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Interactive comment on "Spatiotemporal Variation, Sources, and Secondary Transformation Potential of VOCs in Xi'an, China" *by* Mengdi Song et al.

Anonymous Referee #1

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Song et al. investigated the variation, sources, and chemistry of atmospheric VOCs in Xi'an, China. Field observations were conducted in multiple representative sites in Xi'an. Results showed that vehicle emission was the largest VOC contributor, followed by industrial emissions. Results of backward trajectories coupled with potential source contribution function analysis indicated that Xi'an exhibited a strong local VOC source. In addition, the authors demonstrated that alkenes, aromatics, and OVOCs played dominant roles in the secondary transformation of ambient VOCs in Xi'an. The manuscript is very well written, and the results are clearly presented. Therefore, I would like to recommend its publication in Atmospheric Chemistry and Physics, subject to minor changes.

1. Lines 75-80: GC analysis

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Discussion paper

Please provide the details of GC procedures (e.g., oven temperature program) for the analyses of both low carbon number and high carbon number compounds.

2. Line 85: "VOC gridded sampling was performed at 7:00 China Standard Time (CST) and 15:00 (CST) on July 1 and July 14, 2019, respectively."

This sentence is confusing. Were the samples collected at both 7:00 and 15:00 on both July 1 and July 14? Or the samples were collected at 7:00 on July 1 and 15:00 on July 14? Please clarify.

3. Line 89: "Ambient air was sampled into a 3-L SiloniteTM 90 canister (Entech Instrument, United States)."

How long was the sampling time? Or what was the time resolution of the VOC sampling? How many samples were collected per site? Please clarify.

4. Lines 116-117: "VOC tracers with a data integrity greater than 75% and greater than 65% valid data (concentration $\geq$ MDL) were selected as the input species."

This sentence is confusing. Do you mean "VOC tracers with greater than 65% valid data"?

Please explain why 75% and 65% were used.

5. Equation (4): please provide references for the uncertainty estimation.

6. Lines 172-176: the effects of temperature

As shown in Figure 2, the temperature during polluted periods could be 10-15 °C higher than that in the clean days. An increase in temperature can enhance both the emissions and the oxidation rates of VOCs.

Can the authors estimate how much of the ozone increase was due to the increase of VOC emissions and how much was due to the enhancement of VOC oxidation rates during the polluted periods?

7. Figure 4: spatial variations of VOCs

Were the TVOC concentrations shown in Figure 4 two-day average values of July 1 and July 14? If no, please specify which date the figure represents. If yes, please explain why the author used the average concentrations. Following comment 2 above, if the sampling was conducted at 7:00 on July 1 and at 15:00 on July 14, were the meteorological conditions similar during the two sampling periods? Would the results be the same by analyzing the data collected on each individual day?

8. Lines 192-194: "In addition, the contribution of OVOCs at the YT site was significantly higher than that of the other sites, indicating that the YT site may be significantly affected by ageing sources (Figure 4a)."

a) Please provide the VOC list identified in this study in the supporting information.

b) What were the OVOC composition measured in this study? Throughout the manuscript, the authors tended to attribute higher OVOC concentration to stronger atmospheric oxidation. Although this is reasonable to some extent, there is a possibility that OVOCs were directly emitted. For example, acetone can be emitted from sources such as solvent evaporation, biomass burning, and vehicle emission, as also shown in Figure 8.

Can the authors comment on the primary emissions of OVOCs during the campaign? And how will this affect the conclusion regarding OVOCs in this study?

9. Section 3.2.1 Specific VOC Ratios

The methodology using VOC ratios to investigate potential sources provides useful insights. However, the uncertainty may be huge. For example, the authors mentioned that in the industrial region, the concentration ratio of toluene to benzene ranged from 3.0 to 6.9, using the results obtained from Zhengzhou city in China (Li et al., 2019a), the Pearl River Delta region (Chan et al., 2006), and several other developed coastal regions in China (Zhang et al., 2015). I would expect that the industry type and compo-

sition are likely different between Xi'an and the cities/areas mentioned in the references (e.g., coastal regions). How does the T/B ratio vary from location to location? How will this affect the conclusions of this study?

Similar issues may exist in the T/B ratios for other sources. For example, the T/B ratio for vehicle emissions can be strongly influenced by vehicle type and fuel composition. Please discuss the uncertainty of using these ratios.

10. Figures 6a-6c: what are the green lines?

11. Lines 297-301: "There were two trajectory clusters from the southeast direction, the southeast short distance trajectories (Cluster 2) and southeast medium-long distance trajectories (Cluster 4), accounting for 35.2% and 23.5%, respectively. This result indicated that the VOC concentration in the CB site was significantly affected by the southeast trajectory from the junction of the Shaanxi Province, Hubei Province, and Henan Province in addition to local sources."

The PSCF analysis was based on the results of the 24-h backward trajectories. The lifetimes of different VOCs are different in the atmosphere, as also indicated in Table 2. For example, some OVOC species can have much longer lifetimes than reactive alkenes such as ethylene. The long-lived OVOC species may survive through atmospheric oxidation and get transported to Xi'an over 24 h from surrounding provinces. However, reactive species such as ethylene may not be able to.

Can the authors incorporate the lifetime information of different categories of VOCs into the PSCF analysis?

12. Lines 349-350: "the O3 350 concentration in Xi'an urban areas (CB and DHS) often exceeded the national hourly standard of 200 μg/m3 (approximately 101.9 ppb)."

In lines 43-48, the author used a different national standard (i.e., 160 μg/m3). Please be consistent throughout the manuscript.

13. NOx concentration

This study demonstrated that high VOC concentration is a major concern in reducing ozone pollution in Xi'an. However, in addition to VOCs, NOx also plays an indispensable role in tropospheric ozone production. NOx concentration was measured in this study. However, there was little discussion on the effects of NOx concentration on ozone and the interplay among NOx, VOC, and ozone. With the measurement data available, can the authors briefly comment on which regime (VOC-limiting or NOx-limiting) was discussed in this study (e.g., in the urban sites and the rural sites) and corresponding implications?

Technical comments:

1. Line 11: "as a critical precursors of ozone...", remove "a"

2. Line 76: change "low-carbon" and "high-carbon" to "low carbon number" and "high carbon number"

3. Line 187: "Of the sites, XF site exhibited the highest VOC concentration of 54 ppb, followed by CT, HC, with concentrations of 41.4, and 38.2 ppb, respectively"

Please keep consistent the number of significant figures throughout the manuscript.

4. Line 199: missing "to" between "used" and "preliminarily"