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1 **Measurement report: Seasonality, distribution and sources of**  
2 **organophosphate esters in PM<sub>2.5</sub> from an inland urban city in**  
3 **Southwest China**

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8 **Abstract.** Organophosphate esters (OPEs) are contaminants of emerging concern, and studies have  
9 concluded that urban areas are a significant source of OPEs. Samples were collected from six ground-  
10 based sites located in Chengdu, a typical rapidly developing metropolitan area in Southwest China, and  
11 were analysed for seven OPEs in atmospheric PM<sub>2.5</sub> ( $\Sigma_7$  OPEs). The concentrations of  $\Sigma_7$  OPEs in PM<sub>2.5</sub>  
12 ranged from 5.83 to 6.91 ng m<sup>-3</sup>, with a mean of  $6.6 \pm 3.3$  ng m<sup>-3</sup>, and the primary pollutants were tris-  
13 (2-butoxyethyl) phosphate (TBEP), tri-n-butyl phosphate (TnBP), tris-(2-chloroethyl) phosphate (TCEP)  
14 and tris-(2-chloroisopropyl) phosphate (TCPP), which together made up more than 80% of the  $\Sigma_7$  OPEs.  
15 The concentrations of  $\Sigma_7$  OPEs were higher in autumn/winter than in summer. Nonparametric tests  
16 showed that there was no significant difference in  $\Sigma_7$  OPE concentrations among the six sampling sites,  
17 but the occurrence of unexpectedly high levels of individual OPEs at different sites in autumn might  
18 indicate noteworthy emissions. A very strong correlation ( $R^2 = 0.98$ ,  $p < 0.01$ ) between the OPEs in soil  
19 and in PM<sub>2.5</sub> was observed. Backward trajectory analysis indicated that the OPEs in PM<sub>2.5</sub> were mainly  
20 affected by local sources. Principal component analysis (PCA) revealed that the OPEs in PM<sub>2.5</sub> were  
21 largely sourced from the plastic industry/interior decoration/traffic emission (34.5%) and the chemical,  
22 mechanical and electrical industries (27.8%), while the positive matrix factorization (PMF) model  
23 revealed that the main sources were the plastics industry/indoor source emissions, the food/cosmetics  
24 industry, and industrial emissions. In contrast to coastal cities, sustained and stable high local emissions  
25 in the studied inland city were identified, which is particularly noteworthy. Chlorinated phosphates,  
26 especially TCPP and TCEP, had a high content, and their usage and source emissions should be  
27 controlled.

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## 28 1. Introduction

29 With the prohibition of brominated flame retardants, the production of and demand for organophosphate  
30 esters (OPEs) have rapidly increased in recent years (Wang et al., 2012). OPEs are widely distributed in  
31 the environment and have been detected in air (Guo et al., 2016; Li et al., 2017), water (Wang et al., 2013;  
32 Li et al., 2014), soil (Yin et al., 2016), sediment (Cristale et al., 2013; Celano, et al., 2014) and organisms  
33 (Kim et al., 2011). However, many scholars have found that OPE residues in the environment can cause  
34 toxic effects on organisms (WHO, 1991, 1998, 2000; Kanazawa et al., 2010; Van der Veen & de Boer,  
35 2012; Du et al., 2015). Some countries have enacted legislature to restrict the usage of OPEs (Blum et  
36 al., 2019; Exponent, 2018; State of California, 2020). Nevertheless, the production and usage of OPEs  
37 in China are still on the rise.

38 As OPEs are synthetic substances, the only source of OPEs in the environment is anthropogenic  
39 emissions. The detection of OPEs in Arctic and Antarctic snow samples and atmospheric particulate  
40 matter samples demonstrated that OPEs can be transported over long distances (Möller et al., 2012; Li  
41 et al., 2017). Many studies on OPEs in oceans have been carried out, and the concentrations of particle-  
42 bound OPEs range from tens to thousands of  $\text{ng m}^{-3}$  (Möller et al., 2011; 2012; Cristale & Lacorte, 2013;  
43 Li et al., 2017; McDonough et al., 2018). Some researchers noted that high concentrations of OPEs  
44 (thousands of  $\text{ng m}^{-3}$ ) originated from air flow from the mainland (Möller et al., 2012; Lai et al., 2015).  
45 In addition, studies have proven that urban areas have the highest OPE pollution. However, until now,  
46 only a few papers have reported the concentration and distribution of OPEs in urban atmospheric  $\text{PM}_{2.5}$ .  
47 Concentrations of atmospheric OPEs in most cities were lower than  $10 \text{ ng m}^{-3}$ ; a higher concentration of  
48  $19.2 \text{ ng m}^{-3}$  was observed at a suburban site in Shanghai, and a concentration of  $49.1 \text{ ng m}^{-3}$  was observed  
49 in Hong Kong (Ohura et al., 2006; Salamova et al., 2014b; Marklund et al., 2005; Shoeib et al., 2014;  
50 Yin et al., 2015; Liu et al., 2016; Ren et al., 2016; Guo et al., 2016; Wong et al., 2018). To date, most  
51 studies in China have focused on OPEs in the Yangtze River Delta and Pearl River Delta, especially  
52 eastern coastal cities, while little attention has been paid to western inland cities.

53 Chengdu is a typical inland city located in Southwest China. This megacity is the capital of Sichuan  
54 Province, covers an area of 14,335 square kilometres and has a permanent population of 16.33 million.  
55 As an important national high-tech industrial base, commercial logistics centre and comprehensive  
56 transportation hub designated by the State Council, Chengdu is the most important central city in the

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57 western region (<https://en.wikipedia.org/wiki/Chengdu>). Liu et al. (2016) investigated three chlorinated  
58 OPEs in the atmosphere at 10 urban sites in China during 2013 – 2014 and observed the highest annual  
59 mean concentrations in Chengdu ( $1,300 \pm 2,800 \text{ ng m}^{-3}$ ). However, there is still a lack of information  
60 regarding the levels, sources, and fate of OPEs in Southwest China, which may obviously differ from  
61 those of coastal cities or ocean locations. Our previous study investigated OPE concentrations in  $\text{PM}_{2.5}$   
62 at two sites (urban and suburban sites) in Chengdu (a city experiencing fast economic growth in  
63 Southwest China) and found that the OPE concentrations and profiles were similar at the two sites (Yin  
64 et al., 2015). However, the influencing factors and potential sources of OPEs in  $\text{PM}_{2.5}$  in Chengdu are  
65 still unclear. Therefore, in this study,  $\text{PM}_{2.5}$  was collected over one year (October 2014 to September  
66 2015) at six sites in Chengdu to a) report the levels and composition profiles of OPEs in urban air in a  
67 typical inland city; (b) obtain the seasonal and spatial variations in OPEs in  $\text{PM}_{2.5}$ ; (c) investigate the  
68 relationships and correlations among the target compounds or with influencing factors; and (d) illustrate  
69 the potential sources of OPEs in  $\text{PM}_{2.5}$ .

