Responses to Reviewers

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.

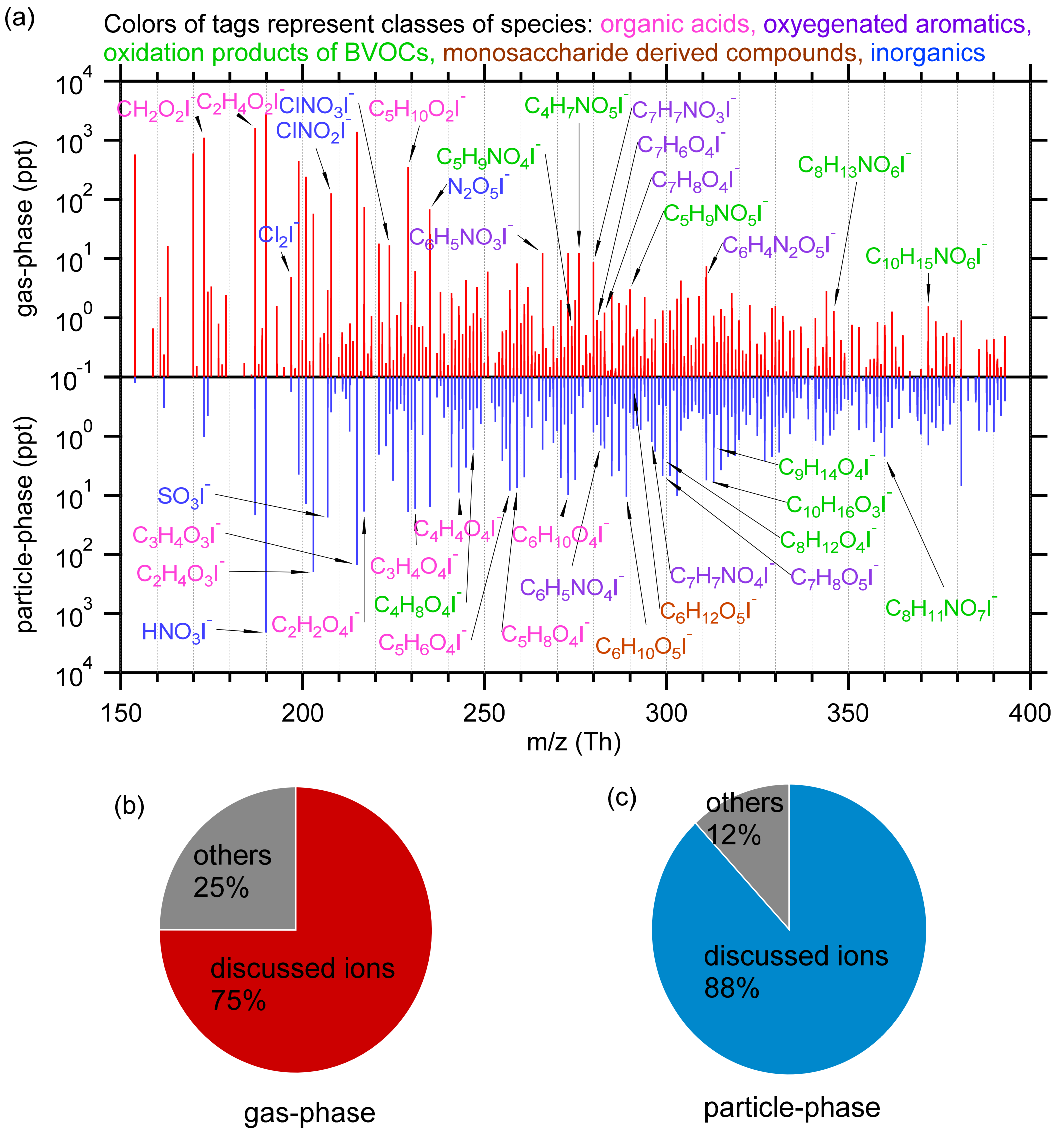


Figure 1. (a) Mass spectra of iodide charged ion within m/z 150-400 Th in gas-phase (red) and particle-phase (blue), respectively. (b) The fraction of I-clusters discussed in the main text (Table 1) in the total gas-phase I-clusters. (c) The fraction of I-clusters discussed in the text in the total particle-phase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

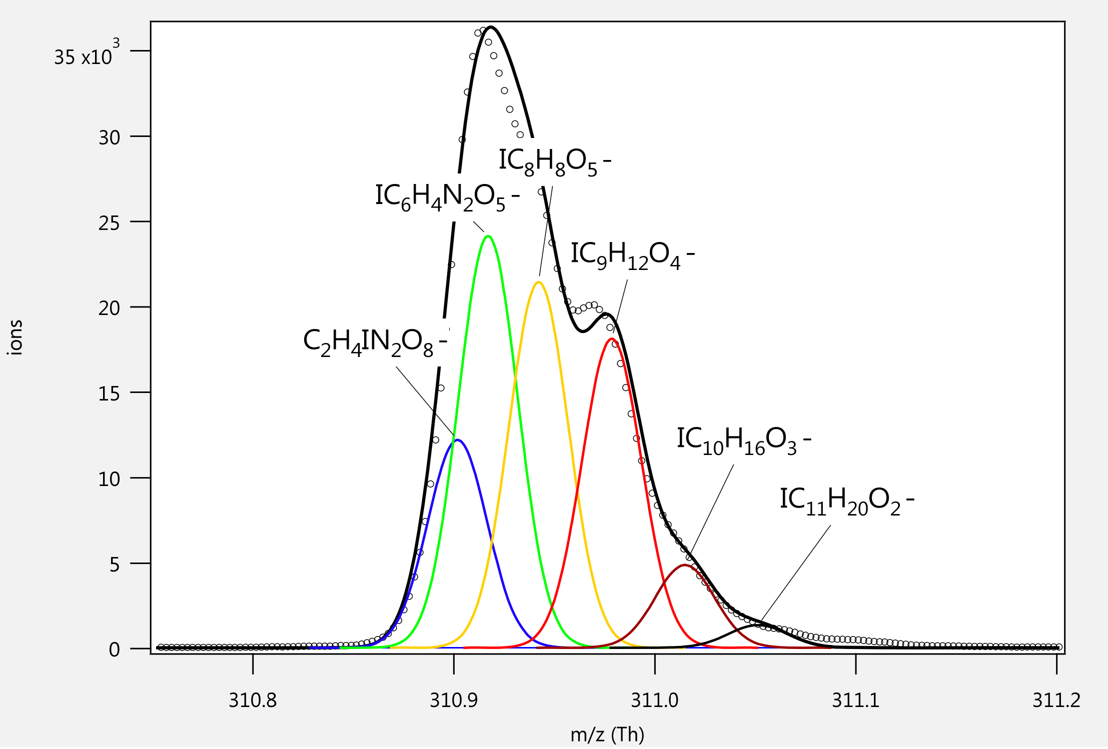


Figure S8. High-resolution peak fittings to the mass spectrum of I-CIMS at m/z 311.

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.

Reviewer #2

Authors Ye et al. comprehensively present here a very nice dataset based on urban measurements using the FIGAERO-I-CIMS. This kind of results are still rather rare, so I think this dataset will be of good interest to readers of ACP, and in particular to users of that instrumentation. I want to positively highlight especially the comprehensive sensitivity calibrations that were done for this study, but are often overlooked or neglected in other studies: direct calibrations for many compounds, including humidity dependence; the voltage scanning method; and determination of the transmission function. Also the figures are well done overall and clear, thanks! Overall, the paper is also well written, especially the intro (compact but detailed enough) and methods sections (detailed enough without being too messy). However, the manuscript does also feel a bit like a collection of snapshot results. It is all interesting bits and pieces, and well supported by the diligent methodology. A storyline, however, is missing; or clearer indications why certain results were chosen to be presented; or deeper investigations of some aspects; or at least some summarizing consolidation showing how the bits and pieces come together... The results are definitely of interest and worth publishing (ideally after addressing some concerns/issues below, but which I should not be dealbreakers). However, I suggest considering publishing the manuscript as a "measurement report", rather than a "research article", at least in its current form. (A random example of that lack of going "deeper" would be in line 488: results are acknowledged to be useful for investigating OA evolution, but that investigation is not actually done. That is a pattern through much of the manuscript. Interesting observations are reported, but not or hardly investigated. Instead, it is the next observation's turn.)

Reply: We thank the reviewer for the insightful comments.

Our manuscript mainly focuses on the interpretation of mass spectra of the FIGAERO-I-CIMS measured in urban environments (Fig. 1a): (1) Sections are organized around the mass spectra. (2) In each section of a specific chemical type, we chose to discuss those species that had high concentrations during the campaign as shown in the mass spectra.

As there is not much work reporting the measurements of oxygenated organic compounds in the urban areas utilizing FIGAERO-CIMS, this work can serve as a valuable reference for the future field studies on urban air quality in China and elsewhere. As suggested by the reviewers, we observed a number of interesting implications from the throughout interpretation of the mass spectra in both gas and particle phases from the FIGAERO-I-CIMS, more detailed investigations on the selected issues are being prepared for further publications. Thus, in our opinion, this manuscript should be a “research article” rather than a “measurement report”.

General comments

1. *I would suggest a slightly more specific title, along the lines of mentioning the actual location of the measurement campaign, and/or time of the year, etc.*

Reply: We thank the reviewer for the comment. The information and location of the measurement campaign have been included in the abstract and also the main text. Our manuscript could be a valuable reference for future studies on the urban atmosphere. It is not just a data report on a specific measurement at a specific place, so we don’t think it is necessary to add the specific information about the measurement campaign to the title.

2. *I wonder if the paper would gain from flipping Chapter 3 (Results), i.e. to start with the more general bulk analysis, and then going into the details, rather than the other way round. But that may also be a matter of taste.*

Reply: We thank the reviewer for the comment. After careful consideration, we still think it is better to arrange results in the current logical order. This manuscript mainly focuses on the interpretation of the mass spectra. We start with an overview of the averaged mass spectra and then discuss the ions associated with the largest signals/concentrations in both gas and particle phases. In addition, the variability and sources of these ions will help to interpret the more general bulk analysis for chemical characteristics of organic compounds.

3. *Table 1 is not referenced in the text, and hence I also found it very late. That should be fixed, as it is a very useful summary table indeed.*

Reply: We thank the reviewer for the suggestion. We add the reference of Table 1 in Line 279 of the revised manuscript:

Table 1 summarizes species discussed in the main text.

4. Throughout the paper there are some minor typos/grammatical erros (e.g., line 106: check prepositions; line 140: missing article; line 145: adverb used instead of adjective; etc.). I tried to point those out for the Abstract only, in my minor comments below, but the issue persists throughout all sections. The paper still reads well, with few exceptions, but those errors should be fixed nonetheless.

Reply: We thank the reviewer for the comment. We went through carefully and corrected all typos and grammatical errors we could find.

Major comments

1. My main major concern is the complete lack of temperature-resolved thermal desorption data ('thermograms)', which the FIGAERO technique typically provides by default. Those thermograms can provide a wealth of additional information (see, e.g. Ylisirniö et al., AMTD, 2020; doi.org/10.5194/amt-2020-254; or Ye et al., Environ. Sci.Technol., 2019; doi.org/10.1021/acs.est.9b03265; many others...). So I am curious as for why they are omitted? I would at least like to see a general discussion of that aspect of the data, possibly depending on the reasons for their absence.

Reply: We thank the reviewer for this comment. We agree that thermograms can provide a wealth of information for volatility of organic compounds in aerosol. As the current manuscript has been already very long as suggested by other reviewers, there is not much room to add more materials. Rather than providing a simple and crude thermogram here, it might be better to present those data in a more systematic and comprehensive way in another manuscript, which we are working on.

2. Related to that, there is hardly a mention of the possible role of thermal decomposition in producing observed compositions, which may be evident from thermograms (e.g., if desorption temperatures are unreasonably high, given the volatility one would expect from a certain composition) or even directly from the composition (if said volatility would suggest a particulate fraction (Fp) much lower than observed). A nonnegligible role of such thermal decomposition has been repeatedly reported from FIGAERO measurements on SOA (e.g. Lopez-Hilfiker et al., 2014, doi.org/10.5194/amt7-983-2014; Stark et al., 2017; doi.org/10.1021/acs.est.7b00160; D'Ambro et al., 2018, doi.org/10.1021/acsearthspacechem.8b00084; etc.), and that issue is indeed on of the *method's major drawbacks, so I would expect similar issues in this study. For example, I would not be surprised if the compositions identified as oxalic and malonic acids (section 3.4) would turn out decomposition products of the thermal desorption process due to their relatively high vapor pressure (although mass loadings presumably were high too, and I have not seen the observed thermograms...)*

Reply: We thank the reviewer for the comments. We agree that thermal decomposition would produce compounds of relatively high vapor pressure, and they are nonnegligible in terms of analyzing volatility or particulate fraction. We also agree that in our measurements, thermal decomposition probably caused the deviation of Fp and other parameters. Considering that space does not permit a relatively complete analysis, we do not put thermograms in our manuscript. Instead, we add the following discussion (Line 531-535 of the revised manuscript) to remind readers of the possible role of thermal decomposition:

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).

3. *There should be some description of the conditions prevailing during the campaign, along with some more general measurement results. Probably in the beginning of section 3. E.g., meteorological data, oxidants/radicals if measured, aerosol mass loadings, time series of the AMS main composition classes (e.g. OA, nitrate, ammonium, sulfate, etc.), and whatever is available and the authors consider might be important for the reader to set the presented results into the appropriate context.*

Reply: We thank the reviewer for the comment. In the revised supplement, we have added a figure (Fig. S1a) showing the time series of meteorological parameters (temperature, relative humidity and wind), trace gases and VOCs (isoprene, monoterpenes, benzene, toluene) during the campaign. The analysis for a few VOCs observed in this campaign has been reported (Wu et al., 2020).

