Response to comments by Reviewer#1

We thank the reviewer for the detailed and constructive comments and suggestions. 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.

General comments:

This manuscript presents measurements of fatty acids and their oxidation products, which are used as a proxy for cooking emissions, at an urban site in Changzhou, China. Aerosol gas chromotography-mass spectrometry (TAG) was used to detect concentrations of these compounds every two hours during three monitoring periods in January – March 2021. The authors explore changes in concentration throughout the diurnal cycle and under the influence of different air masses. Estimates of the effective rate constant are used to suggest that the key night-time oxidant for these fatty acids is ozone.

This paper's specific focus on cooking emissions provides a valuable contribution towards a growing literature base on the chemical composition of urban aerosol. The overall goal of the paper – to quantify the contribution of cooking aerosol and examine its influence under different regimes – is important. However, I found the conclusions in some parts of the paper to be unclear or not fully supported by the data presented. I would also recommend a check through the paper for typos and to improve the clarity of the writing in some places. I would suggest that this paper is suitable for publication in ACP, subject to some edits. Additional comments are provided below

Response: We thank the reviewer for the positive comments. We have carefully checked the manuscript to make sure that the conclusions are clear and could be well supported by the data presented. We have also checked and revised the typos throughout the paper. Revisions are highlighted.

Major comments in detail:

1. Line 95: This would benefit from more information about the process of how sample collection takes place with TAG.

Response: We have added descriptions about sampling to the main text. Please refer to Lines 93-

110.

Lines 93-110: “Quantification of hourly speciated organic markers was achieved using TAG. The operation details and data quality have been described in our previous work (Wang et al., 2020; Zhang et al., 2021). The sampling and analysis sequence of the TAG system includes four steps: (a) $PM_{2.5}$ sampling and synchronous gas chromatography-mass spectrometry (GC-MS) analysis of the previous sample; (b) loading of the internal standards (IS) from the standards (STD) reservoir to a thermal desorption cell; (c) derivatization and thermal desorption of analytes on the collection and thermal desorption (CTD) cell and subsequent preconcentration of the analytes in focusing trap (FT); and (d) loading of analytes into the GC column for GC-MS analysis. The following is a detailed description. Ambient air was sampled at a flow rate of 8.5-9.5 L/min through a cyclone with $PM_{2.5}$ cutting size (BGI Inc., Waltham, MA), a Nafion dryer (PERMA PURE, MD-700-24S-3) to remove moisture, and then through a carbon denuder (model: ADI-DEN2) to remove volatile organics. The sampled particles were collected on the CTD cell at 30°C for 60 min, followed by derivatization and thermal desorption for 8 min as the temperature of the CTD cell increases to 300°C in 2 min and maintains for 6 min, during which a 10 mL/min helium purge flow combined with a 40 mL/min derivatization flow with N-methyl- N-(trimethylsilyl) trifluoroacetamide (MSTFA) flow through for 8 min. Subsequently, the FT was heated to 300°C in 2 min and kept at 300°C for 10 min, transferring the analytes onto the GC column head (DB-5MS, size 30 m × 0.25 μm × 0.25 μm) by carrier gas. After GC separation, the target organics were sent to the MS detector for quantification. The GC-MS analysis duration for each sample was 60 min while collection of the next sample the CTD cell starts. With the current TAG instrumental set-up, samples were collected every even hour. The post-sampling steps, including in-situ derivatization, thermal desorption, GC-MS analysis, and standby step, took 2 h, thus producing 12 samples per day.”

2. Lines 181-184 and Fig. 3: The authors discuss the influence of boundary layer changes on the concentration of fatty acids, suggesting that this is the reason there is no lunchtime increase in fatty acids. I agree that the diurnal pattern shown in Fig. 3 is very characteristic of a parameter influenced by boundary layer dynamics. However, this makes it difficult to discern which changes are related to boundary layer changing and which to fresh emissions. I might suggest that plotting the diurnal of each compound as a fraction of $PM_{2.5}$ or OC would give more insight into the chemical changes.

In fact, this can be seen later in Fig. 12, where there is a more obvious midday peak in the fractional contribution of the cooking factor than in the absolute concentrations.

Response: Thanks for the constructive comment. We have revised the figure to include diurnal trends of TFAs/OC and inserted relative discussions as well, please refer to Lines 205-211.