## 70 **2. Materials and Methods**

### 71 **2.1 Chemicals**

72 The main reagents, such as ethyl acetate, acetone, hexane and acetonitrile, were high-performance liquid  
73 chromatography (HPLC) grade (Kelon Chemical Corp., China). The standard solution (Sigma Aldrich  
74 Corp., USA) included tri-n-butyl phosphate (TnBP), tris-(2-ethylhexyl) phosphate (TEHP), tris-(2-  
75 butoxyethyl) phosphate (TBEP), triphenyl phosphate (TPhP), tris-(2-chloroethyl) phosphate (TCEP),  
76 tris-(2-chloroisopropyl) phosphate (TCPP), and tris-(2,3-dichloropropyl) phosphate (TDCIPP). Copper,  
77 aluminium oxide, silica gel,  $\text{Na}_2\text{SO}_4$  and other chemicals were purchased from Kelon Chemical Corp.,  
78 China. Deionized water was obtained from Milli-Q equipment.

### 79 **2.2. Sample collection**

80 The atmospheric sampling sites were located in the main city area (site B: downtown; site C: south; site  
81 D: east; site E: north; site F: west) and suburban area (site A) of Chengdu, as shown in Fig. S1. The  
82 atmospheric samples were collected by a KC-6120 medium-flow atmospheric comprehensive sampler  
83 with quartz film. The speed was set at  $100 \text{ L min}^{-1}$ , and each collection campaign lasted 23 hours. The  
84 sampling campaign was carried out between October 2014 and September 2015. In each season,

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85 continuous sampling was carried out for approximately one week, except for rainy days. In autumn, the  
86 sampling duration was from October 23 to October 29, 2014 (no samples were obtained due to rain on  
87 October 26 and 27); in winter, the sampling duration was from December 22 to December 30, 2014 (no  
88 samples were obtained due to rain on October 25 and 26); in spring, the sampling duration was from  
89 March 25 to March 30, 2015; and in summer, the sampling duration was from July 16 to July 24, 2015  
90 (no sample was obtained due to rain on July 21). A total of 149 samples were obtained. Most of the  
91 weather conditions were cloudy days, with south/north winds at  $\leq 5.5$  m/s. The temperature ranged from  
92 0 to 35 °C. The weather conditions represented typical seasonal weather conditions.

### 93 **2.3. Sample preparation and analysis**

94 The shredded PM<sub>2.5</sub> sample film was placed in a test tube and incubated in 20 mL ethyl acetate/acetone  
95 (v:v, 3:2) for 12 hours. After ultrasonic extraction for 30 minutes, the liquid was separated, and the  
96 residue was further extracted with 10 mL ethyl acetate/acetone (v:v, 3:2) by ultrasonic extraction for 15  
97 minutes. The extracts were combined, concentrated with vacuum-condensing equipment (Buchi Syncore  
98 Q-101, Switzerland) to approximately 1 mL, and then loaded onto an activated aluminium oxide/silica  
99 gel (v:v, 3:1) column. The column was eluted first with 20 mL hexane to remove impurities, then with  
100 20 mL ethyl acetate/acetone (v:v, 3:2), and the latter eluate (ethyl acetate/acetone) was collected. The  
101 eluate was concentrated to nearly dry by vacuum-condensing equipment and then fixed to 200  $\mu$ L with  
102 hexane for gas chromatography-mass spectrometry (GC-MS) (Shimadzu 2010 plus, Japan) analysis.

103 The GC was equipped with a SH-Rxi-5Sil MS capillary column (30 m  $\times$  0.25  $\mu$ m  $\times$  0.25 mm, Shimadzu,  
104 Japan) and operated with a 280 °C inlet temperature using splitless injection. The MS source was electron  
105 impact (EI), and it was operated in selected ion monitoring (SIM) mode. Helium was used as the carrier  
106 gas with a flow rate of 1.00 mL min<sup>-1</sup>. The GC oven temperature was held at 50 °C for 1 minute, increased  
107 to 200 °C at 15 °C min<sup>-1</sup> and held for 1 minute, increased to 250 °C at 4.00 °C min<sup>-1</sup>, and then increased  
108 to 300 °C at 20 °C min<sup>-1</sup> and held for 4 minutes. The interface temperature was 280 °C, and the ion source  
109 temperature was 200 °C. The respective characteristic ion and reference ions (m/z) of the 7 target  
110 compounds were 155/99, 211, 125 (TnBP), 249/63, 143, 251 (TCEP), 125/99, 201, 277, 157 (TCPP),  
111 75/99, 191, 209, 381 (TDCPP), 326/325, 77, 215 (TPhP), 85/100, 199, 299 (TBEP), 99/113 and 211  
112 (TEHP).

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## 113 2.4. QA/QC

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

## 125 2.5 Statistical analysis

126 Data analysis was done through IBM SPSS 22.0. Parameter test and nonparametric test were used to  
127 analyse the differences between data. Pearson's correlation coefficients were used to evaluate the linear  
128 relationship between the two variables, while Spearman's rank correlation coefficients were used to  
129 evaluate the monotonic relationship between the two variables.

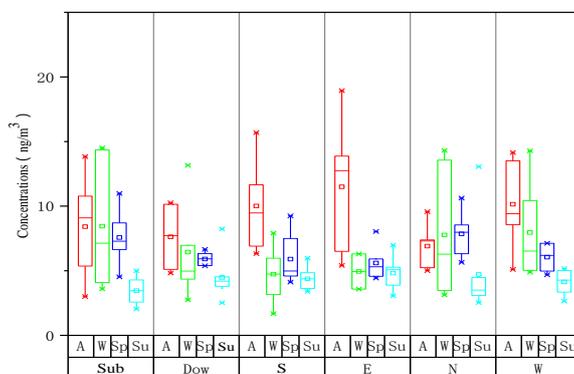
## 130 3. Results and Discussion

### 131 3.1. Levels of OPEs in PM<sub>2.5</sub>

132 OPEs were present in PM<sub>2.5</sub> samples collected across the study area (Fig. S1). The seven OPEs were  
133 found in 96.7% - 100% of the samples (n=149). The high detection frequencies of most OPEs indicated  
134 that OPE contamination was ubiquitous in the air of Chengdu city.

135 The concentrations of  $\Sigma_7$  OPEs in PM<sub>2.5</sub> across the six sites were in the range of 3.5 - 11.5 ng m<sup>-3</sup>, and the  
136 annual median concentration of  $\Sigma_7$  OPEs was 6.5 ± 3.3 ng m<sup>-3</sup> (Fig. 1). The seasonal average value of  
137 OPEs in PM<sub>2.5</sub> at each site was almost at the same level (5.8 ± 1.3 ng m<sup>-3</sup> - 6.9 ± 2.5 ng m<sup>-3</sup>).  
138 Nonparametric tests showed that there was no significant difference in  $\Sigma_7$  OPE concentrations among the  
139 six sampling sites, indicating that the atmosphere was evenly mixed, and there was no particularly heavy-  
140 or light-polluted area in Chengdu city. These data were quite consistent with our previous study, which

141 reported the annual median concentration of OPEs in PM<sub>2.5</sub> from December 2013 to October 2014 (Yin  
 142 et al., 2015). Interestingly, the concentration of Σ<sub>7</sub> OPEs at the suburban site was similar to or even higher  
 143 than those at some urban sites, which indicated more local sources of these compounds in the suburban  
 144 area.