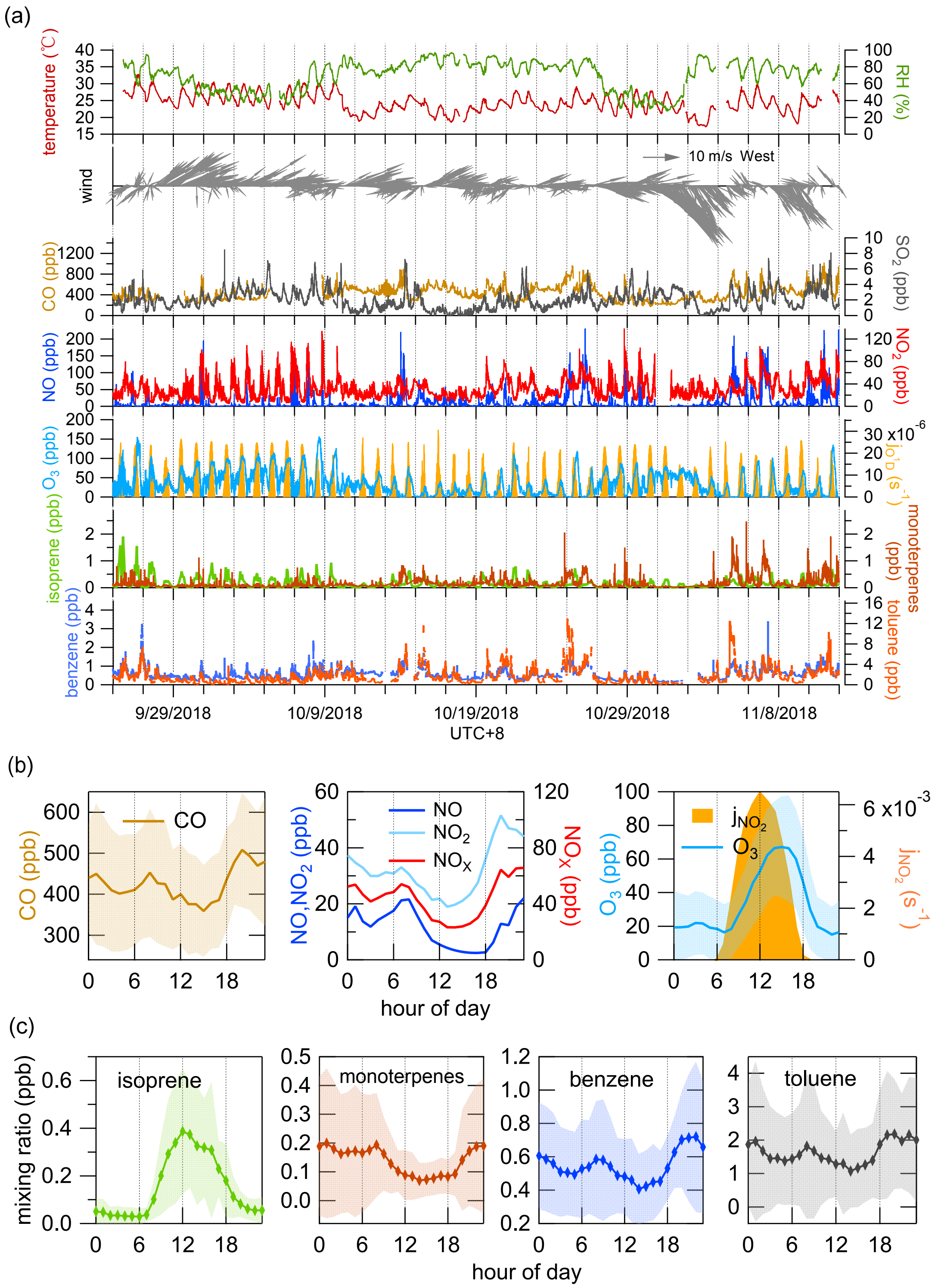


Figure S1. (a) Time series of meteorological parameters (temperature, relative humidity and wind), trace gases (CO, SO_2, NO, NO_2, O_3), VOCs (isoprene, monoterpenes, benzene, toluene) and measured photolysis rate constant (j_{NO_2}) during the campaign. (b) Diurnal trends of trace gases and j_{NO_2}. (c) Diurnal trends of VOCs (Wu et al., 2020). The shaded areas indicate one standard deviation.

4. Also, I have gotten caught switching back and forth between the main text and the supplement. What was the rationale behind which figures are shown in the main text, vs. which in the supplement? That choice appears somewhat random. Indeed I think that the figures discussed in the main text should be included in the main article as well, and rather dismiss those figures to the supplement that the reader does not necessarily need to see while still believing the story.

Reply: Those figures we think are related with important outcomes are shown in the main text. The figures in the supplement provide some support for the results in the main text.

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) In each section of a specific chemical type, we chose to discuss those species that had high concentrations during the campaign as shown in the mass spectra. And this is why there are so many figures.

We make a few modifications to the manuscript. The number and order of pictures in the main text remains unchanged. As for pictures in the SI, we re-order pictures:

(1) Time series of particulate chloride measured by AMS can be displayed with the time series of N2O5 and ClNO2, so we remove it from SI.

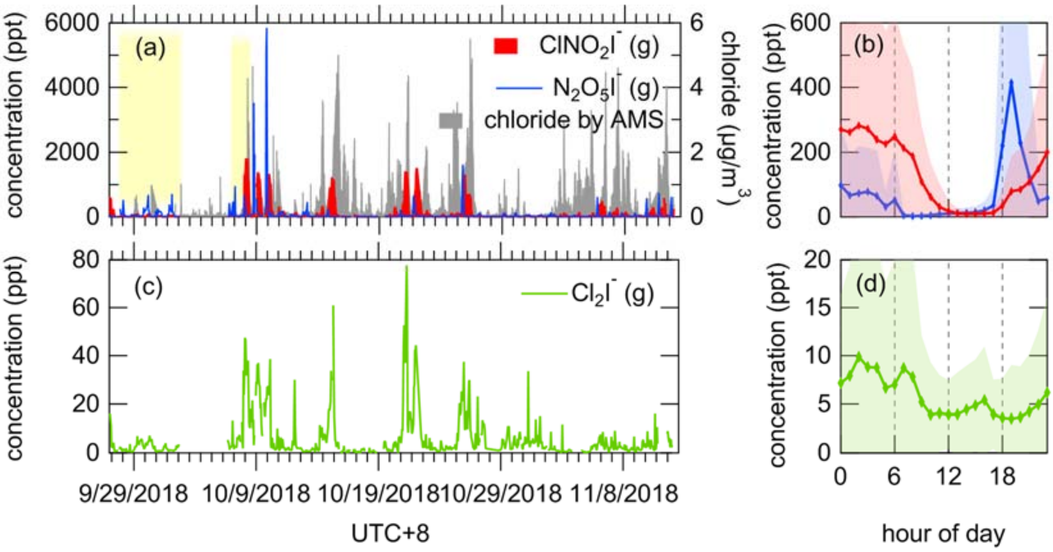


Figure 10. Time series and diurnal variations of humidity-corrected concentrations of N_2O_5 and $ClNO_2$ (a, b) and Cl_2 (c, d). The gray profile is the time series of chloride measured by AMS (mainly non-sea salt). The tinted background indicates the days with high concentrations of N_2O_5 but low concentrations of $ClNO_2$. The shaded areas

indicate one standard deviation.

(2) We add a figure showing an example of the identification of ions with two nitrogen atoms and zero nitrogen atoms which would both lie at odd masses.

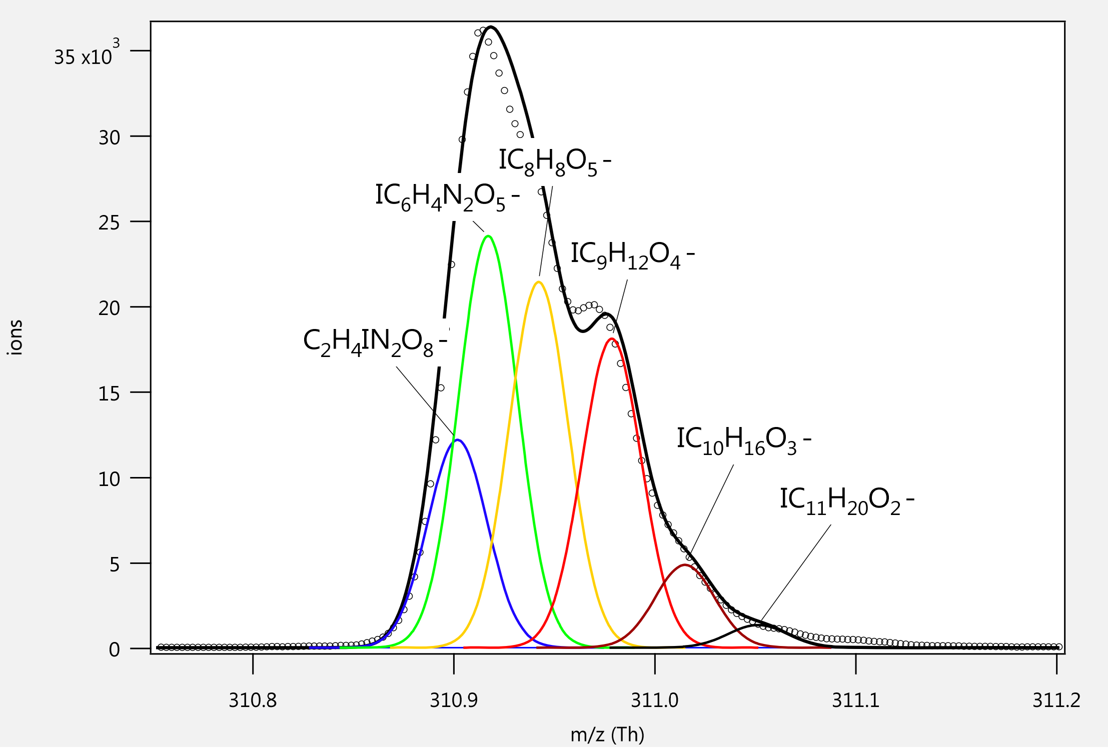


Figure S8. High-resolution peak fittings to the mass spectrum of I-CIMS at m/z 311.

(3) Fig. S13b (time series of C10H15NO6I- in both phases) of the original manuscript is deleted, as other factors may also affect particle-phase concentrations, resulting the difference in the time series of C10H15NO6 in two phases, e.g. OA concentrations, factors possibly influencing the distribution of isomers.

(4) Fig. S14b of the original manuscript is deleted, as the discussions on Fig. S14b was removed but we forgot to remove the corresponding figure.

Minor comments:

1. *Abstract*

- line 29: measurements "by" instead of "of"

Reply: Corrected.

- line 34: typo: "form" -> "from"

Reply: Corrected.

- line 38: missing "of" after "formation"

Reply: Corrected.

- line 42: possibly hint at the uncertainties behind the number 24%?

Reply: In the revised manuscript, the number is modified as fitted coefficient ± one standard deviation, which is “24±0.8%”.

- line 43: "systematically"-> "systematical"

Reply: Corrected.

- line 44: some word or words missing or extraneous around "urban"

Reply: Corrected.

2. Methods

- line 121: unclear procedure (probably due to some wrong language)

Reply: In Line 124-126 of the revised manuscript, the procedure is described as:

Based on AMS data, organic nitrate concentrations were determined by 2-3 times lower NO_2^+/NO^+ ratios for organic nitrate than inorganic nitrate (Fry et al., 2013).

- line 132: j(NO2) should be defined, and could be a bit clearer how it is derived

Reply: Thanks for the comment. In Line 137-140 of the revised manuscript, this sentence is modified:

Time series and diurnal profiles of meteorological parameters, trace gases, the photolysis rate of NO_2 (j_{NO_2}) along with several important VOCs (isoprene, monoterpenes, toluene and benzene) are shown in Figure S1.

In Line 136-137, we mentioned: Photolysis rates were measured by PFS-100 photolysis spectrometer (Focused Photonics Inc.).

- line 148: might be worth pointing out here that only elemental compositions can directly be determined (provided sufficient mass accuracy and resolving power)

Reply: We thank the reviewer for pointing it out. We rephrase the statement in Line 151-155 of the revised manuscript:

Iodide source is a “soft” ionization technique with little ionization-induced

fragmentation and selective detection towards multi-functional organic compounds, providing elemental compositions for thousands of oxygenated compounds in the atmosphere (Hyttinen et al., 2018; Iyer et al., 2016; Lee et al., 2014; Riva et al., 2019).

- line 156: "m/Δm" should possibly be explained

Reply: In Line 161 of the revised manuscript, the sentence has been modified:

…with a mass resolving power of 10000-11000 (m/Δm at 50% height).

- In Section 2.2.1, I would mention in the main text also the temperature range used for the thermal desorption phase. Otherwise, I think the somewhat complex sampling/measurement setup is sufficiently explained with the support by the nice figures in the supplement. (Although I am familiar with the FIGAERO, so that view may be biased.)

Reply: We thank the reviewer for the comment. We add the temperature range used for the FIGAERO thermal desorption in Line 190-192 of the revised manuscript:

The N_2 flow was ramped from ambient temperature to 175℃ in 12 minutes and held for another 20 minutes.

- line 195 (and later): I assume that solution droplets were deposited onto the filter, in which case I believe that "injected" is incorrect.

Reply: Thanks for pointing it out. We replace the "injected" with "deposited".

