Final author comments (ACs): Response to referee comments (RCs)

Manuscript title

Insufficient mass spectrometric detection of synthesized peroxy acids from α-pinene ozonolysis

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Throughout this document, referee comments, author comments, and manuscript changes are identified as RC, AC, and MC, respectively. The first number identifies the referee, and the second identifies the corresponding comment. Where several manuscript changes relate to the same comment, an additional number is used (e.g., MC1.2.1 and MC1.2.2). All page and line numbers cited below refer to the clean revised manuscript.

Dear Editor and Referees,

We sincerely thank both referees for their careful, constructive, and scientifically important evaluations. Their comments helped us distinguish more clearly between what our measurements demonstrate directly and what they support as a mechanistic interpretation. We agree that, although the original manuscript framed decomposition as an interpretation in several places, some key formulations attributed the low peroxy-to-carboxylic-acid signal ratios to ionization too confidently and extended the atmospheric implications too broadly from two moderately oxygenated standards. We have therefore refined the central interpretation, added new control analyses, expanded the experimental details, and narrowed the atmospheric implications while preserving the main findings of the study.

We consider the additional figures presented in this author response to be useful supporting material that should be archived alongside the revised manuscript rather than appearing only in the response. We have therefore prepared a Supplementary Information file containing four figures and their corresponding captions, as presented below.

Response to Anonymous Referee #1

Referee comment RC1.1

This manuscript addresses an important issue in atmospheric measurements by examining the limitations of widely used mass spectrometric OOM measurements, particularly those arising from reagent-ion selectivity and the lack of authentic monomeric standards for hydroperoxides and peroxy acids. The topic is timely and relevant, given the central role of OOMs in secondary organic aerosol formation and new particle growth. The results suggest that peroxy acids may be systematically underestimated due to ionization-related effects, which has important implications for interpreting OOM measurements. However, several aspects of interpretation and the broader atmospheric implications require further clarification.

Author response AC1.1

We thank the referee for recognizing the importance and timeliness of the measurement problem and for identifying where our mechanistic and atmospheric interpretation required greater restraint. We have responded by adding controls, distinguishing observations from hypotheses, and revising the manuscript throughout. The revisions are detailed below, point by point.

Referee comment RC1.2

The central conclusion of the manuscript is that peroxy acids formed during α-pinene oxidation are substantially underdetected by nitrate-CIMS due to decomposition or fragmentation associated with the ionization process. However, the evidence presented does not fully exclude alternative explanations related to the chemical stability of the synthesized standards during storage, handling, or sampling into the instrument. Can the authors provide additional experimental evidence demonstrating that the observed discrepancy between the NMR-derived concentrations and the mass spectrometric response originates specifically from the ionization step?

Author response AC1.2

We thank the referee for raising this central point. We agree that some formulations in the original manuscript attributed the low peroxy-to-carboxylic-acid signal ratios to ionization-associated decomposition more confidently than the available evidence warranted. We have now added three control experiments that substantially narrow the possible explanations. As described in our response to Referee 2 (AC2.3), the pure pinonic acid (PA) experiment shows a slow signal increase consistent with retention during evaporation and transport, whereas the PA signal in the peroxy pinonic acid (PPA) standard rises rapidly together with PPA. This contrast argues against independent evaporation of pre-existing PA and a stronger compound-specific response to PA as the main causes of the reduced ratios, because either explanation would retain the slow PA time response. The temperature controls further exclude thermal degradation in the heated ion transfer tube under the tested conditions. Together with the pronounced dependence on ionization chemistry, these observations support chemical conversion of a common peroxy-acid-derived parent after evaporation, most likely during ionization. However, surface-catalyzed conversion at stainless steel inlet surfaces cannot be fully ruled out as a contributor to the reduced ratios. The corresponding manuscript revisions are detailed in our responses to the relevant comments from both referees.

Manuscript change MC1.2.1, Abstract, p. 1, lines 13–21

These ratios vary strongly across ionization modes, with greater apparent peroxy acid loss under harder (de)protonation and improved, though still incomplete, preservation under softer nitrate and uronium adduct formation. Together with the paired temporal profiles of the peroxy and carboxylic acid signals, the results are consistent with ionization-associated loss of peroxy acid functionality. Notably, uronium provides significantly higher sensitivity for these moderately oxygenated compounds, complementing nitrate's strong selectivity toward highly oxygenated organic molecules (HOMs). Together, our results suggest that peroxy acids formed via α-pinene autoxidation may be systematically under-quantified by commonly used mass spectrometric approaches, with possible implications for molecular assignments, oxygen-to-carbon (O:C) ratios, volatility-basis-set derivations, and inferred rates of nucleation and early particle growth. The broader atmospheric magnitude of these effects remains to be established.