145  
 146 **Figure 1.** Levels and seasonal variation of Σ<sub>7</sub> OPEs in PM<sub>2.5</sub> at six sampling sites. A: autumn, W: winter, Sp: spring,  
 147 Su: summer, Sub: suburbs, Dow: downtown, S: south, E: east, N: north, W: west.

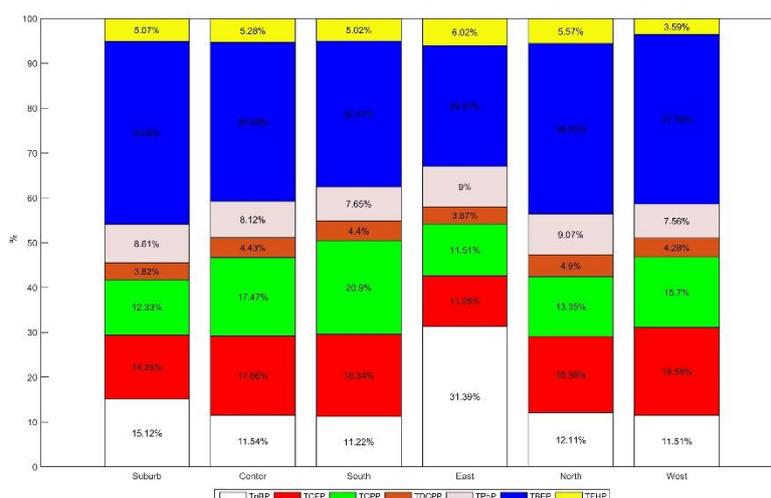
148 The concentrations of OPEs in the particles of Chengdu were comparable to those reported for Beijing  
 149 (0.257 - 8.36 ng m<sup>-3</sup>) (Wang et al., 2018), Σ<sub>6</sub> OPEs for a Shanghai urban site (6.6 ng m<sup>-3</sup>) (Ren et al.,  
 150 2016), and Σ<sub>6</sub> OPEs for Bursa (6.5 ng m<sup>-3</sup>), but higher than those in Houston, US (Σ<sub>12</sub> OPEs, 0.16 - 2.4  
 151 ng m<sup>-3</sup>) (Clark et al., 2017), Dalian (Σ<sub>9</sub> OPEs, 0.32-3.46 ng m<sup>-3</sup>, 1.21 ± 0.67 ng m<sup>-3</sup>) (Wang et al., 2019),  
 152 the European Arctic (0.033 - 1.45 ng m<sup>-3</sup>) (Salamova et al., 2014), the Northern Pacific and Indian Oceans  
 153 (0.23 - 2.9 ng m<sup>-3</sup>) (Moller et al., 2012), the Yellow Sea and Bohai Sea (0.044 - 0.52 ng m<sup>-3</sup>) (Li et al.,  
 154 2017), the South China Sea (0.047 - 0.161 ng m<sup>-3</sup>) (Lai et al., 2015), and the North Atlantic and Arctic  
 155 Oceans (0.035 - 0.343 ng m<sup>-3</sup>) (Li et al., 2017). The detected OPE concentrations were also lower than  
 156 those in Guangzhou and Taiyuan (Σ<sub>11</sub> OPEs, 3.10 - 544 ng m<sup>-3</sup>) (Chen et al., 2020), Bursa, Turkey (Σ<sub>6</sub>  
 157 OPEs, 0.53 - 19.14 ng m<sup>-3</sup>) (Kurtkarakus et al., 2018), and 20 industrial sites in an urban region in  
 158 Guangzhou, China (Σ<sub>12</sub> OPEs, 0.52 - 62.75 ng m<sup>-3</sup>) (Wang et al., 2018).

### 159 3.2. Composition profiles of OPEs in PM<sub>2.5</sub>

160 Nonchlorinated OPEs were the predominant OPEs across Chengdu city. The annual median  
 161 concentrations of total OPEs were fairly uniform at the six sites and were influenced mainly by alkylated  
 162 OPEs. As listed in Table 1, the general trend was that TBEP was the most abundant OPE (annual median  
 163 concentration: 2.3 ng m<sup>-3</sup>, 35.3% of Σ<sub>7</sub> OPEs), followed by TCEP (1.1 ng m<sup>-3</sup>, 16.3%) ≈ TnBP (1.0 ng

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164  $\text{m}^{-3}$ , 15.6%)  $\approx$  TCPP (1.0  $\text{ng m}^{-3}$ , 15.0%) > TPhP (0.5  $\text{ng m}^{-3}$ , 8.4%) > TEHP (0.3  $\text{ng m}^{-3}$ , 5.1%) > TDCPP  
165 (0.3  $\text{ng m}^{-3}$ , 4.3%), with the concentrations of TBEP being approximately 7 - 10 times higher than those  
166 of TDCPP and TEHP. The composition profile of OPEs was similar at all sites except for the east site,  
167 which had a higher contribution of TnBP. However, TBEP, TCEP, TCPP and TnBP were the dominant  
168 OPEs across the city and contributed more than 80% to  $\Sigma_7$  OPEs. This profile was similar to that in  
169 Longyearbyen, Norway, with the primary pollutants being TnBP and TBEP (Möller et al., 2012), as well  
170 as the profiles of OPEs in outdoor urban air (TBEP > TCPP > TCEP > TnBP > TPhP) in Stockholm,  
171 Sweden (Wong et al., 2018) and Turkey (TBEP > TCPP > TPhP > TEHP > TCEP) (Kurtkarakus et al.,  
172 2018). However, these results substantially differed from the report of an urban site in Shanghai that  
173 showed TCEP (0.1 - 10.1  $\text{ng m}^{-3}$ , 1.8  $\text{ng m}^{-3}$ ) > TCPP (0.1 - 9.7  $\text{ng m}^{-3}$ , 1.0  $\text{ng m}^{-3}$ ) > TPhP (0.06 - 14.0  
174  $\text{ng m}^{-3}$ , 0.5  $\text{ng m}^{-3}$ ) > TBP (0.06 - 2.1  $\text{ng m}^{-3}$ , 0.4  $\text{ng m}^{-3}$ ) > TDCPP (Nd. - 23.9  $\text{ng m}^{-3}$ , 0.3  $\text{ng m}^{-3}$ ) and  
175 only detected TBEP in 3 out of 116 samples (Nd. - 0.7  $\text{ng m}^{-3}$ , Nd.) (Ren et al., 2016) and reported data  
176 from the Bohai and Yellow Seas showing TCPP (43 - 530  $\text{ng m}^{-3}$ ; 100  $\text{ng m}^{-3}$ , 50  $\pm$  11%) > TCEP (27 -  
177 150  $\text{ng m}^{-3}$ ; 71  $\text{ng m}^{-3}$ , 25  $\pm$  7%) > TiBP (19 - 210  $\text{ng m}^{-3}$ ; 57  $\text{ng m}^{-3}$ , 14  $\pm$  12%) > TnBP (3.0 - 37  $\text{ng m}^{-3}$ ;  
178 13  $\text{ng m}^{-3}$ ). Li et al. (2014) determined that the primary pollutant of outdoor air in Nanjing was TCEP,  
179 and TBEP was not detected. These differences reflected significant differences in OPE production and  
180 usage in different regions, even in the same country. It should be noted that the concentrations of TCPP  
181 and TCEP were at the same level in this study, failing to indicate the industrial replacement of TCEP by  
182 TCPP in Southwest China; this result differed from the higher concentration of TCPP than TCEP  
183 observed due to the industrial replacement of TCEP by TCPP in Europe (Quednow & Püttmann, 2009).  
184 This absence of industrial replacement was confirmed by the fact that there are manufacturers and sellers  
185 of TCEP and TCPP in Chengdu (<https://show.guidechem.com/hainuowei>,  
186 <http://www.sinostandards.net/index.php>), indicating the production of and demand for both TCPP and  
187 TCEP in this region.



