We thank the referees for taking the time to review our work and providing insightful comments which have improved our manuscript. We believe that the paper now contains clearer language and better presentation of our results. The discussion of several key points, including the composition and formation processes of the observed HOMs, the mechanism of RO_2-RO_2 cross reaction suppression, and the implications of our findings relating to new particle formation (NPF), has been expanded and refined. We have also clarified several crucial aspects of the data analysis methodology and supplemented the discussion regarding the clog of the pinhole, which is vital for the validity of our results. The changes to the introduction more clearly present the relevant background information and provide more context placing this work in the literature.

Responses to individual referee comments are below. We have reproduced each comment and provided our response underneath. Manuscript changes are highlighted. Line numbers refer to the original preprint manuscript. Also note that we have updated the name of the technique used for analysis of fitted binPMF peak centers from "scaled Kendrick mass defect (SKMD) analysis" to "generalized Kendrick analysis (GKA)". This brings our nomenclature in line with the terminology used by Alton et al., (2022) (see the preprint discussion for more information regarding the name change: https://egusphere.copernicus.org/preprints/2022/egusphere-2022-1319/). We have not reproduced these changes in this response document, but they can be found in the tracked changes version of the manuscript.

Referee #1

General comments: In this work, the authors present measurements of atmospheric cations and anions using an APi-TOF at the SGP site. They further deploy the binPMF to aid the identification of ions and find distinct chemical characteristics and temporal behaviors. The neutral species in the atmosphere that can be inferred from ion measurements have meaningful implications on the atmospheric new particle formation and growth, although quantitative studies require further measurement using active chemical ionization schemes. One main difficulty in understanding ion behaviors is that the abundance of ions is a result of both the concentration of respective neutral species and the charging potential (i.e., proton affinity, molecular polarity, etc.). The authors are fully aware of this complexity and the interpretation in this study is careful and reasonable, which I do appreciate. In general, I think this paper has certainly new insights into the understanding of atmospheric ions at this site and presents an excellent example of what we can learn from ion measurements. Therefore, I recommend the acceptance of this manuscript for publication in ACP, after a few minor concerns are addressed.

Our Response: We thank the referee for their thoughtful consideration of our manuscript.

Comment 1.1: Line 21-22. HOMs are spelled as "highly oxidized molecules", while in Line 44, it is spelled as "highly oxygenated molecules". I suggest following the definition by Bianchi et al., i.e., "highly oxygenated organic molecules".

Our Response: We have fixed this wording.

Manuscript changes:

Lines 21-22: Negative ions consist of strong acids including sulfuric and nitric acid, organosulfates, and clusters of NO₃⁻ with highlighted highly oxygenated organic molecules (HOMs) derived from monoterpene (MT) and sesquiterpene (SQT) oxidation.

Line 44: Highly oxygenated organic molecules (HOMs) derived from monoterpenes (MTs) have frequently been observed clustered with ~~sulfate~~ HSO_4^- or ~~nitrate~~ NO_3^- ~~anions~~

Comment 1.2: Line 104-105. The authors mentioned that the pinhole of APi-TOF was clogged partway through the campaign. I wonder whether there is any influence by the clog, for example on the total ion counts? Please add a sentence about this.

Our Response: A different referee also had a question about the pinhole clog (comment 3.3). For clarity we address these comments together at the end of the response document.

Comment 1.3: Line 190. For NPF identification, the cut-off size of SMPS is important. The authors mentioned in Line 214 that the low abundance of higher-order sulfuric acid clusters is consistent with the lack of nanoparticles. According to my experience, the sulfuric acid trimer to dimer ratio is always very low (a few %) even in amine-rich environments, so the ratio of 2% here probably can't be simply taken as indicative of negligible NPF. Could it be possible that SMPS is not able to detect particles down to a few nanometers?

Our Response: We agree that the relationship between sulfuric acid clusters and NPF is more complicated than originally described. Originally line 214 was describing the ratio of the timer to the dimer as 2% in the sulfuric acid dimer binPMF factor. Since we do not believe this factor is related to NPF, we have removed the reference to new particle formation in this location. We have added details to the manuscript (changes described below) about the instrumentation.

In response to other referee comments (see comment 2.4), we have added further discussion of NPF elsewhere in the manuscript. A complete description of particle observations during HI-SCALE is outside the scope of this work, but we have added references to direct readers to the papers focused on this subject.

Manuscript changes:

Lines 190-192: Aerosol size distributions and select trace gases were monitored using a scanning mobility particle sizer (SMPS, cutoff mobility diameter of 14 nm) and quadrupole proton transfer reaction mass spectrometer (PTRMS) respectively as part of the HI-SCALE campaign (Liu and Shilling, 2016a, b). PTRMS measurements have been previously described in Liu et al., 2021. A variety of other instruments were deployed to measure trace gases, aerosols, clouds, and meteorological conditions during HISCALE. Specific results from these instruments were not used in this work and can be found elsewhere (Fast et al., 2019).

Comment 1.4: Line 237. The chemical species with m/z located at 288 could also be C5H10N2O8, a widely-observed peak in isoprene-rich environments. The double-bond-equivalent of C10H10O6, as suggested by the authors, seems too high in my opinion. Please double-check the formula assignment on this nominal mass.

Our Response: We agree that $C_5H_{10}N_2O_8$ is a probable formula assignment and have changed the manuscript to reflect this. We attribute several observed species to oxidation of isoprene (lines 244-245, 324-326, and 330-334), so this formula is consistent with the chemistry we hypothesize to occur at the site and/or during transport to the site. However, the difference between $(C_5H_{10}N_2O_8)NO_3^-$ at *m/z* 288.032 and $(C_{10}H_{10}O_6)NO_3^-$ at *m/z* 288.036 is less than 15 ppm, and therefore neither can be definitively ruled out. These formulas would have different isotopic patterns, but the intensity of the peak at *m/z* 288 is insufficient for isotopic patterns to be distinguishable against the noise. $C_{10}H_{10}O_6$ may be chorismic acid, an important branching point in plant metabolic synthesis (Tzin and Galili, 2010). Discussion of both formulas has been added to the manuscript.

Manuscript changes:

Lines 236-245: The low *m/z* ~~nitrates~~NO_3^- factor is mostly composed of peaks between *m/z* 100 and 300 with major ions attributed to clusters of NO_3^- with non-nitrate organic compounds (e.g. $(C_3H_4O_4)NO_3^-$~~, at *m/z* 166 and~~ $(C_5H_6O_4)NO_3^-$ at *m/z* 192)~~, and $(C_{10}H_{10}O_6)NO_3^-) (m/z 166, and 192, and 288)~~ and clusters of NO_3^- with inorganic acids (e.g. $(H_2CO_3)NO_3^-$ at *m/z* 124 and $(HNO_3)NO_3^-$ at *m/z* 125). Also present are clusters containing two nitrogen atoms which are likely clusters of NO_3^- with small ~~organic nitrates~~ONs (e.g. $(C_5H_7NO_7)NO_3^-$ and $(C_5H_9NO_7)NO_3^-$ at *m/z* 255 and 257). Both $C_5H_7NO_7$, and $C_5H_9NO_7$ have been identified as ~~organic nitrate~~ON products of isoprene oxidation by hydroxyl radicals in the presence of NO_x (Ng et al., 2008; Lee et al., 2016a). The peak at *m/z* 288 is likely $(C_5H_{10}N_2O_8)NO_3^-$, which can also be produced by hydroxyl radical oxidation of isoprene in the presence of NO_x (Lee et al., 2014; Xu et al., 2020). $C_5H_9NO_7$ and $C_5H_{10}N_2O_8$ are also produced by NO_3 radical-initiated oxidation of isoprene (Ng et al., 2008). It should be noted that $(C_{10}H_{10}O_6)NO_3^-$ is also a possible formula for the ion at *m/z* 288. While we consider this formula to be less likely because of the high number of double bond equivalents, $C_{10}H_{10}O_6$ would correspond to chorismic acid, a central branching point in plant cell metabolism (Tzin and Galili, 2010), and cannot be definitively ruled out. While we cannot distinguish between clusters of ~~organonitrates~~ON with ~~nitrate~~ NO_3^- ($ON·NO_3^-$) and clusters of organic compounds with nitric acid and ~~nitrate~~ NO_3^- ($R·HNO_3·NO_3^-$), we suggest that clusters of ~~organonitrates~~ON with ~~nitrate~~ NO_3^- are more likely for ~~these~~ formulas with multiple nitrogen atoms both because we do not observe each of the clusters that would correspond to the organic compound clustered with ~~nitrate~~ NO_3^- ($R NO_3^-$) and because the ~~organonitrate~~ON species have been previously identified in the atmosphere. ~~Both C5H7NO7 and C5H9NO7 have~~

~~been identified as organic nitrate products of isoprene oxidation by hydroxyl radicals in the presence of NOₓ (Ng et al., 2008; Lee et al., 2016; Chen et al., 2020).¶¶~~

Comment 1.5: Line 292-293. "The increased intensity at odd m/z suggests that neutral organonitrate species clusters with NO3- are more abundant than clusters of HOMs with NO3-". This statement isn't right. By definition, organonitrates (with enough oxygen atoms) are a subset of HOMs. Maybe rephrase it as "… than clusters of non-nitrate HOMs with NO3-."

Our Response: We agree and have clarified the wording.

Manuscript changes:

Line 292-293: The increased intensity at odd m/z suggests that neutral ~~organonitrate~~ON HOM species clustered with NO_3^- are more abundant than clusters of non-nitrate HOMs with NO_3^-.

Comment 1.6: Line 295-300. I buy that the nighttime NO3+SQT reaction could be strong, but what about the daytime. SQT reacts with O3 fairly effectively, and if the subsequent RO2 reacts with NO, C15 ONs will also be formed. So, I am a bit surprised that no C15 ONs observed during the day. One possibility could be that C15-ONs do not bind with HSO4- as efficiently as it does with NO3-; in this regard, are there any SQT-originated ONs appear in the daytime high-mass factor in the positive ion mode? Another possibility is that the O3 concentration at SGP site is quite low during the day. It would be very helpful if the concentrations of NO, O3, and NO2 are provided. Anyway, please consider rephrasing this part.

Our Response: After revisiting our analysis to respond to this point, we have decided to restructure parts of the manuscript to give a more complete description of the organonitrate (ON) and non-nitrate HOMs we observed. We have moved the discussion of HOMs to a separate section (Sect. 3.2 HOMs) and supplemented the discussion of the HOMs observed in the high *m/z* NO_3^- factor (previously in in Sect. 3.1) with analysis of the HOMs present in the low *m/z* NO_3^- factor. Due to the number of changes required to create a new section, presenting each individual change would be unwieldy and we instead reproduce the new section below. A complete list of changes can be found in the tracked changes version of the manuscript. Changes made in response to several other comments are found in this new section, and we have indicated this in our responses to these comments.

We do not observe any daytime signals which we attribute to either ON or non-nitrate C15 HOMs. SQT mixing ratios are typically lower during the day than at night both because, as the referee notes, reactions with ozone lead to a short atmospheric lifetime and because of increased boundary layer height. Further, nighttime NO_3 radical chemistry results in much higher ON yields than daytime chemistry. The lack of ON SQT oxidation products in the daytime spectra is therefore not surprising, and we have added more information regarding this point to the manuscript.

