Responses to Reviewer #3

This paper presents a detailed characterization of gas- and particle-phase compounds in Guangzhou, based on FIGAERO-I-CIMS measurements. The presence and behaviour of a large number of different groups of compounds observed during a measurement campaign in October and November 2018 are outlined. Compound classes discussed include those deriving from biomass burning, species formed from oxidation of biogenic and anthropogenic VOCs, sulphate-containing species and others.

This paper will provide a valuable reference for future field studies on urban air quality in China and elsewhere. Only a small number of datasets exist for this instrument in urban environments, which makes detailed results like those presented here a valuable addition to the literature. The breadth and detail of the FIGAERO-I-CIMS calibrations are particularly impressive and the descriptions of how these were done comprise an important resource for future CIMS studies. The experimental setup is well-considered and robust. The number of different compounds and ideas presented in this paper is comprehensive, but to an extent it sacrifices depth and continuity between ideas in order to achieve this. I would therefore recommend revisiting the paper's "bigger picture" and making the links between each section and the next clearer to make the paper more cohesive.

This paper will certainly be of interest for readers of ACP and I therefore recommend publication after the comments outlined below have been addressed.

Reply: We greatly appreciate the reviewer providing the valuable comments and constructive suggestions which inspired us in many ways. Please find the response to individual comments below.

General comments

1. While each of the individual observations presented here is interesting and valuable, they have not been linked together into an overall storyline, which can leave the paper feeling disjointed. It would benefit from more discussion about how these disparate observations are related to one another and a more concise description of the overall picture in the conclusion.

Reply: We thank the reviewer for the comment. Our manuscript mainly focuses on the interpretation of mass spectra of the FIGAERO-I-CIMS measured in urban environments: (1) Sections are organized around the mass spectra. (2) The species

discussed in each section had high concentrations during the campaign as shown in the mass spectra. (3) After going through detailed investigation of chemical types, general chemical characteristics of organic compounds are analyzed.

We agree with the reviewer that we should add a more concise description to make our storyline clearer. In the end of sections of specific chemical types and in the beginning of bulk analyses, we restate the arrangement of individual results:

(1) (Line 303-310) **Based on the mass spectra shown in Fig. 1, we identify a number of ions associated with high concentrations in both gas and particle phases. In the following Section 3.2-3.7, we will perform interpretation of the mass spectra by analyzing variability and correlation of these important ions, including monosaccharide-derived compounds (with brown tags in Fig. 1), oxygenated aromatics (with purple tags), organic acids (with pink tags), oxidation products of biogenic volatile organic compounds (BVOCs, with green tags), sulfur-containing compounds, and inorganics (with blue tags).**

(2) (Line 505-509) **The above discussions on individual chemical groups provide insights into the identification of the mass spectra from FIGAERO-I-CIMS, along with sources and chemistry of oxygenated organic compounds in the urban atmosphere. In this section and the following one, we will provide a bulk analysis of the detected organic compounds.**

2. More could be done to examine the environmental factors leading to each of the observations presented in the paper, as well as discussing the ramifications.

Reply: We agree with the reviewer for the importance of the environmental factors, but the main target of this article is to serve as a reference of mass spectra for measurements of FIGAERO-I-CIMS in the urban atmosphere. We have included a few analyses on the effects of environmental factors. For example, the contribution of 2-methylglyceric acid ($C_4H_8O_4$) to OA is positively related to meteorological conditions with low humidity and strong sunlight (Fig. S13), which is consistent is with the literature that $C_4H_8O_4$ is a commonly reported oxidation product of isoprene formed in high-NO_x conditions (Surratt et al., 2010). As this manuscript is already pretty long, we are planning to analyze these topics in more depth and present the results in the
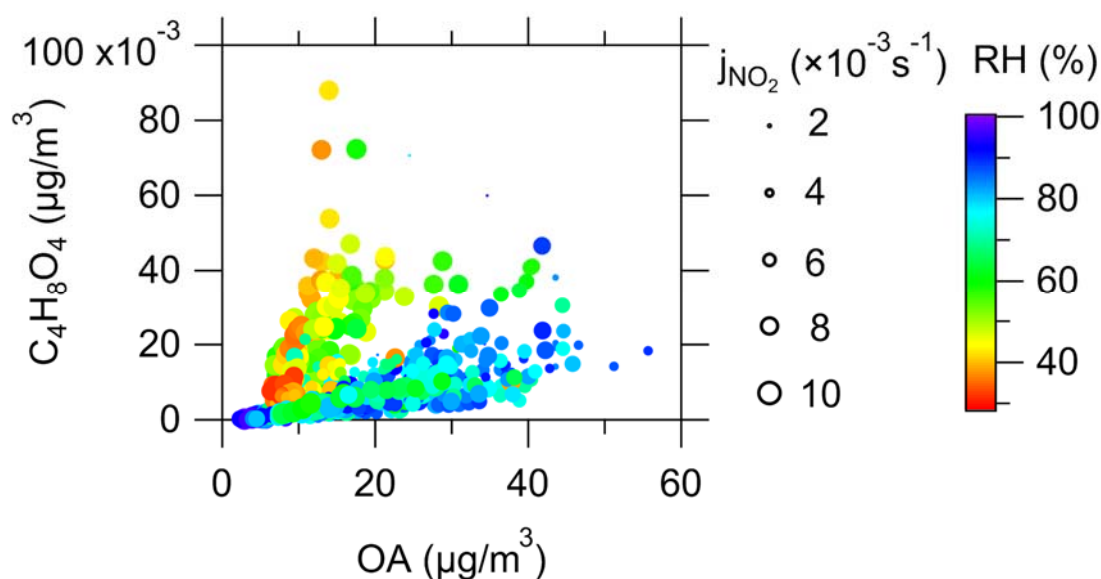
following manuscript.