188

189 **Figure 2.** Percentages of individual OPE contributing to the  $\Sigma_7$  OPEs at each sampling site.

190 **Table 1.** The annual median concentrations of OPEs in PM<sub>2.5</sub> from Chengdu (ng m<sup>-3</sup>).

Sampling sites	TnBP	TCEP	TCPP	TDCPP	TPhP	TBEP	TEHP	$\Sigma_7$ 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

191 Combined with the data from 2013-2014 (Yin et al., 2015), TBEP was always the dominant OPE during  
 192 the two sampling periods (2013 - 2014 and 2014 - 2015). The Kruskal-Wallis test revealed that TnBP  
 193 and TCPP had no significant difference between the two sampling periods, but there were significant  
 194 differences in other kinds of OPEs between the two sampling periods. This result indicated that the  
 195 production and usage of individual OPEs have changed to a certain degree, suggesting that OPEs should  
 196 be better investigated and governed with respect to individual compounds.

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197 OPEs can be categorized by whether they are halogenated, alkylated or aryl OPEs. Of the OPEs measured  
198 in this study, TCEP, TCPP and TDCPP are halogenated OPEs, TBEP, TnBP and TEHP are alkylated  
199 OPEs, and TPhP is an aryl OPE. The OPEs in PM<sub>2.5</sub> at all sites were dominated by alkylated compounds  
200 ( $55.9 \pm 10.1\%$ ), followed by halogenated OPEs ( $35.8 \pm 9.9\%$ ) and aryl OPEs ( $8.3 \pm 4.1\%$ ). Our results  
201 are similar to those observed in Bursa, Turkey (Kurtkarakus et al., 2018), where alkylated OPEs  
202 accounted for 68% - 95% of total OPEs, while halogenated OPEs accounted for 3.1% - 29%, and aryl  
203 OPEs accounted for 1.4% - 3.7%. Wu et al. (2020) also reported that alkyl OPEs dominated the OPE  
204 compositional profiles of urban air collected from Chicago and Cleveland. At Longyearbyen, the  
205 nonchlorinated OPE concentrations comprised 75% of the  $\Sigma_8$  OPE concentrations (Salamova et al.,  
206 2014a). However, our results are obviously different from those of many studies, with the atmospheric  
207 samples collected in urban areas being dominated by chlorinated OPEs (50 - 80%) (Salamova et al.,  
208 2014b; Liu et al., 2016; Guo et al., 2016). In our study, nonchlorinated OPEs were dominant in urban  
209 and suburban areas across the city.

### 210 **3.3. Seasonal and spatial variations in OPEs in PM<sub>2.5</sub>**

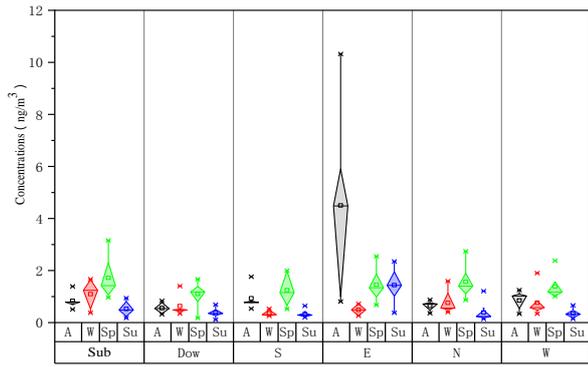
211 The mean seasonal concentrations are plotted for the six sampling sites in Fig. 1. The data were quite  
212 consistent with our previous study from December 2013 to October 2014 (Yin et al., 2015). The  
213 concentrations of OPEs in PM<sub>2.5</sub> were fairly uniform throughout the three studied years. As shown in Fig.  
214 2, the general order of decreasing average  $\Sigma_7$  OPE concentrations in the suburban area was autumn ( $8.4$   
215  $\pm 4.3$  ng m<sup>-3</sup>)  $\approx$  winter ( $8.4 \pm 4.5$  ng m<sup>-3</sup>) > spring ( $7.6 \pm 2.2$  ng m<sup>-3</sup>) > summer ( $3.5 \pm 1.1$  ng m<sup>-3</sup>), while  
216 in the urban area, the order was autumn ( $9.30 \pm 3.89$  ng m<sup>-3</sup>) > winter ( $6.63 \pm 3.65$  ng m<sup>-3</sup>) > spring ( $6.36$   
217  $\pm 1.72$  ng m<sup>-3</sup>) > summer ( $4.60 \pm 1.91$  ng m<sup>-3</sup>). The average concentration of  $\Sigma_7$  OPEs in autumn/winter  
218 was approximately 2 times that in summer. In summer, turbulent flow accelerated the diffusion of  
219 pollutants, leading to the lowest concentration, while higher concentrations of OPEs appeared in autumn  
220 and winter because the inversion layer appeared more frequently in autumn and winter, making the  
221 diffusion and dilution of pollutants more difficult. This seasonal variation was mostly in line with that at  
222 the Shanghai urban site, with an order of autumn ( $8.4$  ng m<sup>-3</sup>) > winter ( $7.6$  ng m<sup>-3</sup>) > spring ( $5.5$  ng m<sup>-3</sup>)  
223 > summer ( $4.4$  ng m<sup>-3</sup>); in that case, the maximum value was also approximately twice the minimum  
224 (Ren et al., 2016). In addition, this finding was similar to that in Xinxiang, which showed no significant  
225 seasonal changes and only exhibited individual high values in winter. In contrast, Wang et al. (2019)

