Response to reviewers' comments

Referee #1: "The authors have responded well and in detail to each of the comments provided by the reviewers, which has resulted in substantial improvements to the text and figures. I believe this manuscript will now provide a valuable addition to the literature. I would therefore recommend publication in ACP, after the minor comments outlined below have been addressed."

We thank all the reviewers for the constructive comments which have helped to improve the paper substantially. We have carefully addressed the minor comments outlined during the second-round review. Below is our point-by-point response to each comment, marked in blue. Changes made to the main text are marked in red. Revisions made to the manuscript are highlighted.

The main concern raised by both reviewers was the limited evidence provided to support the authors' assertion that the predominant source of fatty acids in this environment is cooking. The revised manuscript contains more detailed consideration of alternatives (eg biomass burning, traffic emissions, coal burning, sea spray). Nevertheless, I still feel there could be more acknowledgement that there could be at least some influence from other sources. For example, in lines 227-228, the authors dismiss the possibility of a sea spray contribution based on the oleic acid/stearic acid ratio from a single study (Bikkina et al., 2019). While this certainly provides evidence in favour of the authors' hypothesis, I would argue that it is not strong enough to conclusively rule out the potential contribution, as the authors have done here.

Response: We agree with the reviewer that there are diverse sources of fatty acids besides cooking, such as biomass burning, traffic emissions, coal burning, sea spray etc. Based on the source profiles from literature, and the observed data from TAG, as well as the anthropogenic source characteristics in Changzhou, we conclude that the predominant source of fatty acids in the Changzhou City is likely to be from cooking sources. In lines 227-228, we mentioned that "The oleic acid/stearic acid (O/S) ratio from sea spray aerosol samples is 0.16 (Bikkin et al., 2019), which is obviously lower than the ambient data in this study (1.4)." From this data as well as location of Changzhou (located in the inland YRD, far away from the sea), we believe that sea spray contribution to fatty acid in Changzhou is negligible. We agree that it is not appropriate to conclusively rule out the potential contribution from other sources, therefore, in the revised manuscript, we have softened the language through out the mansucript.

The new Fig. 4 is a valuable addition as it provides more context. It could be interesting to include data points from non-cooking sources in Fig. 4b, if they are available, as well as the campaign average. This could provide supporting evidence for the claim that the majority of the observed fatty

acids originate from cooking.

Response: We thank the reviewer for the constructive comment. We have added data of non-cooking sources in Fig. 4b, and inserted the references to the figure title of Fig.4.
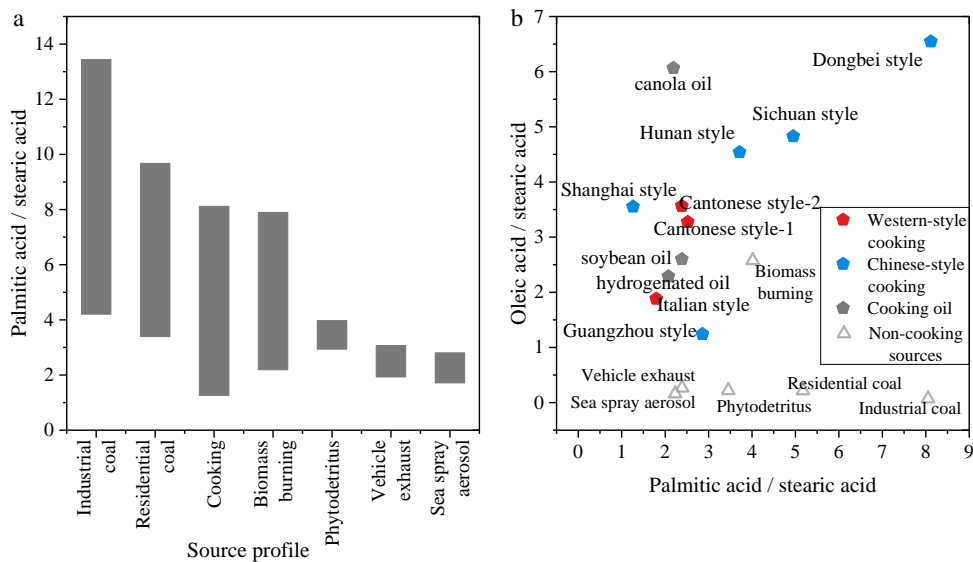

Figure 4. Ratio of fatty acids (P/S) in organic molecular substances emitted directly from different sources (a); Ratio of fatty acids (P/S vs O/S) emitted by different types of cooking sources and non-cooking sources (b). (Bikkin et al., 2019; Cai et al., 2017; Hays et al., 2002; He et al., 2004; Oliveira et al., 2007; Pei et al., 2016; Rogge et al., 1993; Schauer et al., 2001, 2002; Simoneit, 2002; Zhang et al., 2008; Zhao et al., 2007).