Fig. S5: What is the meaning diamonds vs. triangels vs. circles? I think there are some discrepancies with humidity-dependences determined by Lee et al. (EST, 2014; doi.org/10.1021/es500362a), e.g.: 1) missing positive slope for formic acid for very low humidities (or at only at lower ones than in Lee et al.) 2) mostly negative slope for nitric acid (for > 2.5 mmol/mol), whereas positive slope in Lee et al. (for < 8 hPa) 3) the slope of succinic acid is slightly negative, but slightly positive in Lee et al. If I am not mistaken, the range of humidities covered by Lee et al. corresponds to mixing ratios up to 8 mmol/mol, which is only the driest third of the data in Fig. S5. But I think above observations (1-3) still hold. It appears like water has a "more negative impact" on sensitivity overall for Ye et al. here, compared to Lee et al. (2014). Such sensitivity *calibrations, in particular also for humidity dependence, are rare and therefore very useful. But it would be better still if the authors could include some discussion of potential discrepancies to earlier sensitivity calibrations and speculate on their reasons. On a side note, I just wondered what Fig. S5 would look like with logarithmic scales? Could be worth considering if that maybe straightened out some lines, for example.*

Reply: We thank the reviewer for the insightful comments.

(1) We add the description about markers in Fig. S5 caption:

The curves with square markers were obtained from calibrations using the FIGAERO. Other humidity curves were determined via the gas inlet. Diamonds, circles and triangles represent humidity curves of inorganic compounds, simple organic acids and multi-functional organic compounds, respectively.

(2) The discrepancies of humidity dependency in our work and Lee et al. are interesting. We add the discussion on this issue in Section S3 in the SI:

Section S3. Comparison of humidity dependences with literature

Humidity dependence curves for most species shown in Fig. S5 are similar with those determined by Lee et al (2014). There are some discrepancies: e.g. (1) obvious positive slope for formic acid under very low humidity in Lee et al (2014); (2) mostly negative slope for nitric acid (for absolute humidity >2.5 mmol/mol), whereas positive slope in Lee et al (2014) (for water vapor pressure <8 hPa).

These discrepancies probably resulted from the difference of pressures in the IMR between the two work: 90 mbar in Lee et al (2014) versus 380 mbar in this work. Table S3 compares the water vapor pressures used in the two studies. The maximum partial pressure of water in this work is 380 mbar×25 mmol/mol =9.5 mbar, higher than 0.8 mbar in Lee et al. (2014). Therefore, the positive slope for formic acid for low humidity is very narrow in our work. For the same reason, their calibrations did not observe the negative slope for nitric acid as their water pressure <0.8 mbar.

Over all, the humidity dependences in Lee et al (2014) and our work are pretty consistent if considering the water vapor pressure in the IMR. The humidity range used in our calibration experiments is sufficient to cover the humidity variations during the campaign (the range was 8.9-34.4 mmol/mol, and mean value was 22.1±5.3 mmol/mol).

Table S3. Comparison of the water vapor pressure used in Lee et al (2014) and this work

Pressure	Lee et al. (2014)	This work
IMR pressure	90 mbar	380 mbar
Maximum water vapor pressure	0.8 mbar	AH~25 mmol/mol, so P_{H2O} =380 mbar×25×10^{-3} =9.5 mbar
Water vapor pressure of positive slope for CH_2O_2	~ 0.15 mbar	AH=0.32 mmol/mol, so P_{H2O} =380 mbar×0.32×10^{-3} =0.12 mbar
Water vapor pressure of positive slope for HNO_3	~ 0.8 mbar	AH=2.1 mmol/mol, so P_{H2O} =380 mbar×2.1×10^{-3} =0.8 mbar

In the main text of revised manuscript, we also mention the comparison results briefly in Line 218-220:

Considering water vapor pressure in the IMR, our humidity-dependent curves are generally consistent with those reported in Lee et al. (2014) (see detailed discussion in Section S3 in the supplement).

(3) The following figure shows Fig. S5 with logarithmic scales. The curves of logarithmic functions approximate straight lines in logarithmic scales.

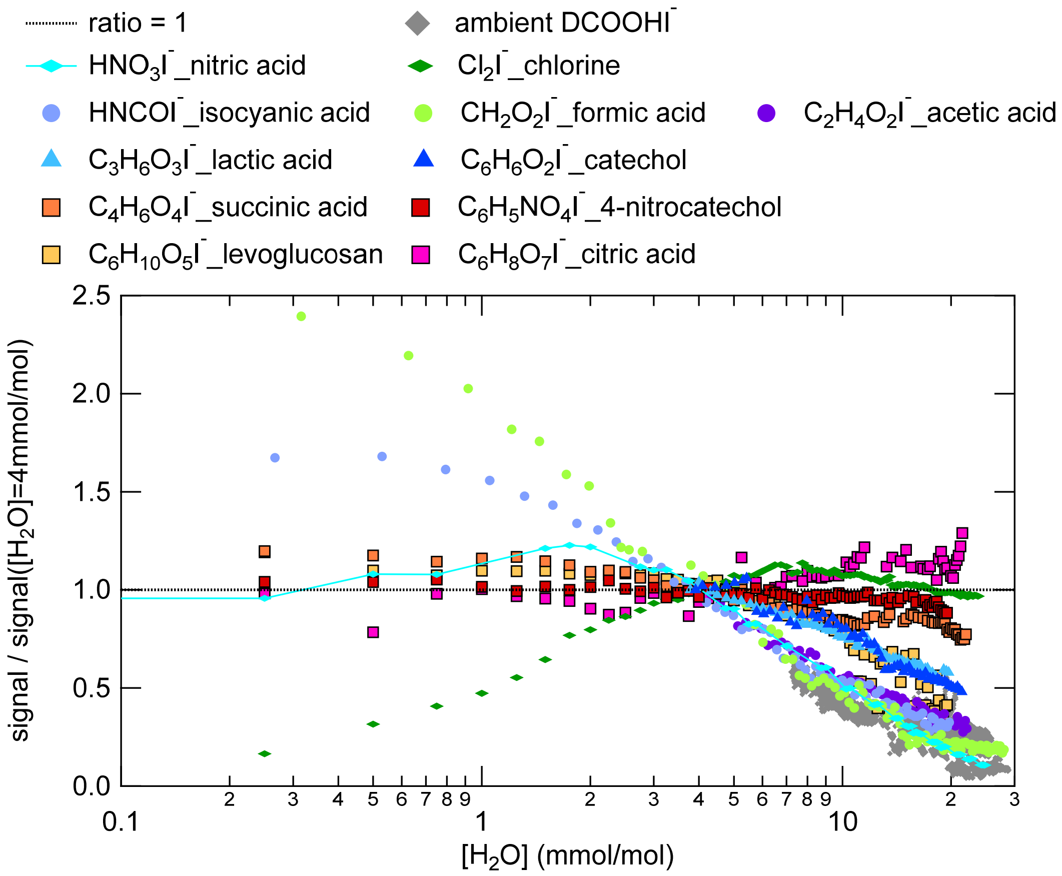


Fig. S6a-f: Would be good to mark in the graphs when the new solution was used. And in light of recent results indicating the importance of solution concentration on Tmax (Ylisirniö et al., AMTD, 2020; doi.org/10.5194/amt-2020-254), it could be interesting to report the concentrations used here (Fig. S6b, d, f; even though it seems like Tmax information was not actually used in this study – not yet anyway).

Reply: We thank the reviewer for the comment.

(1) We use different markers to represent different calibration solutions in the revised manuscript (Fig. S6).

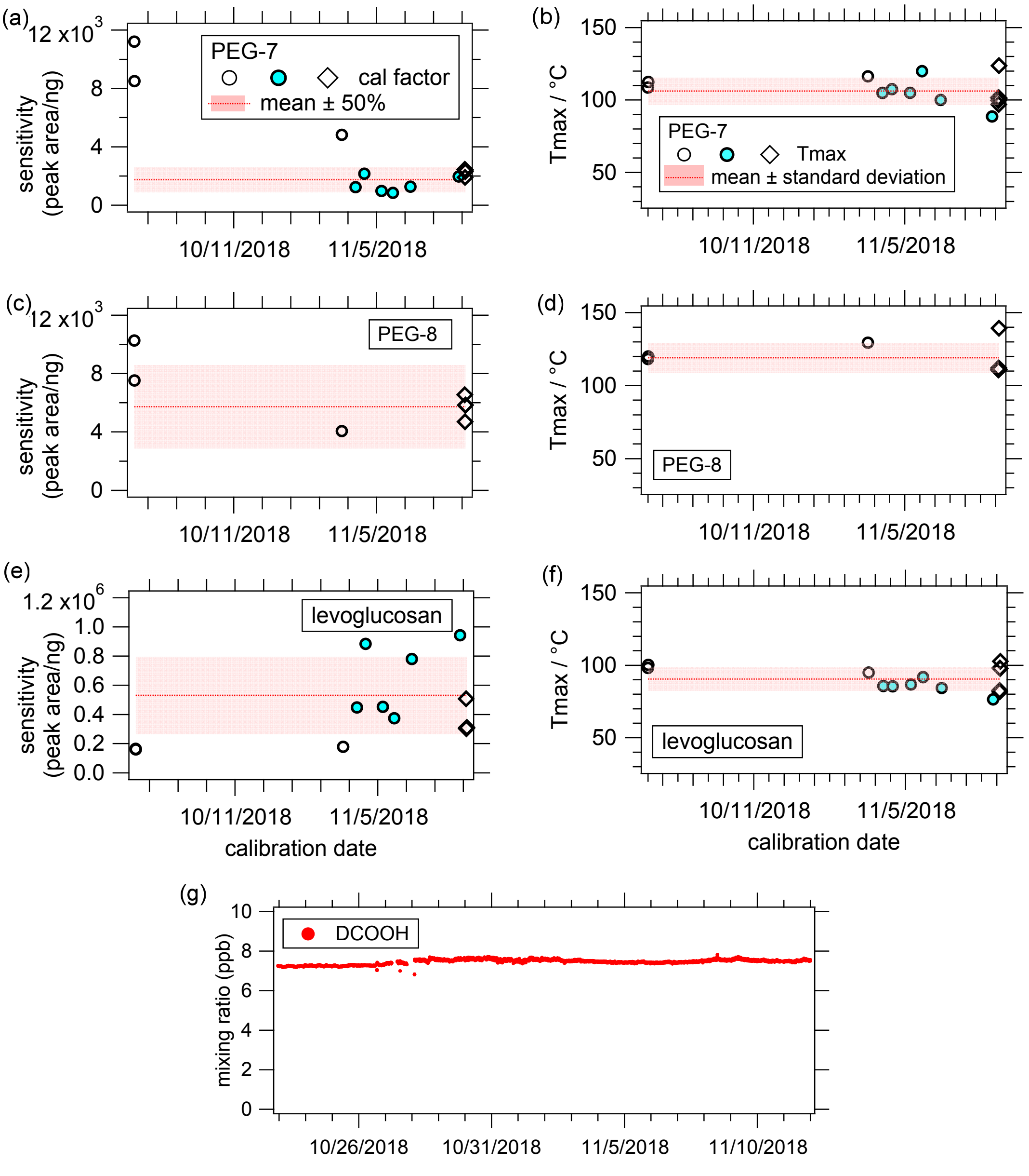


Figure S6. The time series of calibration factors (a, c, e) and T$_{max}$ (b, d, f) of hepaethylene glycol, octaethylene glycol and levoglucosan in the regular calibrations during the campaign. Three markers represent three solutions that were used (Table S2). The concentration of levoglucosan was too high in the solution used in the first two calibrations. Excess levoglucosan severely depleted primary ions, resulting in the underestimation of the response of levoglucosan. On the other hand, low concentrations of primary ions caused the overestimated normalized signals for other ions, and the calibration factors of PEG7 and PEG8 were subsequently overestimated. (g) The measured concentration of DCOOH was steady after applying humidity correction to the signal of DCOOH based on its curve shown in Fig. S5.

(2) Also, the calibration concentrations are summarized in Table S2.

Table S2. The concentrations used in regular calibrations during the campaign

Solution index	Calibration date	Amount deposited on the FIGAERO filter (ng)		
		Levoglucosan	PEG-7	PEG-8
1	2018/09/23	2500	2255	1129
	2018/09/23	5000	4511	2258
	2018/10/29	2500	2255	1129
2	2018/11/01	331.2	1409	
	2018/11/02	331.2	1409	
	2018/11/05	331.2	1409	
	2018/11/07	265.0	1127	
	2018/11/10	397.5	1691	
	2018/11/19	530.0	2254	
3	2018/11/20	6.56	1142	1129
	2018/11/20	13.12	2284	2255
	2018/11/20	19.68	3425	3383
	2018/11/20	26.24	4567	4511
	2018/11/20	31.49	5480	5413

In 2.2.3, 1st paragraph: It is unclear what is meant by "integrating the sum signals" (integrating the signal time series during desorption?) and "peak area" (presumably that same thing?). The latter term is often used for the areas under mass spectral peaks, so I would avoid using it here, unless some more detailed explanation is given (provided I have understood correctly).

Reply: We thank the reviewer for pointing out this confusion. In this manuscript, peak area means the integrated signals under the thermogram profile. This term is ambiguous as the reviewer mentioned, so we have modified the sentence in Line 252-253 of the revised manuscript:

Hourly particle-phase data were obtained by integrating the signals of various ions during each FIGAERO desorption period.

3. Results:

In general, I was thinking the "organic acids" group should be more clearly defined, and possibly renamed. What was the criteria to fall into this group? And it is probably reasonable to assume that also a subset of compounds assigned to other groups qualify as organic acids.

Reply: The section name is modified as "**organic acids and related compounds**".

The only criterium of this manuscript was the mass spectra: sections are organized around the mass spectra, and in each section of a specific chemical type, we chose to discuss those species that had high concentrations, e.g. formic acid, pyruvic acid and dicarboxylic acids. We were not intended to include organic acids as more as possible, or exclude organic acids in other sections.