Figure S13. Scatterplot between particle-phase $C_4H_8O_4$ and OA color-coded by ambient RH and size binned by the daily maximums of photolysis rates of NO_2.

3.   There are a very large number of figures associated with the main text. In addition, some of the supplementary figures actually seem more relevant than those chosen to be included. I would recommend looking again at the figures both in the main paper and in the supplementary materials to establish which are the most important and contribute the most to the overall storyline. Including fewer figures with the main text might make the key results easier for the reader to identify and digest.

Reply: We thank the reviewer for the comments. We went through detailed analyses on individual important species in the mass spectra, which results in relatively large number of graphs in the manuscript. We have considered moving some to the SI, but almost all of the figures have attracted attention from the co-authors and other reviewers. And finally, the 17 figures that are related to the most important results are presented in the main text.

4.   Overall, this paper is well-written and the ideas are clearly-presented. However, there are quite a few typos and grammatical errors, so it would benefit from another read-through to identify and correct these.

Reply: We went through the manuscript again and corrected all typos and grammatical errors we could find.

Specific comments

3

1. Line 3: It might be worth stating the location of the measurements in the title, to give potential readers more context.

Reply: Our manuscript could be a valuable reference for future FIGAERO-I-CIMS studies in the urban atmosphere. It is not just a data report on a specific measurement at a specific place, and thus we don't think it is necessary to add the location of the campaign to the title. In addition, the location of measurements was mentioned in the abstract.

2. Lines 56-7: I don't fully understand the sentence "oxygenated organic compounds provide a vital link between advanced chemical mechanisms and the model-observation discrepancy". Are you saying that OOCs are not accounted for in models and this explains discrepancies between models and observations? If so, how is this shaping the model results? This needs to be a little clearer and more fully-explained.

Reply: Yes, we mean that oxygenated organic compounds are not accounted for in models. We rephrase this sentence in Line 55-58 of the revised manuscript:

Oxygenated organic compounds are not fully accounted in some earlier studies, which may explain some of the discrepancies between observations and models for many unaddressed issues in atmospheric chemistry.

Following Line 58-66 show the examples of the above statement: "Oxygenated organic compounds are supposed to be the top candidates for missing OH reactivity observed in various environments including pristine rainforests and urbanized areas (Noelscher et al., 2016; Yang et al., 2016, 2017). The photolysis of carbonyls serves as a critical radical source driving ozone formation in highly polluted industrialized areas (Edwards et al., 2014; Liu et al., 2012; Xue et al., 2016). Although it has been discovered a long time ago that oxygenated organic compounds make up a substantial fraction of submicron aerosol mass (Kroll and Seinfeld, 2008), enormous difficulty still exists in accurately predicting formation and evolution of SOA (de Gouw et al., 2005; Hodzic et al., 2010; Volkamer et al., 2006)."

3. Lines 120-1: This technique could do with one more sentence of explanation.

Reply: Thanks for the comment. We rephrase the calculation method of particle water of organics (Line 121-124):

LWC of aerosol was taken as the sum of water contributed by inorganic components which was predicted by ISORROPIA II model and organic

components which was calculated based on the organic hygroscopicity parameter (Fountoukis and Nenes, 2007; Guo et al., 2015).

4. Line 132: Here, 'diel' is used to refer to typical changes over a 24 hour period, but elsewhere in the paper 'diurnal' is used for the same concept. Either of these is fine, but it would improve clarity if the same word was used throughout (unless they are being used to mean different things, in which case this should be explained).

