

Review for “Characteristics and sources of VOCs and the O₃-NO_x-VOC relationships in the central plain city, China.

Summary:

This manuscript presents an interesting study, investigating what is driving ozone production in the region of Zhengzhou. The authors have investigated both the reactivity of individual/grouped VOCs as well as a source apportionment analysis, and a box model has been used to produce an ozone production isopleth. Whilst these are the key sections crucial to any exploration of the O₃-NO_x-VOC relationships in an urban centre, the authors could work on adding some more detail to each section. In addition, more work is needed to bring together all of the results sections, with more discussion on what the data is telling us and what this could mean for what is driving ozone production. With these changes in place, I would recommend this manuscript for publication in the Journal of Atmospheric Chemistry and Physics.

This manuscript is generally well written, with a small number of couple of grammatical mistakes (e.g. line 74: is in a VOCs-limited regimes, change to “is in a VOC-limited regime”).

Some conclusions are made throughout the manuscript that are not so clearly backed up by the results. The authors could add some more quantification (e.g. percentage differences), when comparing Case 1, Case 2 and clean days. If the main message is that the sources are the same during both polluted and clean days, this needs to be made clearer. If this is the case, what could be driving the ozone production? Is it elevated concentrations? Could it be temperature? This can all be brought together in the conclusions.

The authors should include an expanded version of Table 1, which shows average mixing ratios for all the VOCs measured. It should also be made clear which of these VOCs are used in which part of the study (e.g. OBM, source apportionment etc.). The should be made available in the supplementary.

The authors should also consider changing the title from “central plain city, China” to the name of the city (Zhengzhou) for clarity.

To improve the coherency of the manuscript, the authors should bring together findings from previous sections into the next section. For example, there are sections on concentrations and sources of a variety of VOCs, but then the last results section ignores that knowledge and just focuses on varying AVOCs by bulk.

The author should incorporate the results from previous sections into this last section. For example, how does O₃ production change when NO_x is varied alongside reductions in each source respectively?

The conclusions should bring together all of the findings of each results section.

Detailed comments:

- 44 Remove “of course”
- 199 Although I recognise that additional details on the GC-MS instrumentation can be found in a previous publication, the authors should include a few more details about instrumentation in the sample collection section. What is the time resolution of samples? How long were samples captured for? What were they captured in, and how long were they left before being analysed by the instrumentation?
- 147 CPF is described as a “new source identification tool”, but papers from 2006 and 2007 are referenced. Is this technique new? Have there been new applications of this?
- 154 The MCM is no longer hosted at the University of Leeds and hasn’t been for a while. I suggest you provide the new working link, hosted by the University of York (<https://mcm.york.ac.uk/MCM/>).
- 164 The authors should also describe how they have calculated $P(O_3)$ from the model, if this was not a direct output. If the authors are using a specific box model (e.g. DSMACC, AtChem2), please specify which one and include the appropriate references.
- 170 Was any interpolation or averaging of the data performed to generate 1 h time resolution data for the model?
- 171 Why was WS constrained in your box model? This parameter is not used by the MCM. Was it used to calculate other factors in your model?
- 172 Please list all the measured VOCs, indicating which ones were selected, in a table. It would also be helpful to see average concentrations for these compounds. All of this should be presented in the supplementary.
- 173 What are the default values for $j(H_2O_2)$ and $j(O_1D)$ and planetary boundary layer? Do you think these are representative of the site? Have any dilution rates been applied to compounds generated in the model, and if so, are these varied based on the default PBLH? The authors need to highlight why these values were used. If measured or modelled values cannot be used, it is important to discuss the uncertainties associated with using default values for your results.
- 180 Please provide more context for why a value of 0.6 indicates the model is performing well. What is the acceptable range for this value to be? Which

- compound did you evaluate the performance of the model using? What was constrained in the model when you did this, and what was the model left to calculate. Much more detail is required here.
- 189 What is meant by “short pollution process”? Do you mean that the pollution event was too short, and you only looked at periods where pollution remained high for at least a week for better data coverage? Please clarify.
- 224 This is a very large proportion of halocarbons. It would be really interesting to see which VOCs are included in each category in your study, and what the average mixing ratios were across the sampling period. Please include this as an expanded version of Table 1 in the supplementary.
- 231 Remove “if”
- 236 Explain what you mean by the “top fifteen VOC species”. Do you mean the highest average mixing ratio? If so, please replace “top” with something like “the fifteen VOCs with the highest average mixing ratio across the observation period.”
- 253 “As illustrated in the following PMF source apportionment”. Where is this? I cannot see any source apportionment in this section, just some discussion of the possible sources of different VOCs from the literature.
- 255 I don’t understand what Figure 2 shows. What does the line represent and what are the bars? What are the authors trying to say using this figure?
- 260 “Major” VOCs – why exactly were these selected? You could either just say “a selection of VOCs”, or if you are pointing out that these are the major ones, you need to explain why.
- 264 “photochemical reaction” – change to “photochemical reactivity”, as there are multiple photochemical reactions happening.
- 271 Explain what you mean by “the daily change was consistent with NO_x ”.
- 273 What are “traditional nighttime activities”?
- 279 Acetone is a “common VOC” – what does this mean? Consider changing the language.
- 297 Could it be that the pentanes come from a mix of sources? The text implies that for Case 1, Case 2 and clean days, the sources are exclusively NG emissions, Vehicular exhaust emissions, and liquid gasoline emissions respectively.
- 311 Was this value 0.5 for all three case? How does this ratio vary with wind speed? Perhaps this could further support the argument of E/X rations indicating that air masses were affected by transport?

- 315 Generally for this section, more discussion of the potential locations of some of these sources would be good to see. There are two solvent factors. Why is this? Different industrial sources? Are there any industrial sources in the northeast and southeast of the site? For factor 7, are there any industrial sites near the observation site? Are the source apportionment factors consistent with the geography of the site?
- 369 This is really interesting. Are you saying that O₃ pollution events appear to be independent of the VOC sources, and these remain broadly similar? If this is the case, then what is driving these O₃ pollution events. Is it the meteorology?
- 383 This is the wrong way around - O₃ formation was more sensitive to biogenic emissions, not “biogenic emissions was more sensitive to O₃ formation”.
- 385 From Figure 6, the RIRs look broadly similar between Case 1, Case 2, and clean. In the text, the authors have suggested there is a difference between clean and polluted days. Could you please quantify what this difference is? For example, what is the percentage difference in RIRs during polluted days, and is this significant?
- 408 Please clarify which data you have used to generate the Isopleth in Figure 7. Have you used the average peak O₃ across the entire observation period? Or is this the average daytime O₃ between particular hours? There is a point for “base case”, but it would be interesting to see where Case1, Case2 and clean days would appear on this isopleth.
- 451 This seems quite general, after the detail you have gone into earlier on the RIRs for VOC groups and looking closely at different sources. I understand why biogenic compounds have not been included, but the impact of these should be further acknowledged in the text as changes to biogenic emissions present a large uncertainty to how O₃ production might change in the future. It would have been interesting to see how O₃ production might change when the different sources are reduced alongside NO_x. This is more useful to policy than just investigating different percentage changes in bulk AVOCs, as it would be challenging to reduce AVOC emissions in this way.
- 441 You say P(O₃) increases respectively, but what is this respective to? Is this per hour?
- 453 The authors could work on bringing all of these results together in the conclusion, rather than just summarising the key result of each section in turn. What is driving O₃ production? Is it related to sources? Is it the meteorology?
- 465 Olefins mentioned here, earlier referred to as alkenes. Please change to alkenes.