Manuscript change MC1.2.2, Results and discussion, p. 10, lines 188–189

These systematic differences across ionization modes support the interpretation that decomposition occurs during ionization, rather than elsewhere in the mass spectrometer;...

Referee comment RC1.3

For example, are there measurements under different ionization conditions or inlet residence times that would help isolate the source of the signal loss?

Author response AC1.3

The multi-scheme chemical ionization inlet (MION) and H-ESI settings were optimized to provide stable, high total ion count (TIC) signals. We did not perform a systematic source-voltage or residence-time series with the synthesized standards because altering these parameters would affect the entire instrument response pattern and require an extensive series of measurements. For example, changing the flow settings would simultaneously influence wall effects and ionization efficiencies, making it difficult to isolate the origin of peroxy acid degradation. Instead, the new pure PA and temperature controls argue against independent evaporation, compound-specific response factors, and ion transfer tube heating as the main explanations under the tested conditions. We revised the conclusions (see AC2.7 in the response to Referee 2) to identify conversion at stainless steel inlet surfaces as the principal not-yet-fully-resolved alternative explanation.

Referee comment RC1.4

Thermal decomposition, wall losses, or inlet-related processes could contribute to the observed discrepancies. Given the known instability of peroxy compounds, can the temperature of ion transfer tube affects the stability of the cluster?

Author response AC1.4

For the peroxy pinonic acid (PPA) standard in nitrate mode, increasing the ion transfer tube temperature from 100 °C to 200 °C increased the peroxy-to-carboxylic-acid nitrate adduct ratio from approximately 0.8 to approximately 1.0, as displayed by Fig. R1. The ratio remained substantially below the NMR ratio of 4.7. In a separate H-ESI experiment with

commercial *meta*-chloroperoxybenzoic acid (*m*CPBA), the ratio of deprotonated *m*CPBA to *meta*-chlorobenzoic acid (*m*CBA) increased from 0.02 at 85 °C to 0.03 at 110 °C and 0.04 at 320 °C, as displayed by Fig. R2. These values remain far below the approximate bulk *m*CPBA/*m*CBA ratio of 3.3, but the direction of change is again opposite to that expected if ion transfer tube heating caused peroxy acid degradation. Across a synthesized aliphatic peroxy acid standard and a more stable aromatic peroxy acid, these controls exclude thermal degradation in the ion transfer tube under the tested conditions.

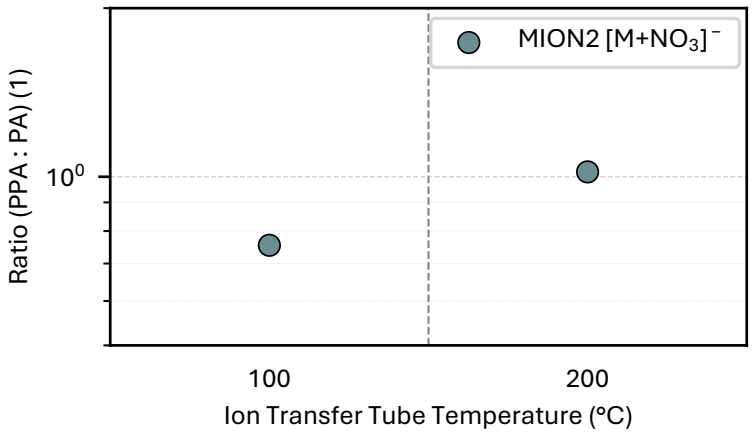

Figure R1: Supplementary Figure S2. Nitrate adduct signal ratio of peroxy pinonic acid (PPA) to pinonic acid (PA) at ion transfer tube temperatures of 100 °C and 200 °C, calculated from 2 min averaged mass spectra. The ratio increases modestly with temperature from approximately 0.8 to approximately 1.0, but remains well below the NMR ratio of 4.7.