Referee #3:

In this study, the authors used TAG techniques to study fatty acid concentrations in the atmosphere, including saturated fatty acids, unsaturated fatty acids, and their oxidative decomposition products. The authors attribute these fatty acid species to emissions from cooking. Their higher time resolution chemical speciation with TAG represents a detailed, valuable dataset, and I appreciate their use of backward trajectories and PMF to understand chemical sources. However, I echo the previous review comments that some of the conclusions here still aren't fully supported by the data. I can see that the authors did carefully address reviewer comments from the first round. I would suggest that the authors further soften the language in the text throughout the manuscript to account for the fact that there is significant uncertainty in the sources of the primary and secondary products observed here. This is a result of field measurements being very challenging to interpret with mixed sources contributing to any one measurement, and I think this needs to be better acknowledged and reflected in the manuscript. I think the manuscript is acceptable for publication in Atmospheric Chemistry and Physics following a careful review of how each conclusion is stated.

Response: We thank the reviewer for the detailed and constructive comments and suggestions. We have carefully checked the manuscript to make sure that the conclusions are clear and could be well supported by the data presented. We agree that it is not appropriate to conclusively rule out the potential contribution from other sources, therefore, in the revised manuscript, we have softened the language. Below is our point-by-point response to each comment, marked in blue. Changes made to the main text are marked in red. Revisions made to the manuscript are highlighted.

Introduction:

1. Line 51: I would be careful with this phrasing, so that you do not attribute all lung cancer to exposure to cooking fumes.

Response: Thanks for the comment. We have revised the description. Please refer to Lines 52-53.

Lines 52-53: "The carcinogenic risk analysis suggested that the potentially adverse health effects induced by cooking sources should not be ignored."

2. Line 62: write out "hydroxyl" and "" and then use the acronyms after you've defined them in words.

Response: We have defined these words in the new manuscript.

Line 61: hydroxyl (OH)

Line 71: "OH and nitrate (NO_3) radicals".

3. I would consider re-organizing the introduction so that you talk about TAG methods (and why

online measurements are important) after introducing cooking emissions more – so perhaps could move lines 55-69 to after lines 70-77.

Response: Thanks for the comment. We have adjusted the order of the TAG methods and cooking emissions in the introduction section. Please refer to Lines 54-78.

Lines 54-78: "Cooking is an important source contributor to $PM_{2.5}$, especially in urban environments. Cooking sources have recently received increasing attention, but they are largely an uncontrolled source of $PM_{2.5}$. Saturated fatty acids (sFAs) and unsaturated fatty acids (uFAs)··The aging of POA markers under atmospheric conditions, however, is still far from being properly understood with few field observations performed in this topic compared to laboratory studies (Bertrand et al., 2018a; Bertrand et al., 2018b). The high timely-resolved observations would help to fill this gap."

Methodology:

4. Line 85: please be more specific about what you mean by "its main chemical constituents as well as organic markers"

Response: We added specific information about "its main chemical constituents as well as organic markers". Please refer to Lines 86-88.

Lines 86-88: "Gaseous pollutants, $PM_{2.5}$ and its main chemical constituents (water soluble ions, carbon components and elements, etc.) as well as organic markers (alkanes, hopanes, polycyclic aromatic hydrocarbons, sugars, alcohols and organic acids, etc.) ·············."

5. Can you comment on any fatty acid losses to your instrument, i.e., in the cyclone, dryer, or denuder?

Response: Thanks for the constructive comment. Regarding the possible material loss during the observation of $PM_{2.5}$ by the TAG instrument, Zhao (2012) conducted relevant experiments at the early stage of the instrument development and explored the collection efficiency of the TAG instrument for different carbon numbers of organic matter and the amount of loss of particles of different particle sizes at the denuder respectively. The results demonstrate that the accuracy of the data obtained from TAG's observations of atmospheric pollutants is high and can accurately reflect the pollution levels of atmospheric pollutants.