We observe non-nitrate C10 HOMs clustered with NO_3^- during the daytime in the low *m/z* NO_3^- factor. Unlike the high *m/z* NO_3^- factor, which is dominated by ON HOMs, the C10 HOMs in

this factor are mostly non-nitrate HOMs. We do not observe any clusters of C10 HOMs with HSO_4^- in any factor. This is difficult to explain because the daytime ambient anion measurements by Bianchi et al. (2017) demonstrate that MT derived ON HOMs and non-nitrate HOMs both cluster efficiently with HSO_4^- and with NO_3^-, so it is unclear why the C10 non-nitrate HOMs that we detect as clusters with NO_3^- in the low m/z NO_3^- factor do not also cluster with HSO_4^-. It is not possible for us to definitively explain the absence of these clusters, but possible explanations have been added to the manuscript.

We do not observe any SQT ONs in the positive ion data. These species generally require high levels of oxygenation to cluster effectively with ambient HSO_4^- and NO_3^-, so the neutral species we observe clustered with NO_3^- in the negative ion data would not have sufficiently high gas phase proton affinities to be present as ambient cations. Unfortunately, there are no measurements of ozone or NO_x at the SGP site during the HISCALE campaign. Ozone measurements from nearby EPA monitoring stations are included below. Monitoring stations located 50-100 km from the SGP site consistently measure ozone at 35-55 ppb during the day and show good agreement.
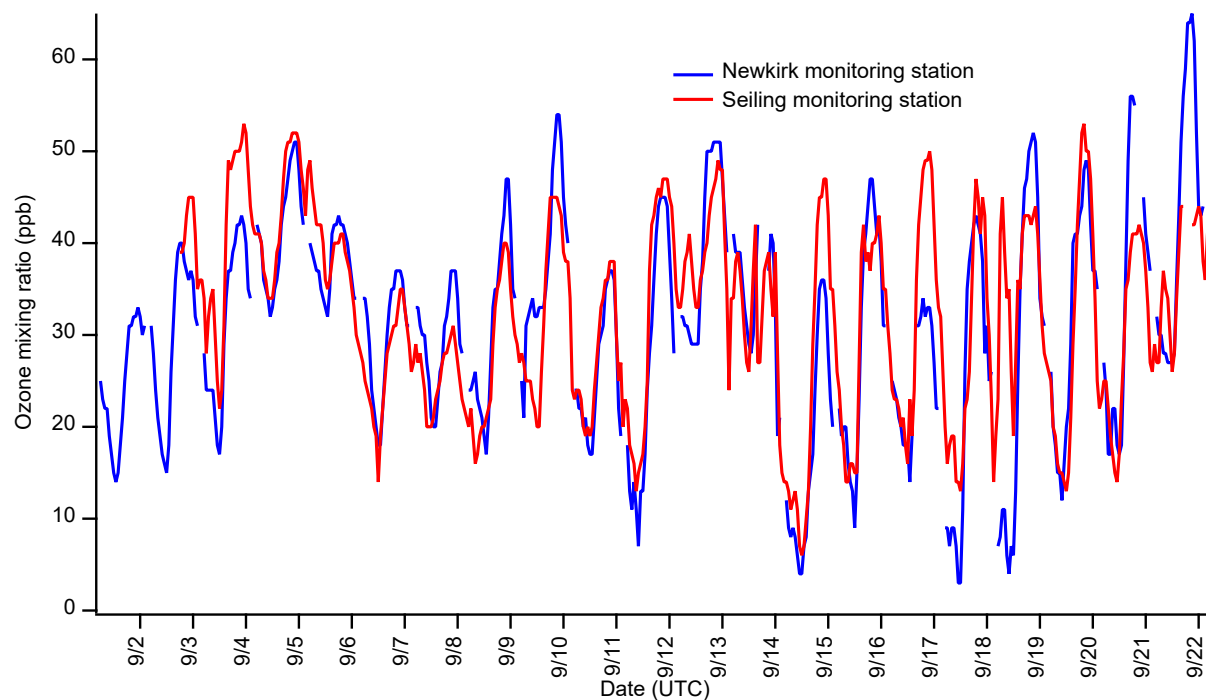
Manuscript changes:

<mark>**3,2 HOMs**</mark>

<mark>The HOMs signals we observe differ from those reported by previous APi-ToF measurements in three ways: i) the intensity of C15 ion clusters is greater than the intensity of C10 ion clusters, ii) the ON HOMs clustered with NO_3^- (odd m/z) peaks are higher in intensity than non-nitrate HOMs clustered with NO_3^- (even m/z), and iii) signals from HOM dimers (e.g., C20 and C30 molecules) are absent from the spectra. In this section we explore potential explanations for these three observations and discuss the implications for particle growth at this site.</mark>

We attribute C10 species to MT oxidation products and C15 species to SQT oxidation products. Clusters of MT non-nitrate HOMs with NO_3^- (Ehn et al., 2012) and MT ON HOMs with NO_3^- (Bianchi et al., 2017) have been observed previously in APi-ToF measurements, but we do not observe the C16-C20 MT dimers that have been previously detected. Similarly, SQT non-nitrate HOMs have been observed as neutral compounds and as ions in the boreal forest (Jokinen et al., 2016). In that study, SQT HOMs contributed only a minor fraction (0.2%) to the total ion signal compared to up to 12% of the total signal observed here. Additionally, C29 and C30 dimers were observed previously, but not in this work. To our knowledge, SQT ON HOMs have not been reported previously in ambient measurements. Although $C_{15}H_{24}O_x$ compounds can be formed from cross reactions of isoprene and MT peroxy radicals (Heinritzi et al., 2020), we would expect the C10 ions to be relatively more intense than the C15 ions if cross-reactions were important. The attribution of the C15 compounds to SQT oxidation products is also consistent with measurements of SQT and MT emissions from agricultural crops. For herbaceous crops such as alfalfa, a species grown in the area (USDA-NASS, 2016), SQT emissions are greater than MT emissions (Ormeño et al., 2010). In general, measurements of SQTs are challenging due to their low concentrations and short lifetimes. Thus, while knowledge of SQT emissions and HOM yield is of most relevance for understanding particle formation and growth, observations of SQT oxidation products are informative. Given the low detection limits of APi-ToF, measurements of SQT oxidation products through ambient anion cluster observations may represent a useful methodology for better understanding the atmospheric fate of SQTs and their ultimate contribution to particle growth.

The high m/z NO_3^- factor accounts for the majority of the HOMs signal. In this factor, both C10 and C15 species ON HOMs (odd masses) are more abundant than non-nitrate HOMs (even masses). Approximately 55% of the signal in the lower m/z series of peaks (C10 compounds) and 60% of the signal in the higher m/z series of peaks (C15 compounds) is found at odd m/z. Based on the assigned formulas for the C15 series, the singly substituted ^{13}C isotopologue ion would account for 25-50% of the signal at the next nominal mass. Therefore, the portion of signal due to ON species is even greater than the percentage of odd m/z signal indicates.

To explain the higher intensity of C10 and C15 ON HOMs compared to non-nitrate HOMs in the high m/z NO_3^- factor, we hypothesize that NO_3 radical chemistry is important for producing the HOMs observed in this factor. The diel profile of the high m/z NO_3^- factor is high at night and decreases to near zero during the day. This profile is broadly consistent with compounds produced via nighttime chemistry, although, as will be discussed below, other explanations are possible for low HOM signals during the day. If ozonolysis were the main HOM production route, we would expect to see higher signals of the non-nitrate HOMs. Production of HOMs (particularly ON HOMs) by NO_3 radical chemistry is also supported by the greater intensity of C10 non-nitrate HOMs than C10 ON HOMs in the low m/z NO_3^- factor. The low m/z NO_3^- factor exhibits increasing intensity in the morning and evening with a dip in the middle of the day. As discussed earlier (Sect. 3.1), this diel profile is suggestive of photochemical production with charge

competition leading to the midday dip. HOMs are observed clustered with NO_3^- in both the high m/z NO_3^- and low m/z NO_3^- factors, and thus the change in the ratio of C10 ON HOMs and C10 non-nitrate HOMs between day and night suggests a change in the ratio of the corresponding neutrals. Since ON yields from NO_3 radical oxidation of MTs and SQTs are larger than ON yields from OH oxidation in the presence of NO_x (Lee et al., 2016b), the changing ratio of ON to non-nitrate HOMs over the course of the day supports our hypothesis that NO_3 radical chemistry is important for HOM formation at night.

The low HOM signal during the day is likely a result of charge competition but may also be due to inefficient clustering of the HOMs with HSO_4^- compared to NO_3^-. Although previous ambient ion measurements have found that both ON and non-nitrate MT oxidation products cluster with NO_3^- and with HSO_4^- (Bianchi et al., 2017), in our work both C10 and C15 species are only observed as clusters with NO_3^-. We are unable to unequivocally explain the lack of HSO_4^- clusters. One possibility is that, as we propose in Sect 3.1, nitric acid is relatively abundant compared to sulfuric acid at the SGP site. The lack of C15 HOMs during the day could potentially be because increased boundary layer height and a short lifetime of SQT HOMs result in SQT oxidation product mixing ratios that are too low to be observed, particularly when coupled with charge competition. While some questions regarding the production pathways and speciation of daytime HOMs remain, the changing ratio of C10 ON HOMs to non-nitrate HOMs between day and night is strong evidence for the importance of NO_3 radical chemistry for nighttime HOM formation. Our observations highlight how combining measurements of ambient ion composition with measurements of neutral HOMs is important for fully understanding the HOMs budget.

The lack of C20 and C30 dimers in the high m/z NO_3^- factor implies that RO_2-RO_2 cross reactions are infrequent at night during the measurement period. Because the observed C15 ONs are likely formed at night when NO is low, the suppression of dimer formation is probably not due to reactions of RO_2 radicals with NO. However, RO_2 radicals terminated by reaction with HO_2 radicals could result in the observed monomers. Measurements of HO_2 radicals were not made during the campaign. Nonetheless, HO_2 radicals are produced at night through oxidation of VOCs by ozone or NO_3 radicals (Stone et al., 2012), and both mechanisms may contribute to nighttime HO_2 radicals present at the SGP site. Although dimers formed via cross-reactions are thought to be important for NPF, monomers can play a role in the growth of new and/or small particles.

A few brief particle growth events were identified during the campaign, but several of these events were detected by aircraft observations and cannot be directly related to APi-ToF observations made at the surface (see Fast et al., 2019 for detailed description of NPF observations). The small number of events and the fact that instrument polarity was switched every 24 hours mean that negative ion data coverage is insufficient during these events to draw conclusions about how the behavior of HOMs contributed to particle growth at SGP during the measurement period. However, we can assess the potential partitioning behavior of the identified HOM species by using the volatility parametrization described by Li et al. (2016), to estimate saturation mass concentrations

Comment 1.7: Line 301-302. Related to my former comment about NO concentration at SGP site. I'd like to see a short discussion on the reason for the suppressed RO2 cross-reactions. If NO3 is present in a considerable amount, NO concentration has to be very low, which shouldn't suppress dimer (C30) formation. Maybe this is due to the RO2+NO3 -> RO + NO2 + O2?

