Responses to Reviewer #1

Review for "Chemical characterization of oxygenated organic compounds in gas-phase and particle-phase using iodide-CIMS with FIGAERO in urban air" by Ye et al.

This manuscript describes the deployment of a FIGAERO-ToF-CIMS with iodide ionization to a polluted urban environment, namely a mega-city (Guangzhou) in China, as part of a coordinated measurement campaign. The authors detail their experimental set up and go into each class or source class of compounds they measured. It is primarily an exploratory paper as urban studies, particularly with a FIGAERO which can measure the chemical composition of the gas and particle phases, are generally underrepresented. In my opinion, the experimental design was well thought out and the measurements were carefully and deliberately performed. For example, performing humidity calibrations is often not done but provides high-quality measurements, and voltage scanning for calibrating unknown compounds goes above and beyond typical studies. Overall, it is a well-written manuscript. The introduction is concise yet informative, and I liked the way the results and discussion section were formatted, with a sub-section for each class of compounds.

Reply: We appreciate the reviewer for the insightful comments, which help us tremendously in improving the quality of our work. Please find the response to individual comments below.

General comments

1. *However, I do have two general comments. First, please read over the paper carefully for grammatical errors. For example, "The systematically interpretation" in the abstract should be "systematic interpretation", and connector words are missing throughout, like "of", "the", and "and".*

Reply: We thank the reviewer for pointing this out. We went through the entire manuscript for a few times and corrected all of the relevant places we found.

2. *Second, I would suggest re-visiting the figures. 17 main-text figures make it difficult*

to discern the message of the paper, and many can be moved to the SI. Further, I think some figures could be included, for example on line 486-487, "The analysis of the OSc - nc space indicates. . ." could include an accompanying figure that could be discussed throughout section 3.8. And I think the way the results/discussion is written, where the spectra are broken down by types of compounds and their origins would lead nicely to a pie chart, stacked bar, or similar showing the relative contributions of each source (maybe in place of Fig. 1).

Reply: We thank the reviewer for the comment. In the main text, we went into the details about individual important species in the mass spectra, which results in relatively larger number of graphs. We have considered moving some from the main text to the SI, but almost all of the figures have attracted attention from the co-authors and other reviewers. And we finally decide to include all of the 17 figures in the main text.

The discussion in section 3.8 revolves around the OSc-nC space (Fig. 12). In the revised manuscript, we add the reference of Figure 12 in the main text:

The composition of organic compounds detected by FIGAERO-I-CIMS was comprehensively characterized with molecular-level details in $\overline{OS_C} - n_C$ space (Fig. 12) which depicts the average oxidation states of carbon for closed-shell $C_xH_yO_z$ and $C_xH_yN_{1,2}O_z$ compounds clustered with iodide as a function of carbon number.

We think the reviewer's suggestion of showing readers a pie chart about the relative contributions is an excellent idea. We calculate the fractions of the I-clusters discussed in the main text (Table 1) in the total I-clusters detected in the gas and particle phases, respectively. The results are shown in pie charts in Fig. 1b&c.