Reply: Thanks for pointing it out. "diel" is replaced with "diurnal" in the revised manuscript.

5. Section 2.2.2: The detail in this section is fantastic, as the FIGAREO-I-CIMS calibrations were carried out much more fully than is typical. This is likely to be extremely valuable as a resource for CIMS users in the future. Given this, it might be beneficial to include a table in the supplement showing the actual conversion factors used for each type of compound.

Reply: Thanks for the comment. We will submit an Excel file summarizing the response factors from voltage scanning, calibration factors, humidity curves as one of the supplements. The functions of voltage scanning results are given in Fig. S7 caption:

(a) Fitting the voltage scanning results as a sigmoidal function of sensitivity relative to maximum sensitivity versus dV_{50} (i.e. the voltage where half of an iodide adducts dissociate). The sigmoidal function is $y = 0.23181 + \frac{0.81488}{1+\exp\left(\frac{2.5492-x}{2.1654}\right)}$. (b) Fitting relative transmission efficiency as a gaussian curve of m/z. The gauss function is $y = 0.27777 + 1.0403 \times \exp\left(-\left(\frac{x-217.4}{147.7}\right)^2\right)$.

6. Fig. 2: This figure is difficult to interpret. The text states that most species have higher concentrations during the daytime, but the way the lines are linked together in Fig. 2 make it look like the opposite is true. I would advise looking for a different way to represent this. Perhaps representing each mz with a marker instead of linking the lines, or even using a completely different type of plot to show this, for example grouping compounds and showing the ratios as box plots. What does it mean for the particle phase to be measured in ppt here?

Reply: Thanks for the comment. We represent each ion with a circle for the revised Figure 2. The numbers in boxes indicate the night/day ratios of the tagged ions that
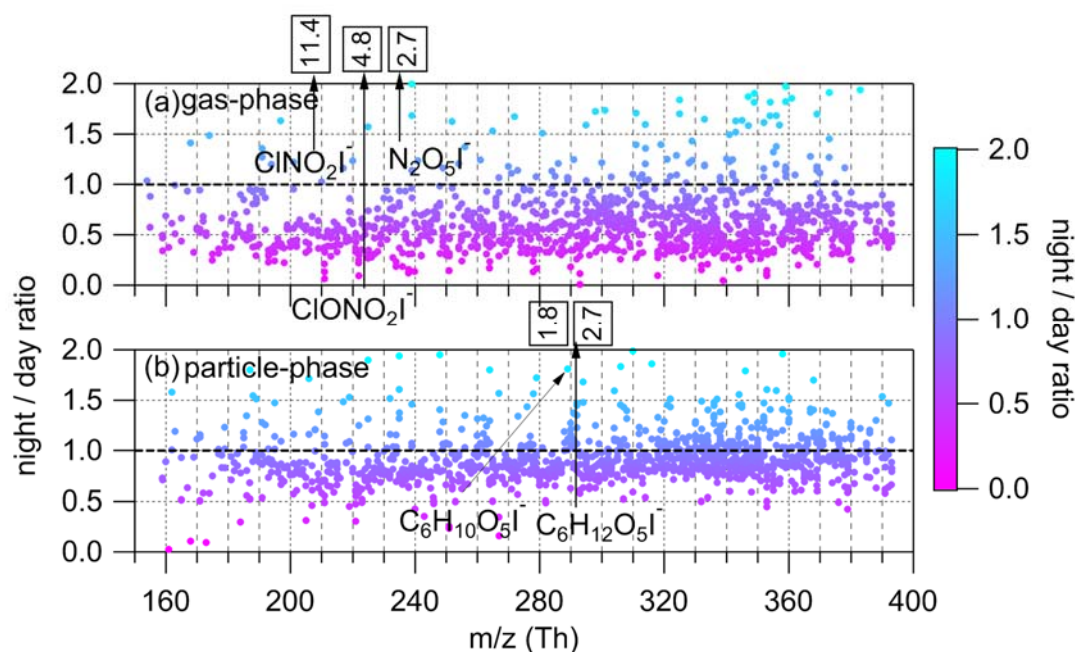
exceed the y-axis ranges.

Figure 2. The ratios of concentrations at night (10 pm - 6 am) to concentrations during the day (10 am - 6 pm) for ions ranging from 150 to 400 Th in gas-phase (a) and particle-phase (b). The range of y-axis is set between 0 and 2 for clarity, although the ratios of some compounds are larger than 2. The numbers in boxes indicate the night/day ratios of tagged ions that exceed the y-axis ranges.

