

## Responses to Reviewers' Comments on Manuscript egusphere-2022-1108

(Characteristics of Negative Cluster Ions in an Urban Environment)

We are grateful for the reviewers' comments and we feel that our responses to these will greatly improve this manuscript. We have addressed the comments in the following paragraphs and made corresponding changes in the revised manuscript. Comments are shown as *blue italic text* followed by our responses. Changes are **highlighted** in the revised manuscript and shown as "quoted underlined text" in our responses.

### Reviewer #1:

*The manuscript by Yin et al. describes measurements of atmospheric ions in Beijing. Notably, they quantify the concentrations of ions of specific composition through a rigorous calibration process. For select ions, a steady-state analysis is applied to show how the time series of these specific ions are well represented by known chemical and physical processes and that condensational loss represents the largest ion loss term. Ion composition is compared to the composition of neutral gases measured by a nitrate chemical ionization mass spectrometer (CIMS) and similar to past findings, it is found that there is generally good agreement in the types of organic molecules identified as ambient ions and as neutral gases albeit with different intensities. These measurements from an urban environment are also compared to measurements from the boreal forest with similarities and differences discussed.*

*In my opinion, the most important contribution of this manuscript is the push towards making quantitative measurements of the chemically resolved composition of ambient ions and in using these quantitative measurements to evaluate our understanding of ion sources and sinks. Quantifying specific ions is a challenging undertaking that few have pursued in recent years (specifically when using time-of-flight mass spectrometers). Although some would argue that the science to effort pay off of such measurements may be minor, I think that there are some important questions that could be addressed if such measurements became more routine. The other aspects of the manuscript (discussion of composition, comparison to other environments, etc.) are only superficially explored and require a more comprehensive analysis before they would provide general insight into atmospheric composition and chemistry. In short, I think this manuscript contributes a technical advancement to the field and thus may be more appropriate for a different journal or as a technical note. In my opinion, to be suitable for publication in a more general journal, more detailed analysis regarding composition is necessary and the scientific motivation and insights of the analysis need to be clearly established in the manuscript.*

**Response:** We appreciate the reviewer for the affirmative comments on our work of ion quantification. As suggested by the reviewer, we have added more detailed discussions on the ion compositions, sources, and sinks for a deeper scientific understanding of ion formation in the revised manuscript, including (1) the charging capacity of  $\text{NO}_3^-$  and  $\text{HSO}_4^-$  in the ambient atmosphere was determined by analyzing ions concentrations as well as organic ion compositions. The ratio of the two ionization forms ( $\text{M}\cdot\text{HSO}_4^-/\text{M}\cdot\text{NO}_3^-$ ) was positively related to the ratio of reagent ions ( $\text{HSO}_4^-/\text{NO}_3^-$ ). Although the molecules clustered with  $\text{HSO}_4^-$  and  $\cdot\text{NO}_3^-$  are similar in composition, we found that  $\text{M}\cdot\text{HSO}_4^-$  formed more efficiently for CHO and  $\text{CHON}_{\text{nonNPs}}$ , while  $\text{M}\cdot\text{NO}_3^-$  formed more efficiently with  $\text{CHON}_{\text{NPs}}$  when targeting the compounds that can be ionized by both  $\text{HSO}_4^-$  and  $\cdot\text{NO}_3^-$ . (2) the relationships between ions and neutral molecules were compared. We found that most organic ions were positively correlated with neutral molecules, resulting in their similar diurnal cycles. For these compounds, the ion concentrations can be roughly estimated through the neutral molecular concentrations and CS. However, an exception was found for  $\text{CHON}_{\text{NPs}}$ , the concentration of which is also significantly influenced by the reagent ions  $\text{NO}_3^-$ . We found that the charge fractions are higher for molecules with higher molecular weight and  $\overline{\text{OS}}_{\text{C}}$ . We also observed a

charging competition between different neutral organic and inorganic compounds, such as the competition between H<sub>2</sub>SO<sub>4</sub> and organic ions. We believe these analyses will largely promote the understanding of the formation of atmospheric ions and formulate important implications on the ionization chemistry of NO<sub>3</sub><sup>-</sup> and HSO<sub>4</sub><sup>-</sup>.

*(1) Sect 2.1: At least a basic overview of the measurements at the boreal forest site needs to be provided so that the reader can understand and correctly interpret the results presented. Given that the measurements have been previously published, it is not necessary to go into a lot of detail, but the basics should be provided so the manuscript stands on its own. These include the dates of the measurements, a brief description of the inlet, how (if?) the transmission efficiency was determined, and any extenuating/unusual circumstances that would influence the measurements and the conclusions drawn here.*

**Response:** Thanks for the suggestions! We have added detailed information about the measurement of cluster ions in Hyytiälä including the measurement periods and the sampling settings in the revised manuscript as below,

**Table S1 in SI**

**Table S1.** The measurement period and time resolution for instruments at AHL/BUCT and SMEAR II stations.

Site, type	Location	Instrument	Time resolution	Measurement period
AHL/BUCT, urban	Beijing, China	APi-HTOF	1 h	Feb 14-Feb 27, 2018
		CI-APi-LTOF	5 min	Jan 23-April 14, 2018
		NAIS	4.5 min	Jan 12-Dec 31, 2018
SMEAR II, boreal forest	Hyytiälä, Finland	APi-HTOF	1 h	April 7-June 8, 2013
		NAIS	4.5 min	Jan 1-Dec 31 2013

[Line 124-126] “Besides, the measurements at a boreal forest station SMEAR II (System for Measurement of forest Ecosystem and Atmospheric Relationships) located at Hyytiälä, Finland were used for comparison. Details of the instruments and their measurement periods in these two stations are given in Table S1.”

[Line 127-129] “The atmospheric negative cluster ion compositions were measured with an atmospheric pressure interface time-of-flight high-resolution mass spectrometers (APi-HTOF) from Feb 14 to Feb 27, 2018, in Beijing, and from April 7 to June 8, 2013 in Hyytiälä (Yan et al., 2018).”

[Line 138-140] “In Hyytiälä, ions were sampled through a core sampling method. It has a wide tube outside and a short coaxial tube inside to minimize the sampling losses with a total flow rate of 5 LPM.”

[Line 157-159] “The ion mobility distribution was measured by a NAIS (NAIS, Airedt Ltd.) ..... from Jan 1<sup>st</sup> to Dec 31<sup>st</sup>, 2013 in Hyytiälä (Kontkanen et al., 2013).”

*(2) Sect 2.1: The dates of the measurements are unclear to me. On line 123, it is stated that the study ran from Jan 14th to Sept 16th, 2018, while on line 126 it states that the API measurements are from Feb 14th to Feb 27th, 2018. Were API measurements only made over this ~2 week period? If so, that needs to be clarified throughout the text. Were the nitrate CIMS measurements made concurrently with the API measurements or are they from a different time period? If a different time period, when exactly was that period and how would that influence the comparison between the API and the CIMS? As it reads now, the manuscript implies the measurements are simultaneous. Further information regarding the nitrate CIMS*

*inlet, sampling protocol, and calibration frequency also need to be given so the reader can judge the likelihood of potential artefacts etc.*

**Response:** The sampling period of APi-TOF measurement was from Feb 14<sup>th</sup> to Feb 27<sup>th</sup>. The measurement period only lasts two weeks because the APi inlet is easy to be blocked by aerosols, dust, or catkin in polluted areas and ion clusters would be hard to be detected, similar to the study of Yao et al. (2018).

A CI-APi-TOF and an APi-TOF were operated side by side to acquire information on the neutral molecules and negative cluster ions simultaneously.

The calibrations, including the sensitivity calibration for H<sub>2</sub>SO<sub>4</sub> and the transmission efficiency calibrations for the mass detectors, were calibrated at the end of the campaign.

Apart from the modification listed in question 1, we have revised the manuscript as below,

[Line 144-148] “It was operated side by side with the APi-TOF to achieve simultaneous measurements of neutral molecules and cluster ions. NO<sub>3</sub><sup>-</sup> and its adducts (HNO<sub>3</sub>)<sub>1-2</sub>NO<sub>3</sub><sup>-</sup> were used as the reagent ions to chemically ionize the gas molecules with a laminar flow ionization source mounted in front of the APi-LTOF (Eisele and Tanner, 1993). Nitric acid is volatilized and carried by a total of 20 LPM sheath flow, then it is exposed to soft X-ray to produce NO<sub>3</sub><sup>-</sup> and its adducts (HNO<sub>3</sub>)<sub>1-2</sub>NO<sub>3</sub><sup>-</sup>.”