Reference: Zhao, Y.: Organic Aerosol Sources and Chemistry: Insights from Development and Application of In-Situ Thermal Desorption Gas Chromatograph for Semi-Volatile Organic Compounds (SV-TAG), 2012.

Results and discussion:

6. Line 164-165: It would help to list out these instruments specifically in your methods section. I would also suggest moving the paragraph where you describe each of these instruments in the SI to your main text. It is a short paragraph and it would help readers understand the measurements you took.

Response: Thanks for the suggestion. We have moved the paragraph regarding description of instruments to the main text, please refer to Lines 89-96.

Lines 89-96: "The meteorological parameters were obtained from a meteorological monitor (WXT520, VAISALA Inc., FL). O3 and NO2 were measured by ozone analyzer (49i-PS, Thermo Fisher Scientific, US) and NOx analyzer (MODEL450i, Thermo Fisher Scientific, US), respectively. $PM_{2.5}$ mass concentration was measured by an online particulate matter monitor (BAM1020. Met One Inc., US); the concentration of the carbon components (Organic carbon, OC; Elemental carbon, EC) was measured using semi-continuous OC/EC analyzer (RT-4, Sunset Laboratory Inc, US) (Nicolosi et al., 2018; Zhang et al., 2017b); water soluble ions were measured by MARGA ionic online analyzer (ADI2080, Metrohm, CHN) (Makkonen et al., 2012) and elements were measured by an atmospheric elements online monitor (EHM-X200, Tianrui, CHN) (Makkonen et al., 2012)."

7. Axes on Figure 2 are very hard to read – can you put more space between each panel? Also your axis breaks are very small, can you make them larger? And finally, can you put a number below your axis break (not just above), so it is more clear what the values are right before and after the break?

Response: We have revised Figure 2 accordingly.
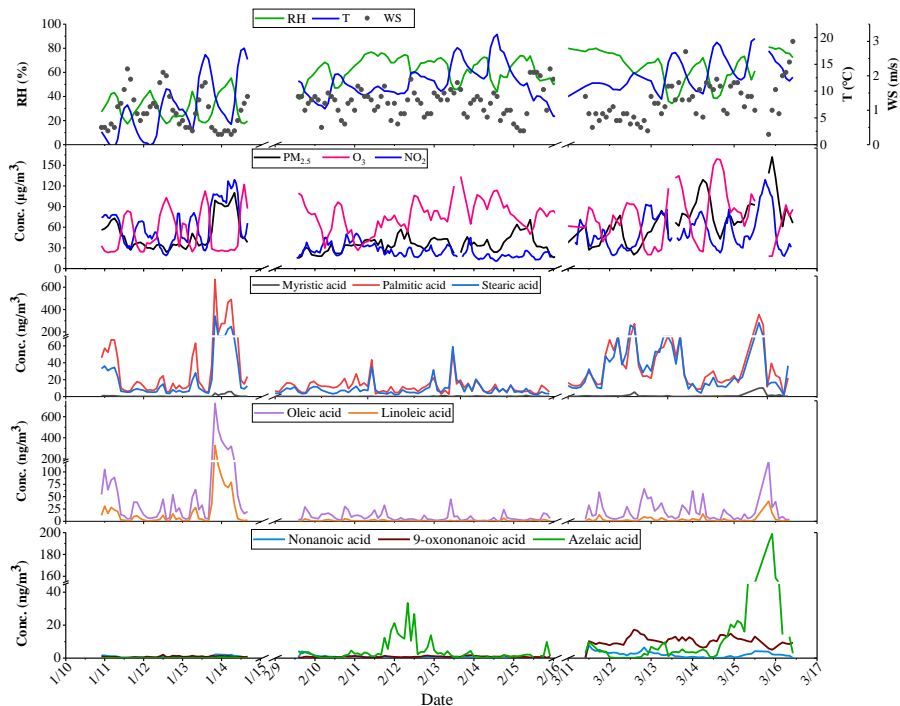
8. Line 180: specify what time of day "dinner time" is

Response: We have clarified the "dinner time" in the manuscript, please refer to Lines 187-188.

Lines 187-188: "It revealed that the composition of $PM_{2.5}$ could dramatically change, especially during the dinner time (18:00-20:00)."

9. Line 183: What meteorological conditions are present in "clean" and "polluted" periods? Are there more emissions during the "polluted period" or simply different meteorological conditions?