7. Line 302: Here, it could be worthwhile to add some more detail to discuss why biomass burning is high at night to give some more context to this observation. Is this typical in cities in China? Does this follow a similar pattern to those observed in different locations? What kind of burning is taking place and for what purposes?

Reply: We thank the reviewer for the comment. In China, residential burning for cooking is an important source of OA in the evening during non-heating seasons or areas. Previous work has observed enhanced emissions of biomass burning OA or tracers in the evening in other regions (Wang et al., 2020; Zhang et al., 2015). We add some details in in Line 324-329 of the revised manuscript:

The mass fraction of $C_6H_{10}O_5$ in OA had a similar diurnal profile, and the ratios of $C_6H_{10}O_5$ to CO increased at night (from 0.17±0.02 to 0.5±0.03 μg·m^{-3}/ppm, Fig. 3c), both suggesting enhanced emissions of this compound were related with combustion activities during the evening, e.g., residential biofuel burning for

cooking as reported by some previous measurements in China (Wang et al., 2020; Zhang et al., 2015)**.**

8.   Line 304: While it is perhaps obvious from context, it should be specified here that it is the diurnal cycle of C6H10O5I- that closely resembles the m60 fragment.

    Reply: We thank the reviewer for pointing it out. The time series of C6H10O5I- and m/z 60 fragment is very similar, as shown in Fig. 3a. The sentence in Line 326-327 of the revised manuscript is modified:

Furthermore, the time variations of particle-phase $C_6H_{10}O_5I^-$ were very similar to that of the m/z 60 fragment in AMS mass spectra (Fig. 3a).
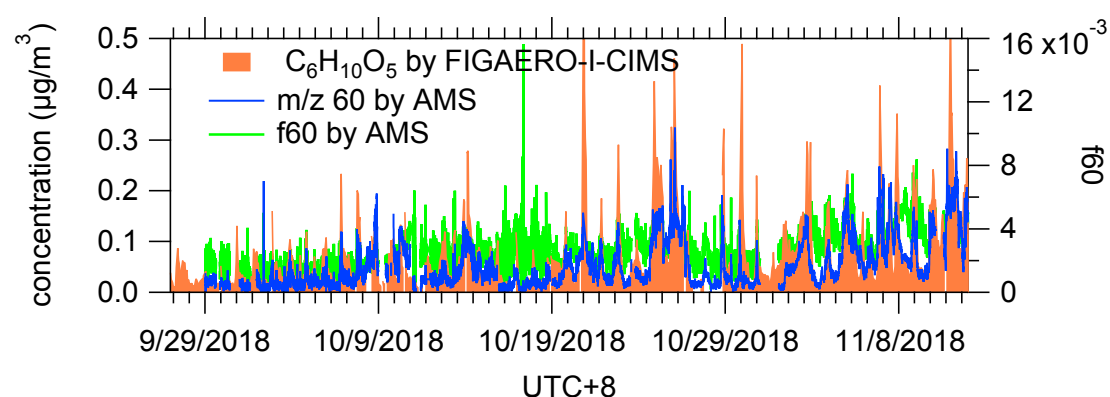

Figure 3. (a) Time series of particulate $C_6H_{10}O_5$ measured by FIGAERO-I-CIMS, m/z 60 fragment and f60 measured by AMS. Background f60=0.3% and background m/z 60=0.3%×OA were subtracted from f60 and m/z 60 (Cubison et al., 2011; Hu et al., 2016).

9.   Fig. 4: This figure would benefit from a reminder in the caption of what the different compounds are.

    Reply: Thanks for the comment. The caption of Figure 4 is revised:

Figure 4. Diurnal variations of oxidized aromatics including nitro-phenols ($C_6H_5NO_3I^-$), nitro-benzenediols ($C_6H_5NO_4I^-$), methyl nitro-phenols ($C_7H_7NO_3I^-$), methyl nitro-benzenediols ($C_7H_7NO_4I^-$), dinitro-phenols ($C_6H_4N_2O_5I^-$), dihydroxy methyl benzoquinone ($C_7H_6O_4I^-$), tetrahydroxy toluene ($C_7H_8O_4I^-$), pentahydroxy toluene and fragments of C9 aromatics ($C_7H_8O_5I^-$). The shaded areas indicate one standard deviation.

10. Line 391: MVK and MACR need to be defined.

Reply: Corrected:

Its daily maxima occurred in the afternoon and correlated moderately with methyl vinyl ketone (MVK) + methacrolein (MACR) measured by PTR-ToF-MS (Fig. 8).