- lines 319-322: It would be good to elaborate on the conclusion of primary and secondary sources from Fig. 5. I fail to see how that distinction can be made here, or under what assumptions.

Reply: (1) Levoglucosan was enhanced in the evening and so it was probably associated with regional biomass burning emissions (section 3.2). We elaborate on this conclusion 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 $\mu g \cdot m^{-3}$/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., 2020c; Zhang et al., 2015).

(2) We elaborate on the conclusion of primary and secondary sources in Line 344-348 of the revised manuscript:

The scatterplot of $C_6H_5NO_4$ as the function of $C_6H_{10}O_5$ exhibits two different slopes (Fig. 5): the lower slope at night (0.088±0.005) indicates the contribution of

biomass burning, while the higher slope during the daytime (0.26±0.02) suggests there were other important sources for nitro-aromatics, potentially secondary formation from photooxidation of aromatics (Jenkin et al., 2003).

Fig. S13a: I suggest expressing also right-hand y-axis in units of ppt C10H15NO6I- and Fig. S13b: What kind of correlation was expected? Certainly, gas phase mixing ratios would not be the only variable affecting particle-phase concentrations. Other factors might play a role too, e.g. OA loading, and factors possibly influencing the distribution of isomers, e.g. NOx and O3. The main text (line 416) points out that the correlation is not good, but I might miss the attempt of explaining that. The following sentences might be the hypothesis, but that would not be clear to me from reading this paragraph. In any case, I think that looking at more data could support the authors' hypotheses.

Reply: Thanks for the comments.

(1) Fig. S13a of the original version is revised as the reviewer suggested.

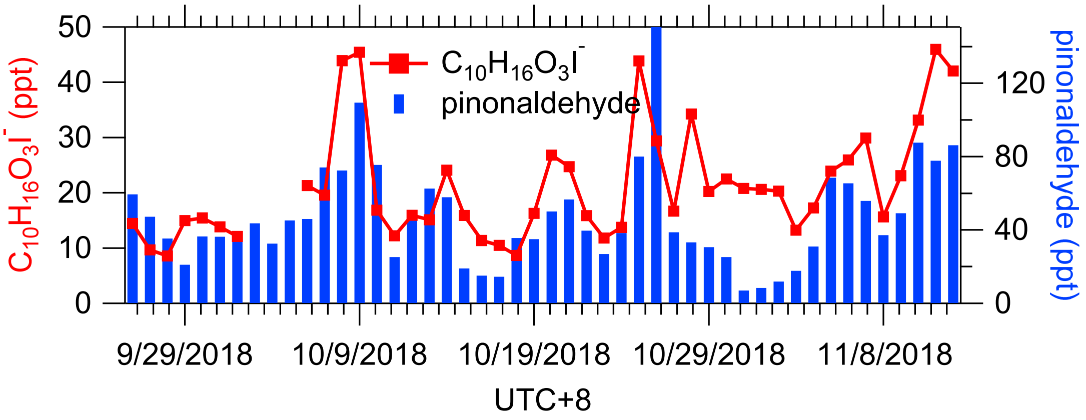


Figure S14. Time series of daily maximum concentrations of gaseous $C_{10}H_{16}O_3I^-$ and pinonaldehyde ($C_{10}H_{16}O_2H^+$, m/z 169.12).

(2) There are two possible isomers for $C_{10}H_{15}NO_6$ according to the literature. We expected that the difference in time series of gas-phase and particle-phase $C_{10}H_{15}NO_6$ may support our hypothesis of different isomers contributing to $C_{10}H_{15}NO_6$. We agree with the reviewer that gas-phase mixing ratios would not be the only variable affecting particle-phase concentrations, so we delete Fig. S13b in the original supplement and modify the corresponding statement in Line 443-451 of the revised manuscript:

However, $C_{10}H_{15}NO_6I^-$ in the gas phase showed a distinct diurnal profile with peak before the noon. Two possible types of compounds were proposed for

$C_{10}H_{15}NO_6$ in previous studies: peroxyacetyl nitrate from pinonaldehyde (Faxon et al., 2018; Nah et al., 2016; Schwantes et al., 2020), or organic nitrates (Bean and Hildebrandt Ruiz, 2016; Boyd et al., 2015). 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.

Fig. S14: Very interesting figure, both panels, yet S14b is not discussed anywhere.

Reply: We delete this figure from the revised manuscript. The discussion about the Fig. S14b of the original manuscript had been removed, but we forgot to remove the corresponding figure.

- lines 427-428: I do not actually see where the cited Lee et al. study reports that organosulfates are detected via deprotonation. Le Breton et al. do make the case, and I believe there are LC-ESI-MS measurements that also detect such compounds in deprotonated form, which might make for more suitable works to cite here in addition.

Reply: In the 4th paragraph of Lee et al. study, it said, "Electron transfer and proton abstraction are essentially negligible except for a few atmospherically relevant compounds, such as nitrate (NO_3) radicals in the case of charge transfer, and sulfuric acid (H_2SO_4) in the case of proton abstraction".

We also cited LC-ESI-MS measurements by Huang et al. (https://doi.org/10.5194/amt-11-3447-2018) in Line 462-463 of the original manuscript:

Previous work observed the sulfite ion radical ($\cdot SO_3^-$) during the ionization of organosulfates (Huang et al., 2018).

- line 432: reference should be specifically to panel b in Fig. S15.

Reply: Thanks for pointing it out. The sentence in Line 461-462 of the original manuscript is modified as the reviewer suggested:

Abundant SO_3I^- was detected in particles, and it correlated well with the ion $C_2H_3SO_6^-$ (Fig. 9b) and sulfates measured by AMS (Fig. S16).

- lines 440-444: I agree that wall losses are an issue, but then what about other likely low-volatility compounds that are reported as concentrations (e.g. Fig. S11)? It

might actually be useful to estimate wall losses, if possible (it has remained unclear, by the way, if the gas-phase sampling flow was laminar or turbulent). Reporting reliable mixing ratios or concentrations is tricky business with these methods. But I think it is OK to report results in those ways, as long as caveats and uncertainties are clearly stated (better yet quantified (or estimated)...)

Reply: Wall loss occurs inside both sampling lines and the instrument. For example, semi-volatility and low-volatility compounds tend to interact with wall surfaces and thus extend response time. Researchers are also trying to improve the designs of the IMR to minimize wall effects (Palm et al., 2019). As accurate estimation for all these gas-wall interactions has remained unclear, we did not correction the effects of wall loss in this work.

We agree with the reviewer that our signals were inevitably influenced by wall losses. We add the details of residence time and Reynolds number of the two sampling lines in section 2.2.1: 1.3 seconds and ~1500 for particle sampling line, 0.24 seconds for gas sampling line.

- Fig. 10, panels b and d lack legends.

Reply: Corrected.

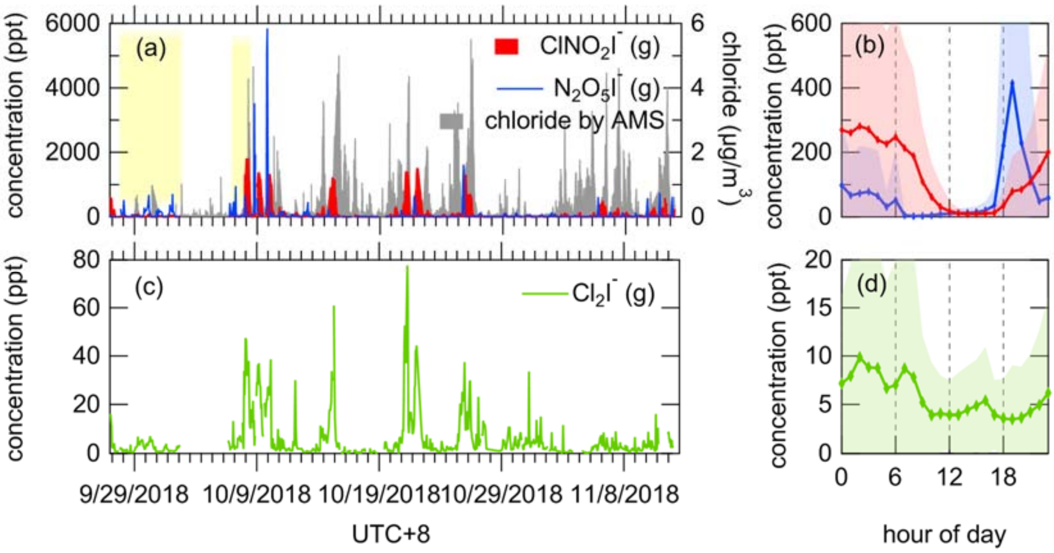


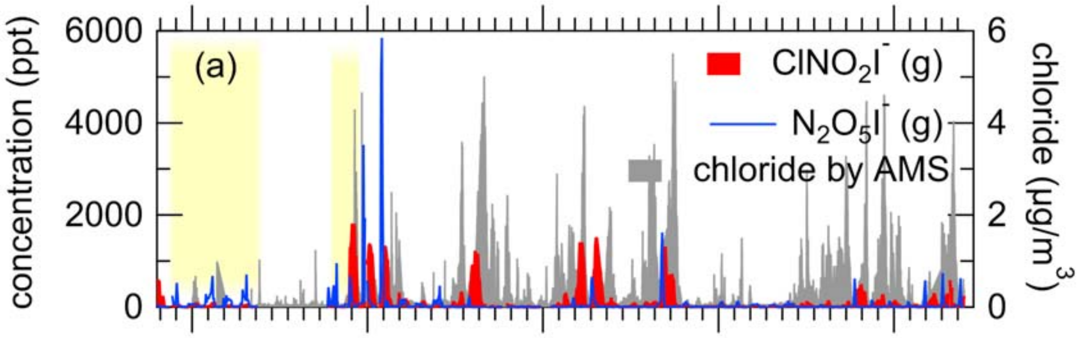
Figure 10. Time series and diurnal variations of humidity-corrected concentrations of N_2O_5 and $ClNO_2$ (a, b) and Cl_2 (c, d). The tinted background indicates the days with high concentrations of N_2O_5 but low concentrations of $ClNO_2$. The shaded areas indicate one standard deviation.

- Fig. S16 lacks explanation of yellow shades.

Reply: The explanation is added to the caption:

The tinted background indicates the days with high concentrations of N_2O_5 but low concentrations of $ClNO_2$.

In addition, we combine Fig. S16 and Fig. 10a in the revised manuscript.



- Reference to Fig. 11 could come sooner.

Reply: Corrected (Line 494-495 of the revised manuscript):

Here, the concentrations of HNO_3I^- in the particle phase were compared with particulate nitrate measured by AMS (Fig. 11c).

- line 486: “augmented” likely not the right word

Reply: We delete “augmented primary”. The sentence in Line 522-523 of revised manuscript has been modified:

However, there was a notable exception in C5 which had a significantly reduced $\overline{OS_C}$, probably as the result of emissions of isoprene.

- line 502: I think that concluding from the abundance of that group of compositions (CxHyN1,2Oz with #O=3) to the abundance of nitrophenols specifically, needs some additional evidence or argumentation or relativization, as other (in particular non-phenolic) compounds are likely member of that group as well.

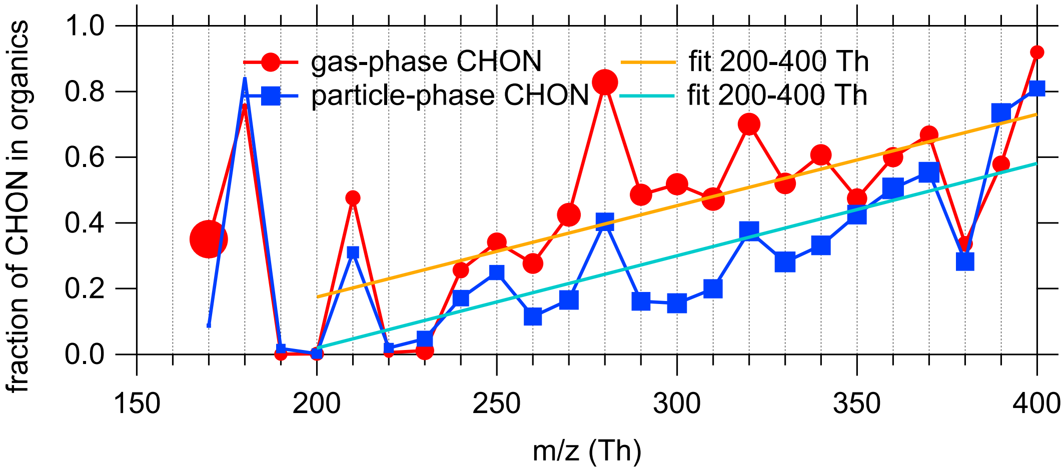
Reply: We thank the reviewer for the comment. To support this conclusion, the fraction of nitrophenols in $C_xH_yN_{1,2}O_3$ is added to Line 543-545 of revised manuscript:

Nitrophenols also contributed significantly to $C_xH_yN_{1,2}O_z$ compounds, as they accounted for 74% of $C_xH_yN_{1,2}O_z$ containing 3 oxygen atoms, which in turn

accounted for 22% of $C_xH_yN_{1,2}O_z$.

- Figs. 14 and S17 (and related discussion): I fail to see the point in this analysis. Please elaborate.

Reply: We fit the points within m/z 200-400 as the following figure shows (the two fitted traces are not displayed in the revised manuscript). It is obvious that the observed fractions of N-containing organic compounds were higher for elevated m/z. Marker sizes indicate the total concentration level in each m/z bin. High concentrations of HNCO resulted in the large marker around m/z 170 (Wang et al., 2020b) (https://doi.org/10.1021/acs.est.0c02843).



~- line 523: why do you think agreement was worse in some periods?

