.1%). Our results are similar to those observed in Bursa, Turkey (Kurtkarakus et al., 2017), whose alkylated

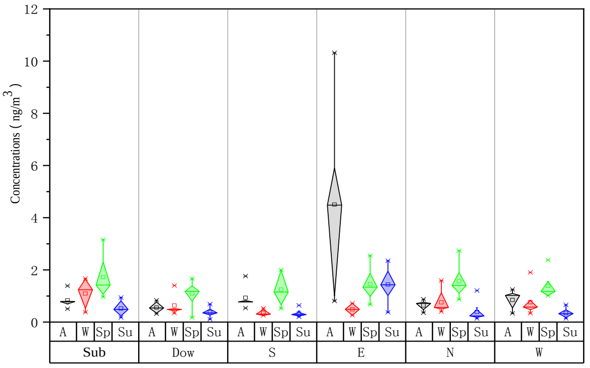
OPEs covered 68% - 95% of total OPEs, while halogenated OPEs covered 3.1% ~ 29%, and aryl OPEs covered 1.4% - 3.7% of total OPEs. Wu et al. (2020) also reported that alkyl OPEs dominated OPE compositional profiles of urban air collected from Chicago and Cleveland. At Longyearbyen, the non-chlorinated OPE concentrations comprised 75% of the Σ_8 OPEs concentrations (Salamova et al., 2014a). However, our results are obviously different from many studies with the atmospheric samples collected in urban areas being dominated by chlorinated OPEs (50 - 80%) (Salamova et al., 2014b; Liu et al., 2016; Guo et al., 2016). In our study, non-chlorinated OPEs were dominant in urban and suburban area across the city.

3.3. Seasonal and spatial variation of OPEs in $PM_{2.5}$

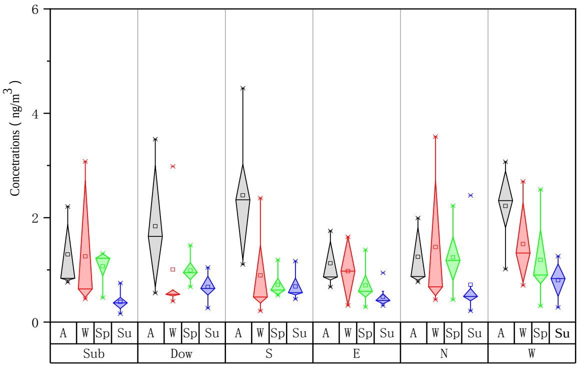
The mean seasonal concentrations were plotted for six sampling sites in Fig. 1. The data were quite consistent with our previous study from December 2013 to October 2014 (Yin et al., 2015). The concentrations of OPEs in $PM_{2.5}$ have been fairly uniform in the past three years. As shown in Fig. 1, the general order of the decreasing average Σ_7 OPEs concentrations in suburban area was autumn (8.4 ± 4.3 ng m^{-3}) ≈ winter (8.4 ± 4.5 ng m^{-3}) > spring (7.6 ± 2.2 ng m^{-3}) > summer (3.5 ± 1.1 ng m^{-3}), while in urban area was autumn (9.30 ± 3.89 ng m^{-3}) > winter (6.63 ± 3.65 ng m^{-3}) > spring (6.36 ± 1.72 ng m^{-3}) > summer (4.60 ± 1.91 ng m^{-3}). The average concentration of Σ_7 OPEs in autumn / winter was approximately 2 times that in summer. In summer, the turbulent flow accelerated the diffusion of pollutants, leading to the lowest concentration, while the higher concentrations of OPEs appeared in autumn and winter because the inversion layer appeared more frequently in autumn and winter, resulting in the pollutants being more difficult to diffuse and dilute. This seasonal variation was mostly in line with that at the Shanghai urban site of autumn (8.4 ng m^{-3}) > winter (7.6 ng m^{-3}) > spring (5.5 ng m^{-3}) > summer (4.4 ng m^{-3}), of which the maximum value was also approximately twice the minimum (Ren et al., 2016). In addition, this finding was similar to that in Xinxiang that no significant seasonal changes and only exhibited individual high values in winter. On the contrary, Wang et al. (2019) found the $PM_{2.5}$ - bound fractions of OPEs varied significantly between seasons in Dalian, China, with their concentrations higher in hot seasons, which may due to the temperature-driven emission or gas-particle partitioning. Wong et al. (2018) reported that most of OPEs in outdoor urban air showed seasonality, with increased concentrations during the warm period in Stockholm, Sweden. Sühring et al. (2016) reported temperature dependence of chlorinated OPEs and EHDPP in Arctic air. Wu et al. (2020)

