

Responses to 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 errors (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 (F_p) 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).

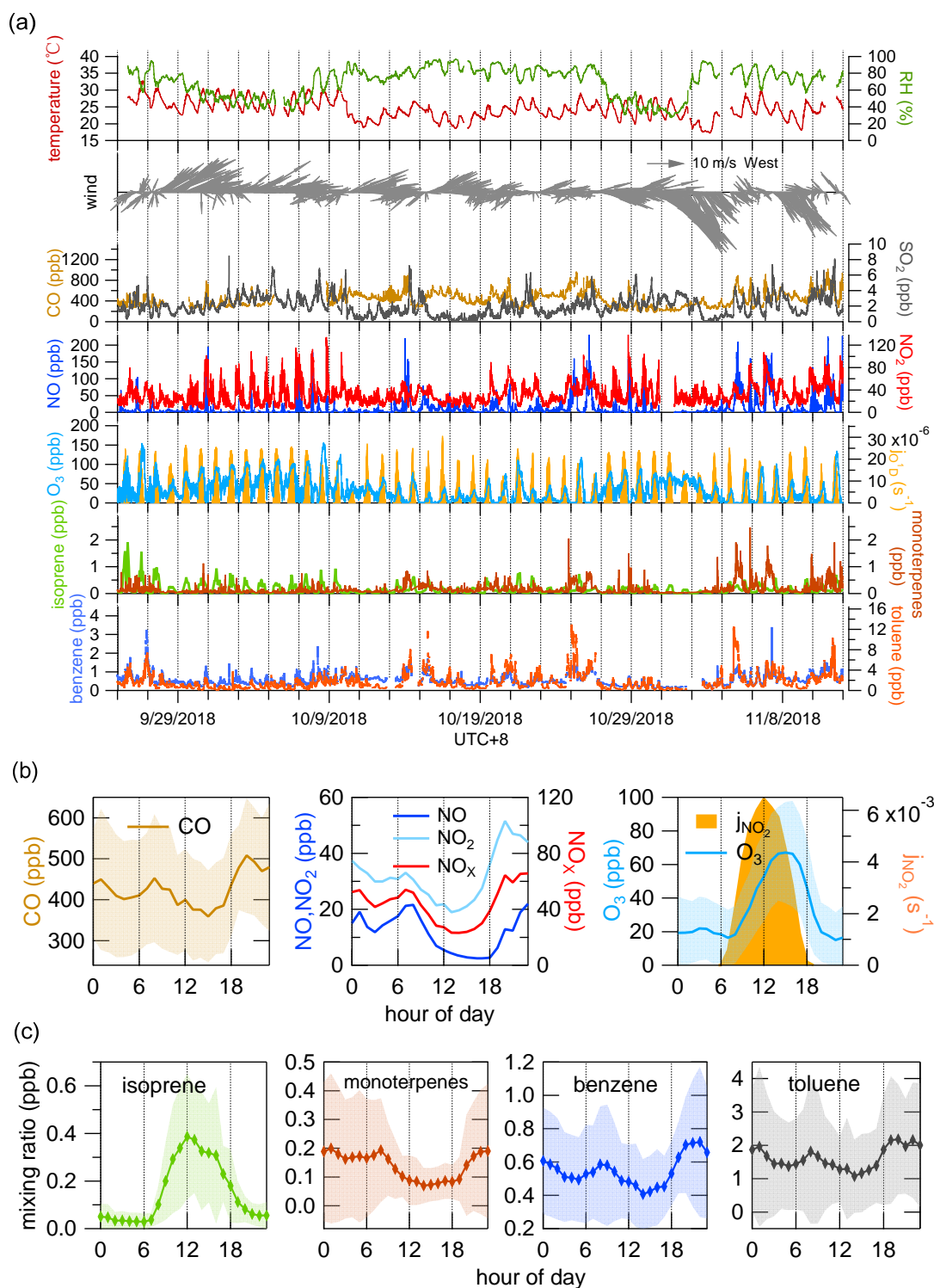


Figure S1. (a) Time series of meteorological parameters (temperature, relative humidity and wind), trace gases (CO , SO_2 , NO , NO_2 , O_3), VOCs (isoprene, monoterpenes, benzene, toluene) and measured photolysis rate constant (j_{NO_2}) during the campaign. (b) Diurnal trends of trace gases and j_{NO_2} . (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 N_2O_5 and ClNO_2 , so we remove it from SI.