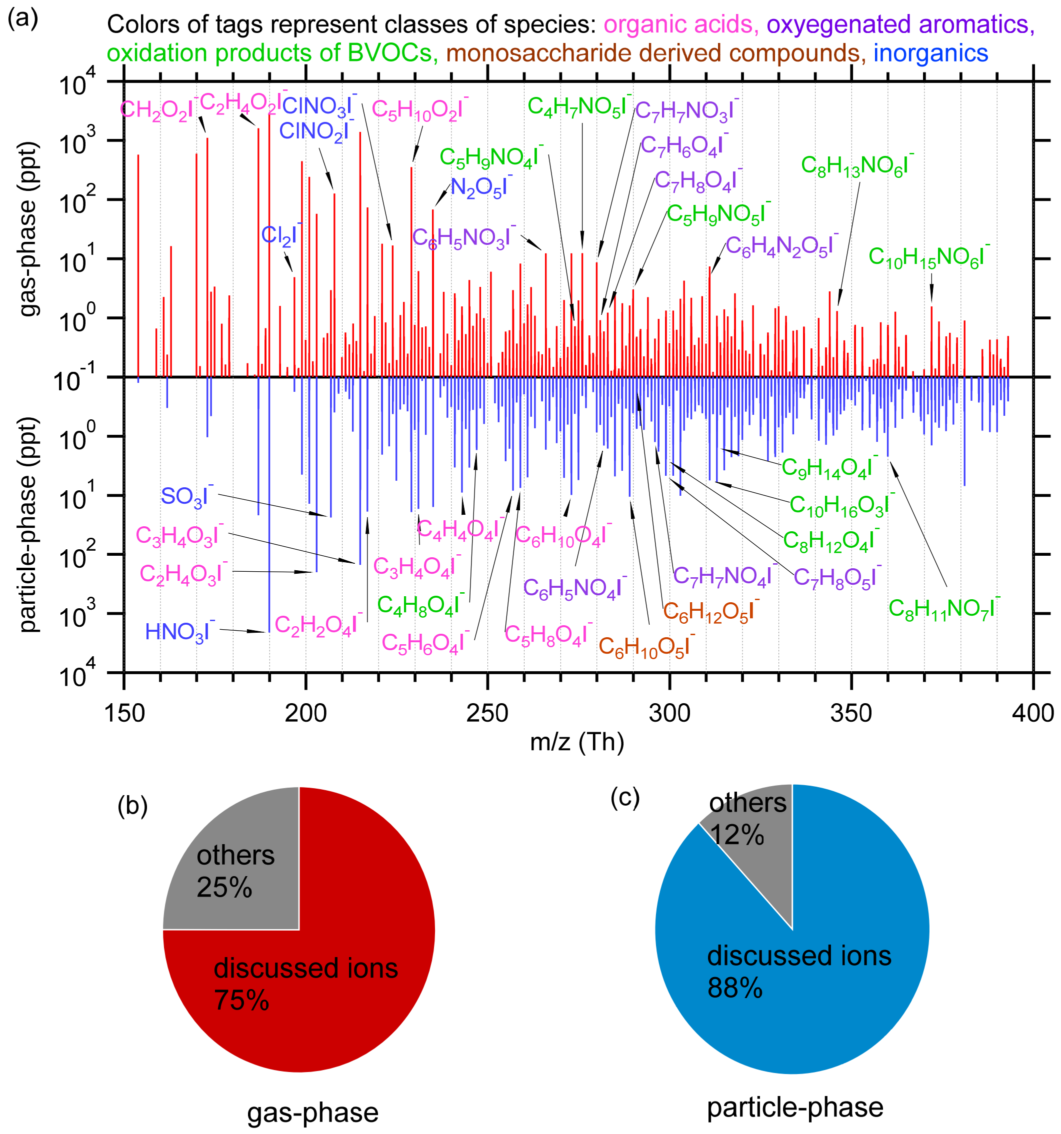

Figure 1. (a) Mass spectra of iodide charged ion within m/z 150-400 Th in gas-phase (red) and particle-phase (blue), respectively. (b) The fraction of I-clusters discussed in the main text (Table 1) in the total gas-phase I-clusters. (c) The fraction of I-clusters discussed in the text in the total particle-phase I-clusters.

Specific comments

1. Throughout the manuscript "～" is used when it should be "-" to identify ranges of values. For example, lines 33 & 156.

Reply: We thank the reviewer for the comment. We corrected them in the revised manuscript.

2. *Line 30-31, "installed with a Filter Inlet for Gases and AEROsols (FIGAERO-I-CIMS) in both gas-phase and particle-phase": this section is worded confusingly. Do you mean that the FIGAERO was utilized to measure both the gas and particle phases?*

Reply: Yes. We mean that we use FIGAERO-I-CIMS to measure species both in the gas and particle phases.