reported that median concentrations of Σ_6 OPEs for summer samples were up to 5 times greater than those for winter samples. The similar seasonal patterns were reported by Salamova et al. (2014a) for the atmospheric particle - phase OPE concentrations in samples collected from the Great Lakes in 2012. A reasonable explanation is that OPEs are not chemically bound to the materials in which they are used and higher temperatures may facilitate their emission from buildings and vehicles. However, Shoeib et al. (2014) did not observe any temperature dependence for the OPEs in urban air in Toronto, Canada. Thus previous reports of temperature dependence of OPEs are not consistent. In our study, the correlation analysis between the temperature, wind speed, wind direction and Σ_7 OPEs concentrations has been done. The results showed statistically significant negative correlations between temperature and Σ_7 OPEs ($R= -0.355$, $p<0.01$). The lowest concentrations of Σ_7 OPEs and individual compound were observed in summer suggesting the OPEs level was not driven by the temperature-driven emission. Gas-particle partitioning and local emission sources may contribute to the variation.

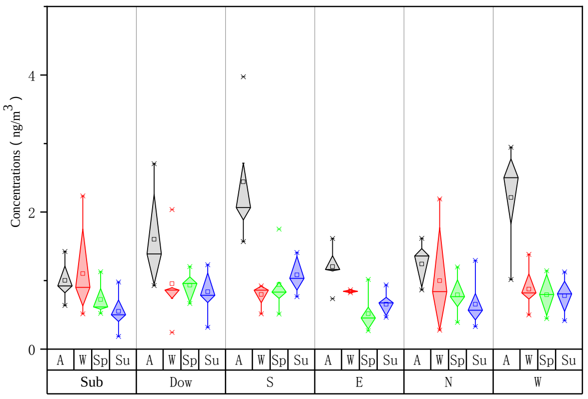
Compared to the coastal cities, the most obvious difference was that concentrations of almost all OPEs monomers in this study (Fig. 3) were highest in autumn / winter and lowest and concentrated in summer suggesting the sustained and stable high local emissions in the inland city which were particularly noteworthy. No point source was identified in summer and the OPEs level was diluted and diffused in summer due to the higher wind speed than in winter in the inland city. This was different from the coastal cities: Liu et al. (2016) reported that the highest TCPP and TCEP concentrations were observed in the summer in Guangzhou and Javier et al. (2018) found the OPEs in spring generally exhibited the lowest concentrations in Bizerte, Tunisia, probably linked to the influence of local meteorological conditions and air mass trajectories to a lesser extent.



