Professor MacKenzie
Editorial Office
Atmospheric Chemistry and Physics

26th October 2018

Dear Professor MacKenzie,

Attached please find our revised manuscript entitled "Characterization of VOCs and their related atmospheric processes in a central China city during severe ozone pollution periods" (Manuscript number: acp-2018-397), as well as a thorough, point-by-point response to each point raised from the reviewers ("Response to Reviewers"). The revisions to the manuscript are highlighted in blue words in the provided Microsoft Word document. Additionally, there is a clean revised manuscript as required.

We greatly appreciate those comments and valuable suggestions from the reviewers. The manuscript has been greatly improved. We do feel that we have demonstrated our efforts in the revised manuscript.

Please do not hesitate to contact me at stevenho@hkpsrl.org or by phone at +00-852-66833994 if you need additional information. Thank you for your time in handling our manuscript.

Sincerely,

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Comment and response #1

The authors thank for all valuable comments and suggestions to our manuscript. We have point-to-point response to each comment as below.

Comment 1:

The title can also be changed, since the influence of VOCs on O_3 formation forms only a small part of the paper. The main focus of the paper is on the measured VOCs.

Response:

Thanks for the suggestion, the title has been revised as：

> "*Characterization of VOCs and their related atmospheric processes in a central China city during severe pollution periods*"

Comment 2:

I am not sure about the use of this acronym for the 57 VOCs. A VOC is a species and PAMS is not

Response:

The term has been replaced by "VOCs".

Comment 3:

A high VOC/NOx ratio usually signifies that an area is NOx sensitive and not VOC sensitive. Changes in VOC concentration do therefore not cause any changes in O_3 concentrations, while increased NOx causes increased O_3.

Response:

According to the ratio of VOCs /NO_x, the ozone formation regime was prone to VOC-limited. The statement has been revised accordingly.

Comment 4:

Which four sites? Where you measured VOC precursor species? You mentioned that VOCs were measured in Zhengzhou City and precursor species were measured at four different sites

Response:

This refers to the four sites located in Zhengzhou city where we collected the samples in this study. The details of sampling location have been described in the main texts.

Comment 5:

A VOC-limited regime is associated with low VOCs not high VOCs. Your high VOC/NOx ratio indicate a NOx limited regime and therefore NOx must be reduced and not VOCs to reduce O_3.However, I think this area is VOC-limited (very high NOx) and reduction on VOCs will result in reduced O_3. And therefore your high VOC/NOx ratio does not make sense

Response:

Sorry for the unclear description in previous statement. Yes, it should be VOC-limited. The related statements have been revised.

Comment 6:

Fuel evaporation? Solvent evaporation, I agree with.

Response:

Solvent (i.e., from industry and household) is a major source of VOCs definitely, while fuel evaporation is also a contributor to VOCs originated from industries or other sources powered by fossil fuels.

Comment 7:

Where? In the USA or in China?

Response:

This refers to worldwide countries, including China and USA.

Comment 8:

This sentence read that the nationwide deterioration of air quality contributes the measurements being scarce. Please improve.

Response:

We have revised the sentence as

> *"In China, the investigations on VOCs including source apportionment, measurement of emission profiles and interpretation of seasonal variations were mainly concentrated in Yangtze River Delta (YRD), Pearl River Delta (PRD) and Beijing-Tianjin (BJT) regions (An et al., 2014;Wang et al., 2014;Chen et al., 2014;Liu et al., 2016a;Guo et al., 2017). Limited studies have been conducted in less developed or developing regions (i.e., southwestern and northwestern China) where prominently impacted by biomass burning and with high abundances of toxic and reactive compounds. (Li et al., 2014;Li et al., 2017a)."*

Comment 9:

These sites are only in the USA

Response:

The term of PAMS was widely used to present the most critical contributors in the production of ozone in the atmosphere. It does not mean the sampling sites.

Comment 10:

This sentence does not fit within the context of this paragraph that is focusing on VOC measurement in China and the gaps in knowledge.

Response:

The original lines 64-66 have been deleted

Comment 11:

why? Due to VOCs/CO or NOx?

Response:

The statement has been revised as

> *"In less developed cities of Heilongjiang and Anhui, biomass combustion had the highest contribution (40% and 36%, respectively) to the O_3 formation potentials due to high quantity of agricultural activities."*

Comment 12:

The first two paragraphs are not well structure and must be improved.

Response:

The paragraphs have been revised, specified in newly lines 37-74.

Comment 13:

Why? Due to increased NOx emissions?

Response:

The sentence has been revised as:

> *"The percentage of VOC-limited regime in North China Plain (NCP) increased from 4% to 6% between 2005-2013, owing to the rapid increases of NO_x emissions (Jin and Holloway, 2015)."*

Comment 14:

please improve

Response:

The sentence has been revised as:

> *“Based on the density of population distribution, locations of industrial facilities, and the prevailing winds, four sites have been selected for sample collection:”*

Comment 15:

If possible, it would be nice to show the major pollutant sources on the map in Fig. 1. This will help a lot with interpretation of results e.g. discussion in Section 1 on the influence of wind direction on the different ΣVOCs measured at each of the sites for all the months.

Response:

This is a good idea. Suggestion taken. The map was improved as below:

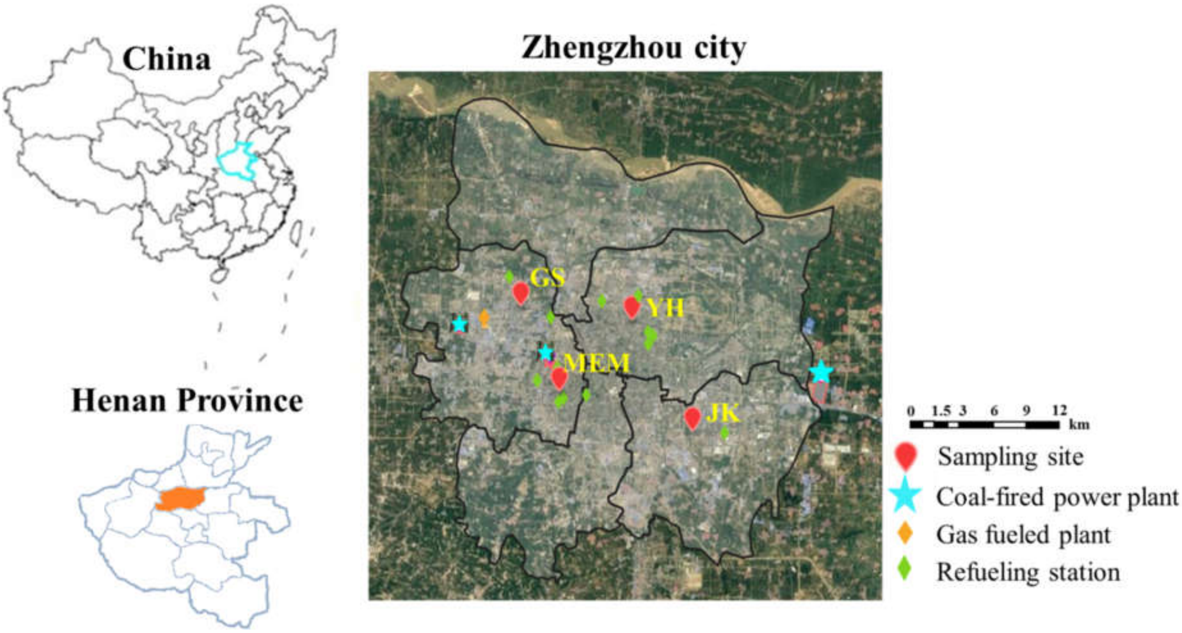


Fig 1. Map of Zhengzhou, China showing the locations of sampling sites.

Comment 16:

Please better explain. Why only 10 days? Were there only ten days in each month that it did not rain?

Response:

The sentence has been revised as:

> *"Ten sampling days with the rainfall record (ca. 0 mm) were chosen in every month during the period of May - September, 2017 consequently, to represent a typical air quality condition in a month."*

Comment 17:

What was considered to be valid samples?

Response:

"Valid samples" means that those samples were not influenced by high humidity, wrong operation, and fault of instrument.

Comment 18:

I do not think that this is a good acronym for your VOC species studied

Response:

Suggestion taken. The term has been replaced in the whole manuscript.

Comment 19:

According to what? Why were only these species considered relevant? Also, I assume from the rest of the discussion in the paper, these 57 species are only hydrocarbons. Therefore rather say that the 57 species included 28 were alkanes, 11 alkenes, acetylene and 17 aromatics.

Response:

The sentence has been revised as:

> *"The standard gas of PAMS (1 ppm; Spectra Gases Inc, NJ, USA) was used to construct the calibration curves for the 57 target VOCs, including 28 alkanes, 11 alkenes, acetylene and 17 aromatics"*

Comment 20:

This sentence and table is not necessary in the document and can be removed. Although it could be included a supplementary material, I do not think these analytical specifications contribute to the main content of this paper.

Response:

Thanks for the suggestion. It has been moved to supporting information, depicted as Table S1.

Comment 21:

Uncertain what is meant here.

Response:

The statement has been revised as:

> *"No obvious disturbances due to improperly activities (such as smoking, spray fumes, etc.) of sample collectors were present during the sampling events."*

Comment 22:

Not sure that this is the correct term

Response:

The term has been replaced by "QC/QA" and moved to supporting information.

Comment 23:

Unnecessary

Response:

It has been deleted

Comment 24:

Please improve the description of the PMF technique (line 166 - 184) Look at the paper Jaars, et al., Atmospheric Environment, 172 133–148, 2018, http://dx.doi.org/10.1016/j.atmosenv.2017.10.047.

Response:

Thanks for the reference. The description has been revised.

Comment 25:

Please structure this entire Section better. Numerous examples of incoherent writing is illustrated in the paragraphs in this section.)

Response:

The section has been revised.

Comment 26:

Air mass does not originate but pass over a source region/city/sources.

Response:

The statement has been revised as:

> *"In May, the largest cluster (27.2%) was passed over from Yinchuan, a central city in northwest China."*

Comment 27:

It will be better here to say that the Σ_{VOCs} different for all the months at all the sites, with the site with highest Σ_{VOCs} not being the same each months. This can be attributed to numerous factors that will be explored later in the paper. And then you can present the influence of prevalent wind direction on concentrations measured.

Response:

The related section has been revised according to the suggestion, specified as:

> *"The Σ_{VOCs} varied at the four sites, where the highest Σ_{VOCs} and their compositions were not identical across the sampling months as well. In May 2017, the highest Σ_{VOCs} was reported at JK (37.65±22.58 ppbv), followed by GS (31.73±18.70 ppbv), YH (30.05±16.43 ppbv) and MEM (29.05±15.34 ppbv), while the Σ_{VOCs} values for the month of June, July, August and September were found to be in the order of: GS>JK>MEM>YH, MEM>GS>JK>YH, YH>MEM>JK>GS, and MEM> YH > GS >JK, respectively. This can be attributed to numerous factors that will be explored later in the paper. Besides the emission sources (to be discussed in Section 3.2), the impacts controlled by meteorological conditions should not be ignored as well."*

Comment 28:

This discussion on the influence of prevailing wind direction and -speed could be significantly improved with an appropriate wind rose overlayed on a map of the city indicating the four sites and the major sources.

Response:

They have been presented in Fig. 4 and Fig S2.

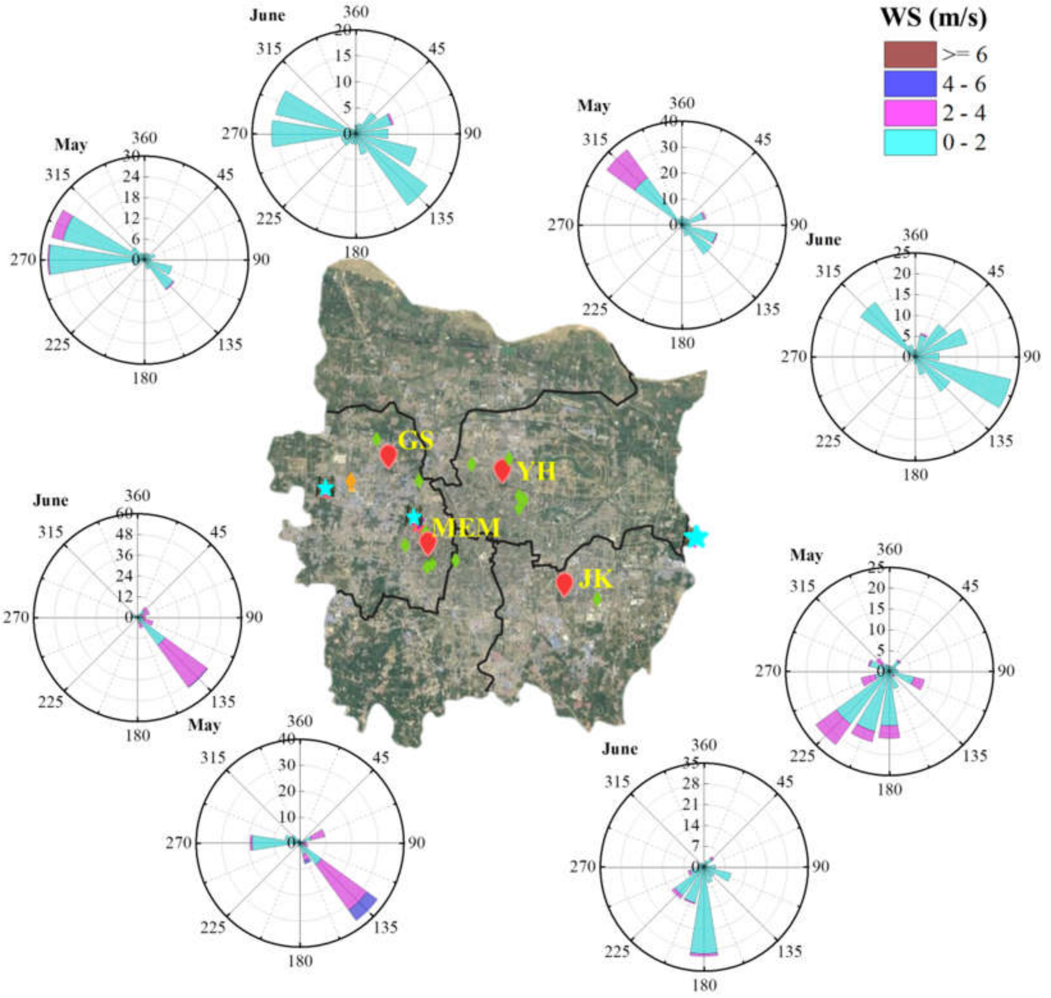


Fig.4 Wind rose at each site in May and June (the wind distribution in other three months were illustrated in Fig S2)

Comment 29:

Can you indicate this on a topographical map of the city?

Response:

A reference contained the topographical map has been added.

> "*Mu, B., Mayer, A. L., He, R., and Tian, G.: Land use dynamics and policy implications in Central China: A case study of Zhengzhou, Cities, 58, 39-49, 10.1016/j.cities.2016.05.012, 2016.*"

Comment 30:

from where

Response:

The statement has been removed because of the adjustment of the newly Table 1 and Fig. 8.

Comment 31:

A figure with meteorological data for the sampling period must be included to assist in the discussion of the data.

Response:

The statement has been removed because of the adjustment of the newly Table 1 and Fig. 8, and the meteorological data was presented in Fig S1.

Comment 32:

The authors must consider to rather include a figure with the statistical distributions (e.g. box and whisker plots with mean, median, as well as 25th, 75th percentiles) of the VOC species presented for the entire sampling period instead of the large Table 3. This will greatly assist in the discussion of concentrations measured at different sites. Table 3 could then only include the ΣVOC for each month at each of the site if they want to elaborate on the influence of wind direction and -speed on VOC concentrations measured at each site.

Response: Thanks for the suggestion, Fig.8 has been added.

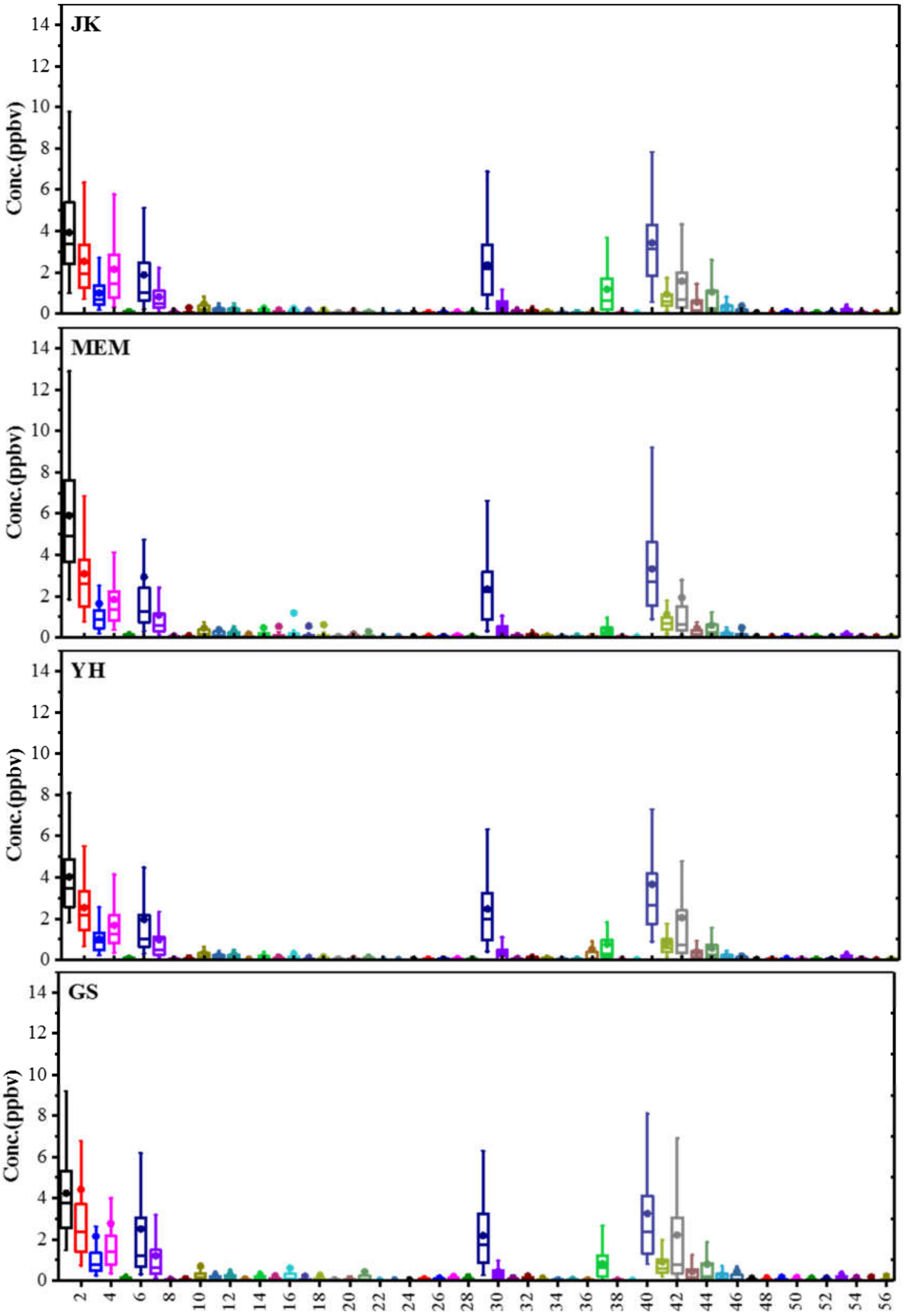


Fig.8 Concentrations of 57 VOCs at each site for the whole sampling period, the whisker was ranged from 5-95%, and the box was 25-75%, the solid points stand for average value, the line in the box represent median value. The number of chemicals can refer from Table S1.

Comment 33:

Nowhere in the text it is indicated that these 57 VOCs were classified into alkane, alkenes, alkynes and aromatics, which are further discussed

Response:

The statement has been revised as

> *"The standard gas of PAMS (1 ppm; Spectra Gases Inc, NJ, USA) was used to construct the calibration curves for the 57 target VOCs, including 28 alkanes, 11 alkenes, acetylene and 17 aromatics."*

Comment 34

why is this?

Response:

It was attributed to the busy traffic in urban city. The sentence was revised as

> *"With regard to the weight percentage of major groups (Table 3), the composition of alkanes was the largest in all cities because of their longer lifetimes and widespread from a variety of pollution sources (Fig. 5)"*

Comment 35:

Which will be nicely indicated in figure as suggested above presenting the statistical data of all VOCs measured at all the sites.

Response:

Suggestion taken. It has been presented in Fig.S3.

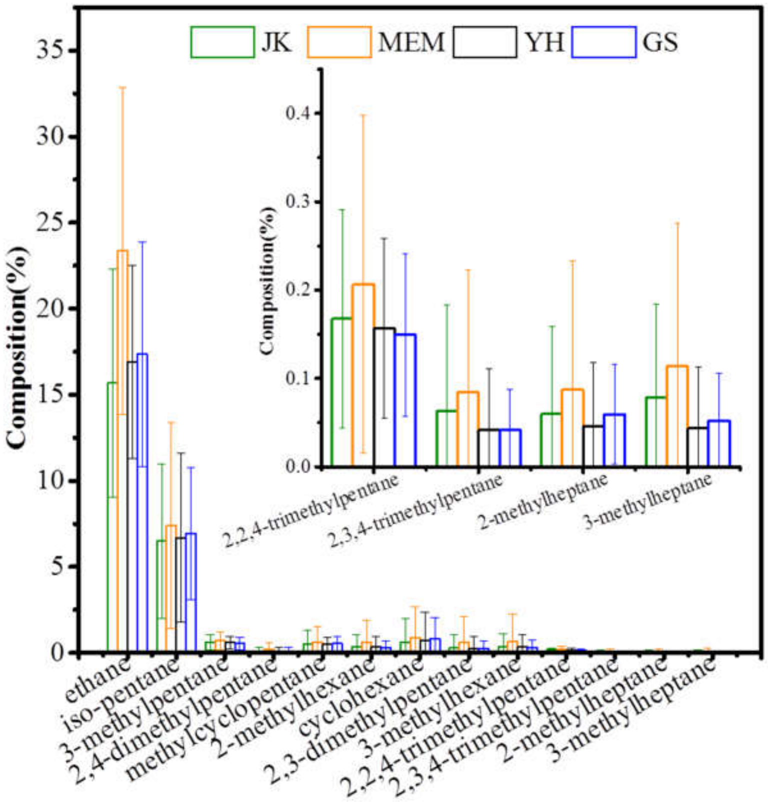


Fig. S3 Compositions of ethane, iso-pentane and C_7-C_8 alkanes at JK, MEM, YH and GS

Comment 36:

What compounds? Alkanes in general, or the species contributing to alkane levels at MEM only? If the latter, why not elaborate on alkanes at the other sites?

Response:

They referred to ethane, isopentane and alkanes with 7-8 carbon atoms, which have been presented in Fig.S3.

Comment 37

missing an introductory sentence on the daytime and night-time concentration that is additionally presented in figure2

Response:

It was revised as:

"Due to the variations of the planet boundary layer (PBL) height, solar radiation and emission sources, the concentrations of VOCs displayed obvious differences between morning and afternoon time (07:00LT and 14:00LT in this study). Compared with morning period, the aromatic compounds showed lower compositions at14:00 LT (Fig. 5), because of the increased planet boundary layer

> *and the active photochemical reactions, while alkenes always peaked in the14:00 LT."*

Comment 38

how so?

Response:

The statement has been revised as

> *"According to the dataset, the increases in alkene compositions (~4.3% uplift) were mainly due to higher contributions of isoprene (~1.4% at morning and 7.6% in the afternoon), which was mainly emitted from biogenic sources and increased exponentially with ambient temperature (Jiang et al., 2018)."*

Comment 39: Please include a table where in these VOC results can be contextualized and compared to other cities. Only Beijing, Nanjing and Guangzhou included in Figure 2. Furthermore, the fact that concentrations for these three cities are included in Fig.2 are also not properly introduced in the text.

Response:

The information has been added in revised Table 3.

Comment 40:

Are you speaking generally here, i.e. all the cities in China?

Response:

It refers to the countries discussed here.

Comment 41

Here again you mention aromatics. An examples of a sentence "coming from nowhere" within the context of a paragraph that is trying to contextualize results.

Response:

The statement has been revised as

> *"With regard to the weight percentage of major groups (Table 3), the composition of alkanes was the largest in all cities because of their longer lifetimes and widespread from a variety of pollution sources (Fig. 5), while the composition of aromatics was lower than alkenes in these cities except for Guangzhou."*

Comment 42:

You are only comparing your results to the three cities included in Fig. 2 and not all the cities listed here in your discussion above

Response:

The results have been shown in Table 3.

Comment 43:

Reference of biofuel as source of acetylene

Response:

A reference has been added.

> *"Zhu, Y., Yang, L., Chen, J., Wang, X., Xue, L., Sui, X., Wen, L., Xu, C., Yao, L., Zhang, J., Shao, M., Lu, S., and Wang, W.: Characteristics of ambient volatile organic compounds and the influence of biomass burning at a rural site in Northern China during summer 2013, Atmospheric Environment, 124, 156-165, 10.1016/j.atmosenv.2015.08.097, 2016."*

Comment 44:

The problem with the dataset is that it does not cover a full year, i.e. all seasons. Therefore rather combine local (wind direction and -speed as done in Section 3.1) and long-range transport (back trajectories as done in Section 3.7) here to explain temporal variation.

Response:

Suggestion taken.

Comment 45:

better to have meteorological parameters in separate fig as indicated in previous comment.

Response:

It has been presented in Fig S1

Comment 46:

Are you sure it is for all pollutants?

Response:

It refers to air pollutants we monitored in this study, including SO_2, CO, NO_2, O_3 and VOCs. We have revised the statement as

> *"The time series of mixing ratios of NO_x, O_3 and Σ_{VOCs} at every site are shown in Fig. 6. The results showed a distinctive temporal characteristic where lower levels of SO_2, CO, NO_x, O_3 and Σ_{VOCs} were observed in July and August (mid-summer) (Table S5)."*

Comment 47

You did not collect VOCs on rainy days as indicated in your experimental section.

Response:

Yes, this observation was referred to the results from other studies.

Comment 48:

This is very difficult to see in Fig. 3. Fig. 3 must be improved to be more legible and easier to observe observations

Response:

It has been changed to newly Fig 6.

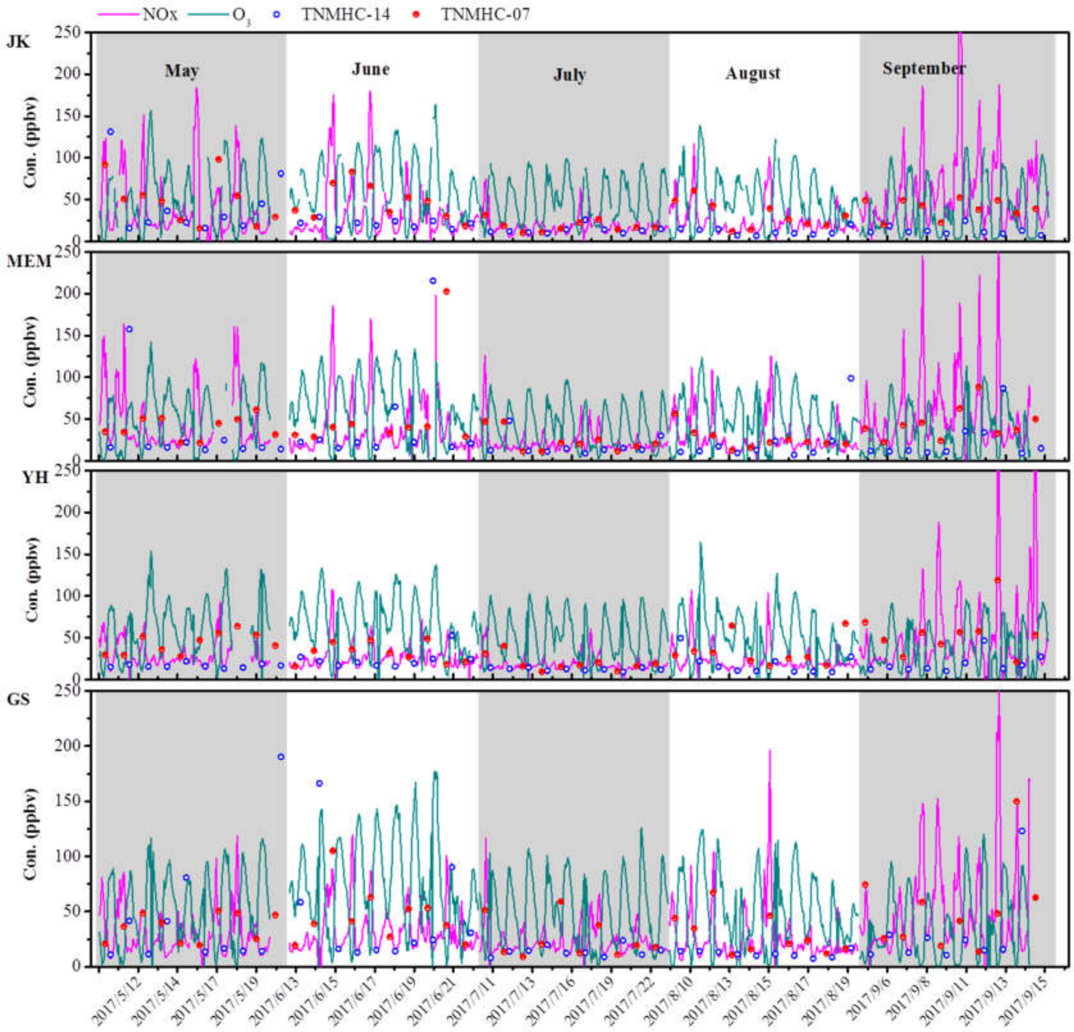


Fig.6 Temporal variations of mixing ratios of Σ_{VOCs}, NOx and O_3 at the four sites during the whole sampling period, in which Σ_{VOCs}-07 stands for the concentration level of Σ_{VOCs} observed at 07:00 LT, and Σ_{VOCs}-14 was that observed at 14:00 LT.

Comment 49:

I cannot see this in Fig. 3

Response:

We have presented it in newly Fig. 7.

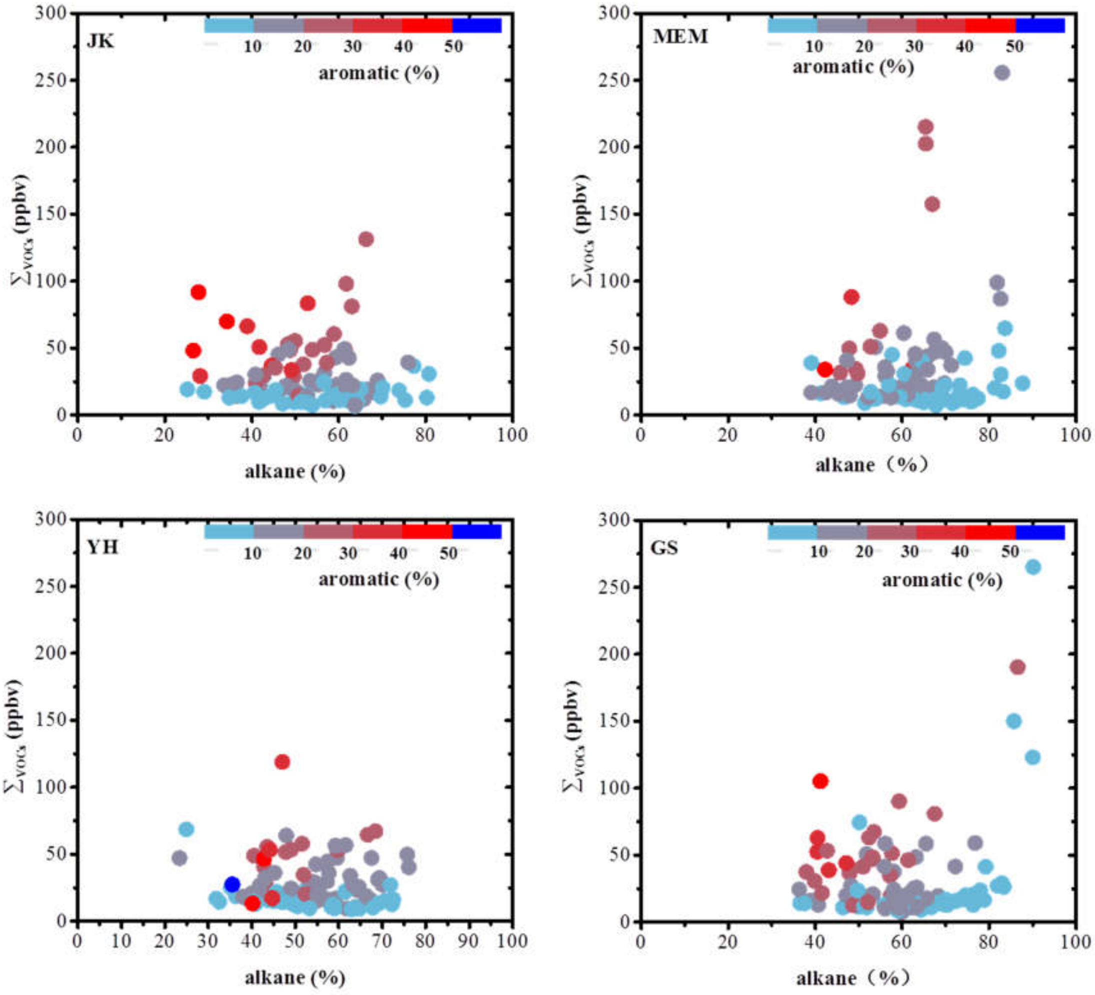


Fig. 7 The relationship between mixing ratio of Σ_{VOCs} and the composition of alkane, the data points were color coded with the composition of aromatic.

Comment 50:

Not easily observed in Fig.3

Response:

We have modified the figure and presented in newly Fig. 7.

Comment 51:

Why? Can you show this?

Response:

The simultaneous increases in concentration of SO_2, CO and NO_x represent the characters of potential combustion source, which could be caused by the nearby thermal power plant.

Comment 52:

(Reason for disturbance?

Response:

During the sampling period, the building where we conducted the sampling had painting activities during June, 2017.

Comment 53:

Wind direction will confirm this

Response:

The wind direction was added as:

> *"The results support the possible impact from a gas-fueled power plant located about 1 km southwest of the site (~18% of prevailing western wind at GS during May to September)."*

Comment 54:

Combine with next paragraph

Response:

We think it is not so appropriate to combine the two paragraphs. The discussion of next paragraph is on alkyne.

Comment 55:

Give a reference for acetylene associated with biomass burning.

Response:

A reference of Zhu et al, 2016 has been added.

> *"Zhu, Y., Yang, L., Chen, J., Wang, X., Xue, L., Sui, X., Wen, L., Xu, C., Yao, L., Zhang, J., Shao, M., Lu, S., and Wang, W.: Characteristics of ambient volatile organic compounds and the influence of biomass burning at a rural site in Northern China during summer 2013, Atmospheric Environment, 124, 156-165, 10.1016/j.atmosenv.2015.08.097, 2016."*

Comment 56:

Instead of Table 4, rather presented a figure with statistical distributions of total VOCs, SO_2, O_3 etc measured at each site. This will greatly assist in discussion. Paragraph in Section 3.1 where different monthly total VOC concentrations at each of the sites are explained with the influence of wind direction and -speed will also better fit within the discussion on spatial variations. The structure of this section must also be improved.

Response:

The original table has been replaced by Fig. 9.

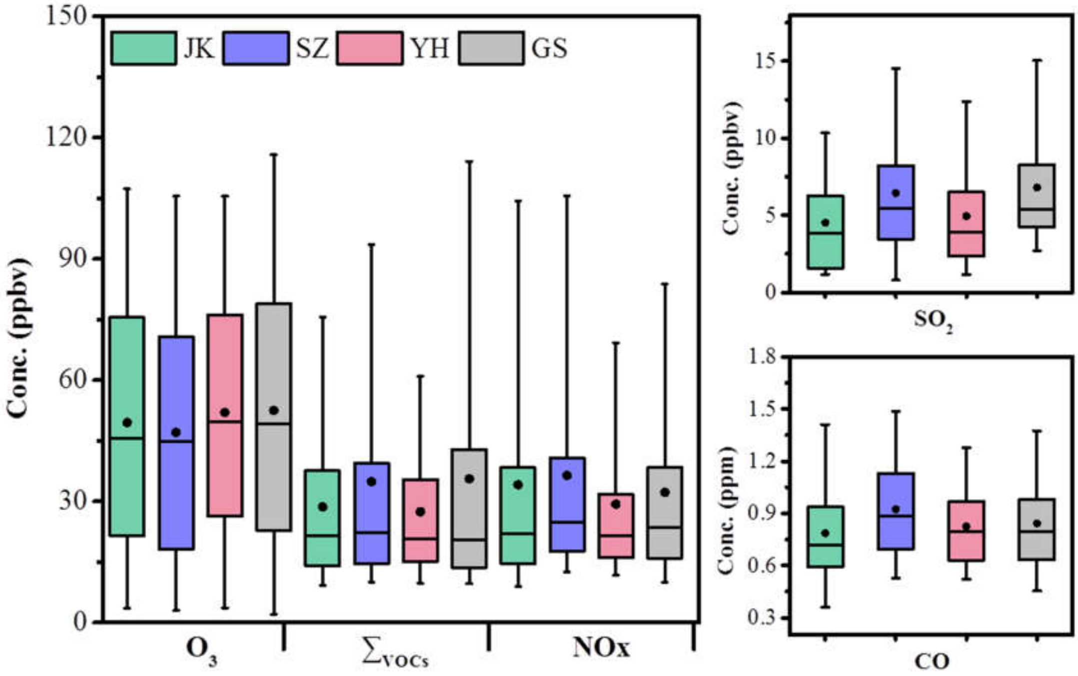


Fig. 9 The distribution of concentration point on O_3, Σ_{VOCs}, NOx, SO_2 and CO at each site, the range of the box was 25%-75%, the black line in the box stands for median level, the black dot represent the average level, the range of whisker was 5-95%.

While the paragraph in Section 3.1 was more focus on meteorological factors, so it has not been moved to this section

Comment 57:

Not really. Differences are marginal

Response:

Yes, we agree that the difference is marginal. However, it is true that GS and JK had higher absolute values, so we have changed it to "*slightly higher*" in the text.

Comment 58:

This is not true. Differences are marginal

Response:

Yes, the difference is marginal. We have thus changed to

> *"Additionally, the air pollutants related to the combustion processes, such as SO_2 and CO, were more abundant, though marginal, in western area of Zhengzhou (GS and MEM) (Fig.9).".*

Comment 59:

Again, marginal differences between sites

Response:

The sentence has been rewritten as

> *"Under high levels of VOCs and sufficient supply of NO_x, the highest average mixing ratio of O_3 was observed at GS, followed by YH where even with the lowest VOCs and NO_x, indicating that there are multiple factors, rather than the absolute concentrations, contributed to the O_3 formation at YH."*

Comment 60:

Inconsequential statement from observation

Response:

The point has been deleted

Comment 61:

This sentence does not fit within the flow of the content

Response:

For in June, the O_3 concentration often exceeded the national standard level of 80 ppbv, meaning severe air pollution caused by ozone during this period, in this section we focus on the period to discuss the relationship between VOCs and O_3 as a result.

Comment 62:

Small differences. Cannot really make this statement.

Response:

We do agree this. The sentence has been thus rewritten as

> *"The weight percentage of aromatics (15.62±12.06%) at GS was higher than those at other sites as well, indicating that the painting and other renovation activities at GS was potentially an important factor for its high O_3 level in June."*

Comment 63:

How is this substantiated?

Response:

Solvent usage is an important source of aromatics. Considering the renovation activity in June at GS, the higher aromatic composition should be caused by the renovation. According to aromatics with high reactivity, we thus suspect that the higher ozone level in June at GS was associated with the renovation activity

Comment 64:

O_3 levels were only higher at GS

Response:

Thank for the pointing out this. The statement has been revised as:

> *"The higher level of O_3 at GS was accompanied with the higher Σ_{VOCs} (39.29±25.37ppbv)."*

Comment 65:

Bad writing

Response:

The statement has been revised as:

> *"Even though both the Σ_{VOCs} and specifically high O_3 formation potential compounds (such as alkenes and aromatics) at MEM were slightly higher than those at YH (Table 4), the O_3 concentration at MEM was not higher."*

Comment 66:

O_3 can only be formed from NO_2.

Response:

We certainly recognize this. However, NO_2 was formed from NO, and NO could consume O_3. Considering that ozone formation involved all the process mentioned above, we do think it is reasonable to address the NO_x impact on ozone formation.

Comment 67:

In China? Give a reference please. Where is Hebei located in relation to Beijing? Sentences 311 - 315 another example of incoherent writing.

Response:

The statement has been revised as:

> *“It is well known that many O_3 episodes were attributable not only to local sources but also to regional transports. For example, Streets et al. (2007) reported that with continuous southern winds, the O_3 level in Beijing was 20-30% contributed from its neighboring cities in Hebei. "*

Comment 68:

From Fig. 3 this surely does not look like the day on which O_3 peaks at all the sites in this study.

Response:

Yes, it is only happened at YH, and the content was revised accordingly in the text.

Comment 69:

VOCs are the important contributors to O_3 formation within a VOC-limited regime, i.e. very high NOx. I am sure that this is the case for the very polluted regions in China.