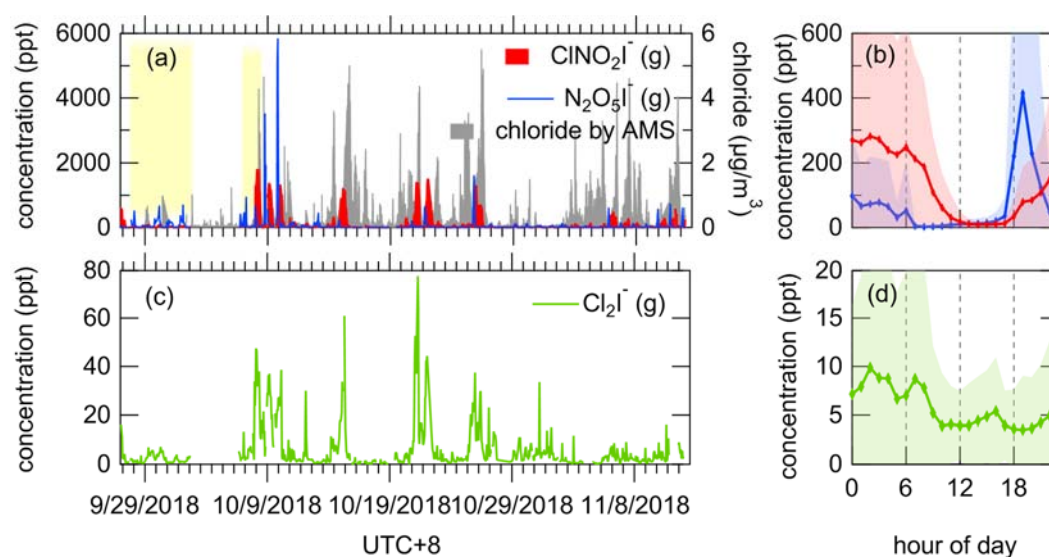


Figure 10. Time series and diurnal variations of humidity-corrected concentrations of N_2O_5 and ClNO_2 (a, b) and Cl_2 (c, d). The gray profile is the time series of chloride measured by AMS (mainly non-sea salt). The tinted background indicates the days with high concentrations of N_2O_5 but low concentrations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