Reply: As organic nitrate by AMS is estimated based on the different NO^+/NO_2^+ ratios between organic nitrate and inorganic nitrate, the uncertainties for determined organic nitrate would be inevitable high when inorganics dominate the total nitrates. Actually, our results also reflect this. We calculate the correlation coefficients between particulate N-containing organic compounds from FIGAERO-I-CIMS and particulate organic nitrates from AMS for the periods below a certain threshold of particulate inorganic nitrate measured by AMS, as shown in figure 15c. The comparison result is added to Line 565-568 of the revised manuscript:

Good agreement was achieved when the concentrations of inorganic nitrate were relatively lower, e.g. below 8 μg/m^3. However, the discrepancies increased when inorganic nitrate were higher, which can affect the determination of organic nitrate from AMS.

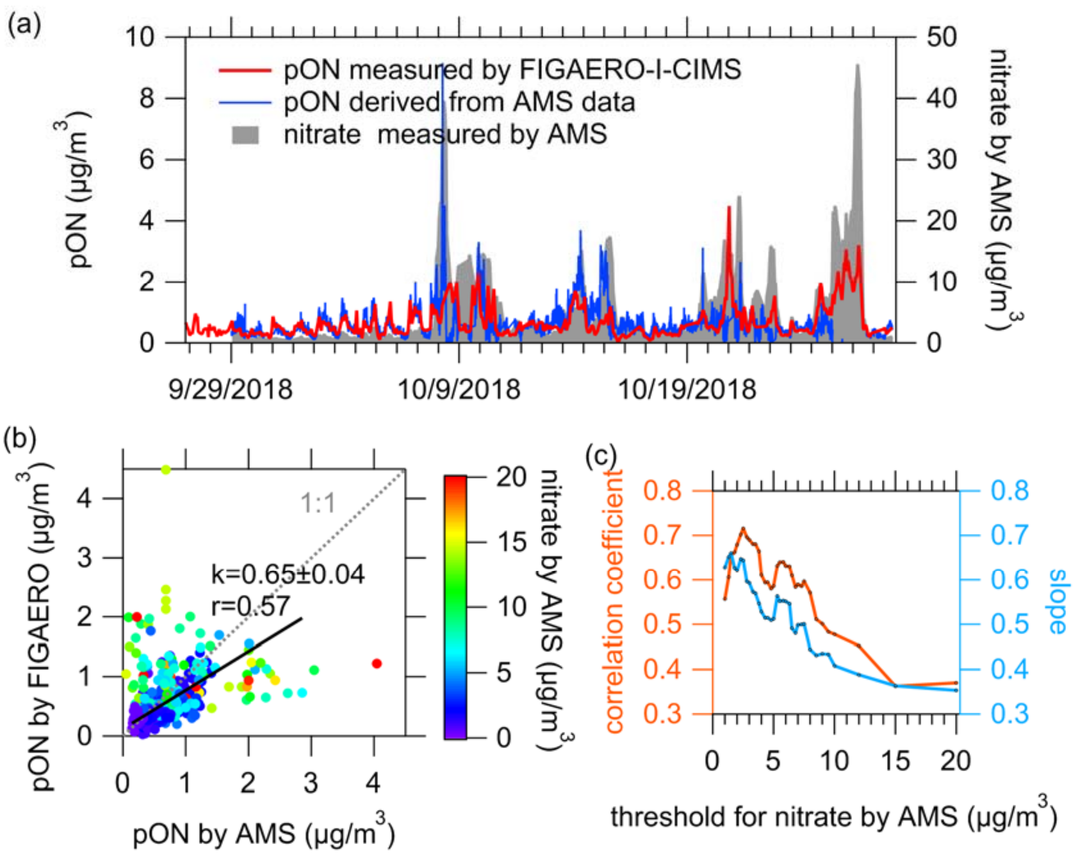


Figure 15. (a) Time series of particulate N-containing organics measured by FIGAERO-I-CIMS (pON by FIGAERO), particulate organic nitrates derived from AMS data (pON by AMS) as well as particulate inorganic nitrate. (b) Comparison of pON by FIGAERO and pON by AMS, color-coded by the concentrations of particulate inorganic nitrate measured by AMS. The black line presents the linear fit for nitrate by AMS below 8 μg/m^3. (c) The determined slopes and correlation coefficients between pON by FIGAERO versus pON by AMS by filtering the data below different thresholds of particulate inorganic nitrate measured by AMS.

Fig. 16a: Could the relatively high absolute humidity also contribute to the lower mass closure, keeping in mind calibration results (Fig. S5)?

Reply: Dry N_2 gas was used for thermal desorption of FIGAERO, so humidity is supposed not to affect the particle phase measurements.

Fig. S18b: Clarify in caption or in the figure that OA is AMS-based.

Reply: The caption is modified:

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.

Conclusions: Should more suitably be called a "Summary."

Reply: Corrected.

- line 575: Unclear connection of BVOC products to NOx

Reply: The sentence In Line 623-625 of the revised manuscript has been modified:

Different diurnal profiles for various BVOC-derived organic nitrates were observed, reflecting their different formation pathways related to NO_X chemistry (i.e. daytime photo-oxidation, nocturnal NO_3 reactions).

Review #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.

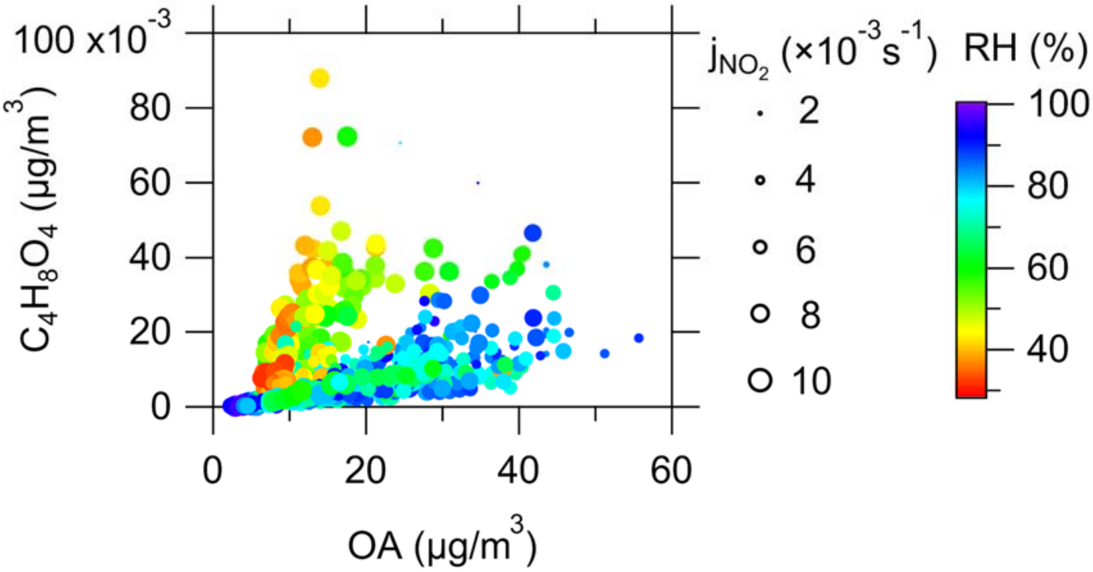


Figure S13. Scatterplot between particle-phase $C_4H_8O_4$ and OA color-coded by ambient RH and size binned by the daily maximums of photolysis rates of NO_2.

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

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 $y = 0.23181 + \frac{0.81488}{1+\exp(\frac{2.5492-x}{2.1654})}$. (b) Fitting relative transmission efficiency as a gaussian curve of m/z. The gauss function is $y = 0.27777 + 1.0403 \times \exp(-(\frac{x-217.4}{147.7})^2)$.

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.

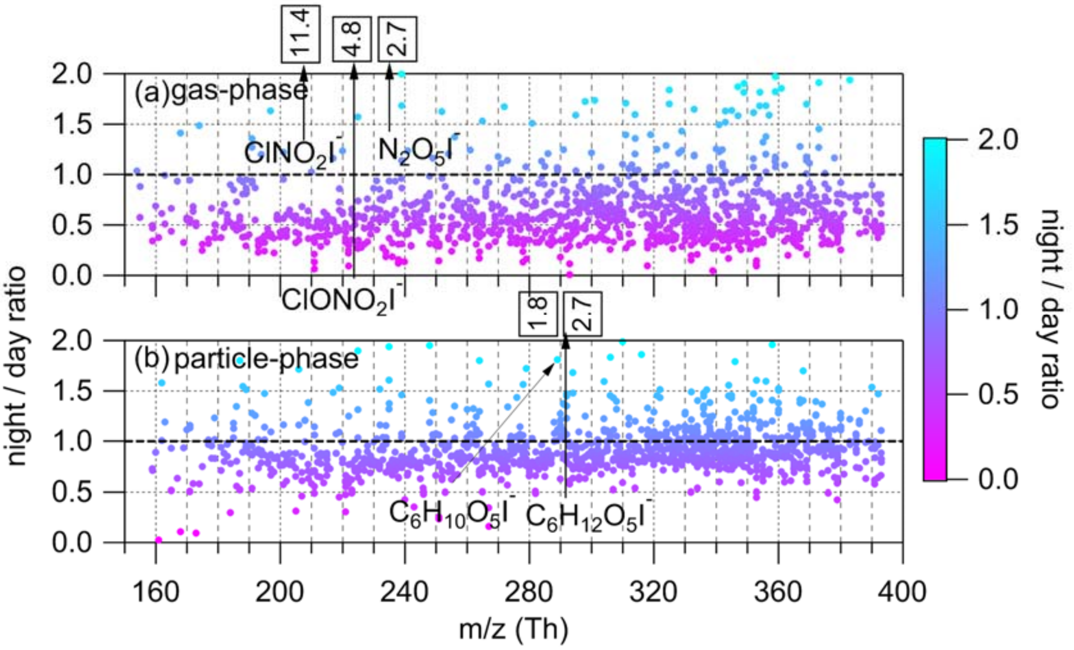


Figure 2. The ratios of concentrations at night (10 pm - 6 am) to concentrations during the day (10 am - 6 pm) for ions ranging from 150 to 400 Th in gas-phase (a) and particle-phase (b). The range of y-axis is set between 0 and 2 for clarity, although the ratios of some compounds are larger than 2. 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., 2020a; 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 $\mu g \cdot m^{-3}$/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., 2020c; 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).

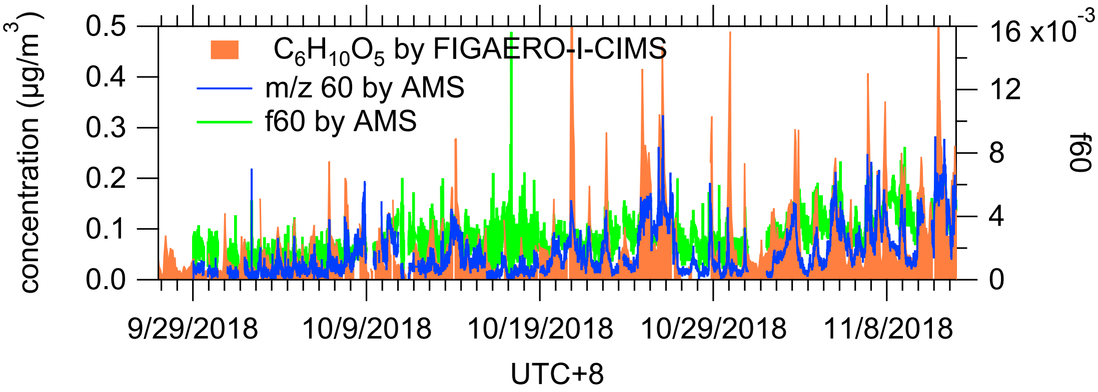


Figure 3. (a) Time series of particulate $C_6H_{10}O_5$ measured by FIGAERO-I-CIMS, m/z 60 fragment and f60 measured by AMS. Background f60=0.3% and background m/z 60=0.3%×OA were subtracted from f60 and m/z 60 (Cubison et al., 2011; Hu et al., 2016).

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.

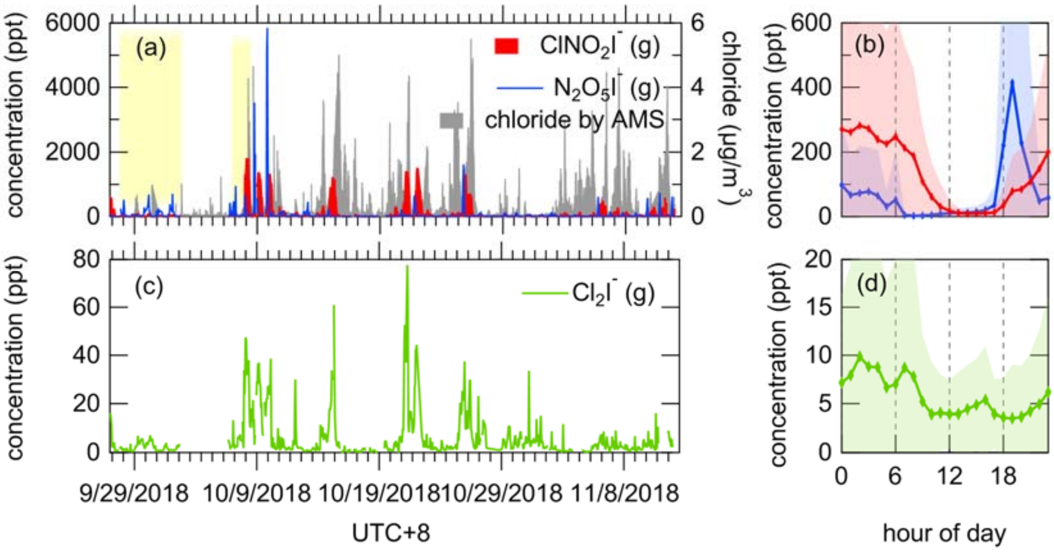


Figure 10. Time series and diurnal variations of humidity-corrected concentrations of N_2O_5 and $ClNO_2$ (a, b) and Cl_2 (c, d). The tinted background indicates the days with high concentrations of N_2O_5 but low concentrations of $ClNO_2$. The shaded areas indicate one standard deviation.

