Response to Reviewer #1

General comment (GC):

Volatile organic compounds (VOCs) and volatile inorganic compounds (VICs) are important target analytes, both in an environmental context and industrial process control. The simultaneous analysis of both compound groups with a high temporal resolution and sensitivity is still challenging. To overcome this challenge, the authors introduce the novel Vocus B Chemical Ionization Time-of-Flight Mass Spectrometer. This instrument can serve as an "all-in-one" solution, quasi-simultaneously targeting both compound groups by rapidly switching between multiple reagent ions and polarities. The manuscript is well-structured and easy to understand. It is also written in clear, appropriate English. The authors provide a comprehensive description of the Vocus B's performance in controlled laboratory tests and three relevant real-world applications. The use cases are well-chosen and presented, demonstrating the device's versatility and usefulness in air pollution research and industrial applications. The results are presented logically and comprehensively, and the advantages over other established measuring devices are clearly highlighted. I therefore favor publishing this manuscript in Atmospheric Measurement Techniques after minor revisions.

Response:

We appreciate Reviewer #1 for your positive assessment of our work and the constructive comments provided. We have addressed each specific point below.

Minor comments (MC):

MC 1: *Line 157: "…, and various aromatics (chlorobenzene, styrene, etc.)" - Styrene and other aromatics are shown in Figure S1. The only (hetero)aromatics in Figure 1 are chlorobenzene and pyridine.*

Response:

Apology for the confusion. We have revised the text to accurately reflect the figures. Furthermore, as suggested in your next comment, we have moved the calibration plots for Styrene, Toluene, and α-pinene from the Supplement to the main Figure 1 to resolve this discrepancy.

