Author Response to Referee 1

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.

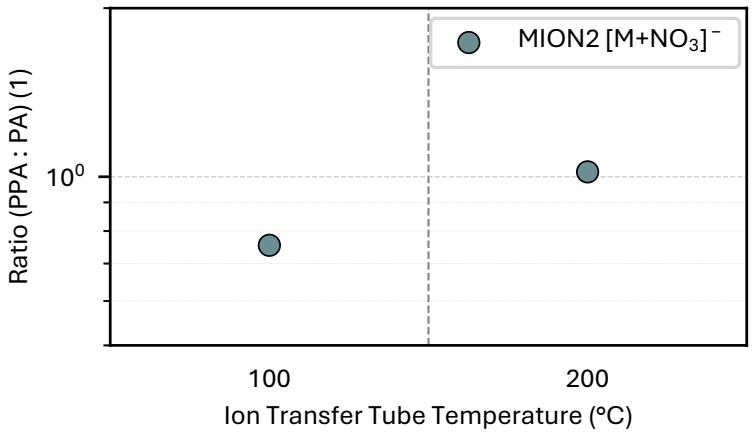

Figure R1: Supplementary Figure S2. Nitrate adduct signal ratio of peroxy pinonic acid (PPA) to pinonic acid (PA) at ion transfer tube temperatures of 100 °C and 200 °C, calculated from 2 min averaged mass spectra. The ratio increases modestly with temperature from approximately 0.8 to approximately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

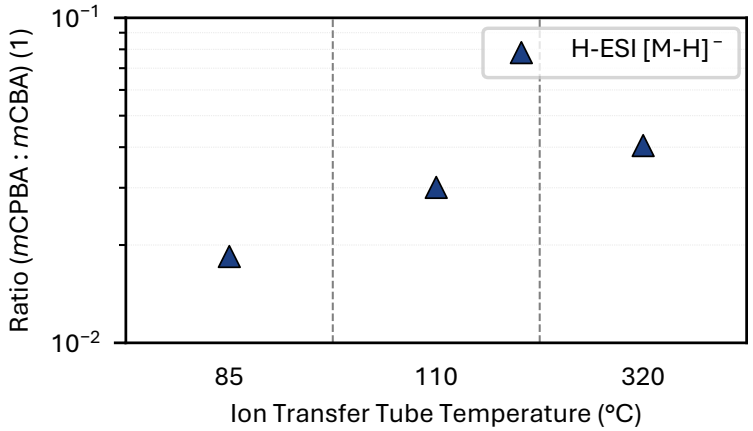

Figure R2: Supplementary Figure S3. Signal ratio of deprotonated *meta*-chloroperoxybenzoic acid (*m*CPBA) to *meta*-chlorobenzoic acid (*m*CBA) measured with heated electrospray ionization (H-ESI) at ion transfer tube temperatures of 85 °C, 110 °C, and 320 °C, calculated from 30 s averaged mass spectra. 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.