Response:

Thank you for the reminder. The evidence has been added as

> *"On that day, the ratios of Σ_{VOCs}/NO_x at the four sites were all less than 6.5 (ppbC/ppbv) (Fig. S4), indicating a regional VOC-control system, and that VOCs are the critical contributors to the formation of O_3 in Zhengzhou"*

Comment 70:

FIg. 4 is poorly introduced in the text and not sufficiently discussed.

Response:

The statement has rewritten as

> *“The reductions in Σ_{VOCs} in the afternoons (around 14:00 LT) compared to mornings (around 07:00 LT) may have been caused from the uptake by O_3 formation, while the reduction of Σ_{VOCs} and active compounds (i.e., aromatic+alkene) at 14:00 relative to 07:00, determined as 35% and 56% respectively, were the least at YH among the four sites (Fig. S4).”*

Comment 71:

You refer to aging in air masses.

Response:

Yes, this can be confirmed with its high E/X ratio (0.91) at 14:00, while the ratio for fresh air usually scattered around 0.3.

Comment 72:

Therefore VOC-limited due to very high NOx

Response:

Yes, it is.

Comment 73:

The construction in this section must also be improved. The authors interchange between T/B ratios and T/B correlations, which are two totally different aspects. Both are indicative of source, but in different manner. T/B ratios can be related to source and aging.

This section also links to your source apportionment section.

Response:

Yes, it is exactly right. The original text may be obscure. The explanation has been improved as below:

> *"In this study, the correlation between benzene and toluene was fairly well at all the sites (R^2=0.70-0.74), except for YH (R^2=0.41) (Fig.14), suggesting the similar sources for benzene and toluene at JK, MEM and GS, while more complex such as variable wind direction at YH. The average ratios of T/B were lied within the range of 1.64-2.29, which were scattered around the character ratio of 2 for vehicle exhaust, illustrating the significance of vehicle emissions at the four sites."*

Comment 74:

Poorly written sentence

Response:

The statement has been rewritten as

> *"Specifically, at JK, MEM and YH, most of T/B ratios were distributed between 0.6 and 3, which were corresponding to character ratios for coal or biomass burning and industrial activities respectively. These reflected the mixture impacts from mobile source and coal/biomass burning at these three sites. However, more values were greater than 3 at GS, suggesting more frequent disturbance from industrial activities at this site."*

Comment 75:

Increased regionally in view of temporal variations?? This deduction does not make sense.

Response:

The statement has been revised as

> *" From the temporal respect, the T/B ratios at 14:00 LT were lower than at 07:00 LT (Fig.15). In fact, the reaction rate constant of toluene (5.63×10-^{12}cm^{3}molecule^{-1}s^{-1}) with •OH is much higher than that for benzene (1.22×10^{-12}cm^{3}molecule^{-1}s^{-1}), representing more rapid consumption of toluene from photochemical reactions and thus resulting in lower T/B ratios at 14:00 LT. Besides, the emission strength of mobile source is often weaker at 14:00 LT, while the coal/biomass burning are increased due to more human activities. Both of the situations can be used to explain the lower T/B ratios observed at 14:00 LT."*

Comment 76:

Please do not confuse T/B ratio and T/B correlations here. T/B correlation is indicative of similar sources, while T/B ratio indicate sources and aging.

What does this mean/imply?

Response:

We agree with this point. The statement has been revised as

> *"In this study, the correlation between benzene and toluene was fairly well at all the sites (R^2=0.70-0.74), except for YH (R^2=0.41) (Fig.14), suggesting the similar sources for benzene and toluene at JK, MEM and GS, while more complex such as variable wind direction at YH."*

Comment 77:

One would start/begin the paragraph with these sentences to indicate to what sources specific ratios of these two compounds can be related to and then you discuss your observed ratios in your study and relate them to these typical ratios. Another example of incoherent writing.

Response:

Newly lines 374-380 have been revised accordingly.

Comment 78:

Toluene is an aromatic species and NOT an alkene.

Response:

Yes, we truly know this. The original statement may lead confusion and it has been revised as

> *"For the individual species, the top 10 most contributors in OFP included ethylene, isoprene, m,p-xylene, toluene , propylene, acetylene, n-butane, i-pentane and propane."*

Comment 79:

What type of combustion? This paragraph is poorly structured and must be improved.

Response:

Based on analysis conducted in other sections, we inferred the combustion source as vehicle emissions and biofuel burning. and the paragraph was restructured.

Comment 80:

The VOC/NOx ratio is used to establish whether a region is VOC or NOx limited. Here you must indicate whether VOCs or NOx are the limiting factors.

High VOC/NOx ratio indicative of region being NOx limited. In such a region NOx determine O3 levels and not VOCs. Higher ratios only indicate high VOCs in relation to NOx. If there is not enough NOx, O3 will not form, since it can only form from NO2. Therefore to say that higher O3 correspond to higher VOC/NOx ratios does not make sense. More VOCs in the absence of NOx will not form O3. Therefore, I think at your site you have high NOx, which is the only scenario where O3 formation is considered VOC sensitive.

Response:

We have added a new section 3.4, which is mainly discussed the variation of VOCs/NOx ratios.

> *"The VOCs/NO_x ratio is often used to distinguish a region is either VOCs or NO_x limited in O_3 formation. According to the general case, the area was loaded in VOC-sensitive regimes when VOCs/NOx ratios were lower than 10 in the morning; and it would be on NOx-sensitive regime when VOCs/NOx ratios were greater than 20 (Sillman, 1999;Hanna et al., 1996). In this study, the mean value of VOCs /NO_x (ppbC/ppbv) were below 5 at all four sites (Fig.10), and 75% of the data points were < 6, indicating that the O_3 formation was sensitive to VOCs*

in Zhengzhou, and the reductions on the emissions of VOCs will be benefit for O_3 alleviation.

The VOCs /NO_x showed differences among the four sites (Fig. 10), with the lowest value at MEM (~3.8) and the highest value at JK (~4.7). The distributions demonstrated that the production of O_3 at MEM was more sensitive to VOCs than JK due to presence of emission from thermal-power plant. Meanwhile, approximately 14% of the VOCs /NO_x ratios of >8.0 were found in the NO_x-limited site of JK, potentially resulting from higher VOCs or lower NO_x emissions than other sites. Both of the mixing ratios and the statistical data showed higher levels of VOCs (with lower NO_x) at GS, where only ~4% of the ratios of > 8 was observed, indicating that there must be other factors (unresolved in this study) impacted the variation of O_3 formation regimes.

From the daily variations of VOCs /NO_x ratios (Fig. 10), higher values were observed at 14:00 LT than 07:00 LT at the four sites, well correlated with less vehicle emissions or more consumption paths for NOx with stronger light intensity. The increment of VOCs /NO_x at 14:00 LT was more obvious at JK and GS, suggesting that more emission sources of VOCs at daytime, and resulting the O_3 formation system shifting to the transition area in the afternoon.

Many researches showed that the O_3 formation depends not only on the abundances of precursors (mainly VOCs and NO_x) and also VOCs to NO_x ratio (Pollack et al., 2013). In this research, the mixing ratio of O_3 at 14:00 LT presented a slightly positive trend ($p<0.05$) with the uplift of VOCs /NOx at JK (Fig. 11), consistent to the results observed at the megacity of Shanghai (Gao et al., 2017), where the O_3 formation was more sensitive to NO_x when high O_3 levels were observed. This can be attributed to the increased O_3 production efficiency at high VOCs /NO_x. There were no discernible trends at other sites, possibly due to the counteraction imposed by other uncertain factors."

Comment 81:

Similar to all other sections, this section can also be better written and structured (section 3.7).

Response:

This section has been re-structed in other parts.

Comment 82:

This section must also be improved. I also suggest to combine this with Section 3.1 where differences in VOC concentrations for different months are discussed and explained with wind direction and -speed. Therefore combine local and long-range transport. Also see general comment at Section 3.1 to include all this in Section 3.2.

Response:

It has been incorporated in section 3.1 and 3.2

Comment 83:

Very busy figure with too much information.

Response:

Suggestion taken. The original figures have been decomposed as Fig.13 and Fig.14.

Comment 84:

Please describe this better. All the figures are small. You mean "smaller" figures.

Response:

Thanks for the reminder. The vertical axis in every small figure represents the mixing ratio of toluene (ppbv), while the horizontal axis stands for benzene level (ppbv).

Comment & response #2

Overview

1. The manuscript requires extensive English language editing. It is not currently suitable for publication as there are too many places in which weaknesses in English make it unclear, ambiguous or difficult to understand the point the authors are making;

Response:

Sorry and thanks for suggestion. The manuscript has been reviewed by a native English speaker.

2. The abbreviation "PAMS" stands for Photochemical Assessment Monitoring Stations, referring to the locations at which VOC sampling and monitoring are conducted. It does not refer to the compounds sampled, for which "VOC" (or VOCp to distinguish those isolated here from the generic term) should be used.

Response:

We had used the term of PAMS for the representation of 57 critical ozone precursors, which are defined in the Photochemical Assessment Monitoring Stations. The term has been replaced in the revised manuscript.

3. My chief concern with this work is the limited (and potentially biased) nature of the data collected, as outlined above. This precludes the authors from reaching robust conclusions regarding meteorological drivers of ozone, inter-annual variability, and the precise cause of the observed increase in ozone in Zhengzhou City, as well as preventing them from being able to offer clear policy advice regarding emissions controls.

Response:

We did understand the concern from the reviewer. However, the study was conducted for five months in a year, covering the entire period troubled with ozone pollution. The scale of sampling campaign is much systematic and larger than any local research conducted in the central China. Certainly, continuous monitoring and extension of the work is necessary while the most efficient policy is being established for emission controls.

4.The authors need to give far more detail of the prevailing meteorology in Zhengzhou, at the very least the typical intra- and inter-annual variability to put the sampling time period into context.

Response:

The manuscript has been revised according to both reviewers' suggestion. The discussion on meteorology has been improved.

5. Some of the analysis techniques used have associated limitations which the authors do not discuss. For example, PMF analysis requires that the inputs (here the concentrations) are independent when that will not be the case here. PMF is a well-established and accepted method for source apportionment analysis but the authors should be clear about its limitations. Likewise, the actual rate of ozone formation from any specific VOC is strongly dependent on both chemical and meteorological conditions and can only be reliably estimated using detailed atmospheric chemistry models. While ozone formation potentials based on constant maximal incremental reactivity (MIR) ratios are a useful indicator of which VOCs may be most important to control they are only an indicator. Again the authors need to be clear about this. The following reference may be of use: "Photochemical ozone creation potentials for organic compounds in northwest Europe calculated with a master chemical mechanism". Derwent, R.G. et al., 1998; doi: 10.1016/S1352-2310(98)00053-3

Response:

The discussions on source apportionment and reactivity of VOCs in ozone formation have been improved. Please refer to those details for the related sections on the point-to-point responses.

6. I cannot over-emphasize the importance of wind direction to the analyses presented here. It is critical in terms of both the transport of longer-lived and secondary pollutants and the local production. Local production is affected by meteorology which is often synoptic in scale and therefore correlated with windspeed and direction. Meteorological conditions will affect both photochemical efficiency and pollutant source strengths. This importance should be reflected in both the text and the figures. The back-trajectories tucked away right at the end as Fig. 10 should be incorporated into Fig. 1 and presented in the text ahead of the analysis of possible local production sources.

Response:

As the same as point (4), we have interpreted the influences on meteorological conditions including wind direction and speed in the explanation of local and regional transfer of pollutants.

7. Following on from this, there is also a real need for a windrose plot showing met conditions of importance (from the text = T, RH, although radiation would also be

useful) and concentrations of the various pollutants for each of the 4 locations and possibly also split out by month. While I appreciate the authors have attempted to highlight the contribution of wind direction (and speed) in Fig. 4 and through various color-coding in Fig. 7 I don't think these give the clear oversight required given the key role winds play. See e.g. http://www.openair-project.org/examples/BivariatePolarPlots.aspx or http://www.openair-project.org/examples/windpollutionroses.aspx for open source visualization tools

Response:

Thanks for the appreciation on our work and we have revised the related figures accordingly.

8. As the manuscript stands, the SI seems rather unnecessary as it consists of a single plot. I have however made several recommendations below regarding moving material out of main text

Response:

Thanks for the reviewer's suggestion and comments on our submitted manuscript. We have made point-to-point responses to each comment as below in detail.

Introduction:

Comment 1

This section is particularly difficult to follow. It is hard to work out which parts refer to previous work and how relevant these are. The authors do not explain how the different regimes reported from e.g. Los Angeles and SE USA relate to Zhengzhou.

Response:

The statement has been revised. The original aim of the statement was to support the importance of VOCs studies in different regions. This has been deleted according to suggestion.

Comment 2

Many of the references are not the most appropriate to the point the authors appear to be making. For example, Capps et al applied a methodology that was developed previously by e.g. Carter et al., Derwent et al., etc.

Response:

We have made more clarification and checked the citations. The reference of Capps et al was replaced by Carter et al.(1994) as suggested.

> *"Carter, W. Development of Ozone Reactivity Scales for Volatile Organic Compounds; J. Air & Waste Manage. Assoc. 1994, 44, 881-899. "*

Comment 3

L81: "one of the most polluted cities" where? In China? Asia? Globally?

Response:

The statement has been revised as:

> *"With the rapid growth of industrial activities, as well as increased vehicle emissions and fuel combustions, air quality in Zhengzhou has notoriously deteriorated. The Air quality index (AQI) for 65% of the days in 2013 exceeded the allowable limits of 100 established by the Air Quality Guideline."*.

Comment 4

L81-2: "its air quality exceeds the allowable limits set by Air Quality Guidelines" - specifically which pollutants exceeded the limits and what are the limits

Response:

The limits are referred to the guideline of air quality index (AQI) in China. In 2012, the Chinese Ministry of Environmental Protection (CMEP) issued the Ambient Air Quality Index (AQI) Technical Provisions (Trial) (HJ 633 - 2012) on the basis of the United States Environmental Protection Agency (U.S.EPA) AQI objective, and it was implemented as the Chinese Ambient Air Quality Standard (CAAQS) (GB 3095-2012). The AQI level is determined by the concentrations of six criteria pollutants including SO_2, NO_2, CO, O_3, $PM_{2.5}$ and PM_{10}. Basically, the AQI acts as a guideline for local government to inform the public and to take proper health protection measures.

Experimental:

Sampling site:

Comment 5

What was the sampling duration and flow rate?

Response:

The description has been revised as

> *"Grab samples were collected minute using 3.2 L stainless-steel canisters (Entech Instrument, Inc., Simi Valley, CA, USA), which were pre-cleaned with high purity nitrogen and pressurized to 20 psi."*.

Comment 6

Why did the authors select 07:00 and 14:00 as the two sampling times? How do these relate with rush hour? Or mealtimes? Or the working day?

Response 6

The statement has been revised as

> *"Two samples, one collected at 07:00 with increasing of human activities and another one collected at 14:00 with well-mixed of ambient air, were obtained on each sampling day."* .

Chemical analysis:

Comment 7

What was the specific compound mix in each of the three standard gases? There are issues regarding extrapolating area: concentration scaling factors from 1 compound to another even for structurally similar compounds and those with similar retention times (see e.g. Ruiz-Hernandez et al., 2018; doi:10.1186/s13007-018-0335-2))

Response:

The 57 VOCs (defined as the most critical contributors for ozone) discussed in this paper were quantified with the PAMS standard gas (1 ppm; Spectra Gases Inc, NJ, USA) containing 28 alkanes, 11 alkenes, acetylene and 17 aromatics. The other two standard gases were used to quantify halocarbons and oxygenated VOCs, but they have not been discussed in this manuscript. In order to avoid confusion, the information for the two standard gases has been removed. The extrapolating method has not been used. The co-eluted compounds of m-xylene and p-xylene were reported as m,p-xylene.

QA/QC:

Comment 8

This text could be moved to the SI if it is retained

Response:

Suggestion taken. The texts have been moved to SI.

PMF:

Comment 9

The authors go into far more detail of the specific equations (which are a standard technique) than is necessary in the main text. I suggest that the mathematical details of PMF are moved to the SI and the authors give more information regarding precisely how it was applied to their data.

The authors also need to include a statement regarding the limitations of applying PMF here.

Response:

Thanks for the suggestion. The mathematical details of PMF were moved to the SI, and the content in Section 2.3 has been rewritten.

Results and discussions

Mixing ratios and meteorological variations:

Comment 10

"VOCs" not "PAMS" Are the reported meteorological data over the entire month or just the 10 days each month when the sampling was conducted?

Response:

The term of "PAMS" has been replaced with "VOCs" in the text. The meteorological data were covered the 10 sampling days in each month.

Comment 11

Are the average VOC concentrations for all samples taken in that month, i.e. combining the 07:00 and 14:00 sampling times? This would be misleading as it would be expected that values and sources differ markedly between those two times of day.

Response:

Yes, the average concentrations represent the values from two sections (i.e., 07:00 and 14:00) for each sampling day.

We do understand the concern about the variations of concentrations and contributions of the sources from time to time. There were many factors impacted the VOCs levels and composition indeed, while in this study we focus on the impacts from meteorological conditions in different month. Therefore, we have depicted the case by the statement as

> "*This can be attributed to numerous factors that will be explored later in the paper. Besides the emission sources (to be discussed in Section 3.2), the impacts controlled by meteorological conditions should not be ignored as well*".

And, the diurnal variations have been discussed in other sections.

Comment 12

The large variability (reported standard deviations and month-to-month differences) indicate the clear need for sampling to continue over a much longer time period, taking in different times of day and for a number of years.

Response:

The objective of this study is to illustrate the characteristics of VOCs during the high ozone level period in a year. The sampling has been conducted for five months in a year, when were sufficiently representative.

Comment 13

L199: "more accumulated at GS"? I don't understand what point the authors are making here. Do they refer to higher concentrations? Greater influence of transported pollution?

Response:

The sentence has been revised as

> "*The average wind speed at GS (0.74±0.33 m* s^{-1}*) was lower than that at MEM (1.84±0.94 m* s^{-1}*) and YH (0.97±0.36 m* s^{-1}*) (Table 3), indicating poor dispersion conditions at GS. The air pollutants emitted from MEM and YH were more liable resulting in a higher level of* Σ_{VOCs} *at GS in June.*"

Comment 14

L205: Likewise I don't understand what the authors mean by "topographical effect"

Response:

Topographical effect is referred to a geographical factor impacted the distribution of VOCs. In this study, the sites of GS and MEM were located at the western part of Zhengzhou, while JK and YH were belong to the eastern part. Since the VOCs levels gradually increased from east to west, we have thus suspected that the concentrations of VOCs could be correlated with the topography.

Comment 15

The authors have used PMF to identify source sectors and present the findings of this analysis in section 3.6. what is presented here is speculation which is entirely superfluous given they have used PMF later.

Response:

Suggestion taken. The paragraph has been revised as

> *"The C_2 - C_5 alkanes, acetylene, ethylene, toluene and benzene were the most abundant VOCs detected at all sites (Fig.8), and the mixing ratios of toluene varied within a wide range at each site, because of its universal emission sources (e.g., vehicle exhaust emissions and solvent usage) (Wang et al., 2014;Barletta et al., 2005). These chemicals contributed >60% for ΣVOCs at each site, illustrating strong combustion-related sources in Zhengzhou."*

Comment 16

It would seem to me to make more sense for the authors to discuss likely influences from long-range transport of pollutants (i.e. HYSPLIT back-trajectory analyses here shown in Section 3.7) BEFORE considering local sources.

Response:

Thanks for the suggestion. This has been moved to Section 3.1.

Comment 17

L208: The authors describe the results as showing "the general consistency of pollution sources in the region" but the large variability in the reported averages do not appear to suggest that.

Response:

Even though the concentrations were variable, the compositions of major compounds were similar at every site. Therefore, we do conclude that there were consistent emission sources for each site.

Comment 18

L221-222: The authors have not convincingly demonstrated this in their presented results.

Response:

The paragraph has been revised as

“The C_2 *-* C_5 *alkanes, acetylene, ethylene, toluene and benzene were the most abundant VOCs detected at all sites (Fig.8), and the mixing ratios of toluene varied within a wide range at each site, because of its universal emission sources (e.g., vehicle exhaust emissions and solvent usage) (Wang et al., 2014;Barletta et al., 2005). These chemicals contributed >60% for* Σ_{VOCs} *at each site, illustrating strong combustion-related sources in Zhengzhou”*

According to results calculated by PMF, except for toluene in which solvent use contributed more about 50%，these compounds were mainly originated from vehicle and coal/biomass burning,

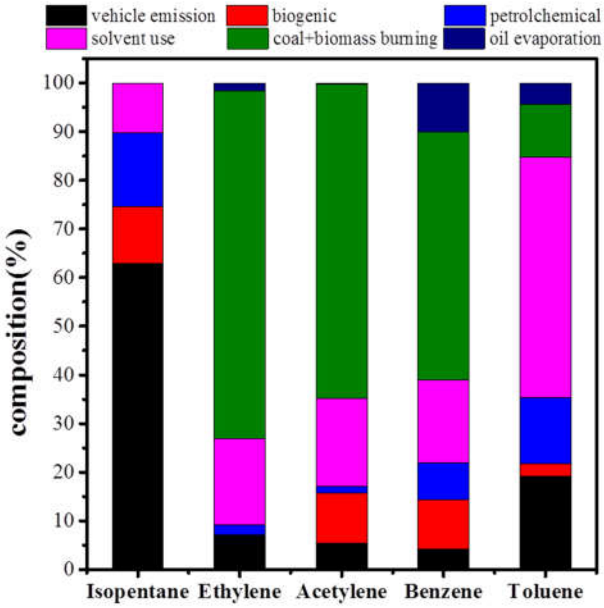


Fig. Major emission sources of abundant compounds apportioned by PMF.

Comment 19

L231-232: Samples were taken at 07:00 and 14:00 only. The authors cannot make general comments about morning and afternoon as they have not presented any data to suggest that the conditions at 07:00 (14:00) persist throughout the morning (afternoon)

Response:

The paragraph has been revised as,

“Due to the variations of the planet boundary layer (PBL) height, solar radiation and emission sources, the concentrations of VOCs displayed obvious differences between morning and afternoon time (07:00LT and 14:00LT in this study). Compared with morning period, the aromatic compounds showed lower compositions at14:00 LT (Fig. 5), because of the increased planet boundary layer and the active photochemical reactions, while alkenes always peaked in the14:00

> *LT. According to the dataset, the increases in alkene compositions (~4.3% uplift) were mainly due to higher contributions of isoprene (~1.4% at morning and 7.6% in the afternoon), which was mainly emitted from biogenic sources and increased exponentially with ambient temperature (Jiang et al., 2018).”*

Temporal variations:

Comment 20

L261: “wash-out” specifically refers to rain which I don’t think is what the authors mean.

Response:

The sentence has been revised as

> *“The occurrences of precipitation and raining were also frequent in most areas of China during summer, resulting in decreasing background level of air pollutants”*

Comment 21

L276: “sharp changes in local emissions” - such as?

Response:

These could be resulted from the local emissions such as coal combustion and leakage of compressed natural gas (CNG) or LPG. We have explained this case in the following statements:

> “*Specifically, at MEM, the distinctive increment was always accompanied with obvious increases of alkanes or aromatics (Fig. 7). Since the T and RH were often consistent during the sampling period, the direct gas evaporations should be constant as well. Therefore, the simultaneous increased concentrations of SO_2, CO and NOx could illustrate the potential impacts from combustion sources, such as emissions from nearby thermal power plant. At GS, the increase of Σ_{VOCs} in June was usually with extremely high levels of aromatics, due to the disturbance from solvent use for building renovation during this period, and the abnormal high levels of Σ_{VOCs} in other months were related to the rising concentrations of C_3-C_4 alkanes, which were mainly originated from consumptions of compressed natural gas (CNG) or LPG (Huang et al., 2015b). The results support the possible impact from a gas-fueled power plant located about 1 km southwest of the site (~18% of prevailing western wind at GS during May to September).”*

Comment 22

L278-9: It is not clear how changes in T and RH lead the authors to conclude combustion sources were enhanced.

Response:

Since the T and RH were often consistent under normal conditions, the contributions from gas evaporation should be also constant. Therefore, the simultaneous change of SO_2, CO and NOx should be caused by the enhancement of combustion sources. In order to avoid confusion, we have rewritten the statement as:

> *"Specifically, at MEM, the distinctive increment was always accompanied with obvious increases of alkanes or aromatics (Fig. 7). Since the T and RH were often consistent during the sampling period, the direct gas evaporations should be constant as well. Therefore, the simultaneous increased concentrations of SO_2, CO and NOx could illustrate the potential impacts from combustion sources, such as emissions from nearby thermal power plant."*

Comment 23

It would be extremely helpful to have a more detailed map of Zhengzhou City showing the 4 sites, key emission sources and prevailing wind.

Response:

Suggestion taken. The newly figure 1 and 4 have been revised as below:

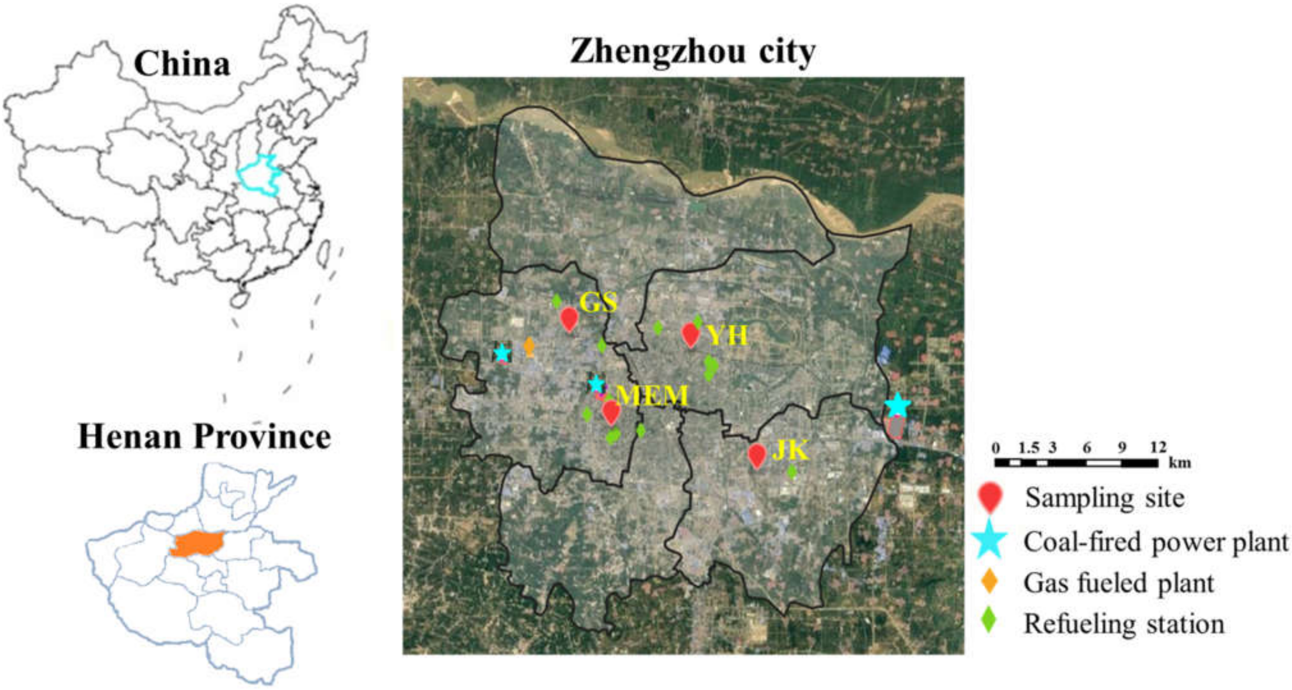


Fig 1. Map of Zhengzhou, China showing the locations of sampling sites.

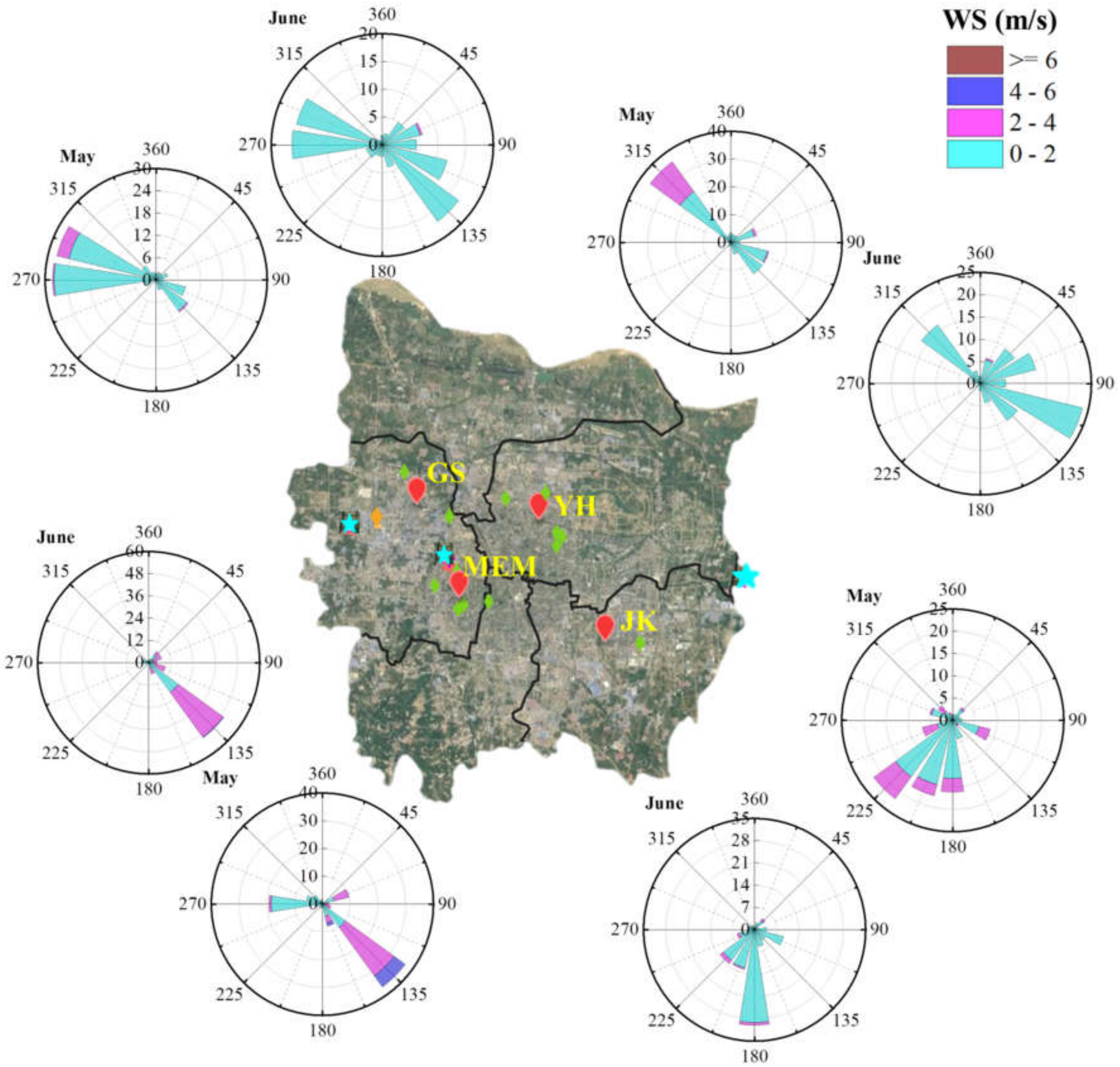


Fig. 4 Wind rose of each site in May and June (the wind distribution in other three months were illustrated in Fig S2)

Spatial variations:

Comment 24

L298-299: O_3-NOx-VOC interactions and reactions are always highly complex and non-linear, hence the development of ozone isopleths (see e.g. Silman, 1999)

Response:

Thanks for the recommend reference. There is a particular section (i.e, section 3.4) for discussion on the ratio of VOCs/NOx.

Comment 25

L300: Is this peak (i.e. hourly) O_3 or 8-hour O_3?

Response:

It is hourly average**.**

Comment 26

L306-307: This sentence appears to contradict the results presented in L301-302.

Response:

There is no contradiction. The original L306-307 just pointed out that a reversible observation on concentrations of O_3 and VOCs/OFP was seen at the two sites of MEM and JH only. There are many different factors controlling the ozone formation. The general trend is unchanged.

Comment 27

L321-323: "when synoptic conditions were favorable" - yet in the abstract and conclusions the authors state categorically that O3 formation in Zhengzhou is VOC-sensitive. If there is a caveat it should also be made clear in these other sections.

Response:

The discussion on ozone formation regime was presented in the newly Section 3.4.

Comment 28

Please give typical T/B ratios for relevant sources.

Response:

We have provided the information as:

> *"T/B is another efficient tool to differentiate between pollution sources, both the tunnel studies and roadside researches indicated that T/B ratio varied within the range of 1 - 2 when the atmosphere was heavily impacted by vehicle emissions (Gentner et al., 2013;Tang et al., 2007;Huang et al., 2015b;Wang et al., 2002), and when the ratio was less than 0.6, it may be due to other sources, such as coal combustion and biomass burning (Tsai et al., 2003;Akagi et al., 2011). The industrial activity would become more important when the value of T/B ratio is higher than 3 (Zhang et al., 2015)".*

Comment 29

L334-336: Without knowing that the emission sources remained constant throughout the time it is not possible to state definitively that the differences were due to photochemistry.

Response:

The relative statements have been revised as:

> *"From the temporal respect, the T/B ratios at 14:00 LT were lower than at 07:00 LT (Fig.15). In fact, the reaction rate constant of toluene ($5.63\times10^{-12}cm^3molecule^{-1}s^{-1}$) with •OH is much higher than that for benzene ($1.22\times10^{-12}cm^3molecule^{-1}s^{-1}$), representing more rapid consumption of toluene from photochemical reactions and thus resulting in lower T/B ratios at 14:00 LT. Besides, the emission strength of mobile source is often weaker at 14:00 LT, while the coal/biomass burning are increased due to more human activities. Both of the situations can be used to explain the lower T/B ratios observed at 14:00 LT. In comparison with other months, higher T/B ratios were found more frequently in September, potentially showing the more strengthen indusial activities during this period."*

Comment 30

L336-337: The authors make many statements such as this without attempting to explain why the observed difference may have occurred.

Response:

The incoherent statements have been deleted.

Comment 31

L340-342: The absolute values should be reported before the R^2 value.

Response:

Thanks for the reminder. The absolute values have been reported.

Comment 32

L349: It would be possible to achieve these values with zero vehicle emissions but a mixture of industrial and biomass burning emissions. Hence my previous comment regarding the superfluity of this speculation given the authors have conducted PMF for source-apportionment. But perhaps other pollutants monitored at the site also provide insight into most likely sources?

Response:

The statement has been revised as

> *"The average ratios of T/B were lied within the range of 1.64-2.29, which were scattered around the character ratio of 2 for vehicle exhaust, illustrating the significance of vehicle emissions at the four sites. Specifically, at JK, MEM and*

YH, most of T/B ratios were distributed between 0.6 and 3, which were corresponding to character ratios for coal or biomass burning and industrial activities respectively. These reflected the mixture impacts from mobile source and coal/biomass burning at these three sites. However, more values were greater than 3 at GS, suggesting more frequent disturbance from industrial activities at this site."

Comment 33

L355: How are the outliers ("abnormal values") identified and removed?

Response:

The abnormal values defined as the data points did not distribute in the range of 5-95%, and thus were not taken into consideration in Section 3.5.

Comment 35

L360-361: As previously noted, a windrose plot would be extremely helpful.

Response:

They have been now presented in newly Fig. 4 and Fig. S2.

Comment 36

L360-361: This might be the prevailing wind, but what about the specific days sampled?

Response:

The prevailing wind directions were often consistent with the wind directions on our 10 sampling days each month.

Comment 37

i-pentane and n-pentane: Is this the ratio of i/n that the authors are reporting from these previous studies?

Response:

In newly L374-380, the ratios from other studies have been added, and the values observed in this study were presented in Fig.12.

Comment 38

I would suggest that the authors reverse the order and discuss i/n ratios first as they are NOT influenced by different reaction rates, and then discuss T/B ratios which are.

Response:

The relative statement has been moved to newly L374-391.

Reactive chemicals:

Comment 39

L389-390: As noted previously, there are caveats associated with OFPs. It is not just the "reactivity" that matters when assessing the contribution of each individual species to overall O3 formation. Different mixtures of VOCs result in competition between different species, leading to different relative yields, different reaction paths, etc.

Response:

The statements have been revised as:

> "*The reactivity of individual species was different, while mixtures of VOCs would have competition the precursors between each other, leading to variations on reaction paths and O_3 formation yields. Ozone formation potential (OFP) is a useful tool to estimate maximum O_3 productions of each compound under optimum conditions, from which the vital species in O_3 formation could be identified.*"

Comment 40

L392-395: The authors need to make it abundantly clear that this is an entirely hypothetical potential (or maximum) possible O_3 formation for each compound in isolation.

Response:

The statement has been revised as:

> "*Ozone formation potential (OFP) is a useful tool to estimate maximum O_3 productions of each compound under optimum conditions, from which the vital species in O_3 formation could be identified (Huang et al., 2017). The calculation of OFP is based on mixing ratios and maximum incremental reactivity (MIR) of individual compound, which are expressed in Eq. (4).*"

Comment 41

L396: The authors should present their own results first and then put them into context against previous studies. It's not clear why they would expect relative abundances and relative contributions to O_3 formation to be the same across different regions with different sources and different meteorological conditions.

Response:

The paragraph has been rewritten as,

> *"In Zhengzhou city, alkenes contribute most (55.91±14.17%) to the sum of OFP, of which ethylene had the largest portion. The results is different with the estimation based on emission inventories by Wu and Xie (2017), in which the largest contributor of total OFP in North China Plain (NCP), YRD and PRD was aromatics, reflecting that there was relatively less surface coating industries in Zhengzhou."*

The estimation was not considered meteorological conditions, and the provincial emissions were calculated using equations:

$$E_t = \sum_{p=1}^{N} \Big(\sum P_{m,n} \times \mathrm{VMT}_{m,n} \times \mathrm{EF}_{m,n} + \sum (1 - R_k) \times \mathrm{EF}_{s,k} \times A_{s,k} \Big) \times 10^{-12}$$

where E_t is the total VOC emission (Tg), $P_{m,n}$ is the vehicular population of category m with emission standard n in province p (N = 31, including all of the provinces, municipalities, and autonomous regions in mainland China), $VMT_{m,n}$ and $EF_{m,n}$ are the corresponding annual average mileage (km) and emission factor (g/km), respectively, R_k is the removal efficiency with technology k, and $EF_{s,k}$ and $A_{s,k}$ are the corresponding emission factors and activity data for source s (except on-road vehicles), respectively.

Comment 42

L401: "fraction" rather than "composition"?

Response:

Yes, it should be "fraction". The statement has been revised as:

> *"the percentage of acetylene (4.51±0.34%) weighted in OFP was higher than many other areas in China"*

Comment 43

L410-411: Demonstrating the caution required in using and interpreting OFPs

Response:

Thanks for the reminder. The statement has been revised as,

> *"Under low RHs and high T and OFP (88.13±30.32 ppbv), the O_3 level at YH was unexpectedly lower than that at MEM on sunny days. Since the OFP was*

estimated with the assumption of reactions that proceeded under optimum conditions, the above phenomenon reflected there were unsatisfied O_3 formation conditions at YH."

Comment 44

L414: And/or increased the importance of local versus long-distance sources.