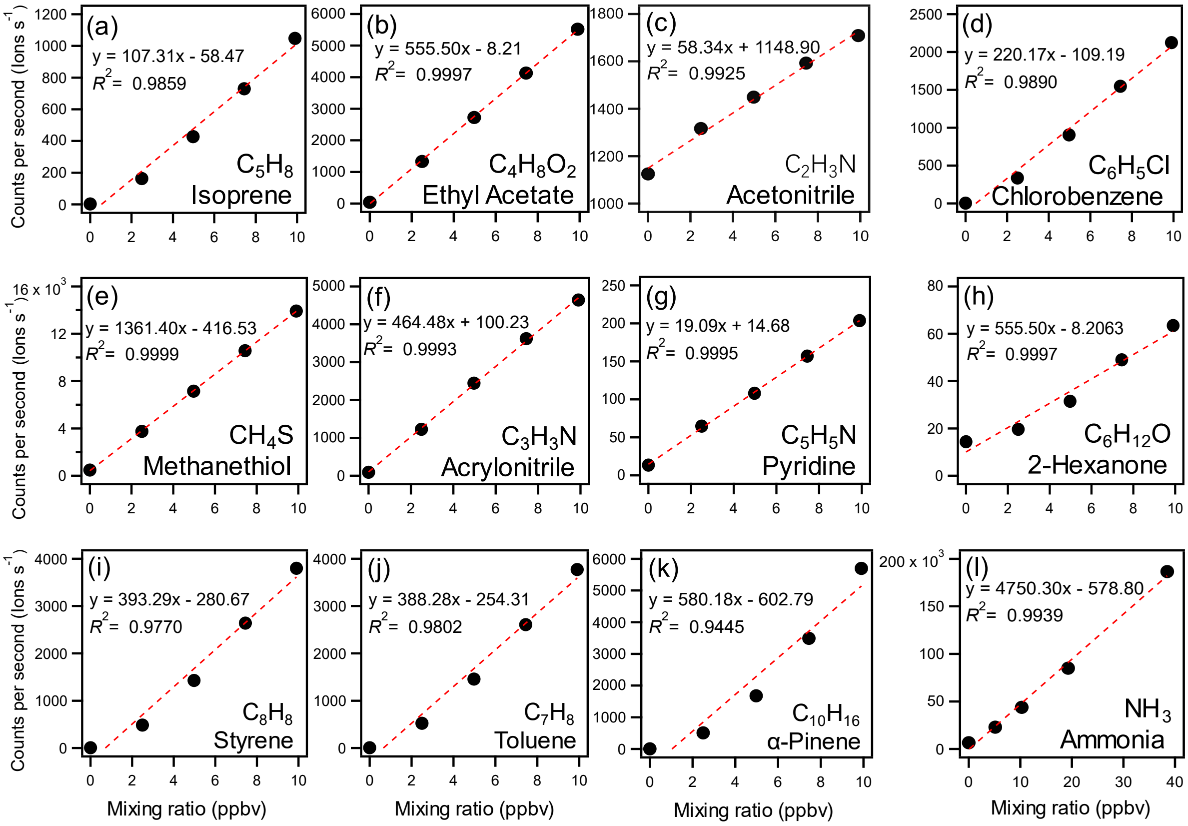


Figure 1. Laboratory calibration curves for (a-k) representative VOCs from a certified gas standard and (l) the key inorganic compound, NH_3. The VOCs were calibrated using the benzene reagent ion mode, while NH_3 was calibrated using the protonated acetone mode.

MC 2: *Figure 1: I suggest adding the plots for toluene and/or o-xylene (representing the BTEX compound group) and α-pinene (representing a major forest VOC) from Figure S1 in the main manuscript. There appears to be sufficient space for three additional plots in the current layout. This would emphasize the relevance and suitability of the proposed instrument for* *environmental research and enhance transparency by including examples with lower, yet still satisfactory linearity.*

Response:

Agree. We have redesigned Figure 1 (see revised Figure 1 above) to include the calibration curves for Styrene, Toluene, and α-pinene, which were previously located in Figure S1. The caption and related text have been updated accordingly.

MC 3: *Lines 196 – 201: Since the calibration curves for ethylamine and dimethylamine are quite distinct, how would you calculate and report the sum of C2-amines? And how does this improve the quantification of an unknown mixture of both analytes?*

Response:

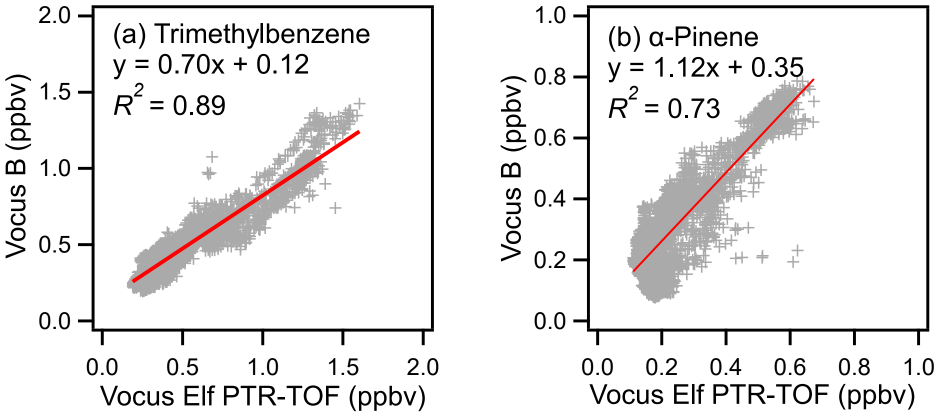
This is an inherent challenge in time-of-flight mass spectrometry without chromatographic separation of the isomers, such as ethylamine and dimethylamine. In our study, we determined the individual sensitivities for both ethylamine and dimethylamine (as shown in Figure 2). When reporting the sum as "C2-amines" for ambient data, we apply an average sensitivity factor derived from the two isomers. While this introduces a degree of uncertainty (approximately ±20-30% based on the slope difference) depending on the actual mixing ratio of the isomers in the air, it provides a "best estimate" total concentration. This approach improves quantification over previous studies that might arbitrarily apply the sensitivity of just one isomer to the total signal.

We have added a sentence in Section 3.1 (around Line 201) clarifying that the "C2-amines" concentration is calculated using the average sensitivity of the two isomers, and we have explicitly acknowledged the uncertainty introduced by the unknown isomeric ratio in ambient samples.