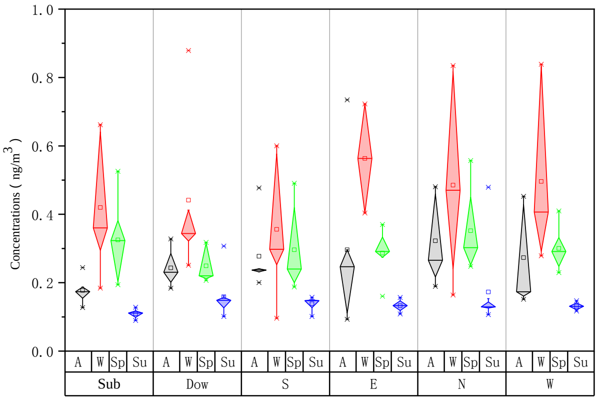
TnBP



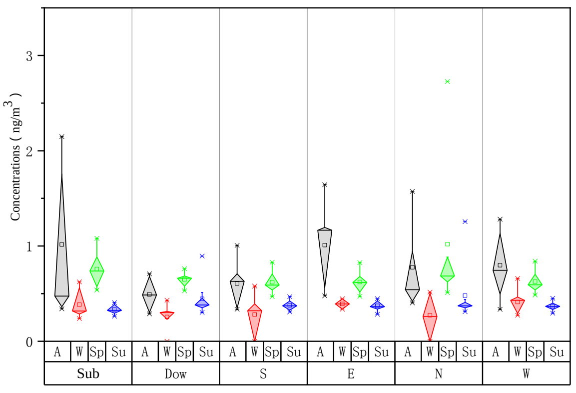
TCEP



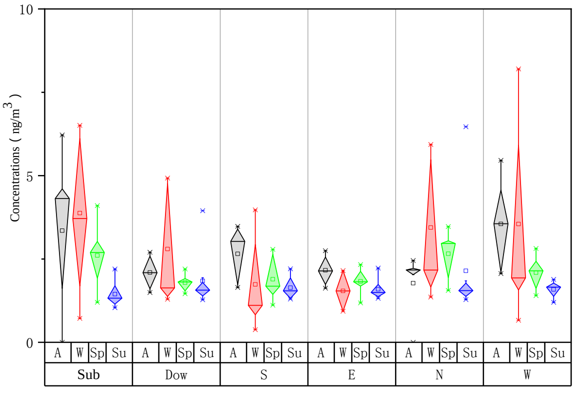
TCPP



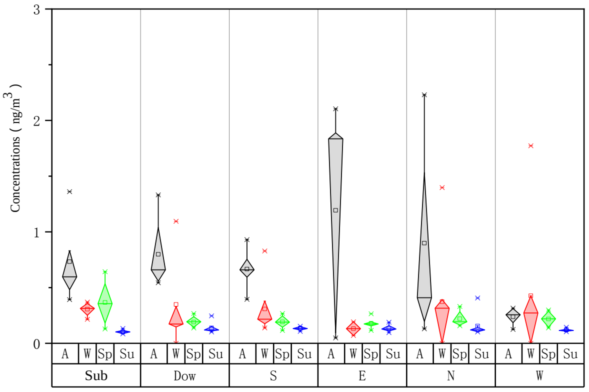
TDCPP



TPhP



TBEP



TEHP

Figure 3. The seasonal variation of monomer individual OPEss in $PM_{2.5}$ from Chengdu city. A:Autumn, W:Winter, Sp:Spring, Su:Summer, Sub:Suburbs, Dow:Dowtown, S:South, E:East,N:North, W:West.

Though Kruskal Wallis test showed that there was no significant variation of Σ_7 OPEs concentrations across the city, the spatial differences were identified in the study. For example, TnBP and TCPP had significant difference among six sites. In addition, the higher concentrations and more dispersed pattern of most OPEs were observed in autumn and winter than in summer (Fig. 3). The concentrations of TEHP in autumn at the eastern and northern sampling site were more dispersed than others. The same dispersion pattern was observed for TBEP in winter at the western sampling site, TPhP in autumn at the suburban sampling site, TnBP in autumn at the eastern sampling site, suggesting that there existed extra emission sources in autumn or winter. Considering the layout of Chengdu which develops from the central area with the loop line (the first ring road, the second ring road and the third ring road), the uniform patterns of OPEs levels and distribution across the city is understandable. Different types of industrial parks in different directions in Chengdu may be the reason for the spatial differences of OPEs. For example, in the east of Chengdu, there are automobile industrial parks and other large industrial parks while logistics and shoemaking industrial parks are located in the suburbs. The occurrence of unexpected high levels of individual OPEs at different sites in autumn might indicate that there was a noteworthy emission. The spatial and seasonal variation of individual OPE suggest that the control and management of OPEs should be taken. Interestingly, in this study, alkyl OPEs dominated both urban and suburban sites. This was extremely different from the results reported by Wu et al.