Response:

The statement has been revised as

> *"The highest total OFP was seen at JK in June, while the highest O_3 levels was observed at GS where located at a downwind position with lowest WS (0.74±0.33 $m\ s^{-1}$). The concentration level of O_3 usually increased with wind speed (Fig.S7), particularly when the eastern wind was dominant, illustrating the disturbance from long-distance sources to urban center".*

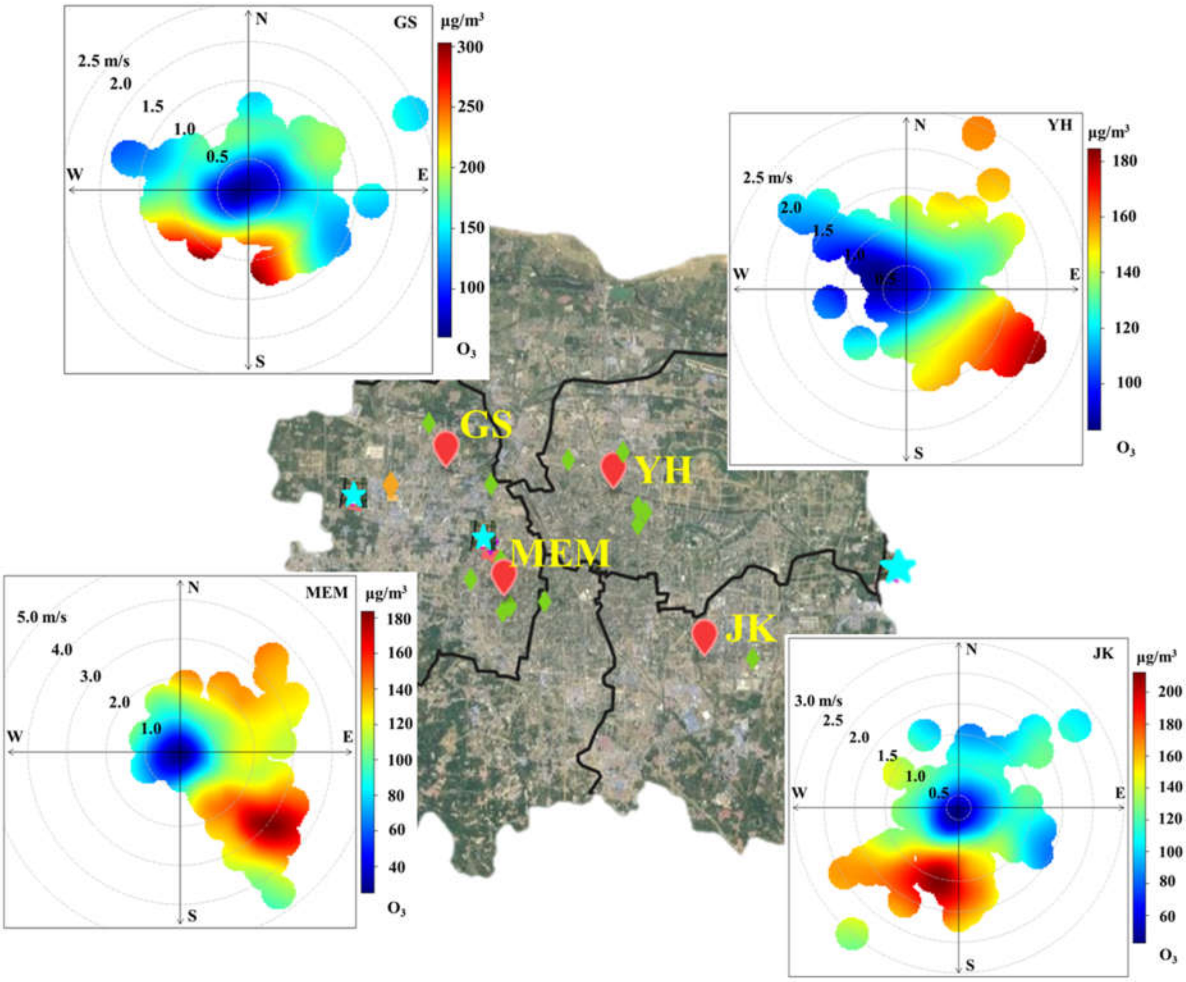


Fig.S7 Relationship among O_3 ($\mu g\ m^{-3}$), wind direction and wind speed ($m\ s^{-1}$) during sampling period in June, 2017

Source apportionment

Comment 45

It would be extremely useful to have a map showing (roughly) the key emission sources for these 7 or 8 factors near each of the 4 sampling sites.

Response:

They have been incorporated in newly Fig.1.

Comment 46

L420-425: These describe the methodology and should be included in Section 2.

Response:

Suggestion taken.

Comment 47

L423-424: As suggested previously, I would move Table 6 to SI together with the detailed mathematical description of the method

Response:

Suggestion taken.

Comment 48

L424-425: Explain how the number of factors was determined.

Response:

The description has been revised as:

> *"Three to nine factors were selected to initiate the running of PMF, the Q/Q(exp) for every site at fixed factor size were presented in Table S4. With the increase of factor number, the ratios Q/Q(exp) were declined due to additional factors. When the factor size changing from 3 to 4, 4 to 5, and 5 to 6, the decrement of Q/Q(exp) were larger (~12-23%), while the change was lower than 10% after factors increased to 7, combined with the field conditions, six factors were defined at each site."*

Comment 49

L427-428: Was it possible to identify specific alkanes or alkenes? Were there any clear differences between sites or times of day?

Response:

Yes, sources can be identified with specific compounds using all of samples collected in this study. The PMF results indicate that coal+biomass burning (about 72%) was the most important source of ethylene, while as to toluene, solvent use (50%) contributed most.

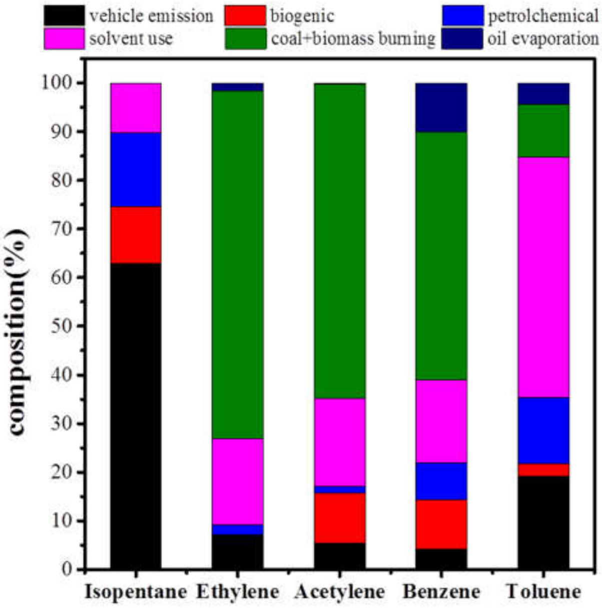


Fig. Major emission sources of abundant compounds apportioned by PMF.

The major emission sources for abundant compounds the four sites were presented below:

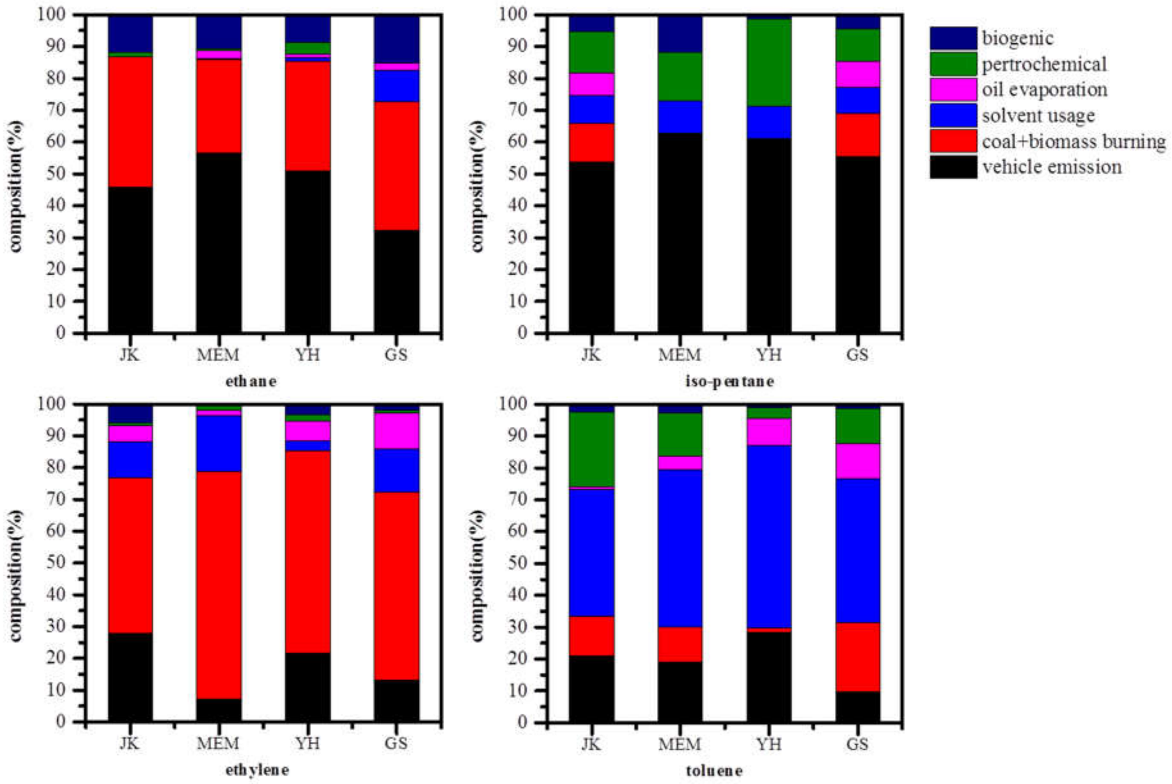


Fig. major sources of ethane, iso-pentane, ethylene and toluene at each site

The major emissions for ethane, iso-pentane and ethylene were combustion-related source. In more specific, vehicle emission and coal+biomass burning were the most important sources for ethane, and vehicle emission contributed more than iso-pentane at each site, while coal and biomass burning contributed most to ethylene regionally. The typical aromatic of toluene is appointed to solvent usage.

Comment 50

I suggest the authors emphasize the differences between the identified factors more than they do. It is the trimethylbenzene that distinguishes the second from the first factor, but it is likely that ratios of e.g. toluene to xylene also differ

Similarly with source 3: it is the ratio of toluene:benzene and other aromatics that makes this distinct from the first factor and leads to the conclusion that one is gasoline and the other diesel.

Does source 4 also correlate with SO_2 which would strengthen the case that this is specifically coal burning rather than another fossil fuel? Again, the fifth factor seems little different from the first three. Emphasize the unique markers of each

Response:

Thanks for the suggestion, we have re-calculated and the correlations are acceptable.

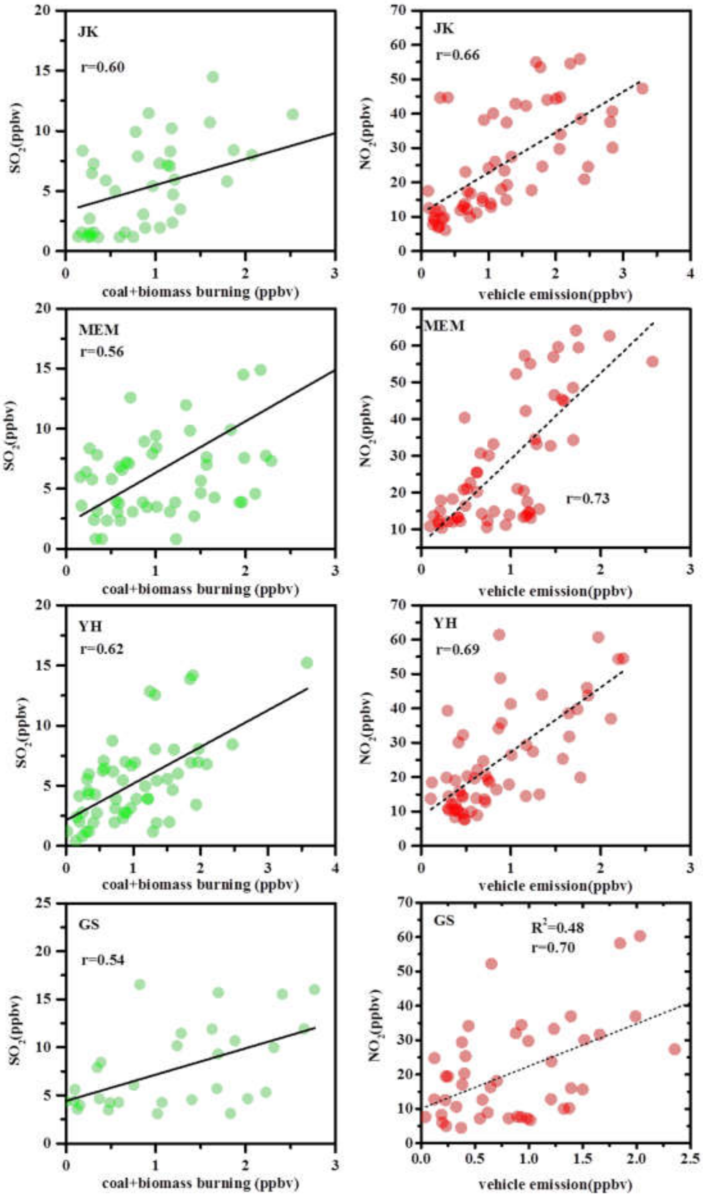


Fig. 16 Correlation analysis between contributions of coal+biomass burning and SO_2, and vehicle emission and NO_2

The revised six sources and the correspondent source markers were summarized as below

Source	**Source category**	**Markers**	**Reference**
1	vehicle emission	C_2-C_5 alkanes, NO_2	(Watson et al., 2001)
2	coal+biomass burning	ethane, ethylene, acetylene, benzene	(Liu et al., 2008;Zhang et al., 2013)
3	solvent usage	toluene, ethylbenzene, xylenes	(Yuan et al., 2010;Wang et al., 2014)
4	oil gas evaporation	C_4-C_5 alkenes, n-heptane	(Wang et al., 2017)
5	petrochemical	methyl-cyclopentane, cyclohexane, 3-Methyl-hexane, 2-Methyl-hexane, styrene	(Liu et al., 2008;Jobson et al., 2004)
6	biogenic	Isoprene	(Millet et al., 2016)

Comment 51

Source 6 seems to exhibit the same compound mix as source 1. How do they differ? Is it that they have very different ratios of some of the compound classes?

Response:

We have rerun the PMF, and the problem has been fixed.

Comment 52

L465: Do the authors mean different vehicle types (e.g. hybrid, LPG, etc) or different styles of driving (e.g. more idling, lower speeds with increased braking, etc)?

Response:

It was pointed to different styles of driving.

Comment 53

It seems to me that Factor 8 is simply a sub-set of Factor 6. How are they distinguishable?

Response:

We have rerun the PMF, and the problem has been fixed.

Comment 54

L482-484: It would be really nice if the authors now brought together the two quantified analyses they have conducted: source-apportionment and OFPs to identify the sectors that were most polluting at each site. Presumably here "important" refers to magnitude but would that also be the most important if considering OFP? Or toxicity?

Response:

We presented the results on calculation based on two methods, one with absolute mixing ratios and the other with OFP, in Fig.17. and a part of description was like this:

> "*On the base of O_3 formation impact, coal+biomass burning, solvent use, and vehicle emission were the three major contributors as well. In contrast to the concentration weighted method, the importance of solvent use estimated with OFP increased 28-65% for each site, and the significance of vehicle emissions decreased 29-53%. At YH and GS, small discrimination (<4%) in contributions of coal+biomass burning between the two methods were found. On the other hand, the variations on coal+biomass burning at JK (a decline of 17%) and MEM (an increase of 29%) were more obvious, due to low abundance of reactive species in this factor at JK and high level of alkenes at MEM. Considering that the aging*

index of xylene/ethylbenzene was high at MEM (2.97) and low at JK (0.01) remarkably, demonstrating that the emission sources related to coal+biomass burning was fresher at MEM than JK.”

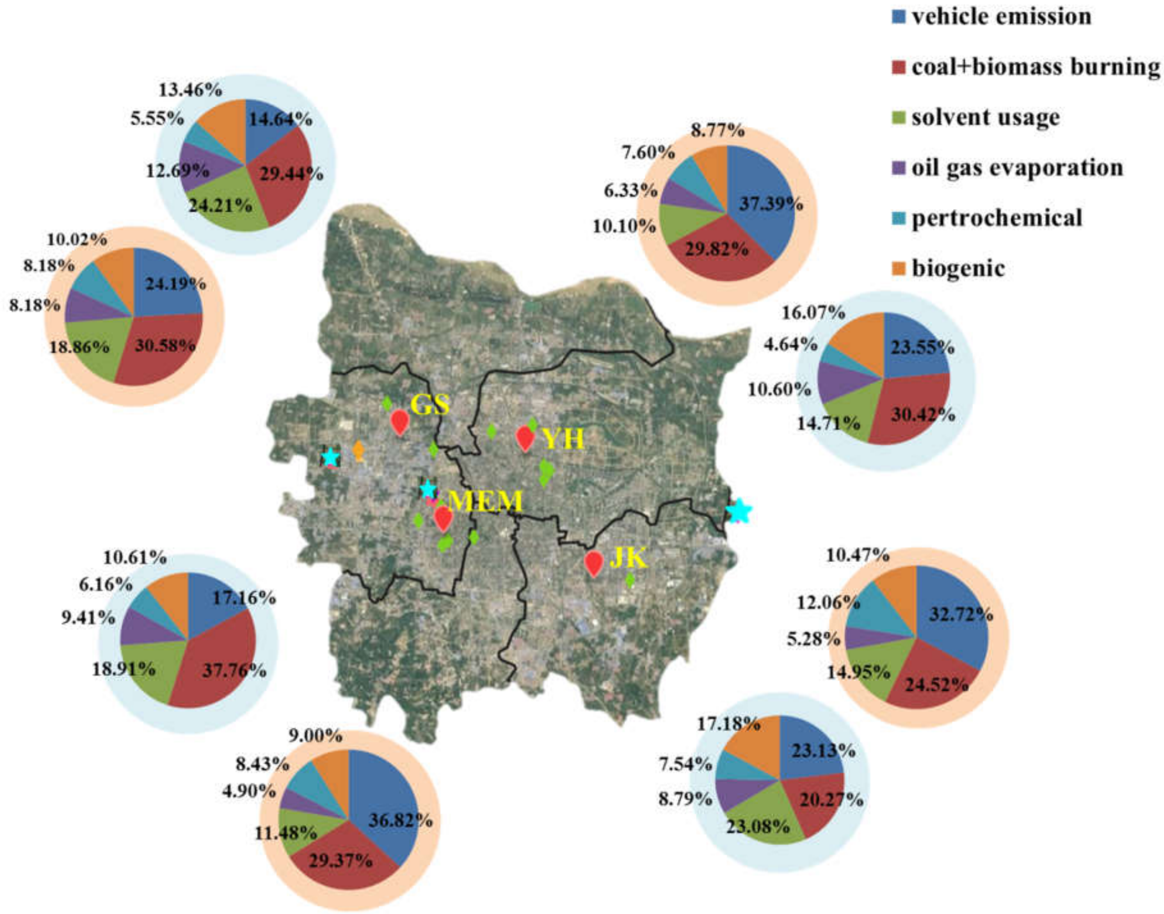


Fig. 17 Source apportionment results during the whole sampling period. The results weighted in observed concentrations were shadowed with pink color, and the results estimated based on OFP were shadowed with light blue color.

Long-range transport:

Comment 55

This entire section should be moved forward and presented ahead of all the sections describing possible local sources of precursor emissions. As O_3 is a secondary pollutant, regional and long-range transport is typically the greatest source.

Response:

This has been moved to Section 3.1.

Figures and Tables

Comment 56

Table 1: Suggest move to SI; not essential for main text. However, MIR should be included in the current Table 5.

Table 2: See comments regarding wind.

Tables 2-4: Should be combined into a site overview table with all met variables discussed within the text, average concentrations of all pollutants, specific VOC concentrations

Table 5: Would suggest to add % contribution to total VOC concentration as a neat comparison against % contribution to OFP and to put MIR in this table as it is used to calculate OFP

Fig. 1: I suggest the authors combine this with Fig. 10; airmass back trajectories are important for virtually all of the analysis presented in this study so should not be relegated to the final figure (and similarly should be included far earlier in the text than they are.

Fig. 2: It is not possible for any individual class of VOC to account for >100% of the composition of total VOCs. Either the authors should be using a stacked bar chart with each segment of the bar representing the different compound classes or a side-by-side bar chart as in the insert for isoprene. I would also suggest that isoprene should be included as part of the chart and not as an insert.

There is no obvious reason why the right-hand and left-hand panels should use different types of chart given they are showing the same thing.

The caption should be expanded to actually explain the figure; it is not just a title. For example, do the bars for YH, GS, etc on the left-hand panel include both 07:00 and 14:00 data? And is that comparable with the data from other cities? The panel would be less cluttered if the authors listed the references as footnotes rather than on the chart itself.

Fig. 3: This figure is very poorly presented. The authors are attempting to fit too much data on each panel with too few different axes scales. Using a reverse scale on the secondary y-axis makes it almost impossible to assimilate the information and see correlations between the different variables. Using an axis ranging from 0 to 200 means that the T (in degC) is compressed to the point of masking any hour-to-hour fluctuations; CO (even scaled to ppm instead of ppb) has become a featureless red

line. Why is SO2 coloured in rather than just presented as a line?

The data requires splitting across additional panels, firstly helping to de-clutter and secondly allowing additional axes for clarity.

Again the caption should be expanded to be more descriptive. What is the significance of the two dates that are shaded? Are the tick marks corresponding to the dates shown at the bottom indicating 00:00 on that date? Or 12:00 (i.e. the middle of the day)?

Fig. 4: Why are the colours used for each class here (and in Fig. 3) different from those used in the left-hand panel of Fig.2 ?

Given that the left-hand panel has a continuous temporal scale on the x-axis would it make more sense to present all 07:00 data before all 14:00 data on right-hand panel rather than splitting by site?

Please include more information in the figure caption.

Fig. 5: Again, the authors are attempting to fit too many different variables on each panel, each with different scales, chart types, symbols and symbol colours. This requires splitting out into separate panels or charts.

Response:

Tables and figures have been revised according to the suggestion.

Change list

Title

Changed as "Characterization of VOCs and their related atmospheric processes in a central China city during severe ozone pollution periods"

Abstract

L17-19 "Canister samples were collected for measurement of fifty-seven VOCs, which are the most important O_3 precursors."

L23-27 "The cluster analysis points out that air masses from cities south of Zhengzhou were cleaner than from other directions. Besides, the molar ratio of VOCs to NO_x indicated that VOCs were more sensitive than NO_x to the O_3 formation in Zhengzhou. Meanwhile, the overall results further implied that photochemical reactions at marginal sites where highly distributed with industries were more efficient than those at other sites."

L30-34 "From Potential Source Contribution Function (PSCF) analysis, the strong emissions from coal+biomass burning and solvent usage were concentrated in southwest of Shanxi and Henan province. The results of this study gather scientific evidences on the pollution sources for Zhengzhou city, benefiting the Government to establish efficient environmental control measures particularly for O_3 pollution."

1. Introduction

L42-49 "In China, the investigations on VOCs including source apportionment, measurement of emission profiles and interpretation of seasonal variations were mainly concentrated in Yangtze River Delta (YRD), Pearl River Delta (PRD) and Beijing-Tianjin (BJT) regions (An et al., 2014;Wang et al., 2014;Chen et al., 2014;Liu et al., 2016;Guo et al., 2017). Limited studies have been conducted in less developed or developing regions (i.e., southwestern and northwestern China) where prominently impacted by biomass burning and with high abundances of toxic and reactive compounds (Li et al., 2014;Li et al., 2017a)."

L50-65 "Fifty-seven VOCs, including C_2 - C_{10} alkanes, alkenes, alkynes and aromatics, which greatly contribute to ambient O_3 formation, have been identified and are regularly monitored by Photochemical Assessment Monitoring Stations (PAMS) (Shao et al., 2016;Chen et al., 2010). Due to characteristic structure and reactivity of these compounds, their contributions in O_3 production were varied accordingly, and it is reported that aromatics and alkenes were responsible for most of the weighted reactivity of VOCs (59.4% and 25.8%, respectively) in Pearl River Delta (PRD) region in China (Ou et al., 2015). Consequently, researchers have deduced that reductions of alkenes and aromatics are profit for O_3 control (Carter, 1994). In addition, with the variations on energy structure, industrial construction and meteorological conditions (Wang et al., 2015;Shao et al., 2011), major emission sources of VOCs at each city are unique. In less developed cities of Heilongjiang and Anhui, biomass combustion had the highest contribution (40% and 36%, respectively) to the O_3 formation potentials due to high quantity of agricultural activities, while in the developed cities such as Shanghai, Beijing and Zhejiang, solvent usage has become more dominant (>20%) than other pollution sources (Wu and Xie, 2017). Therefore, identification on district emission sources of VOCs is necessary to provide scientific-based information for policy-makers who establish efficient strategies to alleviate O_3 pollution."

L66-74 "In addition to the factors discussed above, non-linear relationships between ambient VOCs, nitrogen oxide (NO_x) and O_3 production indicate that the reduction in tropospheric O_3 is more complex than expected (Lin et al., 1998;Hidy and Blanchard, 2015;Li et al., 2018). Many modeling and field studies showed that photochemical O_3 production in several cities in China such as Guangzhou, Shanghai and Beijing with high levels of NO_x were highly sensitive to VOCs (Shao et al., 2009;Gao et al., 2017;Ou et al., 2016). The sensitivity regime is always varied with time and geographical locations (Luecken et al., 2018). The percentage of VOC-limited regime in North China Plain (NCP) increased from 4% to 6% between 2005-2013, owing to the rapid increases of NO_x emissions (Jin and Holloway, 2015)."

L79-82 "The Air quality index (AQI) for 65% of the days in 2013 exceeded the allowable limits of 100 established by the Air Quality Guideline. Particularly, O_3 was the major pollutant in summer and over 50% of the days in a year, the mixing ratio of O_3 exceeded the Grade I standard (100 $\mu g\ m^{-3}$) of daily maximum average 8-hour (DMA8) in Henan (Shen et al., 2017;Gong et al., 2017)."

2. Observation and Methodology

2.1 Sampling site

L93-94 "Based on the density of population distribution, locations of industrial facilities, and the prevailing winds, four sites have been selected for sample collection:"

L106-111 "Ten sampling days with the rainfall record (*ca*. 0 mm) were chosen in every month during the period of May - September, 2017 consequently, to represent a typical air quality condition in a month. Grab samples were collected minute using 3.2 L stainless-steel canisters (Entech Instrument, Inc., Simi Valley, CA, USA), which were pre-cleaned with high purity nitrogen and pressurized to 20 psi. Two samples, one collected at 07:00 with increasing of human activities and another one collected at 14:00 with well-mixed of ambient air, were obtained on each sampling day."

2.2 Chemical Analysis

L128-131 "Target compounds were identified with retention time and mass spectra, and quantified with multi-point calibration curve in this study. The standard gas of PAMS (1 ppm; Spectra Gases Inc, NJ, USA) was used to construct the calibration curves for the 57 target VOCs, including 28 alkanes, 11 alkenes, acetylene and 17 aromatics."

L137-140 "Due to the complex chemical reactions, the application of PMF in VOCs has to be based on a couple of principles: eliminating species with mixing ratios below MDL and excluding species with high reactivity, except for the source markers

(Shao et al., 2016;Guo et al., 2011). Finally, 31 VOC species and NO_2 were chosen for the source apportionment analysis."

2.3 Positive matrix factorization (PMF)

L141-155 "In this study, PMF was performed with fifty base runs for each site, results with the minimum Q value (a parameter used to express uncertainties of PMF results) were considered as optimum solutions. In Table S2 the r^2 between observed values and predicted values of selected VOCs and NO_2 are presented for the four sites, the r^2 for most species (>80%) were higher than 0.6, compounds with $r^2<0.6$ were down weighted when determine factor sources.

During PMF analysis, bootstrap method was used to evaluate stability and uncertainty of the base run solution, setting the minimum correlation R-value at 0.6, 100 bootstrap runs were performed, and the results were showing in Table S3, and acceptable results (>80%) were gained for all the factors.

Three to nine factors were selected to initiate the running of PMF, the Q/Q(exp) for every site at fixed factor size were presented in Table S4. With the increase of factor number, the ratios Q/Q(exp) were declined due to additional factors. When the factor size changing from 3 to 4, 4 to 5, and 5 to 6, the decrement of Q/Q(exp) were larger (~18-25%), while the change was lower than 12% after factors increased to 7, combined with the field conditions, six factors were defined at each site."

2.4 Potential source contribution function (PSCF)

This was a newly section

2.5 Estimation of the initial NO_x and VOCs

This was a newly section

3 Results and discussions

3.1 Meteorological variations and Mixing ratios

L188-200 "Meteorological conditions are important factors that impact both the compositions and levels of VOCs. During the sampling period, the T (RH) was varied from 15°C (15%) to 38°C (100%) (Fig.S1), and the dominant wind was northwestern and southeastern (Fig. 2). The air clusters, analyzed by HYSPLIT model, showed moderate differences in each month (Fig. 3). In May, clusters arriving at Zhengzhou demonstrated longer paths, and included six clusters in total, while in June, the length of clusters were shorter. However, the concentration levels and compositions of VOCs were similar in the two months. In May, the largest cluster (27.2%) was passed over from Yinchuan, a central city in northwest China, then crossing several non-capital cities (i.e., Yanan, Yuncheng and Luoyang) in Shanxi and Sichuan provinces. Such a long-range transport of pollutants might result a less impact on the air quality of Zhengzhou, as comparable level and similar compositions of VOCs were obtained during the period of May - June. In June, August and September, approximately half of the air trajectories originated from the areas of Henan province, indicating the air pollutants in Zhengzhou were impacted by local factors at most time."

L201-203 “The Σ_{VOCs} varied at the four sites, where the highest Σ_{VOCs} and their compositions were not identical across the sampling months as well.”

L207-209 “This can be attributed to numerous factors that will be explored later in the paper. Besides the emission sources (to be discussed in Section 3.2), the impacts controlled by meteorological conditions should not be ignored as well.”

L214-216 “The air pollutants emitted from MEM and YH were more liable resulting in a higher level of Σ_{VOCs} at GS in June.”

L219 “where the elevation was gradually increased from east to west in Zhengzhou (Mu et al., 2016).”

L227 **“**which was mainly emitted from biogenic sources and increased exponentially with ambient temperature (Jiang et al., 2018).”

L235-237 “the composition of alkanes was the largest in all cities because of their longer lifetimes and widespread from a variety of pollution sources (Fig. 5), while the composition of aromatics was lower than alkenes in these cities except for Guangzhou.”

L241-242 “the composition of aromatics in Zhengzhou was the lowest probably due to its less solvent-used manufacturers than in Guangzhou, Hangzhou and Nanjing, and less numbers of vehicles than in Beijing.”

L245-246 “Zhu et al. (2016) observed that the composition of alkyne in the biomass-burning period could be double of that in the non-biomass burning period.”

3.2 Temporal variations

L257-258 “The occurrences of precipitation and raining were also frequent in most areas of China during summer, resulting in decreasing background level of air pollutants.”

L267-274 “Beside local emissions, the long-range air mass also had some impacts on relatively lower level of Σ_{VOCs} in July. As illustrated in Fig.3, different from other months, the air current was originated with the largest portion (*ca*. 88.68%) of clusters from Hubei province, where the average Σ_{VOCs} in its capital city (23.3±0.6 ppbv) (Lyu et al., 2016) was lower than that in Zhengzhou (29.18±23.08 ppbv). In combination with the lower weight percentage of photothermal-reactive aromatics (10.30±4.23%), and the lowest toluene to benzene (T/B) ratio of 1.15±0.99 around this period, it is possible that the cleaner air mass clusters originating from Hubei also contributed to the reduction of Σ_{VOCs} in July.”

L281-285 “Specifically, at MEM, the distinctive increment was always accompanied with obvious increases of alkanes or aromatics (Fig. 7). Since the T and RH were often consistent during the sampling period, the direct gas evaporations should be constant as well. Therefore, the simultaneous increased concentrations of SO_2, CO and NO_x could illustrate the potential impacts from combustion sources, such as emissions from nearby thermal power plant.”

3.3 Spatial variations

L299-308 **“**The C_2 - C_5 alkanes, acetylene, ethylene, toluene and benzene were the most abundant VOCs detected at all sites (Fig.8), and the mixing ratios of toluene varied within a wide range at each site, because of its universal emission sources (e.g., vehicle exhaust emissions and solvent usage) (Wang et al., 2014;Barletta et al., 2005). These chemicals contributed >60% for Σ_{VOCs} at each site, illustrating strong combustion-related sources in Zhengzhou.

Among the four major organic classes, alkane was the most abundant group as a result of its widespread sources and longevity (Fig.5), accounted for 52.9%, 62.5%, 53.4%, 53.4% of the total Σ_{VOCs} at JK, MEM, GS, and YH, respectively. The highest composition of alkane was observed at MEM due to the stronger contributions of ethane, iso-pentane, and C_6-C_8 branched alkanes (Fig. S3), which are emitted from light-duty gasoline vehicles (Wang et al., 2017a)."

L312-315 "Under high levels of VOCs and sufficient supply of NO_x, the highest average mixing ratio of O_3 was observed at GS, followed by YH where even with the lowest VOCs and NO_x, indicating that there are multiple factors, rather than the absolute concentrations, contributed to the O_3 formation at YH."

L320-325 "The higher level of O_3 at GS was accompanied with the higher Σ_{VOCs} (39.29±25.37ppbv). The weight percentage of aromatics (15.62±12.06%) at GS was higher than those at other sites as well, indicating that the painting and other renovation activities at GS was potentially an important factor for its high O_3 level in June. Even though both the Σ_{VOCs} and specifically high O_3 formation potential compounds (such as alkenes and aromatics) at MEM were slightly higher than those at YH (Table 4), the O_3 concentration at MEM was not higher."

L330-334 "For example, Streets et al. (2007) reported that with continuous southern winds, the O_3 level in Beijing was 20-30% contributed from its neighboring cities in Hebei. During this study, a typical regional ozone pollution was happened on August 10th at YH (Fig.6). On that day, the ratios of Σ_{VOCs}/NO_x at the four sites were all less than 6.5 (ppbC/ppbv) (Fig. S4), indicating a regional VOC-control system, and that VOCs are the critical contributors to the formation of O_3 in Zhengzhou."

L339-340 "All of this confirmed that the abnormally high O_3 at YH was caused by the transport of air pollutants from other sites on that day."

3.4 VOCs/NOx ratio

This was a newly added section

3.5 Ratios of specific compounds

L374-380 "The ratio of i-pentane to n-pentane can be used to differentiate potential sources such as consumption of natural gas, vehicle emissions and fuel evaporations. It is claimed that in areas heavily impacted by natural gas drilling, the ratios were lied within the range of 0.82 - 0.89 (Gilman et al., 2013;Abeleira et al., 2017). Higher values were often reported for automobiles, in a range of 2.2 - 3.8 for vehicle emissions, 1.8 - 4.6 for fuel evaporation, and 1.5 - 3.0 for gasoline (Russo et al., 2010;McGaughey et al., 2004;Jobson et al., 2004;Wang et al., 2013), whereas the ratios below unity was found for coal combustion (0.56 - 0.80) (Yan et al., 2017)."

L385-387 "The average ratio at MEM was 2.31, higher than the character ratios of coal combustion, reasonably due to the observation site presented at upwind position of the thermal power plant.”

L390-391 “The average ratios at YH (1.94) and GS (1.63) were lower than those at the above two sites, suggesting the comparatively stronger contribution from coal burning.”

L398-419 “In this study, the correlation between benzene and toluene was fairly well at all the sites (R^2=0.70-0.74), except for YH (R^2=0.41) (Fig.14), suggesting the similar sources for benzene and toluene at JK, MEM and GS, while more complex such as variable wind direction at YH. The average ratios of T/B were lied within the range of 1.64-2.29, which were scattered around the character ratio of 2 for vehicle exhaust, illustrating the significance of vehicle emissions at the four sites. Specifically, at JK, MEM and YH, most of T/B ratios were distributed between 0.6 and 3, which were corresponding to character ratios for coal or biomass burning and industrial activities respectively. These reflected the mixture impacts from mobile source and coal/biomass burning at these three sites. However, more values were greater than 3 at GS, suggesting more frequent disturbance from industrial activities at this site.

From the temporal respect, the T/B ratios at 14:00 LT were lower than at 07:00 LT (Fig.15). In fact, the reaction rate constant of toluene ($5.63\times10^{-12}cm^3molecule^{-1}s^{-1}$) with •OH is much higher than that for benzene ($1.22\times10^{-12}cm^3molecule^{-1}s^{-1}$), representing more rapid consumption of toluene from photochemical reactions and thus resulting in lower T/B ratios at 14:00 LT. Besides, the emission strength of mobile source is often weaker at 14:00 LT, while the coal/biomass burning are increased due to more human activities. Both of the situations can be used to explain the lower T/B ratios observed at 14:00 LT. In comparison with other months, higher T/B ratios were found more frequently in September, potentially showing the more strengthen indusial activities during this period.

Overall, based on the iso-pentane/i-pentane and T/B ratios, the atmospheric VOCs at every site were impacted by a mix of coal/biomass burning and vehicle emissions, whereas GS was more liable impacted by industry-related sources.”

3.6 Relative reactivity of VOCs

L421-426 “The reactivity of individual species was different, while mixtures of VOCs would have competition the precursors between each other, leading to variations on reaction paths and O_3 formation yields. Ozone formation potential (OFP) is a useful tool to estimate maximum O_3 productions of each compound under optimum conditions, from which the vital species in O_3 formation could be identified (Huang et al., 2017). The calculation of OFP is based on mixing ratios and maximum incremental reactivity (MIR) of individual compound,”

L431-435 “In Zhengzhou city, alkenes contribute most (55.91±14.17%) to the sum of OFP, of which ethylene had the largest portion. The results is different with the estimation based on emission inventories by Wu and Xie (2017), in which the largest contributor of total OFP in North China Plain (NCP), YRD and PRD was aromatics, reflecting that there was relatively less surface coating industries in Zhengzhou.”

L449-456 “Under low RHs and high T and OFP (88.13±30.32 ppbv), the O_3 level at YH was unexpectedly lower than that at MEM on sunny days. Since the OFP was estimated with the assumption of reactions that proceeded under optimum conditions, the above phenomenon reflected there were unsatisfied O_3 formation conditions at YH. The highest total OFP was seen at JK in June, while the highest O_3 levels was observed at GS where located at a downwind position with lowest WS (0.74±0.33 m s^{-1}). The concentration level of O_3 usually increased with wind speed (Fig.S7), particularly when the eastern wind was dominant, illustrating the disturbance from long-distance sources to urban center."

3.7 Source apportionment

This whole section has been rewritten

3.8 Consumption of VOCs and correlations with ozone level

This was a newly added section

4. Conclusions

L522-523 "It is found that the weighted percentage of aromatics was lower, while alkyne was higher in Zhengzhou city than in other Chinese cities."

L529-540 "In addition, the impact of aging process was less in Zhengzhou than that in Beijing. The photochemical reactions at JK and GS were more efficient, while the relationships among O_3, NO_x and VOCs at urban sites of MEM and YH were more complex. Either the mixing ratios or calculated OFPs demonstrated that the most important contributors to VOCs were vehicle exhaust, coal+biomass burning and solvent use, illustrating the necessary to conduct emission controls on these pollution sources. Vehicle emission was more dominant at urban center (YH and MEM), while solvent use was more important at the sites (JK and GS) far away from urban center in Zhengzhou. It is further shown that the air pollution in Zhengzhou was mostly impacted by local emissions according to the cluster analysis, and southern air clusters occasionally from Hubei Province was cleaner. In addition, strong emissions for coal+biomass burning were concentrated in southwest of Shanxi, western of Shandong and southwest of Henan provinces according to the PSCF analysis."

Table & Figure

All of the tables and figures were reconstructed thoroughly.

Table1. Concentrations of Σ_{VOCs} (ppbv) at every site during the sampling period

	JK		MEM		GS		YH	
	Mean	**Std.**	**Mean**	**Std.**	**Mean**	**Std.**	**Mean**	**Std.**
May.2017	37.65	22.58	29.30	15.34	31.73	18.70	30.05	16.43
June.2017	34.02	19.89	30.28	12.77	39.29	25.37	28.33	11.94
July.2017	16.01	6.13	20.74	12.66	19.60	13.94	15.95	7.54
Aug.2017	21.54	15.29	24.37	20.79	20.49	15.67	26.03	17.01
Sept.2017	26.20	16.22	34.15	23.85	30.36	19.76	32.56	19.76

Table2. Wind speed (m·s^{-1}) at every site during the sampling period

	JK	MEM	YH	GS
May	1.34±0.65	1.86±1.19	1.27±0.66	0.97±0.49
June	1.07±0.48	1.86±0.94	0.97±0.36	0.74±0.33
July	1.48±0.59	2.62±1.19	1.15±0.45	0.90±0.32
August	1.06±0.48	1.86±0.94	0.95±0.39	0.76±0.35
September	0.80±0.38	1.24±0.80	0.82±0.43	0.62±0.38

Table3. Concentration levels of VOCs and compositions of major groups in Zhengzhou and other cities in China

Items		**Guangzhou**	**Nanjing**	**Beijing**	**Hangzhou**	**Wuhan**	**Zhengzhou**
		March-December, 2005	2011-2012	August, 2006	July-August, 2013	2013-2014	May-September, 2017
Sampling site		residents-commercial -transportation mixed area	transportation-industry mixed area	residents-commercial mixed area	residents-transportation mixed area	urban	urban
Quantified compounds		59 NMHC	56 NMHC	47 NMHC	56 NMHC	99 VOCs	56 NMHC
Total samples		145	_	24	_	_	400
TNMHC (ppbv)		47.3	43.5	65.55±17.44	55.9	23.3±0.5	29.18±23.08
Compositions of major groups (%)	*alkane*	49.0	45.0	52.3	33.2		56±12
	alkene	16	25.3	21.2	25.9		16±7.6
	aromatic	23	22.3	18.1	24.3		14±8.4
	alkyne	12	7.3	8.4	16.6		13±6.7
Reference		(Li and Wang, 2012)	(An et al., 2014)	(Guo et al., 2012)	(Li et al., 2017b)	(Lyu et al., 2016)	this study

Table4. Specific information on VOCs, O$_3$ and NO at the four sites in June, 2017

Composition or conc.	JK	MEM	YH	GS
Aromatic (%)	9.06	11.57	4.72	15.75
Alkene (%)	6.36	4.13	5.52	5.47
Σ_{VOCs} (ppbv)	34.02	30.28	28.33	39.29
O$_3$(ppbv)	74.87	73.50	73.81	87.99
NO(ppbv)	7.10	7.72	2.34	4.47

Table5. Top 10 VOCs ranked according to calculated ozone formation potential (OFP) and their corresponding percentage weighted in mixing ratio

Site	**Species**	**OFP (ppbv)**	**Weighted in OFP (%)**	**Weighted in mixing ratio (%)**	**Site**	**Species**	**OFP (ppbv)**	**Weighted in OFP (%)**	**Weighted in mixing ratio (%)**
JK	Ethylene	18.99	25.54	8.22	MEM	Ethylene	18.44	30.88	7.92
	Isoprene	12.99	21.83	7.31		Isoprene	4.66	10.10	2.36
	m/p-Xylene	6.08	5.89	2.67		Toluene	3.73	6.67	3.99
	Toluene	5.53	5.83	4.22		Propylene	3.60	6.16	1.25
	Propylene	4.03	5.36	1.29		Acetylene	2.82	5.00	12.19
	Acetylene	2.97	4.44	13.54		m/p-Xylene	2.55	4.20	1.40
	n-Butane	2.15	3.05	7.28		n-Butane	1.81	3.20	5.97
	o-Xylene	1.83	2.00	0.88		Isopentane	1.76	3.16	7.39
	Isopentane	1.66	1.95	6.50		Ethane	1.58	2.96	23.35
	Propane	1.17	1.73	9.77		Propane	1.31	2.48	10.64
YH	Ethylene	19.83	28.10	8.88	GS	Ethylene	18.04	25.96	7.51
	Isoprene	7.44	11.30	3.67		Isoprene	8.01	16.75	4.64
	Toluene	6.63	7.75	5.72		Toluene	7.43	7.67	5.49
	m/p-Xylene	3.93	4.38	1.58		Propylene	4.39	5.85	1.26
	Acetylene	3.15	4.38	13.91		m/p-Xylene	4.31	4.57	1.75
	Propylene	3.01	3.60	0.91		Acetylene	2.76	4.24	12.07
	Trans-2-pentene	2.25	2.94	3.43		n-Butane	1.82	2.93	6.39
	n-Butane	1.84	2.80	6.31		Isopentane	1.71	2.68	6.94
	Isopentane	1.59	2.22	6.69		Propane	1.38	2.26	11.61
	Propane	1.18	1.98	10.20		Isobutane	1.13	1.98	4.59

[a] *m*-Xylene and *p*-Xylene are co-eluted in the chromatographic separation.