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.**

Review #4

In this work the authors use a FIGAERO-I-CIMS to make calibrated and uncalibrated measurements of oxygenated organic and inorganic compounds in the urban atmosphere Guangzhou over several days. Their observations demonstrate an effective ability to quantify a number of oxygenated organics in both the gas and particle phases and are well-grounded through supporting measurements made by an aerosol mass spectrometer and PTR-MS, in particular. Their findings highlight the limitation of the I-CIMS analytical toolset in urban environments where fresh emissions of organics are abundant, when the objective is to close the atmosphere organic carbon budget. Their findings also highlight the capacity for the I-CIMS to place limits on the contribution of organics to aerosols, for molecules containing up to 5 O atoms. Overall, this work is highly suited for publication in Atmospheric Chemistry & Physics, pending minor revisions for improved accessibility to the scope of the measurements.

Reply: We are grateful for all the detailed comments and the valuable suggestions, which help us greatly in improving our manuscript. Please find the answers to individual comments below.

Minor Revisions

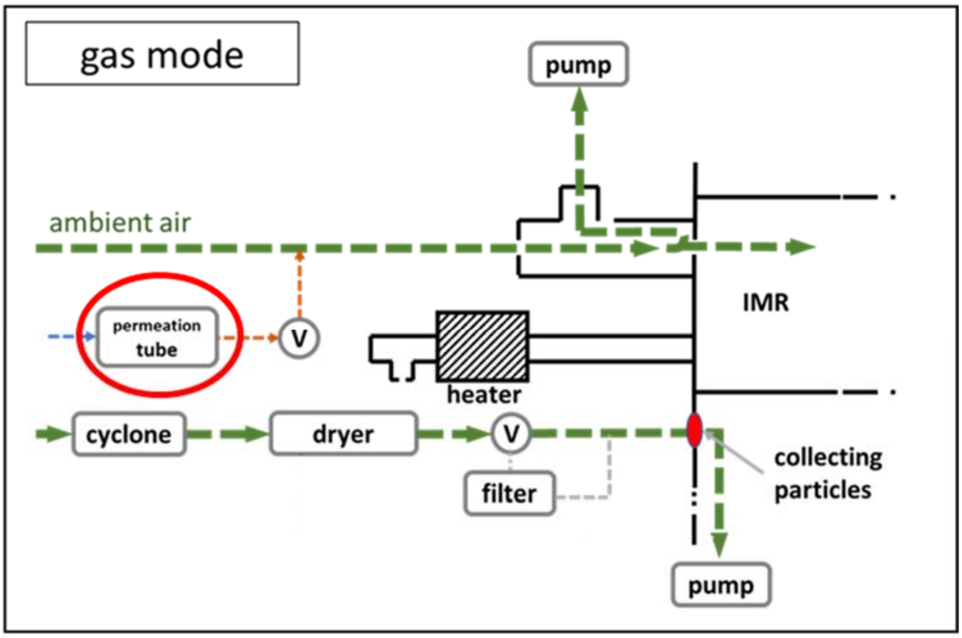
1. Limitations of long inlet lines for gas sampling on instrument response, accuracy of field blanks, or creation of bias from wall loss of aerosols followed by their volatilization are not accounted for in the presented data analysis. The authors go to great extents to conduct calibrations for their target analytes, but do not present response times for a subset of these gases using the full inlet line length under field conditions nor to simulate them in the laboratory. The partitioning and delay of organic gases has been previously demonstrated and warrants some consideration and comment in this work (Deming et al., 2019; Liu et al., 2019). With increasing oxidation of organics, time responses would be expected to increase for analytes traversing the inlet, despite the short residence time of air in it (0.35 s). The authors state the inlet was heated to minimize sorption but do not provide sufficient detail (e.g. what was the temperature? How was it chosen?). The gas inlet has a further concern related to bias introduced from the volatilization of particles lost to the tubing surfaces. Such effects are well documented for NH4NO3 and expected for semi-volatile organics. Were particles excluded from the gas inlet? If yes, how? I no, how was the impact of volatilized particles on the gas phase measurements accounted for? Finally, the *technical details of the DCOOH addition to the instrument during the campaign to track gaseous response factors for all analytes are not given. Was this added to the instrument inlet? Or just in front of the IMR, as per the zero air for blanks?*

One way the authors could have determined an approximation of these effects is by analyzing their signal decays for all ions during the field blanks where the inlet was overflowed with zero air, but the blanks presented in the manuscript appear to be limited at being performed only just upstream of the IMR of the CIMS.

In the case of highly oxygenated organics and inorganics (e.g. HNO3), there is also a concern of long desorption time constants for these molecules during background assessments. Were these quantified in order to set the 3-minute background of the instrument? If yes, can the authors present a summary table of such time constants meeting this criterion using their calibration data? The calibrated compounds cover a nice range of atmospheric species and would strengthen the quality of the dataset.

Reply: We would like to thank the reviewer for the insightful comments.

(1) DCOOH was added before the IMR as shown in Fig. S3a:



(2) The following figure shows how signals of gases decease during the 3-min background. For VOCs and many SIVOCs, 3-min is enough to reach the gas-wall equilibrium, but that's not the case with very "sticky" compounds like nitrophenols. We agree with the reviewer that the method for calculating gas background used in this paper is inevitably influenced by wall effect, especially for "sticky" species, and this impact can be significantly reduced using "fast background" in which the background

maintains for such a short time that the wall interactions can be ignored (Palm et al., 2019). In Line 184-188, we add the reminder to the readers that our method is not the best way to calculate the gas background:

The background measurements for CIMS are inevitably influenced by wall interactions, especially for "sticky" species. Recently, Palm et al. (2019) proposed a new way to determine gas background ("fast background") by fast switching between ambient air and background, which greatly improves accurate determination of CIMS background.

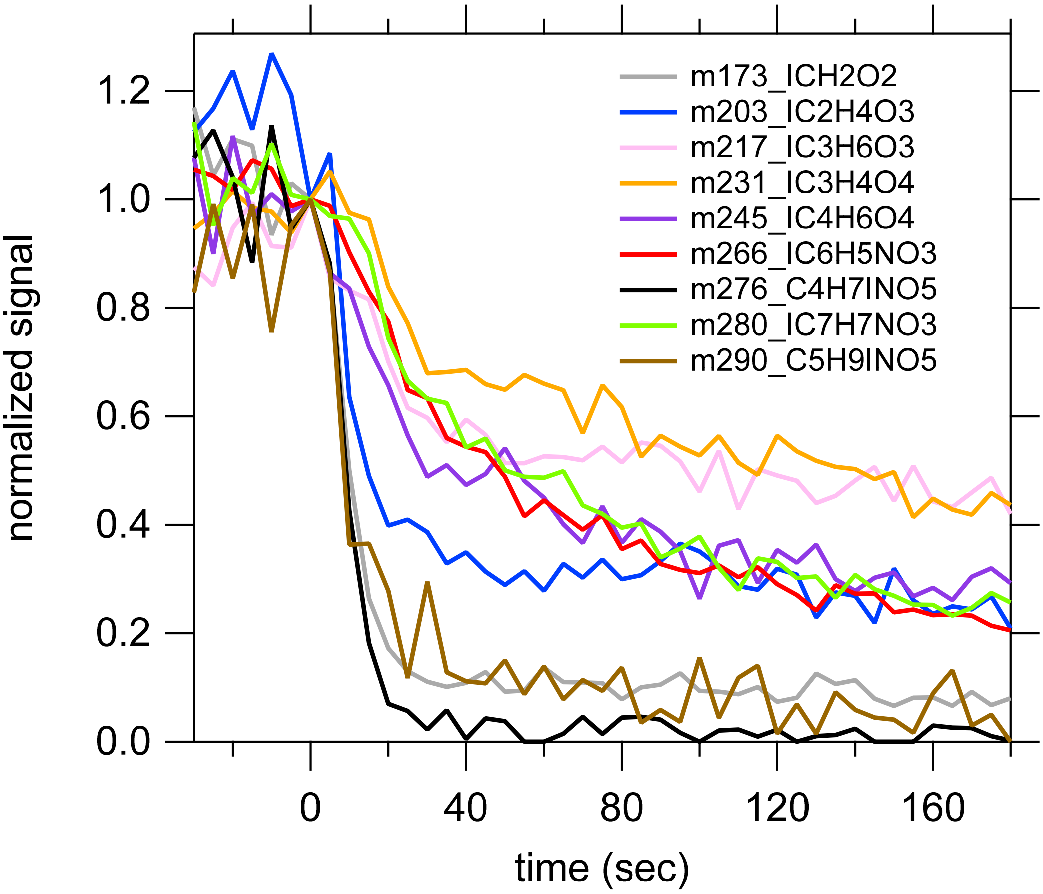


Figure. Gas-phase time profiles measured during a gas background. Time zero is the start time of background. Signals were normalized to the ambient concentrations at Time zero.

(3) We did not remove particles from gas sampling. In Line 166-167 we remind this information:

…and 2 L/min was directly taken into the instrument for gas measurements without removing particles.

(4) Ambient air was drawn via a 3-meter Teflon tubing (1/4-inch OD) at ~9 L/min. The residence time was 0.24 seconds (0.35 seconds was derived based on the

assumption that the ID of tubing was 3/16 inch. Here, we re-calculate the residence time using accurate ID of the tubing). We believe that the volatilization of particles in such a short time while passing through gas inlet is not important, as implied by the following figure (the signals changes during the FIAGERO desorption period), which demonstrates that the increases of signals on a timescale of <1 second is negligible.

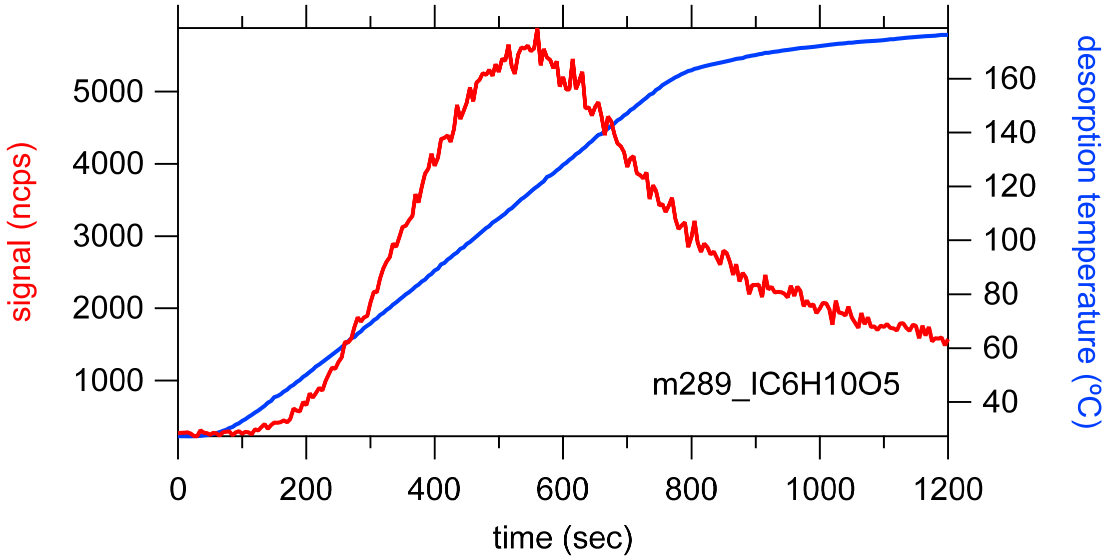


Figure. Time profile of the levoglucosan ion measured during the FIGAERO desorption period of a calibration experiment.

(5) In addition to the above modifications, we also add more information about the sampling system in Section 2.2.1 (experimental setup), including the length of sampling line protruding out the window (~1.5 meters), the Reynolds number and residence time in the particle sampling line (~1500 and 1.3 seconds, respectively).

2. The authors present extensive work to calibrate for many atmospheric gas and particulate species expected in real samples. They present field calibrations for the FIGAERO that have up to 50 % variance in in response, but no discussion on how this may impact the interpretation of their results or improved upon for future work. Some additions need to be made throughout the manuscript to capture the impact that this variance could have (e.g. when evaluating the contribution of the particulate organics detected to the total OA from the AMS, can a +/- on these numbers be derived?).

Reply: We thank the reviewer for the comment. The aim of field calibrations was to check the stability of the instrument, and these calibration factors determined in the campaign were not used for calculating concentration. Thus, the variance up to 50% shown in Fig. S6 would not affect the interpretation for the results.

The variance of calibration factors throughout the campaign actually was caused by the calibration solution. In the first two calibrations, the concentration of levoglucosan in the solution was too high. We add explanation about the effect observed for using of too high concentration in the calibration standards in Figure S6 caption:

The concentration of levoglucosan was too high in the solution used in the first two calibrations. Excess levoglucosan severely depleted primary ions, resulting in the underestimation of the response of levoglucosan. On the other hand, low concentrations of primary ions caused the overestimated normalized signals for other ions, and the calibration factors of PEG7 and PEG8 were subsequently overestimated.

We add the estimated error of fitting to the fraction of the particulate organic compounds detected in the total OA concentrations: 24±0.8%. We did not calculate the uncertainty from the measurements, as it is too complicated to include so many factors, e.g. calibration factors, response factors derived from voltage scanning, wall loss.

