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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Measurement report: Seasonal, distribution and sources of organophosphate esters in $PM_{2.5}$ from an inland urban city in southwest China" *by* Hongling Yin et al.

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Response to Anonymous Referee #2 Dear sir, we gratefully thanks for the precious time the reviewer spent making constructive remarks and totally understand the reviewer's concern. The pre-experiment was carried out before the experiment. We conducted the thorough experiment for the quality control and quality assurance including the blank experiment, recoveries of internal standard (TDCPP-d15 and TPhP-d15) in samples for evaluating the accuracy, blank experiment (field blanks, solvent blanks, matrix blanks), precision experiment, etc.. Due to the limited space of the paper, and the focus

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Discussion paper

of this paper is not on the establishment of analytical methods, it is simplified a lot in the QA/QC part. But we have done all the related experiments for QA/QC, and the results were good. In the revised manuscript, we have added them in QA/QC part. Therefore, there is no need to worry about the accuracy of the data. But it's a pity that there were many grammatical problems and reference problems in the manuscript. We all corrected them and sincerely hope that the manuscript can meet the requirements of Atmospheric Chemistry and Physics after modification. According to your constructive comments, the revisions of the manuscript are as follows:

Major concern: Novelty: There is a similar study previously conducted by the leading author here. What makes this manuscript distinct from that previous one? Authors should elaborate more the novelty of this study. Response: The article we published earlier is a report of our experiment results from only two sampling sites. The purpose of that paper was to report the pollution level and distribution of the atmospheric OPEs at urban and suburban sites. Interestingly, we found the seasonal variations of OPEs were significantly different from PM2.5 concentrations and PM2.5-bound PAHs, etc.. So we carried out a more detailed experiment with six sampling sites in the second year. In this paper, except for reporting the level and seasonal variations of OPEs at six sites, we paid more attention to investigate the relationships and correlations among the target compounds or with influence factors and illustrate the potential sources of OPEs in PM2.5. For example, whether different functional areas affect the distributions of atmospheric OPEs, correlations of OPEs with environmental factors (temperature, wind, vapor pressure, boiling points, etc.), correlations of OPEs with PM2.5 concentrations, correlations of OPEs in PM2.5 and soil, correlations of OPEs in indoor and outdoor air were all discussed. These differences are the innovation of this paper.

QA/QC: 1) As no surrogate standards were spiked prior to sample treatment, how did authors evaluate OPE recoveries from the analytical procedures? Response: "Thorough QA/QC procedures for OPE analysis were conducted to ensure data quality. To evaluate the recovery efficiencies of analytical procedures, all samples were added

with internal standard (TDCPP-d15 and TPhP-d15), 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 7 OPEs and the internal standard were between 78.9% and 122.5%." was added in the manuscript. There are only two internal standards, so we use them to ensure the recovery, but use external standard method to quantify the target compounds. In addition, a matrix blank was run in parallel with every batch of samples for the analysis of OPEs. 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 means 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 correlation coefficients of the standard curves of the seven OPE profiles were all greater than 0.990.These all could ensure the accuracy of the data.

2) How was the matrix effect assessed and compensated? Response: The matrix effect was assessed by the matrix blank experiment. The blank quartz membrane was added with the internal standard (TDCPP-d15 and TPhP-d15) and OPEs standard. After the whole pretreatment process, the recoveries of 7 OPEs and the internal standard were all between 70% and 120%. So the data was not corrected and the matrix effect was not compensated.

