Responses to Reviewer #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

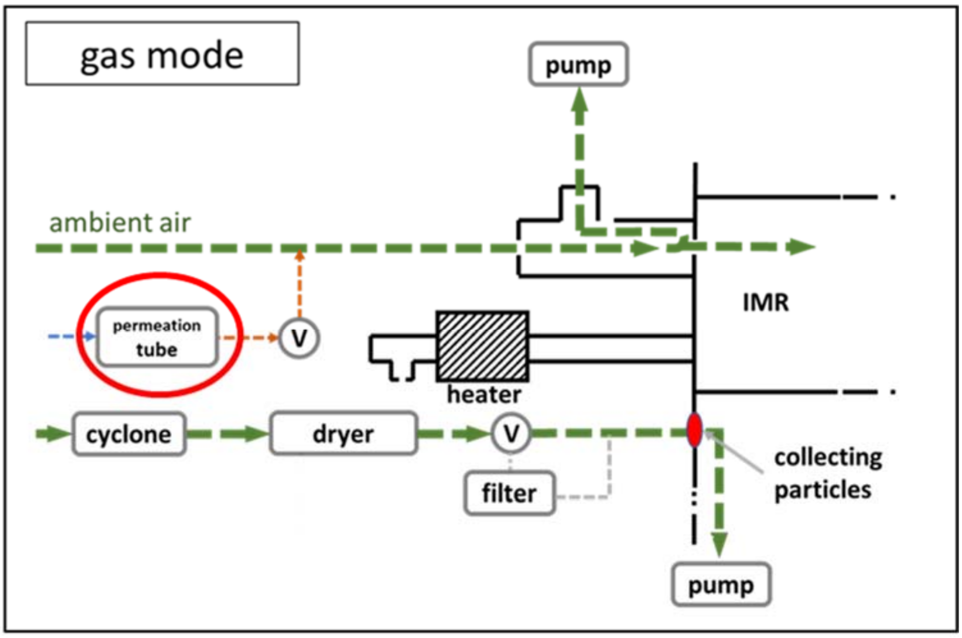
1. Limitations of long inlet lines for gas sampling on instrument response, accuracy of field blanks, or creation of bias from wall loss of aerosols followed by their volatilization are not accounted for in the presented data analysis. The authors go to great extents to conduct calibrations for their 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.