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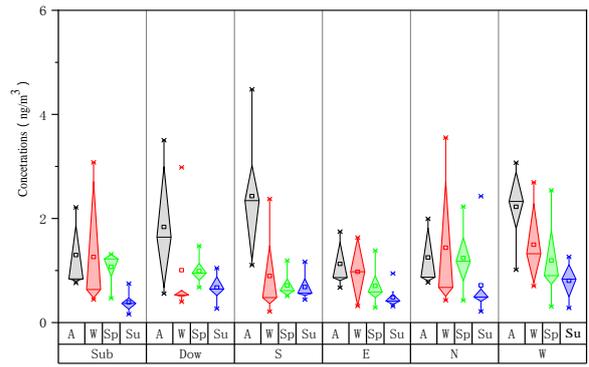
226 found that the PM<sub>2.5</sub>-bound fractions of OPEs varied significantly between seasons in Dalian, China,  
227 with their concentrations being higher in hot seasons, which may be due to temperature-driven emissions  
228 or gas-particle partitioning. Wong et al. (2018) reported that most OPEs in outdoor urban air in  
229 Stockholm, Sweden, showed seasonality, with increased concentrations during the warm period. Sühring  
230 et al. (2016) reported the temperature dependence of chlorinated OPEs and 2-ethylhexyl diphenyl  
231 phosphate (EHDPP) in Arctic air. Wu et al. (2020) reported that median concentrations of  $\Sigma$  OPEs for  
232 summer samples were up to 5 times greater than those for winter samples. Similar seasonal patterns were  
233 reported by Salamova et al. (2014) for atmospheric particle-phase OPE concentrations in samples  
234 collected from the Great Lakes in 2012. A reasonable explanation is that OPEs are not chemically bound  
235 to the materials in which they are used and higher temperatures may facilitate their emission from  
236 buildings and vehicles. However, Liu et al. (2014) did not observe any temperature dependence for OPEs  
237 in urban air in Toronto, Canada. Thus, previous reports of the temperature dependence of OPEs are not  
238 consistent. In our study, correlation analysis between temperature, wind speed, wind direction and  $\Sigma_7$   
239 OPE concentrations was performed. The results showed statistically significant negative correlations  
240 between temperature and  $\Sigma_7$  OPEs ( $R = -0.355$ ,  $p < 0.01$ ). The lowest concentrations of  $\Sigma_7$  OPEs and  
241 individual compounds were observed in summer, suggesting that the OPE level was not dominated by  
242 temperature-driven emissions. Gas-particle partitioning and local emission sources may contribute to this  
243 variation.

244 The most obvious difference between these results and those for coastal cities was that the concentrations  
245 of almost all OPE monomers in this study were highest in autumn/winter and lowest in summer,  
246 suggesting sustained and stable high local emissions in the studied inland city, which is particularly  
247 noteworthy. No point sources were identified in summer, and the OPE levels were diluted and diffused  
248 in summer due to the higher wind speed than that in winter in the studied inland city. This behaviour was  
249 different from that of coastal cities: Liu et al. (2016) observed the highest TCPP and TCEP concentrations  
250 in the summer in Guangzhou, and Javier et al. (2018) found that the OPEs in spring generally exhibited  
251 the lowest concentrations in Bizerte, Tunisia, probably linked to the influence of local meteorological  
252 conditions and, to a lesser extent, air mass trajectories.

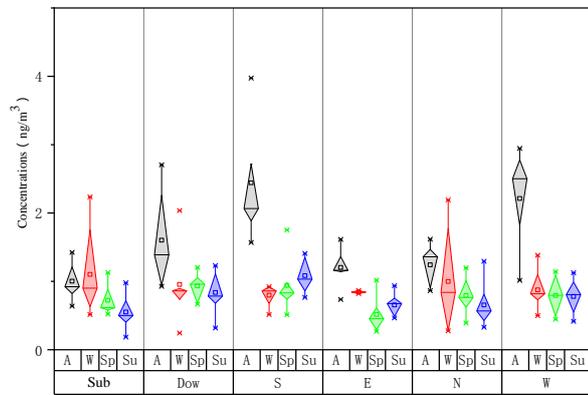
253



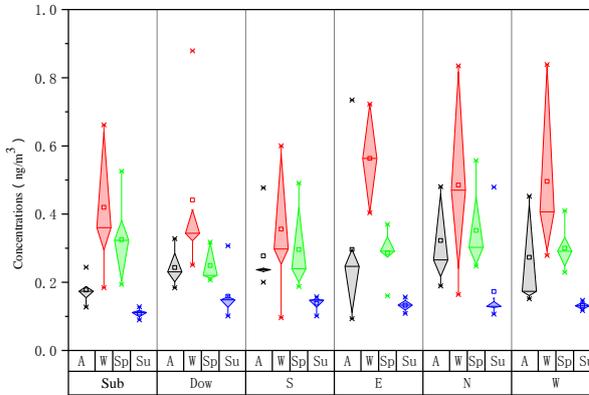
TnBP



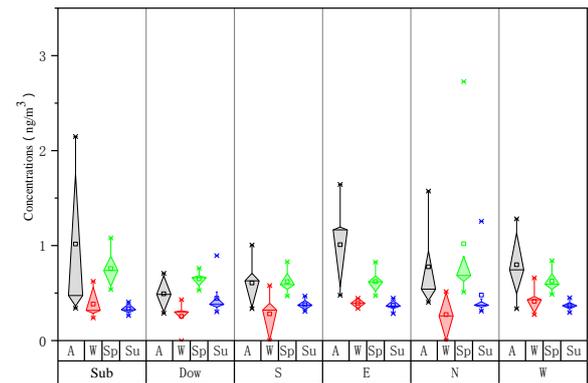
TCEP



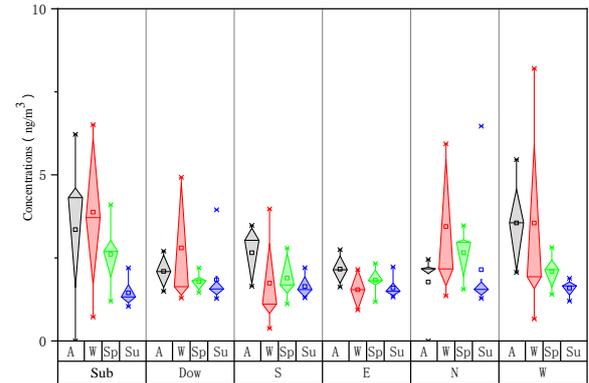
TCPP



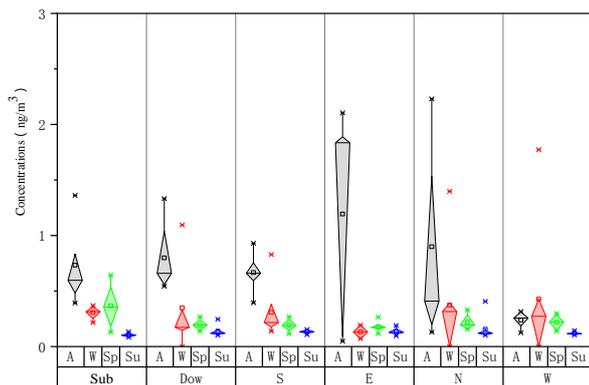
TDCPP



TPhP



TBEP



TEHP

254 **Figure 3.** The seasonal variation of individual OPE in PM<sub>2.5</sub> from Chengdu city. A:Autumn, W:Winter, Sp:Spring,  
 255 Su:Summer, Sub:Suburbs, Dow:Downtown, S:South, E:East,N:North, W:West.