[Line 151-154] “The sensitivity for H<sub>2</sub>SO<sub>4</sub> was calibrated via the controlled reaction between SO<sub>2</sub> and OH at the end of the campaign (Kürten et al., 2012; Li et al., 2019). The relative mass-dependent transmission efficiency of the CI-APi-LTOF was calibrated using the depletion method (Heinritzi et al., 2016).”

[Line 158-159] “In both stations, the measurement periods of NAIS covered the measurement periods of APi-TOF.”

*(3) Sect. 2.1: Please provide more details on the inlet for the NAIS and how the calibration was performed. These details, particularly regarding calibration and inlet colocation/design, are critical for evaluating the API quantification.*

**Response:** A 1.8 m long 4 cm copper tube is used to sample ambient ions with a flow rate of 54 LPM to reduce the losses of ions during sampling. NAIS was calibrated through the method described by Wagner et al. (2016) and both inversion kernel and sampling losses were considered in the data inversion. We added the information to the revised manuscript as below,

[Line 167-171] “In urban Beijing, ambient air is drawn into the system through a 1.8 m long copper tube with a diameter of 4 cm, positioned at the window. The sample flow rate is maintained at 54 LPM. The inversion kernel of NAIS was calibrated based on the method described by Wagner et al. (2016) and sampling losses were further considered in the data inversion. The results of NAIS were calibrated considering both the transfer functions and sampling losses (Mirme and Mirme, 2013; Wagner et al., 2016).”

*(4) Sect. 3.2: While this section provides description of the measurements, the scientific motivation of the analysis as well as how the results can be used to further broaden our understanding of atmospheric composition/chemistry are unclear to me. The comparison between Beijing and Hyytiälä is rather superficial, just presenting averages. There is no discussion on how seasonality, day-night differences, transport, etc. would influence the results and the comparisons. The finding that the two locations differ in composition is unsurprising and doesn't provide new insights at the given level of analysis. I suggest either removing this analysis or significantly expanding it to consider aspects such as how the possible HOM precursors differ and what that implies about HOM molecules that are often important for aerosol growth. Further specific minor comments about this section are listed below.*

**Response:** Thanks for the suggestion. To gain deeper scientific insights into the cluster ion characteristics, we reorganized the contents and added more analysis on the cluster formation processes. For section 3.2, we cut down the comparisons between Beijing and Hyytiälä and only mention data from Hyytiälä as a reference when needed. Now Section 3.2 mainly focuses on the formation of negative cluster ions from the view of both reagent ions and neutral molecules. The formation of cluster ions was analyzed by comparing their concentrations, volatility distributions, and charge fractions with CS, reagent ions, and their corresponding neutral molecules.

The diurnal variations of cluster ions, their corresponding neutral molecules, and the charge fractions were shown in Fig. 7. The diurnal variations of cluster ions and their corresponding neutral molecules in Figure 7a-b reflect the significant role of neutral molecule variations in determining the cluster ion concentration, and the diurnal variations of charging fraction Figure 7c reflect a charging competition between H<sub>2</sub>SO<sub>4</sub> and organic ions.

Transportation of organic ions is considered to be limited due to their short lifetime, and the analysis of seasonality would need a longer measurement period.

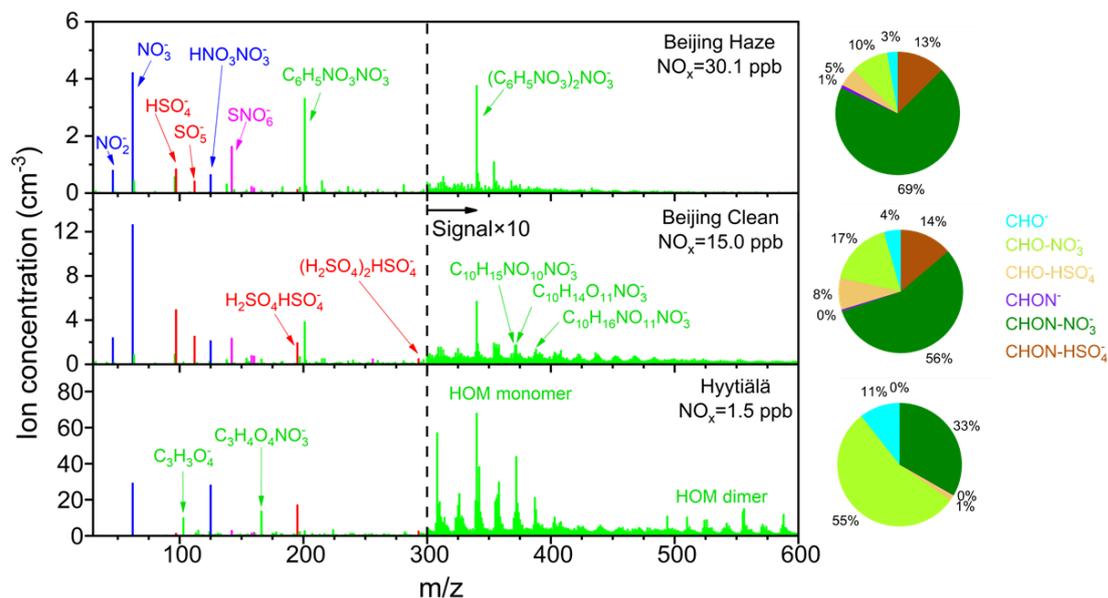
Through the comprehensive quantitative analysis of atmospheric cluster ions, reagent ions, and neutral molecules, we can roughly predict the composition and concentration variations of most atmospheric negative cluster ions from measured neutral molecules and CS, as indicated by Fig. 8. However, as the actual charging fractions for different species differ in a wide range as shown in Fig. 9, the prediction of actual concentrations of atmospheric ions would require more work.

*(5) Lines 330-331: I don't see how this implies that ion-induced nucleation is stronger under clean conditions. Please provide further analysis supporting this statement.*

**Response:** Thanks for the suggestion. Here we meant that the concentration of NPF-related ion clusters including (H<sub>2</sub>SO<sub>4</sub>)<sub>0-2</sub>H<sub>2</sub>SO<sub>4</sub><sup>-</sup>, (H<sub>2</sub>SO<sub>4</sub>)<sub>3</sub>NH<sub>3</sub>H<sub>2</sub>SO<sub>4</sub><sup>-</sup>, and (H<sub>2</sub>SO<sub>4</sub>)<sub>3</sub>C<sub>2</sub>H<sub>7</sub>NHSO<sub>4</sub><sup>-</sup> all increased significantly during clean periods, indicating enhanced ion-induced nucleation. As its relationship with our main topic is weak, this sentence has been removed from the revised manuscript.

*(6) Lines 332-334: Is the nitrogen-containing organic ions referring to CHONNO<sub>3</sub>? If so, I don't understand the point about a higher fraction in Beijing given that Figure 4a shows 27% for Beijing haze while the Hyytiälä pie chart shows 31% suggesting a larger fraction in Hyytiälä. Moreover, from the pie charts in Fig. 4b, there also appears to be more CHON in Hyytiälä than in the Beijing haze.*

**Response:** We apologize for any confusion. 'nitrogen-containing organic ions' refers to the sum of CHON-NO<sub>3</sub><sup>-</sup> and CHON-HSO<sub>4</sub><sup>-</sup>. In the revised manuscript, we use CHON-related ions instead of the original expression. We meant that CHON-related ion fractions **among all organic ions** are more abundant in Beijing than in Hyytiälä, **not among all ions**. To avoid confusion, we revised the pie charts to show the fractions of CHO-related ions and CHON-related ions in the total organic ions, as shown in Fig. 4 in the revised manuscript. It shows that the CHON-related ions account for over 70% of total organic ions in urban Beijing, and only 33% in Hyytiälä on average. The figure and manuscript have been revised as below,



**Figure 4.** The negative cluster ion compositions in Beijing and Hyttiälä..

[Line 335-341] “The negative organic ions are mainly CHO-related or CHON-related organic ions in the form of the adduct with  $\text{NO}_3^-$  or  $\text{HSO}_4^-$  (Fig. 4). Only minor fractions ( $\sim 4\%$ ) are in the deprotonated form of  $\text{CHO}^-$  or  $\text{CHON}^-$ . These indicate that the ionization schematic of organic ions is mainly through ion-molecular reaction with  $\text{NO}_3^-$  or  $\text{HSO}_4^-$  in Beijing. As few neutral sulfur-containing organics were observed, it is unlikely that the identified  $\text{CHON-HSO}_4^-$  is a cluster of sulfur-containing organics and  $\text{NO}_3^-$ , but rather a cluster of nitrogen-containing organics and  $\text{HSO}_4^-$ . Among all negative organic ions,  $\text{CHON}$  organic ions adducted with  $\text{NO}_3^-$  ( $\text{CHON}\cdot\text{NO}_3^-$ ) are the most abundant and account for 56% and 69% during clean and haze periods, respectively.”