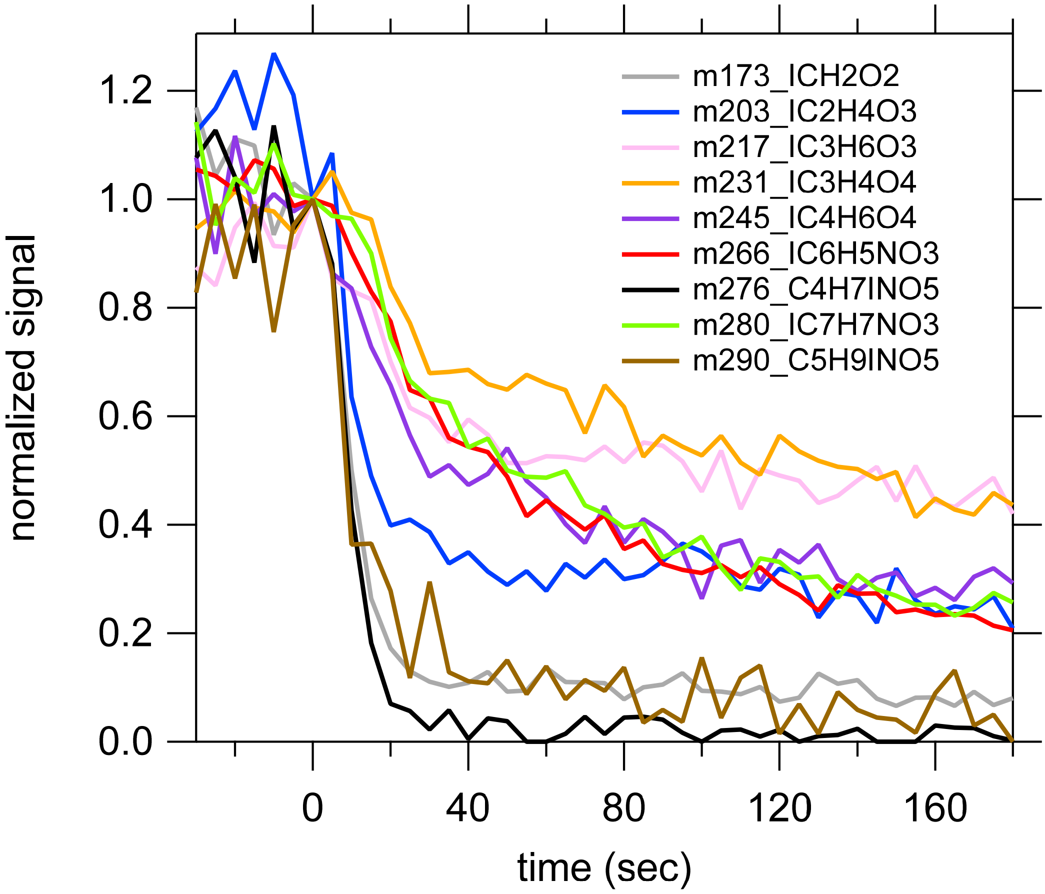


Figure. Gas-phase time profiles measured during a gas background. Time zero is the start time of background. Signals were normalized to the ambient concentrations at Time zero.

(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.

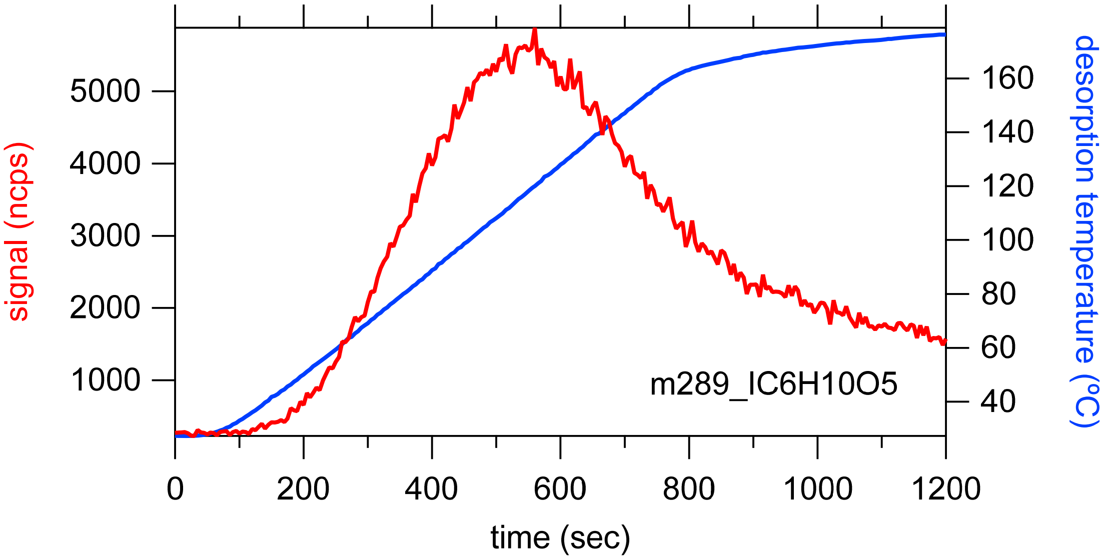


Figure. Time profile of the levoglucosan ion measured during the FIGAERO desorption period of a calibration experiment.

(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).