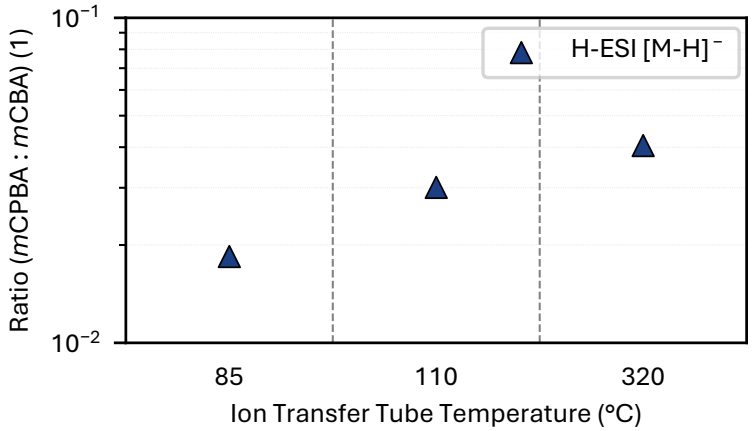

Figure R2: Supplementary Figure S3. Signal ratio of deprotonated *meta*-chloroperoxybenzoic acid (*m*CPBA) to *meta*-chlorobenzoic acid (*m*CBA) measured with heated electrospray ionization (H-ESI) at ion transfer tube temperatures of 85 °C, 110 °C, and 320 °C, calculated from 30 s averaged mass spectra. The ratio increases modestly with temperature, but remains well below the approximate bulk *m*CPBA/*m*CBA ratio of 3.3.

Manuscript change MC1.4, Results and discussion, p. 11, lines 212–217

We further tested the influence of the ion transfer tube temperature. For the PPA standard measured in nitrate mode, increasing the temperature from 100 °C to 200 °C increased the

PPA/PA nitrate adduct ratio from approximately 0.8 to approximately 1.0 (Fig. S02), which remained below the NMR ratio of 4.7. For commercial *m*CPBA measured with H-ESI, the deprotonated *m*CPBA/*m*CBA ratio increased from 0.02 at 85 °C to 0.03 at 110 °C and 0.04 at 320 °C (Fig. S03). In both experiments, higher transfer tube temperatures increased rather than decreased the relative peroxy acid signal. These results therefore exclude thermal degradation of peroxy acids in the ion transfer tube as a cause of the reduced ratios under the tested conditions.

Referee comment RC1.5

Also, I suppose the total signal of the products in nitrate CIMS is the sum of normalized signal intensities of deprotonated as well as the cluster. Does addition of all the related signals (deprotonated + cluster) reduces the discrepancy observed between NMR and MS-derived ratios?

Author response AC1.5

The (de)protonated and adduct channels were evaluated separately throughout our analysis, and both channels independently yielded peroxy-to-carboxylic-acid ratios below the corresponding NMR ratios. Consequently, summing the channels cannot restore the NMR ratio. To provide the requested quantitative comparison, we nevertheless summed the normalized peroxy acid signals from the (de)protonated and adduct channels within each reagent ion mode and divided by the analogously summed carboxylic acid signals. The resulting ratios are 0.4 (nitrate, PNPA), 0.7 (nitrate, PPA), 0.05 (uronium, PNPA), and 0.5 (uronium, PPA). All remain substantially below the corresponding NMR ratios of 4.4 and 4.7 by factors of approximately 10, 6.6, 96, and 10, respectively. Thus, combining both detected channels slightly changes the numerical ratios but does not resolve the Orbitrap and NMR discrepancy.

Referee comment RC1.6

The study relies on two monomeric compounds - peroxy norpinonic acid (PNPA) and peroxy pinonic acid (PPA). This point is particularly important because the broader atmospheric implications discussed in the manuscript rely on the assumption that the behavior of the investigated standards is representative of peroxy acids present in α-pinene ozonolysis and other HOM-forming systems. This study relies on a limited number of synthesized standards, and it is unclear to what extent the results can be generalized to the broader class of highly oxygenated atmospheric peroxy acids formed during α-pinene ozonolysis.

Author response AC1.6

We thank the referee for this important qualification and agree. PNPA and PPA contain four oxygen atoms and are moderately oxygenated molecules. Their value is that they are authentic α-pinene-derived monomer standards containing a peroxy acid functionality; they do not span the oxygenation state or functional group diversity of atmospheric HOMs. We have therefore revised the statement that these standards may be HOM proxies, while identifying the behavior of other peroxy acids as a question for future work.

Manuscript change MC1.6.1, Introduction, p. 3, lines 65–68

Both standards contain four oxygen atoms and are therefore classified as moderately oxygenated molecules (MOMs). Their peroxy acid functionality makes them useful model compounds for probing the detection of peroxy-acid-containing α-pinene-derived oxidation products, including HOMs, but they should not be treated as quantitative proxies for the broader and more highly functionalized HOM population.

Manuscript change MC1.6.2, Introduction, p. 3, lines 71–74

We show that these two peroxy acids exhibit strong variability in instrument response across different ionization schemes, indicating that their abundance may be substantially underestimated in atmospheric studies. Whether comparable response behavior occurs for more highly oxygenated atmospheric peroxy acids remains to be established using additional authentic standards.

Referee comment RC1.7

Minor comments: 1. Expansion of term HOM should be consistently defined upon first use. For example, in Line 17, HOM is expanded as 'highly oxygenated molecules'.