MC 4: *Figure 4: Were the other VOCs also measured with the Vocus Elf PTR-TOF-MS? If so, did you also observe good agreement with the Vocus B data?*

Response:

Yes, the Vocus Elf PTR-TOF measures a wide range of VOCs. For abundant species (for example, a-Pinene and Trimethylbenzene shown below), we observed generally good agreement between the two instruments. However, the Vocus Elf has a much lower resolution and sensitivity compared to the Vocus B CI-TOF, making the comparison less reliable for trace-level species or those near the detection limit of the Elf. We chose to highlight DMF in Figure 4 because its unexpectedly high concentration provided a perfect signal-to-noise ratio for validation and because it was a key finding of the campaign.



A one-to-one ration scatter plots validating Trimethylbenzene (a) and a-Pinene (b) measurements via inter-comparison between co-located Vocus B and Vocus Elf PTR-TOF.

MC 5: *Figure 6: As you stated in lines 173-175, the calibration of highly corrosive, acidic gases is technically challenging. How robust are the results for HF, HCl and SO_2 in this use case? Especially the signals for SO_2 and HCl seem to show a comparably high fluctuation or noise.*

Response:

You are correct that the quantification of sticky, corrosive gases like HF and HCl carries higher uncertainty than standard VOCs. In this specific industrial simulation (FOUP), the “calibration” for these acids relied on relative transmission calculations and semi-quantitative response factors derived from Iodide-adduct thermodynamics, as generating stable dynamic standards for these acids at ppt levels is extremely difficult. The fluctuation and noise observed in Figure 6 are primarily due to the “sticky” nature of these molecules interacting with the FOUP surfaces and sampling lines, as well as the rapid 2-second time resolution used to capture the fast decay. We emphasize that for this application, the relative decay profile and the ability to detect the presence of outgassing in real time are the primary figures of merit, rather than absolute quantitative accuracy.

We have modified the text in Section 3.5 to clarify that the quantification of acidic species is semi-quantitative. We explicitly attribute the signal noise to the surface interactions (stickiness) of these acidic molecules and the high time resolution of the measurement.

Technical comments (TC):

TC 1: *Line 56: “… (PTR-MS)* ***are*** *highly effective …”*

Response:

Corrected accordingly.

TC 2: *Lines 158-168: I suggest to add the reference to Figure S1 here, since the calibration curves of aromatics are presented there.*

Response:

Thank you for the suggestion. We have cited the calibration curves in the Supplementary Information (Supplementary Figure S1) in the text. The citation appears at the end of the paragraph describing the calibrations (lines 163).“…Calibration results for additional VOCs are provided in Supplementary Figure S1…”

Response to Reviewer #2

General comment (GC):

The manuscript presents a detailed and comprehensive evaluation of the Vocus B CIMS for simultaneous measurement of volatile organic compounds (VOCs) and inorganic gaseous species. The study is generally well written and I recommend it for publication after addressing the following comments:

Response:

We thank Reviewer #2 for your recommendation and the insightful comments regarding the instrument’s operation and advantages. We have addressed the concerns as follows.

Specific comment 1:

One of the main advantages of the Vocus B is its ability to measure a wide range of VOCs using different reagent ions. While this study emphasizes the synchronous measurement of VOCs and inorganic species, primarily ammonia, it would be beneficial to include mass spectra for the three reagent ion modes.

Response:

We agree that showing the mass spectra helps visualize the all-in-one capability. We have added a new figure in the Supplementary Material (see attached figure in below and Figure S2) displaying representative mass spectra for the three reagent ion modes, highlighting the primary reagent ions and typical analyte peaks. We have referenced this figure in Section 2.1.