(7) Line 340: In (Bianchi et al., 2017) which are measurements also from Hyttiälä, HOMs were observed as adducts with  $\text{HSO}_4^-$  as well. This should be discussed. This paper is referenced in line 343, however it should be moved earlier and in the context of relatively little adduct formation with  $\text{HSO}_4^-$  observed in the dataset used for the comparison here. Furthermore, in the Bianchi et al measurements it appears that  $\sim 25\text{-}50\%$  of the signal for a given HOM ion was from the HOM  $\text{HSO}_4^-$  adduct during the daytime – I’m not sure I would consider this as being particularly low.

**Response:** Thanks for the suggestion. We agree that during the daytime on the clear days of Hyttiälä, organic ion clusters charged by  $\text{HSO}_4^-$  are non-negligible. But the ratio between organic ions attached to  $\text{HSO}_4^-$  and  $\text{NO}_3^-$  would still be lower than that in urban Beijing. This is mainly due to the higher  $\text{HSO}_4^-/\text{NO}_3^-$  ratio in Beijing ( $\sim 0.36$ ) compared with Hyttiälä ( $\sim 0.05$ ), as illustrated in Fig. S13. We have modified the manuscript as below,

[Line 360-363] “Moreover, a larger fraction of the organic ions are in the form of adducts with  $\text{HSO}_4^-$  in Beijing than in Hyttiälä. This is related to the higher  $\text{HSO}_4^-/\text{NO}_3^-$  ratio in Beijing ( $\sim 0.36$ ) compared with Hyttiälä ( $\sim 0.05$ ). The fraction of  $\text{HSO}_4^-$  adducted ions would increase during clear days in Hyttiälä but its fraction is still lower than those in Beijing (Bianchi et al., 2017).”

(8) Line 341-342: I am not entirely convinced by this argument since in Hyttiälä the  $\text{H}_2\text{SO}_4\text{HSO}_4^-$  peak is relatively more intense compared to  $\text{HSO}_4^-$  than it is in Beijing. Additionally, in Hyttiälä the  $\text{HNO}_3\text{NO}_3^-$  ion is more intense than the  $\text{NO}_3^-$  ion compared to Beijing. This seems to imply that further nuance needs to be considered such as relative binding strengths of  $\text{HNO}_3\text{NO}_3^-$  vs  $\text{HOM}\text{NO}_3^-$  adducts (and likewise for  $\text{HSO}_4^-$  adducts).

**Response:** Thanks for the suggestion. As shown in Table R1, we compared the ratio of  $\text{HSO}_4^-/\text{NO}_3^-$ ,  $\text{HSO}_4^-/(\text{HNO}_3)_{0-2}\text{NO}_3^-$ , and  $(\text{H}_2\text{SO}_4)_{0-2}\text{HSO}_4^-/(\text{HNO}_3)_{0-2}\text{NO}_3^-$  in Beijing and Hyytiälä. The ratio of  $\text{HSO}_4^-/\text{NO}_3^-$  and  $\text{HSO}_4^-/(\text{HNO}_3)_{0-2}\text{NO}_3^-$  is both significantly higher in Beijing than in Hyytiälä. In contrast, the ratio of  $(\text{H}_2\text{SO}_4)_{0-2}\text{HSO}_4^-/(\text{HNO}_3)_{0-2}\text{NO}_3^-$  in Beijing is only slightly higher than in Hyytiälä. This is due to the abundance of  $(\text{H}_2\text{SO}_4)_{1-2}\text{HSO}_4^-$  in Hyytiälä. Thus we think that the low fraction of organic ions containing  $\text{HSO}_4^-$  is attributed to the low ratio of  $\text{HSO}_4^-/\text{NO}_3^-$  or  $\text{HSO}_4^-/(\text{HNO}_3)_{0-2}\text{NO}_3^-$ .  $(\text{H}_2\text{SO}_4)_{1-2}\text{HSO}_4^-$  should contribute little to the charging of OOMs because their formation energies are much lower than those of organic ions charged by  $\text{HSO}_4^-$  (Herb et al., 2018). As the concentration of  $(\text{HNO}_3)_{0-2}\text{NO}_3^-$  is dominated by  $\text{NO}_3^-$  in Beijing, we mainly consider  $\text{NO}_3^-$  as the main reagent ions in the atmosphere in the following analysis.

**Table R1.** The ratio between  $(\text{H}_2\text{SO}_4)_{0-2}\text{HSO}_4^-$  and  $(\text{HNO}_3)_{0-2}\text{NO}_3^-$  in Beijing and Hyytiälä

	$\text{HSO}_4^-/\text{NO}_3^-$	$\text{HSO}_4^-/(\text{HNO}_3)_{0-2}\text{NO}_3^-$	$(\text{H}_2\text{SO}_4)_{0-2}\text{HSO}_4^-/(\text{HNO}_3)_{0-2}\text{NO}_3^-$
Beijing	0.3554	0.3037	0.4459
Hyytiälä	0.0473	0.0240	0.3681

*(9) Figure 4: Was the Hyytiälä data corrected for the API transmission function? If not, these comparisons are not meaningful.*

**Response:** Thanks for the suggestion. In the revised manuscript, we quantified the API-TOF data measured in Hyytiälä using the *in-situ* quantification method with NAIS and updated the spectra as in Fig.4. It is stated in the revised manuscript as below,

[Line 141-142] “For further analysis in this study, we quantified the negative cluster ions in both Beijing and Hyytiälä using the *in-situ* quantification method, as will be discussed in Section 2.2.”

*(10) Sect. 3.3: Similar to Sect. 3.2, I find the analysis in this section too superficial to provide meaningful insights that will improve our understanding of atmospheric chemistry/composition. However, compared to Sect. 3.2, I think this section would require less work to add new insights. With the results presented as averages, overly broad generalizations are made and the text mostly focuses on reporting results rather than discussing the implications of those results. For instance, reporting the average charge fractions as a range of 4 orders of magnitude (line 381) does not provide meaningful information given the significant diel pattern of H2SO4 and the resulting impacts of charge competition. It would be interesting to know what is influencing such a range. For instance, it would seem reasonable that perhaps HOMs present primarily at night (i.e. formed from NO3 radical chemistry) might have higher charged fraction because of less charge competition with H2SO4. Is there a diel dependence evident in this charged fraction? Similarly, one might expect a day vs night dependence to perhaps influence the NO3- vs HSO4- charging (line 385). Delving a little more into the details controlling these wide ranges would allow the reader to gain more generalized insight into the chemistry and would be more helpful in analysis of future datasets. Such an analysis need not focus on all the ions – targeting the a select few (i.e. most intense HOMs) would be appropriate. This section would also benefit from clearly articulating the major scientific conclusions the reader should learn. For instance, is there something to be learned about specific conditions where API is capable of providing insight into diel variations of neutral HOMs versus when it cannot? Further specific minor comments about this section are listed below.*

**Response:** Thanks for the suggestion. In the revised manuscript, we have added deeper discussions on ion formation, its influencing factors, and implications. The sections are thus reorganized. The influence of CS, reagent ions, and neutral molecules on the formation of negative clusters was analyzed in detail. The charge competition between  $\text{H}_2\text{SO}_4$  and neutral molecules was clearly shown, and the charge fractions of organic ions with different compositions increased significantly during nighttime. We further show that molecules with high carbon atom numbers and high average carbon oxidation state are more easily to be charged. The influence of reagent ions,  $\text{NO}_3^-$  and  $\text{HSO}_4^-$ , on the formation of organic ions is mainly through their concentrations, and  $\text{HSO}_4^-$  clusters with organic molecules more efficiently than  $\text{NO}_3^-$ , except for NPs. Thus it

is possible to predict the variation of negative cluster ions based on the measured neutral molecules and CS. Though the ratio between them is highly dependent on their species, the charge fractions observed in our study can be used as a reference for the other urban environments. In addition, it is possible to provide some insight into the differences in charging efficiency of organics measured by using  $\text{NO}_3^-$  and  $\text{HSO}_4^-$  as the reagent ions.