Author response AC1.7

We thank the referee for noting this inconsistency. We now define HOMs at first use as 'highly oxygenated organic molecules' and use the same expansion throughout.

Manuscript change :

See the corresponding change to the abstract in MC1.2.1.

Referee comment RC1.8

2. Figure 5 middle panel figure, why the signal(m/z 247 and 231) persist in the background of the uronium ionization experiments?

Author response AC1.8

We thank the referee for raising this point. The non-zero signals at mass-to-charge ratios (m/z) 247 and 231 during the initial blank are attributed to persistent carryover from trace material retained on inlet and instrument surfaces. Uronium is sufficiently sensitive to detect these residual levels even after routine cleaning. Between experiments, the evaporator, connecting tubing, and inlet components up to the ion transfer tube were cleaned with acetone. We retained the blank signals in Figure 5 rather than suppressing them. Importantly, detection was not assigned from visual inspection of the chromatograms alone: each sample peak had to exceed the corresponding blank mean by three standard deviations (3σ), according to the detection criterion defined in the original manuscript. We clarify the origin of the background, the cleaning procedure, and the statistical criterion.

Manuscript change MC1.8.1, Materials and methods, p. 5, lines 106–107

Between experiments, the evaporator, connecting tubing, and inlet components up to the ion transfer tube were cleaned with acetone.

Manuscript change MC1.8.2, Materials and methods, p. 6, lines 114–115

All analyte peaks were considered detected only when their signal exceeded the corresponding blank mean by three standard deviations (3σ).

Manuscript change MC1.8.3, Results and discussion, p. 8, lines 161–163

The persistent signals at mass-to-charge ratios (m/z) 247 and 231 during the initial uronium blank are attributed to trace carryover retained on inlet or instrument surfaces and detected because of the high sensitivity of uronium; all reported sample signals nevertheless exceeded the corresponding blank-derived 3σ threshold.

Response to Anonymous Referee #2

Referee comment RC2.1

This manuscript describes the synthesis of measurement of 2 peroxy acid-carboxylic acid pairs (peroxy norpinonic acid/norpinonic acid and peroxy pinonic acid/pinonic acid). Commonly used mass spectrometric techniques are employed. The overall science question is important and timely because similar mass spectrometric methods are frequently used in chamber and field studies to identify the organic compounds that contribute to aerosol formation and growth. A lack of authentic molecular standards, however, has limited our ability to understand instrument response factors (i.e. calibration/sensitivity) and to identify how these molecules behave in instruments (i.e. do they stick to walls, fragment upon ionization, etc.). This work begins to address these questions and is an appropriate topic for the journal. A main conclusion of the manuscript is that the peroxy acids undergo fragmentation due to ionization. While that very well may be the case, in my opinion, the evidence presented is not yet conclusive and further experiments may be required.

Author response AC2.1

We thank the referee for recognizing the importance of authentic standards and for emphasizing the distinction between an observed low response and a uniquely demonstrated fragmentation mechanism. We agree that some formulations in the original manuscript attributed the low peroxy-to-carboxylic-acid signal ratios to ionization-associated fragmentation more confidently than the evidence warranted. As detailed in responses AC1.2 and AC1.4 to Referee 1 and in AC2.3 below, the new pure pinonic acid (PA) control argues against independent evaporation and compound-specific response factors as the main causes of the reduced ratios, while the temperature controls exclude thermal degradation in the ion transfer tube under the tested conditions. Taken together with the pronounced variation across ionization modes, these findings support retaining ionization-associated decomposition as the best-supported interpretation, while surface-catalyzed conversion at stainless steel inlet surfaces remains a not-yet-fully-resolved alternative.

Referee comment RC2.2

Before I can recommend publication of the manuscript, I think that the following points require consideration. Major Comments: Much of the attribution that ionization is causing fragmentation comes from the observation that the carboxylic acid species is detected with higher intensity than the peroxy acid species and that the time behavior of the peroxy acid relative to the carboxylic acid is not what one would expect for compounds of different volatility. However, the relative intensities of response are unknown. For nitrate CIMS, these compounds are on the edge of what it is likely to detect well and sensitivities can be unpredictable. Since the carboxylic acids were synthesized as part of the peroxy acid synthesis, would it be possible to perform a standard addition like analysis where the carboxylic acid is spiked into the peroxy acid in order to confirm that the signal increases as expected?

