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Reply on RC1

Shijie Yu et al.

Author comment on "Measurement report: Intra- and interannual variability and source apportionment of volatile organic compounds during 2018–2020 in Zhengzhou, central China" by Shijie Yu et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-1016-AC1, 2022

General comment

The paper reports a discussion of a measurement dataset of VOCs collected in Zhengzhou (China) between 2018 and 2020. Discussion on trends, potential sources is included in the paper. The approach is not particularly new, however, the dataset and the analysis is quite complete and I believe that the paper could be interesting for the scientific community and suitable for the Journal. However, a few aspects are not completely clear or discussed in sufficient details so that a revision would likely improve the paper, see my specific comments.

Response: Thank you for your careful reading of our paper and the valuable comments and constructive suggestions. Below are the point-to-point responses to all the comments (The comments are marked in black font and the responses are marked in dark blue font). The major changes that have been made according to these responses were marked in yellow color in the highlighted copy of the revised manuscript. And our own minor changes were marked in red font. Note that the following line numbers are shown in the corrected version.

Specific comments

Lines 64-66. Here it would be better to use some references, especially for CMB applied to gaseous VOCs. I am quite aware of use of CMB receptor model for particulate matter and several source profiles are available in the scientific literature but, likely, much less information is available for source profile of VOCs.

Response: Thank you for your suggestions. The references have been supplemented.

(Hellén et al., 2003;Plaisance et al., 2017)

Hellén, H., Hakola, H., Aurila, T., 2003. Determination of source contributions ofNMHCs in Helsinki (60 N, 25 E) using chemical mass balance and the Unmixmultivariate receptor models. Atmos. Environ. 37, 1413–1424.

Plaisance, H., Mocho, P., Sauvat, N., Vignau-Laulhere, J., Raulin, K., Desauziers, V., 2017. Using the chemical mass balance model to estimate VOC source contributions in newly

built timber frame houses: a case study. Environ. Sci. Pollut. R. 24, 24156–24166.

Section 2.2 is quite stingy of details and should be enriched. I would suggest to mention the work of Belis et al. (Atmospheric Environment X, 5, 2020, 100053) regarding performances of receptor models and mention if specific constraints were used in the PMF run and how measurement uncertainties were taken into account and what is the total variable used.

Response: Thanks for your suggestions. We have corrected it. The description of PMF has been updated.

"In this study, analysis of the source of the VOCs was performed using the EPA PMF 5.0 model, which is a receptor model used widely for source apportionment (Gao et al., 2018; Yadav et al., 2019). Detailed information regarding this method is available in the user manual (Norris et al., 2014) and other related literature (Song et al., 2019a, 2019b). Two input files are required for PMF: the concentration values and the uncertainty values of the individual VOC species. The uncertainty is calculated using Eq. (1) when the species concentration value is higher than its method detection limit (MDL), or using Eq. (2) when the concentration is less than or equal to the MDL:

Unc =, (1)

Unc = , (2)

where c is the concentration of the individual VOC species, and EF is the error fraction, which was set to 10% of the VOC concentration (Yuan et al., 2012).

Owing to the complexity of the chemical reactions, not all of the VOC species were used in the PMF analysis. Based on previous work, this study adopted the following principles for selection of the VOC species. (1) Species with more than 25% of data missing or below the MDLs were rejected, which follows the methodology of previous studies (Zhou et al., 2019). (2) Species with short atmospheric lifetimes were excluded because they rapidly react away in the atmosphere. (3) Species that represent source tracers of emission sources were retained (e.g., in the case of isoprene). Eventually, 27 VOC species were selected for source apportionment analysis. VOC species were grouped into strong, weak and bad according to their signal/noise ratio (S/N), and there were 23 and 4 species grouped into strong and weak, respectively. It should be noted that the volumetric concentration (ppbv) of the individual VOC species was converted to mass concentration (μg m−3) before being input into the PMF model.

Choosing the optimal number of factors in the model is important. The number of factors depends on Q (ture)/Q (robust) and Q/Qexpected (Qexp). In theory, Q (ture)/Q (robust) < 1.5 and a value close to 1 is considered reasonable (Ulbrich et al., 2009), and the rate of change of Q/Qexp should be stable and the ratio should be close to 1 (Baudic et al., 2016; Hui et al., 2019). In this study, the numbers of factors used for the PMF analysis were tested from three to eight, and the optimum six-factor solution with Q/Qexp = 0.94, (Q (ture)/Q (robust) = 1.0) was selected. Additionally, Fpeak values from −1 to 1 with 0.1 intervals were used in the model, and Fpeak = -0.2 was established as the best solution (as shown in Fig. S1)."

In supplementary material, and related to the previous point. It is mentioned principal component analysis on this dataset but there is not trace of it in the paper. In addition, it should be explained how the number of factors was chosen because Figure 1 with a constantly decreasing Q/Qe does not seem to allow this identification by itself.