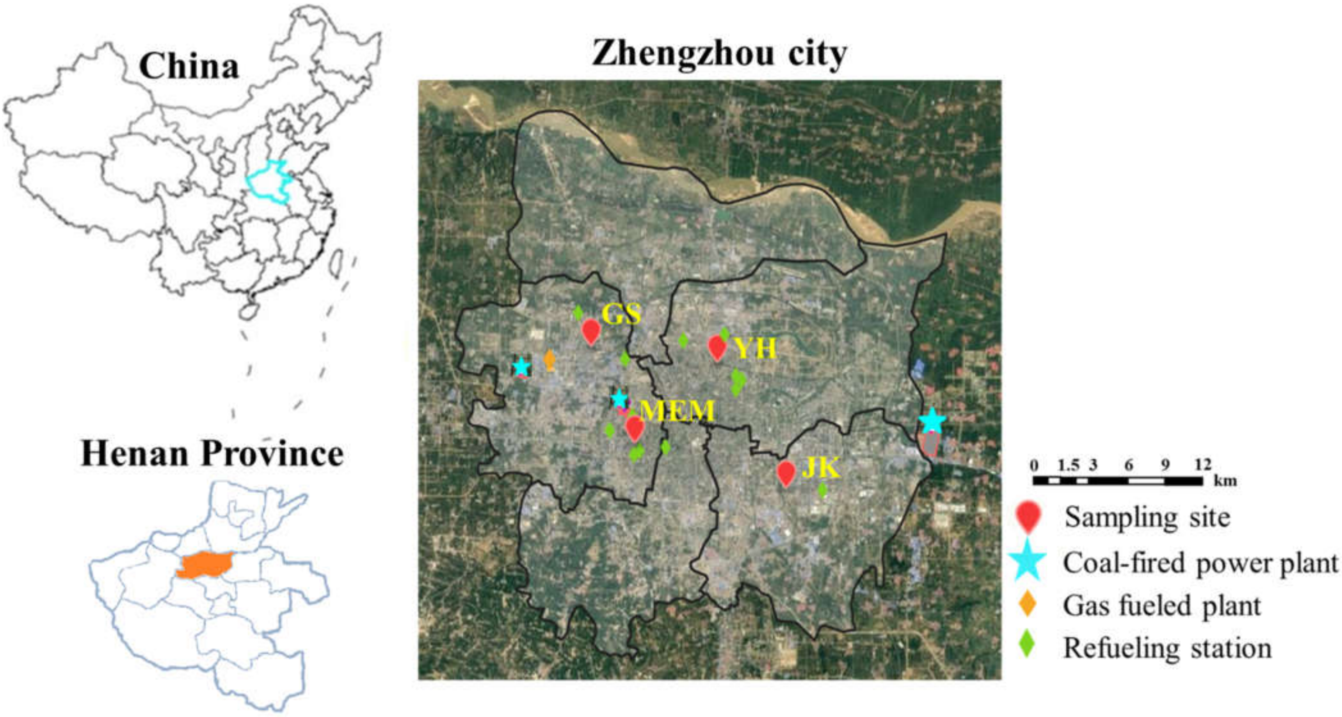


Fig 1. Map of Zhengzhou, China showing the locations of sampling sites.

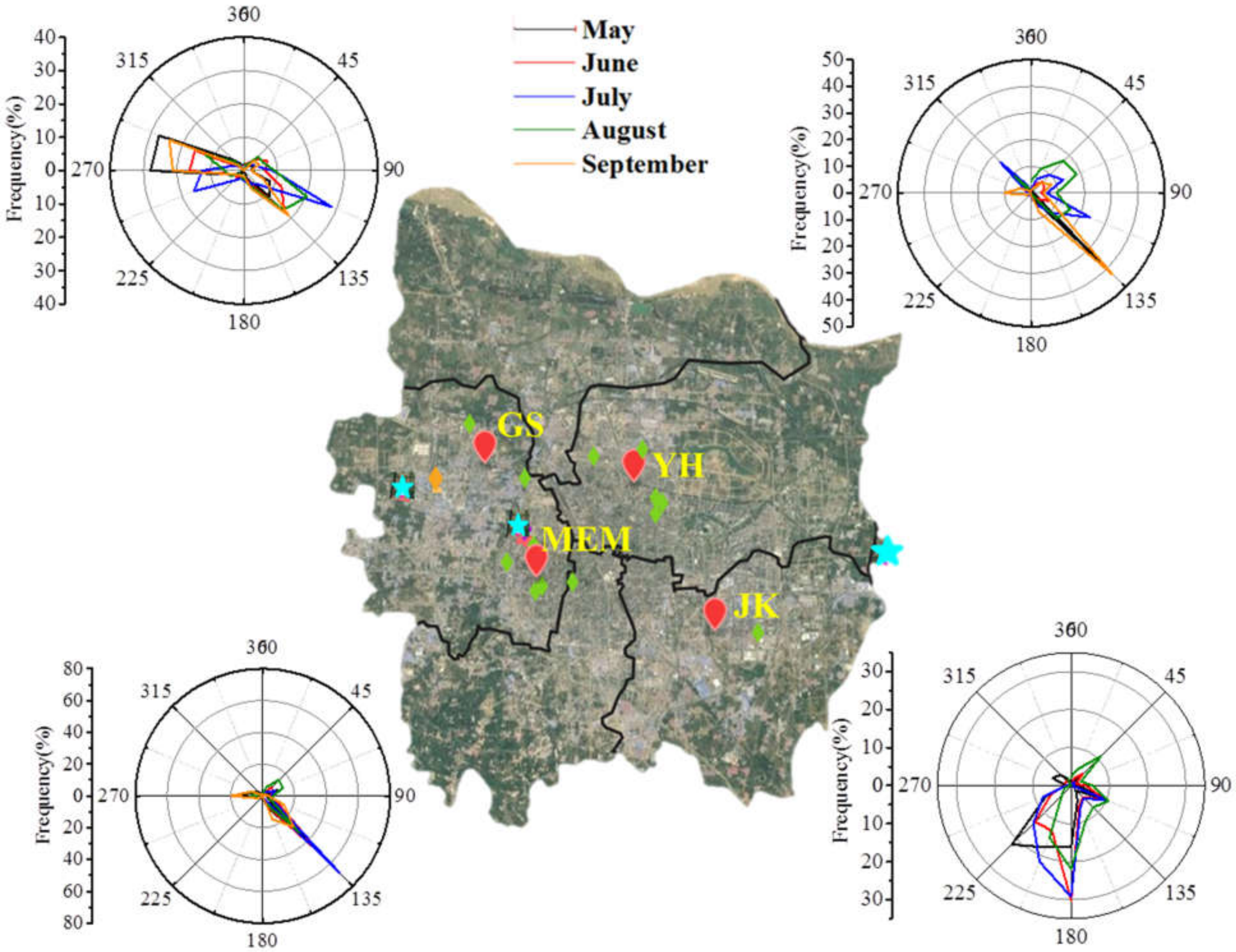
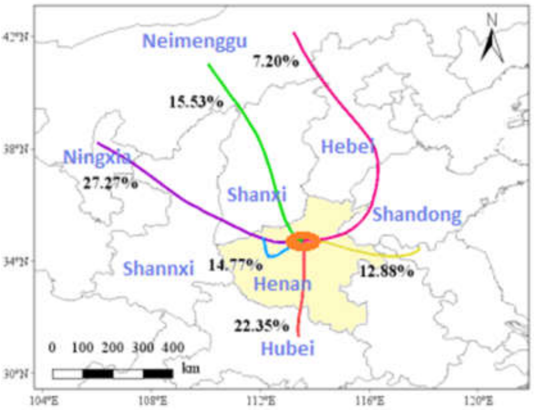
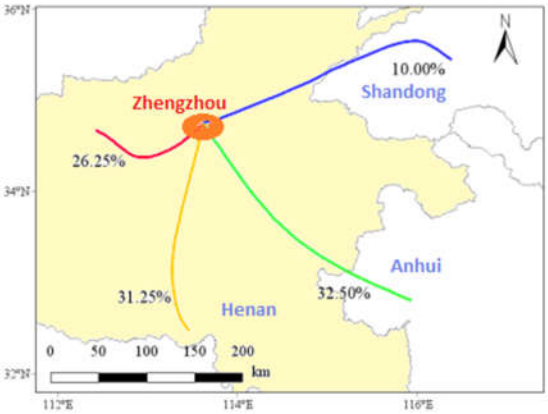


Fig.2 Wind direction for each site during May to September, 2017

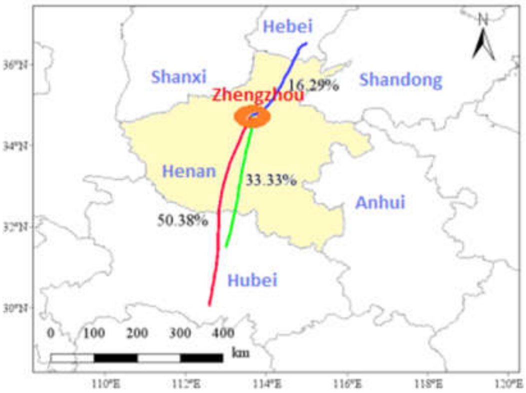
May



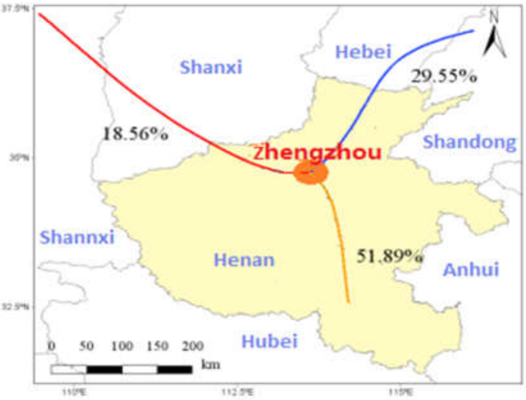
June



July



August



September

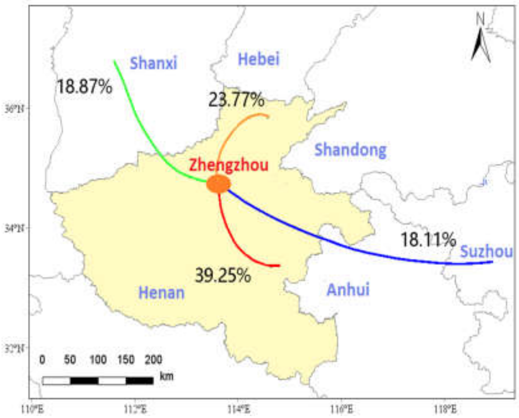


Fig. 3 Cluster analysis of Zhengzhou in each sampling month

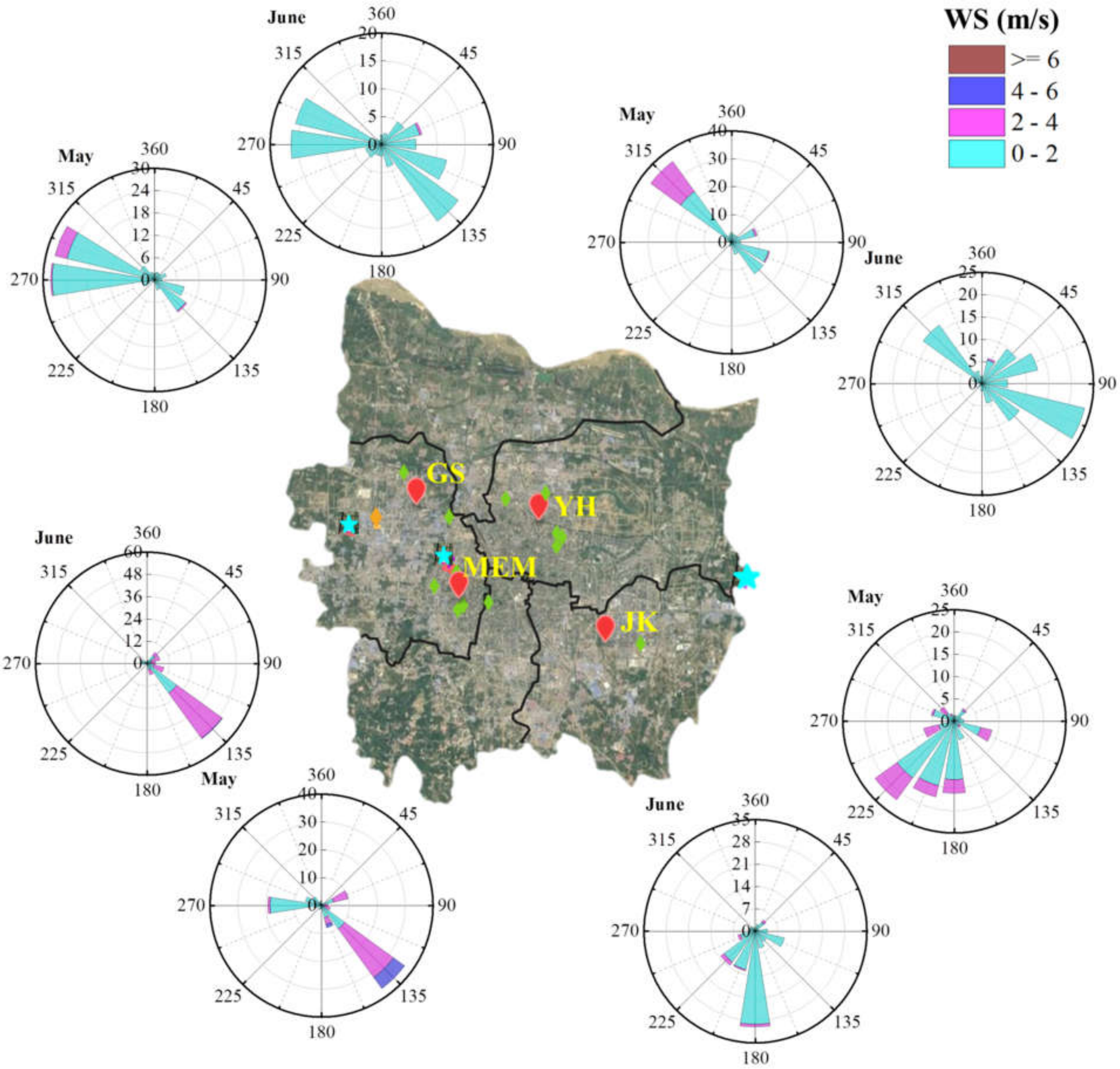


Fig.4 Wind rose at each site in May and June (the wind distribution in other three months were illustrated in Fig S2)

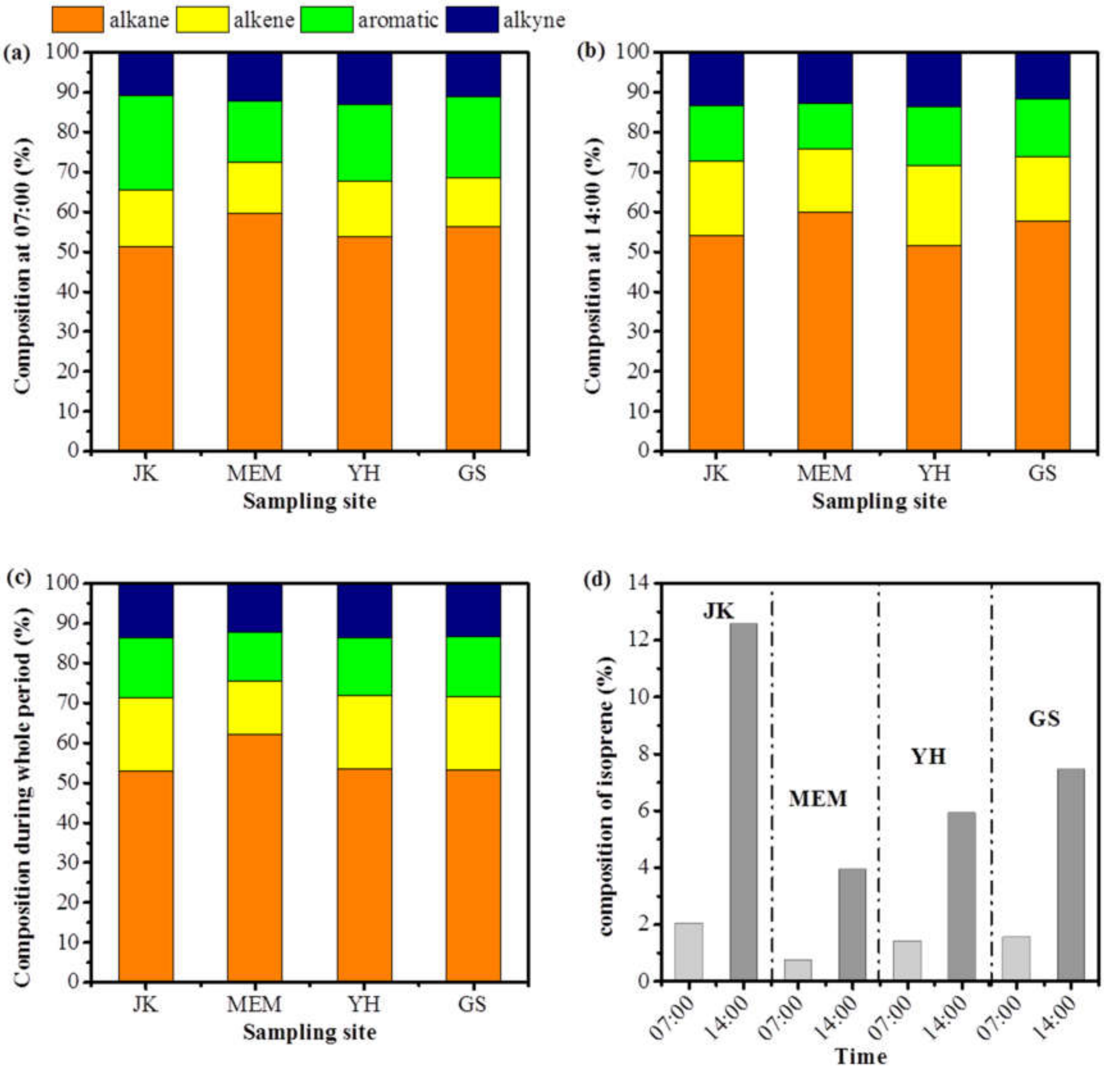


Fig. 5 Compositions of major organic classes at 07:00 LT (a), 14:00 LT (b) and during the whole sampling period (c) at the four sites, and the composition of isoprene at 07:00 LT and 14:00 LT for each site (d).

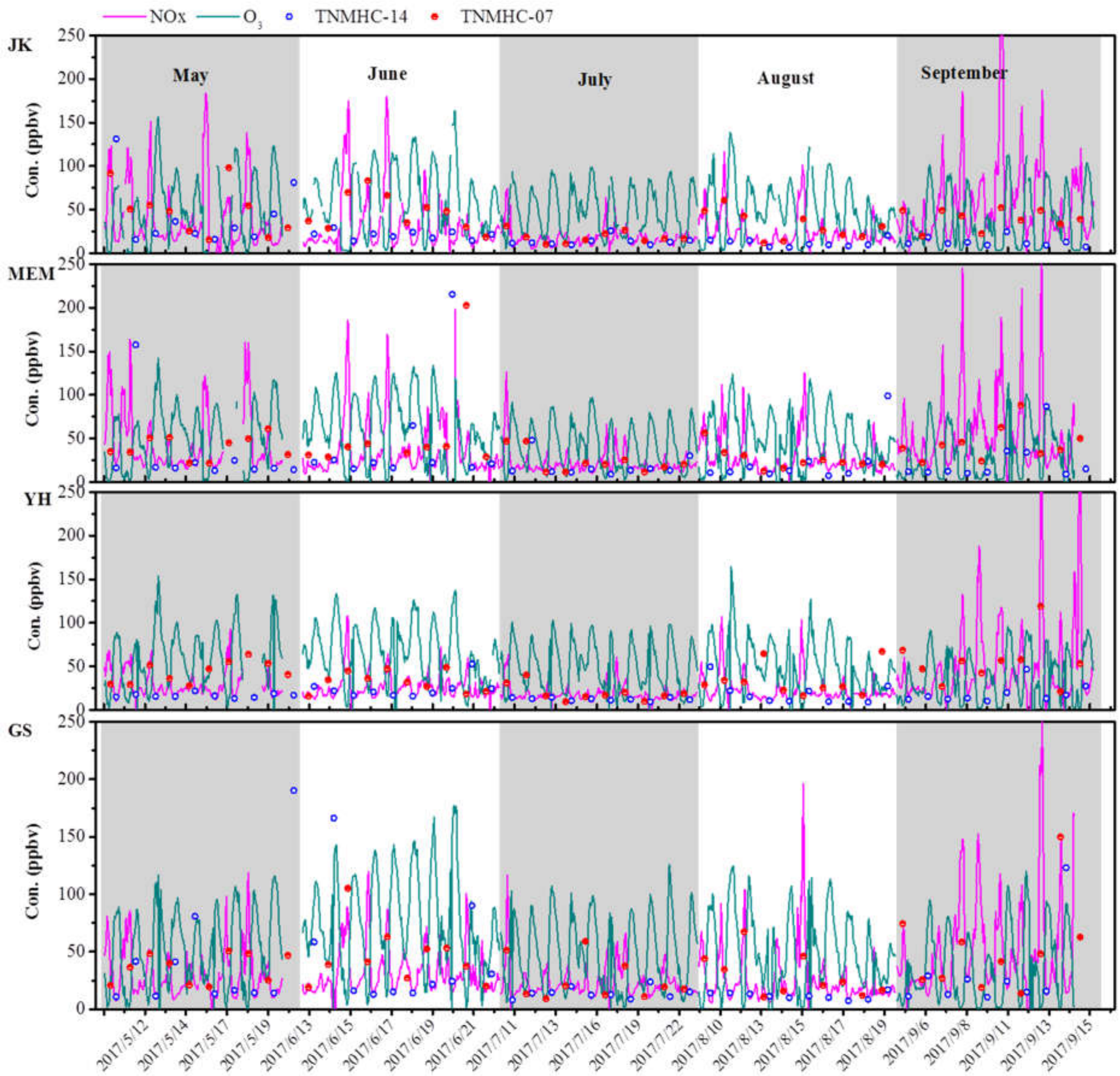


Fig.6 Temporal variations of mixing ratios of Σ VOCs, NOx and O3 at the four sites during the whole sampling period, in which Σ VOCs-07 stands for the concentration level of Σ VOCs observed at 07:00 LT, and Σ VOCs-14 was that observed at 14:00 LT.

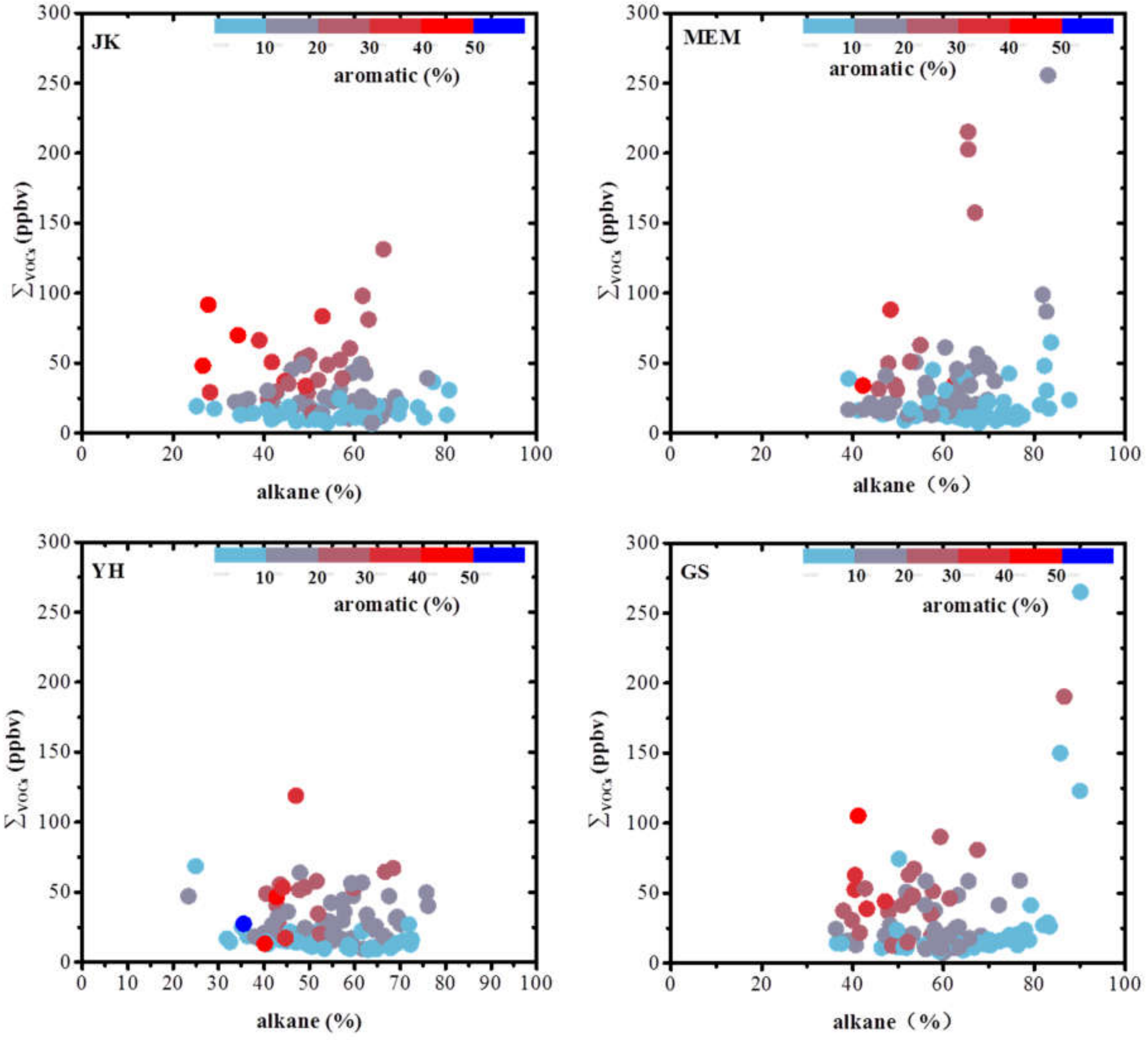


Fig. 7 The relationship between mixing ratio of ΣVOCs and the composition of alkane, the data points were color coded with the composition of aromatic.

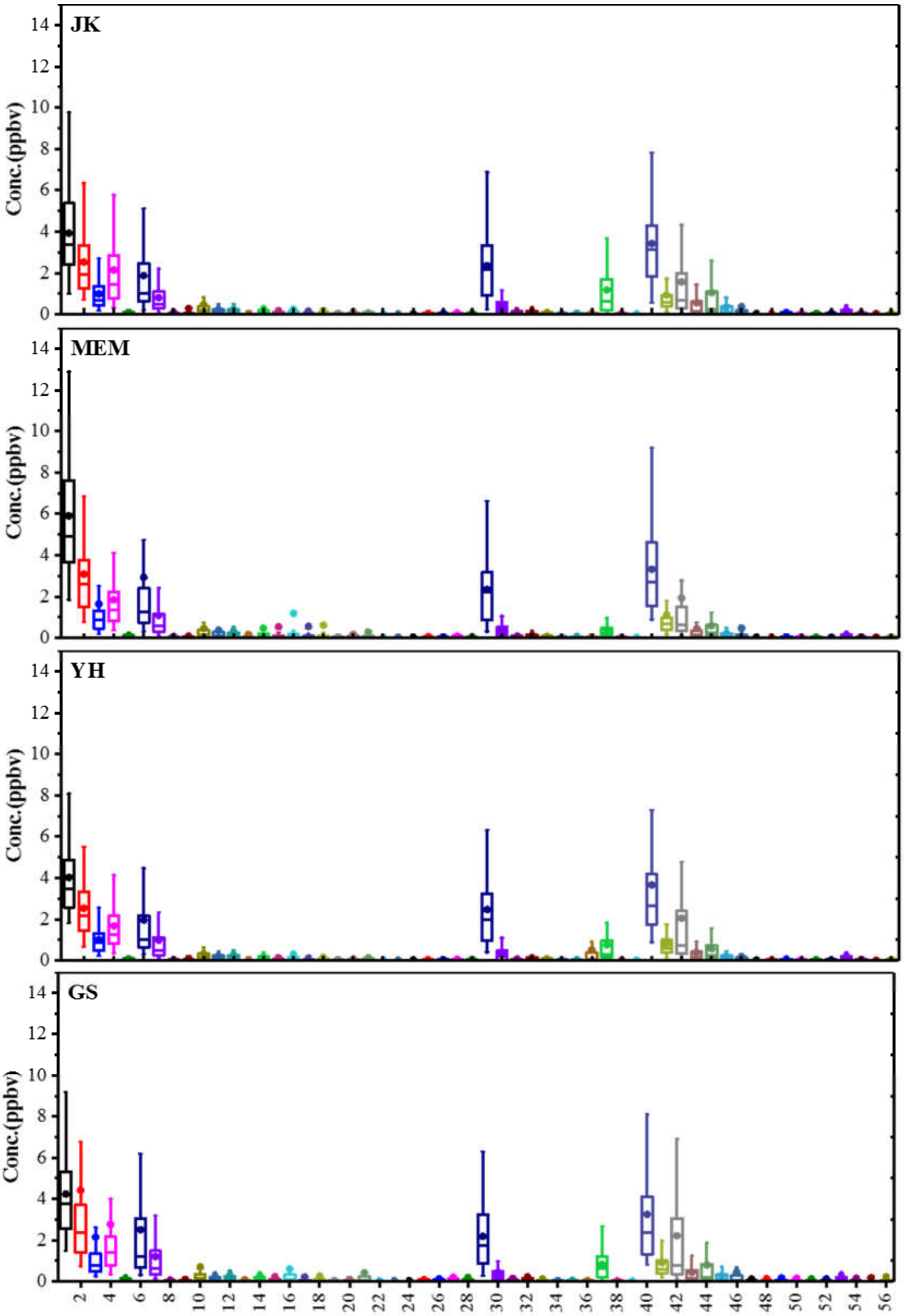


Fig.8 Concentrations of 57 VOCs at each site for the whole sampling period, the whisker was ranged from 5-95%, and the box was 25-75%, the solid points stand for average value, the line in the box represent median value. The number of chemicals can refer from Table S1.

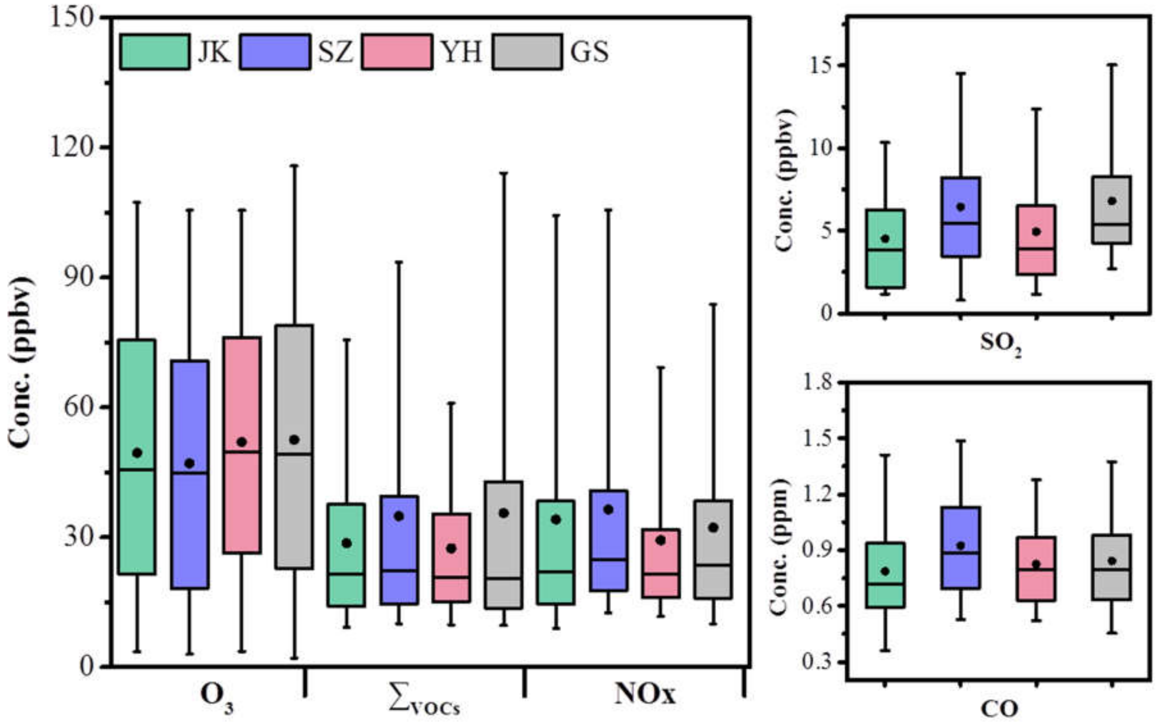


Fig. 9 The distribution of concentration point on O3, ΣVOCs, NOx, SO2 and CO at each site, the range of the box was 25%-75%, the black line in the box stands for median level, the black dot represent the average level, the range of whisker was 5-95%.

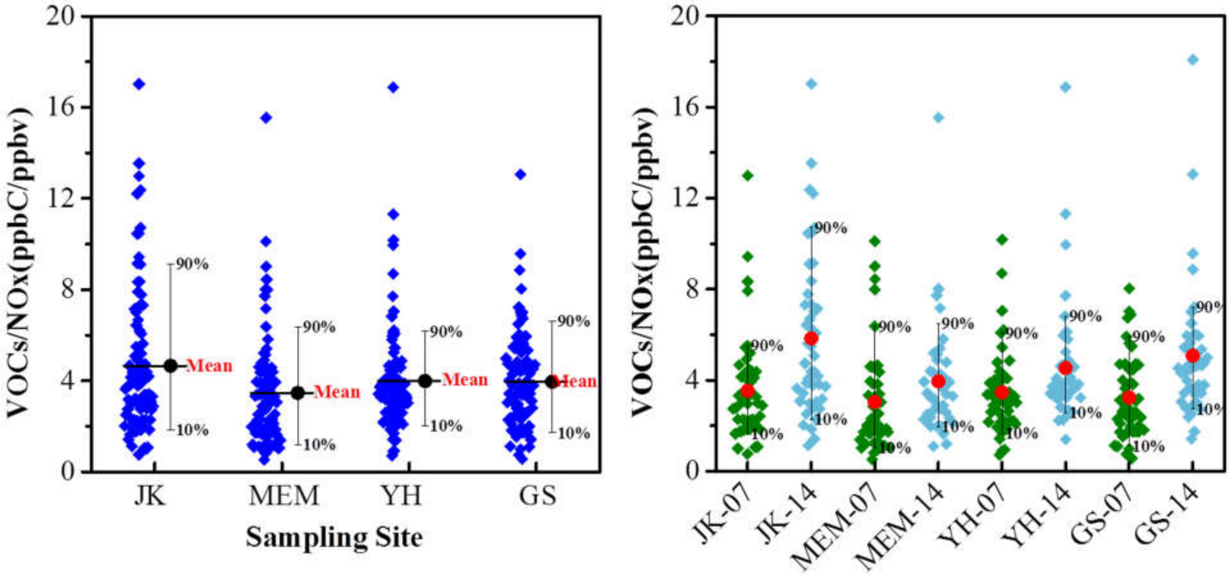


Fig.10 The data distribution of VOCs/NOx(ppbC/ppbv) at the four sites (left), and the ratio observed at 07:00 LT and 14:00 LT were presented (right).