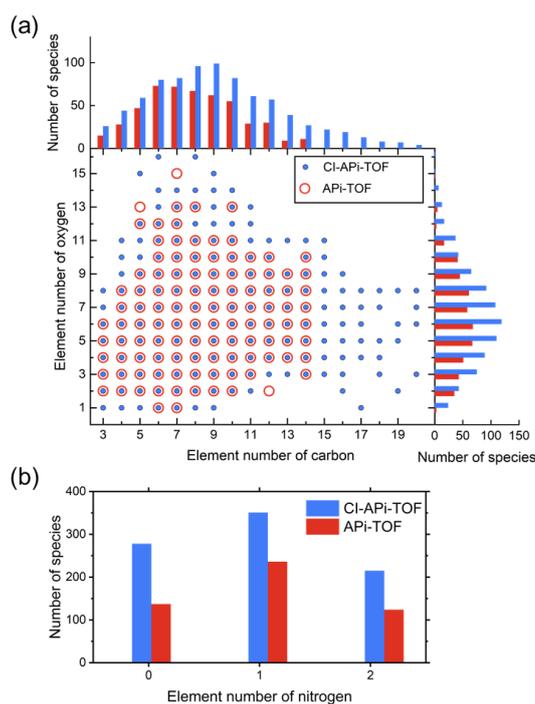
(11) Lines 377-379: What is meant by “neutral molecules detected by the CI-API-TOF containing the same formula of CHO and CHON are treated as their corresponding precursors”? Does that mean the CHO- and CHON- ions were used or is it the formulas after subtracting  $\text{NO}_3^-$  as the reagent ion? The latter seems more appropriate to me.

**Response:** Sorry for the confusion. We meant the latter: the formula of neutral molecules detected by CI-API-TOF was identified by subtracting one  $\text{NO}_3^-$ . We revised the sentence in the manuscript for clearance:

[Line 374] “The neutral molecules detected by CI-API-TOF was identified by subtracting one  $\text{NO}_3^-$ .”

(12) Figure 5: Please explain the histograms in panel b in greater detail. Why are the histograms different intensities overall? Are these total formulas detected? The N atom distribution is not shown in Fig. S6.

**Response:** Sorry for the typo. The ‘Fig. S6’ should be ‘Fig. S9’. The histograms are the number of species containing a certain number of C and O atoms. The number of species differs between API-TOF and CI-API-TOF because the number of peaks identified in API-TOF is less than that in CI-API-TOF. To make it clear, we have modified the figures as below,



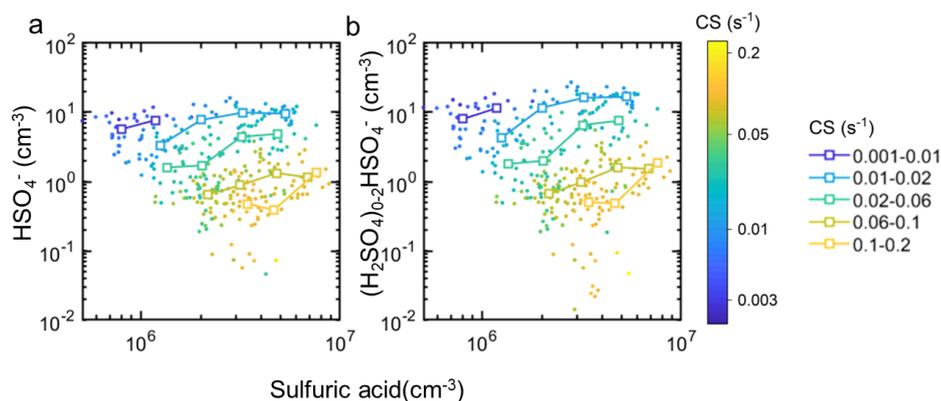
**Figure S12.** Comparison of the organic molecules detected in API-TOF and CI-API-TOF respectively. (a) The distribution of species with different number of carbon atoms and oxygen atoms. (b) The distribution of species with different number of nitrogen atoms.

(13) Figure 6: How was  $\text{HNO}_3$  measured? The fact that the measurements are in a different season should be discussed in the text along with how that could influence the interpretation.

**Response:** The gaseous  $\text{HNO}_3$  is measured by MARGA at the same site, but during a different period. We agree with the reviewer that using data from different seasons would add unknown uncertainties to the analysis. As the analysis of the diurnal cycle of gaseous  $\text{HNO}_3$  does not bring new insights into the formation of ions, we removed it from the manuscript.

*(14) Figure S11: If all the sulfuric acid clusters were included, would there be a better correlation with neutral sulfuric acid?*

**Response:** As shown in Fig. R1, the correlation between sulfuric acid ions and neutral sulfuric acid was not improved by including  $(\text{H}_2\text{SO}_4)_{1-2}\text{HSO}_4^-$ . The ion concentration of  $\text{HSO}_4^-$  was determined by both neutral sulfuric acid and CS. It is shown that after being grouped by CS, the concentration of  $\text{HSO}_4^-$  and other organic ions both increased with the concentration of its corresponding neutral molecules.



**Figure R1.** Scatter plots of the concentrations of  $\text{HSO}_4^-$  and  $(\text{H}_2\text{SO}_4)_{0-2}\text{HSO}_4^-$  measured by APi-TOF and  $\text{H}_2\text{SO}_4$  measured by CI-APi-TOF in urban Beijing, colored by CS.

#### **Other minor comments.**

*(15) In several locations of the manuscript, I think that the wording unnecessarily oversells the impact/implications of the manuscript. In my opinion, this detracts from the work and may make the reader less inclined to appreciate the advancements that the work does make. Examples of this include line 92 and 457. The introduction does not justify why it is particularly urgent to quantify specific ions nor does the manuscript address how these will ultimately aid in human health, air quality, and global climate. These should be removed or should be better justified.*

**Response:** Thank you for your suggestion. In the revised manuscript, we have included further analysis of the charge fractions of organic ions with different species in the atmosphere using the quantification results. Additionally, we have removed sentences that may have overstated our findings.

*(16) Lines 184-190: Since there is overlap in the region where the densities of 1.3 and 1.1 g/cm<sup>3</sup> transition and since at higher masses, the densities appear to go back down to 1.1 g/cm<sup>3</sup>, why not use both 1.1 and 1.3 g/cm<sup>3</sup> to develop a range of possibilities and generate something like a range of values (error bars). This would avoid the sudden, non-physical, stepwise transition and it would avoid implying precision in the answer that isn't there. It would be a better reflection of our current state of understanding.*

**Response:** For the overlap regions from  $m/z$  150 to  $m/z$  200, we accept the reviewer's suggestion and use a gradual transition curve of density instead of stepwise values. But for  $m/z$  larger than 400, we still use 1.3 g/cm<sup>3</sup> because the density of 1.1

$\text{g}/\text{cm}^3$  was for OOMs dimers according to Krechmer et al. (2016). However, in Beijing, OOM dimers are not identified either in neutral molecules or in organic ions. The manuscript is revised as below,

[Line 201-204] “By comparing the measured and calculated mobilities for organic ions with different compositions, densities of 1.1 and 1.3  $\text{g}\cdot\text{cm}^{-3}$  were ultimately used in the mass-mobility conversion of ions with  $m/z$  smaller than 150 or larger than 200, respectively, whereas between  $m/z$  of 150 and 200, a linear curve of density is used.”

*(17) Line 205: How were the sampling losses in the APi determined? This is necessary for others wishing to implement this type of analysis in the future.*

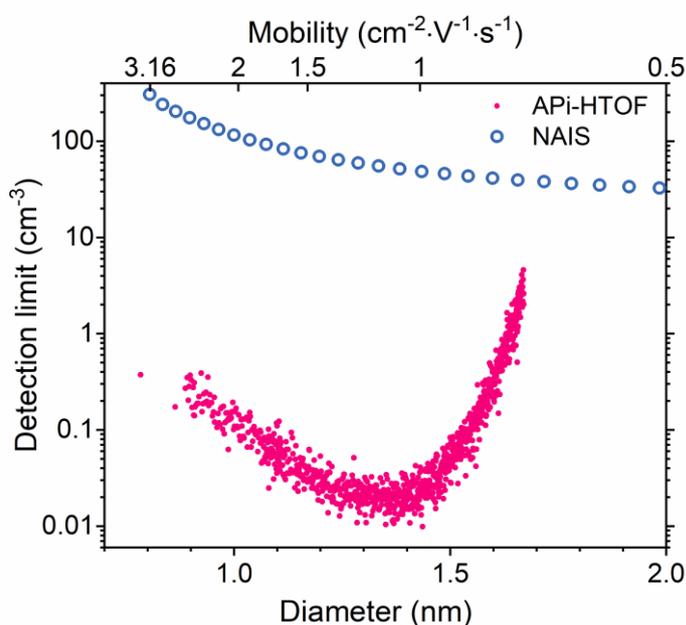
**Response:** We assume that ions measured by APi-TOF have the same sampling losses as neutral particles that have the same sizes.