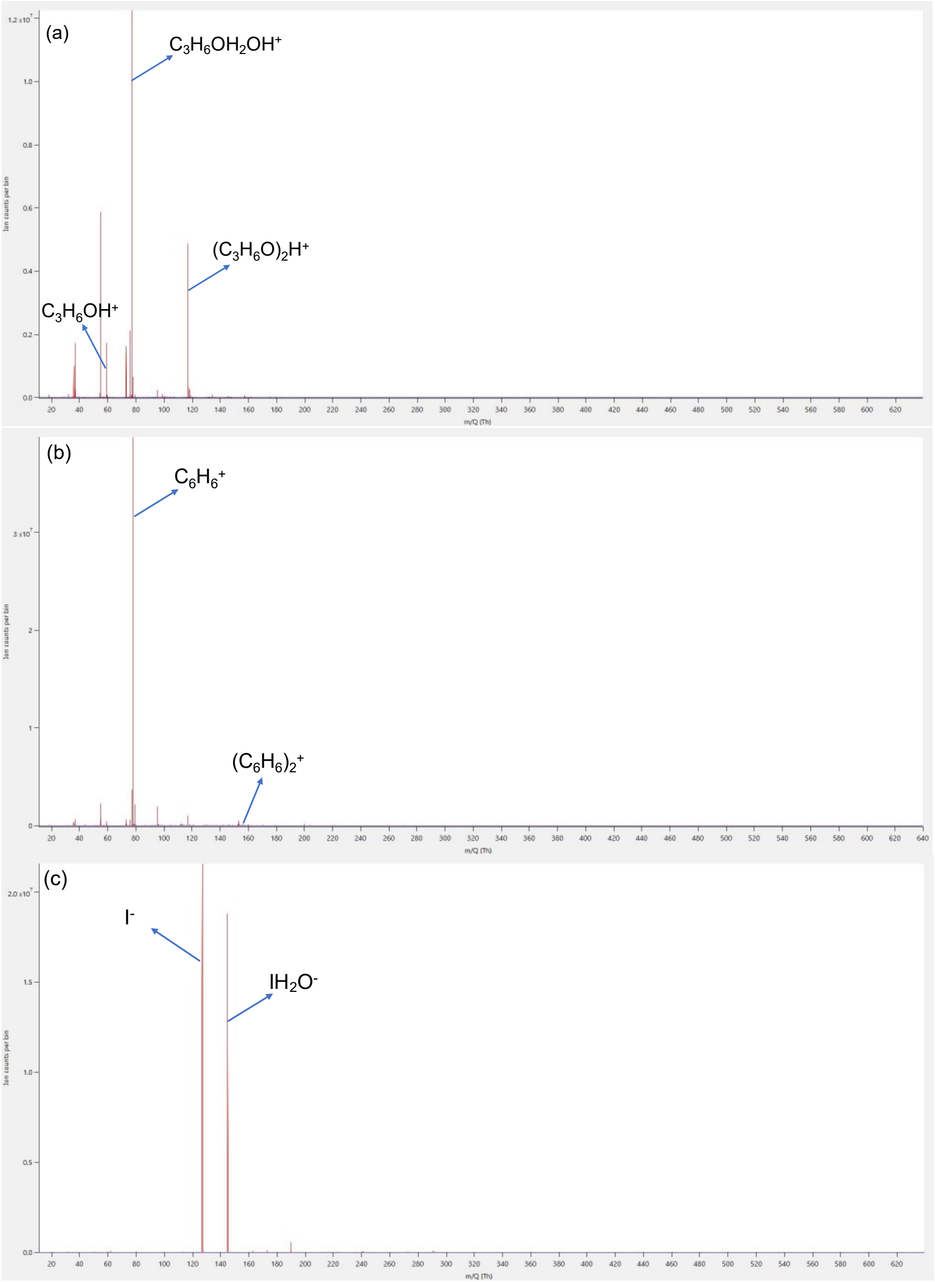


Figure S2. Representative mass spectra of three reagents, acetone (a), benzene (b) and iodine (c), in the ion mode, with the major reagent ion peaks labeled.