Lines 205-211: "Fatty acids showed a clear diurnal variation, with two peaks observed at around 6:00 and 20:00 local time, respectively, and the dinner time peak was especially prominent. In contrast to the previous observations in Shanghai, no peak was observed at lunchtime. The relatively higher boundary layer during the daytime, facilitated the diffusion of pollutants. The weaker oxidation of uFAs emitted at night made the fatty acid concentration peaks more pronounced at dinner time (Wang et al., 2020). Figure 3(b) shows the contribution of various fatty acids to OC. When the influence of the boundary layer height change was eliminated, 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."

3. The authors assume that all fatty acids observed are the result of cooking emissions. This may be a reasonable assumption in this environment; however, I would like to see more justification for this and discussion of other potential sources. For example, palmitic, stearic and oleic acids can all be associated with biomass burning (eg Bertrand et al., 2018; Fujii et al., 2015); and palmitic and stearic acids are released from marine biota in the ocean surface (eg Bikkina et al., 2019), which could be an influence here in CL#2 and CL#4. It seems to me that fatty acids being released at the ocean surface and then oxidised during transport is a more likely explanation for the chemical composition in CL#4.

Response: Thanks for the constructive comment. We have reviewed the molecular marker fingerprinting of fatty acids from different sources (palmitic acid to stearic acid ratio, P/S), and the relationship between P/S and the ratio of oleic acid /stearic acid (O/S) in organic molecular markers emitted from different cooking types (Fig.4). We also examined the profiles of P/S and O/S in fatty acids from sea spray aerosol emissions, and concluded that sea spray aerosol was not a major contributor to fatty acids in urban areas in this study. We could not exclude the impact of aging sea spray aerosol on non-coastal cities. Please refer to Lines 216-231.

Lines 216-231: "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 atmospheric environment 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 had a range 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) studied 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 a significant source of fatty acids in urban areas. 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). Thus, it is reasonable to conclude that biomass burning, vehicle exhaust and sea spray were insignificant sources of fatty acids in urban Changzhou during the observation in this study. 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."

4. Lines 190-193 and Fig. 4a: If I have understood correctly, palmitic acid/stearic acid (on the x-axis) is taken to be a rough indicator of the source of the emissions. If this is the case, it is difficult for the reader to interpret the x-axis here. Could it be more illustrative to label the ratios for a selection of sources on the x-axis? Would you expect to see a relationship between the y-axis and the x-axis?

Response: Palmitic acid (P) and Stearic acid (S) are both saturated FA. Their degradation is much slower than that of oleic acid or linoleic acid. Due to their similar chemical reactivity and volatility and cooking being their common source, the ratio P/S was expected to be relatively constant among different samples. The narrow variation range (ca 0.5-3) shown by the Fig. 4a (now Figure 5a in the revised manuscript) confirmed this point. The main point of Fig. 4a is to contrast the large variation of the oleic/palmitic acid ratio (0.1-10) against the small variation in the P/S ratio, thus highlighting the degradation of oleic acid. Thus, no relationship was expected between the y-axis and x-axis. We now have modified the presentation of this plot by adding an data point (located at the upper right corner) indicating the average ratio of oleic/stearic and P/S ratios for fresh cooking emission. It should also be noted that in the revised manuscript, palmitic acid was replaced with stearic acid as a reference. Please refer to Lines 239-253.

Lines 239-253: "Therefore, the ratio of P/S mainly depends on the sources. 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 (1.2-6.5, with an average of 3.6), while the L/S ratio of 0.25 ± 0.31 was slightly lower than the cooking source profile values (1.1-5.8, and the average was 2.9) (He et al., 2004; Pei et al., 2016; Schauer et al., 2002; Zhao et al., 2007), indicating that linoleic acid is more easily degraded than oleic acid. 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.

The diurnal variations of O/S and L/S are also shown in Fig.5. The ratios were significantly higher during dinner time (18:00-20:00), and were closer to the cooking source profile. Demonstrating that fresh emissions entered into the atmosphere during cooking period, especially dinner time, while uFAs were quickly consumed during aging. The ratio of linoleic acid to stearic acid is consistently lower than what is involved in the source spectrum, which may be influenced by different regions and source characteristics from different types of restaurants."