3) The data from field blanks were missing. PMF model: How were the uncertainties determined? Which references were referred to for identification of sources associated with each factor? I also want to see the source profile of each factor. Response: The field blanks were done which were prepared and installed in the same manner as the regular samples but without turning on the sampler motor. Due to the limited space of the paper, and the focus of this paper is not on the establishment of analytical methods, so it is simplified a lot in the QA/QC part. But we have done all the related experiments

for QA/QC, and the results were good. “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.” was added in the revised manuscript. In PMF, the uncertainty is estimated by three methods: BS, disp and bs-disp. The results are shown in the table below: DISP results showed that the solution was stable because no swaps were present. BS results showed that mapping over 80% of the factors indicated that the BS uncertainties could be interpreted and the number of factors may be appropriate. All of the “Strong” species were selected for the BS-DISP error estimation. The number of DISP and BS-DISP swaps was zero. BS-DISP highlight that the solution may be reliable due to there was no swaps across two factors. Error estimation summary results BS-DISP Diagnostics: # of Cases Accepted: 100 % of Cases Accepted: 100% Largest Decrease in Q: -0.150999993 %dQ: -0.067824623 # of Decreases in Q: 0 # of Swaps in Best Fit: 0 # of Swaps in DISP: 0 Swaps by Factor: 0 0 0 DISP Diagnostics: Error Code: 0 Largest Decrease in Q: -0.005 %dQ: -0.002245848 Swaps by Factor: 0 0 0 BS Mapping: Factor 1 Factor 2 Factor 3 Unmapped Boot Factor 1 100 0 0 0 Boot Factor 2 0 100 0 0 Boot Factor 3 0 0 100 0

The source profile of each factor: Factor Profiles (% of species sum) from Base Run (Convergent Run) TnBP TCEP TCPP TDCPP TPhP TBEP TEHP Factor 1 28.69 70.95 70.72 31.01 58.34 0.00 70.93 Factor 2 0.00 20.31 25.47 44.72 13.97 77.95 26.41 Factor 3 71.31 8.73 3.81 24.27 27.69 22.05 2.66

The references were referred to for identification of sources associated with each factor. “Factor 1 was deduced to be the plastics/electrical industry and indoor source emissions (Esch, 2000; Leisewitz et al., 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., 2005). Factor 3 contributes 71.7% of the total TnBP, which can be deduced as chemical industrial source (Regnery et al., 2011). ”

Minor concern: Line 8: "emerging contaminants"→"contaminant of emerging concern". OPEs have been produced for decades. Response: We're sorry for the improper expression. This expression has been revised to " OPEs are a kind of contaminants of emerging concern in recent years"

Line 9: "centers"→ "areas" Response: Thanks for your advice. "Centers" has been replaced by "areas".

Line 13... which TOGETHER made up..." Response: Thanks for your advice. It has been revised to "which together made up".

Line 18: OPEs can transfer from soil to air particles via suspension and volatilization as well. Actually, authors mentioned this at Lines 303-304. Response: Thanks for your advice. "suggested the atmospheric PM2.5 settlement is an important source of OPEs in soil" has been deleted in line 18.

Lines 32-35: A weird sentence, please rephrase it. Response: Thanks for your advice. After rephrasing, the sentence becomes "However, many scholars found that the residues of OPEs in the environment could cause toxic effects on organisms. (WHO, 1991, 1998, 2000; Kanazawa et al., 2010; Van der Veen and de Boer, 2012; Du et al., 2015)".

Line 35: Reference is needed for the "OPE restrictions". Response: Three references were added for reference: Blum, A.; Behl, M.; Birnbaum, L. S.; Diamond, M. L.; Phillips, A.; Singla, V.; Sipes, N. S.; Stapleton, H. M.; Venier, M. Organophosphate ester flame retardants: Are they a regrettable substitution for polybrominated diphenyl ethers? Environ. Sci. Technol. Lett. 2019, 6, 638-649. Exponent. California bans flame retardants in certain consumer products. 2018, Available at: https://www.exponent.com/knowledge/alerts/2018/09/california-bans-flame-retardants/?pageSize=NaN&pageNum=0&loadAllByPageSize=true (accessed February 15, 2020) State of California. Safer consumer products (SCP) information management system. 2020. Available at:

https://calsafer.dtsc.ca.gov/cms/search/?type=Chemical (accessed February 21, 2020).