(2020) that alkyl OPEs dominated at urban sites, chlorinated OPEs were prevalent at rural sites, and aryl OPEs were most abundant at remote locations. Many studies focused on the halogenated OPEs due to their persistence, bio-accumulation, and potential human health effects, and they dominated the OPEs profile in the air of many cities and other areas (Li et al., 2017). Liu et al. (2016) reported that the sum of the concentrations of the three halogenated OPEs at 10 urban sites ranged from 0.05 to 12 ng m^{-3} suggesting the highest production volume and widest applications of OPEs leading to large emissions of OPEs in China in recent years. However, in our study, the mean concentrations of halogenated, alkylated and aryl OPEs were 2.4 ± 1.4 ng m^{-3}, 3.7 ± 2.1 ng m^{-3}, 0.5 ± 0.4 ng m^{-3}, respectively, which showed the alkylated OPEs dominated the profile of OPEs in $PM_{2.5}$ in Chengdu. In different seasons, the most notable seasonal variation was observed for alkyl phosphate, followed by halogenated OPEs and aryl OPEs. These results were significantly different from those in other studies which reported that the halogenated OPEs had the maximum seasonal variability (Guo et al., 2016; Shoeib et al., 2014).

3.4. Correlation analysis of OPEs

3.4.1 Linkage to environmental factors

Most of OPE monomers concentrations in $PM_{2.5}$ have a strong linear correlation ($R^2 = 0.79$) with their vapor pressure (Fig. 4), suggesting that the vapor pressure is an important factor controlling the levels of OPEs in $PM_{2.5}$ except for TBEP. Generally speaking, the greater the vapor pressure of OPEs, the easier it is to be released into the environment. Therefore, the sources of most OPEs in Chengdu atmospheric $PM_{2.5}$ are mainly both from the production process containing OPEs and the phase transition process before they enter into the atmosphere. The boiling points of OPEs are relatively high, so they tend to be adsorbed in $PM_{2.5}$ after being released to the environment (Wang et al., 2019), and their gas-particle distributions determine their concentration in $PM_{2.5}$. Interestingly, the vapor pressure of TBEP is lower than other OPEs, but its concentration in $PM_{2.5}$ was higher which indicated that there were sustained and stable high emission sources to keep its concentration at a high level which may include the traffic emission source (Chen et al., 2020). Sühring et al. (2016) reported non-halogenated OPE concentrations in Canadian Arctic air appeared to have diffuse sources or local sources close to the land-based sampling stations.

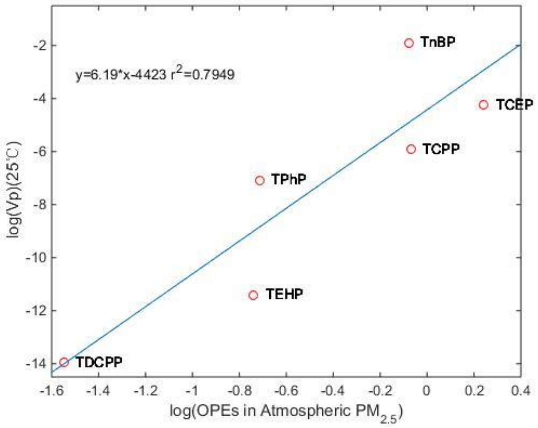


Figure 4. Relationship of individual OPEs concentration in $PM_{2.5}$ and its vapor pressure.