3. *Line 81-82: the use of the word "coatings" here is misleading. The FIGAERO can measure any organics that will evaporate, whether they are coatings, homogeneously mixed, etc.*

Reply: We thank the reviewer for the comment. We have replaced "organic coatings" with "organic compounds".

4. *Line 80-85: the FIGAERO is not the only inlet system that could be described as a "thermal desorption inlet", for example the Micro-Orifice Volatilization Impactor (MOVI) is another example. Please either reword to indicate you're specifically talking about the FIGAERO, or add other examples.*

Reply: We thank the reviewer for the comment. We have added the description about MOVI in Line 80-85 of the revised manuscript:

Installed with a thermal desorption inlet that collects and heats aerosol to evaporate organic compounds, e.g. Filter Inlet for Gases and AEROsols (FIGAERO, Lopez-Hilfiker et al., 2014) and Micro Orifice Volatilization Impactor (MOVI-HRToF-CIMS, Yatavelli et al., 2012), the CIMS instruments are capable of analyzing particle-phase species and gas-particle partitioning in a semi-continuous way (Stark et al., 2017; Stolzenburg et al., 2018).

5. *Line 86-90: actually, much of the published work utilizing a FIGAERO-CIMS has been done in chambers or the laboratory. Please include references to these works or indicate that you are referring to different types of ambient studies.*

Reply: We have included references to the work about using FIGAERO-CIMS in chambers or the laboratory in Line 86-89 of the revised manuscript:

Although FIGAERO-CIMS has gained recent popularity in atmospheric chemistry research, much of the published work was done in chambers or in the laboratory (D'Ambro et al., 2017, 2018; Hammes et al., 2019; Lopez-Hilfiker et al., 2015).

6. *Line 149: I think "complicated" could be removed here or should be explained. Complicated how? Structurally?*

Reply: "complicated" was removed in the revised manuscript.

7. *Line 158-159: how far did the lines protrude out the window? Far enough from the building edge to extend beyond the building laminar layer?*

Reply: The inlet lines protruded out the window for about 1.5 m. We add this information in Line 163-164 in the revised manuscript:

Ambient air was continuously sampled through two inlets protruding about 1.5 meters out of a window on ninth-floor of a building.

8. *Line 193: the (5) is confusing to me, I don't understand the use of parenthesis? Did you calibrate to 5 lower volatility compounds? If so, please list the compounds here or provide a reference to the section or table that lists the compounds.*

Reply: The (5) is the index of calibration methods, not the number of calibrated compounds. We used five methods in total to calibrate multiple chemicals for the instrument.

9. *Line 260 (or 326): how can you be confident you have two nitrogens and not simply a compound with 0 nitrogens, as they would both lie on even masses? Please provide some supporting information to prove this chemical identification âĂŤ maybe a peak fit in the SI and/or reference to previous measurements of dinitrates?*

Reply: We have provided the supporting information as the reviewer suggested in Line 279-281 and Fig. S8 of the revised manuscript:

Although Iodide clusters with two nitrogen atoms and zero nitrogen atoms both lie on odd masses, they can be separated for certain ions with the current resolving power, as demonstrated by the peak fitting results of mass spectrum at

m/z 311 (Fig. S8).