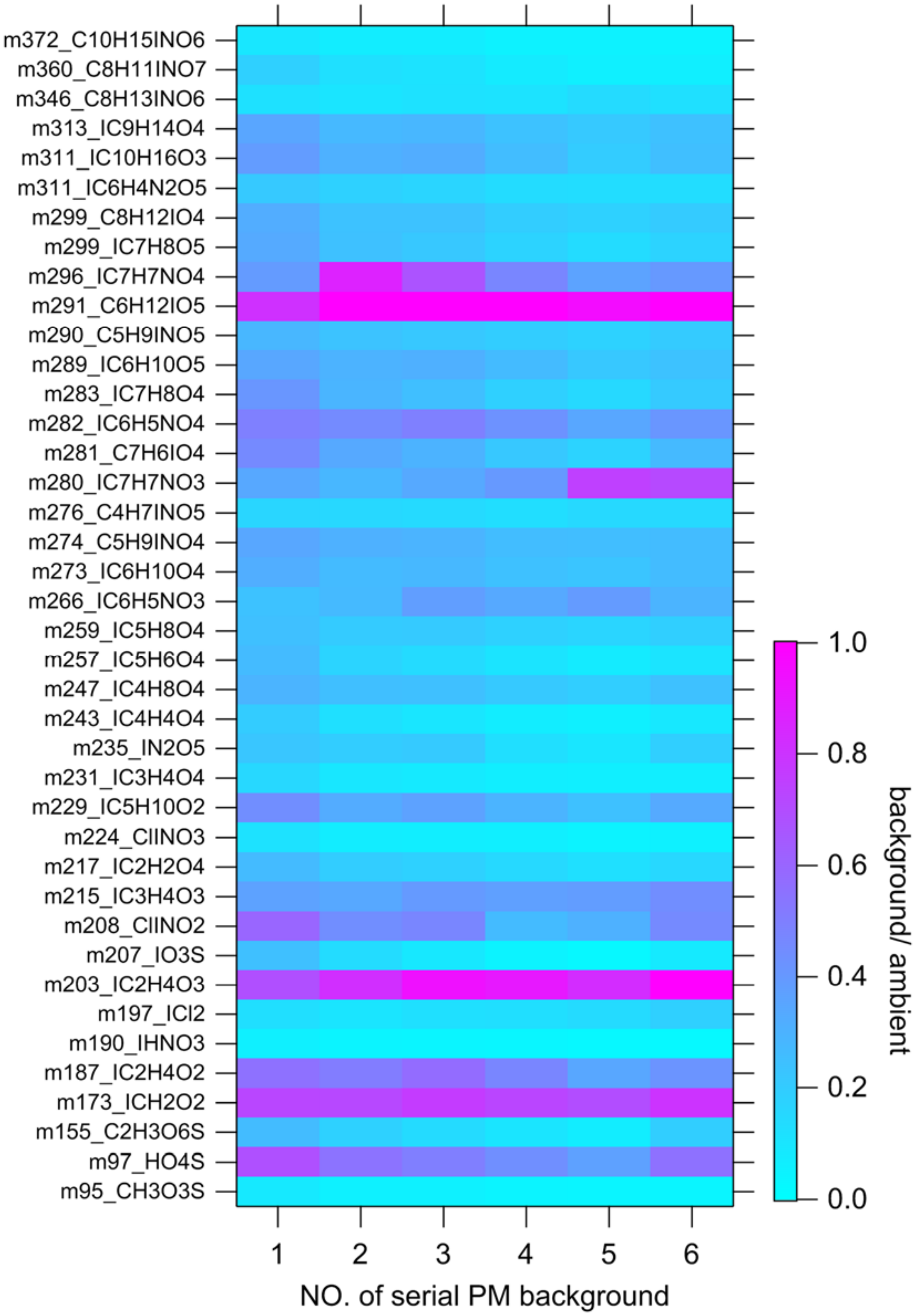
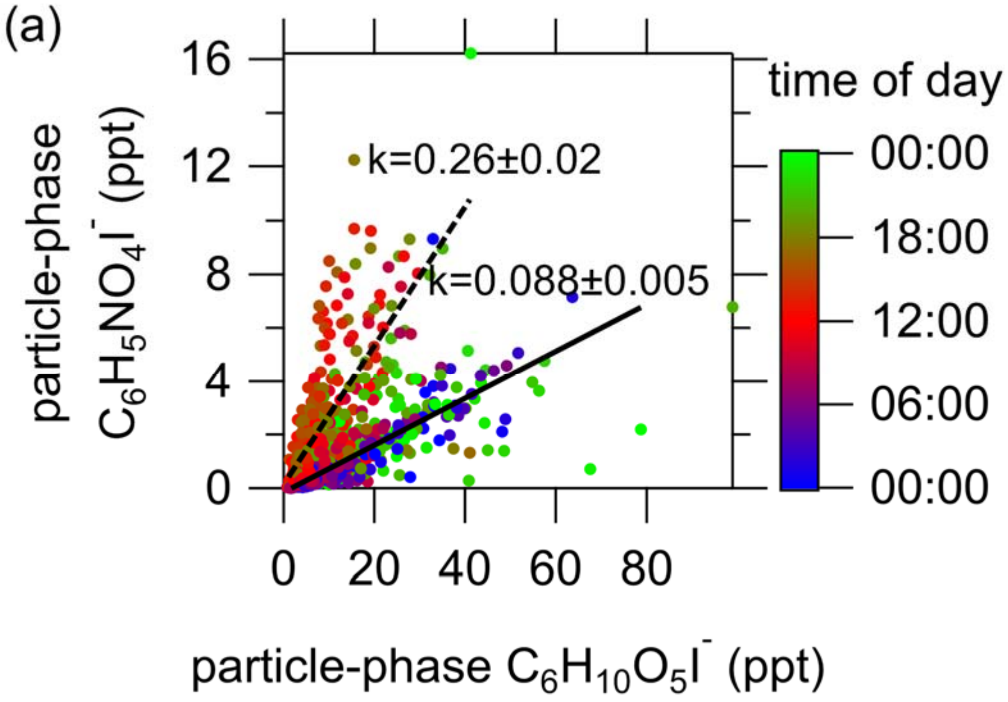


Figure. Ratio of a consecutive series of particle-phase background versus the ambient concentrations for ions discussed in the main text.