Response: Sorry for the mistake. We have corrected it. The description has been corrected to "Choosing the optimal number of factors in the model is important. The number of factors depends on Q (ture)/Q (robust) and Q/Qexpected (Qexp). In theory, Q (ture)/Q (robust) < 1.5 and a value close to 1 is considered reasonable (Ulbrich et al., 2009), and the rate of change of Q/Qexp should be stable and the ratio should be close to 1 (Baudic et al., 2016; Hui et al., 2019). In this study, the numbers of factors used for the PMF analysis were tested from three to eight, and the optimum six-factor solution with Q/Qexp = 0.94, (Q (ture)/Q (robust) = 1.0) was selected. Additionally, Fpeak values from −1 to 1 with 0.1 intervals were used in the model, and Fpeak = -0.2 was established as the best solution (as shown in Fig. S1)".

Fig. S1 The Q/Qexp and Q (ture)/Q (robust) ratios in different solutions (a); the Q/Qexp ratio for different Fpeak value solutions (b).

Lines 215-218. It should be mentioned is the differences in these yearly averages are statistically significant considering the large standard deviations (are STD reported as errors?) indicated.

Response: Thanks for your suggestions. We have corrected it. The description of Line 256-260 has been corrected to "The interannual variation of the VOCs declined gradually as follows: 113.2±65.2 μg/m3 in 2018, 90.7±52.5 μg/m3 in 2019, and 79.1±41.7 μg/m3 in 2020. It should be mentioned is the differences in these yearly averages are statistically significant considering the large standard deviations indicated."

Lines 333-335. To better explain this reasoning, it should be mentioned that CO and NO2 are mainly gases from combustions sources strongly influenced by urban activities such as traffic and domestic heating. Instead, SO2 is generally mainly due to industrial sources or combustion of heavy oils such as fuels used in ships.

Response: Thanks for your suggestions. We have corrected it. The description of Line 368-372 has been corrected to "Meanwhile, this source had correlation with gas tracers of NO_2, SO_2, and CO (R^2 = 0.42, 0.37, and 0.44, respectively). CO and NO2 are mainly gases from combustions sources strongly influenced by urban activities such as traffic and domestic heating. Instead, SO2 is generally mainly due to industrial sources or combustion of heavy oils and coals. Therefore, source 1 was assigned to industrial sources."

Section 3.3.1. This part could be made more strong if related to the diagnostic ratios. For example, the B/T ratio in the different profiles are similar to those found in literature for the specific sources as discussed previously. Actually, the figure 4 is very small and I do not see clearly. I also suggest to increase the size of this figure.

Response: Thanks for your suggestions. Section 3.1 (Source identification) has been rewritten. Meanwhile, Fig. 4 has been drawn at the same time.

Fig.4 Source profiles and contribution percentages during the observation period by PMF model (bar is a mixing ratio and dot is a percentage).

Section 3.3.2. At the end it is not clear if the trends are present and statistically significant. Actually in Figure 5 it seems that rends are not so relevant in relative terms.

Response: Thanks for your suggestions. The concentration contributions of each VOC source during 2018–2020 were updated (as shown in Fig.5). The proportion of vehicle emissions and LPG/NG has increased with each passing year. And the proportion of industrial and solvent sources presented an annual down trend.

Fig. 5 The contributions of each VOC source during 2018-2020.

Line 485. Why here it is mentioned ppbv rather than s-1?

Response: Sorry for the mistake. We have corrected it.

Figures 2 and 3. I suggest to change the vertical scale to maximize the visibility of the data. For example, B is always less than 3 in Figure 3, so why to choose a scale at 6 that compress everything? In addition, in the data in Figure 3 it is missing the results for 20 and 21 (i.e. 8 and 9 pm). The same problems are also present in Fig. 7, Fig. S3.

Response: Sorry for the mistake. We have corrected it. Figures 2 and 3 have been updated. Meanwhile, the standard gas calibrated instrument at 20:00 and 21:00 every day, so there is no data during this period.

Fig. 2 Monthly changes in the concentrations of the typical VOCs species in Zhengzhou. The upper and lower boundaries of the boxes indicate the 75th and 25th percentiles, respectively; the lines within the boxes mark the median; the whiskers above and below the boxes indicate the 90th and 10th percentiles, respectively.

Fig. 3 Diurnal variations in VOCs compounds measured at Zhengzhou. The upper and lower boundaries of the boxes indicate the 75th and 25th percentiles, respectively; the lines within the boxes mark the median; the whiskers above and below the boxes indicate the 90th and 10th percentiles, respectively.

Tables S2, S3, and S4. Better to indicate the measurement units and also explain what is Pr.