Lines 38-39: Reference is needed. Response: Thanks for your advice. References have been added according to your suggestionïijŽ Möller, A.; Xie, Z.; Caba, A.; Sturm, R.; Ebinghaus, R. Organophosphorus flame retardants and plasticizers in the atmosphere of the North Sea. Environ. Pollut. 2011, 159, 3660-3665. Möller, A.; Sturm, R.; Xie, Z.; Cai, M.; He, J.; Ebinghaus, R. Organophosphorus flame retardants and plasticizers in airborne particles over the Northern Pacific and Indian Ocean toward the polar regions: Evidence for global occurrence. Environ. Sci. Technol. 2012, 46, 3127-3134. McDonough, C. A.; De Silva, A. O.; Sun, C.; Cabrerizo, A.; Adelman, D.; Soltwedel, T.;Bauerfeind, E.; Muir, D. C. G.; Lohmann, R. Dissolved organophosphate esters and polybrominated diphenyl ethers in remote marine environments: Arctic surface water distributions and net transport through Fram Strait. Environ. Sci. Technol. 2018, 52, 6208-6216.

Line 45: Which type of matrix is referred to for "Concentrations of OPEs in most cities..."I looked at the references cited, but not all of them talked about PM2.5. Response: This matrix is only for outdoor atmospheric environment. "Concentrations of OPEs in most cities..." has been revised to “Concentrations of atmospheric OPEs in most cities”. Not all of the references we cited talked about PM2.5, but they were all about OPEs in atmospheric particles.

Lines 54-56: How about "Chengdu is an important city in Southwest China due to its role as a national high-tech industrial base, a commercial logistics center, and a comprehensive transportation hub"? Response: Thanks for your advice. This sentence has been added a website: https://en.wikipedia.org/wiki/Chengdu.

Line82: Sampling intervals? Response: 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 day. In autumn, the sampling duration

was from October 23 to October 29, 2014 (no sampling due to rain on October 26 and 27); in winter, the sampling time was from December 22 to December 30, 2014 (no sampling due to rain on October 25 and 26); in spring, 2015, the sampling time was from March 25 to March 30, 2015; in summer, the sampling time was 2015 From July 16 to July 24 (no sampling due to rain on July 21). "has been added in the revised manuscript. Each collection campaign lasted 23 h. The interval of each sample was 1h.

Line 86: Was the analytical method used here applied in any previous studies? Response: Based on the references of Möller et al (2012), we established the quantitative analysis method in the laboratory. This analytical research method has been applied in our previous studies. Li, S. P.; Yin, H. L.; YE, Z. X.; Liang, J. F.; Hao, Y. F. GC-MS determination of 7 organic phosphate ester flame retardants in atmospheric particulates with chromatography purification: PTCA (Part B: Chem Anal). 2015, 051(005):581-585. Yin, H.L., Li, S.P., Ye, Z.X., Yang, Y.C., Liang, J.F., You, J.J. Pollution level and sources of organic phosphorus esters in airborne PM2.5 in Chengdu City, Environ. Sci. (in chinese), 36, 3566-3572, https://doi.org/10.13227/j.hjkx.2015.10.003, 2015. Möller, A.; Sturm, R.; Xie, Z.; Cai, M.; He, J.; Ebinghaus, R. Organophosphorus flame retardants and plasticizers in airborne particles over the Northern Pacific and Indian Ocean toward the polar regions: Evidence for global occurrence. Environ. Sci. Technol. 2012, 46, 3127-3134.

Lines 93-94: How about "The latter eluate was collected and con-centrated by vacuum-condensing..."? Response: The solvent extracts were concentrated to nearly dry by vacuum condensing equipment and then fixed volume to 200 μL with hexane. Then it was placed in a sample bottle to wait for the injection of gas chromatography-mass spectrometry (GC-MS).

Lines 114-118: Could concisely say "detected in virtually all the samples". Response: Thanks for your advice. "Four OPEs (TCPP, TDCPP, TCEP and TnBP) were detected in all samples (n=149), while TBEP was detected in all but one sample. Additionally,

TEHP was detected in 96.7% of samples overall and TPhP was detected in 98% of samples." has been revised to "Seven OPEs were found in 96.7%∼100% of the samples".