Response: We inserted meteorological conditions in the manuscript. Please refer to Lines 192-195 and Table 2. Generally, the meteorological conditions are unfavorable during the "polluted" periods, showing relatively low wind speed and high humidity.

Lines 192-196: "Table 2 shows the mean values of $PM_{2.5}$, OC, TFAs concentrations and meteorological conditions during the clean ($PM_{2.5}$ <35μg/m³) and polluted periods ($PM_{2.5}$ ≥ 35μg/m³). Generally, the meteorological conditions during the polluted period are unfavourable compared to the clean period, showing lower wind speed and higher humidity. The ratios of WS, T and RH during the polluted period to the clean period are 0.9, 1.0 and 1.1 respectively."

Table 2. $PM_{2.5}$ concentration, organic carbon fraction, fatty acids concentration and meteorological conditions during clean and polluted periods.

Species	Clean period	Polluted period	Polluted/clean
$PM_{2.5}$ (μg/m³)	28.29 ± 5.27	62.86 ± 25.67	2.2
OC (μg/m³)	4.05 ± 1.09	8.00 ± 5.23	2.0

TFAs (ng/m^3)	35.28 ± 28.17	147.06 ± 281.66	4.2
sFAs (ng/m^3)	21.60 ± 14.91	92.05 ± 162.75	4.3
uFAs (ng/m^3)	13.68 ± 14.22	55.53 ± 133.82	4.1
TFAs/PM$_{2.5}$ (ng/μg)	1.24 ± 0.91	1.95 ± 2.85	1.6
TFAs/OC (ng/μg)	9.52 ± 7.79	15.33 ± 14.59	1.6
WS (m/s)	1.23 ± 0.45	1.14 ± 0.54	0.9
T (℃)	10.77 ± 4.22	10.99 ± 4.68	1.0
RH (%)	53.41 ± 17.49	56.33 ± 18.55	1.1

10. Line 210: How did you eliminate boundary layer height? Is that what is shown in b?

Response: Thanks for the constructive comment. The diurnal pattern shown in Fig.3(a) is very characteristic of a parameter influenced by boundary layer dynamics. However, it is difficult to discern which changes are related to boundary layer changing and which to fresh emissions. Fig.3(b) showed the diurnal patterns of each compound as a fraction of OC, which can eliminate the influence of the boundary layer height in a relative way, so as to give more insight into the chemical changes. To avoid misunderstanding, we have revised the description. Please refer to Lines 221-222.

Lines 221-222: From the diurnal patterns, it is shown that the proportion of the five fatty acids and TFAs in OC at noon had a weaker peak, which was still smaller than that during the morning and evening mealtimes.

11. Line 212: I agree, but there are also other active sources during these times, as people heat their homes and drive their vehicles to/from work, so I would be careful with this language here. I don't think it is convincing that these are ONLY cooking emissions. The paragraph from lines 224-231 is valuable (discussing ratios of fatty acids from difference sources). Figure 4 is also valuable, depicting this information. But cooking ratios overlap so much with pretty much all other source profiles, so I think you need to be careful how much you emphasize that these are cooking derived-emissions. Also, what references are contributing to figure 4? Please cite them in the figure itself.

Response: We thank the reviewer for the comments and suggestions. We reorganized and softened the language in Line 212, Please refer to Lines 222-224. The source references of the data in the figure are specifically cited in the manuscript, readers can find the references from Lines 227-244. Since the number of cited references is large, and the names of the references cannot be well shown in the figure one by one, we have inserted the references to the figure title of Fig.4.

Lines 222-224: In conclusion, the apparent peaks of TFAs at the dinner time provide evidence for

major source contribution to air pollution from local cooking emissions, although there are mix sources including vehicle exhaust, coal combustion, etc.