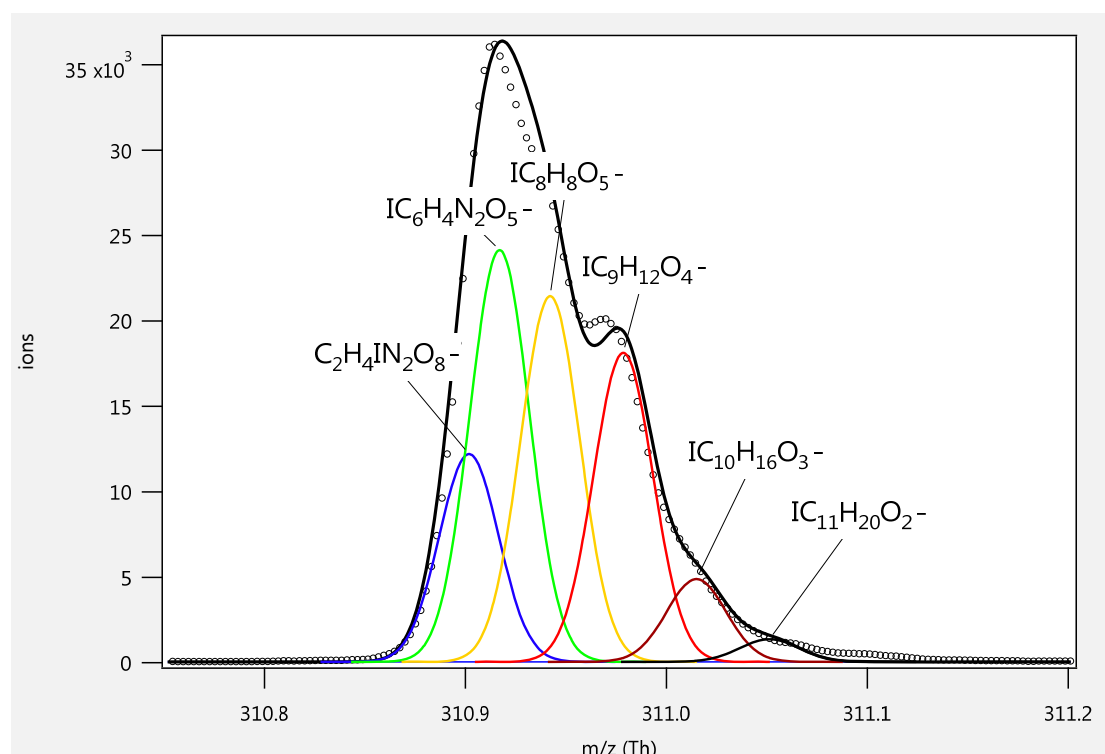


Figure S8. High-resolution peak fittings to the mass spectrum of I-CIMS at m/z 311.

(3) Fig. S13b (time series of $C_{10}H_{15}NO_6I^-$ 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 $C_{10}H_{15}NO_6$ 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 δf "

Reply: Corrected.

- line 34: typo: *form* "→ *from*"

Reply: Corrected.

- line 38: missing δf "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 \pm one standard deviation, which is “ $24 \pm 0.8\%$ ”.

- line 43: *Systematically*"-> *Systematical*"

Reply: Corrected.

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

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 $\text{NO}_2^+/\text{NO}^+$ ratios for organic nitrate than inorganic nitrate (Fry et al., 2013).

- line 132: $j(\text{NO}_2)$ 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 (Hytinen et al., 2018; Iyer et al., 2016; Lee et al., 2014; Riva et al., 2019).

- line 156: $m/\Delta m$ 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 ($m/\Delta m$ 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 N₂ flow was ramped from ambient temperature to 175°C 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. triangles 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 $380 \text{ mbar} \times 25 \text{ mmol/mol} = 9.5 \text{ mbar}$, 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 $22.1 \pm 5.3 \text{ mmol/mol}$).

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 $P_{H_2O} = 380 \text{ mbar} \times 25 \times 10^{-3} = 9.5 \text{ mbar}$
Water vapor pressure of positive slope for CH_2O_2	~ 0.15 mbar	AH=0.32 mmol/mol, so $P_{H_2O} = 380 \text{ mbar} \times 0.32 \times 10^{-3} = 0.12 \text{ mbar}$
Water vapor pressure of positive slope for HNO_3	~ 0.8 mbar	AH=2.1 mmol/mol, so $P_{H_2O} = 380 \text{ mbar} \times 2.1 \times 10^{-3} = 0.8 \text{ mbar}$

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.