3.4.2 Correlation between target analytes

Spearman’s rank correlation coefficients were used to investigate the potential emission sources for OPEs by the relationship between individual OPE in $PM_{2.5}$ (Fig.5, Table 2). Fig. 5 showed no statistically significant positive correlations between OPE monomers ($r<0.50$, $p<0.01$). However, Σ_7 OPEs concentrations were closely related to TBEP, TCEP and TnBP ($r=0.53 - 0.61$, $p<0.01$) which further identified the OPEs levels were influenced mainly by the dominated OPEs compounds. Comparatively, weak correlations between most of OPEs were observed in urban regions (Wang et al., 2018) and Turkey (KurtKarakus et al., 2018). However, strong correlations between individual OPEs were found in Guangzhou and Taiyuan (Chen et al., 2020).

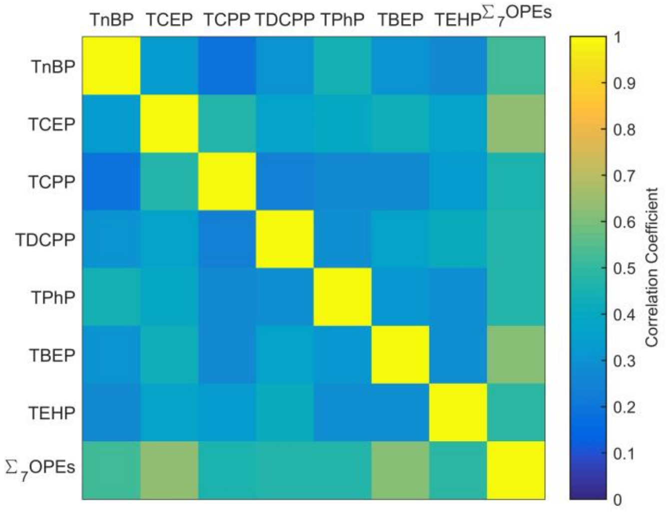


Figure 5. Spearman's rank correlation coefficients between the concentrations of individual OPEs in PM$_{2.5}$ samples.

Table 2. The correlation analysis of individual OPEs in downtown and suburb sampling sites.

		TnBP	TCEP	TCPP	TDCPP	TPhP	TBEP	TEHP
Downtown	TnBP	1	.408*	0.319	0.15	.455*	0.187	0.105
	TCEP	.408*	1	.818**	0.165	0.342	.447*	.449*
	TCPP	0.319	.818**	1	0.184	0.392	.447*	.500*
	TDCPP	0.15	0.165	0.184	1	0.053	0.216	0.175
	TPhP	.455*	0.342	0.392	0.053	1	0.104	-0.081
	TBEP	0.187	.447*	.447*	0.216	0.104	1	0.338
	TEHP	0.105	.449*	.500*	0.175	-0.081	0.338	1
Suburb	TnBP	1	.566**	.476*	.650**	0.269	.417*	0.141
	TCEP	.566**	1	.852**	.683**	0.368	.784**	.423*
	TCPP	.476*	.852**	1	.686**	0.304	.701**	0.297
	TDCPP	.650**	.683**	.686**	1	0.175	.708**	0.158
	TPhP	0.269	0.368	0.304	0.175	1	.512**	.629**
	TBEP	.417*	.784**	.701**	.708**	.512**	1	.434*
	TEHP	0.141	.423*	0.297	0.158	.629**	.434*	1

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed)

Further analysis results were shown in Table 2. Only significant correlation between TCPP and TCEP both at downtown ($r=0.82$, $p<0.01$) and suburban sites ($r=0.85$, $p<0.01$) were observed indicating the high homology between these two compounds. The inland city in China is still using a large number of products containing chlorinated flame retardants, which was confirmed by our previous study of house dust (Liu et al. 2017; Yin et al., 2019). At downtown site, another significant correlation existed between TEHP and TCEP ($r=0.50$, $p<0.01$) while others have weak to moderate correlations ($r<0.46$, $p<0.01$). The downtown area mainly focuses on the light industry and software development, and TCPP, TCEP, TnBP, TBEP and TPhP are used in textile, leather, electronic products and other fields. However, the correlation of each OPE monomer at site A (suburb) was stronger than that in the urban area. The correlations between TnBP and TCEP, TnBP and TDCPP, TCEP and TCPP, TCEP and

TDCPP, TCEP and TBEP, TCPP and TDCPP and TBEP were all extremely significant. This result indicated that the pollution in the suburb was commixed and influenced by many kinds of pollution sources.