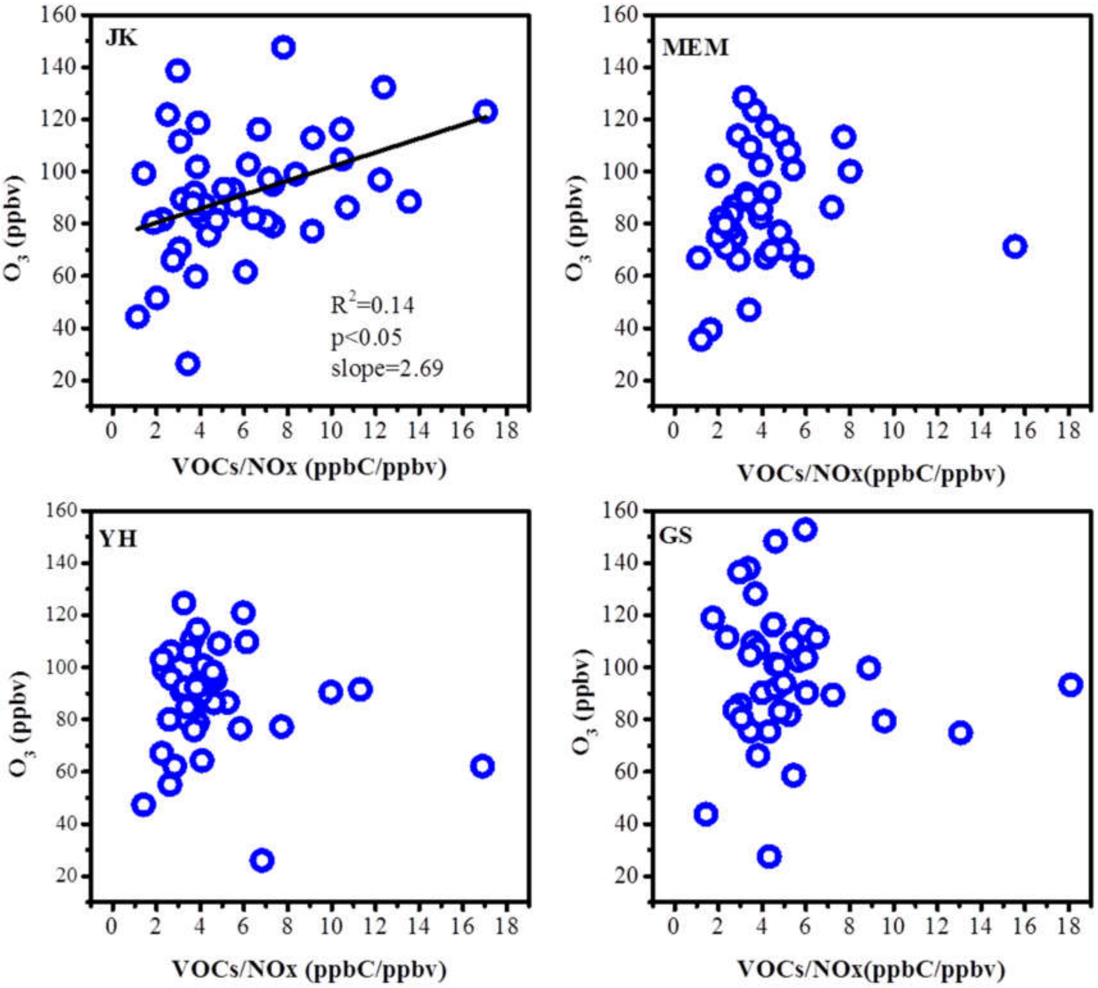


Fig.11 The relationship between O3 and VOCs/NOx at 14:00 LT

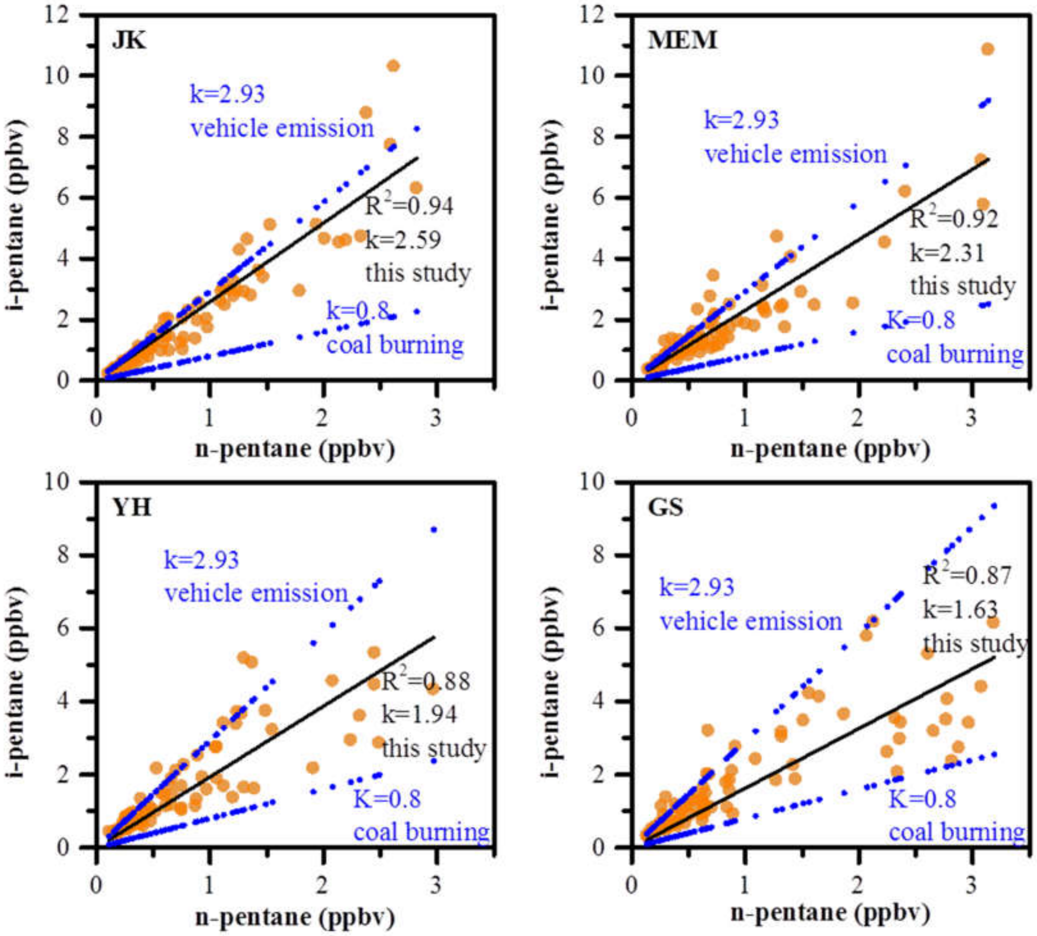


Fig. 12 Ratios of isopentane to n-pentane at every site

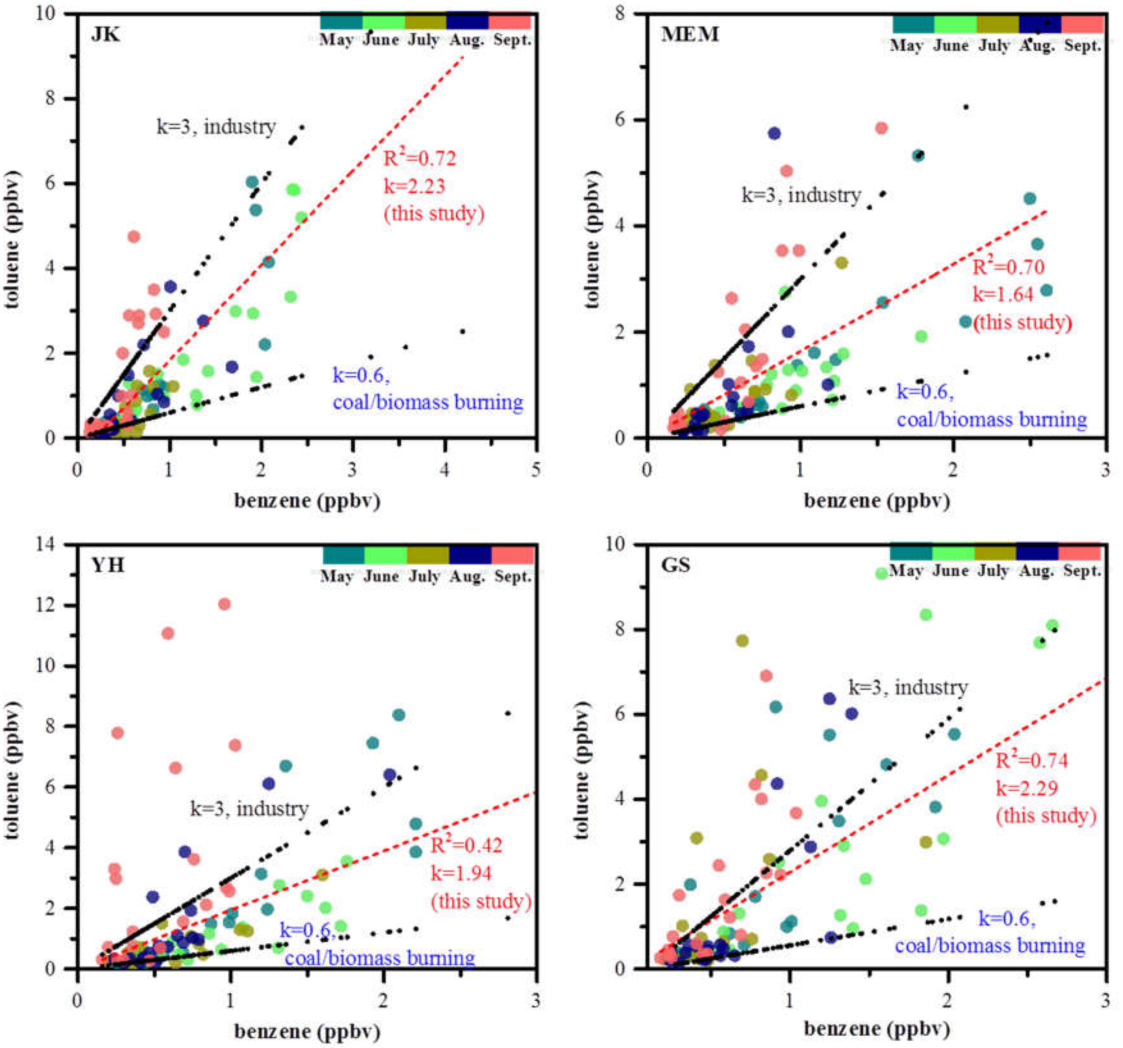


Fig.13 T/B ratios and linear correlation coefficients (R^2) between benzene and toluene at every site, the data points were color mapped with sampling period.

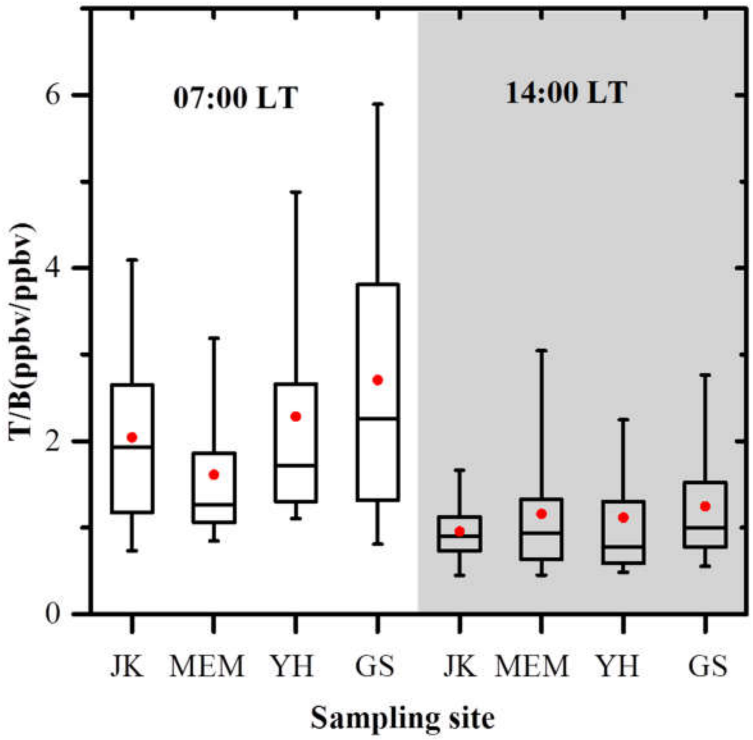


Fig. 14 The average ratio of T/B at 07:00LT and 14:00LT for each site during the whole sampling period

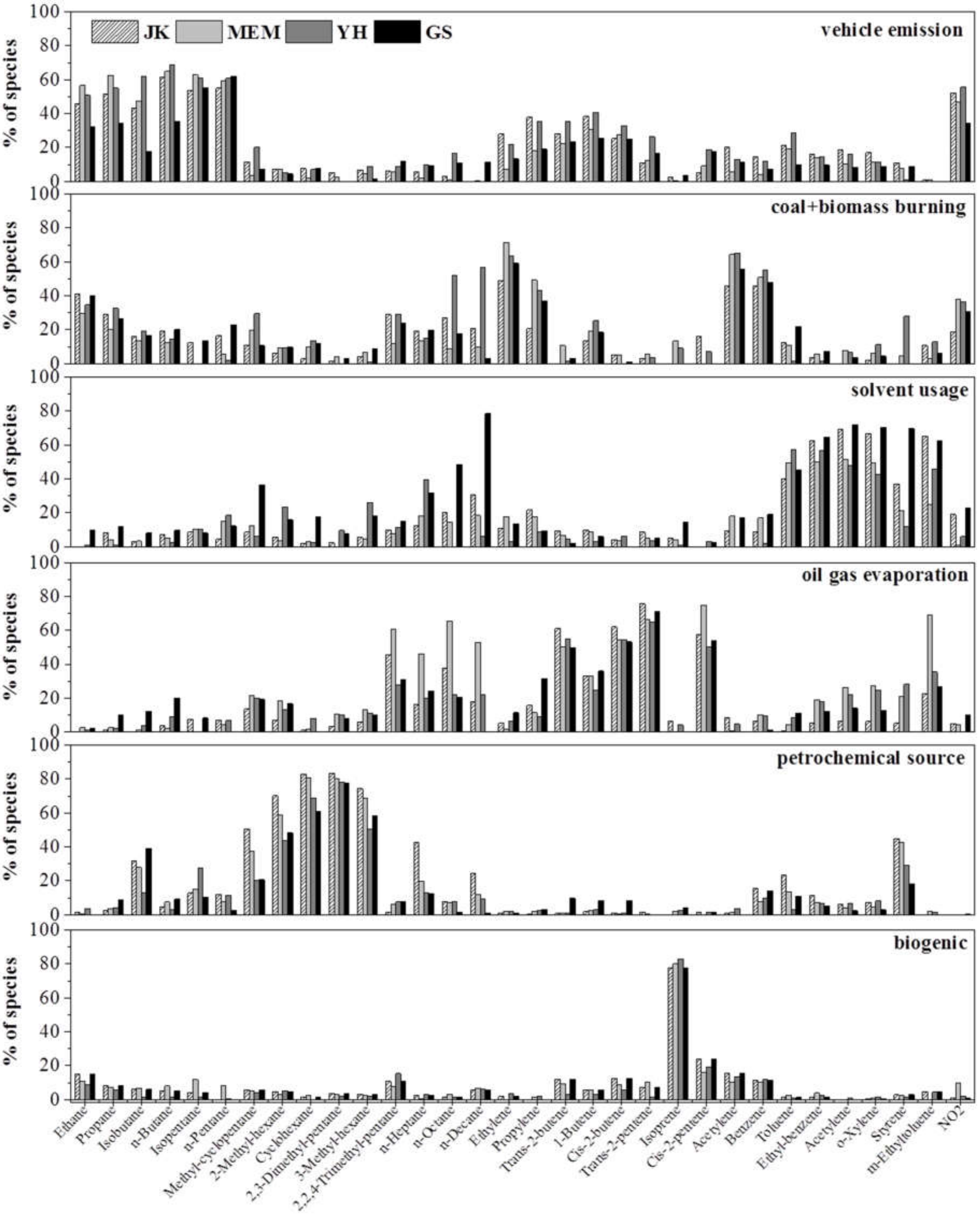


Fig. 15 Explained variations in source profiles as identified by PMF

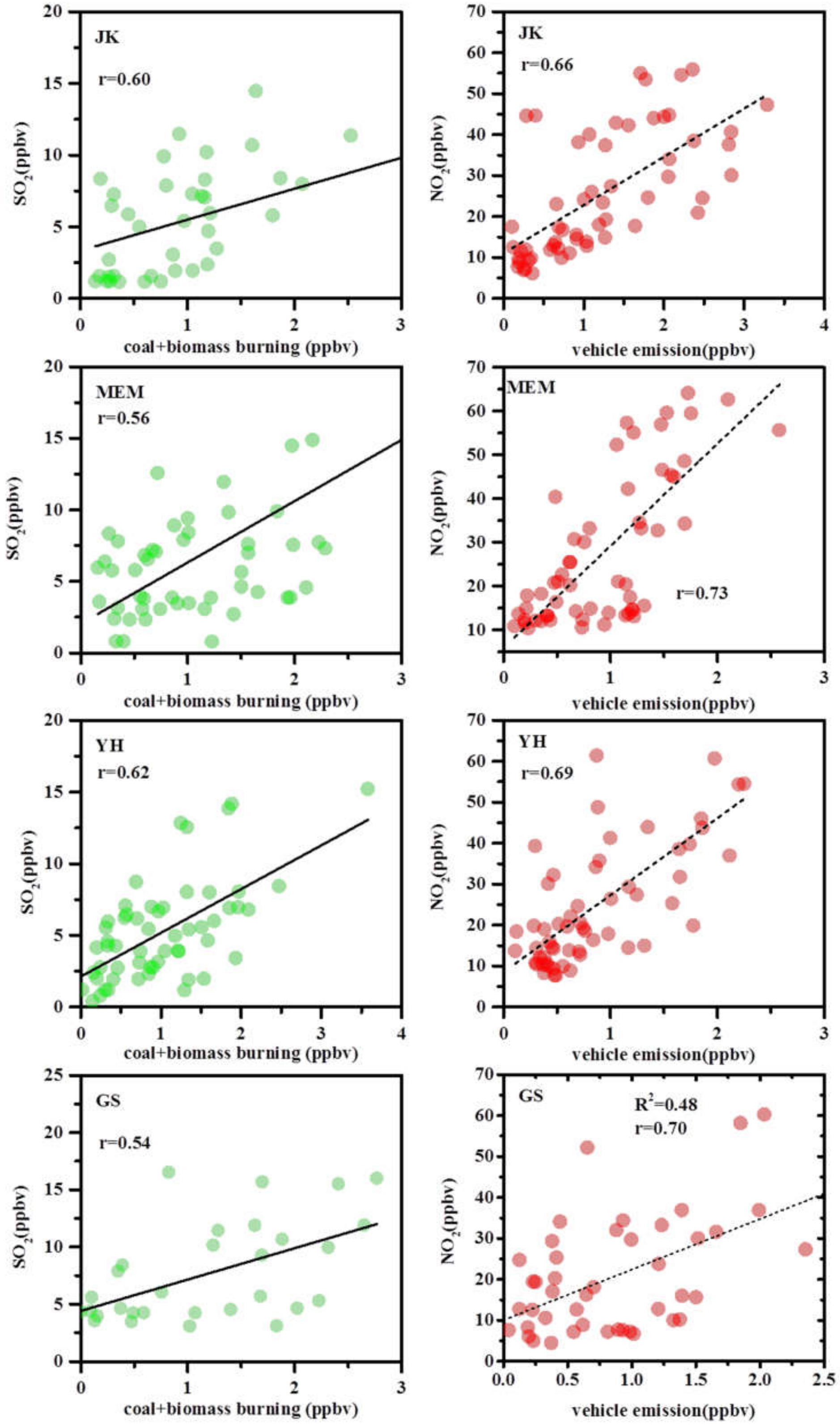


Fig. 16 Correlation analysis between contributions of coal+biomass burning and SO_2, and vehicle emission and NO_2

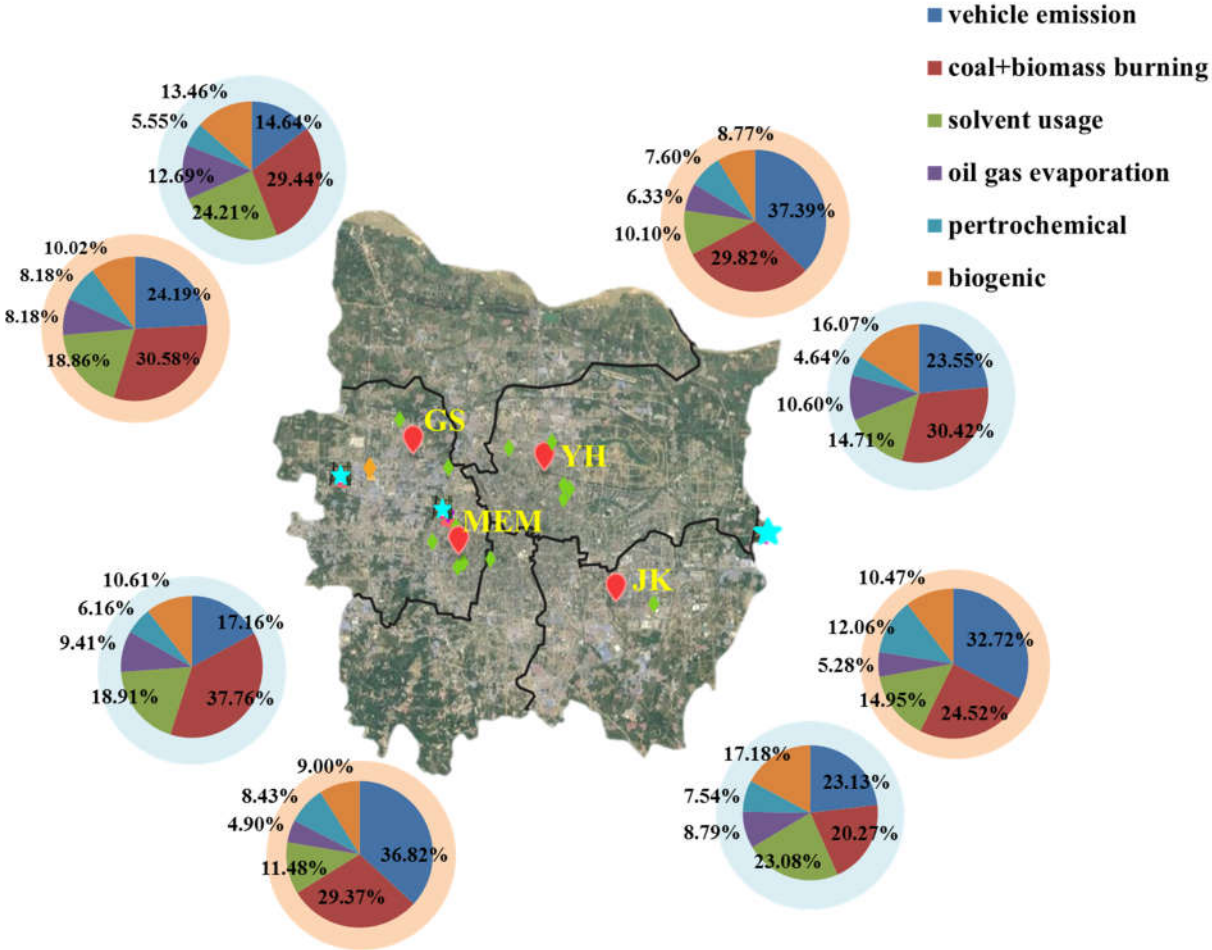


Fig. 17 Source apportionment results during the whole sampling period. The results weighted in observed concentrations were shadowed with pink color, and the results estimated based on OFP were shadowed with light blue color.

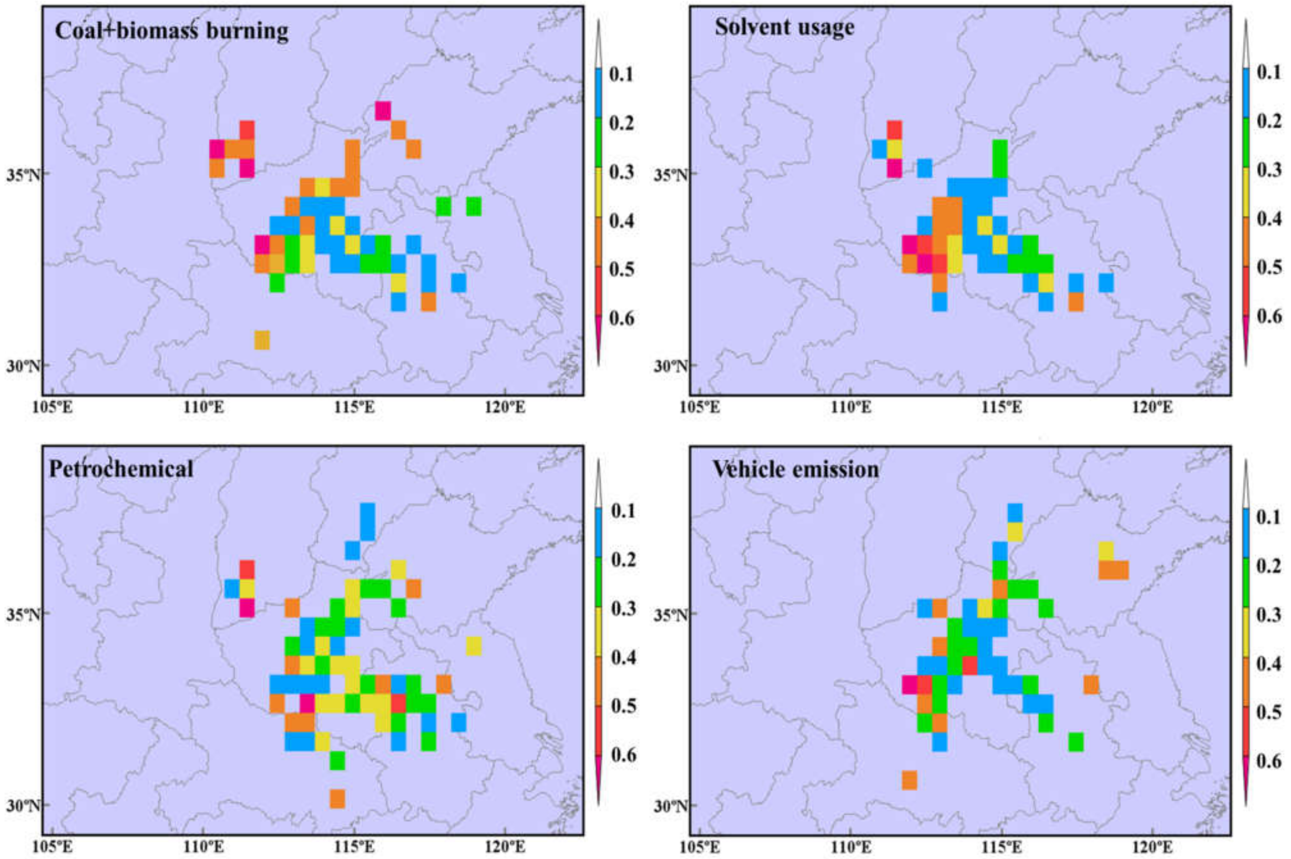


Fig. 18 Probable source regions apportioned by PSCF at Zhengzhou at summer (June-Aug. 2017) during sampling period

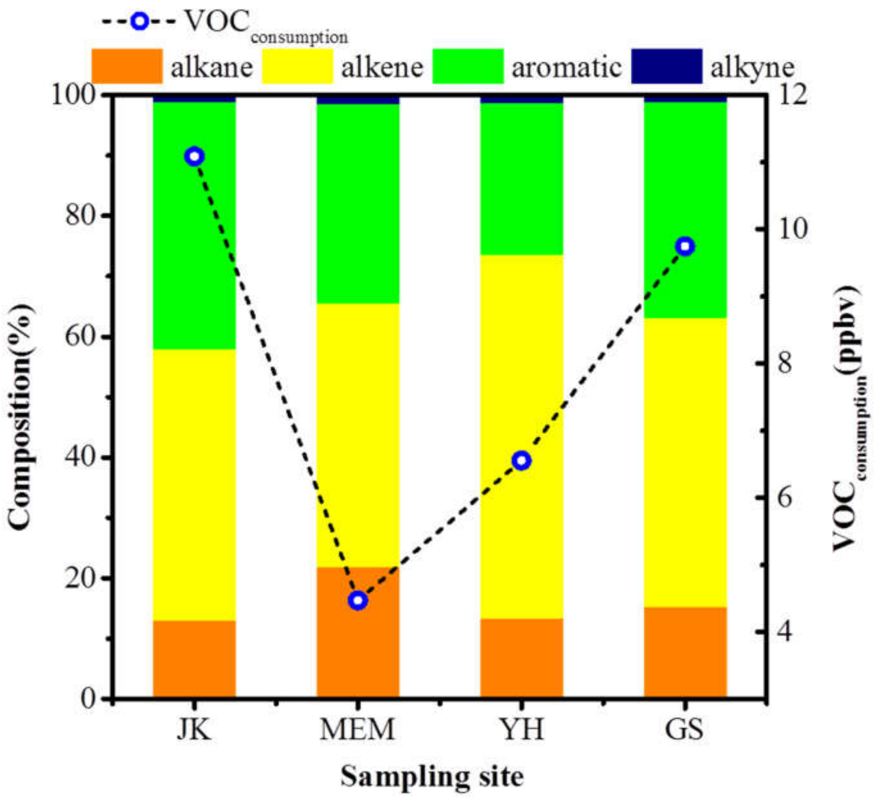


Fig. 19 The composition of major groups based on chemical consumption and the total consumption at each site.

Supporting information

Supplement materials has been added

New reference

Hanna, S. R., Moore, G. E., and Fernau, M.: Evaluation of photochemical grid models (UAM-IV, UAM-V, and the ROM/UAM-IV couple) using data from the Lake Michigan Ozone Study (LMOS) Atmospheric Environment 30, 3265-3279, 1996.

Hopke, P. K., Barrie, L. A., Li, S.-M., M.-D.Cheng, C.Li, and Xie, Y.: Possible sources and preferred pathways for biogenic and non-sea-salt sulfur for the high Arctic Journal of Geophysical Research, 100, 16,595-516,603, 1995.

Mu, B., Mayer, A. L., He, R., and Tian, G.: Land use dynamics and policy implications in Central China: A case study of Zhengzhou, Cities, 58, 39-49, 10.1016/j.cities.2016.05.012, 2016.

Polissar, A. V., Hopke, P. K., Paatero, P., Kaufmann, Y. J., Hall, D. K., Bodhaine, B. A., Dutton, E. G., and Harris, J. M.: The aerosol at Barrow, Alaska: long-term trends and source locations, Atmospheric Environment 33, 2441-2458, 1999.

Shiu, C.-J., Liu, S. C., Chang, C.-C., Chen, J.-P., Chou, C. C. K., Lin, C.-Y., and Young, C.-Y.: Photochemical production of ozone and control strategy for Southern Taiwan, Atmospheric Environment, 41, 9324-9340, 10.1016/j.atmosenv.2007.09.014, 2007.

Sillman, S.: The relation between ozone, NOx and hydrocarbons in urban and polluted rural environments, Atmospheric Environment 33, 1821—1845, 1999.

Sun, J., Wu, F., Hu, B., Tang, G., Zhang, J., and Wang, Y.: VOC characteristics, emissions and contributions to SOA formation during hazy episodes, Atmospheric Environment, 141, 560-570, 10.1016/j.atmosenv.2016.06.060, 2016.

Wang, H.-l., Jing, S.-a., Lou, S.-r., Hu, Q.-y., Li, L., Tao, S.-k., Huang, C., Qiao, L.-p., and Chen, C.-h.: Volatile organic compounds (VOCs) source profiles of on-road vehicle emissions in China, The Science of the total environment, 607-608, 253-261, 10.1016/j.scitotenv.2017.07.001, 2017.

Watson, J. G., Chow, J. C., and Fujita, E. M.: Review of volatile organic compound source apportionment by chemical mass balance, Atmospheric Environment 35, 1567-1584, 2001.

Zhu, Y., Yang, L., Chen, J., Wang, X., Xue, L., Sui, X., Wen, L., Xu, C., Yao, L., Zhang, J., Shao, M., Lu, S., and Wang, W.: Characteristics of ambient volatile organic compounds and the influence of biomass burning at a rural site in Northern China during summer 2013, Atmospheric Environment, 124, 156-165, 10.1016/j.atmosenv.2015.08.097, 2016.

Marked manuscript

Characterization of VOCs and their related atmospheric processes in a central China city during severe ozone pollution periods

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Abstract

A five-month campaign (from May to September 2017) was conducted to characterize volatile organic compounds (VOCs) for the first time at four sites in Zhengzhou City, Henan Province, China, where ozone (O_3) concentration has shown an increasing trend in recent years. Canister samples were collected for measurement of fifty-seven VOCs, which are the most important O_3 precursors. During the same period, O_3 and its precursor gases were monitored online simultaneously. The results indicated that the average mixing ratio of total quantified VOCs (Σ_{VOCs} , 28.83±22.05 ppbv) in Zhengzhou was lower than that in the other Chinese megacities, while alkyne was in a higher proportion. The abundances, compositions and ratios of typical VOCs showed clear spatial and temporal variations. The cluster analysis points out that air masses from cities south of Zhengzhou were cleaner than from other directions. Besides, the molar ratio of VOCs to NO_x indicated that VOCs were more sensitive than NO_x to the O_3 formation in Zhengzhou. Meanwhile, the overall results further implied that photochemical reactions at marginal sites where highly distributed with industries were more efficient than those at other sites. The source apportionmemt was conducted with Positive Matrix Factorization (PMF), and it was found that vehicle exhaust, coal and biomass burning, and solvent usage were the major sources for ambient VOCs at all four sites. From Potential Source Contribution Function (PSCF) analysis, the strong emissions from coal+biomass burning and solvent usage were concentrated in southwest of Shanxi and Henan province. The results of this study gather scientific evidences on the pollution sources for Zhengzhou city, benefiting the Government to establish efficient environmental control measures particularly for O_3 pollution.

1. Introduction

Volatile organic compounds (VOCs) are diverse and reactive chemicals. Vehicle exhausts, fuel combustion and evaporation, and solvent usage are the known major anthropogenic sources of VOCs (Zhang et al., 2014;Liu et al., 2017;Sahu et al., 2017). VOCs play a crucial role in the ground-level ozone (O_3) pollution, which has troubled many rapid economy-growth urban cities (Wang et al., 2017b;Nagashima et al., 2017). Many related studies are thus being conducted globally (Wei et al., 2014;Malley et al., 2015;Ou et al., 2015). In China, the investigations on VOCs including source apportionment, measurement of emission profiles and interpretation of seasonal variations were mainly concentrated in Yangtze River Delta (YRD), Pearl River Delta (PRD) and Beijing-Tianjin (BJT) regions (An et al., 2014;Wang et al., 2014;Chen et al., 2014;Liu et al., 2016;Guo et al., 2017). Limited studies have been conducted in less developed or developing regions (i.e., southwestern and northwestern China) where prominently impacted by biomass burning and with high abundances of toxic and reactive compounds (Li et al., 2014;Li et al., 2017a).

Fifty-seven VOCs, including C_2 - C_{10} alkanes, alkenes, alkynes and aromatics, which greatly contribute to ambient O_3 formation, have been identified and are regularly monitored by Photochemical Assessment Monitoring Stations (PAMS) (Shao et al., 2016;Chen et al., 2010). Due to characteristic structure and reactivity of these compounds, their contributions in O_3 production were varied accordingly, and it is reported that aromatics and alkenes were responsible for most of the weighted reactivity of VOCs (59.4% and 25.8%, respectively) in Pearl River Delta (PRD) region in China (Ou et al., 2015). Consequently, researchers have deduced that reductions of alkenes and aromatics are profit for O_3 control (Carter, 1994). In addition, with the variations on energy structure, industrial construction and meteorological conditions (Wang et al., 2015;Shao et al., 2011), major emission sources of VOCs at each city are unique. In less developed cities of Heilongjiang and Anhui, biomass combustion had the highest contribution (40% and 36%, respectively) to the O_3 formation potentials due to high quantity of agricultural activities, while in the developed cities such as Shanghai, Beijing and Zhejiang, solvent usage has become more dominant (>20%) than other pollution sources (Wu and Xie, 2017). Therefore, identification on district emission sources of VOCs is necessary to provide scientific-based information for policy-makers who establish efficient strategies to alleviate O_3 pollution.

In addition to the factors discussed above, non-linear relationships between ambient VOCs, nitrogen oxide (NO_x) and O_3 production indicate that the reduction in tropospheric O_3 is more complex than expected (Lin et al., 1998;Hidy and Blanchard, 2015;Li et al., 2018). Many modeling and field studies showed that photochemical O_3 production in several cities in China such as Guangzhou, Shanghai and Beijing with high levels of NO_x were highly sensitive to VOCs (Shao et al., 2009;Gao et al., 2017;Ou et al., 2016). The sensitivity regime is always varied with time and geographical locations (Luecken et al., 2018). The percentage of VOC-limited regime in North China Plain (NCP) increased from 4% to 6% between 2005-2013, owing to the rapid increases of NO_x emissions (Jin and Holloway, 2015).

Zhengzhou City is an important developing city in the mid-west of the Huanghe-Huaihe river flood plain in China. As the capital city of Henan Province, it is densely populated with more than seven million residents in 2010 (Geng et al., 2013). With the rapid growth of industrial activities, as well as increased vehicle emissions and fuel combustions, air quality in Zhengzhou has notoriously deteriorated. The Air quality index (AQI) for 65% of the days in 2013 exceeded the allowable limits of 100 established by the Air Quality Guideline. Particularly, O_3 was the major pollutant in summer and over 50% of the days in a year, the mixing ratio of O_3 exceeded the Grade I standard (100 $\mu g\ m^{-3}$) of daily maximum average 8-hour (DMA8) in Henan (Shen et al., 2017;Gong et al., 2017). As one of the major precursors of O_3, the study on VOCs is of significance for Zhengzhou, since no related researches are published in peer-reviewed literature. In this work, a comprehensive sampling campaign for VOCs measurement and characterization has been conducted at four monitoring stations during the time period of May - September 2017. The spatial and temporal variations in VOCs in Zhengzhou were determined. The contributions of major emission sources were quantified, and the relationship among O_3-VOCs-NO_x was discussed in details. The results and implications from this study can provide useful guidance for policy-makers to alleviate ozone pollution in Zhengzhou, China.

2. Observation and Methodology

2.1 Sampling site

Based on the density of population distribution, locations of industrial facilities, and the prevailing winds, four sites have been selected for sample collection: Jingkai community (JK; 113.73°E, 34.72°N), municipal environmental monitoring station (MEM; 113.61°E, 34.75°N), Yinhang school (YH; 113.68°E, 34.80°N) and Gongshui company (GS; 113.57°E, 34.81°N), which are located at the southeastern, southwestern, northeastern and northwestern of Zhengzhou, respectively (Fig. 1). There is a main airport highway and heavy-traffic ring roads approximately 500 m west of JK. Furthermore, the site is at a distance of 2 km from an industrial area, which involves packaging and printing plants, and material distribution factories. It is noteworthy that there were three coal-fired power plants in the urban area of Zhengzhou city. One of the power plants with the highest production was 1.6 km northwest of MEM. Both the MEM and YH include a mix of commercial and condensed residential areas, whereas the apartments around YH are more aged. The GS site is surrounded by several manufacturing plants, including pharmaceuticals, materials, foods and machineries.

Ten sampling days with the rainfall record (*ca.* 0 mm) were chosen in every month during the period of May - September, 2017 consequently, to represent a typical air quality condition in a month. Grab samples were collected minute using 3.2 L stainless-steel canisters (Entech Instrument, Inc., Simi Valley, CA, USA), which were pre-cleaned with high purity nitrogen and pressurized to 20 psi. Two samples, one collected at 07:00 with increasing of human activities and another one collected at 14:00 with well-mixed of ambient air, were obtained on each sampling day. There was a total of 400 samples collected in this study. The chemical analysis was accomplished within two weeks after the collection of samples. Real-time data for trace gases, including SO_2, CO, NO_2 and O_3, and synchronous meteorological data, such as temperature (T), relative humidity (RH), wind direction (WD) and wind speed (WS), were recorded at each air monitoring station.

2.2 Chemical Analysis

In this study, the measurement of VOCs was based on Compendium Method TO-15, which was established by U.S. EPA. Air in the canister was concentrated using liquid-nitrogen at -160 °C in a cryogenic pre-concentrator (7100A, Entech Instrument, Inc.). Both the CO_2 and H_2O were removed from the transfer line. The air was then thermally desorbed at 120 °C and transferred for analysis to a gas chromatography (GC, 7890A, Agilent Technologies, Santa Clara, CA, USA) coupled with dual detectors, i.e. a mass spectrometric detector (MSD) and a flame ionization detector (FID) (5977E, Agilent Technology). Dual columns were applied for the simultaneous analysis of C_2 - C_{11} hydrocarbons. A PLOT column (15 m, internal diameter of 0.32 mm and film thickness of 3.0 μm) was connected to the FID for detection of C_2 - C_5 NMHCs, whereas C_5 - C_{10} NMHCs, oxygenated VOCs (OVOCs) and halocarbons were separated using a DB-624 column (30 m×0.25 mm inner diameter × 3.0 μm film thickness), which was connected to the MSD. Target compounds were identified with retention time and mass spectra, and quantified with multi-point calibration curve in this study. The standard gas of PAMS (1 ppm; Spectra Gases Inc, NJ, USA) was used to construct the calibration curves for the 57 target VOCs, including 28 alkanes, 11 alkenes, acetylene and 17 aromatics. Detailed information on the target analyses involved in this study and their corresponding linearity of calibration (R^2), measurement relative standard deviation (RSD), method detection limit (MDL), maximum increment reactivity (MIR, carter, 2010) are presented in Table S1.

2.3 Positive matrix factorization (PMF)

The U.S. EPA PMF 5.0 software was used for source apportionment (Lau et al., 2010;Abeleira et al., 2017;Xue et al., 2017). Due to the complex chemical reactions, the application of PMF in VOCs has to be based on a couple of principles: eliminating species with mixing ratios below MDL and excluding species with high reactivity, except for the source markers (Shao et al., 2016;Guo et al., 2011). Finally, 31 VOC species and NO_2 were chosen for the source apportionment analysis.

In this study, PMF was performed with fifty base runs for each site, results with the minimum Q value (a parameter used to express uncertainties of PMF results) were considered as optimum solutions. In Table S2 the r^2 between observed values and predicted values of selected VOCs and NO_2 are presented for the four sites, the r^2 for most species (>80%) were higher than 0.6, compounds with $r^2<0.6$ were down weighted when determine factor sources.

During PMF analysis, bootstrap method was used to evaluate stability and uncertainty of the base run solution, setting the minimum correlation R-value at 0.6, 100 bootstrap runs were performed, and the results were showing in Table S3, and acceptable results (>80%) were gained for all the factors.

Three to nine factors were selected to initiate the running of PMF, the Q/Q(exp) for every site at fixed factor size were presented in Table S4. With the increase of factor number, the ratios Q/Q(exp) were declined due to additional factors. When the factor size changing from 3 to 4, 4 to 5, and 5 to 6, the decrement of Q/Q(exp) were larger (~18-25%), while the change was lower than 12% after factors increased to 7, combined with the field conditions, six factors were defined at each site.

2.4 Potential source contribution function (PSCF)

In this study, the probability of air clusters with source concentration higher than a certain value was estimated (Hopke et al., 1995). Briefly, the PSCF value in ijth grid was the ratio of the number of endpoints with higher source concentration relative to the total number of endpoints in ijth grid cell. The criterion value, equal to 75th percentile of the targeted source concentration in this study, was used to verdict whether the value was higher or not. The 48-hour back trajectories was calculated with Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model. While there are many grid cells with small values, which could result in high uncertainty, the weight function (Wij) was introduced to gain optimized PSCF results (WPSCF) (Polissar et al., 1999). According to average values of end points in each cell, in this case, Wij was presented as below.

$$Wij=\begin{cases} 1.0 & nij>30 \\ 0.7 & 10<nij\leq 30 \\ 0.42 & 5<nij\leq 10 \\ 0.05 & nij\leq 5 \end{cases}$$

2.5 Estimation of the initial NO_x and VOCs

With the assumption that chemical loss of NO_x and VOCs were mainly due to their reactions with hydroxyl radical (•OH), the initial mixing ratio of NO_x can be calculated with the equation as (Shiu et al., 2007;Shao et al., 2009):

$$[NO_x]=[NO_x]_0 \exp(-k\,[\bullet OH]\,\Delta t) \qquad (1)$$

where k stands for the reaction rate between NO_x and [•OH]. In this study, k was set as the observed average ratio of NO_2/NO_x during this campaign.

The photochemical age Δt was usually displayed as the ratio between the two compounds, which emitted from common source, but owning different reaction rate with •OH. For this case, the photochemical age clock was performed with ethylbenzene (E) and m,p-xylene (X) (Sun et al., 2016).

$$[\bullet OH]\ \Delta t=1/(k_x-k_E)\ [\ln(C_X/C_E)-\ln(X_0/E_0)] \qquad (2)$$

which k_x and k_E represent their rate constants with •OH, C_X and C_E correspond to the observed mixing ratios; X_0 and E_0 were their initial concentrations. The X_0/E_0 was prescribed at 5 percentile of the observed ratios at 07:00 in this paper.