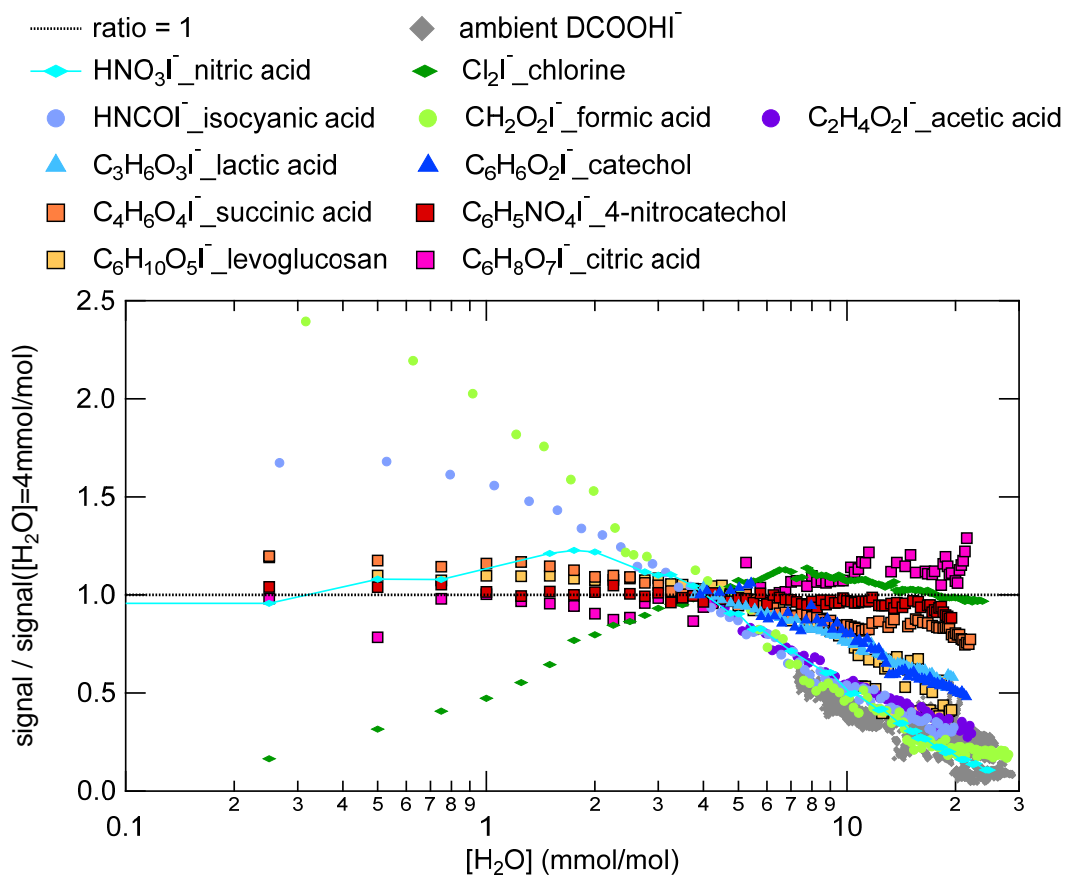


Fig. S6a-f: Would be good to mark in the graphs when the new solution was used. And in light of recent results indicating the importance of solution concentration on T_{\max} (Ylisirniö et al., AMTD, 2020; doi.org/10.5194/amt-2020-254), it could be interesting to report the concentrations used here (Fig. S6b, d, f; even though it seems like T_{\max} 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).