3.4.3 Correlation analysis of OPEs and $PM_{2.5}$ concentrations

The SPSS software scatter diagram was used to analyse the relationship between the concentrations of OPE monomers and $PM_{2.5}$. As displayed in Fig. S2, only weak to moderate correlation were observed between most of OPEs and $PM_{2.5}$ except significant correlation was found between TDCPP and $PM_{2.5}$ ($r=0.53$, $p<0.01$) which suggest the continuous and relative constant local sources were the main sources. This result was found similar with that reported from Taiyuan (Guo et al., 2016), where no correlation was between the concentrations of OPEs and the concentration of particulate matter. However, this result differed from that in Xinxiang (Shen et al., 2016), which showed that the concentrations of OPEs and $PM_{2.5}$ had significant correlation ($r=0.85$), and a high value of OPEs / $PM_{2.5}$ was related to the contribution of the air mass from the heavily polluted area (Henan and Jiangsu province), while low OPEs / $PM_{2.5}$ was due to the air mass from Shanxi-Gansu and Neimenggu Province. Chen et al. (2020) found there was a significant correlation ($p<0.05$) between the concentrations of Σ_{11} OPEs and $PM_{2.5}$ in some sampling sites but not a site located in the urban region in Guangzhou with potential additional pollution sources.

3.4.4 Correlation analysis of OPEs in $PM_{2.5}$ and soil

Due to the low detection frequency of TCPP and TDCPP in the soil (Yin et al., 2016), the relationship of other five OPE monomers in the soil and in atmospheric $PM_{2.5}$ were presented in Fig. 6. A very strong linear relationship was obtained between the OPEs in soil and in $PM_{2.5}$ ($R^2 = 0.98$, $p<0.01$), indicating that the atmospheric $PM_{2.5}$ settlement is an important source of OPEs in the soil, so does the soil be a source for OPEs in the air.

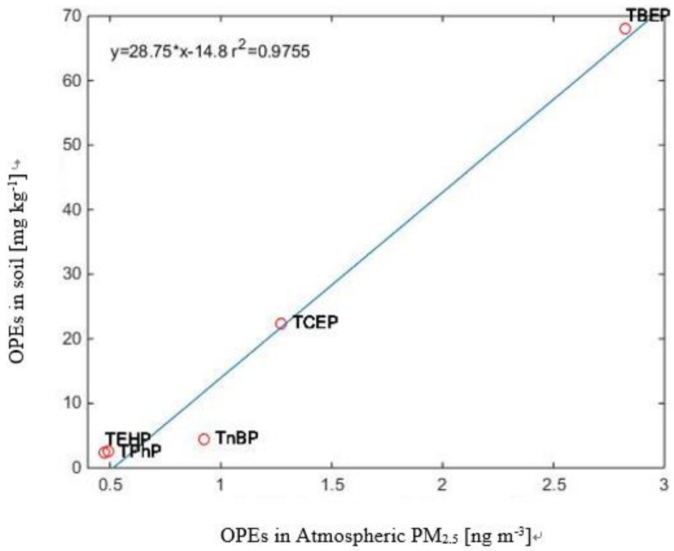


Figure 6. Relationship between OPEs in atmospheric $PM_{2.5}$ and in soil.