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:



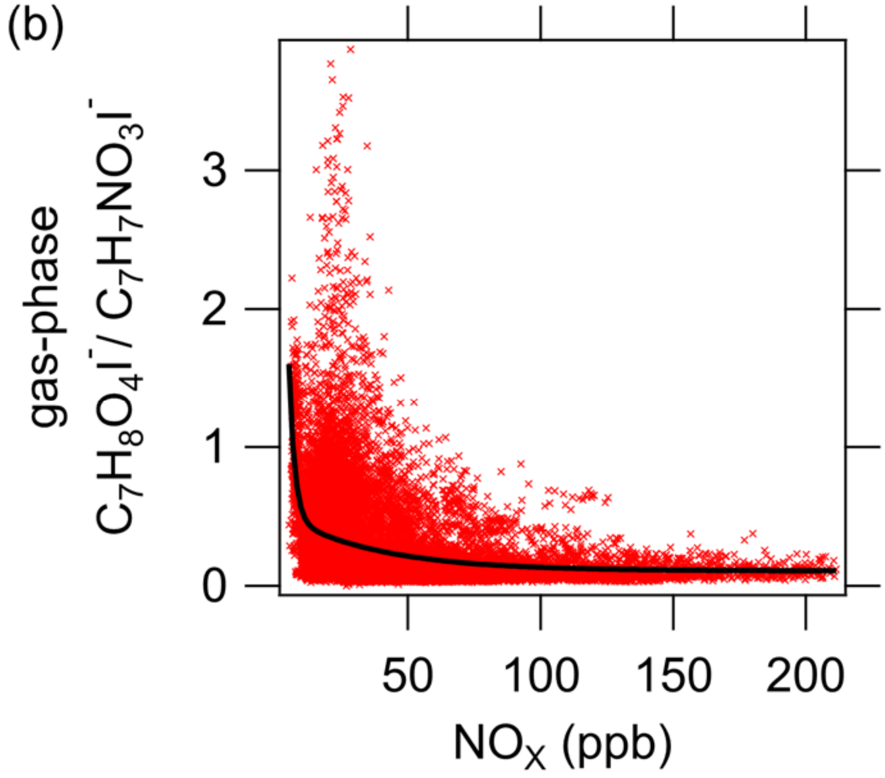


Figure 5. (a) Correlation between particle-phase $C_6H_5NO_4I^-$ and $C_6H_{10}O_5I^-$. The data points are color-coded using the time of the day. Solid and dash lines represent the slopes during the nighttime and daytime, respectively. (b) Relative concentration of $C_7H_8O_4I^-$ and $C_7H_7NO_3I^-$ 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.