256 Although the Kruskal-Wallis test showed no significant variation in  $\Sigma_7$  OPE concentrations across the  
 257 city, spatial differences were identified in this study. For example, TnBP and TCPP had significant  
 258 differences among the six sites. In addition, higher concentrations and more dispersed patterns of most  
 259 OPEs were observed in autumn and winter than in summer (Fig. 3). The concentrations of TEHP in  
 260 autumn at the eastern and northern sampling sites were more dispersed than those at other sites. The same  
 261 dispersion pattern was observed for TBEP in winter at the western sampling site, TPhP in autumn at the  
 262 suburban sampling site, and TnBP in autumn at the eastern sampling site, suggesting that extra emission  
 263 sources existed in autumn or winter. Considering the layout of Chengdu, which spreads out from the  
 264 central area along the loop line (the first ring road, the second ring road and the third ring road), the  
 265 uniform patterns of OPE levels and distribution across the city are understandable. Different types of  
 266 industrial parks in different directions in Chengdu may be the reason for the spatial differences in OPEs.  
 267 For example, in eastern Chengdu, there are automobile industrial parks and other large industrial parks,  
 268 while logistics and shoemaking industrial parks are located in the suburbs. The occurrence of  
 269 unexpectedly high levels of individual OPEs at different sites in autumn might indicate noteworthy  
 270 emissions. The spatial and seasonal variations in individual OPEs suggest that OPE control and  
 271 management measures should be taken. Interestingly, in this study, alkyl OPEs dominated at both urban  
 272 and suburban sites. This finding was extremely different from the results reported by Wu et al. (2020),

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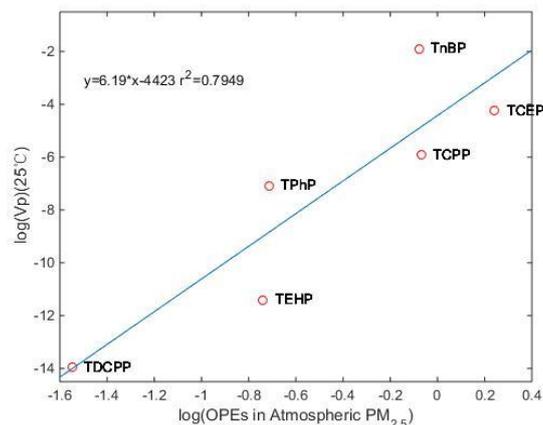
273 in which alkyl OPEs dominated at urban sites, chlorinated OPEs were prevalent at rural sites, and aryl  
274 OPEs were most abundant at remote locations.

275 Many studies have focused on halogenated OPEs due to their persistence, bioaccumulation, and potential  
276 human health effects, and they dominate the OPE profile in the air of many cities and other areas (Li et  
277 al., 2017). Liu et al. (2016) reported that the sum of the concentrations of three halogenated OPEs at 10  
278 urban sites ranged from 0.05 to 12 ng m<sup>-3</sup>, suggesting that the highest production volume and widest  
279 application of OPEs have led to large emissions of OPEs in China in recent years. However, in our study,  
280 the mean concentrations of halogenated, alkylated and aryl OPEs were 2.4 ± 1.4 ng m<sup>-3</sup>, 3.7 ± 2.1 ng m<sup>-3</sup>,  
281 and 0.5 ± 0.4 ng m<sup>-3</sup>, respectively, which showed that alkylated OPEs dominated the profile of OPEs  
282 in PM<sub>2.5</sub> in Chengdu. The most notable seasonal variation was observed for alkyl phosphates, followed  
283 by halogenated OPEs and aryl OPEs. These results were significantly different from those in other studies  
284 that reported that halogenated OPEs had the maximum seasonal variability (Guo et al., 2016; Shoeib et  
285 al., 2014).

### 286 **3.4. Correlation analysis of OPEs**

#### 287 **3.4.1 Linkage to environmental factors**

288 Most OPE monomer concentrations in PM<sub>2.5</sub> have a strong linear correlation ( $R^2 = 0.79$ ) with vapor  
289 pressure (Fig. 4), suggesting that vapor pressure is an important factor controlling the levels of OPEs in  
290 PM<sub>2.5</sub>, except for TBEP. Generally, the greater the vapor pressure of an OPE is, the more easily the  
291 compound can be released into the environment. Therefore, the main sources of most OPEs in Chengdu  
292 atmospheric PM<sub>2.5</sub> are production processes including OPEs and the phase transition process before they  
293 enter into the atmosphere. The boiling points of OPEs are relatively high, so they tend to be adsorbed  
294 onto PM<sub>2.5</sub> after being released to the environment (Wang et al., 2019), and their gas-particle distributions  
295 determine their concentrations in PM<sub>2.5</sub>. Interestingly, the vapor pressure of TBEP is lower than that of  
296 other OPEs, but its concentration in PM<sub>2.5</sub> was higher, which indicated that sustained and stable high  
297 emission sources, possibly including traffic emission, kept its concentration at a high level (Chen et al.,  
298 2020). Sühring et al. (2016) reported that nonhalogenated OPE concentrations in Canadian Arctic air  
299 appeared to have diffuse sources or local sources close to the land-based sampling stations.

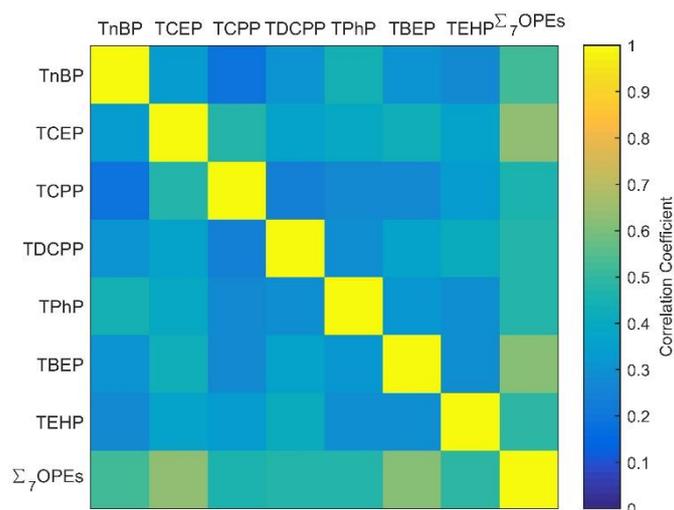


300

301 **Figure 4.** Relationship of individual OPE concentration in PM<sub>2.5</sub> and its vapor pressure.