Our Response: We agree that the suppression of RO_2-RO_2 reactions warrants further discussion and have added this to the manuscript. (these changes can be found in the new Sect 3.2, see Comment 1.6). The proposed NO_3 nighttime chemistry does require NO to be low, but there are several possible fates for RO_2 radicals. It is difficult to provide an unequivocal explanation of the lack of dimers without supporting measurements which are not available, but a likely possibility is RO_2 radical termination by reactions with HO_2. SQT oxidation initiated by NO_3 radicals and terminated by HO_2 radicals could produce the observed ON HOMs. Nighttime sources of HO_2 radicals include oxidation of VOCs by ozone and NO_3 radicals (Stone et al., 2012) which are both possible at the SGP site. We do not observe monomers terminated by any pathway during the day, suggesting that SQT mixing ratios, and thus SQT-derived RO_2 radicals, are reduced during the day.

Manuscript changes: See Comment 1.6.

Comment 1.8: I find the discussion on the positive HOM ions a bit unclear. How many HOM-related ions are identified, what are they, and how different are they from the daytime SQT ones and why? I hope to see some discussion on these points.

Our Response: We have made changes to the manuscript to clarify the relationship between daytime cations and HOM-derived anion clusters. We do not refer to the ions identified in the positive ion data as HOMs. Our proposed formulas for high *m/z* positive mode species are not highly oxidized, containing at most five oxygen atoms and O/C ≤ 0.35. We also do not attribute any daytime ions in positive ion or negative ion data to SQTs.

Manuscript changes:

> Lines 469-477: Although the exact composition cannot be determined, the most reasonable formulas for all observed peaks are organic compounds with one nitrogen atom, 13-24 carbon atoms, 2-5 oxygen atoms, and 2-7 double bond equivalents. All

formulas have O/C ≤ 0.35, meaning these compounds are not considered HOMs. The identified carbon numbers are inconsistent with clusters of ammonia with isoprene, ~~monoterpene~~MT, or ~~sesquiterpene~~SQT oxidation products, and therefore we propose that they are organic reduced nitrogen compounds. The range of double bond equivalents is similar to the range of double bond equivalents for the most intense peaks observed by Junninen et al. (2010). However, the species we observe show increased intensity at higher m/z and have more negative Kendrick mass defects, suggesting that they are more highly oxygenated than those observed by Junninen et al. (2010). Although formulas with one nitrogen atom can explain most of the peaks, formulas with three nitrogen atoms fit well for some peaks and may account for some of the observed signal. The proton affinities required for species to be present as ambient cations are much higher than those required to be present as ambient anions, so it is unsurprising that these species do not appear to be chemically related to the highly oxidized isoprene, MT, and SQT oxidation products observed in the negative ion data.

Referee #2

General comments: This study used APi-TOF to measure the ambient ion chemical composition with the newly developed bin-PMF method and scaled Kendrick mass defect. In general, the manuscript is well-written and within the scope of ACP. I would recommend it be published as a measurement report after some minor revisions.

Our Response: We thank the referee for their valuable feedback. We believe that this work should be published as a research article rather than a measurement report. Several aspects of this work constitute substantial progress in the analysis of APi-ToF data and the understanding of the impacts of agricultural processes on atmospheric chemistry. Our binned positive matrix factorization and modified Kendrick analysis approach allows us to perform the most detailed chemical analysis of APi-ToF data presented in the current literature and should be widely applicable to similar ambient ion datasets. The sesquiterpene (SQT) organonitrate oxidation products we report using this method have not been previously identified as ambient ion clusters and provide new insight into the role of SQTs in NPF and growth in agricultural regions. Considering the dearth of measurements in agricultural regions and that SQTs are emitted by a wide variety of herbaceous crops, this observation in particular may have far-reaching implications. The detection of organosulfates, similarly sheds new light on sulfur chemistry. The bases we detect as cations and the constraints placed on positive mode high *m/z* species are both significant, especially because ambient cation chemistry as a whole remains poorly understood. As this study presents a powerful new data analysis technique and addresses key gaps in the current knowledge regarding agricultural reactive nitrogen chemistry and in the precursors for new particle formation, we consider this work to be substantial enough to warrant publication as a research article.

Comment 2.1: In the introduction section, the authors focused too much on the background of atmospheric ion chemistry. Some discussions related to the gaseous vapors from agricultural regions in previous literature are needed. The authors should clearly state the remaining questions related to that field. I noticed some of such discussions are in the results sections but they should also be summarized in the introduction section.

Our Response: We thank the referee for this comment and agree that in addition to focusing on ion chemistry we should elaborate particularly on the chemistry of agricultural regions. We elect to keep the background on ion chemistry since it is a more specialized area that not all readers may be familiar with, and the knowledge is essential for correctly interpreting the results. We have added discussion of agricultural emissions to the introduction.

Manuscript changes:

> Lines 66-68: While croplands and rangelands account for ~41% of global land area (Ellis et al., 2020), the atmospheric chemistry of trace gases and aerosols remains relatively understudied for these land use categories. In general, agricultural emissions and their impacts on aerosols, air quality, and the nitrogen cycle are insufficiently understood. Agricultural activities and processes are known to emit reduced nitrogen, sulfur, and carbon species that are thought to play a role in NPF; however, large uncertainties remain in the emissions inventories and chemical fates of these compounds (Aneja et al., 2009). Agricultural regions are a promising location to investigate the potential importance of atmospheric bases to NPF because reduced nitrogen compounds used in fertilizers represent the largest source of anthropogenic nitrogen (Fowler et al., 2013), and some organic reduced nitrogen compounds, particularly amines, have been identified in regions of the atmosphere impacted by agriculture (Ge et al., 2011). Although several bases have been hypothesized to contribute to NPF (Glasoe et al., 2015; Jen et al., 2016; Olenius et al., 2017; Myllys et al., 2019; Cai et al., 2022), many of these bases have yet to be measured in the ambient atmosphere. Emissions of certain VOCs, such as methanol and acetone, have been well-studied in agricultural regions (Loubet et al., 2022). However, it is the VOCs that are more reactive, albeit typically less abundant, and their associated oxidation products that will be most important for aerosol budgets and which remain poorly understood. Measurements that constrain reduced nitrogen and reactive carbon species are therefore required for a more complete understanding of NPF, aerosol growth, and overall organic aerosol mass in agricultural regions.

Comment 2.2: It is interesting to see that HSO4- signal is much lower than (H2SO4)HSO4- signal at the measurement site, which is quite different from the existing atmospheric ion studies (e.g., Ehn et al., 2010, Bianchi et al., 2016, and Frege et al., 2017). The HSO4- and NO3- are typically the predominant ions in the negative ion spectra determined from APi-TOF observation in the aforementioned studies because of their relatively abundant parent neutral species (HNO3 and H2SO4 in the day). Thus, a detailed explanation/discussion may be needed here, especially since the authors mention that fairly abundant HNO3 concentrations are expected (line 233) based on the PMF results.

Our Response: Each APi-ToF dataset presented in the literature was collected by an instrument with unique tuning. The distinct tuning of each instrument will impact both the *m/z* transmission function and the extent of declustering which occurs within the APi-ToF. Without calibration to account for these factors, the data collected by different instruments cannot be directly compared. It is not always clear if data presented in the literature have been corrected for

transmission. We did not apply a transmission correction to our data, and we have added emphasis on this point in the manuscript.

Because of the transmission and clustering effects described above, the ratio of ions in APi-ToF spectra does not necessarily reflect the ratio of the same ions in the ambient atmosphere. Our instrument was tuned to more efficiently transmit higher *m/z* species, and thus the ratio of the intensities of the sulfuric acid dimer anion cluster to the bisulfate anion would be increased in our spectra relative to the ambient air. Thus, the higher dimer signal is at least partly due to transmission effects and may have little atmospheric significance. We have added to the manuscript to better describe these effects.

We also note that the visualization of the PMF factors may influence the apparent ratio of the dimer and monomer. The mass spectrum recorded at any time point contains variable contributions from each factor but does not exactly match any one factor. Both the sulfuric acid dimer factor and the sulfur species factor contain some signal from the monomer and the dimer, so the intensity of each factor must be considered when evaluating the ratio of these species. The sulfuric acid dimer factor has a much higher ratio of the dimer to the monomer than the average daytime mass spectrum, which also contains significant contribution to the monomer signal from the sulfur species factor.

Manuscript changes:

> Lines 105-108: Mass spectra were collected over a range of *m/z* 10 – 1700 at a rate of 0.1 Hz. The APi-ToF was operated in "high mass" mode, which enhances transmission of ions at higher (> 200) *m/z*. It was switched between positive and negative polarity approximately every 24 hours. Mass resolving power was approximately 7100 for positive ~~mode~~ ion and 6500 for negative ~~mode~~ ion data. We note that direct comparisons of measurements by APi-ToF instruments are difficult because the tuning of each instrument will result in unique *m/z* transmission functions and differing degrees of cluster fragmentation. A transmission correction was not applied to the data presented in this work.

Comment 2.3: The authors observed evident levels of C15 compounds (CHOs and CHONs) and attribute a substantial fraction of them to sesquiterpene-related HOM in the "high m/z nitrate factor". While a substantial level of sesquiterpene can be emitted from the herbaceous crops around the measurement site, direct observational evidence (e.g., sesquiterpene measurements) may be needed to support such a conclusion.

Our Response: We agree with the referee that direct observational evidence would add certainty to our hypothesis, but no such observations of SQTs are available for this campaign. We attribute these C15 species to SQTs both because SQTs are known to be emitted by the crops found near the SGP site and because species with carbon numbers of 15, which are rare in the atmosphere, have been shown to be produced by SQT oxidation in laboratory experiments (e.g., Richters et al., 2016). While there are other sources which could result in atmospheric C15 compounds (such as a reaction of a MT-derived RO2 with an isoprene-derived RO2), we explored this

possibility in the manuscript (lines 282-284) and determined it to be unlikely. In the absence of other reasonable explanations for our observations, we attribute them to SQTs.

SQTs are typically present at very low mixing ratios due to their high reactivity. Typical SQT concentrations are low enough that direct SQT observations are not always possible, and sometimes only the SQT oxidation products can be detected. We have expanded the discussion in the new Sect 3.2 (see Comment 1.6) to include more context about the difficulty of direct SQT observations and resulting importance of SQT oxidation products.

Manuscript changes: See Comment 1.6

Comment 2.4: Similarly, the authors conclude that more insight into NPF precursors can be provided by applying bin-PMF based on APi-TOF dataset. While this may be true, no NPF event has been observed/reported in this study. More evidence is required to support such a conclusion. Some background information such as pre-existing particles and NOx can also be added in SI.

Our Response: For NPF to occur, atmospheric composition (including trace gases and preexisting particles), atmospheric physical properties, and transport must align to create favorable conditions. Given these complexities, it is worth understanding the processes that are important for NPF even if not all of the atmospheric properties align to result in NPF. It is well known that strong acids, strong bases, and HOMs are important for NPF and subsequent growth, and these are the types of species we detect as ambient ions. Improving our predictive capabilities for NPF requires improving our understanding of the precursors of particle formation, even in the absence of NPF events. We have added more explanation of how our observations relate to our understanding of NPF (see Comment 1.6).