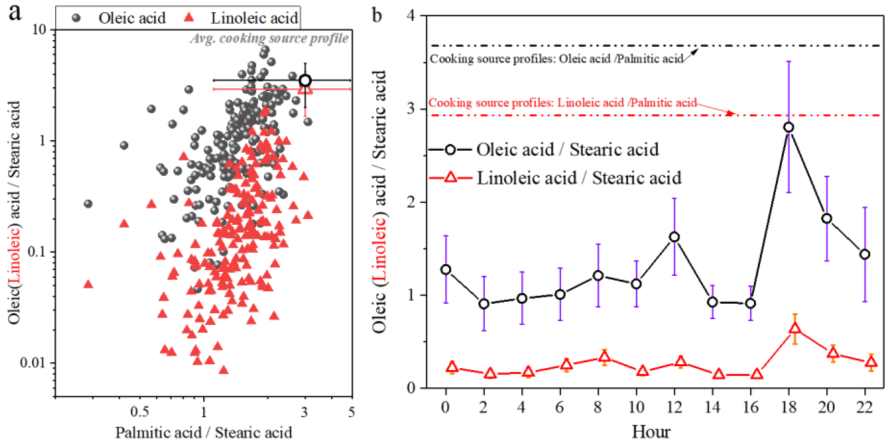


Fig.5. The oleic/ stearic acid and linoleic/ stearic acid ratios compared to the palmitic/stearic acid ratio (a); diurnal variation in the ratio of oleic (linoleic) acid to stearic acid concentration (b).

5. Section 3.3 and Fig. 7: From Fig. 7, there does not appear to be a relationship at all between the concentration of fatty acids and that of $PM_{2.5}$, which makes it difficult to discern the key scientific conclusion from this analysis. In the text, the authors point to a link between the air mass cluster and the behavior of TFAs vs $PM_{2.5}$. I would suggest clarifying the main conclusion from this section and ensuring that it is clearly supported by the figure.

Responses: Thanks for pointing this out. After a careful re-analysis of the data and figures, we agree that no clear scientific conclusions could be drawn from the original Fig 7. Therefore, we have reorganized this in the manuscript. Specifically, the first half of section 3.3 (Original lines 248-263 and Table 2) was retained and moved to subsection 3.1 (New manuscript, lines 183-201 and table 2).

6. Fig. 8: The correlations shown here appear to be quite weak; conclusions taken from them would be strengthened with further statistical analysis. I might suggest:

a. Considering a log-log axis,

b. Carrying out a t-test in each case to establish whether the correlations are statistically significant,

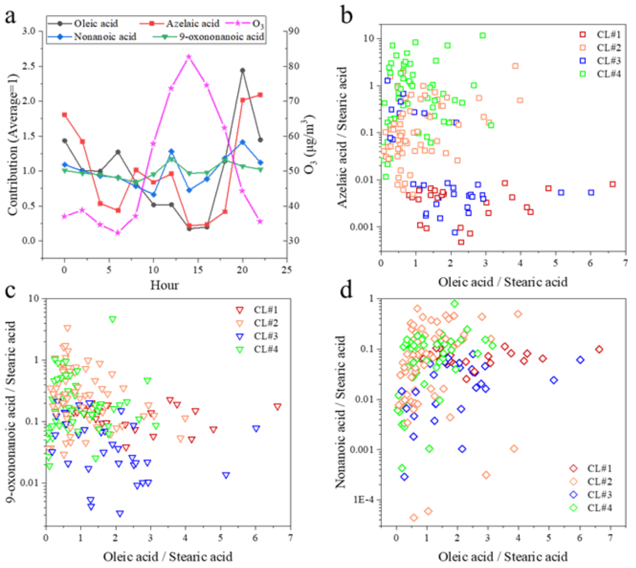
c. Stating correlation co-efficients in the plots.

7. The purpose of the correlation plots (Fig. 8b-d) is not clearly explained in the text.

Responses: Thanks for the comments. We adjusted the section "Atmospheric aging of cooking markers" by merging the original Fig 8 - Fig 9 and removing Fig.8. The logarithmic form is used for the y-axis to better distinguish the differences in ODPs/Stearic acid under different air mass clusters. Although no correlation analysis was conducted in Fig.8 such that a t-test was not performed, we agree with the reviewer to use significance analysis in other sections of this manuscript to make the results more convincing. Please refer to Lines 299-302.

Lines 299-302: “Fig.8(a) shows the diurnal variation of ozone, oleic acid, and ODPs. The ozone concentration started to rise in the morning (06:00) and peaked in the late afternoon (14:00). The diurnal trend of oleic acid was opposite to that of ozone. The diurnal trend of ODPs was also different from oleic acid, the small peak of ODPs was found at around 12:00 in the daytime, which was earlier than that of ozone.”