Author response AC2.2

We thank the referee for this important suggestion. We agree that the original manuscript did not establish relative molar response factors and therefore could not infer the extent of conversion quantitatively from signal intensity alone. A matched standard-addition experiment and independent calibration of both members of each pair would be the strongest

approach for that purpose. We did not perform a standard-addition series for this revision because the peroxy acid standards could not be fully isolated from their corresponding carboxylic acids. Future work should therefore determine full response curves for both the peroxy acid and the corresponding carboxylic acid.
However, the new pure PA experiment presented in AC2.3 directly tests whether a stronger response to PA, without peroxy pinonic acid (PPA) conversion, could explain the low PPA/PA ratio. Pure PA shows a slow signal increase consistent with retention during evaporation and transport, whereas the PA signal in the PPA standard rises rapidly together with PPA. If the reduced ratio arose primarily from a stronger compound-specific response to independently evaporated PA, that PA signal would retain the slow pure-PA time response. The observed temporal behavior therefore argues against compound-specific response factors as the main cause of the reduced ratios, although response-factor calibration remains necessary to quantify the conversion.
As an additional control, four *m*CPBA concentration levels measured in nitrate mode yielded a linear concentration–response relationship for the deprotonated *m*CPBA channel ($R^2 = 0.982$, $n = 4$) within the relevant range of low normalized and absolute intensities. This result supports that the low nitrate signals respond systematically to analyte concentration rather than representing random noise. In addition, the synthesized peroxy acid adduct signals reported in the manuscript were, on average, factors of 34 in nitrate mode and 18 in uronium mode above their respective blank-derived 3σ thresholds. These checks do not establish equal response factors for PPA/PA or PNPA/NPA, but, together with the pure PA temporal response, they show that compound-specific response factors are unlikely to be the principal cause of the observed ratios. The low-signal concentration–response control is presented in Fig. R3.

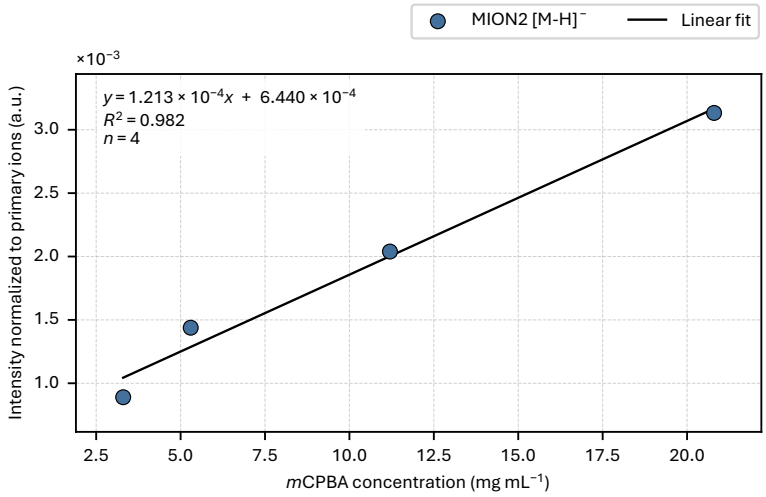

Figure R3: Supplementary Figure S4. Nitrate mode response of the deprotonated *meta*-chloroperoxybenzoic acid (*m*CPBA) signal across four solution concentrations. Points represent 9 min mean intensities normalized to nitrate primary ions. The linear fit is $y = 1.213 \times 10^{-4}x + 6.440 \times 10^{-4}$ ($R^2 = 0.982$; $n = 4$). This control demonstrates a systematic low-intensity response for *m*CPBA in nitrate mode.

Manuscript change MC2.2, Results and discussion, p. 11, lines 237–242

As a limited validation of the nitrate response at low signal intensity, four *m*CPBA solution concentrations were measured. The deprotonated *m*CPBA signal was averaged over 9 min

and normalized to the nitrate primary ions (Fig. S04). The response was described by $y = 1.213 \times 10^{-4}x + 6.440 \times 10^{-4}$ ($R^2 = 0.982$; $n = 4$). This result demonstrates a systematic concentration response for *m*CPBA within the relevant low-intensity regime. It does not determine the relative molar response factors of PNPA/NPA or PPA/PA; however, the pure PA temporal response shows that compound-specific response factors cannot account for the observed time profiles and are therefore unlikely to be the principal cause of the reduced ratios.

Referee comment RC2.3

Measuring the carboxylic acid alone to see if the time response is as expected would also be beneficial.