The initial mixing ratio of VOC was estimated with the method as NO_x (Shiu et al., 2007):

$$[VOC]_0=[VOC]_t \exp(k_i\,[\bullet OH]\,\Delta t) \qquad (3)$$

where $[VOC]_t$ was the observed mixing ratio of i^{th} species and k_i was the correspondent rate constant with •OH.

3 Results and discussions

3.1 Meteorological variations and Mixing ratios

Meteorological conditions are important factors that impact both the compositions and levels of VOCs. During the sampling period, the T (RH) was varied from 15°C (15%) to 38°C (100%) (Fig.S1), and the dominant wind was northwestern and southeastern (Fig. 2). The air clusters, analyzed by HYSPLIT model, showed moderate differences in each month (Fig. 3). In May, clusters arriving at Zhengzhou demonstrated longer paths, and included six clusters in total, while in June, the length of clusters were shorter. However, the concentration levels and compositions of VOCs were similar in the two months. In May, the largest cluster (27.2%) was passed over from Yinchuan, a central city in northwest China, then crossing several non-capital cities (i.e., Yanan, Yuncheng and Luoyang) in Shanxi and Sichuan provinces. Such a long-range transport of pollutants might result a less impact on the air quality of Zhengzhou, as comparable level and similar compositions of VOCs were obtained during the period of May - June. In June, August and September, approximately half of the air trajectories originated from the areas of Henan province, indicating the air pollutants in Zhengzhou were impacted by local factors at most time.

The total concentrations of VOCs (Σ_{VOCs}) are presented in Table 1. The Σ_{VOCs} varied at the four sites, where the highest Σ_{VOCs} and their compositions were not identical across the sampling months as well. In May 2017, the highest Σ_{VOCs} was reported at JK (37.65±22.58 ppbv), followed by GS (31.73±18.70 ppbv), YH (30.05±16.43 ppbv) and MEM (29.05±15.34 ppbv), while the Σ_{VOCs} values for the month of June, July, August and September were found to be in the order of: GS>JK>MEM>YH, MEM>GS>JK>YH, YH>MEM>JK>GS, and MEM> YH > GS >JK, respectively. This can be attributed to numerous factors that will be explored later in the paper. Besides the emission sources (to be discussed in Section 3.2), the impacts controlled by meteorological conditions should not be ignored as well. For instance, the prevailing wind in May was northwestern at GS and YH, while the southwestern wind was dominant at JK (Fig 4). The transport of air pollutants from urban center and industrial plants should be resulted in the highest level of Σ_{VOCs} at JK. In June 2017, the prevailing wind was southeastern at MEM, YH and GS (Fig. 4). The average wind speed at GS (0.74±0.33 m s^{-1}) was lower than that at MEM (1.84±0.94 m·s^{-1}) and YH (0.97±0.36 m s^{-1}) (Table 2), indicating poor dispersion conditions at GS. The air pollutants emitted from MEM and YH were more liable resulting in a higher level of Σ_{VOCs} at GS in June. It should be noted that, when Σ_{VOCs} at JK was higher than that of GS, the level at YH was higher than that of MEM, and vice versa. Except for the discriminations between the pollution sources at every site, the above phenomenon might be a result of the topography, where the elevation was gradually increased from east to west in Zhengzhou (Mu et al., 2016).

Due to the variations of the planet boundary layer (PBL) height, solar radiation and emission sources, the concentrations of VOCs displayed obvious differences between morning and afternoon time (07:00LT and 14:00LT in this study). Compared with morning period, the aromatic compounds showed lower compositions at14:00 LT (Fig. 5), because of the increased planet boundary layer and the active photochemical reactions, while alkenes always peaked in the14:00 LT. According to the dataset, the increases in alkene compositions (~4.3% uplift) were mainly due to higher contributions of isoprene (~1.4% at morning and 7.6% in the afternoon), which was mainly emitted from biogenic sources and increased exponentially with ambient temperature (Jiang et al., 2018).

The average Σ_{VOCs} values in Zhengzhou (28.83±22.05 ppbv) were significantly lower than those in Beijing (65.55 ppbv), Hangzhou (55.9 ppbv), Guangzhou (47.3 ppbv) and Nanjing (43.5 ppbv), and higher than that in Wuhan (23.3±0.5ppbv) (Table 3). Factors, including population density, industrial activity, fuel composition, local stringent regulations for environmental protection, terrain, and weather are the potential reasons for the discrimination of VOCs concentrations in those cities. With regard to the weight percentage of major groups (Table 3), the composition of alkanes was the largest in all cities because of their longer lifetimes and widespread from a variety of pollution sources (Fig. 5), while the composition of aromatics was lower than alkenes in these cities except for Guangzhou. It is well known that aromatics mainly originate from solvent usage and vehicle exhaust in summer. The large amount of shoemaking and shipbuilding industries involving large amounts of solvent usage may be the main reason for the higher composition of aromatics in Guangzhou. In comparison with other four cities, the composition of aromatics in Zhengzhou was the lowest probably due to its less solvent-used manufacturers than in Guangzhou, Hangzhou and Nanjing, and less numbers of vehicles than in Beijing. Alkyne contributes least to VOCs in cities listed in Table 3, with higher level observed in Zhengzhou, where ranked second after Hangzhou. Alkyne typically originates from combustion sources. Zhu et al. (2016) observed that the composition of alkyne in the biomass-burning period could be double of that in the non-biomass burning period (Zhu et al., 2016). As Henan is the largest agricultural province in China and the sampling duration covered the crop harvest season, the residents often used crop residues as the biofuel for their subsistence and a higher alkyne composition in Zhengzhou was thus resulted.

3.2 Temporal variations

The time series of mixing ratios of NO_x, O_3 and Σ_{VOCs} at every site are shown in Fig. 6. The results showed a distinctive temporal characteristic where lower levels of SO_2, CO, NO_x, O_3 and Σ_{VOCs} were observed in July and August (mid-summer) (Table S5). These results were similar to those obtained for other urban areas (Li and Wang, 2012;Cheng et al., 1997;Na et al., 2001). Changes in PBL height, human activities, and abundance of hydroxyl radicals (•OH) were the potential causes for the phenomenon. Pal et al. (2012) reported that the PBL height was positively correlated with temperature. The occurrences of precipitation and raining were also frequent in most areas of China during summer, resulting in decreasing background level of air pollutants. Additionally, a series of effective local policies, such as prohibition of painting and coating in open air and limitations on fuel supply between 10:00 -17:00 LT during hot summer days assisted in suppressing the emissions of VOCs. Meanwhile, many organizations, such as schools, institutes and scattered private workshops, were closed due to summer vacations. Some large-scale industries also stopped manufacturing processes for two weeks during this period. Consequently, the anthropogenic emissions were reduced, which in turn resulted in a decrease in VOCs, SO_2, and NO_x emissions. The reduction of precursor levels and unfavorable photochemical conditions (such as, higher RH) resulted in the lower O_3 levels in July and August.

Beside local emissions, the long-range air mass also had some impacts on relatively lower level of Σ_{VOCs} in July. As illustrated in Fig.3, different from other months, the air current was originated with the largest portion (*ca*. 88.68%) of clusters from Hubei province, where the average Σ_{VOCs} in its capital city (23.3±0.6 ppbv) (Lyu et al., 2016) was lower than that in Zhengzhou (29.18±23.08 ppbv). In combination with the lower weight percentage of photothermal-reactive aromatics (10.30±4.23%), and the lowest toluene to benzene (T/B) ratio of 1.15±0.99 around this period, it is possible that the cleaner air mass clusters originating from Hubei also contributed to the reduction of Σ_{VOCs} in July.

As demonstrated in Fig. 6, the observed Σ_{VOCs} values at 07:00 LT were often higher than those at 14:00 LT. The accumulation of pollutants during night-time and the temperature inversion in the morning were the most reasonable explanations for this phenomenon. Stronger photochemical reaction during noon-time led to the reduction in atmospheric VOCs. It should be noted that pronounced Σ_{VOCs} were occasionally observed at MEM and GS (Fig. 7), which were potentially ascribed to sharp changes in local emissions and meteorological conditions. Specifically, at MEM, the distinctive increment was always accompanied with obvious increases of alkanes or aromatics (Fig. 7). Since the T and RH were often consistent during the sampling period, the direct gas evaporations should be constant as well. Therefore, the simultaneous increased concentrations of SO_2, CO and NO_x could illustrate the potential impacts from combustion sources, such as emissions from nearby thermal power plant. At GS, the increase of Σ_{VOCs} in June was usually with extremely high levels of aromatics, due to the disturbance from solvent use for building renovation during this period, and the abnormal high levels of Σ_{VOCs} in other months were related to the rising concentrations of C_3-C_4 alkanes, which were mainly originated from consumptions of compressed natural gas (CNG) or LPG (Huang et al., 2015). The results support the possible impact from a gas-fueled power plant located about 1 km southwest of the site (~18% of prevailing western wind at GS during May to September).

It is of interest to note that on the morning of 5th September, acetylene was found in extremely high concentrations (14.65 - 39.42 ppbv). Its mixing ratio in most of the urban areas was <10 ppbv (Louie et al., 2013;Duan et al., 2008;Guo et al., 2012). It was learnt that the 5th September is a festival day for the people who worship their ancestors. A large number of incenses and offerings, made up of wood and paper, were burnt during the festival, resulting in an elevation of acetylene all over the Zhengzhou city (Zhu et al., 2016).

3.3 Spatial variations

The C_2 - C_5 alkanes, acetylene, ethylene, toluene and benzene were the most abundant VOCs detected at all sites (Fig.8), and the mixing ratios of toluene varied within a wide range at each site, because of its universal emission sources (e.g., vehicle exhaust emissions and solvent usage) (Wang et al., 2014;Barletta et al., 2005). These chemicals contributed >60% for Σ_{VOCs} at each site, illustrating strong combustion-related sources in Zhengzhou.

Among the four major organic classes, alkane was the most abundant group as a result of its widespread sources and longevity (Fig.5), accounted for 52.9%, 62.5%, 53.4%, 53.4% of the total Σ_{VOCs} at JK, MEM, GS, and YH, respectively. The highest composition of alkane was observed at MEM due to the stronger contributions of ethane, iso-pentane, and C_6-C_8 branched alkanes (Fig. S3), which are emitted from light-duty gasoline vehicles (Wang et al., 2017a).

The average Σ_{VOCs} were slightly higher at industrially impacted sites of GS (31.66±28.73 ppbv) and JK (28.63±22.04 ppbv) than those at MEM and YH (Fig.9). Additionally, the air pollutants related to the combustion processes, such as SO_2 and CO, were more abundant, though marginal, in western area of Zhengzhou (GS and MEM) (Fig.9). Under high levels of VOCs and sufficient supply of NO_x, the highest average mixing ratio of O_3 was observed at GS, followed by YH where even with the lowest VOCs and NO_x, indicating that there are multiple factors, rather than the absolute concentrations, contributed to the O_3 formation at YH.

In June, the O_3 concentration often exceeded the national standard level of 80 ppbv, representing severe air pollution during this period. The average mixing ratio of O_3 during daytime (07:00-18:00 LT) in June, 2017 at JK, MEM, YH, and GS were 74.87±39.55 ppbv, 73.50±40.59 ppbv, 73.81±35.69 ppbv, and 87.99±46.11 ppbv, respectively (Table 4). The higher level of O_3 at GS was accompanied with the higher Σ_{VOCs} (39.29±25.37ppbv). The weight percentage of aromatics (15.62±12.06%) at GS was higher than those at other sites as well, indicating that the painting and other renovation activities at GS was potentially an important factor for its high O_3 level in June. Even though both the Σ_{VOCs} and specifically high O_3 formation potential compounds (such as alkenes and aromatics) at MEM were slightly higher than those at YH (Table 4), the O_3 concentration at MEM was not higher. This could be attributed to other critical precursors such as NO. NO at MEM (7.72ppbv) was significantly higher than that at YH (2.57 ppbv) during daytime, indicating that the titration reaction between O_3 and NO was more efficient at MEM.

It is well known that many O_3 episodes were attributable not only to local sources but also to regional transports. For example, Streets et al. (2007) reported that with continuous southern winds, the O_3 level in Beijing was 20-30% contributed from its neighboring cities in Hebei. During this study, a typical regional ozone pollution was happened on August 10th at YH (Fig.6). On that day, the ratios of Σ_{VOCs} /NO_x at the four sites were all less than 6.5 (ppbC/ppbv) (Fig. S4), indicating a regional VOC-control system, and that VOCs are the critical contributors to the formation of O_3 in Zhengzhou. The reductions in Σ_{VOCs} in the afternoons (around 14:00 LT) compared to mornings (around 07:00 LT) may have been caused from the uptake by O_3 formation, while the reduction of Σ_{VOCs} and active compounds (i.e., aromatic+alkene) at 14:00 relative to 07:00, determined as 35% and 56% respectively, were the least at YH among the four sites (Fig. S4). On the other hand, based on the dispersion of wind direction, between 08:00 - 15:00 LT on August 10th, YH was at the downwind position to the other three sites (Fig. S4). All of this confirmed that the abnormally high O_3 at YH was caused by the transport of air pollutants from other sites on that day.

3.4 VOCs/NOx ratio

The VOCs/NO_x ratio is often used to distinguish whether a region is VOCs or NO_x limited in O_3 formation. According to the general case, the area was loaded in VOC-sensitive regimes when VOCs/NO_x ratios were lower than 10 in the morning; and it would be on NO_x-sensitive regime when VOCs/NO_x ratios were greater than 20 (Sillman, 1999;Hanna et al., 1996). In this study, the mean value of VOCs /NO_x (ppbC/ppbv) were below 5 at all four sites (Fig.10), and 75% of the data points were < 6, indicating that the O_3 formation was sensitive to VOCs in Zhengzhou, and the reductions on the emissions of VOCs will be benefit for O_3 alleviation.

The VOCs /NO_x showed differences among the four sites (Fig. 10), with the lowest value at MEM (~3.8) and the highest value at JK (~4.7). The distributions demonstrated that the production of O_3 at MEM was more sensitive to VOCs than JK due to presence of emission from thermal-power plant. Meanwhile, approximately 14% of the VOCs /NO_x ratios of >8.0 were found in the NO_x-limited site of JK, potentially resulting from higher VOCs or lower NO_x emissions than other sites. Both of the mixing ratios and the statistical data showed higher levels of VOCs (with lower NO_x) at GS, where only ~4% of the ratios of > 8 was observed, indicating that there must be other factors (unresolved in this study) impacted the variation of O_3 formation regimes.

From the daily variations of VOCs /NO_x ratios (Fig. 10), higher values were observed at 14:00 LT than 07:00 LT at the four sites, well correlated with less vehicle emissions or more consumption paths for NO_x with stronger light intensity. The increment of VOCs /NO_x at 14:00 LT was more obvious at JK and GS, suggesting that more emission sources of VOCs at daytime, and resulting the O_3 formation system shifting to the transition area in the afternoon.

Many researches showed that the O_3 formation depends not only on the abundances of precursors (mainly VOCs and NO_x) and also VOCs to NO_x ratio (Pollack et al., 2013). In this research, the mixing ratio of O_3 at 14:00 LT presented a slightly positive trend ($p<0.05$) with the uplift of VOCs /NO_x at JK (Fig. 11), consistent to the results observed at the megacity of Shanghai (Gao et al., 2017), where the O_3 formation was more sensitive to NO_x when high O_3 levels were observed. This can be attributed to the increased O_3 production efficiency at high VOCs /NO_x. There were no discernible trends at other sites, possibly due to the counteraction imposed by other uncertain factors.

3.5 Ratios of specific compounds

Ratios of specific VOCs are useful indicators to identify the emission sources (Raysoni et al., 2017;Liu et al., 2015;Ho et al., 2009). In order to characterize the differences in the contribution of various sources at each site, two ratios of i-pentane/n-pentane and T/B ratios are discussed.

The ratio of i-pentane to n-pentane can be used to differentiate potential sources such as consumption of natural gas, vehicle emissions and fuel evaporations. It is claimed that in areas heavily impacted by natural gas drilling, the ratios were lied within the range of 0.82 - 0.89 (Gilman et al., 2013;Abeleira et al., 2017). Higher values were often reported for automobiles, in a range of 2.2 - 3.8 for vehicle emissions, 1.8 - 4.6 for fuel evaporation, and 1.5 - 3.0 for gasoline (Russo et al., 2010;McGaughey et al., 2004;Jobson et al., 2004;Wang et al., 2013), whereas the ratios below unity was found for coal combustion (0.56 - 0.80) (Yan et al., 2017).

In this study, i-pentane and n-pentane were highly correlated (R^2=0.87 - 0.94) throughout the whole sampling campaign (Fig. 12), indicating constant pollution sources for these two compounds. The highest ratio of i/n-pentane was found at JK (2.59), which was comparable to the value of 2.93 reported in a Pearl River Tunnel (Liu et al., 2008), thus indicating strong impacts from traffic-related sources. The average ratio at MEM was 2.31, higher than the character ratios of coal combustion, reasonably due to the observation site presented at upwind position of the thermal power plant. Additionally, it is remarkable that MEM was surrounded by a main road with four traffic lanes. The distance between the nearest traffic light and the sampling site was just 200 m. Frequent idling may cover up the contribution from coal combustion, reflecting the impact of traffic emissions. The average ratios at YH (1.94) and GS (1.63) were lower than those at the above two sites, suggesting the comparatively stronger contribution from coal burning.

The T/B ratio is another efficient tool to differentiate pollution sources. Both the tunnel and roadside researches indicated that T/B ratio varied within the range of 1 - 2 when the atmosphere was heavily impacted by vehicle emissions (Gentner et al., 2013;Tang et al., 2007;Huang et al., 2015;Wang et al., 2002). The ratio of <0.6 was ascribed to other sources such as coal combustion and biomass burning (Tsai et al., 2003;Akagi et al., 2011). The industrial activity would be more dominant when the T/B ratio is greater than 3 (Zhang et al., 2015).

In this study, the correlation between benzene and toluene was fairly well at all the sites (R^2=0.70-0.74), except for YH (R^2=0.41) (Fig.14), suggesting the similar sources for benzene and toluene at JK, MEM and GS, while more complex such as variable wind direction at YH. The average ratios of T/B were lied within the range of

1.64-2.29, which were scattered around the character ratio of 2 for vehicle exhaust, illustrating the significance of vehicle emissions at the four sites. Specifically, at JK, MEM and YH, most of T/B ratios were distributed between 0.6 and 3, which were corresponding to character ratios for coal or biomass burning and industrial activities respectively. These reflected the mixture impacts from mobile source and coal/biomass burning at these three sites. However, more values were greater than 3 at GS, suggesting more frequent disturbance from industrial activities at this site.

From the temporal respect, the T/B ratios at 14:00 LT were lower than at 07:00 LT (Fig.15). In fact, the reaction rate constant of toluene ($5.63\times10^{-12}cm^3molecule^{-1}s^{-1}$) with •OH is much higher than that for benzene ($1.22\times10^{-12}cm^3molecule^{-1}s^{-1}$), representing more rapid consumption of toluene from photochemical reactions and thus resulting in lower T/B ratios at 14:00 LT. Besides, the emission strength of mobile source is often weaker at 14:00 LT, while the coal/biomass burning are increased due to more human activities. Both of the situations can be used to explain the lower T/B ratios observed at 14:00 LT. In comparison with other months, higher T/B ratios were found more frequently in September, potentially showing the more strengthen indusial activities during this period.

Overall, based on the iso-pentane/i-pentane and T/B ratios, the atmospheric VOCs at every site were impacted by a mix of coal/biomass burning and vehicle emissions, whereas GS was more liable impacted by industry-related sources.

3.6 Relative reactivity of VOCs

The reactivity of individual species was different, while mixtures of VOCs would have competition the precursors between each other, leading to variations on reaction paths and O_3 formation yields. Ozone formation potential (OFP) is a useful tool to estimate maximum O_3 productions of each compound under optimum conditions, from which the vital species in O_3 formation could be identified (Huang et al., 2017). The calculation of OFP is based on mixing ratios and maximum incremental reactivity (MIR) of individual compound, which are expressed in Eq. (4).

$$OFP=C_i\times MIR \qquad (4)$$

where C_i represents the concentration level of i^{th} species, while MIR is a constant taken from Carter (2010) (Table S1).

In Zhengzhou city, alkenes contribute most (55.91±14.17%) to the sum of OFP, of which ethylene had the largest portion. The results is different with the estimation based on emission inventories by Wu and Xie (2017), in which the largest contributor of total OFP in North China Plain (NCP), YRD and PRD was aromatics, reflecting that there was relatively less surface coating industries in Zhengzhou.

For the individual species, the top 10 most contributors in OFP included ethylene, isoprene, m,p-xylene, toluene , propylene, acetylene, n-butane, i-pentane and propane. Their contributions to the sum of OFP was lied within the range of 69.44 - 77.60% (Table 5), with 61.30-76.46% of total VOCs weighted in concentration, highlighting the importance of reduction on emissions of these VOCs no matter based on relative reactivity or mixing ratios. Additionally, it is worth noting that, the percentage of acetylene (4.51±0.34%) weighted in OFP was higher than many other areas in China, including Guangzhou (2.20%) and YRD (2.37%) (Li and Wang, 2012;Jia et al., 2016), demonstrating that it is necessary to conduct emission controls on sources related to combustion (i.e., vehicle emissions and biofuel burning) in Zhengzhou city .

Zhengzhou was suffered from the severest O_3 pollution in June, 2017. The relationships between OFP of each organic group, Σ_{VOCs}, and the ambient concentrations of NO_x and O_3, as well as the corresponding meteorological conditions, are shown in Fig. S5-6. At 07:00 LT, generally lower WS was seen than that at 14:00 LT, offered a favorite condition for local O_3 propagation. Under low RHs and high T and OFP (88.13±30.32 ppbv), the O_3 level at YH was unexpectedly lower than that at MEM on sunny days. Since the OFP was estimated with the assumption of reactions that proceeded under optimum conditions, the above phenomenon reflected there were unsatisfied O_3 formation conditions at YH. The highest total OFP was seen at JK in June, while the highest O_3 levels was observed at GS where located at a downwind position with lowest WS (0.74±0.33 m s^{-1}). The concentration level of O_3 usually increased with wind speed (Fig.S7), particularly when the eastern wind was dominant, illustrating the disturbance from long-distance sources to urban center.

3.7 Source apportionment

The factor profiles given by PMF for each site were presented in Fig.15. The six factors were resolved as vehicle emissions, coal+biomass burning, solvent use, oil evaporation, petrochemical and biogenic source (detailed characterization can be referred to supporting information) on the base of the correspondent markers for each source categories, which were summarized in Table S6. Meanwhile, the correlation coefficients, expressed in Pearson's r, were varied from 0.54 to 0.62 and 0.66 to 0.73 for SO_2 with coal+biomass burning, and NO_2 with vehicle emission, respectively (Fig. 16), proved the precise results gained in this study.

The weight percentage of each factor calculated with two criteria (absolute concentrations and OFPs) at the four sites were presented in Fig.17. At every site, vehicle emission, coal+biomass burning and solvent use were the top three contributor to VOCs abundance in ambient air. Compared to JK and YH, even though the distances between thermal power plant and the observation site was the shortest at MEM, vehicle emission (36.82%) showed the largest portion instead. Coal+biomass burning (30.58%) had the highest contribution at GS, attributed to its downwind position and nearby suburbs that biomass burning occurred more frequently. The contributions from vehicle emission at the two urban centers of MEM (36.82%) and YH (37.39%) were comparable, but higher than those at JK and YH. The consumptions of solvent at GS (18.86%) and JK (14.95%) were higher than those at YH (10.1%) and MEM (11.48%), due to restriction on development of new industrial enterprises in urban center in recent years. Emissions from oil evaporation, petrochemical and biogenic emission were scarce, and their contributions were below 10% at every site.

On the base of O_3 formation impact, coal+biomass burning, solvent use, and vehicle emission were the three major contributors as well. In contrast to the concentration weighted method, the importance of solvent use estimated with OFP increased 28-65% for each site, and the significance of vehicle emissions decreased 29-53%. At YH and GS, small discrimination (<4%) in contributions of coal+biomass burning between the two methods were found. On the other hand, the variations on coal+biomass burning at JK (a decline of 17%) and MEM (an increase of 29%) were more obvious, due to low abundance of reactive species in this factor at JK and high level of alkenes at MEM. Considering that the aging index of xylene/ethylbenzene was high at MEM (2.97) and low at JK (0.01) remarkably, demonstrating that the emission sources related to coal+biomass burning was fresher at MEM than JK.

Except for oil gas evaporation and biogenic sources, in which major emitted compounds with shorter life span, potential source regions for the other four identified sources (i.e., coal+biomass burning, vehicle emission, solvent usage and petrochemical) apportioned by PSCF method were presented in Fig. 18. Southwest of Shanxi province, western of Shandong province, and southwest of Henan province were identified as hot spots for the coal+biomass burning. The active emission areas for solvent use were concentrated in Henan province, and mainly located in southwest of Zhengzhou. The most contribution area for petrochemical was found in southwest of both Shanxi and Henan, northwest of Anhui, and southeast of Hubei provinces. For vehicle emissions, the strongest emission point was scattered in southwest of Henan, while Shandong, Anhui and Hubei provinces also distributed with strong emission points.

3.8 Consumption of VOCs and correlations with ozone level

The consumption of a VOC in the atmosphere could be presented as the difference from its initial mixing ratio and the observed value. The groups of alkenes and aromatics had larger consumption than alkanes, particularly at JK and GS (Fig.19), which was consistent to stronger impacts from solvent usage at the two sites.

The average value of VOC consumption at urban center (MEM and YH, 4-6ppbv) was lower than that at marginal area (JK and GS, 9-11ppbv), and the average increment of O_3 at 14:00 LT was higher than that at 07:00 LT in marginal area, suggesting more efficient photochemical reactions at JK and GS. Meanwhile, the average values of $[\bullet OH]\Delta t$ for each site, ranked in the same order with VOCs consumption, were varied in a range of 2.9×10^{10} to $4.71\times10^{10}cm^{-3}$ s. The values were slightly lower than the results of $4.9\times10^{10}cm^{-3}$ s measured at Beijing in August-September, 2010 (Yuan et al., 2012), indicating that comparatively less aging process in Zhengzhou.

Taken the decrement of VOCs and NO_x as independent variable and the increment of O_3 as dependent variable, the multiple regression analysis was performed. The results for JK and GS were presented as:

$[O_3]_{increment}=0.41[VOC]_{decrement}+0.20[NO_x]_{decrement}+53.44$ (JK, $R^2=0.44$)

$[O_3]_{increment}=0.34[VOC]_{decrement}+0.39[NO_x]_{decrement}+59.29$ (GS, $R^2=0.38$)

The F values for JK and GS were 16.1 and 10.1 respectively, indicating the regression results at the two sites were acceptable. However, the relationships among O_3, NO_x and VOCs could not be expressed in this way at MEM and YH, where the low values for both R^2 (0.12, 0.09) and F values (2.7, 2.8). This potentially attributed to more constant disturbance from fresh emission sources at urban center.

4. Conclusions

In this study, VOC samples were collected at four sites in Zhengzhou, Henan (China) for the first time and analyzed for 57 species. It is found that the weighted percentage of aromatics was lower, while alkyne was higher in Zhengzhou city than in other Chinese cities. C2 - C5 alkanes, acetylene, ethylene, toluene and benzene were the most abundant VOCs in the region, suggesting widespread combustion-related sources in the city. On the basis of monthly average, the maximum Σ_{VOCs} was observed at GS site, where occasionally impacted from the nearby gas fueled plant. Approximately 75% of VOCs/NO_x ratios were below 6 at each site, indicating that the O_3 formation was driven by VOCs regionally. Different from other megacities, alkenes were the biggest contributors to OFP, and acetylene was particularly critical at each site. In addition, the impact of aging process was less in Zhengzhou than that in Beijing. The photochemical reactions at JK and GS were more efficient, while the relationships among O_3, NO_x and VOCs at urban sites of MEM and YH were more complex. Either the mixing ratios or calculated OFPs demonstrated that the most important contributors to VOCs were vehicle exhaust, coal+biomass burning and solvent use, illustrating the necessary to conduct emission controls on these pollution sources. Vehicle emission was more dominant at urban center (YH and MEM), while solvent use was more important at the sites (JK and GS) far away from urban center in Zhengzhou. It is further shown that the air pollution in

Zhengzhou was mostly impacted by local emissions according to the cluster analysis, and southern air clusters occasionally from Hubei Province was cleaner. In addition, strong emissions for coal+biomass burning were concentrated in southwest of Shanxi, western of Shandong and southwest of Henan provinces according to the PSCF analysis. Due to less anthropogenic emissions and more favorable dispersion conditions, most of the air pollutants had the lowest levels in the mid-summer month of July. This study provides the first-hand information on the characteristics of VOCs and assists in overcoming the O_3 pollution issue in Zhengzhou city, China.

Acknowledgements

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Table & Figure

Table1. Concentrations of Σ_{VOCs} (ppbv) at every site during the sampling period

	JK		**MEM**		**GS**		**YH**	
	Mean	**Std.**	**Mean**	**Std.**	**Mean**	**Std.**	**Mean**	**Std.**
May.2017	37.65	22.58	29.30	15.34	31.73	18.70	30.05	16.43
June.2017	34.02	19.89	30.28	12.77	39.29	25.37	28.33	11.94
July.2017	16.01	6.13	20.74	12.66	19.60	13.94	15.95	7.54
Aug.2017	21.54	15.29	24.37	20.79	20.49	15.67	26.03	17.01
Sept.2017	26.20	16.22	34.15	23.85	30.36	19.76	32.56	19.76

Table2. Wind speed ($\mathrm{m\cdot s^{-1}}$) at every site during the sampling period

	JK	**MEM**	**YH**	**GS**
May	1.34±0.65	1.86±1.19	1.27±0.66	0.97±0.49
June	1.07±0.48	1.86±0.94	0.97±0.36	0.74±0.33
July	1.48±0.59	2.62±1.19	1.15±0.45	0.90±0.32
August	1.06±0.48	1.86±0.94	0.95±0.39	0.76±0.35
September	0.80±0.38	1.24±0.80	0.82±0.43	0.62±0.38

Table3. Concentration levels of VOCs and compositions of major groups in Zhengzhou and other cities in China

Items		**Guangzhou**	**Nanjing**	**Beijing**	**Hangzhou**	**Wuhan**	**Zhengzhou**
		March-December, 2005	2011-2012	August, 2006	July-August, 2013	2013-2014	May-September, 2017
Sampling site		residents-commercial-transportation mixed area	transportation-industry mixed area	residents-commercial mixed area	residents-transportation mixed area	urban	urban
Quantified compounds		59 NMHC	56 NMHC	47 NMHC	56 NMHC	99 VOCs	56 NMHC
Total samples		145	_	24	_	_	400
TNMHC (ppbv)		47.3	43.5	65.55±17.44	55.9	23.3±0.5	29.18±23.08
Compositions of major groups (%)	*alkane*	49.0	45.0	52.3	33.2		56±12
	alkene	16	25.3	21.2	25.9		16±7.6
	aromatic	23	22.3	18.1	24.3		14±8.4
	alkyne	12	7.3	8.4	16.6		13±6.7
Reference		(Li and Wang, 2012)	(An et al., 2014)	(Guo et al., 2012)	(Li et al., 2017b)	(Lyu et al., 2016)	this study

Table4. Specific information on VOCs, O_3 and NO at the four sites in June, 2017

Composition or conc.	JK	MEM	YH	GS
Aromatic (%)	9.06	11.57	4.72	15.75
Alkene (%)	6.36	4.13	5.52	5.47
Σ_{VOCs} (ppbv)	34.02	30.28	28.33	39.29
O_3(ppbv)	74.87	73.50	73.81	87.99
NO(ppbv)	7.10	7.72	2.34	4.47

Table5. Top 10 VOCs ranked according to calculated ozone formation potential (OFP) and their corresponding percentage weighted in mixing ratio

Site	Species	OFP (ppbv)	Weighted in OFP (%)	Weighted in mixing ratio (%)	Site	Species	OFP (ppbv)	Weighted in OFP (%)	Weighted in mixing ratio (%)
JK	Ethylene	18.99	25.54	8.22	MEM	Ethylene	18.44	30.88	7.92
	Isoprene	12.99	21.83	7.31		Isoprene	4.66	10.10	2.36
	m/p-Xylene	6.08	5.89	2.67		Toluene	3.73	6.67	3.99
	Toluene	5.53	5.83	4.22		Propylene	3.60	6.16	1.25
	Propylene	4.03	5.36	1.29		Acetylene	2.82	5.00	12.19
	Acetylene	2.97	4.44	13.54		m/p-Xylene	2.55	4.20	1.40
	n-Butane	2.15	3.05	7.28		n-Butane	1.81	3.20	5.97
	o-Xylene	1.83	2.00	0.88		Isopentane	1.76	3.16	7.39
	Isopentane	1.66	1.95	6.50		Ethane	1.58	2.96	23.35
	Propane	1.17	1.73	9.77		Propane	1.31	2.48	10.64
YH	Ethylene	19.83	28.10	8.88	GS	Ethylene	18.04	25.96	7.51
	Isoprene	7.44	11.30	3.67		Isoprene	8.01	16.75	4.64
	Toluene	6.63	7.75	5.72		Toluene	7.43	7.67	5.49
	m/p-Xylene	3.93	4.38	1.58		Propylene	4.39	5.85	1.26
	Acetylene	3.15	4.38	13.91		m/p-Xylene	4.31	4.57	1.75
	Propylene	3.01	3.60	0.91		Acetylene	2.76	4.24	12.07
	Trans-2-pentene	2.25	2.94	3.43		n-Butane	1.82	2.93	6.39
	n-Butane	1.84	2.80	6.31		Isopentane	1.71	2.68	6.94
	Isopentane	1.59	2.22	6.69		Propane	1.38	2.26	11.61
	Propane	1.18	1.98	10.20		Isobutane	1.13	1.98	4.59

[a] *m*-Xylene and *p*-Xylene are co-eluted in the chromatographic separation.

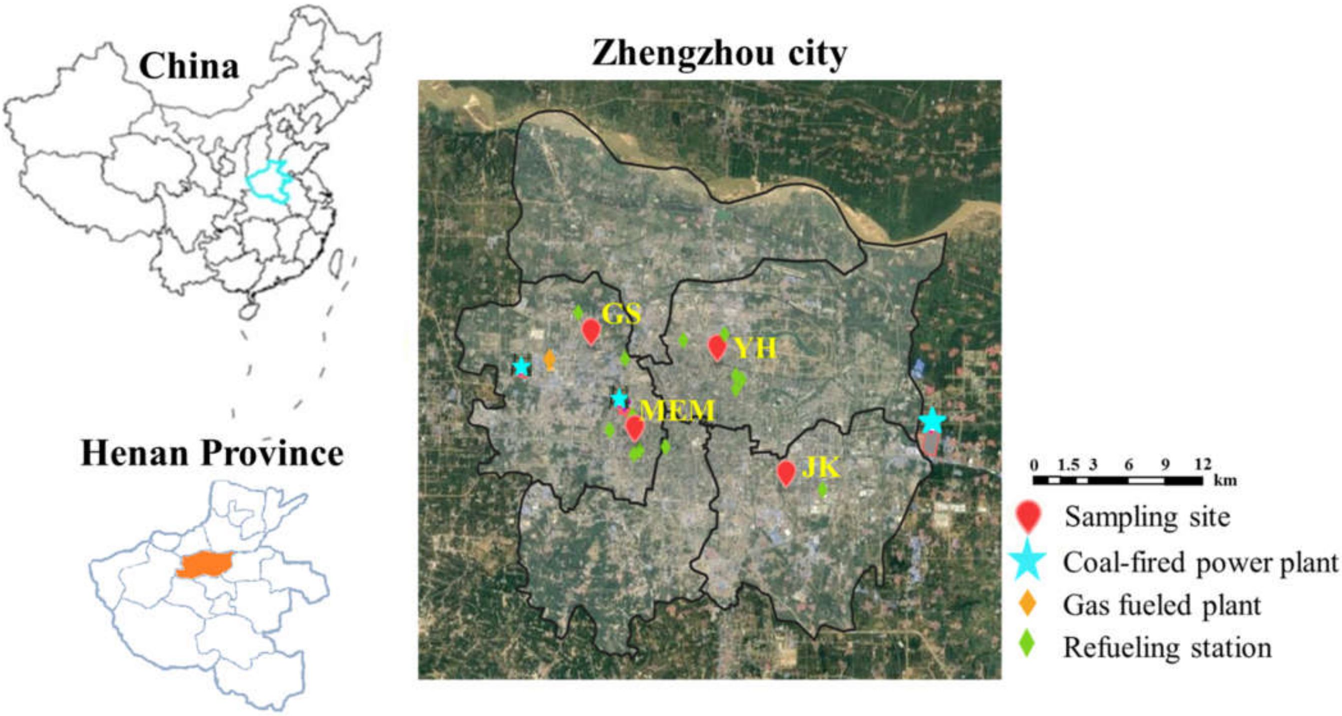


Fig 1. Map of Zhengzhou, China showing the locations of sampling sites.

