Deployment and evaluation of an NH$_4^+$/$\text{H}_3\text{O}^+$ reagent-ion switching chemical ionization mass spectrometer for the detection of reduced and oxygenated gas-phase organic compounds

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Abstract. Reactive organic carbon (ROC) is diverse in its speciation, functionalization, and volatility, with varying implications for ozone production and secondary organic aerosol formation and growth. Chemical ionization mass spectrometry (CIMS) approaches can provide in situ ROC observations and the CIMS reagent-ion controls the detectable ROC species. To expand the range of detectable ROC, we describe a method for switching between the reagent-ions NH$_4^+$ and H$_3$O$^+$ in a Vocus chemical ionization time-of-flight mass spectrometer (Vocus-CI-ToFMS). We describe optimization of ion-molecule reactor conditions for both reagent-ions, at the same temperature, and compare the ability of NH$_4^+$ and H$_3$O$^+$ to detect a variety of volatile organic compounds (VOCs), semi-volatile, and intermediate volatility organic compounds (S/IVOCs) including oxygenates and organic sulfur compounds. Sensitivities are comparable to other similar instruments (up to $\sim$5 counts s$^{-1}$ ppt$_v^{-1}$) with detection limits on the order of 1-10 s of ppt$_v$. We deploy NH$_4^+$/$\text{H}_3\text{O}^+$ reagent-ion switching in a rural pine forest in central Colorado, US, and report a method for characterizing and filtering periods of hysteresis following each reagent-ion switch. We use our ambient measurements to compare the capabilities of NH$_4^+$ and H$_3$O$^+$ in the same instrument, without interferences from variation in instrument and inlet designs. We find that H$_3$O$^+$ optimally detects reduced ROC species with high volatility, while NH$_4^+$ improves detection of functionalized ROC compounds, including organic nitrates and oxygenated S/IVOCs that are readily fragmented by H$_3$O$^+$.

1 Introduction

Tropospheric aerosol formation, oxidant reactivity, and ozone production are driven by the molecularly diverse pool of atmospheric reactive organic carbon (ROC; all organic species excluding methane) (Heald and Kroll, 2020). Speciation of atmospheric ROC is an ongoing analytical challenge (e.g., Goldstein and Galbally, 2007; Hunter et al., 2017), especially at time resolutions relevant to atmospheric mixing and chemistry. While reduced volatile organic compounds (VOCs, with saturation vapor concentration, $C^*$, $> 3 \times 10^6$ µg m$^{-3}$) are an important fraction of ROC, functionalized species with lower volatility (semi-volatile and intermediate volatility organic compounds, S/IVOCs with $C^*$ between 0.3 and $3 \times 10^6$ µg m$^{-3}$) are major contributors to ozone production and aerosol formation (e.g., Xu et al., 2021; Heald and Kroll, 2020; Bianchi et al., 2019; Donahue et al., 2011). For example, near comprehensive measurements of ROC at a forested site showed that S/IVOCs contribute approximately one third of ·OH-reactivity and potential secondary organic aerosol production (Hunter et al., 2017). Further,
semi-volatile and oxygenated VOCs contribute to marine secondary aerosol formation (Burkart et al., 2017; Mungall et al., 2017; Croft et al., 2019, 2021), and oxygenated species such as furans contribute significantly to ·OH-reactivity and aerosol production in wildfire plumes (Xu et al., 2021). In many urban environments, volatile chemical products and other classes of IVOCs make a growing contribution to aerosol and ozone production (Coggon et al., 2021; Zhao et al., 2014b). However, owing to limitations in analytical techniques, and partitioning to inlet and instrument surfaces (Deming et al., 2019; Pagonis et al., 2019), oxygenated and otherwise functionalized S/IVOCs are often unmeasured.