Lines 316-322: “Fig.8(b) to (d) show the relationship between ODPs / stearic acid ratio and oleic acid/stearic acid. In CL#2 and CL#4, 9-oxononanoic acid / stearic acid ratio is larger than that in CL#1 and CL#3, and azelaic acid /stearic acid ratio have the same characteristic. The nonanoic acid / stearic acid ratio is not well characterized, probably because most of the nonanoic acid is present in the gas phase. Bikkina et al. (2019) found that the O/S ratio exhibited a nonlinear (power) inverse relationship with azelaic acid in remote marine aerosols. This feature was not found in this study, which is possibly due to the single source class of fatty acids and ODPs in remote marine areas, the diversity of emission sources in urban areas, and their vulnerability to transport.”



(new) Fig.8. Diurnal variation of C9 products and oleic acid in environmental samples compared to O3 (a); Correlation of C9 products azelaic acid (b), 9-oxononanoic acid (c), and nonanoic acid

(d) with oleic acid.

Minor comments

1. Line 30: The meaning of the term ‘rising period’ is unclear

Response: We have revised the manuscript and made corrections to the abstract. “During the rising period of $PM_{2.5}$······”) was removed.

2. Line 56-8: Quantifying the concentration of fatty acids will not reduce their impact, though it may inform policy. The phrasing needs to be reconsidered here.

Response: We have revised the relevant description, please refer to Lines 56-59:

Lines 56-59, “By clarifying the characteristics of cooking emissions, quantifying the concentrations of pollutants emitted from cooking and its contribution to urban OA on the diurnal time scales, we build up data and process knowledge about cooking-sourced $PM_{2.5}$ pollution, which in turn help us evaluate the option of controlling cooking emissions in the overall pollution prevention for urban environments.”

3. Sometimes ‘fatty acids’ is written out fully (eg line 176), and sometimes it’s abbreviated to ‘FA’ (line 174). I would recommend using the same approach each time.

Response: We have checked the entire manuscript, and changed all the ‘FA’ to ‘fatty acids’ consistently.

4. Fig. 4b: I don’t completely follow where the source profiles come from here. It would be good to outline the origin of these more clearly in the text.

Response: Thanks for pointing this out. We have inserted detailed descriptions to make it clear, please refer to Lines 216-231:

Lines 216-231: “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 atmospheric environment 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 had a range 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) studied 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 a significant source of fatty acids in urban areas. 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). Thus, it is reasonable to conclude that biomass burning, vehicle exhaust and sea spray were insignificant sources of fatty acids in urban Changzhou during the observation in this study. 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."

5. Fig. 5: This figure shows the chemical influences of the different clusters very clearly. However, I would recommend rearranging slightly so that the pie charts do not block the back trajectories, and so that the text is slightly larger in some places. It is currently very difficult to read the percentages on CL#1 and CL#4.

Response: Thanks for the suggestion, the figure has been revised accordingly.