Lines 120-121: Did "The average value... four seasons mean "annual average level"? Response: It means "seasonal average concentration", not "annual average level". It is so sorry that the expression is not concise enough. We have checked other places throughout the manuscript.

Line 141: Rephrase the first sentence. Response: Thanks for your advice. It has been revised to "Non-chlorinated OPEs were the predominant OPEs across Chengdu city".

Lines 143-145: Explain the meaning of values in the parentheses. Response: Thank you very much for your reminder. The expression in the parentheses has been changed to "(annual media concentration: 2.3 ng m-3, 35.3% of Σ7 OPEs)".

Lines: 165-167: References? Response: Thanks for your advice. Two company websites for producing and selling OPEs have been added: https://show.guidechem.com/hainuowei, http://www.sinostandards.net/index.php

Lines182-184: A recent study measuring an extended list of OPEs in the Great Lakes atmosphere also found that alkyl OPEs dominated OPE compositional profiles of urban air collected from Chicago and Cleveland (Wu et al. 2020; 10.1021/acs. est.9b07755). Response: Thank you for your reminder. We have referred to the results of this study. For example, (1)"Wu et al. (2020) reported that median concentrations of ΣOPEs for summer samples were up to 5 times greater than those for winter samples. The similar seasonal patterns were reported by Salamova et al. (2014) 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." has been added in the revised manuscript. (2)"Wu et al. (2020) also reported that alkyl OPEs dominated OPE compositional profiles of urban air collected

from Chicago and Cleveland."(3) "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. " has been added in the revised manuscript.

Line 208-210: OPE levels can be surely affected by temperature, so I suppose the authors would like to say "seasonal variations in OPE levels". Additionally, would meteorological parameters other than temperature result in the seasonal variations found in the present study? Response: Thanks for your advice. Based on our experience, we also strongly agree that temperature and other meteorological factors will affect the level of pollutants in PM2.5. However, the concentration of OPEs found in this study did not varied much in the four seasons, which was significantly different from other pollutants. Some literatures showed that the seasonal variations of OPEs in some coastal cities were significantly affected by temperature (Liu et al., 2016; Wang et al., 2019). For example, Wang et al. (2019) reported seasonality was discovered for OPEs in both gas phase and PM2.5 with their concentrations higher in hot seasons in Dalian, which may due to the temperature-driven emission or gas-particle partitioning. However, "In our study, the correlation analysis between the temperature, wind speed, wind direction and Σ7OPEs concentrations has been done. The results showed statistically significant negative correlations between temperature and Σ7OPEs ($R = -0.355$, $p<0.01$). The lowest concentrations of Σ7OPEs 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." These have been added in the revised manuscript. In addition, other meteorological parameters with high contributions to the seasonal variations were not found in the present study.

Lines 236-238: Has been mentioned before. Lines 238-248: Out of place here. Could be moved to section 3.1. Response: Thanks for your advice. Lines 236-238 have been

deleted.

Line 257: Need reference to support "they tend to be adsorbed in PM 2.5". Response: Thanks for your advice. References have been added: (Wang et al., 2019) Wang, Y., Bao. M. J., Tan. F., Qu. Z. P., Zhang. Y. W., Chen. J. W.: Distribution of organophosphate esters between the gas phase and PM2.5 in urban Dalian, China, Environ. Pollut., https://doi.org/10.1016/j.envpol.2019.113882, 2019.

Line 315: Other factors may lead to such difference 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. Response: Of course, other factors may also cause differences in the content of indoor and outdoor OPEs. The reasons for the difference in indoor and outdoor OPEs content have been supplemented and improved as follows: “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 (Wong, 2018) 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.”

Lines 350-356: References are required for identification of possible sources associated with each factor. Response: Thanks for your advice. References have been added in the manuscript. “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., 2005; 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; Leisewitz et al., 2000; Stevens et al., 2006; Wei et al., 2015)."

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