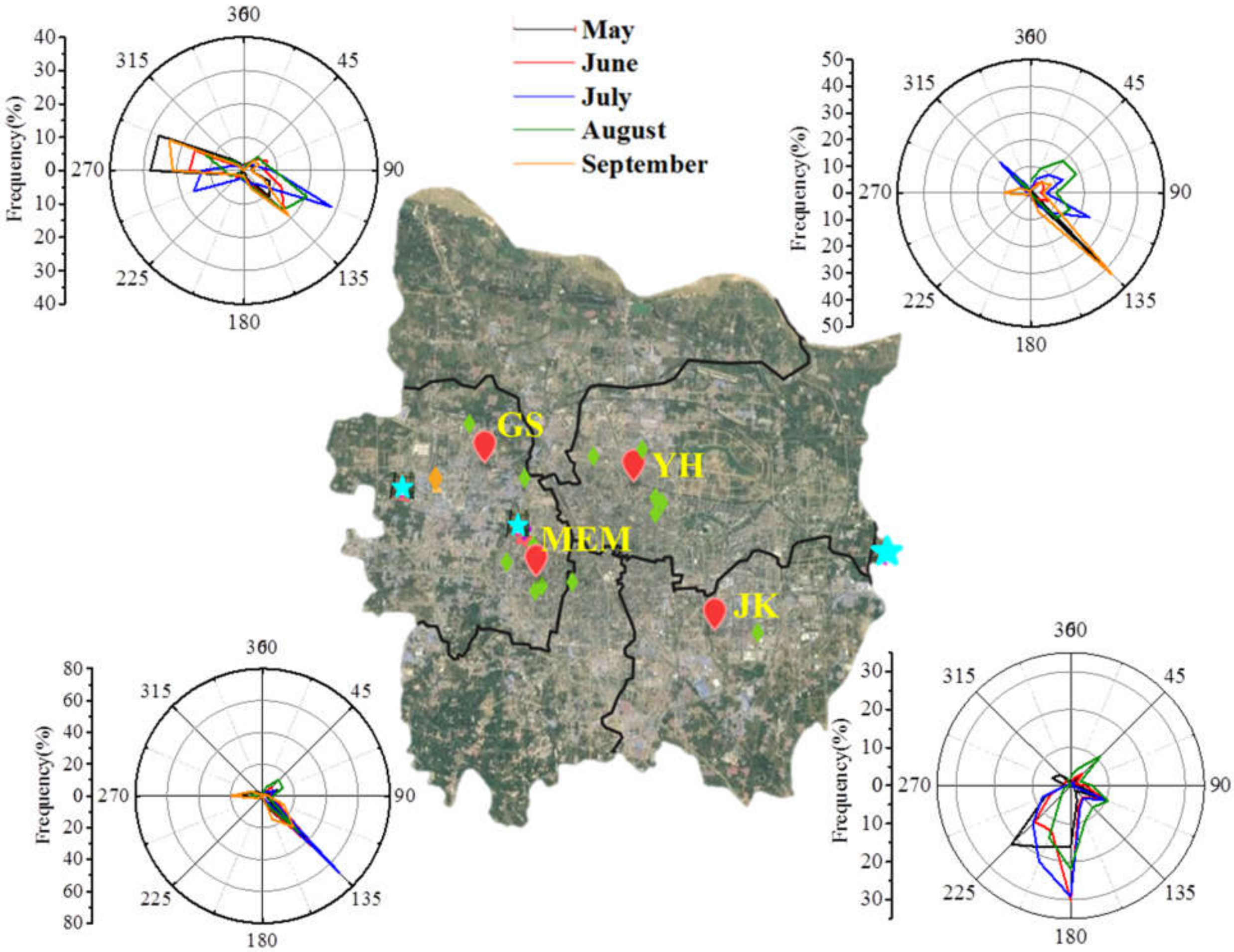
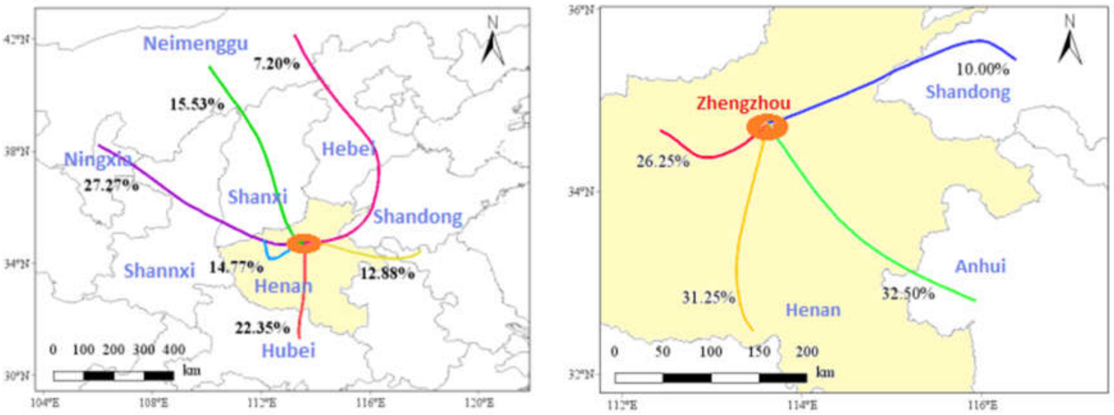
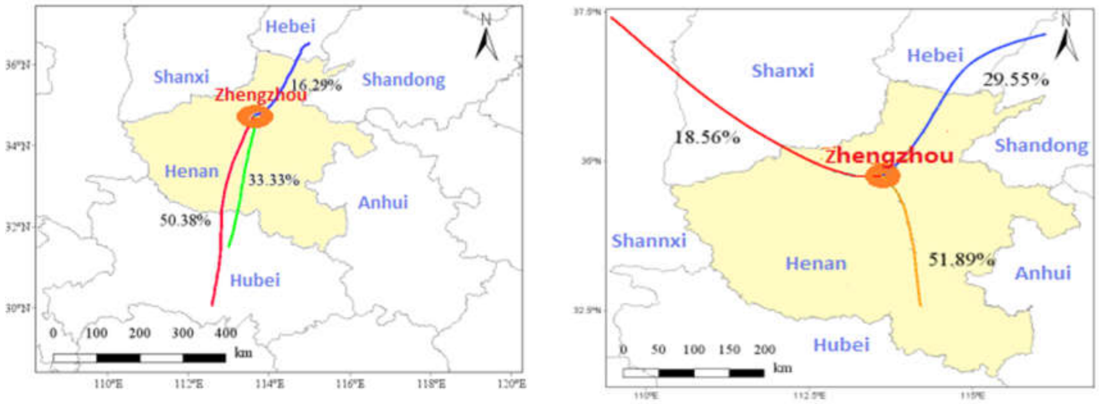


Fig.2 Wind direction for each site during May to September, 2017



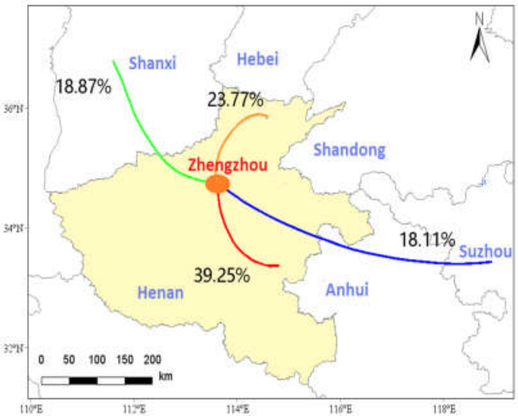
May

June



July

August



September

Fig. 3 Cluster analysis of Zhengzhou in each sampling month

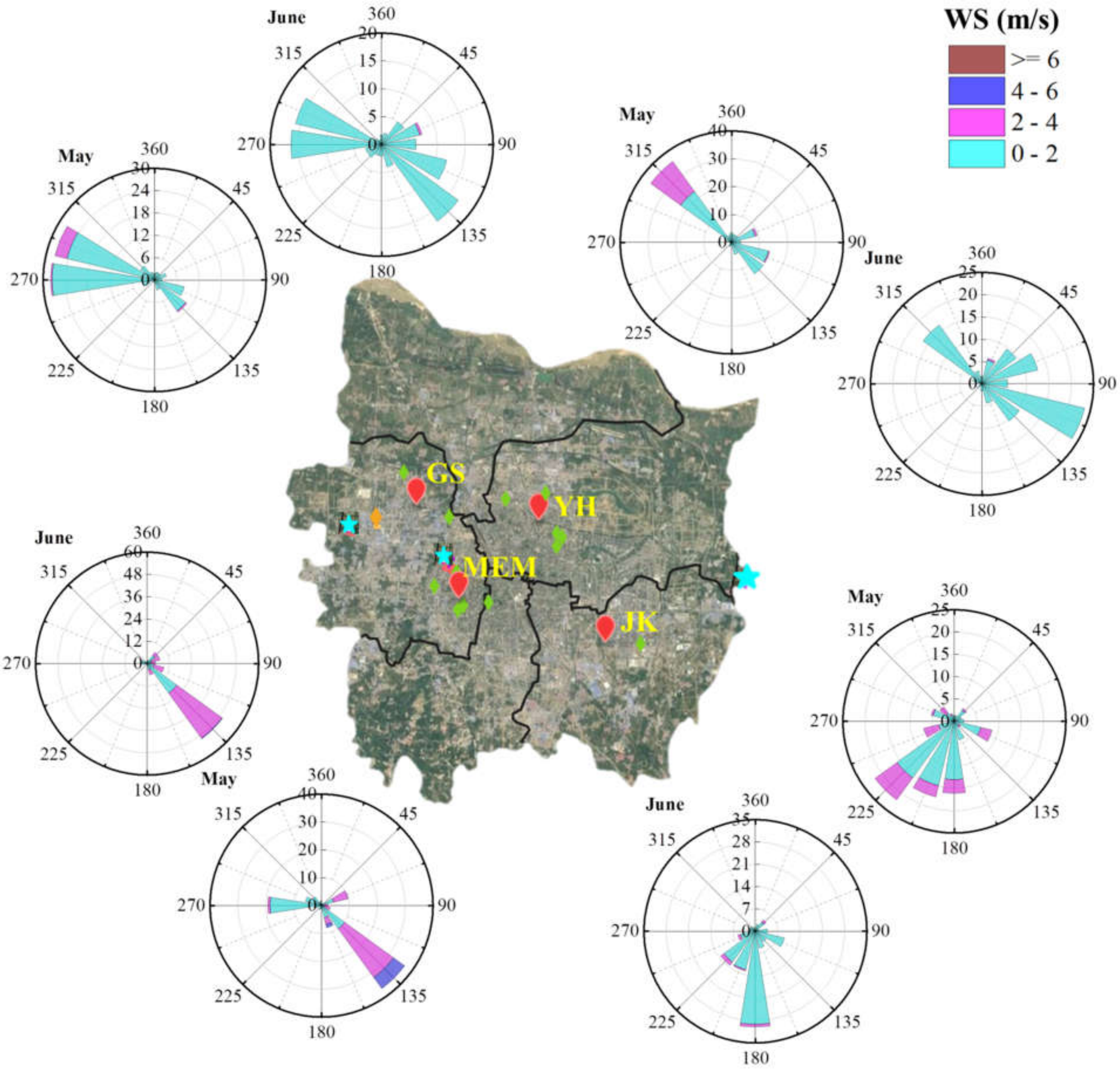


Fig.4 Wind rose at each site in May and June (the wind distribution in other three months were illustrated in Fig S2)

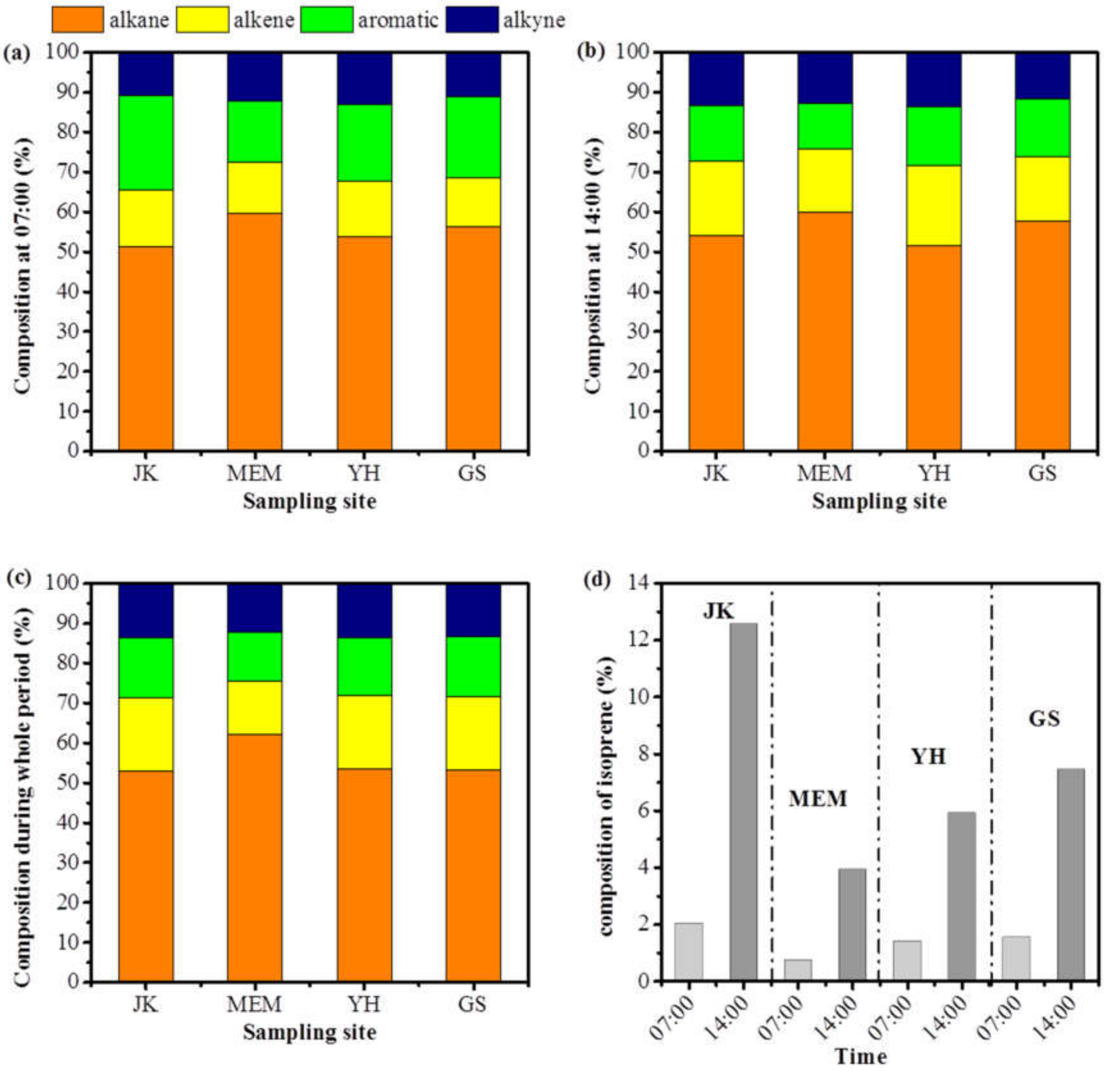


Fig. 5 Compositions of major organic classes at 07:00 LT (a), 14:00 LT (b) and during the whole sampling period (c) at the four sites, and the composition of isoprene at 07:00 LT and 14:00 LT for each site (d).

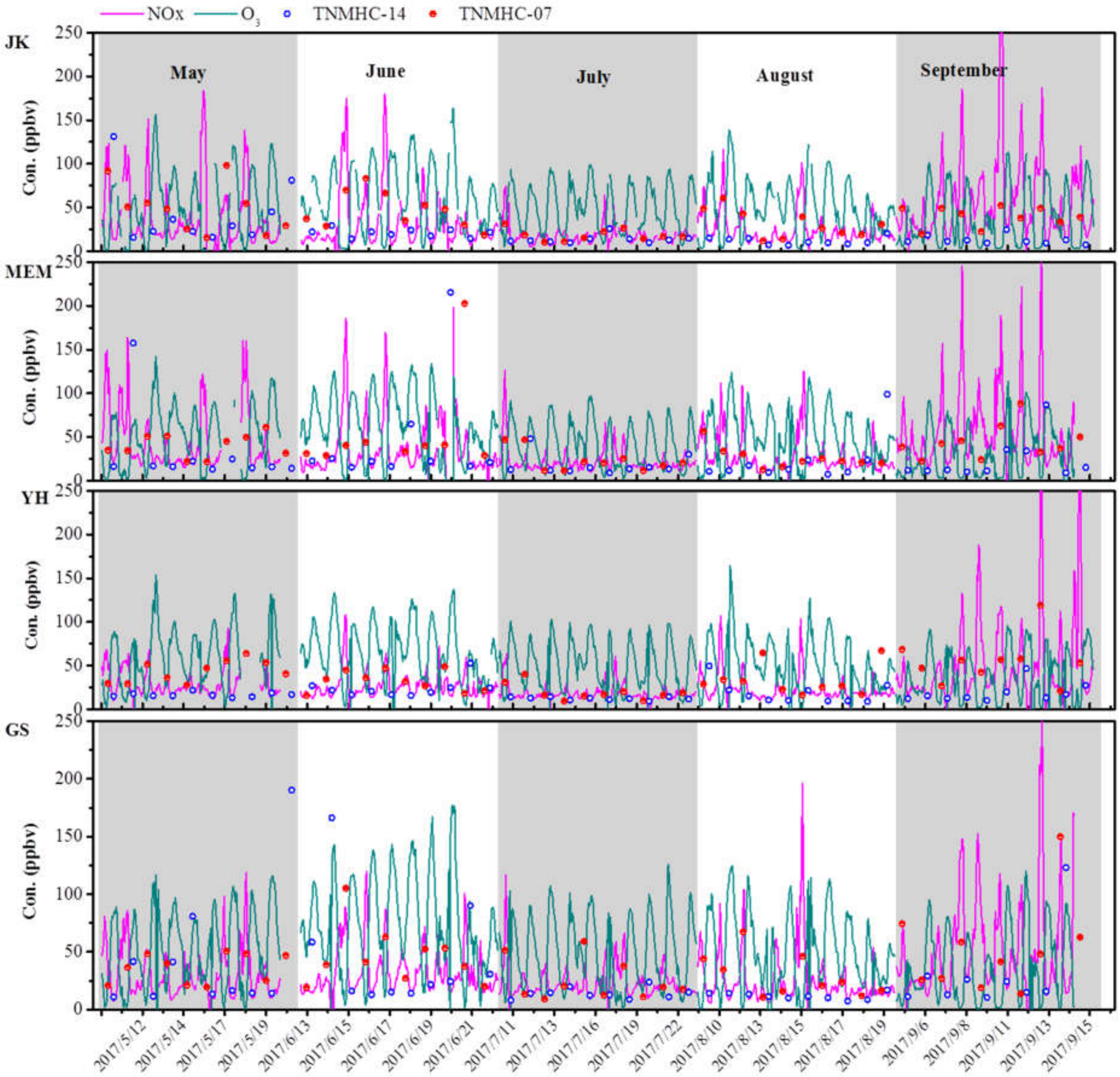


Fig.6 Temporal variations of mixing ratios ofΣ_{VOCs}, NO_x and O_3 at the four sites during the whole sampling period, in which Σ_{VOCs}-07 stands for the concentration level of Σ_{VOCs} observed at 07:00 LT, and Σ_{VOCs}-14 was that observed at 14:00 LT.

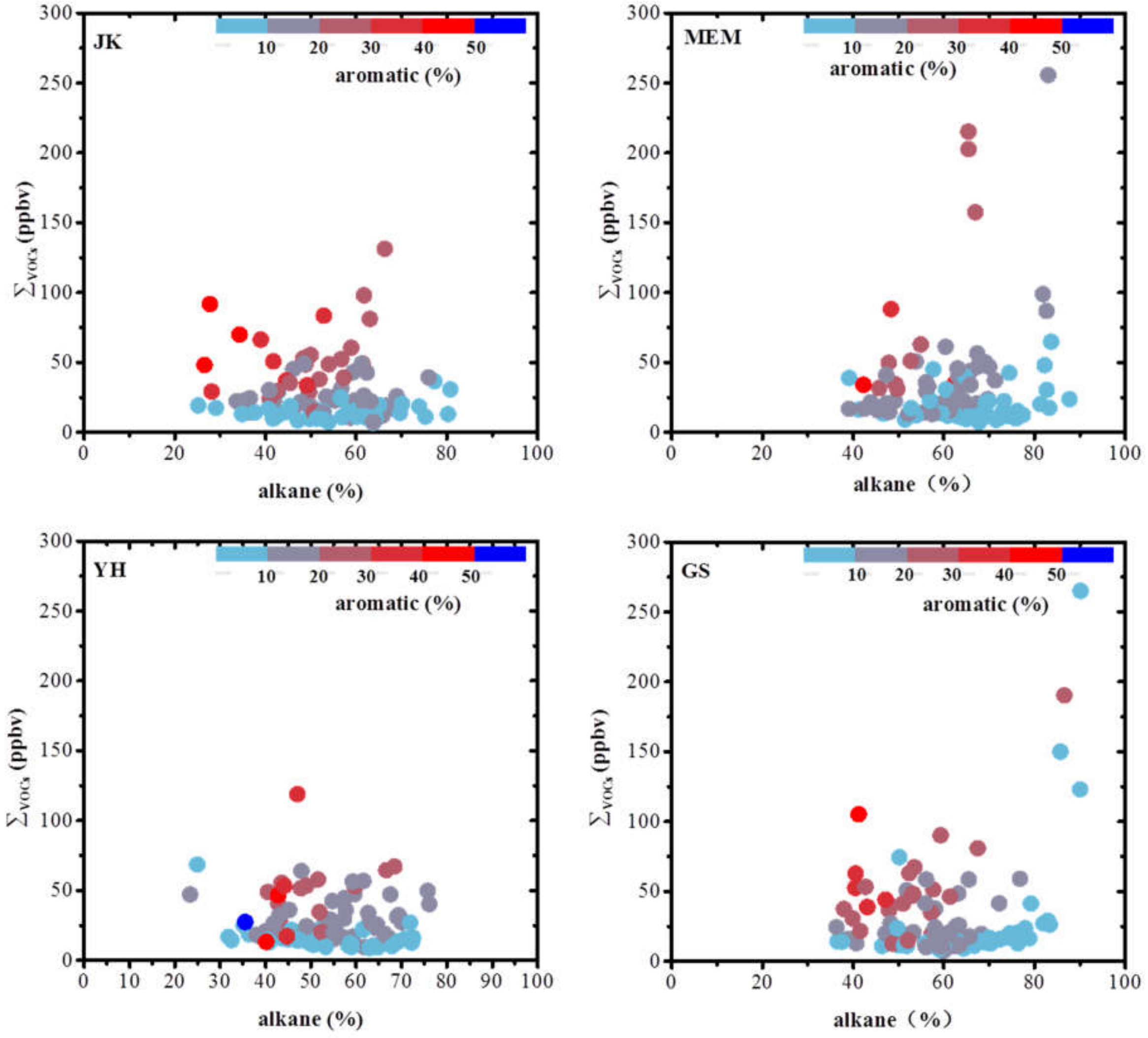


Fig. 7 The relationship between mixing ratio of Σ_{VOCs} and the composition of alkane, the data points were color coded with the composition of aromatic.

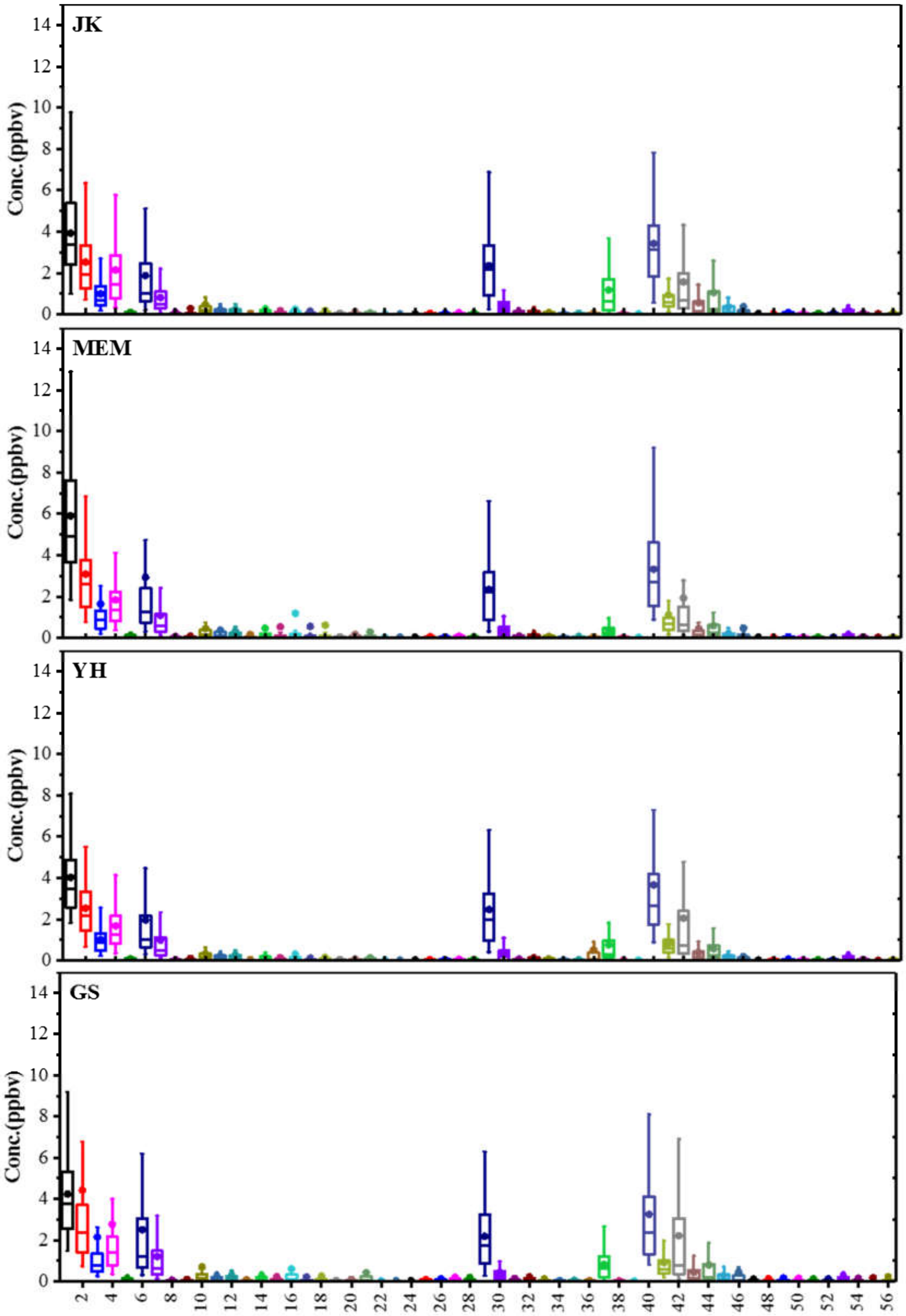


Fig.8 Concentrations of 57 VOCs at each site for the whole sampling period, the whisker was ranged from 5-95%, and the box was 25-75%, the solid points stand for average value, the line in the box represent median value. The number of chemicals can refer from Table S1.

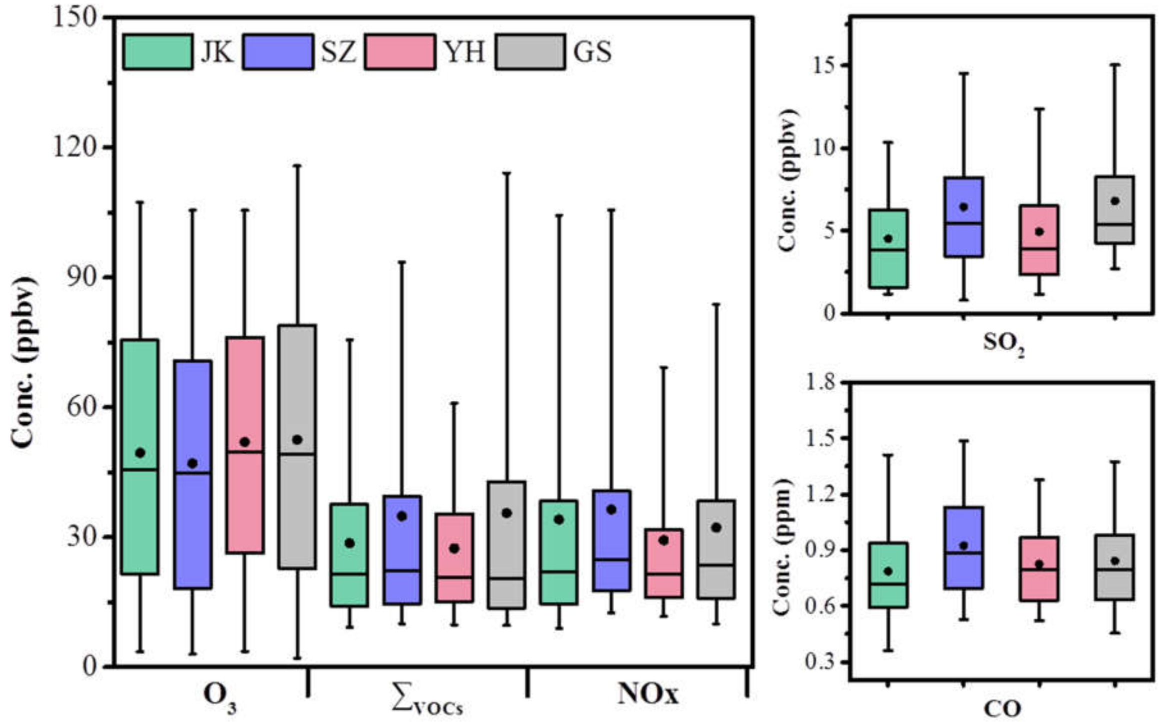


Fig. 9 The distribution of concentration point on O_3, Σ_{VOCs}, NO_x, SO_2 and CO at each site, the range of the box was 25%-75%, the black line in the box stands for median level, the black dot represent the average level, the range of whisker was 5-95%.

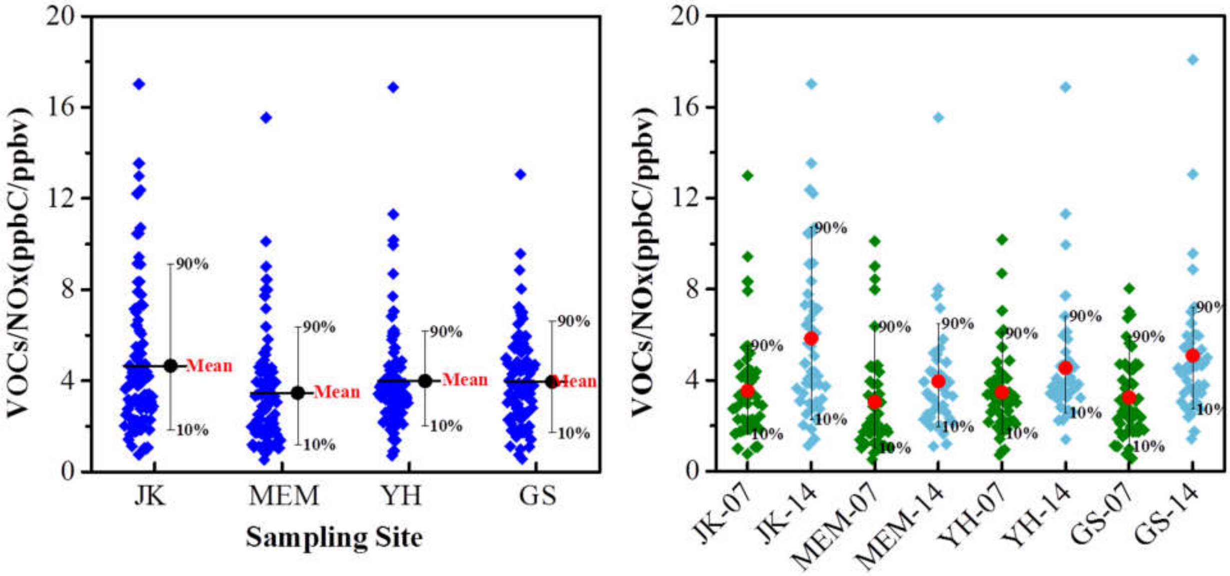


Fig.10 The data distribution of VOCs/NO_x(ppbC/ppbv) at the four sites (left), and the ratio observed at 07:00 LT and 14:00 LT were presented (right).

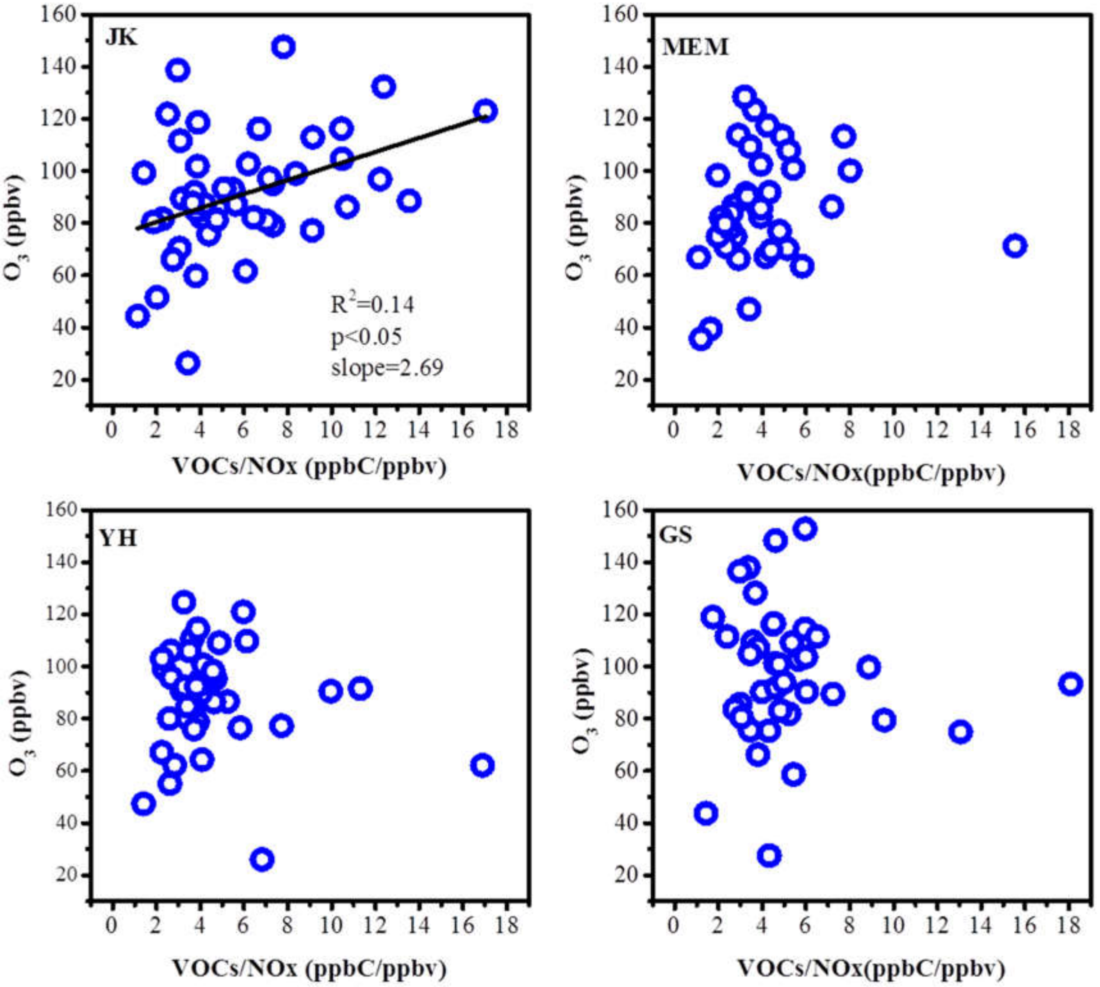


Fig.11 The relationship between O_3 and VOCs/NO_x at 14:00 LT

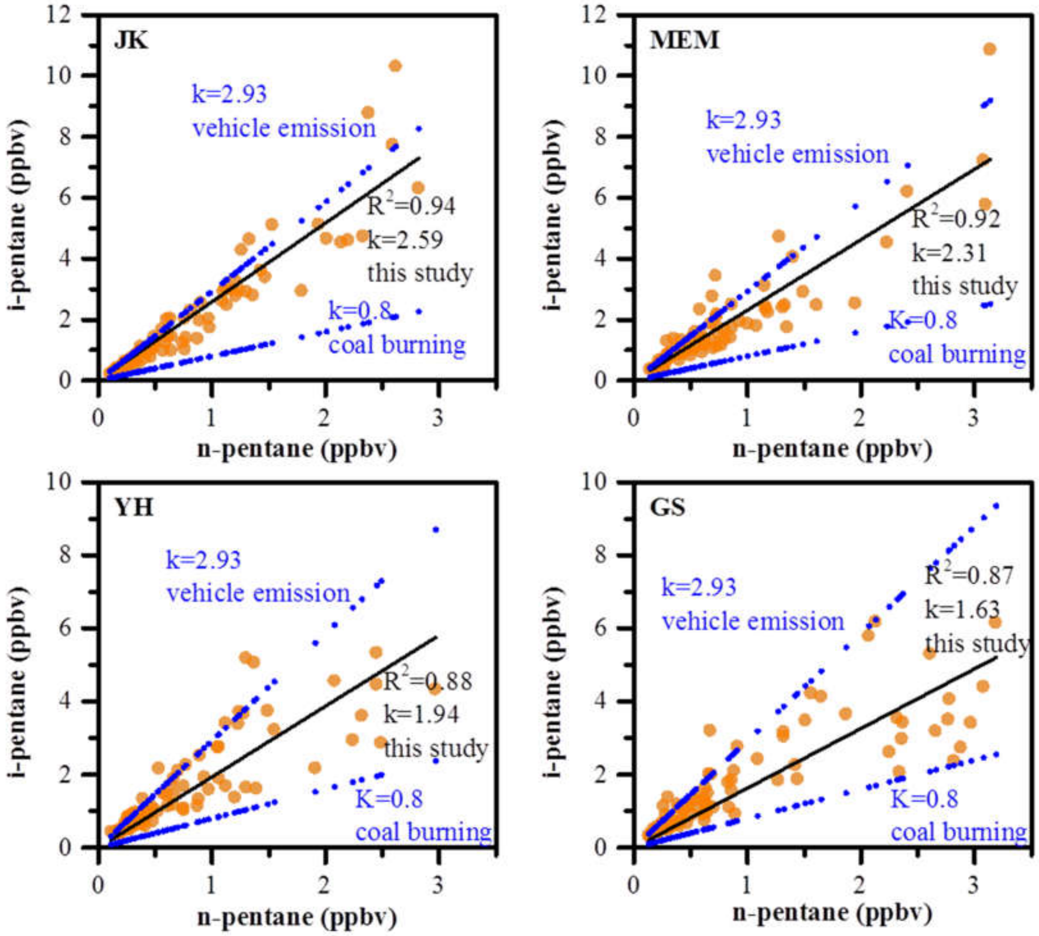


Fig. 12 Ratios of isopentane to n-pentane at every site

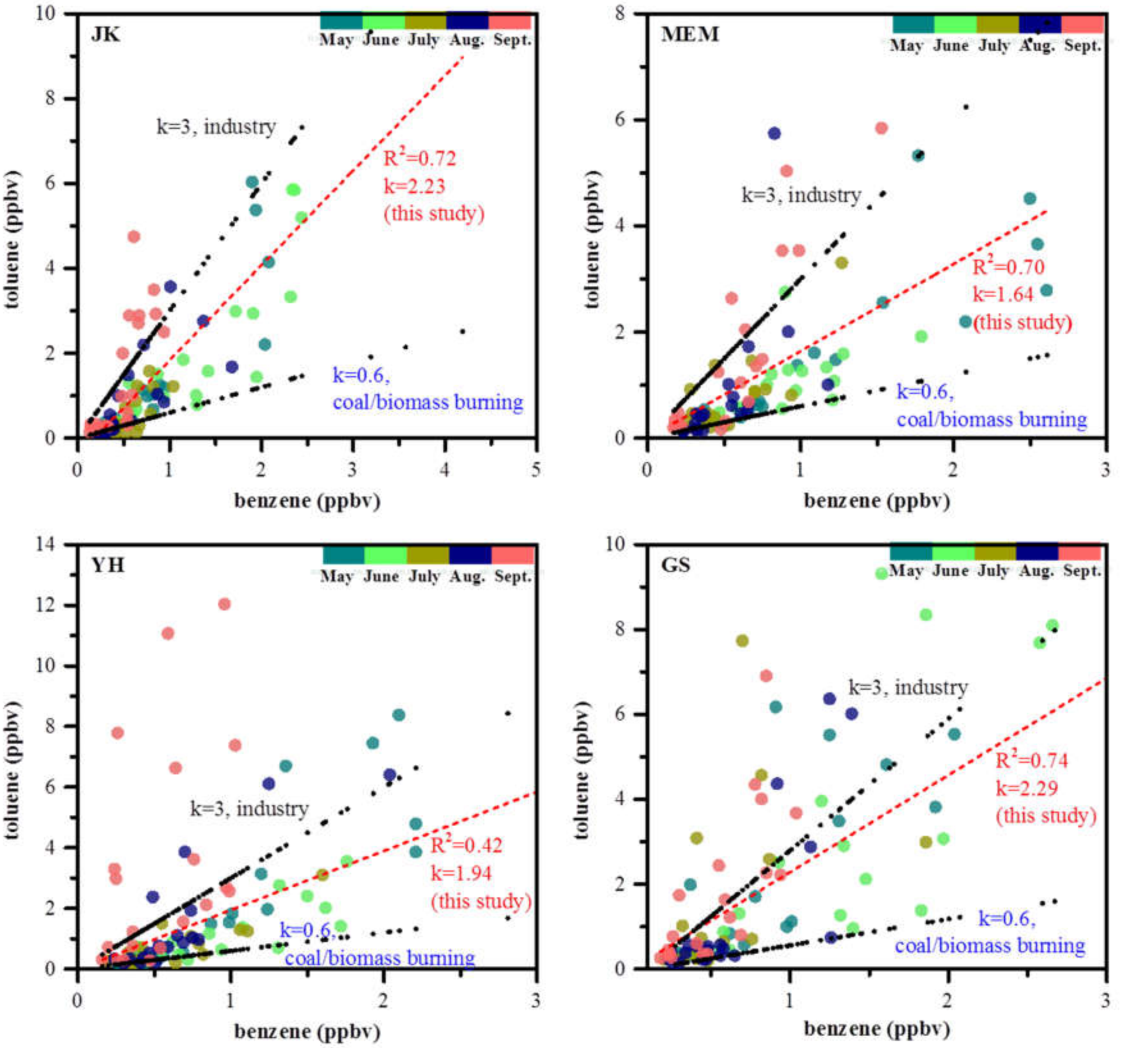


Fig.13 T/B ratios and linear correlation coefficients (R^2) between benzene and toluene at every site, the data points were color mapped with sampling period.