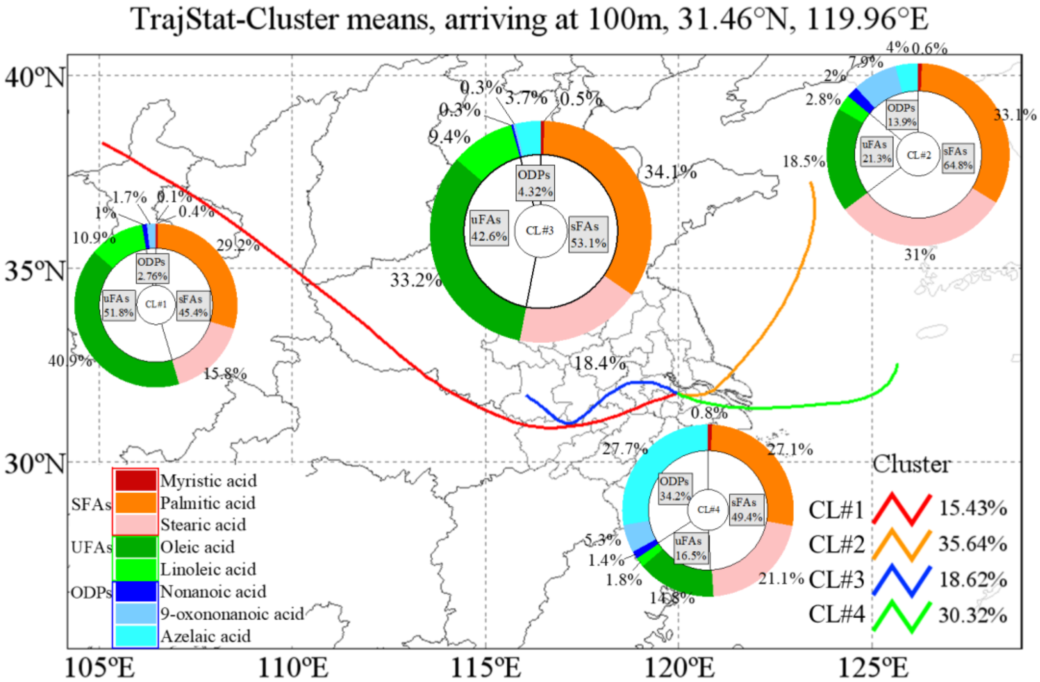


Fig. 6 Sources for each air mass during the sampling period. The colored lines in the map show the contribution of each directional air mass source to the total trajectory as resolved by the TrajStat model.

6. Lines 235-239: I might suggest rephrasing both of these reasons, as they are currently quite difficult to understand. What is meant by the “CL#4 air mass [being] under the influence of CL#4”, for example?

Response: Thanks for the questions and suggestions, we have corrected the description in the manuscript.

Lines 284-290: “The value of uFAs /sFAs in CL#2 and CL#4 was less than that in CL#1 and CL#3 and less than the ratio in sources. In addition, the proportion of ODPs in CL#2 and CL#4 is greater than that in CL#1 and CL#3. This result may be explained by the following two reasons: first, under the influence of transport, the air masses brought more sFAs, ODPs, and the air masses were more aged; second, under the influence of CL#2 and CL#4 air masses, in which the ozone concentration was higher than other air masses, the decomposition reaction of uFAs was more active and could produce more ODPs. In addition, the oxidative reaction of uFAs could be influenced by meteorological conditions as well.”

7. Lines 281-2: It could be helpful to remind the reader what the conclusion referenced here was.

Response: Please refer to the response to comment 5, where we have revised section 3 of the original manuscript. The related paragraph has been removed.

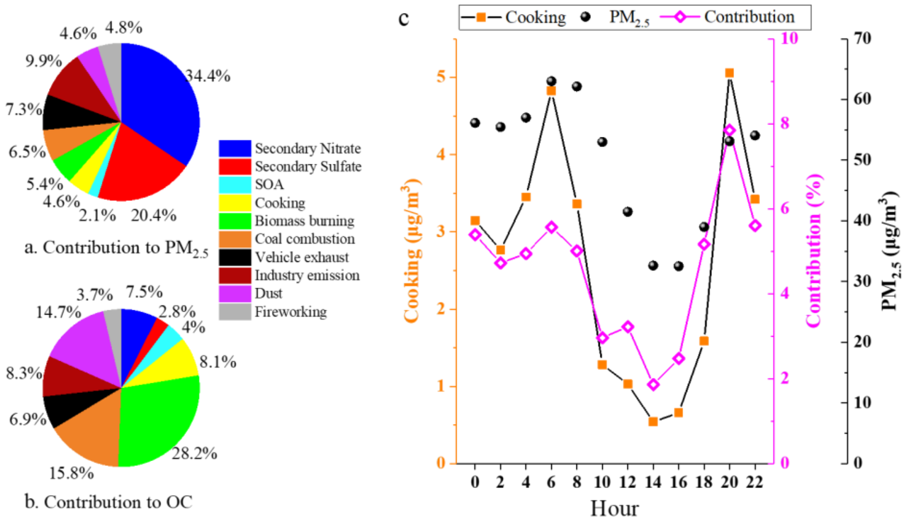
8. Line 351: What does Ox refer to, in this context? How was it measured/observed?

Response: O_x refers to the total oxidant, which is usually used to indicate the atmospheric oxidative capacity and can be calculated by summing NO_2 and O_3 (Dai. et al., 2019; Zhao. et al., 2020; Fu. Et al., 2020).

Line 341: O_x is the total oxidant, calculated from $Ox = NO_2 + O_3$.

9. Fig. 12: It's difficult to interpret the relative size of sections on a 3D pie chart. I would strongly advise making this 2D.

Response: The figure has been revised accordingly.



a. Contribution to $PM_{2.5}$

b. Contribution to OC

Fig.11 Comparison of individual factor contributions to $PM_{2.5}$ (a) and OC (b); diurnal variation of cooking source (c).