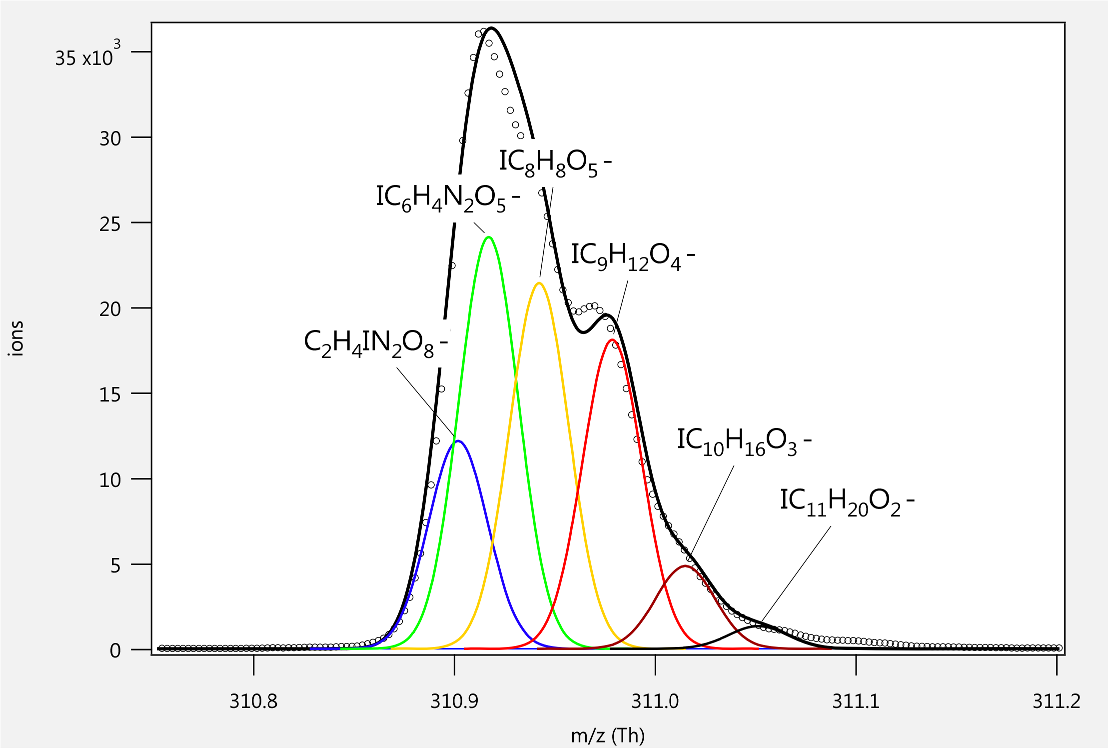

Figure S8. High-resolution peak fittings to the mass spectrum of I-CIMS at m/z 311.

10. Line 298: should Fp be defined explicitly here as "the fraction in the particle phase"? Not sure the abbreviation would be commonly understood by all readers.

Reply: We thank the reviewer for the comment. We have added the definition of Fp in Line 321-323 of the revised manuscript:

In this campaign, $C_6H_{10}O_5$ was detected mostly in the particle phase (the fraction in the particle phase F_p=0.83±0.08) with an average concentration of 0.073±0.076 μg/m^3.

11. Line 381-382 (and throughout results & discussion section): what if these ions have multiple sources? Or different sources produce different isomers of the same composition?

Reply: We thank the reviewer for the comment. We agree with the reviewer that good correlation with tracers, indicators or precursors do not rule out the contributions from other sources. We have revised the statement in Line 406-409 of the revised manuscript:

Our measurements showed that temporal trends of $C_4H_4O_4$ and $C_5H_6O_4$ followed well with those of aromatic hydrocarbons (Fig. S11b), and thus oxidation

of aromatics could be an important contributor to $C_nH_{2n-4}O_4$ in the urban air.

12. Line 490-508/ section 3.8: noticeably lacking is a discussion of small compounds (C4 or less) with a high OSc which have been shown in several publications to be a result of thermal decomposition during desorption. For example line 492-494, please indicate that these C2-C3 compounds that make up 55% of the particle phase signal do not actually exist in the particle-phase as C2-C3, but rather thermal decomposition products, likely arising from the decomposition of very low volatility material such as accretion products or ELVOC. This was first shown by Lopez-Hilfiker et al 2016 (https://pubs.acs.org/doi/abs/10.1021/acs.est.5b04769), and others since.