302 **3.4.2 Correlation between target analytes**

303 Spearman's rank correlation coefficients were used to investigate the potential emission sources for  
 304 OPEs according to the relationship between individual OPEs in PM<sub>2.5</sub> (Fig. 5, Table 2). Fig. 5 shows no  
 305 statistically significant positive correlations between OPE monomers ( $r < 0.50$ ,  $p < 0.01$ ). However,  $\Sigma_7$ OPE  
 306 concentrations were closely related to TBEP, TCEP and TnBP ( $r = 0.53$ - $0.61$ ,  $p < 0.01$ ), which further  
 307 indicated that OPE levels were influenced mainly by the dominant OPE compounds. Comparatively,  
 308 weak correlations between most OPEs were observed in urban regions (Wang et al., 2018) and Turkey  
 309 (KurtKarakus et al., 2018). However, strong correlations between individual OPEs were found in  
 310 Guangzhou and Taiyuan (Chen et al., 2020).



311

312 **Figure 5.** Spearman's rank correlation coefficients between the concentrations of individual OPE in PM<sub>2.5</sub> samples.

313 **Table 2.** The correlation analysis of individual OPE 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

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

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

316 Further analysis results are shown in Table 2. Significant correlations between only TCPP and TCEP at  
 317 both downtown ( $r=0.82, p<0.01$ ) and suburban sites ( $r=0.85, p<0.01$ ) were observed, indicating the high  
 318 homology between these two compounds. The studied inland city in China still uses a large number of  
 319 products containing chlorinated flame retardants, which was confirmed by our previous study of house

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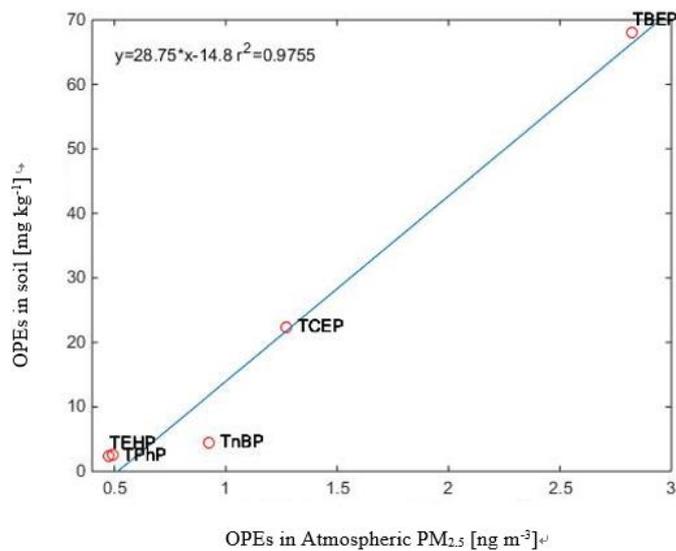
320 dust (Liu et al., 2017; Yin et al., 2019). At the downtown site, another significant correlation existed  
321 between TEHP and TCEP ( $r=0.50$ ,  $p<0.01$ ), while other compounds had weak to moderate correlations  
322 ( $r<0.46$ ,  $p<0.01$ ). The downtown area is mainly focused on light industry and software development, and  
323 TCPP, TCEP, TnBP, TBEP and TPhP are used in textiles, leather, electronic products and other fields.  
324 However, the correlations of each OPE monomer at site A (suburb) were stronger than those in the urban  
325 area. The correlations between TnBP and TCEP, TnBP and TDCPP, TCEP and TCPP, TCEP and TDCPP,  
326 TCEP and TBEP, TCPP and TDCPP, TCPP and TBEP were all extremely significant. This result  
327 indicated that the pollution in the suburbs was commixed and influenced by many kinds of pollution  
328 sources.

### 329 **3.4.3 Correlation analysis of OPEs and PM<sub>2.5</sub> concentrations**

330 SPSS software was used to produce scatter plots to analyse the relationship between the concentrations  
331 of OPE monomers and PM<sub>2.5</sub>. As displayed in Fig. S2, only weak to moderate correlations were observed  
332 between most OPEs and PM<sub>2.5</sub>, except for a significant correlation between TDCPP and PM<sub>2.5</sub> ( $r=0.53$ ,  
333  $p<0.01$ ), which suggests that continuous and relatively constant local emissions were the main sources.  
334 This result was similar to that reported for Taiyuan (Guo et al., 2016), where no correlation was found  
335 between the concentrations of OPEs and the concentration of particulate matter. However, this result  
336 differed from that in Xinxiang (Shen et al., 2016), where the concentrations of OPEs and PM<sub>2.5</sub> had a  
337 significant correlation ( $r=0.85c$ ), and high values of OPEs/PM<sub>2.5</sub> were related to the contribution of air  
338 masses from heavily polluted areas (Henan and Jiangsu Provinces), while low OPEs/PM<sub>2.5</sub> values were  
339 due to air masses from Shanxi-Gansu and Neimenggu Provinces. Chen et al. (2020) found that there was  
340 a significant correlation ( $p < 0.05$ ) between the concentrations of  $\Sigma_{11}$  OPEs and PM<sub>2.5</sub> at some sampling  
341 sites but not at a site located in the urban region in Guangzhou with potential additional pollution sources.

### 342 **3.4.4 Correlation analysis of OPEs in PM<sub>2.5</sub> and soil**

343 Due to the low detection frequency of TCPP and TDCPP in the soil (Yin et al., 2016), the relationships  
344 of the other five OPE monomers in the soil and in atmospheric PM<sub>2.5</sub> are presented in Fig. 6. A very  
345 strong linear relationship was obtained between the OPEs in soil and in PM<sub>2.5</sub> ( $R^2 = 0.98$ ,  $p<0.01$ ),  
346 indicating that atmospheric PM<sub>2.5</sub> settling is an important source of OPEs in the soil, just as soil is a  
347 source for OPEs in the air.



348

349 **Figure 6.** Relationship between OPEs in atmospheric PM<sub>2.5</sub> and in soil.