11. Line 416: 'Did not resemble well' – the meaning of this is unclear.

Reply: Sorry for the confusion. In revised version, Fig. S13b (time series of $C_{10}H_{15}NO_6I^-$) is removed, and this sentence is subsequently deleted. Instead, diurnal cycles are used to support our hypothesis in Line 441-450 of the revised manuscript:

Given the distinct diurnal profiles of $C_{10}H_{15}NO_6I^-$ in the gas and particle phases, and the fact that peroxyacetyl nitrate is supposed to dissociate during the FIGAERO heating (Slusher et al., 2004), we speculate that both compounds contributed to this ion.

12. Fig. 10: In the text, the authors hypothesis that the low ClNO2 days are related to low chloride salt concentrations in the aerosol. Given this, it would be beneficial to show the AMS chloride concentrations in this figure alongside ClNO2, instead of in a separate figure in the supplement.

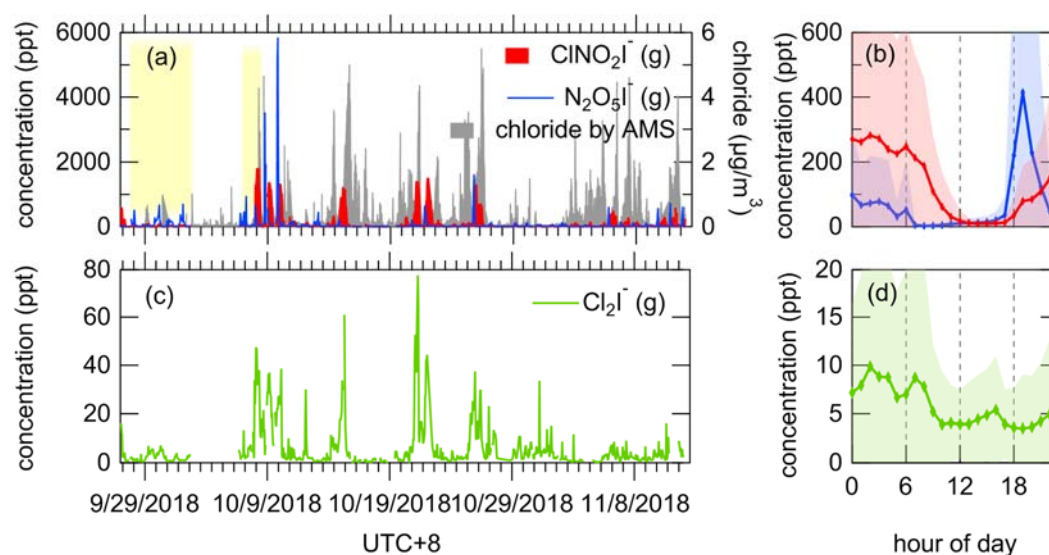Reply: Thanks for the comment. Here is the modified figure.

Figure 10. Time series and diurnal variations of humidity-corrected concentrations of N_2O_5 and $ClNO_2$ (a, b) and Cl_2 (c, d). The tinted background indicates the days with high concentrations of N_2O_5 but low concentrations of $ClNO_2$. The shaded areas indicate one standard deviation.

13. Fig. S17: It is not clear what message is being shared by including this figure. It would be helpful to elaborate in the figure caption or in the text.

Reply: Thanks for pointing it out. We elaborate on Fig. S17 in Line 553-555 of the revised manuscript:

It is clear that the observed fractions of N-containing organic compounds are higher for elevated m/z (Fig. 14) and N-containing ions commonly dominate at even nominal masses (Fig. S17).

14. Lines 536-9: This sentence is difficult to understand; consider revising.

Reply: Sorry for the confusion. The sentence in Line 582-586 of the revised manuscript is modified:

As shown in Fig. 16a, organic compounds measured by FIGAERO-I-CIMS account for higher fractions in OA concentrations by AMS for more aged OA, which is consistent with the fact that I-CIMS are more sensitive to oxygenated organic compounds with multiple functional groups (Lee et al., 2014; Lopez-Hilfiker et al., 2016).

15. Lines 556-7: Would these compounds not be fragmented in the AMS?

Reply: Sorry for the confusion. Fig. S18b shows the correlation coefficients between the total OA concentrations measured by AMS and ion signals measured by FIAGEARO CIMS. We have added "mass concentration" after the word "OA" to avoid confusion:

(in Line 604-606 of the revised manuscript) **The correlation coefficients between the particle-phase concentrations at unit masses by FIGAERO-I-CIMS and OA mass concentration by AMS are calculated (Fig. S18b).**

(in Figure S18b caption) **Correlation coefficients between OA mass concentration measured by AMS and particle-phase signals of unit mass resolution (UMR) measured by FIGAERO-I-CIMS, plotted as a function of m/z.**

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