Technical Revisions

1. *Page 4, Line 105: The quantitative threshold for 'sufficient sunshine' should be presented here in place of these words.*

Reply: Thanks for pointing it out. The sentence in Line 105-108 of the revised manuscript is modified:

Affected by the subtropical monsoon climate, the weather in the region was characterized by high temperatures and relative humidity (RH) as well as sufficient sunshine (global solar radiation of the Pearl River Delta region in Fall, 2016 was ~1200 MJ/m^2, Liu et al., 2018).

2. *Page 4, Line 106: 'south to the mountains' should be 'south of the mountains'*

Reply: Corrected.

3. *Page 5, Line 108: delete 'in Guangzhou' as it is redundant.*

Reply: Corrected.

4. *Page 6, Line 145: 'thermally' should be 'thermal'*

Reply: Corrected.

5. *Page 6, Line 146: 'very' is not required here. Delete.*

Reply: Corrected.

6. *Page 7, Lines 172-173: 'overflushing' should be 'overflowing'*

Reply: Corrected.

7. *Page 7, Line 174: It would be useful to provide a basic description of the TD program in the text (e.g. ramping rate and max temp).*

Reply: Thanks for the comment. We add the information of the TD program in Line 190-191 of the revised manuscript:

The N_2 flow was ramped from ambient temperature to 175℃ in 12 minutes and held for another 20 minutes.

8. *Page 7, Line 177: The description of the particle background measurements is unclear. Please revise for clarity.*

Reply: Thanks for pointing it out. In Line 192-194 of the revised manuscript:

Particle background was determined every 6th 1-hour running cycles in which ambient air passed over a filter (Parker Balston, model 9922-11-CQ) in front of the FIGAERO filter.

9. *Page 8, Lines 197-199: This is good, but could matrix effects from other particle components change the sensitivity of a given analyte? Have standard additions for particulate organics been previously performed to provide context on the validity of this approach? Please provide some additional rationale on the robustness of this calibration technique here.*

Reply: Thanks for the comment. The role of solvent is to dissolve standards. The criteria for choosing the solvent are: 1) it cannot be detected efficiently by the CIMS; 2) it evaporates quickly. This syringe deposition method for FIGAERO calibration has been widely used in the work of FIGAERO-CIMS (Lopez-Hilfiker et al., 2014). Recently a new method using atomizer to generate particles was proposed to calibrate FIGAERO-CIMS (Ylisirniö et al., 2021). However, this study also prove that the performance in terms of sensitivity of the syringe deposition method applied in this study is in excellent agreement with the atomization method, and even better when the calibration concentration is high (Ylisirniö et al., 2021).

10. *Page 9, Lines 225-226: Was the concentration too high for all the analytes? Figure*

S6 says this was the case only for levoglucosan. Please explain the effect observed for the use of too high concentration in the calibration standards, such that the community can benefit from this observation.

Reply: Thanks for the comment. The concentration was too high only for levoglucosan. We add explanation about the effect observed for the use of too high concentration in the calibration standards in Figure S6 caption:

The concentration of levoglucosan was too high in the solution used in the first two calibrations. Excess levoglucosan severely depleted primary ions, resulting in the underestimation of the response of levoglucosan. On the other hand, low concentrations of primary ions caused the overestimated normalized signals for other ions, and the calibration factors of PEG7 and PEG8 were subsequently overestimated.

11. Page 9, Lines 236-238: Depending on the time responses of the analytes in the instrument for desorption (see Minor Comment 1 above), many of these background corrections may be much higher than if the blanks had been performed for a longer period of time. Overall, the impact of this is not particularly serious because the result is a conservative estimate of mixing ratios and mass loadings (i.e. the presented values may be lower than they truly are due to over-correcting). It would be nice to see the data for the backgrounds of species spanning the range of calibrated analytes in the SI.

Reply: Thanks for the comment. We made six particle-phase background in a row in the campaign. The following figure shows the ratio of a consecutive series of particle-phase background versus the ambient concentrations for ions discussed in the main text. Most chemicals can be almost entirely removed in the first background stage, except for a few low-molecular-weight species. The reason why $C_6H_{12}O_5I^-$ (m/z 291) did not behave as we expected is that its ambient concentration was very low at that time (6 am).

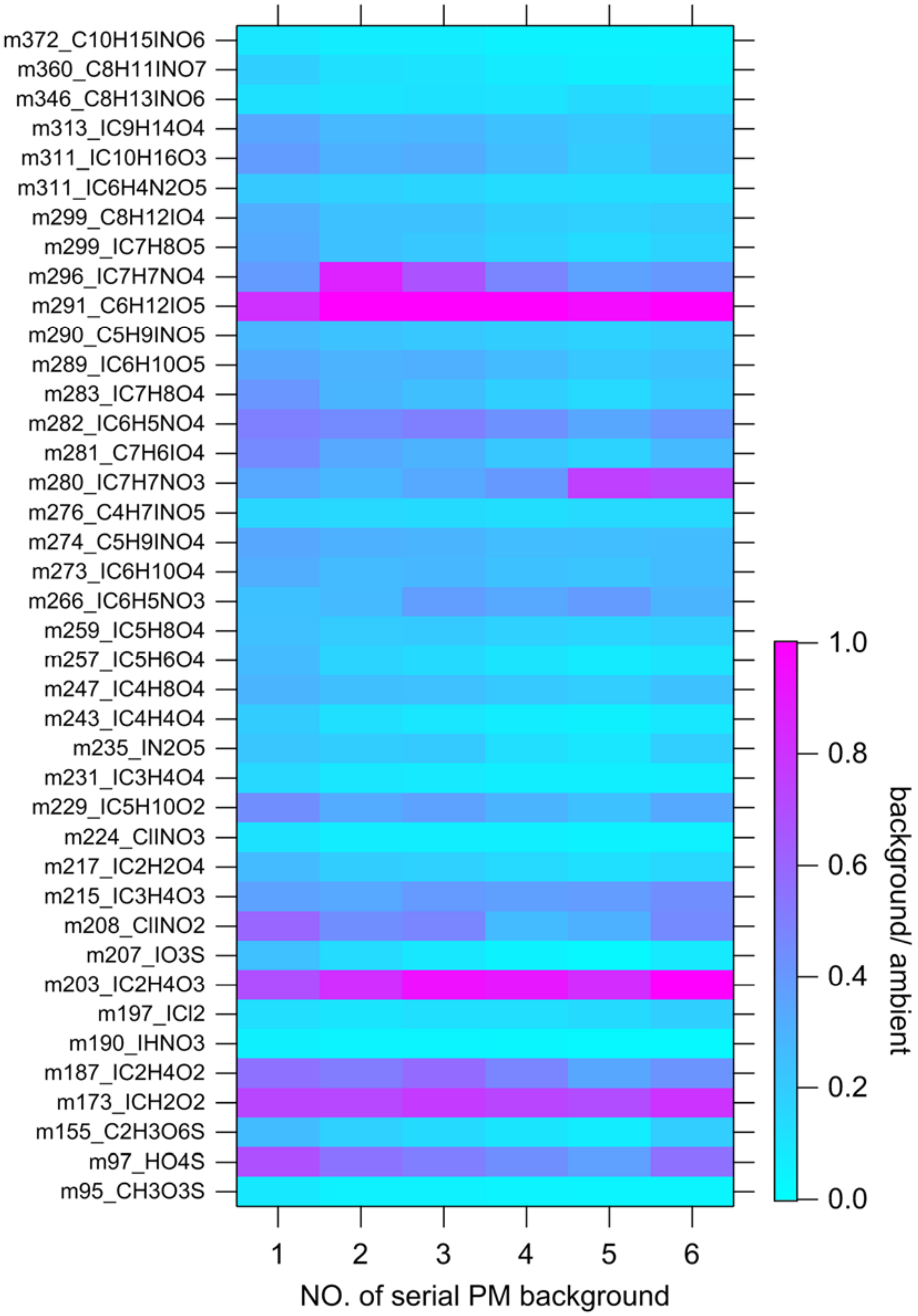


Figure. Ratio of a consecutive series of particle-phase background versus the ambient concentrations for ions discussed in the main text.

12. Page 12, Lines 319-322: There are no lines on Figure 5 depicting the two different slopes. Suggest adding these.

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

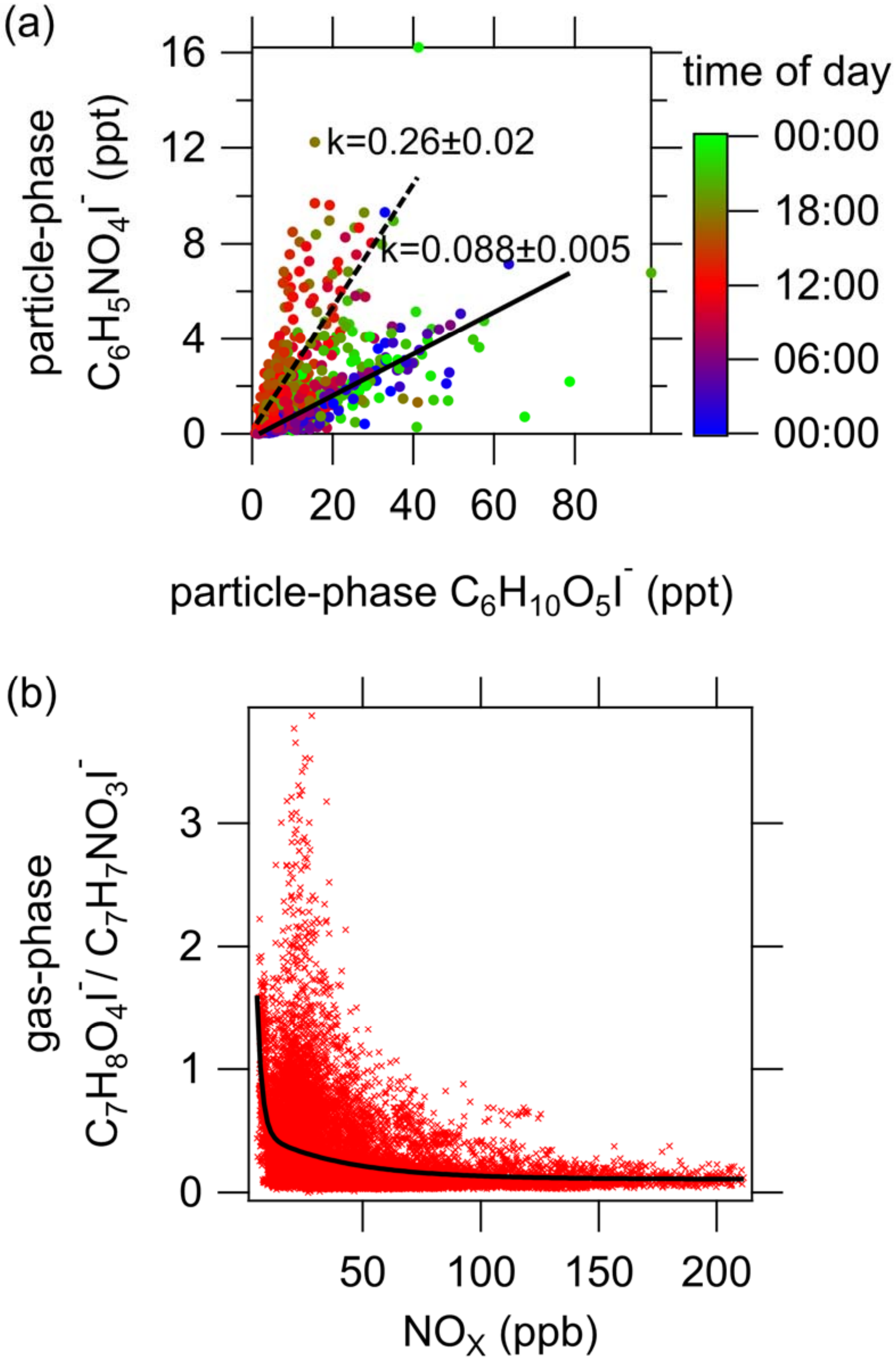


Figure 5. (a) Correlation between particle-phase $C_6H_5NO_4I^-$ and $C_6H_{10}O_5I^-$. The data points are color-coded using the time of the day. Solid and dash lines represent the slopes during the nighttime and daytime, respectively. (b) Relative concentration of $C_7H_8O_4I^-$ and $C_7H_7NO_3I^-$ in the gas phase as a function of NO_X concentration. The black line is the fitted curve using a double exponential function.

13. Page 14, Lines 389-390: 'with 4 or 5 carbon atoms' for a molecular formula denoted as C4. Revise.

Reply: Thanks for pointing it out. The sentence in Line 415-416 of the revised manuscript is revised:

The ion $C_4H_7NO_5I^-$ was the most abundant N-containing C4 organic compounds that were detected in the gas phase.

14. Page 15, Lines 415-416: Revise for clarity.

Reply: Sorry for the confusion. In the revised manuscript, 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 447-450 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.

15. Page 16, Lines 432-435: Can the authors specify or expand on the relative roles of thermolytic versus ionization cleavage of the S-O bond for particulate organosulfates?

Reply: We thank the reviewer for the comment. A few recent studies reported S-containing compounds measured by FIGAERO CIMS (Le Breton et al., 2018; Huang et al., 2018), and we believe it would be interesting to report their behavior from our measurements. Actually, we have not investigated the ionization of S-containing compounds in I-CIMS in the laboratory.

16. Page 16, Lines 452-454: Is the AMS data inclusive of NaCl-detection (Ovadnevaite et al., 2012)? Or is the chloride detected here mostly derived from NH4Cl? If it is the latter, then the presence or absence of aerosol chloride may be more ambiguous than stated and this should be clarified here.

Reply: Thanks for the comment. Chloride detected by AMS is mostly derived from NH_4Cl for two reasons. Firstly, according to Ovadnevaite et al., 2012, the humidity would significantly affect the AMS collection efficiency (CE): the CE of sea salt is likely 0.25 at RH <70%. In our campaign, the aerosol sampled into the AMS was dried. Secondly, we barely see NaCl ion in AMS mass spectra in this campaign.