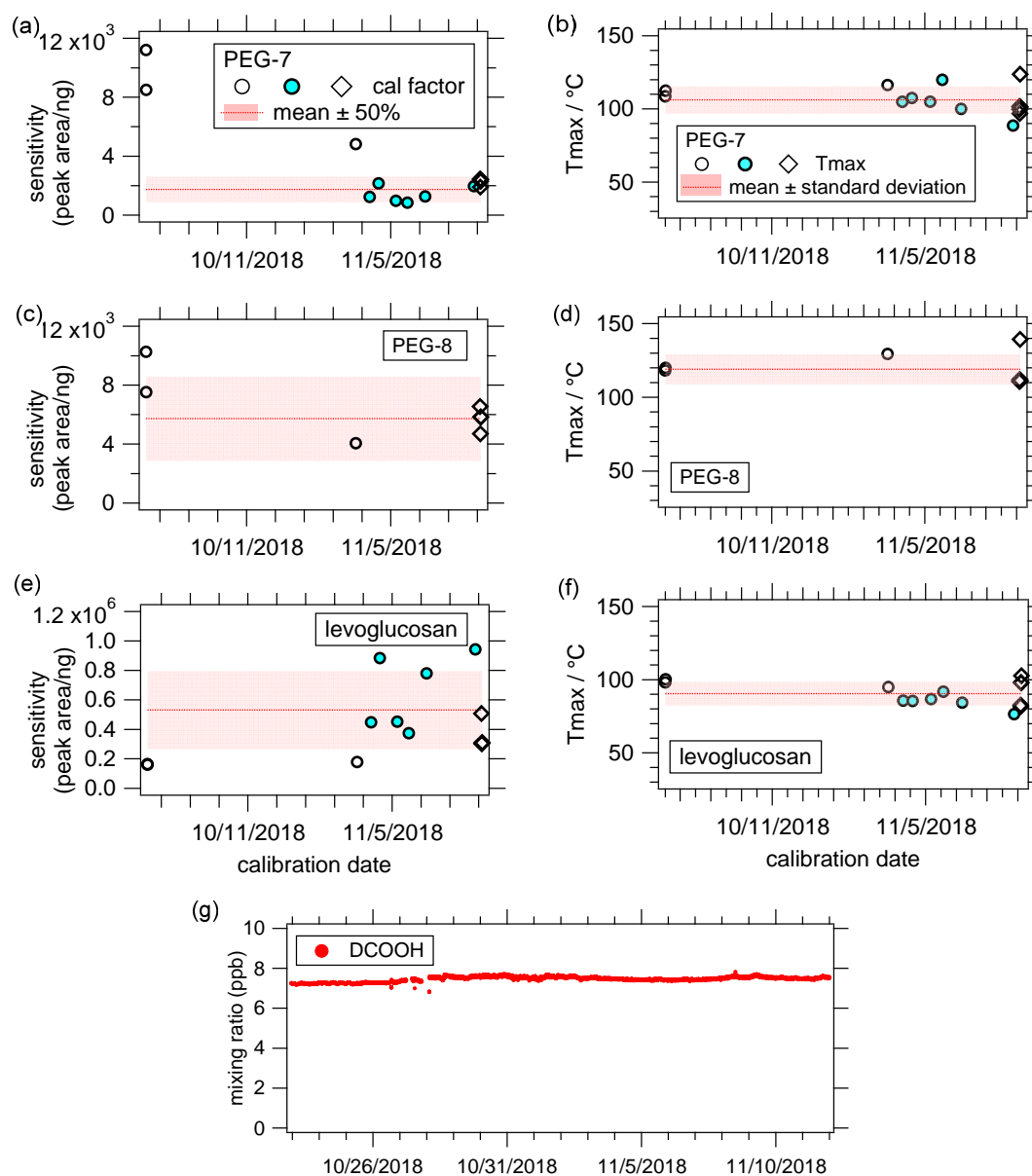


Figure S6. The time series of calibration factors (a, c, e) and T_{\max} (b, d, f) of hepaethylene glycol, octaethylene glycol and levoglucosan in the regular calibrations

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 $0.5 \pm 0.03 \mu g \cdot m^{-3} / ppm$, 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., 2020a; 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 $C_{10}H_{15}NO_6I^-$ 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. NO_x and O_3 . 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.

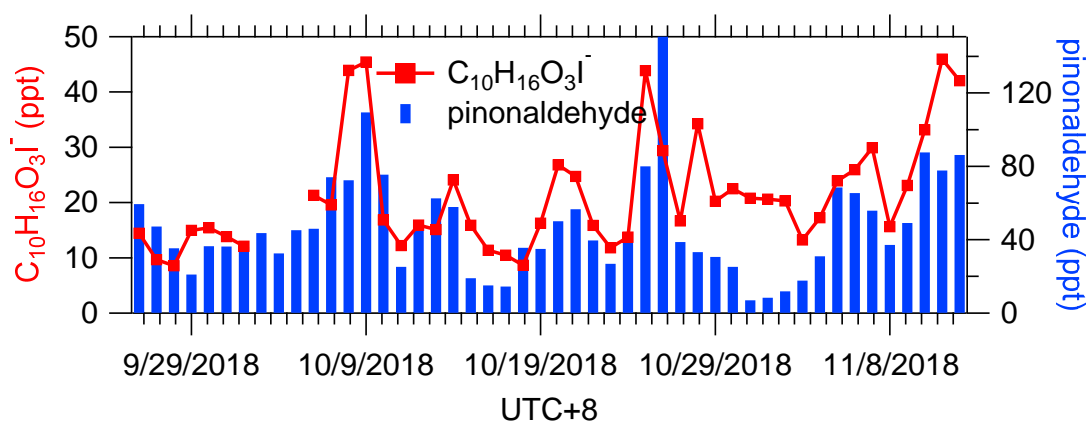


Figure S14. Time series of daily maximum concentrations of gaseous $C_{10}H_{16}O_3I^-$ and pinonaldehyde ($C_{10}H_{16}O_2H^+$, m/z 169.12).

(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 correct 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.