[Line 223-225] “The sampling losses of ions in the APi-TOF is assumed the same as those of neutral particles with the same sizes (Mahfouz and Donahue, 2021).”

*(18) Lines 222-232: Please include the time resolution required for the stated detection limits. I think it would also be more meaningful to provide the range of the APi detection limit (given the  $m/z$  dependent transmission) rather than focusing just on the minimum. The range would be more comparable to the range given for the NAIS.*

**Response:** Thanks for the suggestion. The detection limit of the NAIS is determined according to the noise of the electrometer and its transfer function, and the noise of the electrometer was assumed to be 0.006 fA in this study. The detection limit of the APi-HTOF first decrease and then increase with the increase in  $m/z$ , as shown in Figure S4. Under a minimum diameter of 0.9 nm and a maximum of 1.7 nm, the detection limits of APi-HTOF were  $\sim 0.4$  and  $\sim 4 \text{ cm}^{-3}$ , respectively. We added this information in the revised manuscript as below,

[Line 242-245] “The detection limit of the APi-HTOF is the lowest at a diameter of 1.4 nm, which is  $\sim 0.02 \text{ cm}^{-3}$ , and it increases when the detected ions move to lower or higher sizes due to the decrease in detection efficiency. Under a minimum diameter of 0.9 nm and a maximum of 1.7 nm, the detection limits of APi-HTOF were  $\sim 0.4$  and  $\sim 4 \text{ cm}^{-3}$ , respectively.”



**Figure S4.** The detection limit of APi-HTOF and NAIS for negative cluster ions. The detection limit of APi-HTOF is determined using data with a resolution of 1 hour, and the detection limit of NAIS is determined using data with a resolution of 2 min. The detection limit of the APi-HTOF is determined according to the noise of microchannel plate (MCP) detector and the detection efficiency. The detection limit of the NAIS is determined according to the noise of the electrometer and its transfer function, and the noise of the electrometer was assumed to be 0.006 fA in this study.

*(19) Figure 1: What is causing the dip in the data from m/z 200-300? How does the relatively poor fit in that range affect the interpretation?*

**Response:** Actually, we are uncertain about the causes. There could be several reasons. As we explained in the manuscript, “The discrepancy between the absolute and relative transmission efficiency at small values of m/z may be caused by the uncertainty of small ion measurements in the NAIS, sampling efficiency calculation, or the influences of CI-inlet, as the voltage settings remain the same during the calibration experiment.” This would result in an uncertainty of ~28% for the quantification of ions with an m/z between 200 and 300. We mentioned this uncertainty in the revised manuscript.

[Line 229-230] “It would result in an uncertainty of ~28% for the quantification of small ions.”

*(20) Line 48: The Lee et al 2004 reference is for indoor air quality and uses artificially generated ions. This is very different from what is implied by the current sentence structure and I recommend removing the reference or clarifying what the study actually shows.*

**Response:** This reference has been removed.

*(21) Lines 87-88: I recommend citing some of the seminal work by Arnold et al as well. For instance (but not limited to), Arnold et al., 1982, 1978.*

**Response:** We have added several works of Arnold et al. in the manuscript.

[Line 90-92] “Quadrupole mass spectrometers with approximate unit mass resolution have been applied in a series of ion composition measurements (Arnold et al., 1978; Arnold and Viggiano, 1982; Eisele, 1989; Eisele et al., 2006; Eisele and Tanner, 1990; Viggiano, 1993)”

*(22) Lines 87-88 & 89-90: I recommend starting these lines of references with “e.g.” to indicate that these are non-exhaustive.*

**Response:** Thanks for the suggestion. We have modified the sentences.

*(23) The data availability statement is not aligned with the journal standards*

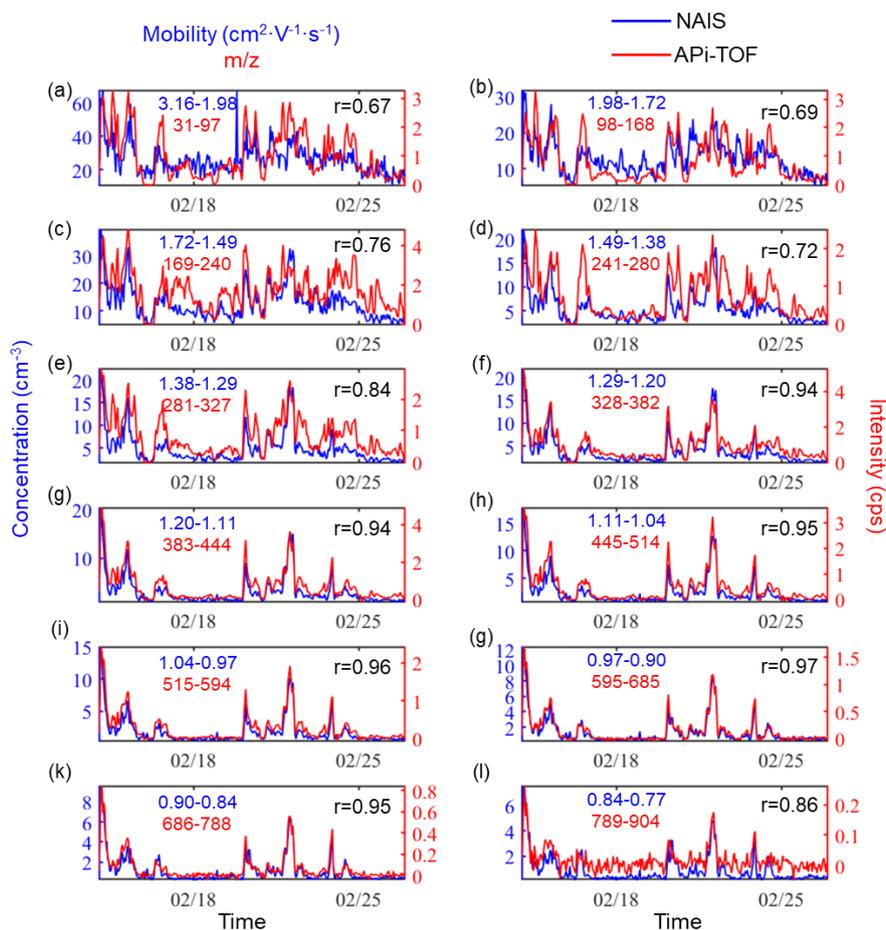
[https://www.atmospheric-chemistry-and-physics.net/policies/data\\_policy.html](https://www.atmospheric-chemistry-and-physics.net/policies/data_policy.html)

**Response:** Thank for the suggestion. We have modified the availability statement.

[Line 531-533] “The detection efficiency of API-TOF, the time series of total negative cluster ions and CS in urban Beijing, and the average spectrums of negative clusters ions measured by API-TOF during haze and clean periods in urban Beijing are available from <https://zenodo.org/record/7791785>.”

(24) Figure S2: I recommend moving the API labels (red text) to the right y-axis to improve readability.

**Response:** Thanks for the suggestion. The figure has been modified as below,



(25) Line 253: I would tend to call these mass balance equations. I also recommend specifying that you are assuming steady-state in deriving equations 6 and 7.

**Response:** Thanks for the suggestion. This statement has been modified here and in other parts of the manuscript. The manuscript is revised as below,

[Line 253-254] “To quantitatively address the sources and sinks of air ions, we simulate the concentration of ions using the mass balance equation and identify their dominant production and loss pathways.”

(26) Lines 319-321: Why not compare the detection of organosulfur molecules with the nitrate CIMS in Beijing rather than citing other measurements that are from significantly different atmospheric conditions?

**Response:** Thanks for the suggestion. The manuscript is revised as below,

[Line 337-339] “As few neutral sulfur-containing organics were observed (Qiao et al., 2021), it is unlikely that the identified CHON-HSO<sub>4</sub><sup>-</sup> is a cluster of sulfur-containing organics and NO<sub>3</sub><sup>-</sup>, but rather a cluster of nitrogen-containing organics and HSO<sub>4</sub><sup>-</sup>.”

*(27) Line 324: Please include in the text, not just the figure legend, how haze periods are identified.*

**Response:** Thanks for the suggestion. The manuscript is revised as below,

[Line 341-342] “Here the haze periods were identified based on whether PM<sub>2.5</sub> concentration is higher than 75 μg·m<sup>-3</sup>.”