We also note that several NPF events did occur during the campaign (Fast et al., 2019). Several events occurred at altitude and were detected by aircraft observations which cannot be directly related to the surface observations made with our APi-ToF. There is also some evidence of particle growth events at the surface, but because there were so few events and data coverage is only 50% (since the instrument was alternated between positive and negative mode) we do not have sufficient data to make conclusive statements about how the observed species impacted NPF during the campaign. For example, NPF was observed on 9/11 and 9/17 (Fast et al., 2019), but negative ion APi-ToF measurements were not made during these events. We have added information to the manuscript about the NPF and particle growth observed during the HISCALE (see Comment 1.6). Although we are unable to link our observations to specific NPF events, the ON HOMs we observe are consistent with the ELVOCs that represent one of the main aerosol growth pathways at SGP (Hodshire et al. 2016). NO_x was not measured at SGP during the campaign.

Manuscript changes: See Comment 1.6.

Comment 2.5: As the authors suggested, the bin-PMF could be a very useful tool in analyzing APi-TOF data in the future. The authors should explain more clearly how it is conducted with Tofware, which could be quite important information for potential Tofware users. Also, the peak

list of the ions, the corresponding neutral species, their potential sources, and the average mass spectra from different trajectory sectors would also be needed in SI.

Our Response: Further details regarding Tofware methods have been added to the manuscript. We have also added a table to SI with peak assignments for the formulas discussed in the manuscript. We do not have a typical peak list because we didn't do high-resolution peak fitting. Generalized Kendrick analysis (GKA) allows us to assign the formulas of peaks in aggregate based on trends in their composition, usually that they vary by the addition of the chemical base unit. While this is a powerful tool for elucidating the underlying chemistry that gives rise to the overall spectrum, the nature of the GKA formula assignment is fundamentally different from HR peak fitting in that we do not use the exact position of a single peak to identify its formula. We instead use the fact that certain peaks form a line on the GKA plot to constrain the formulas of all aligned peaks. In other words, we first establish that only one formula with a varying base unit will explain all of the peaks in a series, then try to determine the best formula to fit all peaks at the same time. Once we identify the formula that explains one series of peaks we can use other trends, such as lines of peaks parallel to the first series, to infer how peaks are related to each other. This is what makes GKA analysis a powerful and useful tool – the trends in the plot constrain peaks that we would not be able to conclusively identify through HR peak fitting alone.

In our opinion the addition of average mass spectra for the trajectory analysis would not clarify the methodology or add to the scientific findings of the paper. Many mass spectra would be required because, at least for the negative ions, daytime and nighttime spectra are very dissimilar. The information about observed ion composition contained in these spectra would ultimately be similar to the information already found in the plots of contributions of each factor to the signal observed from each trajectory. However, we have added the HYSPLIT trajectory classification for each time point to the public data in the CU Scholar repository so that others may create these figures if of sufficient interest.

Manuscript changes:

> Line 126: Binning was performed in Tofware using the Binned Data Export v3.2.5 workflow contained in the Tofware software package. The workflow follows the description given by Zhang et al., (2019) and helps with exporting binned raw mass spectral data. It allows the user to reduce the sizes of data matrices by specifying the *m/z* range, the region to be binned at each *m/z*, and the bin size. The data can be output as Igor binary waves or text files for further processing using existing PMF tools.

> Line 149: These uncertainties were taken into consideration when evaluating potential formula assignments. The fitted binPMF peak centers and corresponding assigned formulas for all peaks highlighted below can be found in Tables S1 and S2 (Sect. S3).

> Line 520: PMF results, HYSPLIT trajectory classifications for each time point, ~~are~~ and time-series for ions shown in the SI are available at the CU scholar repository: https://scholar.colorado.edu/concern/datasets/g158bj60n.

Comment 2.6: Line 229: What is the reason for the nighttime HSO4- signal?

Our Response: It is typical to observe bisulfate at night (see e.g. Ehn et al., 2010, Fig 1b, Frege et al., 2017, Fig. 1b). Sulfuric acid is lost primarily by physical processes, i.e., condensation onto surfaces. The sulfuric acid mixing ratio decreases during nighttime when it is no longer being produced, but it is not expected to reach zero if the timescale for loss to surfaces is sufficiently long. At the SGP site aerosol surface aera is generally lower than in regions with high pollution and leaf area is substantially reduced compared to forested areas. Both factors contribute to a longer timescale for surface losses.

Comment 2.7: Line 357: What is the diurnal variation of the total ion counts of the observed negative ions?

Our Response: Total daytime negative charges varied by approximately 20% day-to-day, and we have added this information to the manuscript. The plot below shows the diel TIC for negative ions. Markers represent the median, and the region between the 25th and 75th quartiles is shaded.
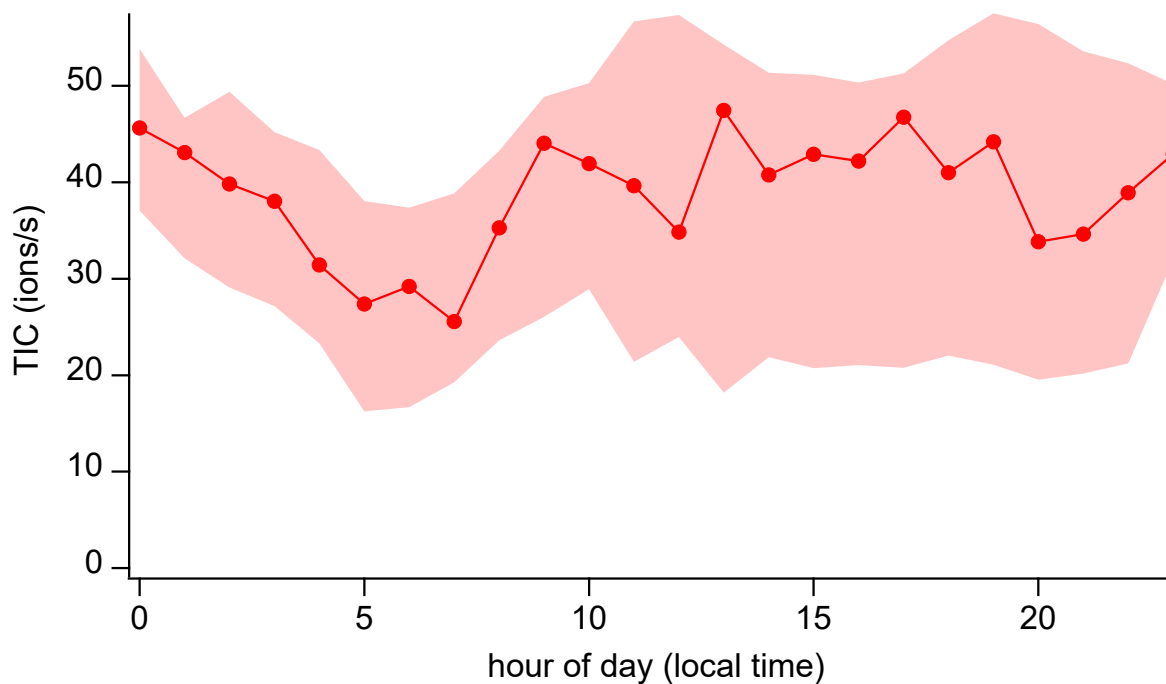
Manuscript changes:

Lines 357: Given that ~~there is an approximately constant number of~~ daytime total negative charges <mark>are approximately constant (~20% daily variation in total negative ions 10:00-14:00 LT)</mark>, we interpret the change in signal partitioning between the low *m/z* ~~nitrate~~NO_3^- and sulfur species factor as reflecting changes in the relative abundance of nitric acid and SO_2/H_2SO_4.

Comment 2.8: Figure 5: The difference between the signal fraction of each m/z is not evidently shown in the figure. A different color code in the log scale is recommended here.

Our Response: The goal of this figure is to demonstrate the overall trend that in positive mode daytime high *m/z* factor most peaks, and all the most intense peaks, appear at even *m/z*. We have added text to the manuscript to clarify this intension. We agree that a different color scale would benefit the figure and have changed it.

Manuscript changes:

> Lines 458-459: A basis of CH_2 and a scaling factor of 35 for the ~~SKMD~~GKA plot of the daytime high *m/z* factor (Fig. 5) were selected such that all species at even nominal masses have negative ~~SKMD~~GKA values (i.e., they appear in the lower half of the plot) and all species at odd nominal masses have positive ~~SKMD~~GKA values (i.e., they appear in the upper half of the plot). A detailed description of how the selection of this scaling factor splits even and odd masses can be found in Alton et al., (2022). The purpose of the GKA plot in Fig. 5 is to illustrate the trend in even and odd masses; a GKA plot which provides insight into the chemical composition of the ions and their relative intensities is included in Sect. S14. Figure 5 ~~The plot~~ demonstrates that the majority of peaks, and all of the highest intensity peaks, are found at even nominal masses.

Previous version of Figure 5:
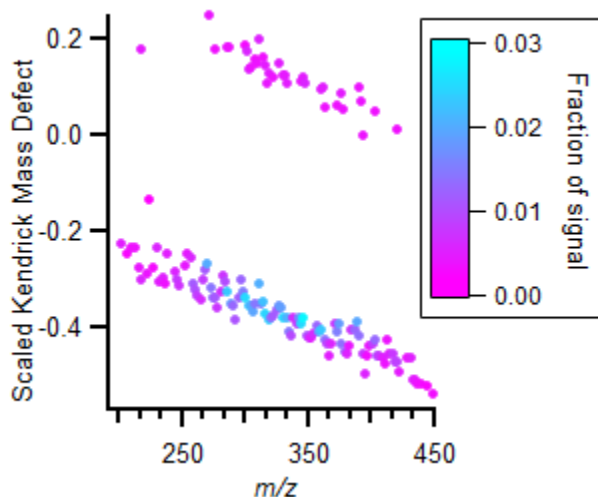
New version of Figure 5:
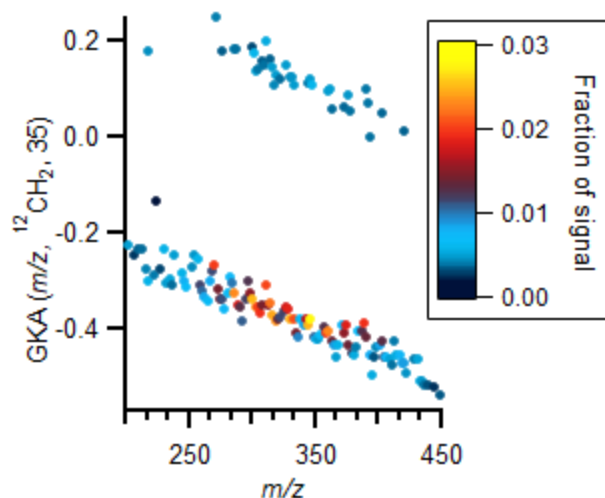
Comment 2.9: Line 482: Why m/z 240 is removed before doing bin-PMF? A further discussion is expected here (Section 3.4) according to the method section (Line 131).