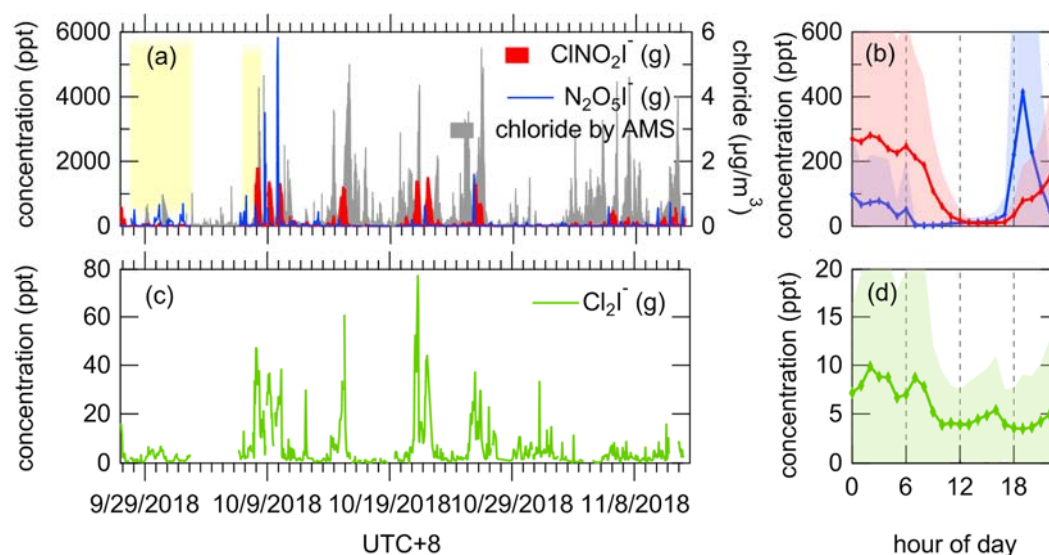


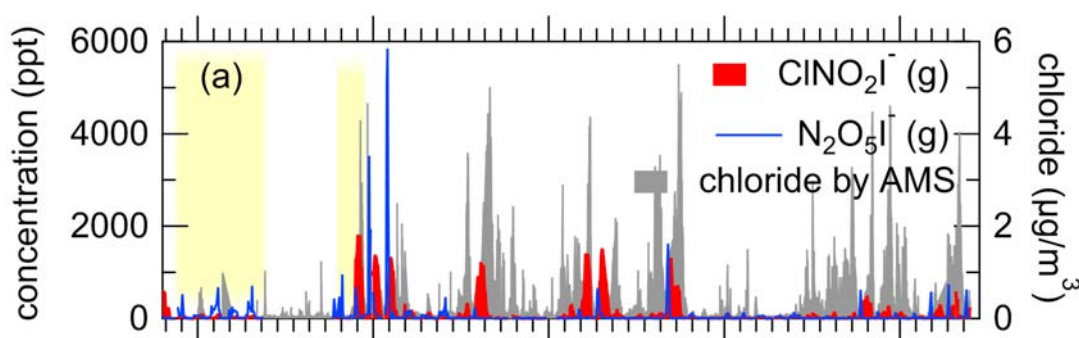
Figure 10. Time series and diurnal variations of humidity-corrected concentrations of N_2O_5 and ClNO_2 (a, b) and Cl_2 (c, d). The tinted background indicates the days with high concentrations of N_2O_5 but low concentrations of ClNO_2 . The shaded areas indicate one standard deviation.

- 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 $\overline{\text{OS}}_{\text{C}}$, probably as the result of emissions of isoprene.

- line 502: *I think that concluding from the abundance of that group of compositions ($\text{C}_x\text{H}_y\text{N}_{1,2}\text{O}_z$ 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.*

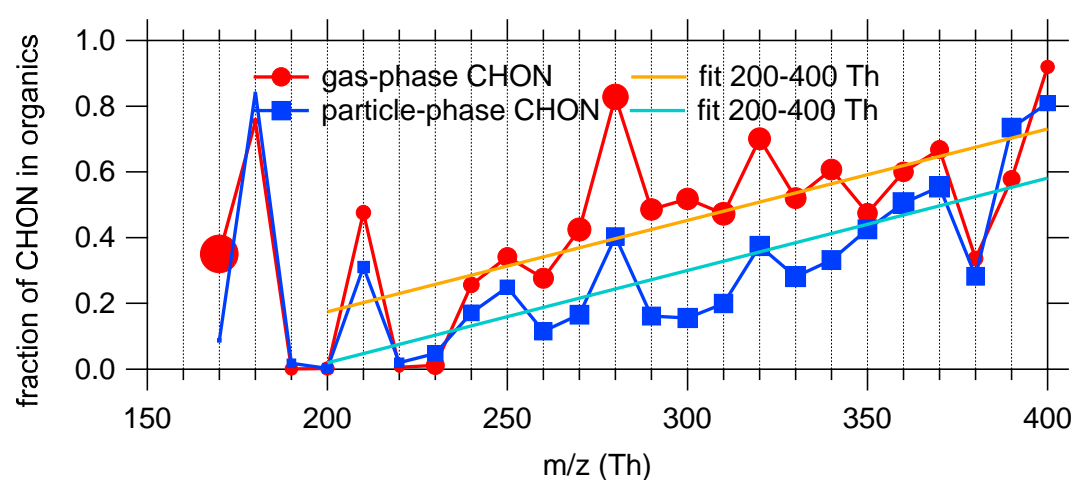
Reply: We thank the reviewer for the comment. To support this conclusion, the fraction of nitrophenols in $\text{C}_x\text{H}_y\text{N}_{1,2}\text{O}_3$ is added to Line 543-545 of revised manuscript:

Nitrophenols also contributed significantly to $\text{C}_x\text{H}_y\text{N}_{1,2}\text{O}_z$ compounds, as they accounted for 74% of $\text{C}_x\text{H}_y\text{N}_{1,2}\text{O}_z$ 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 $8 \mu g/m^3$. However, the discrepancies increased when inorganic nitrate were higher, which can affect the determination of organic nitrate from AMS.

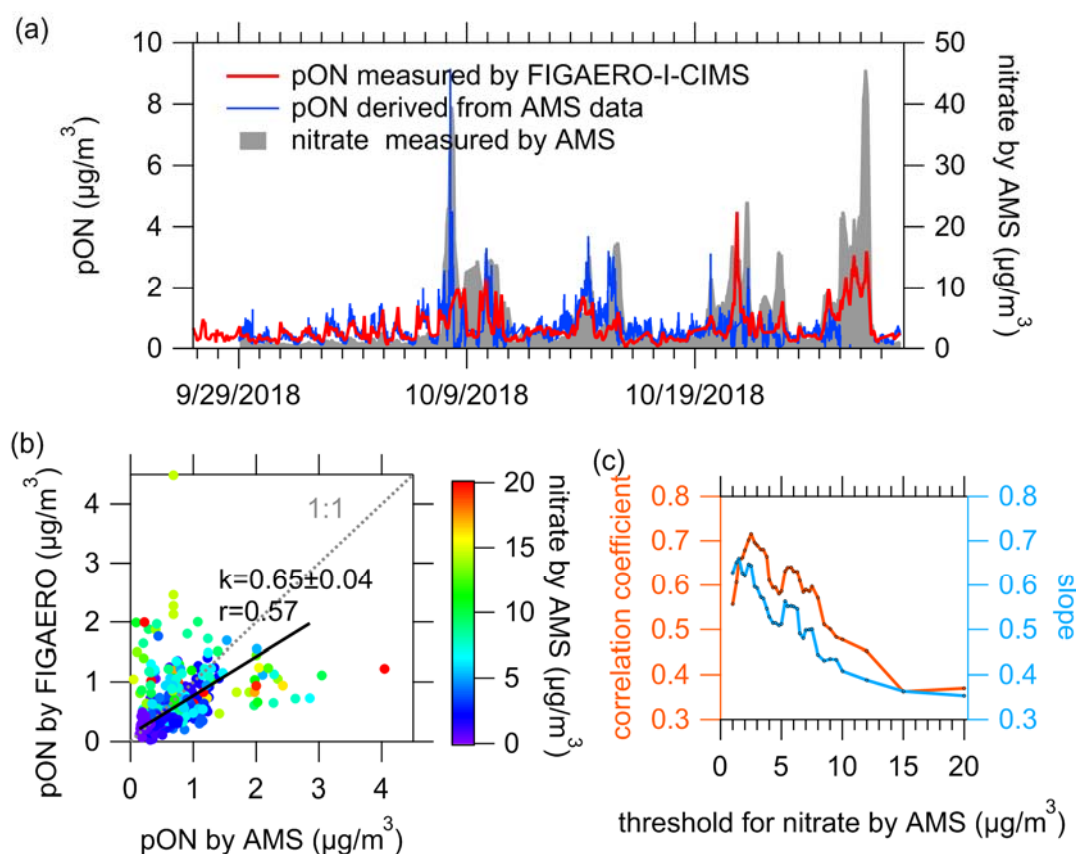


Figure 15. (a) Time series of particulate N-containing organics measured by FIGAERO-I-CIMS (pON by FIGAERO), particulate organic nitrates derived from AMS data (pON by AMS) as well as particulate inorganic nitrate. (b) Comparison of pON by FIGAERO and pON by AMS, color-coded by the concentrations of particulate inorganic nitrate measured by AMS. The black line presents the linear fit for nitrate by AMS below $8 \mu\text{g}/\text{m}^3$. (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 NO_x

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 NO₃ reactions).

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