*(28) Line 328: The C<sub>10</sub>H<sub>16</sub>NO<sub>11</sub>NO<sub>3</sub><sup>-</sup> formula would correspond to an open shelled neutral assuming NO<sub>3</sub><sup>-</sup> as the charging ion. Is there a typo here and in Figure 4?*

**Response:** We have checked this peak assignment again and its mass accuracy is within 1.4 ppm. This peak has also been observed in a previous study by Yan et al. (2020) investigating the HOMs formation under high NO<sub>x</sub> conditions in the chamber. Considering the high NO<sub>x</sub> in urban Beijing, this compound is highly likely to exist in cluster ions, and it might be an open-shelled neutral adduct with NO<sub>3</sub><sup>-</sup>.

*(29) Line 354-355: As the (HNO<sub>3</sub>)<sub>x</sub>NO<sub>3</sub><sup>-</sup> ions are formed as part of the reagent ion generation, I don't think it is appropriate to include them in this list.*

**Response:** Thanks for the suggestion. We have removed this sentence.

*(30) Lines 398-400: This point about the phenol related ions should be made at the beginning of the discussion so the reader understands the parameters of the analysis.*

**Response:** Thanks for the suggestion. We added the description and analysis of nitrated phenols in the revised manuscript. This sentence is revised as below,

[Line 348-351] “NPs have high signals in urban Beijing and their properties are different from most other CHON compounds, such as volatilities and charging efficiencies as will be discussed below. Thus, CHON species were divided into CHON<sub>NPs</sub> and CHON<sub>nonNPs</sub> groups in the following analysis (Nie et al., 2022).”

*(31) Line 415: What specifically is meant by “total ion clusters”? Please clarify.*

**Response:** Here the total ion clusters refer to the total concentration of negative ion clusters. The manuscript has been modified as below,

[Line 396-398] “NO<sub>3</sub><sup>-</sup> maintains a relatively constant proportion (15%±5%) in the total negative cluster ions during the whole sampling period in urban Beijing, while the fraction of HSO<sub>4</sub><sup>-</sup> varies significantly due to the strong diurnal variation of H<sub>2</sub>SO<sub>4</sub>.”

## **Reviewer #2:**

*Yin et al. report measurements of negative atmospheric ions in Beijing. They used an improved calibration technique by*

*comparing the API-TOF signal with NAIS. Concentration and composition of atmospheric ions in Beijing are reported and are further compared with those measured in a boreal forest environment. Sources and sinks of ions are discussed and the concentrations of select ions are simulated, the results of which agree well with measurements. I find the results presented in this work interesting and the manuscript can be accepted after the following comments are addressed.*

*(1) Is it possible to relate the sampling efficiency to more fundamental parameters, e.g., sampling tube length and flowrates? The current method requires that one has to have a well-calibrated NAIS to calibrate an API-TOF, which is demanding on available instruments for a lot of observation sites.*

**Response:** The detection efficiency of API-TOF is highly dependent on its voltage and sampling settings, making it difficult to relate only to basic parameters. In the absence of a NAIS, a high-resolution differential mobility analyzer (DMA) and electrometer are required to calibrate the API-TOF to obtain its detection efficiency (Heinritzi et al., 2016).

*(2) It is not clear to me why only negative ions are discussed, which makes the story not complete. Are there problems with positive ions measurements?*

**Response:** We agree that measuring both positive and negative ions would be ideal for a comprehensive study of ion chemistry in Beijing. However, due to the low concentrations of ions in Beijing, we needed to average the spectra of at least 1 h for better identification of the high-resolution peaks. This is already a relatively low time resolution for real-time measurement. Therefore, we chose not to switch between positive and negative ion modes. In addition, measuring negative ions alone can already provide many valuable insights into the ion composition and sources in Beijing, especially when combined with neutral molecules measurement from nitrate CI-API-TOF.

*(3) It is stated that organic ions with the HSO<sub>4</sub><sup>-</sup> adduct is one of the most abundant organic ions, doesn't this imply that HSO<sub>4</sub><sup>-</sup> clustering with organics should be included in the kinetic model for HSO<sub>4</sub><sup>-</sup>? From Fig. 4a it seems that this sink should be comparable to the H<sub>2</sub>SO<sub>4</sub> + HSO<sub>4</sub><sup>-</sup>*

**Response:** We tried to consider the reactions between HSO<sub>4</sub><sup>-</sup> and organics in our kinetic model for HSO<sub>4</sub><sup>-</sup>. However, the ion-molecule reaction rates between HSO<sub>4</sub><sup>-</sup> and the various organic neutral molecules are unknown. Our manuscript shows that the charge fraction of neutral organic molecules by HSO<sub>4</sub><sup>-</sup> varies significantly among different species. Thus it is difficult to include all these processes in the model. Alternatively, the reviewer inspired us with another solution. That is to estimate the contribution of HSO<sub>4</sub><sup>-</sup> reaction with organics by comparing it with the reaction between H<sub>2</sub>SO<sub>4</sub> and HSO<sub>4</sub><sup>-</sup> through the measured concentration ratio of M·HSO<sub>4</sub><sup>-</sup>/H<sub>2</sub>SO<sub>4</sub>·HSO<sub>4</sub><sup>-</sup>. The corrected loss contributions of condensational loss onto aerosol particles, ion-molecule reaction with H<sub>2</sub>SO<sub>4</sub>, ion-molecule reaction with organics, and ion-ion recombination losses were 62%, 15%, 18%, and 5 %, respectively, which do not change our main conclusion that condensational loss onto aerosol particles is the main loss pathway of ions in urban Beijing. However, as this estimation also introduced large uncertainties and needs to be further evaluated, it is not included in the main manuscript. Instead, we have added a sentence in the manuscript to state the ignorance of the reactions with organics.

[Line 270-271] “The ion-molecule reactions between HSO<sub>4</sub><sup>-</sup> and organic molecules are not considered in this model due to the lack of reaction rate constants.”

*(4) The concentration of ions is determined by the balance between the source and sink terms. Is there any available*

*information on the comparison between ion production rates between Hyytiälä and Beijing?*

**Response:** Thanks for the suggestion. We have calculated the ion production rate in Beijing based on the ion balance method described in Tammet et al. (2006) that uses the measured atmospheric ion size distributions to calculate the ion production rate. In urban Beijing, the ion production rate is estimated to be  $1.65 \text{ cm}^{-3}\cdot\text{s}^{-1}$  during our measurement. In Hyytiälä, the ion production rate is estimated to be  $5.6 \text{ cm}^{-3}\cdot\text{s}^{-1}$  based on the same method (Tammet et al., 2006), which is higher than that in our study.

However, this method may underestimate the ion production rate (Laakso et al., 2004). Direct measurements of radon and global radiation are needed in urban Beijing to obtain a more accurate value of the ion production rate.

*(5) Line 129: how were the voltages adjusted to minimize fragments? Which ion fragmentation is minimized? Please add sentences to provide these details since ion fragmentation is quite important for the current study.*

**Response:** The voltages of the APi-HTOF were adjusted to minimize fragmentation by adding a CI inlet in front of the APi-HTOF. The ratio between  $\text{HNO}_3\text{NO}_3^-$  and  $\text{NO}_3^-$  was minimized with consideration for sensitivity and resolution. Additionally, according to Passananti et al. (2019), critical voltages for minimizing SA cluster fragmentation include Lens Skimmer, Skimmer, Q2-Front, and Q2-Back. They found that when the difference between Lens Skimmer and Skimmer ( $\Delta V_1$ ) is larger than 9 V and the difference between Skimmer and Q2-Front ( $\Delta V_2$ ) is smaller than 3 V, fragmentation is minimized. In our study,  $\Delta V_1$  and  $\Delta V_2$  of the APi-HTOF were 15.5 V and 2.6 V respectively, indicating that our instruments were tuned to minimize fragmentation. The manuscript is modified as below,

[Line 131-133] “The APi-HTOF was operated in the negative ion mode to measure negative ions and its voltages were adjusted to reduce cluster fragmentations.”