Author response AC2.3

We performed the experiment suggested by the referee and measured pure pinonic acid (PA, $C_{10}H_{16}O_3$), the carboxylic acid counterpart of our peroxy pinonic acid standard (PPA, $C_{10}H_{16}O_4$), using pathway (a) in Fig. 2. As displayed by Fig. R4, the pure PA signal continued to rise throughout the approximately 25 min uronium interval and retained a slightly increasing trend during a further approximately 20 min in nitrate mode, suggesting retention of the sample during evaporation and transport. In contrast, the PA signal in the PPA standard rose rapidly together with the PPA signal and approached a plateau within approximately 4 min. Because the pure PA experiment directly characterizes the temporal response of PA under the same experimental conditions, this difference shows that the PA signal in the PPA sample does not arise predominantly from pre-existing PA that evaporates independently. The composition of the mixture may influence absolute evaporation rates, but it does not readily explain the rapid, nearly identical time profiles of the PPA and PA signals or the absence of the PA signal retention observed in the pure PA experiment. If the reduced PPA/PA ratio resulted primarily from a stronger compound-specific response to PA, the PA signal would still be expected to show the slower temporal response of independently evaporating PA. This comparison therefore argues against independent evaporation and compound-specific response factors as the main causes of the observed ratios and supports conversion from a common PPA-derived parent after evaporation and transport.

Manuscript change MC2.3, Results and discussion, p. 10, lines 200–211

A pure pinonic acid (PA) control experiment showed a markedly different temporal response from the PA signal in the PPA standard (Fig. S01). Pure PA continued to increase throughout the approximately 25 min uronium interval and retained a slightly increasing trend during the subsequent approximately 20 min nitrate interval, suggesting retention of the less volatile PA during evaporation and transport. In contrast, the PPA and PA signals in Fig. 5b rose rapidly together and approached a plateau within approximately 4 min. Because pure PA was measured using the same experimental setup and conditions, this difference argues against the PA signal in the synthesized sample arising predominantly from independently evaporating PA already present in the mixture. Although mixture composition may influence absolute evaporation rates, it does not readily explain the rapid, nearly identical profiles of the PPA and PA channels or the absence of the PA signal retention observed in the pure PA experiment. If the reduced PPA/PA ratio resulted primarily from a stronger compound-specific response to PA, the PA signal would still be expected to show the slower temporal response of independently evaporated PA. The comparison therefore argues against independent evaporation and compound-specific response factors as the main causes of

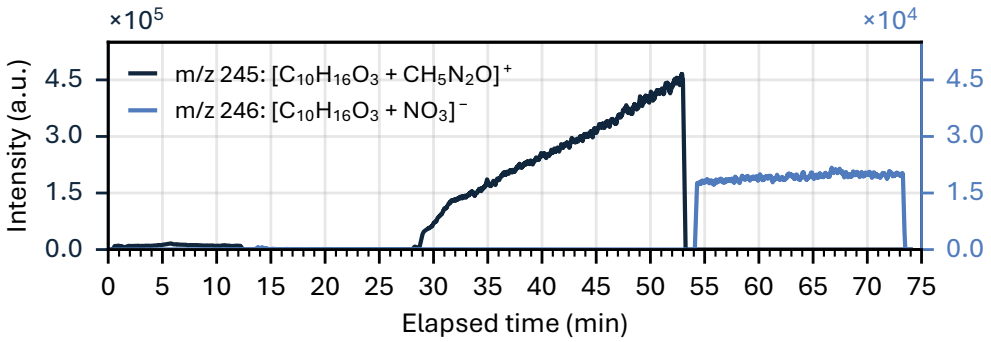

Figure R4: Supplementary Figure S1. Extracted-ion chromatogram of pure pinonic acid (PA; $C_{10}H_{16}O_3$). The uronium adduct channel $[PA+CH_5N_2O]^+$ was recorded first; the abrupt change at approximately 54 min marks the switch to nitrate, after which the nitrate adduct channel $[PA+NO_3]^-$ is shown. Absolute intensities are displayed on separate axes. The pure PA signal continues to rise throughout the approximately 25 min uronium interval and retains a slightly increasing trend during the subsequent approximately 20 min nitrate interval, rather than reaching the rapid plateau observed for the paired peroxy pinonic acid (PPA) and PA signals in Fig. 5b.

the observed ratios and supports conversion from a common PPA-derived parent after evaporation and transport.

Referee comment RC2.4

There are locations of elevated temperature that could be degrading the molecules. Has thermal degradation, for instance in the ion transfer tube, been ruled out by conducting experiments at different temperatures?

Author response AC2.4

We thank the referee for raising this concern. We now add the two temperature control experiments presented in AC1.4 of our response to Referee 1. Increasing the ion transfer tube temperature did not lower the relative peroxy acid signal in either control; the ratio instead increased modestly. These results therefore exclude thermal degradation in the ion transfer tube as a cause of the low peroxy-to-carboxylic-acid ratios under the tested conditions.

Manuscript change :

See the corresponding manuscript change in MC1.4 of our response to Referee 1.

Referee comment RC2.5

Could the stainless steel inlet be influencing the decomposition of the compounds? A quick check could be replacing the PTFE tubing with SS tubing.