Our Response: The signal at *m/z* 240 was removed prior to binPMF analysis because it is an intense and variable signal, meaning that binPMF solutions identify and resolve this signal as its own factor with minimal contributions from other ions. It is possible that a binPMF solution with a sufficiently high number of factors would account for this by correctly allocating distinct signals into different factors, but this is not always possible in practice due to factor "splitting." As described in Sect. S8 (now Sect. S10), we found that too many factors resulted in binPMF solutions that were not interpretable. Separating the peak at *m/z* 240 into its own factor does not give us any new information because the behavior of the factor almost exactly matches the behavior of *m/z* 240. By removing *m/z* 240 prior to binPMF analysis, a binPMF solution can be found which captures nearly all other signals without the inclusion of specious factors.

To improve the manuscript, we have clarified that on line 131 we are referring to further discussion about *m/z* 240 and not of the PMF solutions. We have rephrased line 482 to clarify that the C13 compound referenced in lines 487 and 510 is the peak at *m/z* 240.

Manuscript changes:

> Lines 129-131: The peak at *m/z* 240, identified as $(C_{13}H_{21}NO_3)H^+$, was also removed because it has a very strong signal that dominates PMF results and obscures the behavior of other species (further discussion of *m/z* 240 in Sect. 3.45).

> Lines 480-482: Despite these limitations, the C18, daytime, and nighttime factors all increase towards the end of the measurement period (see Sect. S911) as does the signal at m/z 240 (which was removed prior to calculating binPMF solutions) identified as a C13 compound: $(C_{13}H_{21}NO_3)H^+$.

Line 511, add after end of paragraph: <mark>In particular, the C13 compound $(C_{13}H_{21}NO_3)H^+$) observed at *m/z* 240 is consistently among the most intense cations, but has highly variable signal intensity that could be indicative of emissions or chemistry yet to be identified.</mark>

Referee #3

General comments: This manuscript presents ambient ion composition measurements from the Southern Great Plains. The analysis does not lead to very far-reaching conclusions, but ambient ion composition is a result of a multitude of factors, and as such analyses tend to be more qualitative than quantitative. That being said, the analytical methods are very appropriate, the results are presented in a clear and logical fashion, and the conclusions are to the point. I enjoyed reading the manuscript and only have a few minor comments for the authors to consider before final publication.

Our Response: We thank the referee for taking the time to review our work and providing discerning feedback.

Comment 3.1: Line 32: Does one of the references discuss examples of how ions can "affect neutral gas-phase chemistry through ion-neutral interactions"? It does not sound like a very common reaction mechanism, and therefore it would be interesting to hear more explicitly what kind of reactions are referred to here.

Our Response: Since this mechanism is only of significant importance at higher altitudes, we agree that for a discussion of tropospheric chemistry it should be removed. We have revised this sentence to provide a more accurate description of tropospheric ion chemistry.

Manuscript changes:

> Lines 31-33: Ambient gas-phase ions, both molecular ions and ion-molecule clusters, determine atmospheric electrical properties<mark>, affect neutral gas-phase chemistry through ion-neutral interactions,</mark> and promote new particle formation (NPF) (Hirsikko et al., 2011; Shuman et al., 2015; Kirkby et al., 2016).

Comment 3.2: Line 102: Would be useful to state also the length of the 10mm tube, though I expect it to be very short.

Our Response: We have added this information to the manuscript.

Manuscript changes:

> Lines 101-102: From the 9 SLPM flow, 3 SLPM was subsampled through <mark>an 8 cm stainless steel tube with a 10 mm outer diameter.</mark>

Comment 3.3: Line 105: The clog of the inlet is acknowledged, and the impacts are discussed in different parts of the manuscript. While I don't expect that there will be any impact on any of the

conclusions in this work, it would be useful to add a bit more discussion about the topic. In particular, since on line 131 in the SI it is stated that the primary effect would be lowered signal, I feel that there is a risk that readers might underestimate the potential severity of such a change. For one part, if the SSQ pressure is not controlled to be constant, a change in inlet flow would change the pressure in this (and subsequent) chambers, potentially causing large changes in mass-dependent transmission and declustering strength. The authors should state whether this pressure was controlled or not. Even in the case of an unchanged pressure, the dynamics of the expansion from the pinhole will change, and potentially again affecting the same properties (in addition to the absolute signal strength, which the authors already mention).

Our Response: A different referee also had a question about the pinhole clog (comment 1.2). For clarity we address these comments together at the end of the response document.

Comment 3.4: Lines 122-125: While I am quite familiar with these subjects, I still have a hard time understanding the message of either of these two sentences, in particular the second one. Please try to reformulate. Is "stable isotopes" the correct term here? Why exactly is redundant information minimized?

Our Response: The redundant information we refer to are the signals produced by isotopologues of the same ion (e.g., $H^{32}SO_4^-$ and $H^{34}SO_4^-$). These signals are redundant because each isotopic composition will vary identically in time (with the exception of the noise component to the signal). This is not a problem with high-resolution peak fitting because the less abundant isotopologues are typically removed prior to PMF. The less abundant isotopologues are not removed by binPMF because the input data does not contain a priori information on chemical compositions. This is problematic because different isotopic combinations provide no additional insight when interpreting binPMF factors and add noise that may be interpreted as signal, leading to degradation of the quality of the PMF results. Issues relating to the inclusion of different isotopic compositions are minor in this work as compared to analysis of chemical ionization data because our dataset has a sufficiently low signal-to-noise for the monoisotopic molecular ions that even the most abundant isotopic peaks usually are not detected. This is not always the case, notably for the $H_2^{34}SO_4$ isotopes of sulfuric acid clusters which are detected in the negative ion data during the day.

Manuscript changes:

> Lines 122-125: ~~binPMF is especially useful for low signal-to-noise datasets because the intensity of the stable isotopes is sufficiently low that redundant information (i.e., an ion and its ^{13}C isotope) is minimized in the PMF input. This also has the added benefit of simplifying the process of chemical formula assignment because the convolution of a peak with signal from isotopes of lower m/z species usually has a minor effect on the peak for a given species.~~ A potential drawback of binPMF is that signals from different isotopic compositions of the same ion (e.g., the $^{13}C_1C_2H_4O_4$ isotope of $C_3H_4O_4$) are not removed prior to analysis. Removal of such signals is common practice when performing PMF analysis on high-resolution datasets. These signals do not provide additional insight because in theory each isotopologue should vary identically in time, but in practice there will be slight differences due to random noise. Thus, these signals add no additional

Comment 3.5: Line 136 onward: Since the authors clearly know the peak shape and resolution functions from Tofware, it is not clear to me why these are not used, instead of the method outlined in this paragraph. I expect the results would be nearly identical, but I feel it would be good state the reason for this approach.

Our Response: The low signal-to-noise of the dataset makes determining the peak shape function difficult. Given the low signal, determining peak shape with Tofware requires extensive time averaging which may lead to artificial peak broadening. A similar argument applies for peak widths. We chose to use a simpler method to avoid introducing a possible bias and because we found that the results were very similar. Additionally, due to the low frequency of isobaric ions, we were not concerned about peak area allocation. Both peak shapes (Fig S2) and peak widths (lines 146-148) were compared against results from Tofware functions, and no major discrepancies were identified. Our simulations conclude that the error in peak position introduced by fitting Gaussian peak shapes was negligible compared to error introduced by uncertainty in the mass calibration (lines 145-146), so use of the Tofware peak shape would not have meaningfully improved the uncertainty of the method. We note that in the case of significant peak asymmetry or if peak area allocation of isobaric ions is warranted then it would likely be preferable to use peak widths and shapes determined by Tofware (or similar analysis programs). We have expanded our discussion of peak widths in response to Comment 3.6, see the response below.

Manuscript changes:

Lines 137: To identify exact masses in the binPMF factors, we fit a Gaussian function in *m/z* space to the bins at each nominal mass with signal of sufficient intensity. The width of the Gaussian was not constrained. We selected a Gaussian function rather than the peak shape determined using Tofware to avoid the potential for bias associated with the required long averaging times required to achieve a well-defined shape in Tofware.

Comment 3.6: Lines 149-150: This is stated as a general truth here, but there is no a priori reason why this should always be the case. If this sentence was a conclusion based on the authors own data, it should be said more clearly. I also think there is a word missing in the sentence.

Our Response: We agree that PMF will not always separate isobaric ions into separate factors. While several isobaric ions were resolved in our binPMF solutions, this did not play a major role in our analysis. In addition, the fact that only one peak was fit per mass has little significance. If two peaks were resolved at the same nominal mass in a given binPMF factor we would have been able to fit and interpret both. Further, the previous sentence did not clearly explain the

implication of peak widths for formula assignments. We have reworked several sentences to clarify these points.

Manuscript changes:

> Lines 146-150: Our goal in peak fitting was only to determine which compounds were present, not attribute signal to each specific ion. Thus, we were concerned with identification of the peak centers rather than precise quantitation of peak areas. However, fitting a Gaussian to a peak consisting of insufficiently resolved isobaric ions may cause the fitted peak center to be shifted. Such peaks would be identifiable because they would be wider than expected. Peak width as a function of *m/z* was evaluated by comparing the fitted widths of the binPMF peaks to the peak width calculated within Tofware, and the full widths at half maximum were found to agree to within 20%. The agreement of peak widths therefore confirms that the peaks in the binPMF spectra mostly contain signal from one ion. This is expected because isobaric ions occur at much lower frequency in APi spectra than CIMS spectra. We note that the use of Tofware peak shapes and peak widths would be preferable for datasets in which peaks are asymmetrical, interference of isobaric ions is significant, and/or when peak area allocation is desired. ~~Only the positions of peaks were used to find possible formulas, so errors in peak width do not directly affect the formula assignments. binPMF solutions effectively separate peaks at the same nominal mass into separate factors and only peak was fit at each nominal mass.~~

Comment 3.7: Section 3: Concerning the naming of factors, I believe the "nitrates" factors are named based on them being clusters with NO3- (?), but "nitrates" is also used in relation to organic nitrates. I suggest to go through the manuscript to make sure that every usage of "nitrate" is unambiguous concerning which type of nitrate compound is meant. I also suggest to avoid using terms of the type "negative/positive binPMF factors". Since the "P" already stands for positive, there is the risk for confusion. I suggest to always include the word "ion" or "mode" after positive/negative. This includes the SI, where e.g. "positive binPMF" is used several times.

Our Response: We thank the referee for this suggestion at improving clarity. We agree and have edited the manuscript to remove ambiguity by using "NO_3^-" to refer to nitrate anions, "NO_3 radical" to refer to nitrate radicals, and "organonitrate (ON)" to refer to organic nitrate compounds. We have also changed the names of the "nitrate" factors to "NO_3^-" factors to reflect that they consist mainly of clusters with NO_3^- as opposed to organonitrates. Due to the number of changes, we do not reproduce them here.

Comment 3.8: Line 257: "Formulas are presented as clusters with the nitrate anion". Do you mean that you did not remove the (potential) NO3- from the given formulas?