*(6) Line 23, ‘We demonstrate the feasibility of quantifying cluster ion compositions with simultaneous in-situ measurements by a neutral cluster and air ion spectrometer.’ I find this sentence hard to understand, why is ion composition measurement dependent on neutral cluster spectrometer?*

**Response:** Thanks for the suggestion. A neutral cluster and air ion spectrometer (NAIS) is the name of the instrument we use to measure the ion mobility distributions. The manuscript is modified as below,

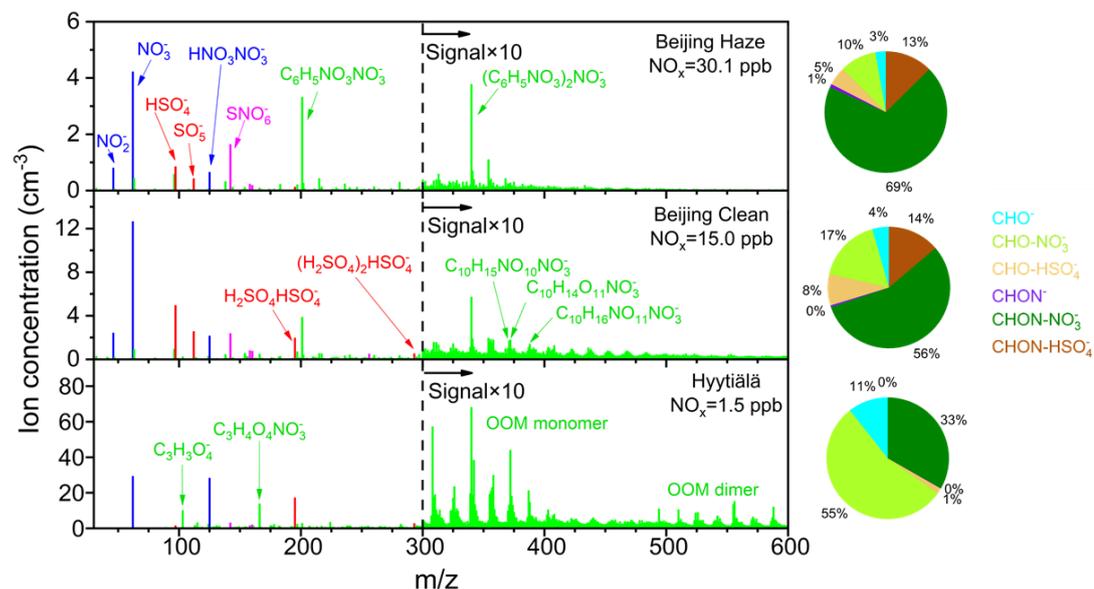
[Line 26-28] “We demonstrate the feasibility of quantifying cluster ions with different compositions using *in-situ* measured ion mobility distributions from a neutral cluster and air ion spectrometer (NAIS).”

*(7) Line 332: This sentence is misleading since nitrogen containing organic ions do not seem to be in higher fractions in Beijing.*

**Response:** We apologize for any confusion. We meant that the relative fraction of nitrogen-containing organic ions compared to CHO-related ions is higher in Beijing than in Hyytiälä. For clearance, we use the fraction of CHON-related ions in the total organic ions, instead of in the total ions, in the revised manuscript. The pie chart in Figure 4 was correspondingly changed to show the fractions in total organic ions.

[Line 335-341] “The negative organic ions are mainly CHO-related or CHON-related organic ions in the form of the adduct with  $\text{NO}_3^-$  or  $\text{HSO}_4^-$  (Fig. 4). Only minor fractions (~4%) are in the deprotonated form of  $\text{CHO}^-$  or  $\text{CHON}^-$ . These indicate that the ionization schematic of organic ions is mainly through ion-molecular reaction with  $\text{NO}_3^-$  or  $\text{HSO}_4^-$  in Beijing. As few

neutral sulfur-containing organics were observed, it is unlikely that the identified  $\text{CHON-HSO}_4^-$  is a cluster of sulfur-containing organics and  $\text{NO}_3^-$ , but rather a cluster of nitrogen-containing organics and  $\text{HSO}_4^-$ . Among all negative organic ions,  $\text{CHON}$  organic ions adducted with  $\text{NO}_3^-$  ( $\text{CHON}\cdot\text{NO}_3^-$ ) are the most abundant and account for 56% and 69% during clean and haze periods, respectively.”



**Figure 4.** The negative cluster ion compositions in Beijing and Hyytiälä.

(8) Line 430: *The reaction between  $\text{H}_2\text{SO}_4$  and  $\text{HSO}_4^-$  does not transform ions back to neutral molecules.*

**Response:** Thanks for pointing this out. We have revised the statement to be more specific: “(line 486-487) The transformation from  $\text{C}_3\text{H}_3\text{O}_4^-$  back to  $\text{C}_3\text{H}_4\text{O}_4$  indicates that the conversion of ions back to neutral molecules is also significant.”

(9) Line 412: *I’m not really sure if this the  $\text{NO}_3^-$  has ‘opposite’ diurnal variations from CS. If the author wants to make this statement, please show their correlation quantitatively.*

**Response:** My apologies for not being clear.  $\text{NO}_3^-$  maintains a constant fraction in the total concentration of negative ion clusters in Beijing (Figure S13a). It has been shown that the total negative ion clusters vary inversely with CS. As a result, the variation of  $\text{NO}_3^-$  is also inversely related to CS in Beijing. However, we have removed this sentence in the revised manuscript as its relationship to our main topic is weak.

(10) Line 257: *typo, should be n+*

**Response:** Corrected.

(11) Line 319: *I would replace ‘distinguished’ by ‘misidentified’.*

**Response:** Thanks for the suggestion, the manuscript is modified as below,

[Line 337-339] “As few neutral sulfur-containing organics were observed, it is unlikely that the identified CHON-HSO<sub>4</sub><sup>-</sup> is a cluster of sulfur-containing organics and NO<sub>3</sub><sup>-</sup>, but rather a cluster of nitrogen-containing organics and HSO<sub>4</sub><sup>-</sup>.”

## References

- Arnold, F. and Viggiano, A. A.: Combined mass spectrometric composition measurements of positive and negative ions in the lower ionosphere—I. Positive ions, *Planetary and Space Science*, 30, 1295-1305, [https://doi.org/10.1016/0032-0633\(82\)90103-9](https://doi.org/10.1016/0032-0633(82)90103-9), 1982.
- Arnold, F., Böhringer, H., and Henschen, G.: Composition measurements of stratospheric positive ions, *Geophys. Res. Lett.*, 5, 653-656, <https://doi.org/10.1029/GL005i008p00653>, 1978.
- Bianchi, F., Garmash, O., He, X., Yan, C., Iyer, S., Rosendahl, I., Xu, Z., Rissanen, M. P., Riva, M., Taipale, R., Sarnela, N., Petäjä, T., Worsnop, D. R., Kulmala, M., Ehn, M., and Junninen, H.: The role of highly oxygenated molecules (HOMs) in determining the composition of ambient ions in the boreal forest, *Atmos. Chem. Phys.*, 17, 13819-13831, 10.5194/acp-17-13819-2017, 2017.
- Eisele, F. L.: Natural and Anthropogenic Negative-Ions in the Troposphere, *J. Geophys. Res.: Atmos.*, 94, 2183-2196, DOI 10.1029/JD094iD02p02183, 1989.
- Eisele, F. L. and Tanner, D. J.: Identification of Ions in Continental Air, *J. Geophys. Res.: Atmos.*, 95, 20539-20550, DOI 10.1029/JD095iD12p20539, 1990.
- Eisele, F. L. and Tanner, D. J.: Measurement of the gas phase concentration of H<sub>2</sub>SO<sub>4</sub> and methane sulfonic acid and estimates of H<sub>2</sub>SO<sub>4</sub> production and loss in the atmosphere, *J. Geophys. Res.: Atmos.*, 98, 9001-9010, <https://doi.org/10.1029/93JD00031>, 1993.
- Eisele, F. L., Lovejoy, E. R., Kosciuch, E., Moore, K. F., Mauldin III, R. L., Smith, J. N., McMurry, P. H., and Iida, K.: Negative atmospheric ions and their potential role in ion-induced nucleation, 111, <https://doi.org/10.1029/2005JD006568>, 2006.
- Heinritzi, M., Simon, M., Steiner, G., Wagner, A. C., Kürten, A., Hansel, A., and Curtius, J.: Characterization of the mass-dependent transmission efficiency of a CIMS, *Atmos. Meas. Tech.*, 9, 1449-1460, 10.5194/amt-9-1449-2016, 2016.
- Herb, J., Nadykto, A. B., Nazarenko, K. M., Korobov, N. A., and Yu, F.: Clustering of sulfuric acid, bisulfate ion and organonitrate C<sub>10</sub>H<sub>15</sub>O<sub>10</sub>N: Thermodynamics and atmospheric implications, *Computational and Theoretical Chemistry*, 1133, 40-46, 10.1016/j.comptc.2018.04.012, 2018.
- Kontkanen, J., Lehtinen, K. E. J., Nieminen, T., Manninen, H. E., Lehtipalo, K., Kerminen, V. M., and Kulmala, M.: Estimating the contribution of ion-ion recombination to sub-2 nm cluster concentrations from atmospheric measurements, *Atmos. Chem. Phys.*, 13, 11391-11401, 10.5194/acp-13-11391-2013, 2013.
- Krechmer, J. E., Groessl, M., Zhang, X., Junninen, H., Massoli, P., Lambe, A. T., Kimmel, J. R., Cubison, M. J., Graf, S., Lin, Y.-H., Budisulistiorini, S. H., Zhang, H., Surratt, J. D., Knochenmuss, R., Jayne, J. T., Worsnop, D. R., Jimenez, J.-L., and Canagaratna, M. R.: Ion mobility spectrometry-mass spectrometry (IMS-MS) for on- and offline analysis of atmospheric gas and aerosol species, *Atmos. Meas. Tech.*, 9, 3245-3262, 10.5194/amt-9-3245-2016, 2016.
- Kürten, A., Rondo, L., Ehrhart, S., and Curtius, J.: Calibration of a chemical ionization mass spectrometer for the measurement of gaseous sulfuric acid, *J. Phys. Chem. A*, 116, 6375-6386, 10.1021/jp212123n, 2012.
- Laakso, L., Petäjä, T., Lehtinen, K. E. J., Kulmala, M., Paatero, J., Hörrak, U., Tammet, H., and Joutsensaari, J.: Ion production rate in a boreal forest based on ion, particle and radiation measurements, *Atmos. Chem. Phys.*, 4, 1933-1943, 10.5194/acp-4-1933-2004, 2004.
- Li, X., Chee, S., Hao, J., Abbatt, J. P. D., Jiang, J., and Smith, J. N.: Relative humidity effect on the formation of highly oxidized molecules and new particles during monoterpene oxidation, *Atmos. Chem. Phys.*, 19, 1555-1570, 10.5194/acp-19-1555-2019, 2019.
- Mahfouz, N. G. A. and Donahue, N. M.: Technical note: The enhancement limit of coagulation scavenging of small charged particles, *Atmos. Chem. Phys.*, 21, 3827-3832, 10.5194/acp-21-3827-2021, 2021.