Lines 227-243: "Fatty acids in urban atmospheres are influenced by various anthropogenic (e.g., biomass burning, vehicle exhaust) (Hays et al., 2002; Schauer et al., 2001; Simoneit, 2002; Wang et al., 2009) and biogenic sources (Oliveira et al., 2007; Rogge et al., 2006). The main sources of fatty acid-like substances in the ambient air of the study area can be discerned on the basis of characteristic ratios between fatty acids emitted from different sources (Fig.4) (He et al., 2004; Pei et al., 2016; Rogge et al., 1993; Zhao et al., 2015; Zhao et al., 2007). The palmitic acid to stearic acid (P/S) ratios observed in this study ranges between 0.49 and 3.08 (average value: 1.49), significantly lower than those associated with residential coal combustion and industrial coal combustion, while partially overlapping those from biomass burning, vehicle exhaust and sea spray aerosol (Bikkin et al., 2019; Cai et al., 2017; Ho et al., 2015; Zhang et al., 2008; Zhang et al., 2007). Ho et al. (2015) investigated urban areas in Beijing where fatty acid concentrations were elevated during traffic restrictions compared to non-restricted periods, suggesting that motor vehicle exhaust is not the largest source of fatty acids in urban areas. The information on fatty acid emissions from biomass burning source is closer to that of cooking sources (Hays et al., 2002; Schauer et al., 2001; Zhang et al., 2008), however, in the study of Simoneit (2002), no oleic acid was detected in organic molecular substances from biomass burning. The oleic acid/stearic acid (O/S) ratio from sea spray aerosol samples is 0.16 (Bikkin et al., 2019), which is obviously lower than the ambient data in this study (1.4). Hence, during the observation in this study, vehicle exhaust and sea spray were not the most important sources of fatty acids emissions in urban Changzhou. Especially during the dinner period, when the O/S ratio was significantly higher and close to the ratio in the organics emitted from traditional culinary types in the Yangtze River Delta region."
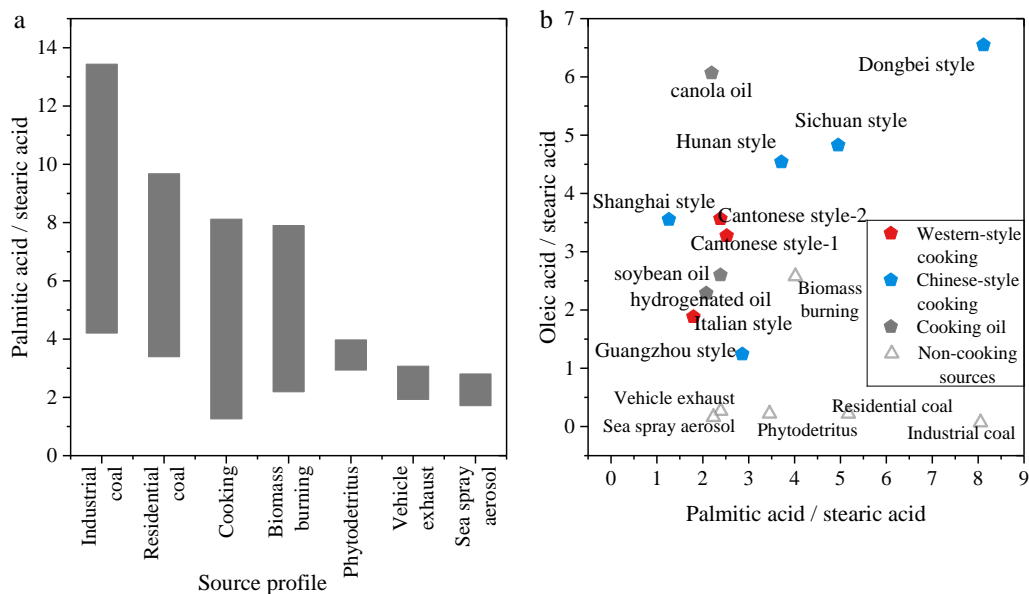
Fig.4

Figure 4. Ratio of fatty acids (P/S) in organic molecular substances emitted directly from different sources (a); Ratio of fatty acids (P/S vs O/S) emitted by different types of cooking sources and non-cooking sources (b). (Bikkin et al., 2019; Cai et al., 2017; Hays et al., 2002; He et al., 2004; Oliveira et al., 2007; Pei et al., 2016; Rogge et al., 1993; Schauer et al., 2001, 2002; Simoneit, 2002; Zhang et al., 2008; Zhao et al., 2007).

12. Line 246: Can you prove this with ozone reactivities? Linoleic acid has an extra double bond than oleic acid so it makes sense it would degrade in the atmosphere more rapidly.

Response: Thanks for the constructive comment. Moise & Rudich (2002) and Thornberry & Abbatt (2004) illustrate the degradation rates of two unsaturated fatty acids in terms of ozone loss kinetics and the specific reactions of oleic and linoleic acids with ozone. We have added literature citations related to this in the manuscript. Please refer to Lines 260-263 and References (Moise and Rudich, 2002; Thornberry and Abbatt, 2004).