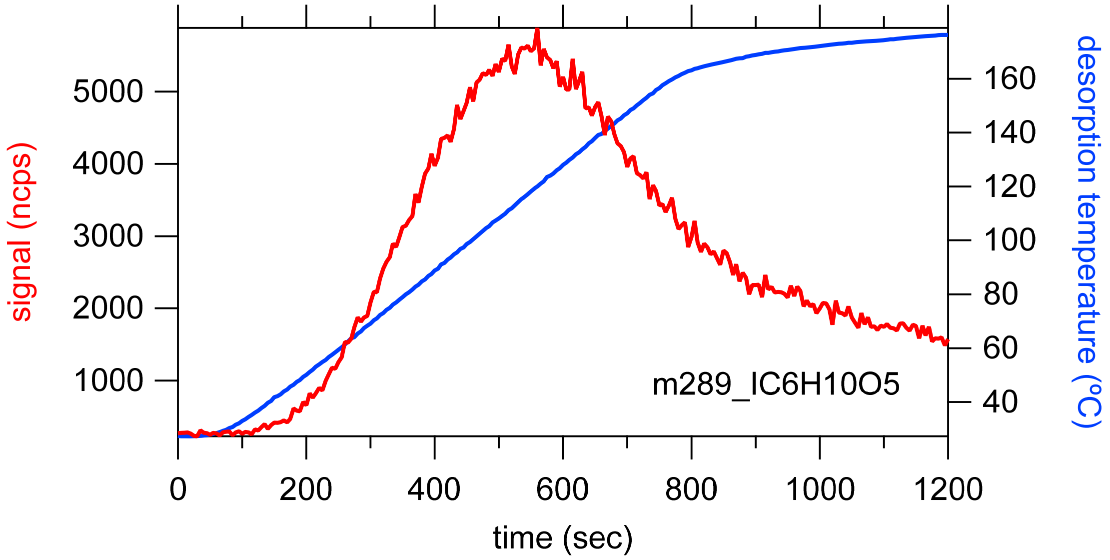


Figure. Time profile of the levoglucosan ion measured during the FIGAERO desorption period of a calibration experiment.

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:

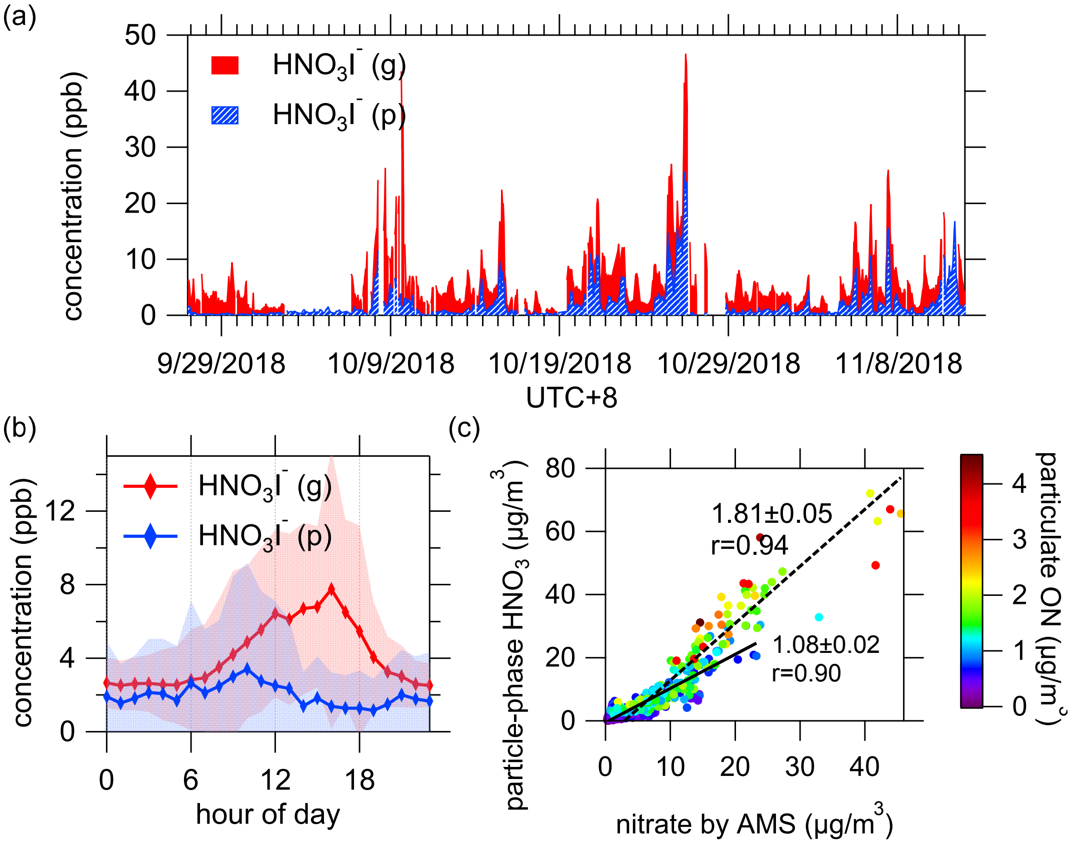


Figure 11. (a) Time series of humidity-corrected HNO_3I^- in both phases. (b) Diurnal variation of humidity-corrected HNO_3I^-. The shaded areas indicate one standard deviation. (c) Comparison of particle-phase HNO_3I^- and nitrate measured by AMS. The color scale denotes particulate N-containing organic 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.