17. Page 17, Lines 457-461: The long lines and known volatility of NH4NO3 under atmospheric conditions could result in a significant bias to the gaseous HNO3 measurement, which is suggested from the early morning shoulder in the presented diurnal HNO3 data in Figure 11b. This growth of this shoulder corresponds to the period when most aerosol nitrate is observed. While it may not be possible to correct for this bias, its existence and impact should be stated and assessed.

Reply: We thank the reviewer for the comment. It is possible that the dissociation of NH_4NO_3 resulted the overestimation of gaseous HNO_3. However, we believe that the volatilization of particles in such a short time while passing through gas inlet (0.24 seconds) is not important, as implied by the following figure (the signals changes during the FIAGERO desorption period), which demonstrates that the increases of signals on a timescale of <1 second is negligible.

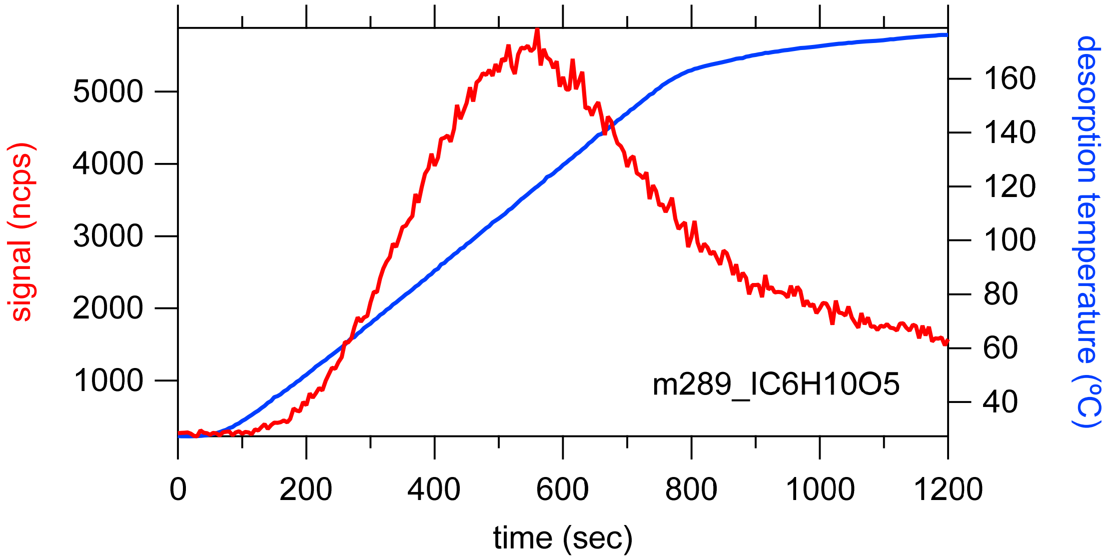


Figure. Time profile of the levoglucosan ion measured during the FIGAERO desorption period of a calibration experiment.

18. Page 17, Lines 464-471: This argument for the bias in particulate nitrate quantitation can be strengthened by separating the dataset around a threshold of 1 ug/m3 or orgN (I determined this by visually inspecting the figure. There may be a better value that can be applied and the authors should identify the best value.). Do the slopes and correlations have marked differences and how can that be related to the AMS ON measurement? Can the authors propose a reasonable correction to account for this bias if AMS ON data is available for other FIGAERO users?

Reply: We thank the reviewer for the insightful comments. The discussions on the threshold of pON in Line 494-499 of the revised manuscript:

Strong correlation was observed (r=0.93), but the concentrations measured by FIGAERO-I-CIMS were higher (slope=1.6), especially for higher concentrations of organic nitrates. Using a threshold of 1 μg/m^3 for organic nitrates, the slopes and correlations were higher for the data points with particulate organic nitrates larger than 1 μg/m^3 (slope=1.8, r=0.94) than those with less than 1 μg/m^3 (slope=1.1, r=0.90).

Fig 11c is also revised:

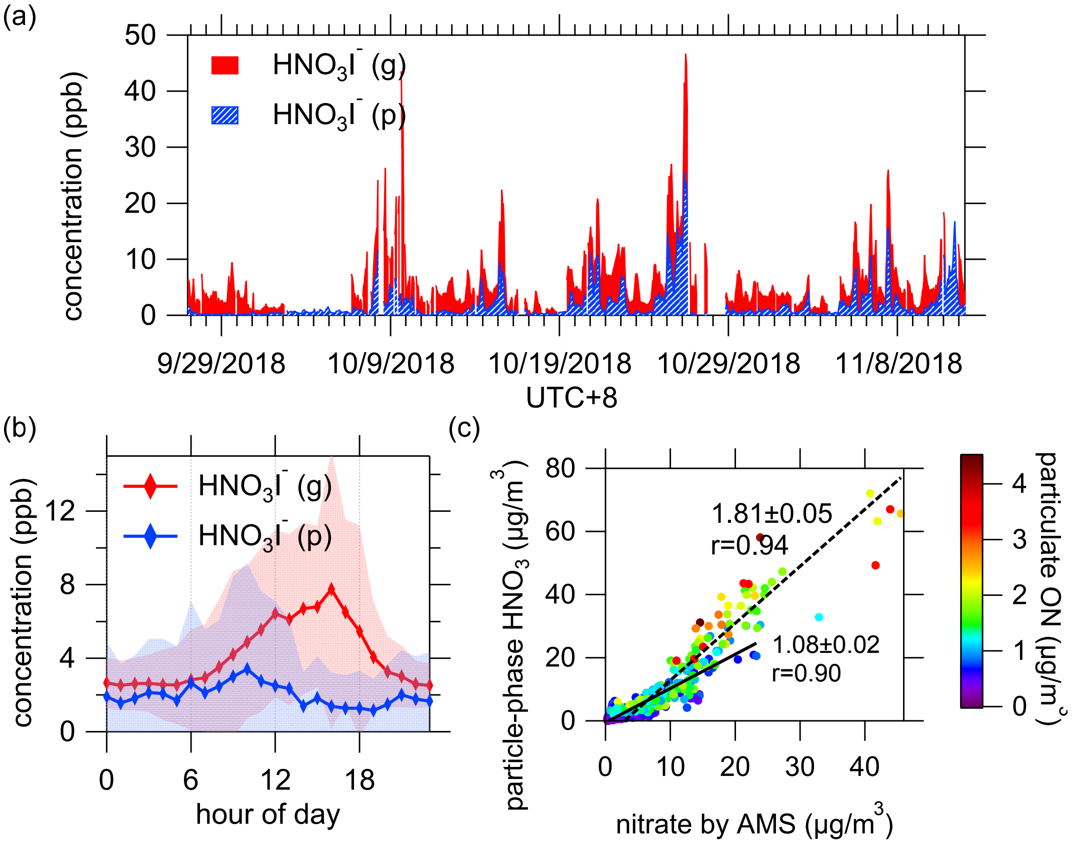


Figure 11. (a) Time series of humidity-corrected HNO_3I^- in both phases. (b) Diurnal variation of humidity-corrected HNO_3I^-. The shaded areas indicate one standard deviation. (c) Comparison of particle-phase HNO_3I^- and nitrate measured by AMS. The color scale denotes particulate N-containing organic compounds measured by FIGAERO-I-CIMS (pON). The solid and dash lines show the fitted results for the datasets of pON less than 1 μg/m^3 and more than 1 μg/m^3, respectively. The concentration of gaseous HNO_3I^- shown here only included the last 5-minute of

every gas-phase working mode, as high level of HNO_3 came out of aerosol which then passed through the CIMS in a short time during particle analysis and a substantial amount would subsequently accumulate on the inner surfaces, leading to a persistent carried over signal that was long enough to disturb the next gas measurement cycle (Palm et al., 2019).

19. Page 19, Lines 522-523: Expand the analysis here. Again, it may be worthwhile to determine the range of pON for both instruments where the relationship is more robust (visual inspection suggests 5 ug/m3?).

Reply: We thank the reviewer for this constructive comment. We display the comparison results of pON for the datasets below a certain threshold of particulate inorganic nitrate. The right axis is the ratio of pON by FIGAERO versus pON by AMS.

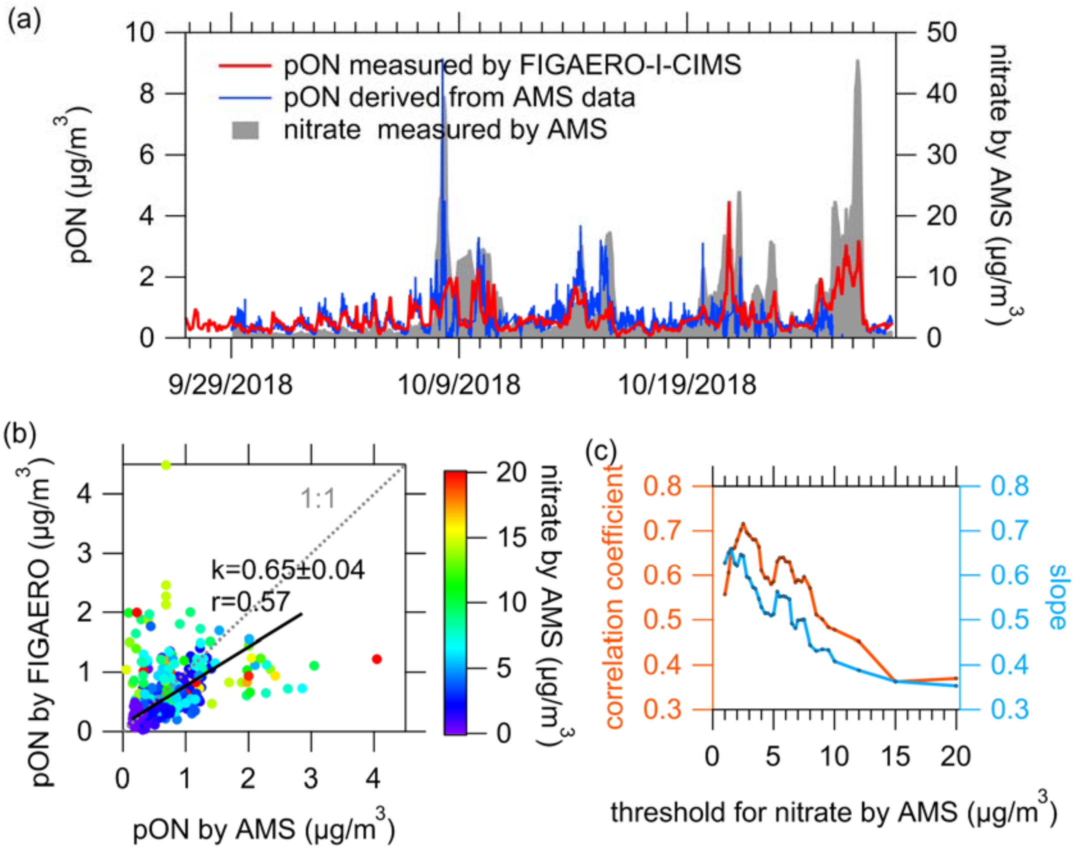


Figure 15. (a) Time series of particulate N-containing organics measured by FIGAERO-I-CIMS (pON by FIGAERO), particulate organic nitrates derived from AMS data (pON by AMS) as well as particulate inorganic nitrate. (b) Comparison of pON by FIGAERO and pON by AMS, color-coded by the concentrations of particulate

inorganic nitrate measured by AMS. The black line presents the linear fit for nitrate by AMS below 8 μg/m^3. (c) The determined slopes and correlation coefficients between pON by FIGAERO versus pON by AMS by filtering the data below different thresholds of particulate inorganic nitrate measured by AMS.

The comparison result is presented in Line 565-568 of the revised manuscript:

Good agreement was achieved when the concentrations of inorganic nitrate were relatively lower, e.g. below 8 μg/m^3. However, the discrepancies increased when inorganic nitrate were higher, which can affect the determination of organic nitrate from AMS.

20. Page 20, Line 549: 'of' at the end of the sentence is not needed. Delete.

Reply: Corrected.

21. Page 20, Lines 559-564: In the figure the abbreviation UMR is used, but it is not defined here or in the figure caption. Please do so.

Reply: We thank the reviewer for pointing it out. We define the abbreviation UMR in Fig. S18 caption:

Figure S18. (a) Van Krevelen diagrams for particle-phase $C_xH_yO_z$ compounds detected by FIGAERO-I-CIMS. The size of circles represents the campaign-averaged concentration of this compound in particles. (b) 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. Star markers from left to right denote $CH_2O_2I^-$, HNO_3I^-, $C_4H_6O_4I^-$, $C_9H_{14}O_4I^-$, $C_9H_{13}NO_7I^-$ and $C_{10}H_{14}N_2O_9I^-$.

22. Figures: When stating 'standard deviation' the number should be presented (e.g. one standard deviation).

Reply: Corrected.

23. References: Given the extensive number of references, the authors are highly encouraged to thoroughly assess their correctness.

Reply: Thanks for reminding. We went through the manuscript again to check the references.

Reference

Bean, J. K. and Hildebrandt Ruiz, L.: Gas-particle partitioning and hydrolysis of organic nitrates formed from the oxidation of alpha-pinene in environmental chamber experiments, Atmos. Chem. Phys., 16(4), 2175–2184, doi:10.5194/acp-16-2175-2016, 2016.

Boyd, C. M., Sanchez, J., Xu, L., Eugene, A. J., Nah, T., Tuet, W. Y., Guzman, M. I. and Ng, N. L.: Secondary organic aerosol formation from the β-pinene+NO3 system: effect of humidity and peroxy radical fate, Atmos. Chem. Phys., 15(13), 7497–7522, doi:10.5194/acp-15-7497-2015, 2015.

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