Author response AC2.5

We thank the referee for highlighting the possible role of surface chemistry. We agree that stainless steel could contribute to surface-catalyzed conversion and that the present

experiments do not exclude this. A 70 mm PTFE connector leads to a 260 mm stainless steel transfer tube that must remain centered within the downstream stainless steel sheath-flow inlet assembly. Replacing the short PTFE section with stainless steel would increase stainless steel contact but would not remove the unavoidable downstream stainless steel surfaces; it would therefore be a sensitivity test rather than a clean isolation of the inlet contribution. Conversely, replacing the centered stainless steel transfer tube with flexible PTFE would compromise the inlet geometry and protected sheath-flow configuration. We have clarified the construction and now identify surface-catalyzed conversion at stainless steel inlet surfaces explicitly as a possible contributor to the reduced ratios.

Manuscript change :

The PTFE connector and stainless steel inlet dimensions are clarified using the wording in manuscript change MC2.9. The revised Results and discussion and Conclusions now identify surface-catalyzed conversion at stainless steel inlet surfaces as a possible contributor to the reduced ratios, as outlined in MC2.7.1 and MC2.7.2.

Referee comment RC2.6

Minor Comments: What is the source of the background (first 10ish minutes) in the uronium adduct mode in Figure 5?

Author response AC2.6

We thank the referee for this question. As explained in AC1.8 of our response to Referee 1, the persistent blank is attributed to trace carryover on inlet and instrument surfaces that remains visible because of the high sensitivity of uronium. We now describe the origin of the background and the routine cleaning and emphasize that sample peaks were accepted only above the blank-derived 3σ threshold.

Manuscript change :

See manuscript changes MC1.8.1, MC1.8.2, and MC1.8.3 in our response to Referee 1.

Referee comment RC2.7

While overall there is effort not to generalize too much and to identify the limitations, there are some points in the manuscript where the implications seem to be extended a bit too far. The compounds measured here are lightly oxygenated and thus are not expected to be detected well by a nitrate CIMS. Further functionalized could also very well alter fragmentation pathways. I suggest a careful review of the manuscript to avoid over generalization. For example, on line 232 “imply” might be better changed to “suggest” and in the conclusions section the limitations should be discussed.

Author response AC2.7

We thank the referee for this important correction and agree. We call PNPA and PPA moderately oxygenated molecules, explain that nitrate has limited sensitivity in this chemical space, and avoid treating these structures as representative of all HOM peroxy acids. We changed “imply” to “suggest” and revised the Conclusions as detailed below. We clarify that the two standards do not represent the full HOM population. We also integrate

the new controls: the pure PA temporal response argues against independent evaporation and compound-specific response factors as the main causes of the observed ratios, and the temperature controls exclude degradation in the ion transfer tube under the tested conditions. The remaining uncertainty concerns surface-catalyzed conversion at stainless steel inlet surfaces as a possible contributor to the reduced ratios. Finally, we state that the magnitude of potential response-bias-induced errors in inferred atmospheric nucleation and particle growth rates cannot be determined directly from the two moderately oxygenated standards studied here.

Manuscript change MC2.7.1, Results and discussion, p. 11, lines 218–223

Considering all experiments and controls, the systematically reduced peroxy-to-carboxylic-acid Orbitrap intensity ratios relative to NMR, the paired temporal profiles of the synthesized standards, and the strong dependence on ionization chemistry are consistent with ionization-associated loss of peroxy acid functionality. The pure PA control argues against independent evaporation of pre-existing PA and compound-specific response factors as the main explanations, and the temperature controls exclude thermal degradation in the ion transfer tube under the tested conditions. However, surface-catalyzed conversion at stainless steel inlet surfaces cannot be ruled out as a contributor to the reduced ratios.

Manuscript change MC2.7.2, Conclusions, p. 12–13, lines 252–291

In this work, we synthesized two monomeric OOM standards from α-pinene ozonolysis containing a peroxy acid functionality. With four oxygen atoms, they are moderately oxygenated molecules (MOMs). Because peroxy acid functionalities often occur in OOMs, including highly oxygenated organic molecules (HOMs), these standards can provide useful qualitative insight into their analytical behavior. However, they should not be regarded as quantitative proxies for the broader population of HOMs. We characterized their detectability with a nitrate- and uronium-based MION-Orbitrap and compared these two gas-phase ionization schemes with liquid H-ESI.