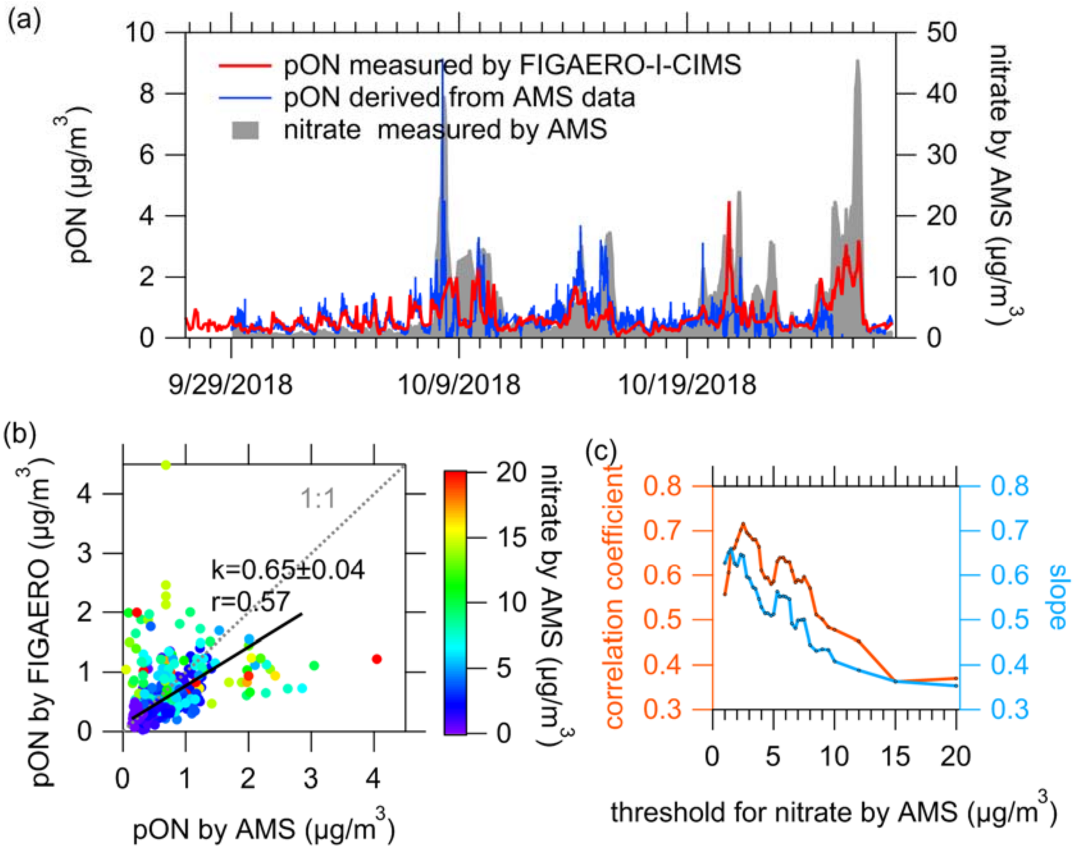


Figure 15. (a) Time series of particulate N-containing organics measured by FIGAERO-I-CIMS (pON by FIGAERO), particulate organic nitrates derived from AMS data (pON by AMS) as well as particulate inorganic nitrate. (b) Comparison of pON by FIGAERO and pON by AMS, color-coded by the concentrations of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

Le Breton, M., Wang, Y., Hallquist, Å. M., Pathak, R. K., Zheng, J., Yang, Y., Shang, D., Glasius, M., Bannan, T. J., Liu, Q., Chan, C. K., Percival, C. J., Zhu, W., Lou, S., Topping, D., Wang, Y., Yu, J., Lu, K., Guo, S., Hu, M. and Hallquist, M.: Online gas- and particle-phase measurements of organosulfates, organosulfonates and nitrooxy organosulfates in Beijing utilizing a FIGAERO ToF-CIMS, Atmos. Chem. Phys., 18(14), 10355–10371, doi:10.5194/acp-18-10355-2018, 2018.

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Palm, B. B., Liu, X., Jimenez, J. L. and Thornton, J. A.: Performance of a new coaxial ion-molecule reaction region for low-pressure chemical ionization mass spectrometry with reduced instrument wall interactions, Atmos. Meas. Tech., 12(11), 5829–5844, doi:10.5194/amt-12-5829-2019, 2019.

Slusher, D. L., Huey, L. G., Tanner, D. J., Flocke, F. M. and Roberts, J. M.: A thermal dissociation–chemical ionization mass spectrometry (TD-CIMS) technique for the simultaneous measurement of peroxyacyl nitrates and dinitrogen pentoxide, J. Geophys. Res. Atmos., 109(D19), doi:10.1029/2004JD004670, 2004.

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