Mirme, S. and Mirme, A.: The mathematical principles and design of the NAIS – a spectrometer for the measurement of cluster ion and nanometer aerosol size distributions, *Atmos. Meas. Tech.*, 6, 1061-1071, 10.5194/amt-6-1061-2013, 2013.

Nie, W., Yan, C., Huang, D. D., Wang, Z., Liu, Y., Qiao, X., Guo, Y., Tian, L., Zheng, P., Xu, Z., Li, Y., Xu, Z., Qi, X., Sun, P., Wang, J., Zheng, F., Li, X., Yin, R., Dallenbach, K. R., Bianchi, F., Petäjä, T., Zhang, Y., Wang, M., Schervish, M., Wang, S., Qiao, L., Wang, Q., Zhou, M., Wang, H., Yu, C., Yao, D., Guo, H., Ye, P., Lee, S., Li, Y. J., Liu, Y., Chi, X., Kerminen, V.-M., Ehn, M., Donahue, N. M., Wang, T., Huang, C., Kulmala, M., Worsnop, D., Jiang, J., and Ding, A.: Secondary organic aerosol formed by condensing anthropogenic vapours over China's megacities, *Nature Geoscience*, 15, 255-261, 10.1038/s41561-022-00922-5, 2022.

Passananti, M., Zapadinsky, E., Zanca, T., Kangasluoma, J., Myllys, N., Rissanen, M. P., Kurten, T., Ehn, M., Attoui, M., and Vehkamäki, H.: How well can we predict cluster fragmentation inside a mass spectrometer?, *Chem. Commun.*, 55, 5946-5949, 10.1039/c9cc02896j, 2019.

Qiao, X., Yan, C., Li, X., Guo, Y., Yin, R., Deng, C., Li, C., Nie, W., Wang, M., Cai, R., Huang, D., Wang, Z., Yao, L., Worsnop, D. R., Bianchi, F., Liu, Y., Donahue, N. M., Kulmala, M., and Jiang, J.: Contribution of Atmospheric Oxygenated Organic Compounds to Particle Growth in an Urban Environment, *Environ. Sci. Technol.*, 55, 13646-13656, 10.1021/acs.est.1c02095, 2021.

Tammet, H., Hörrak, U., Laakso, L., and Kulmala, M.: Factors of air ion balance in a coniferous forest according to measurements in Hyytiälä, Finland, *Atmos. Chem. Phys.*, 6, 3377-3390, 10.5194/acp-6-3377-2006, 2006.

Viggiano, A. A.: IN-SITU MASS-SPECTROMETRY AND ION CHEMISTRY IN THE STRATOSPHERE AND TROPOSPHERE, *Mass Spectrometry Reviews*, 12, 115-137, 10.1002/mas.1280120203, 1993.

Wagner, R., Manninen, H. E., Franchin, A., Lehtipalo, K., Mirme, S., Steiner, G., Petäjä, T., and Kulmala, M.: On the accuracy of ion measurements using a Neutral cluster and Air Ion Spectrometer, 2016.

Yan, C., Dada, L., Rose, C., Jokinen, T., Nie, W., Schobesberger, S., Junninen, H., Lehtipalo, K., Sarnela, N., Makkonen, U., Garmash, O., Wang, Y., Zha, Q., Paasonen, P., Bianchi, F., Sipilä, M., Ehn, M., Petäjä, T., Kerminen, V.-M., Worsnop, D. R., and Kulmala, M.: The role of H<sub>2</sub>SO<sub>4</sub>-NH<sub>3</sub> anion clusters in ion-induced aerosol nucleation mechanisms in the boreal forest, *Atmos. Chem. Phys.*, 18, 13231-13243, 10.5194/acp-18-13231-2018, 2018.

Yan, C., Nie, W., Vogel, A. L., Dada, L., Lehtipalo, K., Stolzenburg, D., Wagner, R., Rissanen, M. P., Xiao, M., Ahonen, L., Fischer, L., Rose, C., Bianchi, F., Gordon, H., Simon, M., Heinritzi, M., Garmash, O., Roldin, P., Dias, A., Ye, P., Hofbauer, V., Amorim, A., Bauer, P. S., Bergen, A., Bernhammer, A. K., Breitenlechner, M., Brilke, S., Buchholz, A., Mazon, S. B., Canagaratna, M. R., Chen, X., Ding, A., Dommen, J., Draper, D. C., Duplissy, J., Frege, C., Heyn, C., Guida, R., Hakala, J., Heikkinen, L., Hoyle, C. R., Jokinen, T., Kangasluoma, J., Kirkby, J., Kontkanen, J., Kurten, A., Lawler, M. J., Mai, H., Mathot, S., Mauldin, R. L., 3rd, Molteni, U., Nichman, L., Nieminen, T., Nowak, J., Ojdanic, A., Onnela, A., Pajunoja, A., Petaja, T., Piel, F., Quelever, L. L. J., Sarnela, N., Schallhart, S., Sengupta, K., Sipilä, M., Tome, A., Trostl, J., Vaisanen, O., Wagner, A. C., Ylisirnio, A., Zha, Q., Baltensperger, U., Carslaw, K. S., Curtius, J., Flagan, R. C., Hansel, A., Riipinen, I., Smith, J. N., Virtanen, A., Winkler, P. M., Donahue, N. M., Kerminen, V. M., Kulmala, M., Ehn, M., and Worsnop, D. R.: Size-dependent influence of NO<sub>x</sub> on the growth rates of organic aerosol particles, *Sci. Adv.*, 6, eaay4945, 10.1126/sciadv.aay4945, 2020.

Yao, L., Garmash, O., Bianchi, F., Zheng, J., Yan, C., Kontkanen, J., Junninen, H., Mazon, S. B., Ehn, M., Paasonen, P., Sipilä, M., Wang, M., Wang, X., Xiao, S., Chen, H., Lu, Y., Zhang, B., Wang, D., Fu, Q., Geng, F., Li, L., Wang, H., Qiao, L., Yang, X., Chen, J., Kerminen, V. M., Petaja, T., Worsnop, D. R., Kulmala, M., and Wang, L.: Atmospheric new particle formation from sulfuric acid and amines in a Chinese megacity, *Science*, 361, 278-281, 10.1126/science.aao4839, 2018.