Reply: Thanks for reminding us to mention the possible results of thermal decomposition which is one of the method's major drawbacks. See Line 531-535 of the revised manuscript:

It is unexpected that C2-C3 compounds made up such a significant portion of the particle phase, indicating a non-negligible role of thermal decomposition from low volatility compounds such as accretion products or extremely low volatile organic compounds which were reported from FIGAERO measurements on SOA (D'Ambro et al., 2018; Lopez-Hilfiker et al., 2014; Stark et al., 2017).

13. Line 556: should the aerosol concentrations of the FIGAERO correlate with the concentrations of the same ion an AMS would measure? Doesn't the AMS decompose compounds when vaporizing, so that what they measure is not what would be in the aerosol phase, in contrast to the FIGAERO which would (typically) measure the parent compound?

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.

14. Line 559: can you provide values for "moderate and strong"?

Reply: Here we attribute r>0.7 to "moderate and strong" correlations. This value has been added in Line 67-608 of the revised manuscript:

Moderate and strong correlations (r>0.7) were observed for the ions between m/z 200 and m/z 400.

15. Line 561-564: this rationale doesn't make sense to me. Decomposition in the FIGAERO, the AMS, or both? Requires references. And the heaviest compounds with m/z 400+ should not be evaporating, and if they are you would expect much higher evaporation rates of everything less than m/z 400. Please reconsider this justification.

Reply: We agree with the reviewer that the volatility may not lead to the difference of correlations. In revised version, the explanation in Line 611-613 is modified:

The possible reason for the lower correlations of heavier compounds (m/z >400) with OA mass loadings is that these compounds might be related to specific sources or certain chemical processes, which might not contribute at large fractions to the total OA concentration.

16. Line 586: doesn't the FIGAERO typically explain ~50% of the AMS-detected OA (e.g. Lopez-Hilfiker et al. ACP 2015, the FIGAERO accounted for ~25-50% of OA measured by the AMS)? Is 24% standard for the urban atmosphere? Can you please compare to previous studies?

Reply: Here, we determine the average fractions of OA detected by FIGAERO-CIMS in OA measured by AMS. The result is from a linear fit from the whole campaign, which reflects the average conditions of the whole campaign. We modified the statement in Line 576-579 of the revised manuscript:

The total organic compounds measured by FIGAERO-I-CIMS explained 24±0.8% (fitted slope ± one standard deviation) of the total OA in average (Fig. 16a), which is lower than the average fractions (~50%) reported previously in boreal and temperate forests (Lopez-Hilfiker et al., 2016; Stark et al., 2017)**.**

We also explore the possible reason for the difference in the ratios in the urban and forest areas in Line 579-588 of the revised manuscript:

The lower fractions determined here might be as the result of larger contributions to OA from primary emissions in urban air, which are composed of large number of compounds with little signal in I-CIMS (Zhao et al., 2016). 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). Furthermore, we expect this fraction to change with the relative contributions of primary emissions and secondary formation for organic compounds in the atmosphere.

Reference

Lopez-Hilfiker, F. D., Iyer, S., Mohr, C., Lee, B. H., Ambro, E. L. D., Kurtén, T. and Thornton, J. A.: Constraining the sensitivity of iodide adduct chemical ionization mass spectrometry to multifunctional organic molecules using the collision limit and thermodynamic stability of iodide ion adducts, Atmos. Meas. Tech., 9, 1505–1512, doi:10.5194/amt-9-1505-2016, 2016.

Stark, H., Yatavelli, R. L. N., Thompson, S. L., Kang, H., Krechmer, J. E., Kimmel, J. R., Palm, B. B., Hu, W., Hayes, P. L., Day, D. A., Campuzano-Jost, P., Canagaratna, M. R., Jayne, J. T., Worsnop, D. R. and Jimenez, J. L.: Impact of Thermal Decomposition on Thermal Desorption Instruments: Advantage of Thermogram Analysis for Quantifying Volatility Distributions of Organic Species, Environ. Sci. Technol., 51(15), 8491–8500, doi:10.1021/acs.est.7b00160, 2017.