Response: Thanks for your suggestions. Tables S4-S7 were indicated the measurement units. And Pr means precipitation.

Table S4 Variations in the monthly average of meteorological parameters (T, RH, UV, and WS) and pollutant gases (O_3, NO_2, CO, and TVOC).

Month	RH	Pr	T	WS	UV	TVOC	NO_2	O_3	CO
	(%)	(mm)	(□)	□m/s)	(W/m^2)	($\mu g/m^3$)	($\mu g/m^3$)	($\mu g/m^3$)	(mg/m^3)
1	46.4±22.7	0.1	3.1±3.3	1.3±0.8	85±33.8	145±80.7	65.4±29.4	22.6±19.5	1.4±0.7
2	55.9±16.1	3.9±0	4.3±5	1.2±1	114.5±45.3	99.8±62.4	45.3±29.5	50.4±35.5	1.2±0.6
3	38.1±16.7	3.3±0.1	13.9±4.8	1.6±0.8	206.5±55	91.6±44.7	48.4±29.3	65.2±42.8	0.5±0.3
4	52.2±19.7	20.2±0.2	16.7±5.3	1.9±1.1	238.5±86.6	95.4±37.8	41.4±23.6	76.7±49.1	0.8±0.4
5	40.9±17.6	0.2±0	24.8±5.5	1.5±0.9	315.2±62.6	72.2±35.8	39±29.4	100.1±62.1	0.7±0.3
6	48.4±22.3	20.6±0.2	30±7.6	0.6±0.4	291.6±112	76.1±32.6	32.9±23.1	114±63.9	0.6±0.3
7	60±15.3	18.2±0.3	30.6±4.6	0.4±0.2	305.6±70.3	81.3±38.3	36.4±27.8	110.4±66.9	0.7±0.3
8	70±18	60.5±0.6	27.8±3.7	0.4±0.2	265±80.1	65.3±25.1	32.6±20.6	95.5±58.5	0.8±0.3

9	65±19.2	1.9±0	23.8±4.3	1.2±0.8	208.3±85.9	80.6±39.3	45.7±35.8	95±73.3	0.9±0.4
10	63±21.5	81.8±0.5	16.8±4.8	1.5±1.3	160±61.8	86.5±56	49.3±30	54.6±49.7	0.9±0.5
11	54.9±22.4	4±0.1	11.3±5.3	1.6±1.3	118.7±42.3	91.2±51.6	55.4±30	35±31.6	1±0.5
12	58.5±23.8	3.4±0	5.6±3.9	1.4±0.8	102.9±41.7	104.5±55.2	49.8±24.5	28.2±25	1.2±0.6

Table S5 The OH reactivity towards the total VOCs and the comparison with other studies (unit: s^{-1}).

	The OH reactivity of the total VOCs	The OH reactivity of the total OVOCs	The OH reactivity after deducting OVOCs	References
Zhengzhou	6.7	-	6.7	This study
Xianghe	7.9	2.4	5.5	Yang et al., 2020
Beijing	15.5	7.2	8.3	Yang et al., 2021
Heshan	18.3	4.7	13.6	Yang et al., 2017

Shanghai	6.21	2.97	3.24	Tan et al., 2019
Guangzhou	10.9	4.6	6.4	Tan et al., 2019
Chongqing	8.9	2.136	6.8	Tan et al., 2019

Table S6 The detailed contribution of each VOC group to the total OH reactivity during the sampling periods (unit: s^{-1}).

Species	2018	Species	2019	Species	2020	Species	Average
Isoprene	1.7	Isoprene	1.1	Isoprene	1.1	Isoprene	1.8
Ethene	1.4	Ethene	0.8	Ethene	0.9	Ethene	1.1
cis-2-Butene	0.6	Propene	0.6	m/p-Xylene	0.5	Propene	0.5
m/p-Xylene	0.6	m/p-Xylene	0.5	Propene	0.4	m/p-Xylene	0.5
Propene	0.6	Styrene	0.3	Styrene	0.4	Styrene	0.4
Styrene	0.6	trans-2-Bu	0.3	Toluene	0.2	cis-2-Bute	0.3

		tene				ne	
trans-2-Bu tene	0.4	cis-2-Bute ne	0.2	trans-2-Bu tene	0.2	trans-2-Bu tene	0.3
Toluene	0.3	Toluene	0.2	cis-2-Bute ne	0.2	Toluene	0.3
i-Pentane	0.2	i-Pentane	0.2	1-Butene	0.1	i-Pentane	0.2
n-Pentane	0.2	1-Butene	0.2	i-Pentane	0.1	1-Butene	0.2
Cyclopenta ne	0.2	trans-2-Pe ntene	0.2	n-Butane	0.1	n-Butane	0.1
1-Hexene	0.2	n-Butane	0.2	Propane	0.1	trans-2-Pe ntene	0.1
1,3,5-Trim ethylbenze ne	0.2	Propane	0.1	trans-2-Pe ntene	0.1	Propane	0.1
cis-2-Pente ne	0.2	n-Pentane	0.1	o-Xylene	0.1	n-Pentane	0.1
trans-2-Pe ntene	0.2	o-Xylene	0.1	1,2,4-Trim ethylbenze ne	0.1	o-Xylene	0.1

