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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Impact of VOCs on the formation of ozone in a central China city during severe pollution periods" *by* Bowei Li et al.

Anonymous Referee #2

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The authors present the results from a measurement campaign conducted over 5 months (May-Sept 2017) at 4 locations in Zhengzhou City during which VOCs were collected and analysed using whole air sampling techniques. This is the first such study to be carried out in Zhengzhou and authors are able to identify the key source sectors of the principal VOCs using positive matrix factorization (PMF).

However, the dataset is limited: whole air samples were collected at two specific times on 10 days of each month and for only a single year. The authors do not present any evidence that meteorological conditions in Zhengzhou in 2017 were typical of the local long-term climate. While PMF does identify the main pollution sources for those sites and those days it is hard to draw long-term conclusions from this study. In particular, the 10 sampling days each month were chosen to ensure optimum sampling conditions

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which would suggest certain synoptic conditions (air mass origins) would be favoured over others introducing a bias into the results.

The authors state their motivation for the study is the trend of increasing ozone in Zhengzhou yet this data and their analysis do not address this, and are unable to with only a single year.

Before commenting further on the details of the study I would like to raise two points:

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.

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.

Major concerns:

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.

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.

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

I cannot over-emphasise 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 refelected 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.

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 colour-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 visualisation tools.

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.

Specific comments:

Given the need for English editing and proof-reading I make only general comments or questions about each section here.

Introduction:

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.

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.

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

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

Experimental:

Sampling site:

What was the sampling duration and flow rate?

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?

Chemical analysis:

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))

QA/QC:

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

PMF:

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.

Results and discussions

Mixing ratios and meteorological variations:

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

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.

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

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? . . .

L205: Likewise I don’t understand what the authors mean by “topographical effect”

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The authors now devote a great deal of time to presenting mixing ratios and relative abundances of a range of VOCs and attributing this to possible local sources. I have two comments regarding this:

1. 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.

2. 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.

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.

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

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)

Temporal variations:

L261: "wash-out" specifically refers to rain which I don't think is what the authors mean

L276: "sharp changes in local emissions" - such as?

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

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

Spatial variations:

L298-299: O3-NOx-VOC interactions and reactions are always highly complex and non-linear, hence the development of ozone isopleths (see e.g. Silman, 1999)

L300: Is this peak (i.e. hourly) O3 or 8-hour O3?

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

L321-323: “when synoptic conditions were favourable” - 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.

Ratios of specific compounds:

Please give typical T/B ratios for relevant sources.

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.

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

L340-342: The absolute values should be reported before the R2 value.

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?

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

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

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

Presumably the wind direction differed between days.

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

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.

Reactive chemicals:

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.

L392-395: The authors need to make it abundantly clear that this is an entirely hypothetical potential (or maximum) possible O3 formation for each compound in isolation.

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 O3 formation to be the same across different regions with different sources and different meteorological conditions.

L401: "fraction" rather than "composition"?

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

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

Source apportionment:

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.

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

L423-424: As suggested previously, I would move Table 6 to SI together with the de-

tailed mathematical description of the method

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

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

I suggest the authors emphasise 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 SO2 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. Emphasise the unique markers of each.

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?

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)?

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

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?

Long-range transport:

This entire section should be moved forward and presented ahead of all the sections describing possible local sources of precursor emissions. As O3 is a secondary pollutant, regional and long-range transport is typically the greatest source.

Figures and Tables

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.

Fig. 6: This plot is unacceptably crowded making it too complex to be easily interpreted. There are 4 different symbols each with 5 different colours to decipher. It is far too small to make out most of the points on it and to add to the difficulty each site uses a different scale! At the very least one separate plot is required for each site. The caption should explain the different colours used and point out that the scales vary.

Fig. 7: See previous comments regarding the use of reverse vertical axes.

A windrose plot would be a far more useful way to present the data (see previous comments regarding the importance of wind direction).

The authors have not explained in the main text the significance of RH<45%

Fig. 8: The caption needs expanding and clarifying (or rather I don't understand it)

Fig. 9: It would also be useful to see a month-by-month breakdown as the authors have reported differences in VOCs and in O3 across the sampling period.

Fig. 10: This should be included with Fig. 1 (see previous comments regarding the importance of air mass origin)

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