3.4.5 Correlation analysis of OPEs indoor and outdoor air

The OPEs profile in outdoor air in this study were: TBEP> TCEP > TnBP> TCPP > TPhP> TEHP> TDCPP, which was different with indoor dust reported from our previous study (Liu et al., 2017): TPhP>TCPP>TnBP> TDCPP >TBEP> TCEP > TEHP. TPhP is used as one of important alternatives for technical decabrominated diphenyl ether (deca - BDE) product, which is typically used as a flame retardant in electrical and electronic products. In addition, the use of plastic film and rubber may be an important source of TPhP. Thus OPEs in indoor dust mainly comes from indoor environment and related to human activities, not from outdoor air. Except for the different usage of OPEs, many factors may also lead to differences between indoor and outdoor OPEs. For example, TBEP has the shortest atmospheric half-lives, which may explain why its dominance in indoor samples was not observed for the outdoor counterparts. Studies in Swedish (Wong et al., 2018) reported the concentrations of OPEs in indoor air were TCPP > TCEP > TBEP > TnBP> TPhP, and in outdoor urban air were TBEP > TCPP > TCEP > TnBP > TPhP which also indicated the differences of OPEs profile in indoor and outdoor air. They found that activities in the building, e.g. floor cleaning, polishing, construction, introduction of new electronics and changes in ventilation rate could be key factors in controlling the concentration of indoor air pollutants, while the observed seasonality for OPEs in outdoor air was due to changes in primary emission.

3.5 Source apportionment of OPEs

3.5.1 Analysis of backward trajectory model

The backward trajectory cluster analysis (HYSPLIT4) combines the horizontal and vertical motion of the atmosphere, which can analyse the transport, migration and diffusion of atmospheric pollutants, were used in this study. The height of AGL500m can better represent the characteristics of the process wind field, and HYSPLIT4 was used to obtain the 24 hours backward trajectory of AGL500m during the sampling period of Chengdu. During the sampling period, the air mass was mainly from the northeastern and southern parts of Sichuan Province, including Mianyang, Deyang, Renshou and Chengdu, and a few of the trajectories came from Chongqing and other places in Gansu Province. Therefore, during the sampling period, Chengdu was mainly affected by the air mass of the eastern Sichuan.

In different seasons, the air sources always came from the southern or the northern regions of Chengdu. In spring, Chengdu was influenced by air mass from the southern region, which could be divided into three paths: (a) from Ya'an through Renshou to Chengdu; (b) from Leshan and Yibin; and (c) from Chongqing through Ziyang to Chengdu. The concentrations of OPEs at the northern and suburban site were relatively high in spring. During the summer period, Chengdu was mainly influenced by air masses from both the southern areas (Yibin, Zigong and others) and the northern areas (Gansu Province, Guangyuan and Mianyang), but there was no significant difference in OPE concentrations at each sampling site, nor in autumn and winter. Combined with the backward trajectory cluster analysis and the concentrations of OPEs at each sampling site, the concentrations of OPEs had no obvious change. This result suggested that OPEs were not affected by exogenous pollution but were mainly affected by the local sources of Chengdu. These results are consistent with the meteorological and topographic conditions. Chengdu's wind has always been breezy with much smaller strength than coastal cities or other inland cities (https://baike.baidu.com/item/%E6%88%90%E9%83%BD/128473?fr=aladdin). The wind direction is relatively constant, mainly from the south and the north. In addition, Chengdu is a city located in the interior of China, which was surrounded by the Qinghai-Tibet Plateau, the Qinling Mountains, etc. These topographic and meteorological conditions block the influence of foreign sources on Chengdu's atmosphere, which further explained that the pollution of OPEs in $PM_{2.5}$ was controlled by endogenous pollution, not by exogenous pollution.