Specific comment 2:

A discussion on the advantages of measuring VOCs with the Vocus B compared to previous *versions of the instrument would be important. Specifically, it is challenging to assess whether the Vocus B offers a clear advantage in measuring ammonia when compared to a more compact and relatively lower-cost alternative, such as the Picarro instrument.*

Response:

The primary advantage of the Vocus B is not only that it measures ammonia better than the Picarro (which is indeed a gold-standard, specialized instrument), but also measures ammonia comparably very well while simultaneously measuring hundreds of VOCs and other VICs (such as acids like HCl, HNO_3 and HF) that the Picarro cannot detect. The clear advantage is the consolidation of three separate instruments (a standard PTR for VOCs, a specialized analyzer for NH_3, and a negative-ionization (I^-) CIMS for acids) into a single platform. Compared to previous Vocus versions, the Vocus B utilizes a new AIM reactor with a conical design that minimizes wall losses, which is critical for the fast response times required for sticky molecules like amines and ammonia, as demonstrated in our mobile measurements.

We have expanded the discussion in the Introduction (near Line 65) and Conclusion to explicitly state that the main advantage is the All-in-One versatility and the reduction of instrumental footprint/complexity, rather than superior performance for a single species compared to a specialized analyzer.

Revised Introduction: "...To overcome the need for such analytical compromises, here we introduce the Vocus B Chemical Ionization Time-of-Flight Mass Spectrometer (CI-TOF-MS)... **Unlike specialized analyzers (e.g., CRDS) that offer benchmark precision but are limited to single species, the Vocus B is engineered to provide a unified "all-in-one" solution.** This platform consolidates the capabilities of multiple separate analyzers by measuring both VOCs and VICs simultaneously with sub-second switching between optimized reagent ions. This significantly reduces the instrumental footprint and operational complexity while preserving the temporal correlation between chemically diverse species."

Revised Text:

"...It effectively addresses the long-standing analytical challenge of concurrently measuring VOCs and VICs. **While specialized techniques like CRDS remain the gold standard for ultimate precision of individual species like NH_3, the Vocus B offers a crucial advantage in versatility.** By successfully integrating the measurement of organic and inorganic compounds into a single platform, it minimizes the logistical burden and synchronization errors associated with deploying multiple separate instruments. The instrument's success across three distinct applications..."

Specific comment 3:

Additionally, a detail that seems to be missing is the cycling process between the three ionization modes. How long does the instrument operate in each mode? Could the authors clarify the time allocated to each mode in the cycling process?

Response:

We apologize for the omission. The instrument is capable of switching modes in under 500 ms. In the field campaigns presented here, we typically employed a cycle where the instrument dwelt in each mode for approximately 500 ms to 1 second, resulting in a total cycle time (and data resolution) of approximately 2 seconds (0.5 Hz) for the full suite of measurements.

We have added specific details about the duty cycle and dwell times used in our experiments to Section 2.1 (Materials and Methods).

Specific comment 4:

Furthermore, the calibration of VOCs was conducted using the benzene reagent ion mode. It would be helpful to know if the authors have also conducted calibration for VOCs using the other two reagent ion modes (Figure 1). This would allow for a comparison of results across the different modes and provide insight into the consistency of measurements.

Response:

While some VOCs can indeed be detected in positive Acetone and negative Iodide modes, the Benzene mode (Charge Transfer) is chemically optimized for the broad detection of non-polar and aromatic VOCs with the highest sensitivity. Therefore, we focused our calibration and quantification of VOCs on the Benzene mode. Calibrating all VOCs in all modes is not standard practice for this instrument, as we prioritize the data from the mode best suited for each compound class (Benzene for VOCs, Acetone for Amines/NH3, Iodide for Acids/Oxygenates).

Specific comment 5:

The term "volatile inorganic compounds" may not be entirely appropriate in this context. I suggest using "inorganic gaseous species" or another more specific term, especially since the focus in this study is primarily on ammonia.

Response:

We appreciate the reviewer's suggestion regarding terminology. Respectfully, we have decided to retain the term "Volatile Inorganic Compounds (VICs)" in this manuscript. Our reasoning is twofold:

First, the term "VICs" provides a direct and logical parallel to "VOCs" (Volatile Organic Compounds), which is the other main subject of this study. Using "VOCs and VICs" highlights that both groups are gas-phase constituents with comparable volatility that are being measured simultaneously by the same mass spectrometric technique.

Second, the abbreviation "VICs" significantly improves the flow and conciseness of the text, particularly when discussing the co-existence and interaction of organics and inorganics repeatedly throughout the manuscript.