Our Response: An incorrect copy of figure 2 was included in the manuscript. It has been replaced with the correct figure, shown below. What we mean by "formulas are presented as clusters with the nitrate anion" is that the formula assignment in the figure has been written to show the proposed constituents of the cluster, one neutral species and one nitrate anion, rather than the sum formula (e.g. $C_wH_xN_yO_z \cdot NO_3^-$ rather than $C_wH_xN_{y+1}O_{z+3}^-$).
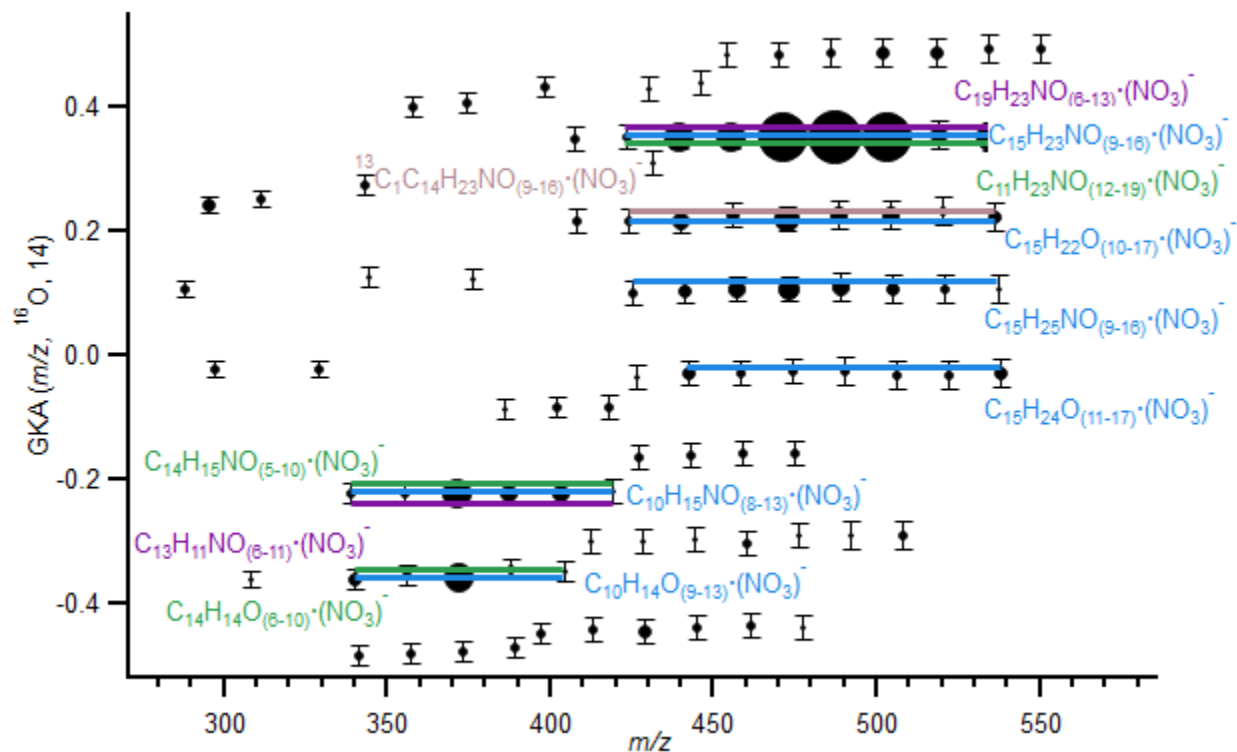
Manuscript changes:
Incorrect Figure 2 (now removed):
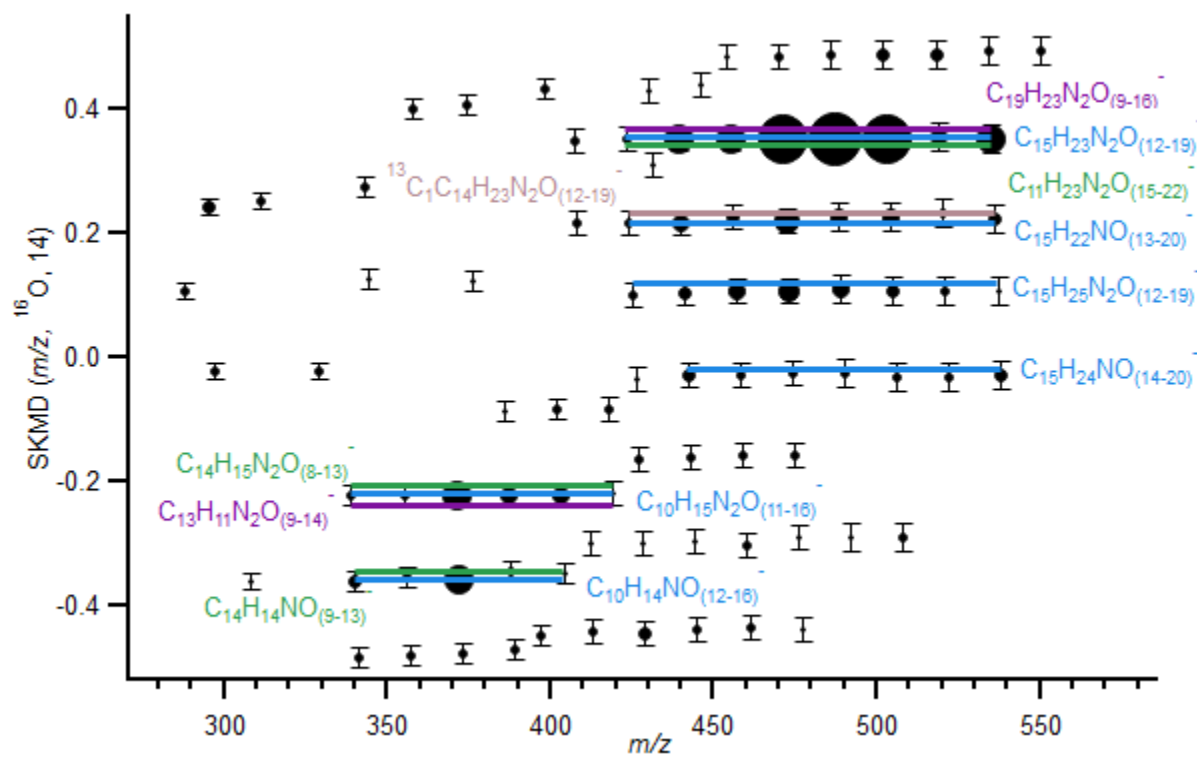
Corrected Figure 2:

Comment 3.9: Lines 292-293: This sentence confuses me. Organic nitrates can also be HOM, so what is actually being compared?

Our Response: We agree with this comment, which is similar is comment 1.5. See the manuscript changes made above.

Comment 3.10: Lines 296-297: This conclusion may be true, but it may also be due to the ON not clustering as efficiently with bisulfate, or that bisulfate just prefers to cluster with other species.

Our Response: This is similar to Comment 1.6, see the above discussion and associated manuscript changes.

Comment 3.11: Line 302: The lack of dimers is very intriguing, and I would like to see some speculation on the reasons. To my knowledge only NO has been shown to kill dimer formation, but since the authors suggest NO3 oxidation to be important, the NO should be very low.

Our Response: This comment is similar to comment 1.7 and we have modified the document in response to these comments. Please see our response to comment 1.7 above.

Comment 3.12: Lines 400-402: If pyridine has a lifetime of 40 days, it should be quite well mixed vertically as well, so why would BL dynamics deplete the signal?

Our Response: We agree that a species with an atmospheric lifetime of 40 days would not be depleted by boundary layer dynamics. We do not detect pyridinium in the positive mode spectra and for clarity we have removed the mention of its lifetime. The detected alkylpyridinium species have shorter lifetimes ($\leq$ 10 days). If emissions of these species are local and continuous then they will not be well-mixed. This type of emission seems reasonable given that these species can be emitted from agricultural processes such as pesticide usage, but sources of alkylpyridiniums are not well-known.

Manuscript changes:

> Lines 400-402: Alkylpyridine species have relatively long atmospheric lifetimes against OH oxidation, on the order of ~~40 days for pyridine,~~ ten days for methylpyridine~~,~~ and five days for ethylpyridine (Yeung and Elrod, 2003)and thus the midday depletion in signal is likely the result of boundary layer dynamics.

Comment 3.13: Lines 455-459: I don't understand why this scaling will result in differences between odd and even masses.

Our Response: This has been discussed in detail in Alton et al., 2022 (AMTD), and we have added a reference to direct readers to this information. Briefly, the formula for generalized Kendrick analysis is:

$$\text{GKA}\left(\frac{m}{z}, \text{R}, \text{X}\right) = \frac{m}{z} \times \frac{X}{R} - round\left(\frac{m}{z} \times \frac{X}{R}\right)$$

With R = 14.0157 and X = 35, the ratio of X/R is close to, but slightly less than, 2.5. The formula for GKA essentially reduces to the *m/z* multiplied by 2.5. An even unit mass multiplied by just under 2.5 will result in $\frac{m}{z} \times \frac{X}{R}$ values that are slightly less than integers and odd unit masses will result in values that are slightly less than half-integers (if multiplied by exactly 2.5 they would be exactly integers and half-integers). With $\frac{m}{z} \times \frac{X}{R}$ less than an integer (even *m/z*) the rounded value will be higher and the GKA will be negative. An $\frac{m}{z} \times \frac{X}{R}$ slightly less than a half-integer (odd *m/z*) will be rounded down and the GKA will be positive. The diagonal pattern results from using exact *m/z,* not unit *m/z*, in the calculation.

Manuscript changes:

> Lines 455-459: A basis of CH_2 and a scaling factor of 35 for the ~~SKMD~~GKA plot of the daytime high *m/z* factor (Fig. 5) were selected such that all species at even nominal masses have negative ~~SKMD~~GKA values (i.e., they appear in the lower half of the plot) and all species at odd nominal masses have positive ~~SKMD~~GKA values (i.e., they appear in the upper half of the plot). A detailed description of how the selection of this scaling factor splits even and odd masses can be found in Alton et al., 2022.

Technical corrections:

> "SGP" is used in the abstract before it is defined.

Line 128: The use of "either" seems misplaced?

Our Response: We thank the reviewer for these corrections.

Manuscript changes:

Lines 14-15: …at the United States Department of Energy Atmospheric Radiation Measurement facility in the Southern Great Plains (SGP), an agricultural region.

Lines 127-128: Several ions were removed from the positive mode data before performing PMF ~~either~~ because they provide little chemical insight.

Discussion of the pinhole clog

Comment 1.2: Line 104-105. The authors mentioned that the pinhole of APi-TOF was clogged partway through the campaign. I wonder whether there is any influence by the clog, for example on the total ion counts? Please add a sentence about this.

Comment 3.3: Line 105: The clog of the inlet is acknowledged, and the impacts are discussed in different parts of the manuscript. While I don't expect that there will be any impact on any of the conclusions in this work, it would be useful to add a bit more discussion about the topic. In particular, since on line 131 in the SI it is stated that the primary effect would be lowered signal, I feel that there is a risk that readers might underestimate the potential severity of such a change. For one part, if the SSQ pressure is not controlled to be constant, a change in inlet flow would change the pressure in this (and subsequent) chambers, potentially causing large changes in mass-dependent transmission and declustering strength. The authors should state whether this pressure was controlled or not. Even in the case of an unchanged pressure, the dynamics of the expansion from the pinhole will change, and potentially again affecting the same properties (in addition to the absolute signal strength, which the authors already mention).

Our response: We do not believe the clog influenced our measurements in a way that meaningfully impacts our conclusions. We have added information on changes to the total ion count to the manuscript. However, our analysis and conclusions are grounded in changes in ion composition which would not be impacted by small changes in total ion counts. We have added a new section to the SI, Sect. S1, to address the effects of the clog.