Lines 260-262: "The results of Moise and Rudich (2002) showed that the reactant activity is directly related to the concentration of unsaturated bonds, with linoleic acid having an extra double bond than oleic acid, indicating that linoleic acid is more easily degraded than oleic acid (Moise and Rudich, 2002; Thornberry and Abbatt, 2004).

References: Moise, T., and Rudich, Y.: Reactive uptake of ozone by aerosol-associated unsaturated fatty acids: Kinetics, mechanism, and products, Journal of Physical Chemistry A, 106(27), 6469–6476, doi.org/10.1021/jp025597e, 2002.

Thornberry, T., and Abbatt, J. P. D.: Heterogeneous reaction of ozone with liquid unsaturated fatty acids: detailed kinetics and gas-phase product studies, PCCP, 6(1), 84-93, doi:10.1039/b310149e,

2004.

13. Figure 5 caption: Please provide more details on how this cooking source profile was determined.

Response: Thanks for the constructive comment. We have made corresponding citations to the cooking source literature in the manuscript, along with additional descriptions in the caption of Figure 5. Please refer to Lines 254-265 and Fig.5.

Lines 254-265: "Fig.5 shows the O/S ratios and linoleic acid/ stearic acid (L/S) versus P/S, respectively. The average value of P/S was 1.49±0.49, which was within the range of cooking source profile values measured from direct emissions from different restaurants and cooking types (1.3-8.1) (He et al., 2004; Pei et al., 2016; Schauer et al., 2002; Zhao et al., 2007), and similar to the ratio of P/S in atmospheric $PM_{2.5}$ in Shanghai (1.9) (Li et al., 2020; Wang et al., 2020). In this study, the O/S ratio (1.4 ± 1.1) of the ambient samples was overall in the range of the cooking source profile (3.6 ± 1.6), while the L/S ratio of 0.25 ± 0.31 was slightly lower than the cooking source profile values (2.9 ± 1.8) (He et al., 2004; Pei et al., 2016; Schauer et al., 2002; Zhao et al., 2007). The results of Moise and Rudich (2002) showed that the reactant activity is directly related to the concentration of unsaturated bonds, with linoleic acid has an extra double bond than oleic acid, indicating that linoleic acid is more easily degraded than oleic acid (Moise and Rudich, 2002; Thornberry and Abbatt, 2004). The O/S ratio of the ambient samples in this study was higher than those measured in Beijing (0.65) (He et al., 2004) from January to October and in Shanghai (0.83) (Li et al., 2020; Wang et al., 2020) during winter."

Figure 5. The oleic/ stearic acid and linoleic/ stearic acid ratios compared to the palmitic/stearic acid ratio (a); diurnal variation in the ratio of oleic (linoleic) acid to stearic acid concentration (b). (The cooking source profile values were measured from direct emissions from different restaurants and cooking types.) (He et al., 2004; Pei et al., 2016; Schauer et al., 2002; Zhao et al., 2007).

14. Line 272: should say "Figure 6"

Response: Thanks for pointing this out. "Fig.5" has been revised to "Fig.6". Please refer to Line 291.

Line 291: "The concentrations of sFAs, uFAs and their oxidation products under each cluster are shown in Fig.6."

15. Lines 286-290: What about primary sources of these ODPs from the ocean? I don't think these are solely attributable to oxidation, and I suggest softening the language here.
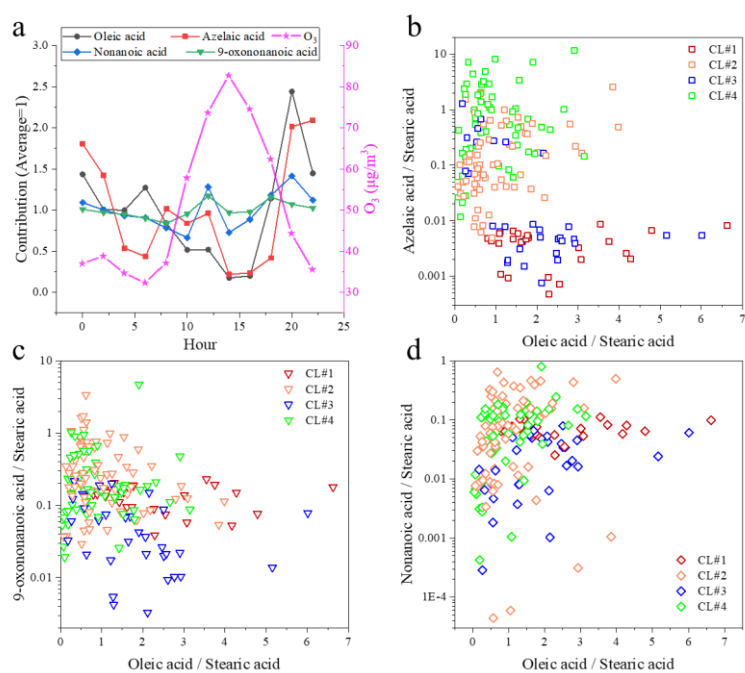
Response: Thanks for the constructive comment. We have revised the language description and