10. Lines 416-8: The authors state what was observed; it would be good to state the conclusions drawn from these observations as well.

Response: Corrections have been made in the manuscript, please refer to Lines 404-408.

Lines 404-408: "The linoleic acid /stearic acid and oleic acid /stearic acid ratios exhibited a significant peak during dinnertime, which was close to the cooking source profile values, and a relatively smaller peak at lunchtime. Cooking sources during dinner hours are the most important contributors to the concentration of fatty acids in $PM_{2.5}$ during the study period. Diurnal trend of ODPs was different from that of uFAs, and the concentration of ODPs increased significantly at noon."

11. Line 422: It would help here to remind the reader that CL#3 was the slower-moving, more local cluster. The same goes for the other clusters when they are mentioned in the conclusion

Response: Thanks for the comment. Revisions have been made, please refer to Lines 279-284.

Lines 279 -284: "CL#3 was a slowly moving, local cluster. Under this air mass clustering, local emissions contribute significantly to fatty acids as well as $PM_{2.5}$ concentration. The air mass of CL#1 exhibits the longest range, the concentrations of ODPs were relatively small among all air masses, and the low ODPs concentration was inconsistent with other literature findings of more aging aerosol production from long-range transport (Wang et al., 2020). The lowest $PM_{2.5}$ concentrations and cleaner air masses during air mass CL#1 suggested that long-range air mass transport from the northwest was not the main source of fatty acids and ODPs in Changzhou during the observation."

Lines 412-413: "Highest total concentrations of sFAs, uFAs and ODPs were found under the local air mass cluster (CL#3), indicating significant local emissions contributing to fatty acids as well as $PM_{2.5}$."

12. Line 425-6: Why would this be the case? Is it because these clusters provide more ozone?

Response: Please refer to response to comment 6, we have modified the discussion. See Lines 285-290 and Lines 413-417.

Lines 285-290: "In addition, the proportion of ODPs in CL#2 and CL#4 is greater than that in CL#1 and CL#3. This result may be explained by the following two reasons: first, under the influence of transport, the air masses brought more sFAs, ODPs, and the air masses were more aged; second, under the influence of CL#2 and CL#4 air masses, in which the ozone concentration was higher than other air masses, the decomposition reaction of uFAs was more active and could produce more ODPs. In addition, the oxidative reaction of uFAs could be influenced by meteorological conditions as well."

Lines 413-417: "And the percentages of TFAs in CL#1 and CL#3 were larger than that in CL#2 and CL#4. The proportion of ODPs in CL#2 and CL#4 was greater than that in CL#1 and CL#3. This is mainly because under the influence of transportation, the air masses brought more sFAs, ODPs. The air masses were more aged, and the higher ozone concentration and more active uFAs decomposition reaction occurred in these two air mass clusters."

13. Line 430-1: The statement here, that "O_3 and NO_3 are the main nighttime oxidants for uFAs in Changzhou City" contradicts the statement in Lines 373-4 that "O_3 was the most likely oxidant for the nighttime uFAs oxidation in the urban area of Changzhou"

Response: Thanks for pointing this out. The description has been revised in the text and in the conclusion. Please refer to Lines 340-345.

Lines 340-345: "Fig.9 shows the effective rate constants of the oxidative decomposition of oleic (k_O) and linoleic (k_L) acids in relation to air oxidants (O_3, NO_2, O_x and NO_3^*, etc. Ox is the total oxidant, calculated from $O_x = NO_2 + O_3$.). It should be noted that the NO_3^*, calculated by multiplying O_3 by NO_2, is a substitution for NO_3^* radical, which is not available in this campaign. Both k_O and k_L had a significant positive correlation (The P values of significance tests were all less than 0.05) with O_3, and no correlation was observed with other air oxidants (O_x, NO_3^* and NO_2). Ozone acted as the predominant oxidant for the oxidative decomposition of uFAs, which was consistent with the conclusion in Shanghai."

Lines 418-421: "The k_O ranged from 0.08 to 0.57 h^{-1}, which was overall smaller than k_L (0.16-0.80 h^{-1}). It was observed that both k_O and k_L had a significant positive correlation with O_3. The relative reaction coefficients k_L /k_O (1.6 ±0.3) of linoleic and oleic acids in this study are close to k_L /k_O measured for O_3 in laboratory studies, indicating that O_3 was the main nighttime oxidants for uFAs in Changzhou City."