3.5.2 Principal Component Analysis

The principal component analysis (PCA) of OPEs was carried out by SPSS. The normalized correlation coefficient matrix of the original data of each sampling site showed that there was a strong correlation between TCPP and TCEP, TCEP and TBEP, and TnBP and TPhP, which satisfied the condition of dimensionality reduction of PCA. Two principal component factors were obtained in this study. The cumulative contribution of the two principal component factors was 62.3%, which can basically reflect the data information. The results were shown in Table S1. For factor 1, there was a large load on TCEP,TCPP,TBEP and a moderate load on TDCPP. Factor 1 can represent the sources of OPEs from the plastic industry, interior decoration and traffic emission, with the contribution ratio of 34.5% (Marklund et al., 2007; Regnery et al., 2011; CEFIC, 2002). Factor 2 has higher load on TnBP, TEHP and TPhP. The highest load was on TnBP, which is often used as a high-carbon alcohol defoamer, mostly in industries that do not come in contact with food and cosmetics, as well as in antistatic agents and extractants of rare earth elements. TEHP can be used as an antifoaming agent, hydraulic fluid and so on. TPhP is typically used in electrical and electronic products, or plastic film and rubber (Esch, 2000; Stevens et al., 2006; Wei et al., 2015). Factor 2 can be considered the chemical, mechanical and electrical industry, and its contribution ratio was 27.8%.

3.5.3 PMF model analysis

The basic principle of the PMF method is to decompose the sample matrix into a factor contribution matrix and factor component spectrum. The source type of the factor is judged according to the factor component spectrum, and then the contribution ratio of source is determined. The uncertainty is estimated by three methods: BS, disp and bs-disp. From 149 samples collected in Chengdu, 132 valid samples were selected to participate in the model calculation and three factors were determined. TPhP was the only chemical with residual (4.0) greater than 3. Concentrations of OPEs satisfied the normal distribution. The components of factor 1 were complex. Factor 1 contributes 71.0%, 70.7% and 70.9% to TCEP, TCPP and TEHP, respectively, and 58.3% to TPhP. Factor 1 was deduced to be the plastics/electrical industry and indoor source emissions (Esch, 2000; Stevens et al., 2006). Factor 2 contributed the most to TBEP (78.0%), followed by TDCPP (44.7%), while it did not contribute to TnBP. Therefore, factor 2 was deduced as the food / cosmetics industry and traffic emissions (Marklund et al., 2007). Factor 3 contributes 71.7% of the total TnBP, which can be deduced as chemical industrial source (Regnery et al., 2011).

4. Conclusions and Implications

Compared to the levels of OPEs in other cities, the levels of OPEs measured in this study were comparable or even higher than most of other studies. This suggests that during the shift of labour-intensive manufacturing from the coastal developed areas to inland regions, OPEs were widely used in industrial and manufacturing processes in southwest China which needs concern.

This intensive sampling campaign of urban and suburban area found no significant spatial variability of Σ_7 OPEs across Chengdu, China, but the most notable seasonal variation was observed for alkyl phosphate, followed by halogenated OPEs and aryl OPEs. Higher concentrations and more dispersed pattern of OPEs in autumn / winter than that in summer, with TBEP, TCEP, TCPP and TnBP being the dominant compounds. The occurrence of unexpected high level of individual OPEs at different sites in autumn might indicate that there was a noteworthy emission. PCA analysis showed the main sources of OPEs in $PM_{2.5}$ include plastic industry / interior decoration / traffic emission (34.5%) and chemical, mechanical and electrical industry (27.8%). PMF showed the main sources were the plastics / electrical industry and indoor source emissions. OPEs have a wide range of physical and chemical properties, combined with differences in its behavior identified in this study, the management of OPEs as individual compounds instead of a single chemical class should be considered. In addition, due to the special topography and meteorological conditions of the inland city, the distribution and seasonal variation of OPEs in the air in this study were significantly different from that of most coastal cities and over the sea. The sustained and stable high local emissions are particularly noteworthy. The chlorinated phosphate, especially TCPP and TCEP, which are highly toxic and persistent in the environment, have high concentrations in this study. Their usage and source emissions should be controlled.

Data availability. Some or all data, models, or code generated or used during the study are available in a repository or online in accordance with funder data retention policies (Provide full citations that include URLs or DOIs.)

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Author contribution. Hongling Yin designed the experiments and Jinfeng Liang and Shiping Li carried them out. Shiping Li visualized the data and Di Wu wrote the original Draft. Hongling Yin prepared the manuscript with contributions from all co-authors.

Competing interests. The authors declare that they have no conflict of interest.

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