We believe that in the context of this "All-in-One" instrument paper, this terminology effectively conveys the intended message.

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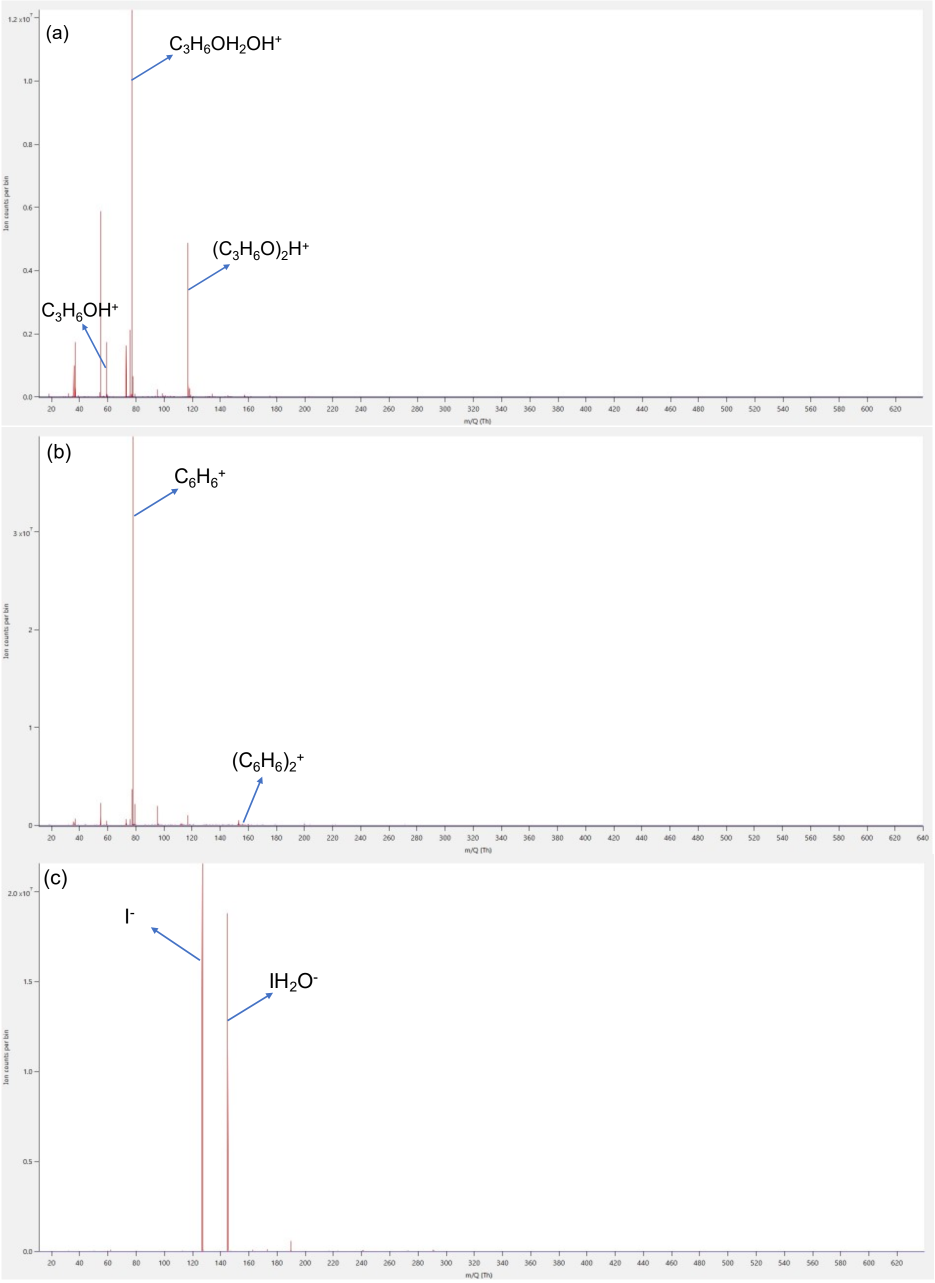

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