added references. Please refer to Lines 307-309.

Lines 307-309: "··········for example, marine heterotrophic bacteria releases sFAs and uFAs into the water column, however the mono/polyunsaturated fatty acids (e.g., oleic acid, linoleic acid) in seawater rapidly oxidizes to form initially oxocarboxylic acids, azelaic acid etc. (Bikkin et al., 2019); ···········"

16. Figure 8: The color of O_3 in the legend and in the figure is different

Response: Thanks for pointing this out. We have made the appropriate changes. Please refer to Figure 8.

17. Line 302: How can you be certain that this is just driven by oxidative decomposition, not dilution or lower emissions? The language here needs to be softened.

Response: Thanks for the constructive comment. We have reorganized the language and made additions to the manuscript. Please refer to Lines 323-325.

Lines 323-325: "····· ····· At the same time, oxidative decomposition, atmospheric dilution and lower emissions caused significant decrease in the concentration of oleic acid until night when large amounts of fresh emissions enter the atmosphere again. ····· ······"

18. Line 305: How can you be certain that the ONLY sources of these two species is oleic acid ozonolysis? The language here needs to be softened to account for the other possible sources.

Response: Thanks for the comment. We have revised accordingly, please refer to Lines 326-331.

Lines 326-331: "C9 ω-oxo acid and diacids (e.g., nonanoic acid, 9-oxononanoic acid and azelaic acid) in the atmospheric environment originate from plant volatilization, combustion emissions, and

cooking processes (Kawamura et al., 2013; Tian et al., 2020), and they were established in chamber studies as major atmospheric oxidation products from uFAs ozonolysis (Kawamura et al., 2013; Moise and Rudich, 2002; Thornberry and Abbatt, 2004). The diurnal variations of Nonanoic acid and 9-oxononanoic acid were similar and both peaked around noon, while the production of 9-oxononanoic acid and azelaic acid are in competition (Thornberry and Abbatt, 2004)."

19. Line 334: What about the impact of plume dilution during this time? In addition to oxidative decay?

Response: Thanks for the constructive comment. We studied the oxidative decay of unsaturated fatty acids using the method of Donahue et al (2005) and Wang & Yu (2021). And among the quantified sFA and uFA cooking markers, palmitic acid was selected as the reference molecule for normalization. Wang and Yu (2021) suggested that using the concentration ratio (uFAs / sFAs) eliminates the interference from atmospheric dilution and deposition. Please refer to Lines 146-150 and References: Donahue et al (2005) and Wang & Yu (2021).

Lines 146-150: "C_i and C_s are the particle-phase concentration of species i and sFAs, respectively. Among the quantified sFA and uFA cooking markers, palmitic acid was selected as the reference molecule for normalization. Using the concentration ratio eliminates the interference from atmospheric dilution and deposition. Fitting the ambient C_i/C_s data versus t with an exponential function provides an estimate for k, the effective pseudo-first order decay rate (h−1). k_{ri} is the second-order reaction rate constant of species i against an oxidant. C_{OX} is the average oxidant concentration in the aerosol."

References: Donahue, N. M., Robinson, A. L., Huff Hartz, K. E., Sage, A. M., and Weitkamp, E. A.: Competitive oxidation in atmospheric aerosols: The case for relative kinetics, Geophys. Res. Lett., 32(16), doi:10.1029/2005gl022893, 2005.

Wang, Q. Q., and Yu, J. Z.: Ambient Measurements of Heterogeneous Ozone Oxidation Rates of Oleic, Elaidic, and Linoleic Acid Using a Relative Rate Constant Approach in an Urban Environment, Geophys. Res. Lett., 48(19), doi:10.1029/2021GL095130, 2021.