Across all techniques, NMR confirmed that the freshly synthesized standards were dominated by peroxy acids, whereas Orbitrap measurements consistently yielded substantially lower peroxy-to-carboxylic-acid ratios, contradicting the SIMPOL.1 expectation that the higher volatility of peroxy acids should produce ratios even greater than those measured by NMR. Crucially, the time evolution of these ratios supports peroxy acid decomposition: after a brief stabilization period, the peroxy-to-carboxylic-acid ratios reach a constant level rapidly, and the peroxy and carboxylic acid signals exhibit nearly identical temporal profiles. In contrast, pure pinonic acid (PA), measured using the same experimental conditions, continued to increase over approximately 45 min and did not show the rapid plateau observed for the peroxy pinonic acid (PPA) standard, suggesting retention of the less volatile PA during evaporation and transport. This argues against independent evaporation and compound-specific response factors as the main causes of the reduced ratios and instead supports the interpretation that both signals originate from a common PPA-derived parent, with conversion occurring after evaporation. Increasing the ion transfer tube temperature did not decrease the relative peroxy acid response for either the PPA standard or *m*CPBA, excluding thermal degradation in the ion transfer tube under the tested conditions. Together with the divergence between sample-preserving NMR and sample-modifying mass spectrometric measurements, and with the pronounced variability across ionization modes, these observations are consistent with ionization-associated loss of peroxy-acid functionality. Such loss appears more pronounced under harder ionization pathways such as (de)protonation. Softer ionization routes such as nitrate and uronium adduct formation appear to preserve the peroxy acid functionality more

effectively; nevertheless, even these channels yield ratios substantially below the bulk values, and the relative responses vary with reagent-ion chemistry and the molecular structure of the analyte, as indicated by the pronounced shifts in the peroxy-to-carboxylic-acid ratios for the two standards under uronium ionization. However, surface-catalyzed conversion at stainless steel inlet surfaces cannot be excluded as a possible contributor to the reduced ratios, highlighting the need for dedicated experiments assessing the influence of inlet material. Finally, our findings highlight that uronium adduct ionization captures this class of moderately oxygenated compounds far more efficiently than nitrate, underscoring its value as a complementary reagent for expanding molecular coverage beyond the HOM-biased selectivity of nitrate-CIMS.
Our results suggest that peroxy acids formed via autoxidation of α-pinene – and potentially other biogenic VOCs – may often be inaccurately quantified across commonly used mass spectrometric techniques. Because nitrate-CIMS is the most prevalent method for gas-phase HOM detection in new particle formation studies, analogous response biases could translate into substantial uncertainties when deriving atmospheric process rates, including nucleation and growth rates of freshly formed particles. For example, in volatility-basis-set derivations from atmospheric measurements, misidentifying peroxy acids as carboxylic acids would artificially lower their assigned oxygen number, thereby underestimating O:C ratios for OOMs and propagating systematic errors in inferred volatilities. The magnitude and broader atmospheric relevance of these effects cannot be inferred directly from the two moderately oxygenated standards studied here and will require investigation using additional authentic standards. These findings underscore the need for calibration procedures capable of capturing such compound-specific effects, together with continued exploration of novel reagent-ion chemistries that provide broader and more uniform coverage across the full range of molecular oxygenation states present in the atmosphere.

Referee comment RC2.8

Technical Comments: Figures 4 & 5: The two dark blue colors are challenging to distinguish on my monitor. Since two traces are shown in each figure, I suggest pairing a dark color with a light color in each subpanel rather than pairing dark with dark and light with light.

Author response AC2.8

We thank the referee for raising this important accessibility issue. Although the original palette was selected from Fabio Crameri's scientifically tested color schemes, we agree that the two dark traces are difficult to distinguish at typical screen brightness and in small panels. We have revised Figures 4 and 5 so that each time-series panel uses one dark and one light trace.

Manuscript change MC2.8, Figures 4 and 5

The paired traces in each subpanel are recolored to use a dark-light combination.

Referee comment RC2.9

Line 86: "PTFE tube connecting the evaporator to the stainless steel inlet measuring 70 mm." Is the inlet or the PTFE tube 70 mm. How long is the other tube?

Author response AC2.9

We thank the referee for identifying the ambiguity. The PTFE connector is 70 mm long and 6 mm in diameter. It connects to a stainless steel transfer tube that is 260 mm long and 6 mm in diameter. This tube is centered within the downstream stainless steel sheath-flow inlet assembly, which is 240 mm long and 24 mm in diameter. We rewrote the Materials and methods sentence so that each dimension is attached unambiguously to the corresponding component.

Manuscript change MC2.9, Materials and methods, p. 4, lines 90–93

The sample lines were kept as short as practicable. A 70 mm long, 6 mm diameter PTFE tube connected the evaporator to a 260 mm long, 6 mm diameter stainless steel transfer tube. This tube was centered within the front side of the downstream stainless steel sheath-flow inlet assembly, which was 240 mm long and 24 mm in diameter.