The SSQ pressure was adjusted, and we have added this note below. There are strong signals in the positive mode from protonated water and water clusters (removed prior to binPMF) which can be used to evaluate effects of the clog on both m/z transmission and declustering. The plot below shows the timeseries of the fractional contribution of several water clusters (m/z 19-109, $(H_2O)_nH^+$, n = 1-6) to the total observed water cluster signal. A large change after September 13th in these fractions would indicate changing transmission or declustering resulting from the clog. The consistent fractional contribution of each water cluster before and after the clog suggests that these effects were minimal.
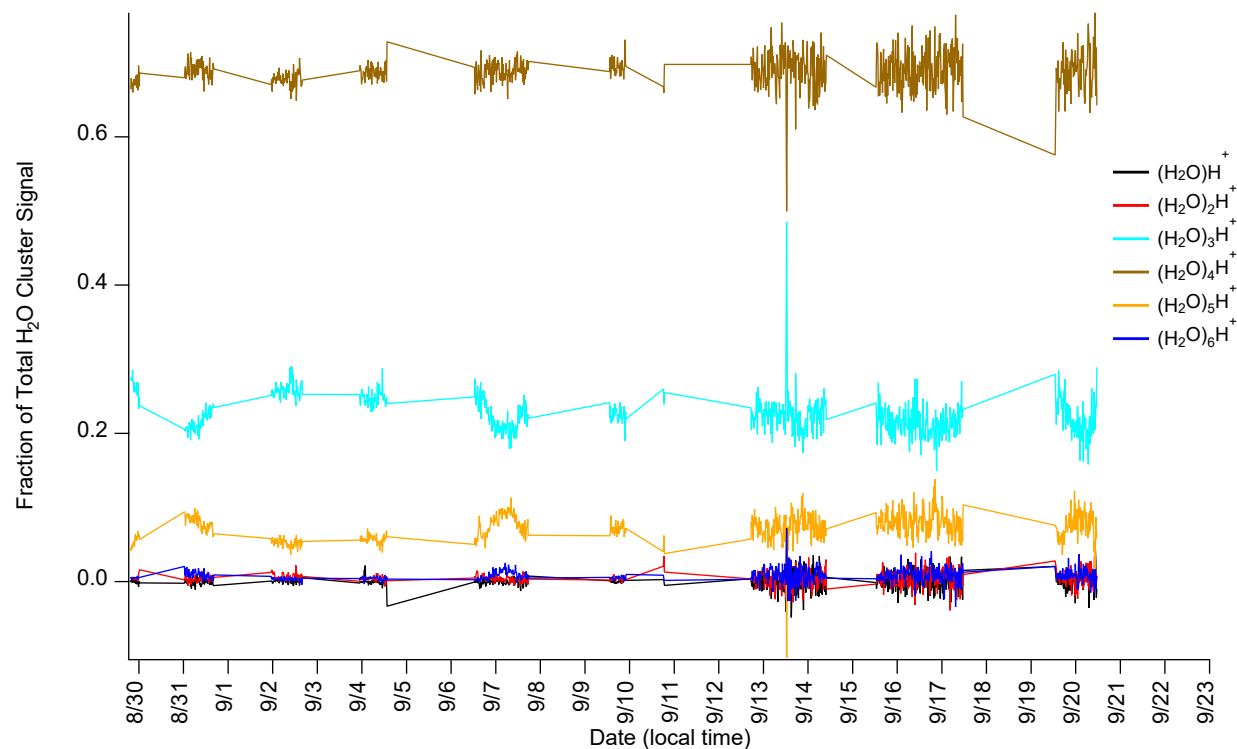
Manuscript changes:

Lines 104-105: Partway through the campaign the inlet became clogged. The clog could not be completely resolved, and the sample flow was reduced to 0.5 SLPM during the second half of the field campaign (13 September 2016 – 23 September 2016). The pressure in the small segmented quadrupole (SSQ), the first chamber of the APi-ToF, was adjusted to be approximately constant before and after the clog. The potential effects of the clog on expansion and declustering within the APi-ToF were evaluated using water clusters in the positive mode and found to be minimal (see Sect. S1). A slight decrease (~ 10%) in total positive ion counts was observed while total negative ion counts remained approximately constant. Slight changes in total ions do not have direct implications for the results of this work which are based on changes in ion composition that would not result from a clog. We discuss the changes and the potential impacts on the measurements and interpretation in greater detail in Sect. S1.

SI Line 5:
S1 Pinhole clog

We carefully considered how the clog of the pinhole on September 13th might influence our conclusions and failed to find evidence of artifacts. We expect that the main effect of a clog would be a reduction in total ions measured by the APi-ToF. Following the clog, total positive ion counts decreased slightly (~ 10%) while total negative ion counts were unaffected. One reason for the minimal change in total negative ion counts may be that the clog roughly coincided with a shift in chemical composition of ions towards higher mass species. We believe this change in ion composition is real because it corresponds

with changes in the composition of neutral trace gases (see Sect. S9). The transmission function of our instrument results in better transmission of higher m/z species, so we would expect to see more total negative ions if charges shift to higher m/z clusters even if the ambient ion concentration remains unchanged. Our work is grounded in analysis of changes in ambient ion composition rather than absolute quantification of ions, so by itself a small change in total ion counts has no direct influence on our conclusions. As noted in the main text, the pressure in the small segmented quadrupole (SSQ) was adjusted such that it did not change significantly following the clog. The SSQ is the first chamber in our differentially pumped instrument, so this would also regulate downstream pressures in a similar manner.

While the main effect of the clog would be a reduction total ion counts, it is also possible that a pinhole clog could affect the ion expansion. To investigate this potential effect, the timeseries of several strong peaks in the positive mode spectra consisting of protonated water or water clusters were evaluated. These clusters were selected because they are consistently strong signals. A substantial change in the ratio of these clusters coinciding with the clog would be evidence of changing declustering due to changes in the expansion. The ratios of these clusters change by less than 2% before and after the clog. This finding suggests that the clog has minimal impact on our conclusions.

References

Alton, M. W., Stark, H., Canagaratna, M. R., and Browne, E. C.: Generalized Kendrick Analysis for Improved Visualization of Atmospheric Mass Spectral Data, Atmospheric Meas. Tech., 1–15, https://doi.org/10.5194/egusphere-2022-1319, 2022.

Aneja, V. P., Schlesinger, W. H., and Erisman, J. W.: Effects of agriculture upon the air quality and climate: Research, policy, and regulations, Environ. Sci. Technol., 43, 4234–4240, https://doi.org/10.1021/es8024403, 2009.

Anon: USDA National Agriculture Statistics Service Cropland Data Layer, 2016.

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, Atmospheric Chem. Phys., 17, 13819–13831, https://doi.org/10.5194/acp-17-13819-2017, 2017.

Cai, R., Yin, R., Yan, C., Yang, D., Deng, C., Dada, L., Kangasluoma, J., Kontkanen, J., Halonen, R., Ma, Y., Zhang, X., Paasonen, P., Petäjä, T., Kerminen, V.-M., Liu, Y., Bianchi, F., Zheng, J., Wang, L., Hao, J., Smith, J. N., Donahue, N. M., Kulmala, M., Worsnop, D. R., and Jiang, J.: The missing base molecules in atmospheric acid–base nucleation, Natl. Sci. Rev., 9, nwac137, https://doi.org/10.1093/nsr/nwac137, 2022.

Ehn, M., Junninen, H., Petäjä, T., Kurtén, T., Kerminen, V. M., Schobesberger, S., Manninen, H. E., Ortega, I. K., Vehkamäki, H., Kulmala, M., and Worsnop, D. R.: Composition and temporal behavior of ambient ions in the boreal forest, Atmospheric Chem. Phys., 10, 8513–8530, https://doi.org/10.5194/acp-10-8513-2010, 2010.

Ehn, M., Kleist, E., Junninen, H., and Pet, T.: Gas phase formation of extremely oxidized pinene reaction products in chamber and ambient air, Atmospheric Chem. Phys., 5113–5127, https://doi.org/10.5194/acp-12-5113-2012, 2012.

Fast, J. D., Berg, L. K., Alexander, L., Bell, D., D'Ambro, E., Hubbe, J., Kuang, C., Liu, J., Long, C., Matthews, A., Mei, F., Newsom, R., Pekour, M., Pinterich, T., Schmid, B., Schobesberger, S., Shilling, J., Smith, J. N., Springston, S., Suski, K., Thornton, J. A., Tomlinson, J., Wang, J., Xiao, H., and Zelenyuk, A.: Overview of the HI-SCALE Field Campaign: A New Perspective on Shallow Convective Clouds, Bull. Am. Meteorol. Soc., 100, 821–840, https://doi.org/10.1175/BAMS-D-18-0030.1, 2019.

Fowler, D., Coyle, M., Skiba, U., Sutton, M. A., Cape, J. N., Reis, S., Sheppard, L. J., Jenkins, A., Grizzetti, B., Galloway, J. N., Vitousek, P., Leach, A., Bouwman, A. F., Butterbach-Bahl, K., Dentener, F., Stevenson, D., Amann, M., and Voss, M.: The global nitrogen cycle in the twenty-first century, Philos. Trans. R. Soc. B-Biol. Sci., 368, 20130164, https://doi.org/10.1098/rstb.2013.0164, 2013.

Frege, C., Bianchi, F., Molteni, U., Tröstl, J., Junninen, H., Henne, S., Sipilä, M., Herrmann, E., Rossi, M. J., Kulmala, M., Hoyle, C. R., Baltensperger, U., and Dommen, J.: Chemical

characterization of atmospheric ions at the high altitude research station Jungfraujoch (Switzerland), Atmospheric Chem. Phys., 17, 2613–2629, https://doi.org/10.5194/acp-17-2613-2017, 2017.

Ge, X., Wexler, A. S., and Clegg, S. L.: Atmospheric amines – Part I. A review, Atmos. Environ., 45, 524–546, https://doi.org/10.1016/j.atmosenv.2010.10.012, 2011.

Glasoe, W. A., Volz, K., Panta, B., Freshour, N., Bachman, R., Hanson, D. R., McMurry, P. H., and Jen, C.: Sulfuric acid nucleation: An experimental study of the effect of seven bases, J. Geophys. Res. Atmospheres, 120, 1933–1950, https://doi.org/10.1002/2014JD022730, 2015.

Heinritzi, M., Dada, L., Simon, M., Stolzenburg, D., Wagner, A. C., Fischer, L., Ahonen, L. R., Amanatidis, S., Baalbaki, R., Baccarini, A., Bauer, P. S., Baumgartner, B., Bianchi, F., Brilke, S., Chen, D., Chiu, R., Dias, A., Dommen, J., Duplissy, J., Finkenzeller, H., Frege, C., Fuchs, C., Garmash, O., Gordon, H., Granzin, M., El Haddad, I., He, X., Helm, J., Hofbauer, V., Hoyle, C. R., Kangasluoma, J., Keber, T., Kim, C., Kürten, A., Lamkaddam, H., Laurila, T. M., Lampilahti, J., Lee, C. P., Lehtipalo, K., Leiminger, M., Mai, H., Makhmutov, V., Manninen, H. E., Marten, R., Mathot, S., Mauldin, R. L., Mentler, B., Molteni, U., Müller, T., Nie, W., Nieminen, T., Onnela, A., Partoll, E., Passananti, M., Petäjä, T., Pfeifer, J., Pospisilova, V., Quéléver, L. L. J., Rissanen, M. P., Rose, C., Schobesberger, S., Scholz, W., Scholze, K., Sipilä, M., Steiner, G., Stozhkov, Y., Tauber, C., Tham, Y. J., Vazquez-Pufleau, M., Virtanen, A., Vogel, A. L., Volkamer, R., Wagner, R., Wang, M., Weitz, L., Wimmer, D., Xiao, M., Yan, C., Ye, P., Zha, Q., Zhou, X., Amorim, A., Baltensperger, U., Hansel, A., Kulmala, M., Tomé, A., Winkler, P. M., Worsnop, D. R., Donahue, N. M., Kirkby, J., and Curtius, J.: Molecular understanding of the suppression of new-particle formation by isoprene, Atmospheric Chem. Phys., 20, 11809–11821, https://doi.org/10.5194/acp-20-11809-2020, 2020.