### 350 3.4.5 Correlation analysis of OPEs in indoor and outdoor air

351 The OPE profile in outdoor air in this study was TBEP > TCEP > TnBP > TCPP > TPhP > TEHP > TDCPP,  
 352 which was different from that of indoor dust reported in our previous study (Liu et al., 2017):  
 353 TPhP > TCPP > TnBP > TDCPP > TBEP > TCEP > TEHP. TPhP is used as an important alternative to  
 354 decabrominated diphenyl ether (deca-BDE), which is typically used as a flame retardant in electrical and  
 355 electronic products. In addition, plastic films and rubber may be important sources of TPhP. Thus, OPEs  
 356 in indoor dust mainly come from the indoor environment and are related to human activities, not from  
 357 outdoor air. In addition to the different usages of OPEs, many factors may also lead to differences  
 358 between indoor and outdoor OPEs. For example, TBEP has the shortest atmospheric half-life, which may  
 359 explain why its dominance in indoor samples was not observed for its outdoor counterparts. Studies in  
 360 Sweden (Wong et al., 2018) reported that the concentrations of OPEs in indoor air followed the order  
 361 TCPP > TCEP > TBEP > TnBP > TPhP, and those in outdoor urban air followed the order TBEP > TCPP >  
 362 TCEP > TnBP > TPhP (Wong, 2018), which also indicated differences in OPE profiles in indoor and  
 363 outdoor air. They found that activities in buildings, e.g., floor cleaning, polishing, construction,  
 364 introduction of new electronics and changes in ventilation rate, could be key factors controlling the  
 365 concentration of indoor air pollutants, while the observed seasonality for OPEs in outdoor air was due to  
 366 changes in primary emissions.

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## 367 3.5 Source apportionment of OPEs

### 368 3.5.1 Backward trajectory model analysis

369 Backward trajectory cluster analysis (HYSPLIT4), which combines the horizontal and vertical motion  
370 of the atmosphere and can analyse the transport, migration and diffusion of atmospheric pollutants, was  
371 used in this study. The height of 500 m above ground level (AGL) can best represent the characteristics  
372 of the wind field associated with this process, and HYSPLIT4 was used to obtain the 500 m AGL 24-  
373 hour backward trajectory during the sampling period in Chengdu. During the sampling period, the air  
374 masses were mainly from the north-eastern and southern parts of Sichuan Province, including Mianyang,  
375 Deyang, Renshou and Chengdu, and a few of the trajectories came from Chongqing and other places in  
376 Gansu Province. Therefore, during the sampling period, Chengdu was mainly affected by air masses  
377 from eastern Sichuan.

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

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395 atmosphere, which further explains why the pollution of OPEs in PM<sub>2.5</sub> was controlled by endogenous  
396 pollution, not by exogenous pollution.

### 397 **3.5.2 Principal component analysis**

398 Principal component analysis (PCA) of OPEs was carried out by SPSS. The normalized correlation  
399 coefficient matrix of the original data for each sampling site showed that there was a strong correlation  
400 between TCPP and TCEP, TCEP and TBEP, and TnBP and TPhP, which satisfied the condition of  
401 dimensionality reduction of PCA. Two principal component factors were obtained in this study. The  
402 cumulative contribution of the two principal component factors was 62.3%, which can basically explain  
403 the data. The results are shown in Table S1. For factor 1, there was a large load on TCEP, TCPP, and  
404 TBEP and a moderate load on TDCPP. Factor 1 can represent sources of OPEs from the plastic industry,  
405 interior decoration and traffic emissions, with a contribution ratio of 34.5% (Marklund et al., 2005;  
406 Regnery et al., 2011; CEFIC, 2002). Factor 2 has a higher load on TnBP, TEHP and TPhP. The highest  
407 load was on TnBP, which is often used as a high-carbon alcohol defoamer, mostly in industries that do  
408 not come into contact with food and cosmetics, as well as in antistatic agents and extractants of rare earth  
409 elements. TEHP can be used as an antifoaming agent, hydraulic fluid and so on. TPhP is typically used  
410 in electrical and electronic products, plastic films and rubber (Esch, 2000; Stevens et al., 2006; Wei et  
411 al., 2015). Factor 2 can be attributed to the chemical, mechanical and electrical industries, and its  
412 contribution ratio was 27.8%.

### 413 **3.5.3 PMF model analysis**

414 The basic principle of the PMF method is to decompose a sample matrix into a factor contribution matrix  
415 and factor component spectrum. The source type of the factor is judged according to the factor component  
416 spectrum, and then the contribution ratio of the source is determined. The uncertainty is estimated by  
417 three methods: bootstrapping (BS), displacement (DISP) and BS-DISP. From the 149 samples collected  
418 in Chengdu, 132 valid samples were selected to participate in the model calculation, and three factors  
419 were determined. TPhP was the only chemical with a residual (4.0) greater than 3. The concentrations of  
420 OPEs satisfied the normal distribution. The components of factor 1 were complex. Factor 1 contributed  
421 71.0%, 70.7% and 70.9% to TCEP, TCPP and TEHP, respectively, and 58.3% to TPhP. Factor 1 was  
422 deduced to be the plastics/electrical industry and indoor source emissions (Esch, 2000; Stevens et al.,

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423 2006). Factor 2 contributed the most to TBEP (78.0%), followed by TDCPP (44.7%), while it did not  
424 contribute to TnBP. Therefore, factor 2 was deduced to be the food/cosmetics industry and traffic  
425 emissions (Marklund et al., 2005). Factor 3 contributed 71.7% of the total TnBP, and was deduced to be  
426 a chemical industrial source (Regnery et al., 2011).

#### 427 **4. Conclusions and implications**

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

432 This intensive sampling campaign of urban and suburban areas found no significant spatial variability in  
433  $\Sigma_7$  OPEs across Chengdu, China, but the most notable seasonal variation was observed for alkyl  
434 phosphate, followed by halogenated OPEs and aryl OPEs. Higher concentrations and more dispersed  
435 patterns of OPEs were observed in autumn/winter than in summer, with TBEP, TCEP, TCPP and TnBP  
436 being the dominant compounds. The occurrence of unexpectedly high levels of individual OPEs at  
437 different sites in autumn might indicate that there were noteworthy emissions. PCA showed that the main  
438 sources of OPEs in  $PM_{2.5}$  include plastic industry/interior decoration/traffic emission (34.5%) and the  
439 chemical, mechanical and electrical industries (27.8%). PMF showed that the main sources were the  
440 plastics/electrical industry and indoor source emissions. OPEs have a wide range of physical and  
441 chemical properties, and combined with the differences in their behaviour identified in this study, the  
442 management of OPEs as individual compounds instead of a single chemical class should be considered.

443 In addition, due to the special topography and meteorological conditions of the studied inland city, the  
444 distribution and seasonal variation of OPEs in the air in this study were significantly different from those  
445 of most coastal cities and ocean locations. The sustained and stable high local emissions are particularly  
446 noteworthy. Chlorinated phosphates, especially TCPP and TCEP, which are highly toxic and persistent  
447 in the environment, had high concentrations in this study. Their usage and source emissions should be  
448 controlled.

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

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451 *Team list.* Hongling Yin, Jinfeng Liang, Di Wu, Shiping Li, Yi Luo, Xu Deng.

452 *Author contribution.* Hongling Yin designed the experiments. Jinfeng Liang and Shiping Li carried them out.

453 Shiping Li visualized the data and Di Wu wrote the original Draft. Hongling Yin prepared the manuscript with  
454 contributions from all co-authors.

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

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