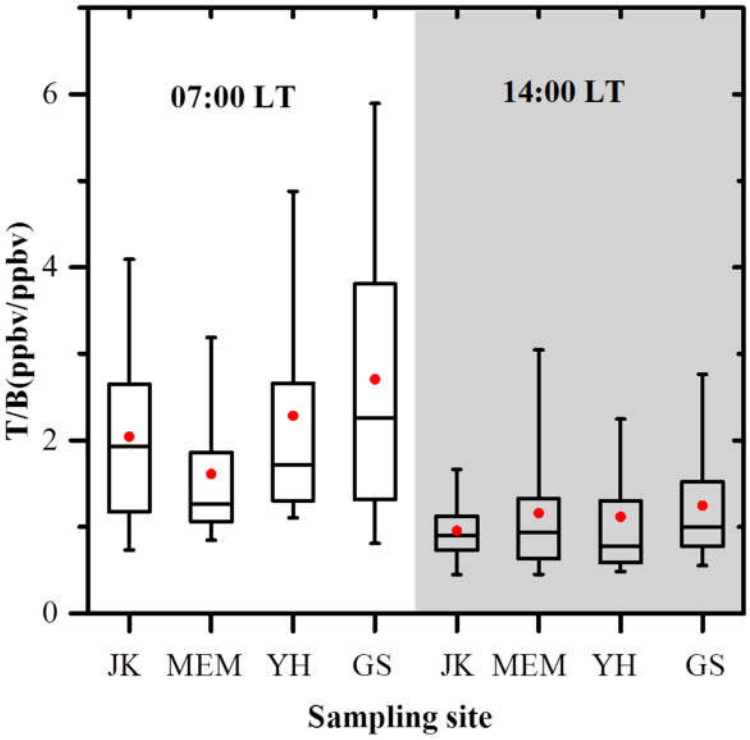


Fig. 14 The average ratio of T/B at 07:00LT and 14:00LT for each site during the whole sampling period

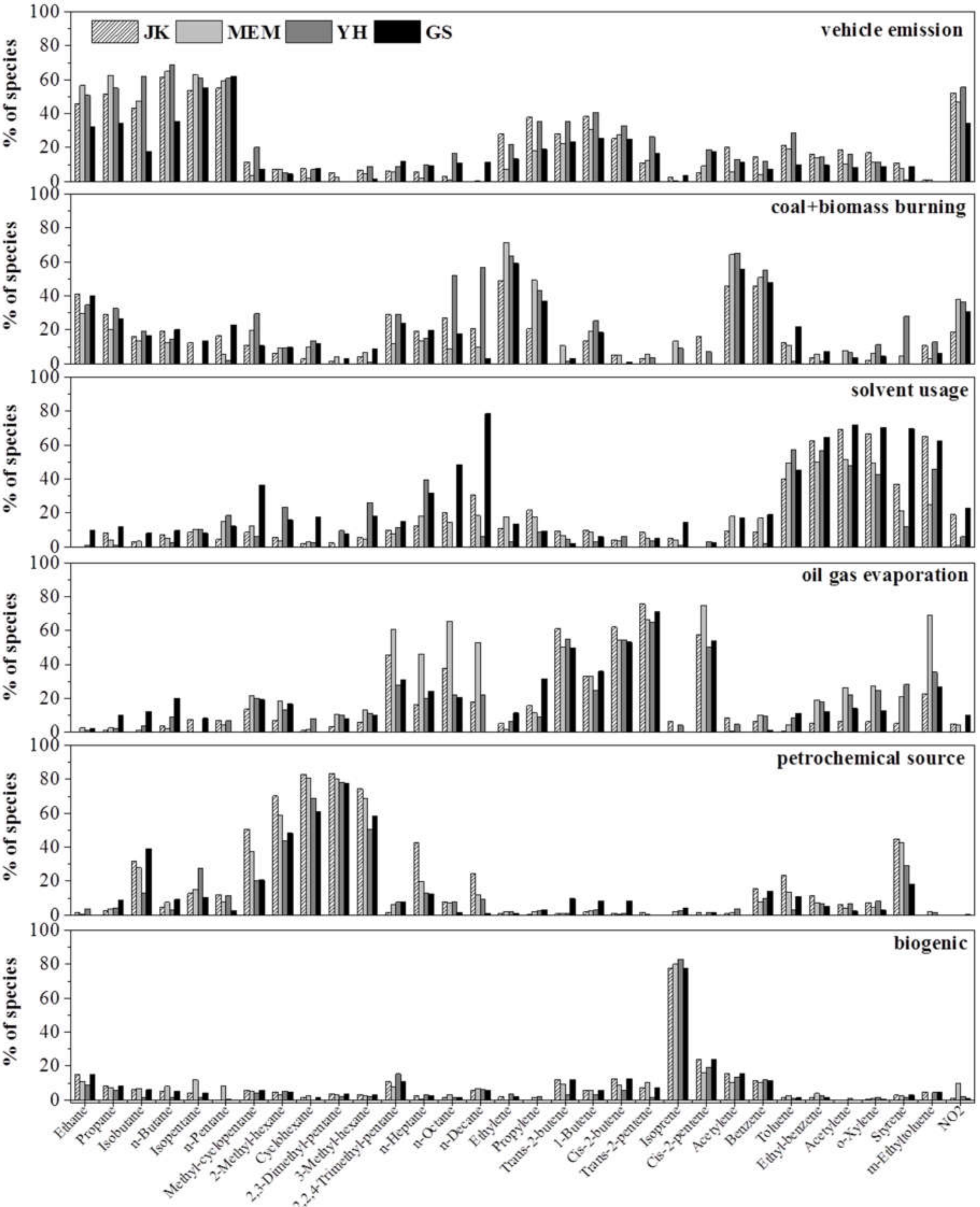


Fig. 15 Explained variations in source profiles as identified by PMF

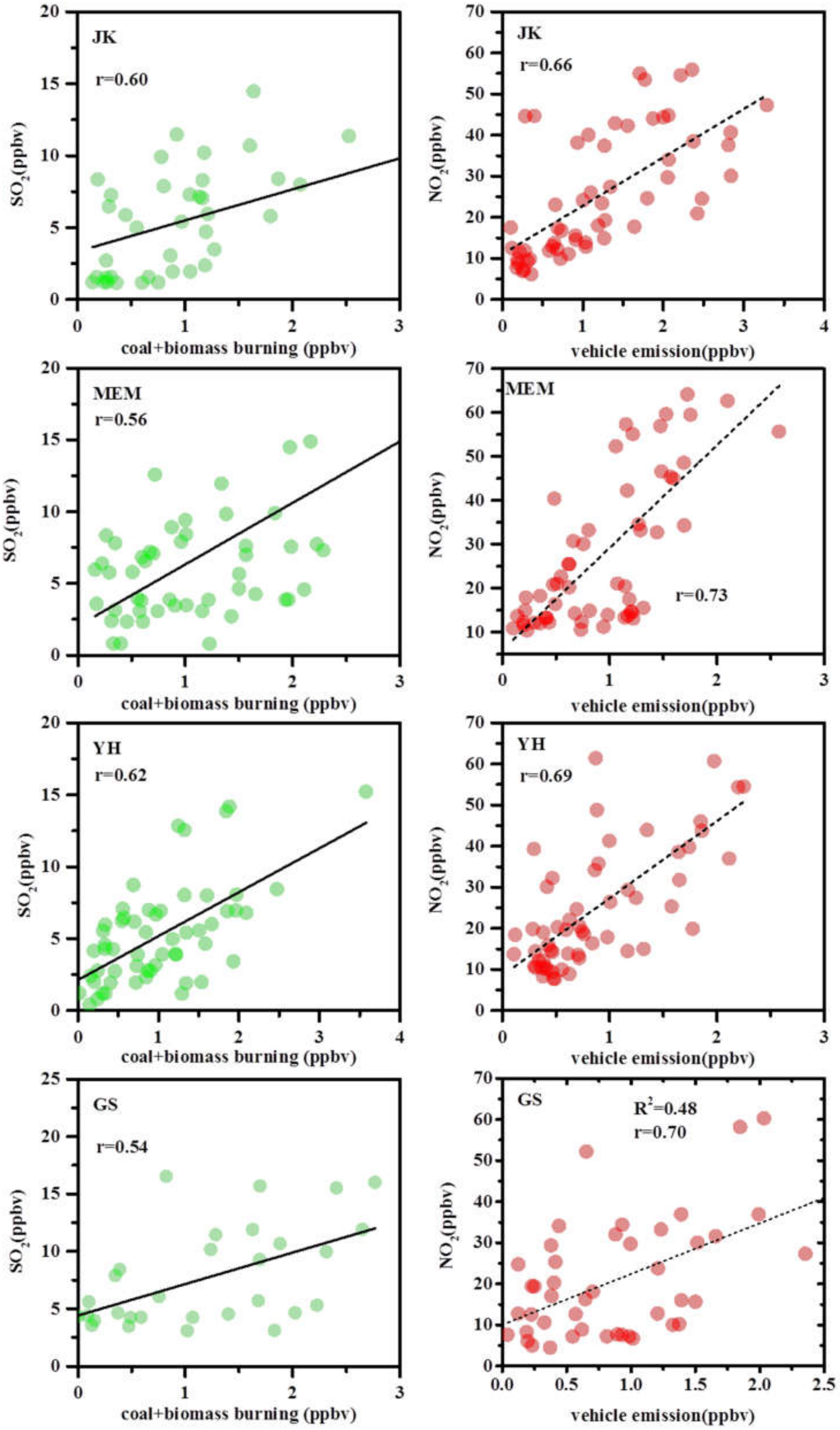


Fig. 16 Correlation analysis between contributions of coal+biomass burning and SO_2, and vehicle emission and NO_2

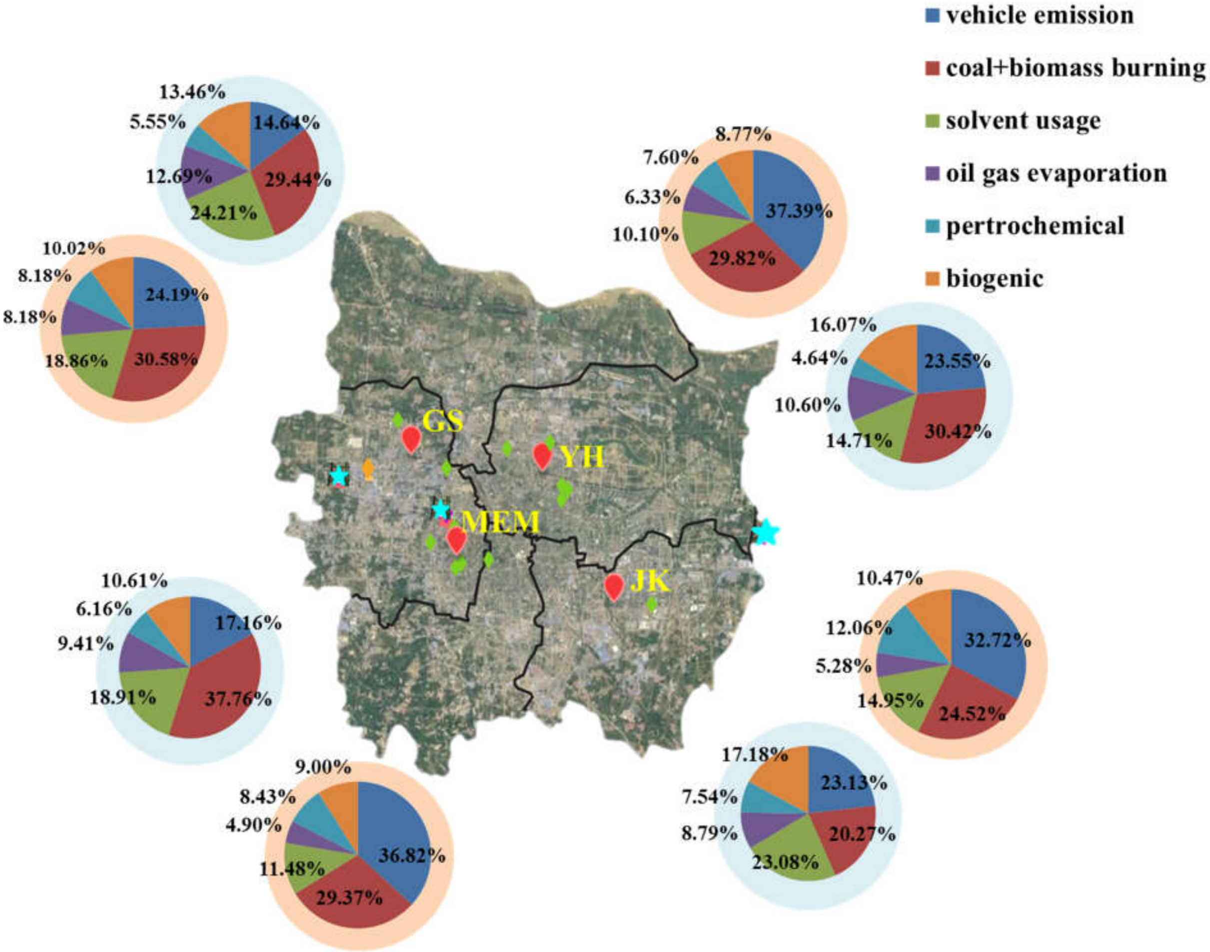


Fig. 17 Source apportionment results during the whole sampling period. The results weighted in observed concentrations were shadowed with pink color, and the results estimated based on OFP were shadowed with light blue color.

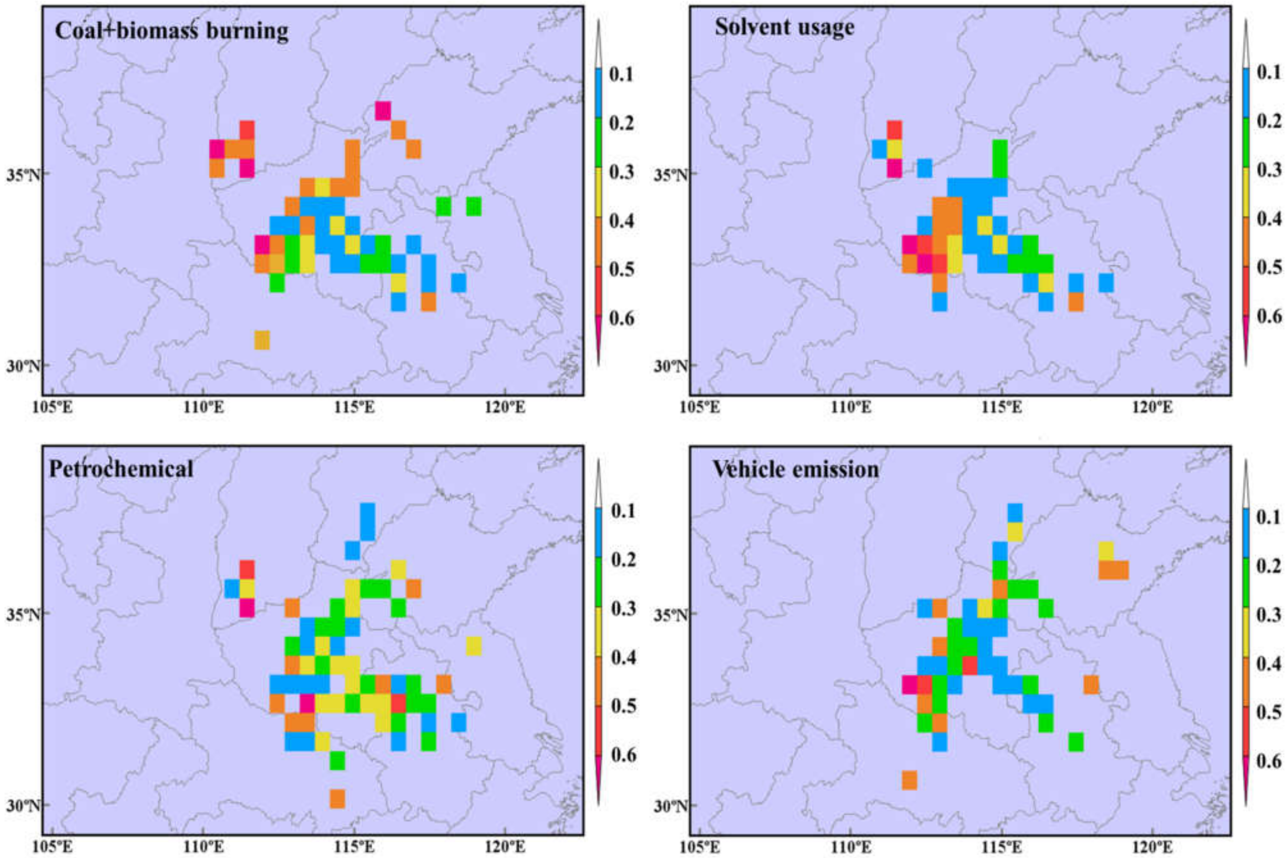


Fig. 18 Probable source regions apportioned by PSCF at Zhengzhou at summer (June-Aug. 2017) during sampling period

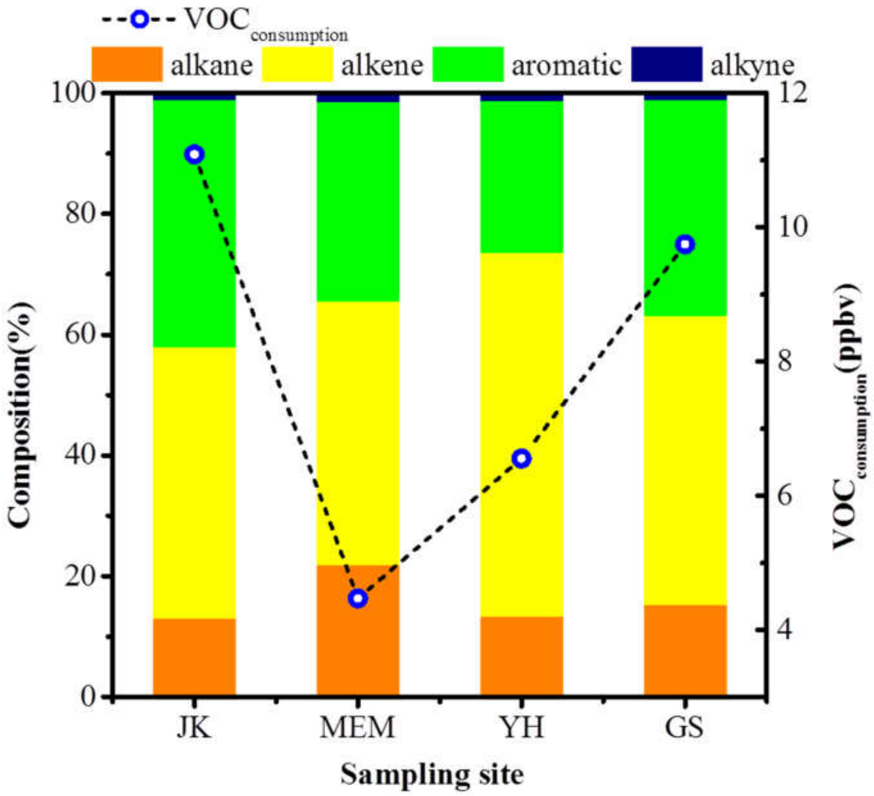


Fig. 19 The composition of major groups based on chemical consumption and the total consumption at each site.

Reference

Abeleira, A., Pollack, I. B., Sive, B., Zhou, Y., Fischer, E. V., and Farmer, D. K.: Source characterization of volatile organic compounds in the Colorado Northern Front Range Metropolitan Area during spring and summer 2015, Journal of Geophysical Research: Atmospheres, 10.1002/2016jd026227, 2017.

Akagi, S. K., Yokelson, R. J., Wiedinmyer, C., Alvarado, M. J., Reid, J. S., Karl, T., Crounse, J. D., and Wennberg, P. O.: Emission factors for open and domestic biomass burning for use in atmospheric models, Atmospheric Chemistry and Physics, 11, 4039-4072, 10.5194/acp-11-4039-2011, 2011.

An, J., Zhu, B., Wang, H., Li, Y., Lin, X., and Yang, H.: Characteristics and source apportionment of VOCs measured in an industrial area of Nanjing, Yangtze River Delta, China, Atmospheric Environment, 97, 206-214, 10.1016/j.atmosenv.2014.08.021, 2014.

Barletta, B., Meinardi, S., Sherwood Rowland, F., Chan, C.-Y., Wang, X., Zou, S., Yin Chan, L., and Blake, D. R.: Volatile organic compounds in 43 Chinese cities, Atmospheric Environment, 39, 5979-5990, 10.1016/j.atmosenv.2005.06.029, 2005.

Carter, W. P. L.: Development of Ozone Reactivity Scales for Volatile Organic Compounds, Air & Waste Manage., 44, 881-899, 1994.

Carter, W.P.L., 2010. Development of the SAPRC-07 chemical mechanism and updated ozone reactivity scale. Available at: http://www.cert.ucr.edu/ wcarter/SAPRC.

Chen, S.-P., Liu, T.-H., Chen, T.-F., Yang, C.-F. O., Wang, J.-L., and Chang, J. S.: Diagnostic Modeling of PAMS VOC Observation, Environ. Sci. Technol., 44, 4635–4644, 2010.

Chen, W. T., Shao, M., Lu, S. H., Wang, M., Zeng, L. M., Yuan, B., and Liu, Y.: Understanding primary and secondary sources of ambient carbonyl compounds in Beijing using the PMF model, Atmospheric Chemistry and Physics, 14, 3047-3062, 10.5194/acp-14-3047-2014, 2014.

Cheng, L., Fu, L., Angle, R. P., and Sandhu, H. S.: Seasonal variations of volatile organic compounds in Edmonton, Alberta, Atmospheric Environment, 31, 239-246, 1997.

Duan, J., Tan, J., Yang, L., Wu, S., and Hao, J.: Concentration, sources and ozone formation potential of volatile organic compounds (VOCs) during ozone episode in Beijing, Atmospheric Research, 88, 25-35, 10.1016/j.atmosres.2007.09.004, 2008.

Gao, W., Tie, X., Xu, J., Huang, R., Mao, X., Zhou, G., and Chang, L.: Long-term trend of O3 in a mega City (Shanghai), China: Characteristics, causes, and interactions with precursors, The Science of the total environment, 603-604, 425-433, 10.1016/j.scitotenv.2017.06.099, 2017.

Geng, N., Wang, J., Xu, Y., Zhang, W., Chen, C., and Zhang, R.: PM2.5 in an industrial district of Zhengzhou, China: Chemical composition and source apportionment, Particuology, 11, 99-109, 10.1016/j.partic.2012.08.004, 2013.

Gentner, D. R., Worton, D. R., Isaacman, G., Davis, L. C., Dallmann, T. R., Wood, E. C., Herndon, S. C., Goldstein, A. H., and Harley, R. A.: Chemical composition of gas-phase organic carbon emissions from motor vehicles and implications for ozone production, Environmental science & technology, 47, 11837-11848, 10.1021/es401470e, 2013.

Gilman, J. B., Lerner, B. M., Kuster, W. C., and de Gouw, J. A.: Source signature of volatile organic compounds from oil and natural gas operations in northeastern Colorado, Environmental science & technology, 47, 1297-1305, 10.1021/es304119a, 2013.

Gong, M., Yin, S., Gu, X., Xu, Y., Jiang, N., and Zhang, R.: Refined 2013-based vehicle emission inventory and its spatial and temporal characteristics in Zhengzhou, China, The Science of the total environment, 599-600, 1149-1159, 10.1016/j.scitotenv.2017.03.299, 2017.

Guo, H., Cheng, H. R., Ling, Z. H., Louie, P. K., and Ayoko, G. A.: Which emission sources are responsible for the volatile organic compounds in the atmosphere of Pearl River Delta?, Journal of hazardous materials, 188, 116-124, 10.1016/j.jhazmat.2011.01.081, 2011.

Guo, H., Ling, Z. H., Cheng, H. R., Simpson, I. J., Lyu, X. P., Wang, X. M., Shao, M., Lu, H. X., Ayoko, G., Zhang, Y. L., Saunders, S. M., Lam, S. H. M., Wang, J. L., and Blake, D. R.: Tropospheric volatile organic compounds in China, The Science of the total environment, 574, 1021-1043, 10.1016/j.scitotenv.2016.09.116, 2017.

Guo, S., Tan, J., Duan, J., Ma, Y., Yang, F., He, K., and Hao, J.: Characteristics of atmospheric non-methane hydrocarbons during haze episode in Beijing, China, Environmental monitoring and assessment, 184, 7235-7246, 10.1007/s10661-011-2493-9, 2012.

Hanna, S. R., Moore, G. E., and Fernau, M.: Evaluation of photochemical grid models (UAM-IV, UAM-V, and the ROM/UAM-IV couple) using data from the Lake Michigan Ozone Study (LMOS) Atmospheric Environment 30, 3265-3279, 1996.

Hidy, G. M., and Blanchard, C. L.: Precursor reductions and ground-level ozone in the Continental United States, Journal of the Air & Waste Management Association, 65, 1261-1282, 10.1080/10962247.2015.1079564, 2015.

Ho, K. F., Lee, S. C., Ho, W. K., Blake, D. R., Cheng, Y., Li, Y. S., Ho, S. S. H., Fung, K., Louie, P. K. K., and Park, D.: Vehicular emission of volatile organic compounds (VOCs) from a tunnel study in Hong Kong, Atmos. Chem. Phys., 9, 7491–7504, 2009.

Hopke, P. K., Barrie, L. A., Li, S.-M., M.-D.Cheng, C.Li, and Xie, Y.: Possible sources and preferred pathways for biogenic and non-sea-salt sulfur for the high Arctic Journal of Geophysical Research, 100, 16,595-516,603, 1995.

Huang, X., Zhang, Y., Yang, W., Huang, Z., Wang, Y., Zhang, Z., He, Q., Lü, S., Huang, Z., Bi, X., and Wang, X.: Effect of traffic restriction on reducing ambient volatile organic compounds (VOCs): Observation-based evaluation during a traffic restriction drill in Guangzhou, China, Atmospheric Environment, 161, 61-70, 10.1016/j.atmosenv.2017.04.035, 2017.

Huang, Y., Ling, Z. H., Lee, S. C., Ho, S. S. H., Cao, J. J., Blake, D. R., Cheng, Y., Lai, S. C., Ho, K. F., Gao, Y., Cui, L., and Louie, P. K. K.: Characterization of volatile organic compounds at a roadside environment in Hong Kong: An investigation of influences after air pollution control strategies, Atmospheric Environment, 122, 809-818, 10.1016/j.atmosenv.2015.09.036, 2015.

Jia, C., Mao, X., Huang, T., Liang, X., Wang, Y., Shen, Y., Jiang, W., Wang, H., Bai, Z., Ma, M., Yu, Z., Ma, J., and Gao, H.: Non-methane hydrocarbons (NMHCs) and their contribution to ozone formation potential in a petrochemical industrialized city, Northwest China, Atmospheric Research, 169, 225-236, 10.1016/j.atmosres.2015.10.006, 2016.

Jiang, X., Guenther, A., Potosnak, M., Geron, C., Seco, R., Karl, T., Kim, S., Gu, L., and Pallardy, S.: Isoprene emission response to drought and the impact on global atmospheric chemistry, Atmospheric Environment, 183, 69-83, 10.1016/j.atmosenv.2018.01.026, 2018.

Jin, X., and Holloway, T.: Spatial and temporal variability of ozone sensitivity over China observed from the Ozone Monitoring Instrument, Journal of Geophysical Research: Atmospheres, 120, 7229-7246, 10.1002/2015jd023250, 2015.

Jobson, B. T., Berkowitz, C. M., Kuster, W. C., Goldan, P. D., Williams, E. J., Fesenfeld, F. C., Apel, E. C., Karl, T., Lonneman, W. A., and Riemer, D.: Hydrocarbon source signatures in Houston, Texas: Influence of the petrochemical industry, Journal of Geophysical Research, 109, 10.1029/2004jd004887, 2004.

Lau, A. K., Yuan, Z., Yu, J. Z., and Louie, P. K.: Source apportionment of ambient volatile organic compounds in Hong Kong, The Science of the total environment, 408, 4138-4149, 10.1016/j.scitotenv.2010.05.025, 2010.

Li, B., Ho, S. S. H., Xue, Y., Huang, Y., Wang, L., Cheng, Y., Dai, W., Zhong, H., Cao, J., and Lee, S.: Characterizations of volatile organic compounds (VOCs) from vehicular emissions at roadside environment: The first comprehensive study in Northwestern China, Atmospheric Environment, 161, 1-12, 10.1016/j.atmosenv.2017.04.029, 2017a.

Li, K., Chen, L., Ying, F., White, S. J., Jang, C., Wu, X., Gao, X., Hong, S., Shen, J., Azzi, M., and Cen, K.: Meteorological and chemical impacts on ozone formation: A case study in Hangzhou, China, Atmospheric Research, 10.1016/j.atmosres.2017.06.003, 2017b.

Li, L., and Wang, X.: Seasonal and diurnal variations of atmospheric non-methane hydrocarbons in Guangzhou, China, International journal of environmental research and public health, 9, 1859-1873, 10.3390/ijerph9051859, 2012.

Li, L., Chen, Y., Zeng, L., Shao, M., Xie, S., Chen, W., Lu, S., Wu, Y., and Cao, W.: Biomass burning contribution to ambient volatile organic compounds (VOCs) in the Chengdu–Chongqing Region (CCR), China, Atmospheric Environment, 99, 403-410, 10.1016/j.atmosenv.2014.09.067, 2014.

Li, Q., Zhang, L., Wang, T., Wang, Z., Fu, X., and Zhang, Q.: "New" Reactive Nitrogen Chemistry Reshapes the Relationship of Ozone to Its Precursors, Environmental science & technology, 52, 2810-2818, 10.1021/acs.est.7b05771, 2018.

Lin, X., Traner, M., and Liu, S. C.: On the Nonlinearity of the Tropospheric Ozone Production, Journal Of Geophysical Research, 93, 15879-15888, 1998.

Liu, B., Liang, D., Yang, J., Dai, Q., Bi, X., Feng, Y., Yuan, J., Xiao, Z., Zhang, Y., and Xu, H.: Characterization and source apportionment of volatile organic compounds based on 1-year of observational data in Tianjin, China, Environmental pollution, 218, 757-769, 10.1016/j.envpol.2016.07.072, 2016.

Liu, C., Ma, Z., Mu, Y., Liu, J., Zhang, C., Zhang, Y., Liu, P., and Zhang, H.: The levels, variation characteristics, and sources of atmospheric non-methane hydrocarbon compounds during wintertime in Beijing, China, Atmospheric Chemistry and Physics, 17, 10633-10649, 10.5194/acp-17-10633-2017, 2017.

Liu, Y., Shao, M., Fu, L., Lu, S., Zeng, L., and Tang, D.: Source profiles of volatile organic compounds (VOCs) measured in China: Part I, Atmospheric Environment, 42, 6247-6260, 10.1016/j.atmosenv.2008.01.070, 2008.

Liu, Y., Yuan, B., Li, X., Shao, M., Lu, S., Li, Y., Chang, C. C., Wang, Z., Hu, W., Huang, X., He, L., Zeng, L., Hu, M., and Zhu, T.: Impact of pollution controls in Beijing on atmospheric oxygenated volatile organic compounds (OVOCs) during the 2008 Olympic Games: observation and modeling implications, Atmospheric Chemistry and Physics, 15, 3045-3062, 10.5194/acp-15-3045-2015, 2015.

Louie, P. K. K., Ho, J. W. K., Tsang, R. C. W., Blake, D. R., Lau, A. K. H., Yu, J. Z., Yuan, Z., Wang, X., Shao, M., and Zhong, L.: VOCs and OVOCs distribution and control policy implications in Pearl River Delta region, China, Atmospheric Environment, 76, 125-135, 10.1016/j.atmosenv.2012.08.058, 2013.

Luecken, D. J., Napelenok, S. L., Strum, M., Scheffe, R., and Phillips, S.: Sensitivity of Ambient

Atmospheric Formaldehyde and Ozone to Precursor Species and Source Types Across the United States, Environmental science & technology, 52, 4668-4675, 10.1021/acs.est.7b05509, 2018.

Lyu, X. P., Chen, N., Guo, H., Zhang, W. H., Wang, N., Wang, Y., and Liu, M.: Ambient volatile organic compounds and their effect on ozone production in Wuhan, central China, The Science of the total environment, 541, 200-209, 10.1016/j.scitotenv.2015.09.093, 2016.

Malley, C. S., Braban, C. F., Dumitrean, P., Cape, J. N., and Heal, M. R.: The impact of speciated VOCs on regional ozone increment derived from measurements at the UK EMEP supersites between 1999 and 2012, Atmospheric Chemistry and Physics, 15, 8361-8380, 10.5194/acp-15-8361-2015, 2015.

McGaughey, G. R., Desai, N. R., Allen, D. T., Seila, R. L., Lonneman, W. A., Fraser, M. P., Harley, R. A., Pollack, A. K., Ivy, J. M., and Price, J. H.: Analysis of motor vehicle emissions in a Houston tunnel during the Texas Air Quality Study 2000, Atmospheric Environment, 38, 3363-3372, 10.1016/j.atmosenv.2004.03.006, 2004.

Mu, B., Mayer, A. L., He, R., and Tian, G.: Land use dynamics and policy implications in Central China: A case study of Zhengzhou, Cities, 58, 39-49, 10.1016/j.cities.2016.05.012, 2016.

Na, K., Kim, Y. P., Moon, K.-C., Moon, I., and Fung, K.: Concentrations of volatile organic compounds in an industrial area of Korea, Atmospheric Environment 35, 2747-2756, 2001.

Nagashima, T., Sudo, K., Akimoto, H., Kurokawa, J., and Ohara, T.: Long-term change in the source contribution to surface ozone over Japan, Atmospheric Chemistry and Physics, 17, 8231-8246, 10.5194/acp-17-8231-2017, 2017.

Ou, J., Zheng, J., Li, R., Huang, X., Zhong, Z., Zhong, L., and Lin, H.: Speciated OVOC and VOC emission inventories and their implications for reactivity-based ozone control strategy in the Pearl River Delta region, China, The Science of the total environment, 530-531, 393-402, 10.1016/j.scitotenv.2015.05.062, 2015.

Ou, J., Yuan, Z., Zheng, J., Huang, Z., Shao, M., Li, Z., Huang, X., Guo, H., and Louie, P. K.: Ambient Ozone Control in a Photochemically Active Region: Short-Term Despiking or Long-Term Attainment?, Environmental science & technology, 50, 5720-5728, 10.1021/acs.est.6b00345, 2016.

Pal, S., Xueref-Remy, I., Ammoura, L., Chazette, P., Gibert, F., Royer, P., Dieudonné, E., Dupont, J. C., Haeffelin, M., Lac, C., Lopez, M., Morille, Y., and Ravetta, F.: Spatio-temporal variability of the atmospheric boundary layer depth over the Paris agglomeration: An assessment of the impact of the urban heat island intensity, Atmospheric Environment, 63, 261-275, 10.1016/j.atmosenv.2012.09.046, 2012.

Polissar, A. V., Hopke, P. K., Paatero, P., Kaufmann, Y. J., Hall, D. K., Bodhaine, B. A., Dutton, E. G., and Harris, J. M.: The aerosol at Barrow, Alaska: long-term trends and source locations, Atmospheric Environment 33, 2441-2458, 1999.

Pollack, I. B., Ryerson, T. B., Trainer, M., Neuman, J. A., Roberts, J. M., and Parrish, D. D.: Trends in ozone, its precursors, and related secondary oxidation products in Los Angeles, California: A synthesis of measurements from 1960 to 2010, Journal of Geophysical Research: Atmospheres, 118, 5893-5911, 10.1002/jgrd.50472, 2013.

Raysoni, A. U., Stock, T. H., Sarnat, J. A., Chavez, M. C., Sarnat, S. E., Montoya, T., Holguin, F., and Li, W. W.: Evaluation of VOC concentrations in indoor and outdoor microenvironments at near-road schools, Environmental pollution, 231, 681-693, 10.1016/j.envpol.2017.08.065, 2017.

Russo, R. S., Zhou, Y., White, M. L., Mao, H., Talbot, R., and Sive, B. C.: Multi-year (2004–2008) record of nonmethane hydrocarbons and halocarbons in New England: seasonal variations and regional sources, Atmospheric Chemistry and Physics, 10, 4909-4929, 10.5194/acp-10-4909-2010, 2010.

Sahu, L. K., Tripathi, N., and Yadav, R.: Contribution of biogenic and photochemical sources to ambient VOCs during winter to summer transition at a semi-arid urban site in India, Environmental pollution, 229, 595-606, 10.1016/j.envpol.2017.06.091, 2017.

Shao, M., Lu, S., Liu, Y., Xie, X., Chang, C., Huang, S., and Chen, Z.: Volatile organic compounds measured in summer in Beijing and their role in ground-level ozone formation, Journal of Geophysical Research, 114, 10.1029/2008jd010863, 2009.

Shao, M., Wang, B., Lu, S., Yuan, B., and Wang, M.: Effects of Beijing Olympics Control Measures on Reducing Reactive Hydrocarbon Species, Environ. Sci. Technol., 45, 514-519, 2011.

Shao, P., An, J., Xin, J., Wu, F., Wang, J., Ji, D., and Wang, Y.: Source apportionment of VOCs and the contribution to photochemical ozone formation during summer in the typical industrial area in the Yangtze River Delta, China, Atmospheric Research, 176-177, 64-74, 10.1016/j.atmosres.2016.02.015, 2016.

Shen, F., Ge, X., Hu, J., Nie, D., Tian, L., and Chen, M.: Air pollution characteristics and health risks in Henan Province, China, Environmental research, 156, 625-634, 10.1016/j.envres.2017.04.026, 2017.

Shiu, C.-J., Liu, S. C., Chang, C.-C., Chen, J.-P., Chou, C. C. K., Lin, C.-Y., and Young, C.-Y.: Photochemical production of ozone and control strategy for Southern Taiwan, Atmospheric Environment, 41, 9324-9340, 10.1016/j.atmosenv.2007.09.014, 2007.

Sillman, S.: The relation between ozone, NOx and hydrocarbons in urban and polluted rural environments, Atmospheric Environment 33, 1821-1845, 1999.

Streets, D. G., Fu, J. S., Jang, C. J., Hao, J., He, K., Tang, X., Zhang, Y., Wang, Z., Li, Z., Zhang, Q., Wang, L., Wang, B., and Yu, C.: Air quality during the 2008 Beijing Olympic Games, Atmospheric Environment, 41, 480-492, 10.1016/j.atmosenv.2006.08.046, 2007.

Sun, J., Wu, F., Hu, B., Tang, G., Zhang, J., and Wang, Y.: VOC characteristics, emissions and contributions to SOA formation during hazy episodes, Atmospheric Environment, 141, 560-570, 10.1016/j.atmosenv.2016.06.060, 2016.

Tang, J. H., Chan, L. Y., Chan, C. Y., Li, Y. S., Chang, C. C., Liu, S. C., Wu, D., and Li, Y. D.: Characteristics and diurnal variations of NMHCs at urban, suburban, and rural sites in the Pearl River Delta and a remote site in South China, Atmospheric Environment, 41, 8620-8632, 10.1016/j.atmosenv.2007.07.029, 2007.

Tsai, S. M., Zhang, J. J., Smith, K. R., Ma, Y., Rasmussen, R. A., and Khalil, M. A. K.: Characterization of Non-methane Hydrocarbons Emitted from Various Cookstoves Used in China, Environ. Sci. Technol., 37, 2869-2877, 2003.

Wang, H.-l., Jing, S.-a., Lou, S.-r., Hu, Q.-y., Li, L., Tao, S.-k., Huang, C., Qiao, L.-p., and Chen, C.-h.: Volatile organic compounds (VOCs) source profiles of on-road vehicle emissions in China, The Science of the total environment, 607-608, 253-261, 10.1016/j.scitotenv.2017.07.001, 2017a.

Wang, H., Qiao, Y., Chen, C., Lu, J., Qiao, L., and Lou, S.: Source Profiles and Chemical Reactivity of Volatile Organic Compounds from Solvent Use in Shanghai, China, Aerosol and Air Quality Research, 10.4209/aaqr.2013.03.0064, 2014.

Wang, M., Shao, M., Lu, S.-H., Yang, Y.-D., and Chen, W.-T.: Evidence of coal combustion contribution to ambient VOCs during winter in Beijing, Chinese Chemical Letters, 24, 829-832, 10.1016/j.cclet.2013.05.029, 2013.

Wang, M., Shao, M., Chen, W., Lu, S., Liu, Y., Yuan, B., Zhang, Q., Zhang, Q., Chang, C. C., Wang, B., Zeng, L., Hu, M., Yang, Y., and Li, Y.: Trends of non-methane hydrocarbons (NMHC) emissions in Beijing during 2002–2013, Atmospheric Chemistry and Physics, 15, 1489-1502, 10.5194/acp-15-1489-2015, 2015.

Wang, T., Xue, L., Brimblecombe, P., Lam, Y. F., Li, L., and Zhang, L.: Ozone pollution in China: A review of concentrations, meteorological influences, chemical precursors, and effects, The Science of the total environment, 575, 1582-1596, 10.1016/j.scitotenv.2016.10.081, 2017b.

Wang, X.-m., Sheng, G.-y., Fu, J.-m., Chan, C.-y., Lee, S.-C., Chan, L. Y., and Wang, Z.-s.: Urban roadside aromatic hydrocarbons in three cities of the Pearl River Delta, People's Republic of China, Atmospheric Environment, 36, 5141–5148, 2002.

Wei, W., Cheng, S., Li, G., Wang, G., and Wang, H.: Characteristics of ozone and ozone precursors (VOCs and NOx) around a petroleum refinery in Beijing, China, Journal of Environmental Sciences, 26, 332-342, 10.1016/s1001-0742(13)60412-x, 2014.

Wu, R., and Xie, S.: Spatial Distribution of Ozone Formation in China Derived from Emissions of Speciated Volatile Organic Compounds, Environmental science & technology, 51, 2574-2583, 10.1021/acs.est.6b03634, 2017.

Xue, Y., Ho, S. S. H., Huang, Y., Li, B., Wang, L., Dai, W., Cao, J., and Lee, S.: Source apportionment of VOCs and their impacts on surface ozone in an industry city of Baoji, Northwestern China, Scientific Reports, 7, 9979, 10.1038/s41598-017-10631-4, 2017.

Yan, Y., Peng, L., Li, R., Li, Y., Li, L., and Bai, H.: Concentration, ozone formation potential and source analysis of volatile organic compounds (VOCs) in a thermal power station centralized area: A study in Shuozhou, China, Environmental pollution, 223, 295-304, 10.1016/j.envpol. 2017.01. 026, 2017.

Yuan, B., Shao, M., de Gouw, J., Parrish, D. D., Lu, S., Wang, M., Zeng, L., Zhang, Q., Song, Y., Zhang, J., and Hu, M.: Volatile organic compounds (VOCs) in urban air: How chemistry affects the interpretation of positive matrix factorization (PMF) analysis, Journal of Geophysical Research: Atmospheres, 117, n/a-n/a, 10.1029/2012jd018236, 2012.

Zhang, J., Sun, Y., Wu, F., Sun, J., and Wang, Y.: The characteristics, seasonal variation and source apportionment of VOCs at Gongga Mountain, China, Atmospheric Environment, 88, 297-305, 10.1016/j.atmosenv.2013.03.036, 2014.

Zhang, Z., Wang, X., Zhang, Y., Lu, S., Huang, Z., Huang, X., and Wang, Y.: Ambient air benzene at background sites in China's most developed coastal regions: exposure levels, source implications and health risks, The Science of the total environment, 511, 792-800, 10.1016/j.scitotenv.2015.01.003, 2015.

Zhu, Y., Yang, L., Chen, J., Wang, X., Xue, L., Sui, X., Wen, L., Xu, C., Yao, L., Zhang, J., Shao, M., Lu, S., and Wang, W.: Characteristics of ambient volatile organic compounds and the influence of biomass burning at a rural site in Northern China during summer 2013, Atmospheric Environment, 124, 156-165, 10.1016/j.atmosenv.2015.08.097, 2016.