n-Butane	0.2	i-Butane	0.1	Ethylbenzene	0.1	1,3,5-Trimethylbenzene	0.1
1-Butene	0.1	Ethylbenzene	0.1	i-Butane	0.1	cis-2-Pentene	0.1
o-Xylene	0.1	3-Methylpentane	0.1	1,3,5-Trimethylbenzene	0.1	Ethylbenzene	0.1
Propane	0.1	n-Hexane	0.1	n-Pentane	0.1	1-Hexene	0.1
Ethylbenzene	0.1	cis-2-Pentene	0.1	1,2,3-Trimethylbenzene	0.1	Cyclopentane	0.1

Table S7 The detailed contribution of each VOC group to the total OH reactivity in different seasons (unit: s^{-1}).

Species	Winter	Species	Spring	Species	Summer	Species	Autumn
Ethene	1.3	Isoprene	1.2	Isoprene	2	Isoprene	0.6
Propene	1	Ethene	1.1	m/p-Xylene	0.5	Propene	0.6

m/p-Xylene	0.6	Propene	0.5	Propene	0.4	m/p-Xylene	0.5
Isoprene	0.5	trans-2-Butene	0.5	Styrene	0.3	Styrene	0.4
Styrene	0.4	m/p-Xylene	0.4	Ethene	0.2	Ethene	0.4
cis-2-Butene	0.3	cis-2-Butene	0.3	cis-2-Butene	0.2	Toluene	0.3
trans-2-Butene	0.3	Styrene	0.2	Toluene	0.2	trans-2-Butene	0.2
Toluene	0.3	1-Butene	0.2	trans-2-Butene	0.2	n-Butane	0.2
1-Butene	0.3	Toluene	0.2	i-Pentane	0.2	Propane	0.2
i-Pentane	0.2	trans-2-Pentene	0.2	1-Butene	0.2	i-Pentane	0.2
trans-2-Pentene	0.2	i-Pentane	0.2	trans-2-Pentene	0.1	1-Butene	0.2
Propane	0.2	Acetylene	0.1	n-Butane	0.1	cis-2-Butene	0.1

n-Butane	0.2	n-Butane	0.1	3-Methylpentane	0.1	trans-2-Pentene	0.1
n-Pentane	0.1	Propane	0.1	Ethylbenzene	0.1	1,3,5-Trimethylbenzene	0.1
cis-2-Pentene	0.1	o-Xylene	0.1	o-Xylene	0.1	n-Pentane	0.1
i-Butane	0.1	n-Pentane	0.1	Propane	0.1	i-Butane	0.1
n-Hexane	0.1	3-Methylpentane	0.1	m-Ethyltoluene	0.1	o-Xylene	0.1
o-Xylene	0.1	cis-2-Pentene	0.1	n-Hexane	0.1	Ethylbenzene	0.1
Ethane	0.1	n-Hexane	0.1	n-Pentane	0.1	Cyclopentane	0.1
Acetylene	0.1	i-Butane	0.1	cis-2-Pentene	0.1	3-Methylpentane	0.1

Figure S2. Please correct Mixing on the y-axis label.

Response: Sorry for the mistake. Figures S2 have been updated.

Fig. S2 Monthly changes in the concentrations of VOCs in Zhengzhou.

Line 56. Better contributors to.

Response: Thanks for your suggestions.. We have corrected it. The description of Line 57-60 has been corrected to "In many regions, alkanes represent the dominant VOC species, while studies which do not report OVOCs usually identify aromatics and alkenes as better contributors of ozone formation potential (OFP) (Li et al., 2019b; Yan et al., 2017)."

Line 73. Better hot topic.

Response: Thanks for your suggestions.. We have corrected it. The description of Line 74-76 has been corrected to "In addition to the study of VOC characteristics and source apportionment, analysis of atmospheric oxidation characteristics is another area of hot topic. "

Line 415. Probably it is night time.

Response: Thanks for your suggestions.. We have corrected it.The description of Line 435-437 has been corrected to "The diurnal variation of this factor was characterized by apparent increase at night, which could be related to the accumulation of pollutants associated with nighttime heating."

Line 477. Remove the t in excess.

Response: Sorry for our carelessness. We have corrected it.

Please also note the supplement to this comment:
https://acp.copernicus.org/preprints/acp-2021-1016/acp-2021-1016-AC1-supplement.pdf