Hirsikko, A., Nieminen, T., Gagné, S., Lehtipalo, K., Manninen, H. E., Ehn, M., Hõrrak, U., Kerminen, V. M., Laakso, L., McMurry, P. H., Mirme, A., Mirme, S., Petäjä, T., Tammet, H., Vakkari, V., Vana, M., and Kulmala, M.: Atmospheric ions and nucleation: A review of observations, Atmospheric Chem. Phys., 11, 767–798, https://doi.org/10.5194/acp-11-767-2011, 2011.

Hodshire, A. L., Lawler, M. J., Zhao, J., Ortega, J., Jen, C., Yli-Juuti, T., Brewer, J. F., Kodros, J. K., Barsanti, K. C., Hanson, D. R., McMurry, P. H., Smith, J. N., and Pierce, J. R.: Multiple new-particle growth pathways observed at the US DOE Southern Great Plains field site, Atmospheric Chem. Phys., 16, 9321–9348, https://doi.org/10.5194/acp-16-9321-2016, 2016.

Jen, C. N., Bachman, R., Zhao, J., Mcmurry, P. H., and Hanson, D. R.: Diamine-sulfuric acid reactions are a potent source of new particle formation, 867–873, https://doi.org/10.1002/2015GL066958.Received, 2016.

Junninen, H., Ehn, M., Pet, T., Kulmala, M., and Worsnop, D. R.: A high-resolution mass spectrometer to measure atmospheric ion composition, Atmospheric Meas. Tech., 1039–1053, https://doi.org/10.5194/amt-3-1039-2010, 2010.

Kirkby, J., Duplissy, J., Sengupta, K., Frege, C., Gordon, H., Williamson, C., Heinritzi, M., Simon, M., Yan, C., Almeida, J., Trostl, J., Nieminen, T., Ortega, I. K., Wagner, R., Adamov,

A., Amorim, A., Bernhammer, A. K., Bianchi, F., Breitenlechner, M., Brilke, S., Chen, X., Craven, J., Dias, A., Ehrhart, S., Flagan, R. C., Franchin, A., Fuchs, C., Guida, R., Hakala, J., Hoyle, C. R., Jokinen, T., Junninen, H., Kangasluoma, J., Kim, J., Krapf, M., Kurten, A., Laaksonen, A., Lehtipalo, K., Makhmutov, V., Mathot, S., Molteni, U., Onnela, A., Perakyla, O., Piel, F., Petaja, T., Praplan, A. P., Pringle, K., Rap, A., Richards, N. A. D., Riipinen, I., Rissanen, M. P., Rondo, L., Sarnela, N., Schobesberger, S., Scott, C. E., Seinfeld, J. H., Sipila, M., Steiner, G., Stozhkov, Y., Stratmann, F., Tomé, A., Virtanen, A., Vogel, A. L., Wagner, A. C., Wagner, P. E., Weingartner, E., Wimmer, D., Winkler, P. M., Ye, P., Zhang, X., Hansel, A., Dommen, J., Donahue, N. M., Worsnop, D. R., Baltensperger, U., Kulmala, M., Carslaw, K. S., and Curtius, J.: Ion-induced nucleation of pure biogenic particles, Nature, 533, 521–526, https://doi.org/10.1038/nature17953, 2016.

Lee, B. H., Mohr, C., Lopez-hilfiker, F. D., Lutz, A., Hallquist, M., Lee, L., Romer, P., Cohen, R. C., Iyer, S., Kurtén, T., Hu, W., Day, D. A., Campuzano-jost, P., Jimenez, J. L., Xu, L., Lee, N., Guo, H., Weber, R. J., Wild, R. J., Brown, S. S., Koss, A., Gouw, J. D., Olson, K., Goldstein, A. H., Seco, R., Kim, S., Mcavey, K., Shepson, P. B., Starn, T., Baumann, K., Edgerton, E. S., Liu, J., Shilling, J. E., Miller, D. O., Brune, W., Schobesberger, S., Ambro, E. L. D., and Thornton, J. A.: Highly functionalized organic nitrates in the southeast United States : Contribution to secondary organic aerosol and reactive nitrogen budgets, PNAS, 113, 1–6, https://doi.org/10.1073/pnas.1508108113, 2016a.

Lee, B. H., Mohr, C., Lopez-hilfiker, F. D., Lutz, A., Hallquist, M., Lee, L., Romer, P., Cohen, R. C., Iyer, S., Kurtén, T., Hu, W., Day, D. A., Campuzano-jost, P., Jimenez, J. L., Xu, L., Lee, N., Guo, H., Weber, R. J., Wild, R. J., Brown, S. S., Koss, A., Gouw, J. D., Olson, K., Goldstein, A. H., Seco, R., Kim, S., Mcavey, K., Shepson, P. B., Starn, T., Baumann, K., Edgerton, E. S., Liu, J., Shilling, J. E., Miller, D. O., Brune, W., Schobesberger, S., Ambro, E. L. D., and Thornton, J. A.: Highly functionalized organic nitrates in the southeast United States : Contribution to secondary organic aerosol and reactive nitrogen budgets, PNAS, 113, 1–6, https://doi.org/10.1073/pnas.1508108113, 2016b.

Lee, L., Teng, A. P., Wennberg, P. O., Crounse, J. D., and Cohen, R. C.: On Rates and Mechanisms of OH and O3 Reactions with Isoprene-Derived Hydroxy Nitrates, J. Phys. Chem. A, 118, 1622–1637, https://doi.org/10.1021/jp4107603, 2014.

Li, Y., Pöschl, U., and Shiraiwa, M.: Molecular corridors and parameterizations of volatility in the chemical evolution of organic aerosols, Atmospheric Chem. Phys., 16, 3327–3344, https://doi.org/10.5194/acp-16-3327-2016, 2016.

Loubet, B., Buysse, P., Gonzaga-Gomez, L., Lafouge, F., Ciuraru, R., Decuq, C., Kammer, J., Bsaibes, S., Boissard, C., Durand, B., Gueudet, J.-C, Fanucci, O., Zurfluh, O., Abis, L., Zannoni, N., Truong, F., Baisnée, D., Sarda-Estève, R., Staudt, M., and Gros, V.: Volatile organic compound fluxes over a winter wheat field by PTR-Qi-TOF-MS and eddy covariance, Atmospheric Chem. Phys., 22, 2817–2842, https://doi.org/10.5194/acp-22-2817-2022, 2022.

Myllys, N., Kubečka, J., Besel, V., Alfaouri, D., Olenius, T., Smith, J. N., and Passananti, M.: Role of base strength, cluster structure and charge in sulfuric-acid-driven particle formation, Atmospheric Chem. Phys., 19, 9753–9768, https://doi.org/10.5194/acp-19-9753-2019, 2019.

Ng, N. L., Kwan, A. J., Surratt, J. D., Chan, A. W. H., Chhabra, P. S., Sorooshian, A., Pye, H. O. T., Crounse, J. D., Wennberg, P. O., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol (SOA) formation from reaction of isoprene with nitrate radicals (NO$_3$), Atmospheric Chem. Phys., 8, 4117–4140, https://doi.org/10.5194/acp-8-4117-2008, 2008.

Olenius, T., Halonen, R., Kurtén, T., Henschel, H., Kupiainen-Määttä, O., Ortega, I. K., Jen, C. N., Vehkamäki, H., and Riipinen, I.: New particle formation from sulfuric acid and amines: Comparison of monomethylamine, dimethylamine, and trimethylamine, J. Geophys. Res. Atmospheres, 122, 7103–7118, https://doi.org/10.1002/2017JD026501, 2017.

Ormeño, E., Gentner, D. R., Fares, S., Karlik, J., Park, J. H., and Goldstein, A. H.: Sesquiterpenoid Emissions from Agricultural Crops: Correlations to Monoterpenoid Emissions and Leaf Terpene Content, Environ. Sci. Technol., 44, 3758–3764, https://doi.org/10.1021/es903674m, 2010.

Richters, S., Herrmann, H., and Berndt, T.: Highly Oxidized RO2 Radicals and Consecutive Products from the Ozonolysis of Three Sesquiterpenes, Environ. Sci. Technol., 50, 2354–2362, https://doi.org/10.1021/acs.est.5b05321, 2016.

Shuman, N. S., Hunton, D. E., and Viggiano, A. A.: Ambient and Modified Atmospheric Ion Chemistry: From Top to Bottom, Chem. Rev., 115, 4542–4570, https://doi.org/10.1021/cr5003479, 2015.

Stone, D., Whalley, L. K., and Heard, D. E.: Tropospheric OH and HO2 radicals: field measurements and model comparisons, Chem. Soc. Rev., 41, 6348–6404, https://doi.org/10.1039/C2CS35140D, 2012.

Tzin, V. and Galili, G.: The Biosynthetic Pathways for Shikimate and Aromatic Amino Acids in Arabidopsis thaliana, Arab. Book Am. Soc. Plant Biol., 8, e0132, https://doi.org/10.1199/tab.0132, 2010.

Xu, Z. N., Nie, W., Liu, Y. L., Sun, P., Huang, D. D., Yan, C., Krechmer, J., Ye, P. L., Xu, Z., Qi, X. M., Zhu, C. J., Li, Y. Y., Wang, T. Y., Wang, L., Huang, X., Tang, R. Z., Guo, S., Xiu, G. L., Fu, Q. Y., Worsnop, D., Chi, X. G., and Ding, A. J.: Multifunctional Products of Isoprene Oxidation in Polluted Atmosphere and Their Contribution to SOA, Geophys. Res. Lett., 48, e2020GL089276, https://doi.org/10.1029/2020GL089276, 2020.

Yeung, L. Y. and Elrod, M. J.: Experimental and computational study of the kinetics of OH + pyridine and its methyland ethyl-substituted derivatives, J. Phys. Chem. A, 107, 4470–4477, https://doi.org/10.1021/jp027389s, 2003.

Zhang, Y., Peräkylä, O., Yan, C., Heikkinen, L., Äijälä, M., Daellenbach, K. R., Zha, Q., Riva, M., Garmash, O., Junninen, H., Paatero, P., Worsnop, D., and Ehn, M.: A novel approach for simple statistical analysis of high-resolution mass spectra, Atmospheric Meas. Tech., 12, 3761–3776, https://doi.org/10.5194/amt-12-3761-2019, 2019.