Chemical ionization mass spectrometry (CIMS) represents a family of analytical techniques applied to detect and characterize organic and inorganic trace gases in whole air at high time resolution (e.g., Zhang et al., 2023; Yuan et al., 2017; Huey, 2007). The choice of reagent-ion determines the scope of the measurement in terms of ROC functionality and chemistry, while instrument construction and design impacts the range of detectable species in terms of volatility and reactivity (e.g., Riva et al., 2007). The choice of reagent-ion determines the scope of the measurement in terms of ROC functionality and chemistry, while instrument construction and design impacts the range of detectable species in terms of volatility and reactivity (e.g., Riva et al., 2019; Krechmer et al., 2018). A range of reagent-ions are in common use and are selective toward specific ROC classes. Oxygenated, multi-functional organic gases can be detected as negative ions using iodide (I−/(H2O)n, I−) (Lee et al., 2018, 2014), acetate (CH3O−) (Brophy and Farmer, 2015; Roberts et al., 2010), CF3O− (Crounse et al., 2013, 2006), sulfur hexafluoride (SF6) (Nah et al., 2018; Huey, 2007), nitrate (NO3−) and bromide (Br−) (Rissanen et al., 2019; Bianchi et al., 2019) reagent-ions. Highly oxygenated organic species (with C+ \* 0.3 \times 10^6 \ \mu g \ \text{m}^{-3}), together with low volatility inorganic species (e.g., H2SO4), can be detected with nitrate and bromide ionization at ambient pressure (Bianchi et al., 2019; Rissanen et al., 2019; Riva et al., 2019). CF3O− effectively detects organic peroxides (Crounse et al., 2013, 2006), while I−, Br−, NO3− and SF6 detect a range of polar and acidic gases (Riva et al., 2019; Lee et al., 2018, 2014). Reduced VOCs, small oxygenated VOCs (e.g., methanol, ethanol, acetone, acetaldehyde) and reduced sulfur compounds (e.g., dimethyl sulfide and methanethiol) are readily detected as positive ions via proton transfer with hydronium (H3O+) reagent-ions (e.g., Kilgour et al., 2022; Pagonis et al., 2019; Krechmer et al., 2018; Yuan et al., 2017). NO+ and O2+ allow detection of reduced VOCs, with proton affinities below that of water, that are generally not detectable with H3O+ (Jordan et al., 2009; Smith and Spanel, 2005). While H3O+ can detect functionalized VOCs, fragmentation is common and complicates the interpretation of mass spectra from complex samples (e.g., Coggon et al., 2024; Kilgour et al., 2024; Li et al., 2021; Pagonis et al., 2019; Yuan et al., 2017). To overcome some of the limitations induced by H3O+ ionization, fast separation techniques have been coupled to proton-transfer instruments (Claffin et al., 2021; Stockwell et al., 2021; Vermeuel et al., 2023b; Coggon et al., 2024; Kilgour et al., 2024), and other positive polarity reagent-ions have been applied to functionalized ROC. Benzene (C6H6) reagent-ions detect dimethyl sulfide, monoterpenes and sesquiterpenes with reduced fragmentation and higher selectivity compared to H3O+ (Kim et al., 2016). Water clusters (i.e., (H2O)nH+) can detect a small subset of species detected by H3O+, such as dimethyl sulfide, with high selectivity (Blomquist et al., 2010). An array of oxygenated, multi-functional compounds in the intermediate to semi-volatile range can be detected using ammonium reagent-ions (e.g., Xu et al., 2022; Khare et al., 2022; Muller et al., 2020; Hansel et al., 2018), which provide some overlap in the fractions of ROC detected by negative polarity reagent-ions such as I− and CF3O−.
recently shown that NH\textsuperscript{+}\textsubscript{4} ionization can detect organic nitrates (Xu et al., 2022), while laboratory studies have demonstrated detection of organic peroxides (Zhou et al., 2018) and peroxy radicals (Hansel et al., 2018). Selected ion flow tube mass spectrometry (SIFT-MS) studies show that NH\textsuperscript{+}\textsubscript{4} ions form the strongest associations with carbonyl groups, relative to other oxygenates (e.g., alcohols and ethers) (Adams 2003). However, the conditions under which reagent-ions form and ion-molecule reactions occur determine the dominant reagent-ion and ionization mechanism, which in turn controls the scope of detectable compounds and associated sensitivity. Possible reagent-ions include NH\textsubscript{4} \cdot X\textsuperscript{n+} (where X = H\textsubscript{2}O or NH\textsubscript{3} and n = 0, 1, 2, ...).

In practice, multiple reagent-ions can be present, with NH\textsubscript{4} \cdot H\textsubscript{2}O\textsuperscript{+} providing optimal sensitivity to oxygenated compounds (Xu et al., 2022). Reactions with neutral analytes occur through ligand switching (Reaction R1), where the evaporation of X promotes softer adduct formation compared to NH\textsubscript{4}\textsuperscript{+} alone (i.e., n = 0) (Xu et al., 2022; Canaval et al., 2019; Adams et al., 2003).

\[
\text{NH}_4 \cdot X^+ + A^+ \rightarrow A \cdot NH_4^+ + X
\]

Given an analyte, A, with larger NH\textsubscript{4}\textsuperscript{+} affinity (i.e., the negative enthalpy of the reaction: NH\textsubscript{4}\textsuperscript{+} + A \rightarrow A \cdot NH\textsubscript{4}\textsuperscript{+}; e.g., Xu et al. (2022)) than X, the ionization reaction (R1) is exothermic (Adams et al., 2003). Therefore, NH\textsubscript{4} \cdot X\textsuperscript{+} ligand switching reactions will proceed efficiently at or near the collision limit, with little importance of the reverse reaction unless reaction timescales are long or the reaction is endothermic (Xu et al., 2022; Zaytsev et al., 2019a). Reaction R1 is exothermic for the majority of oxygenates and multi-functional compounds (Xu et al., 2022; Adams et al., 2003; Canaval et al., 2019; Zaytsev et al., 2019a) (Table S1, Edward P. Hunter and Sharon G. Lias; Michael M. Meot-Ner (Mautner) and Sharon G. Lias)); however, ion-molecule reactor (IMR) conditions must be selected to promote pure ion chemistry, optimize sensitivity, and minimize fragmentation.

Many CIMS reagent-ions provide access to complementary fractions of ambient ROC, and combining multiple reagent-ions in a single CIMS instrument can provide several advantages. First, reagent-ion switching can maintain the benefits of selectivity afforded by specific reagent-ions, while expanding the number of detectable compounds. For example, H\textsubscript{3}O\textsuperscript{+} and NO\textsuperscript{+}/O\textsubscript{2} are combined in proton-transfer reaction (PTR) and SIFT-MS instruments to expand detection capabilities to a broad range of alkanes, alkenes, aromatics, and some oxygenated species (e.g., Agarwal et al., 2014; Smith and Spanel, 2005). Further, the combination of nitrate and bromide reagent-ions allows detection of a wide range of highly oxygenated molecules along with hydroperoxyl radicals, iodine compounds and sulfuric acid (He et al., 2023; Rissanen et al., 2019). Iodide, acetate and water cluster reagent-ions have been combined in laboratory studies, using repeated experiments rather than active reagent switching, to expand the range of detectable ROC (Aljawhary et al., 2013) and inform development of reaction mechanisms (e.g., Zhao et al., 2014a). Thus, combining reagent-ions can decrease the potentially large number of instruments required to characterize a broad range of ROC classes (e.g., Heald and Kroll, 2020). Second, combining reagent-ions in a single instrument allows for direct comparison between the fractions of ROC detected by each chemical ionization reagent (e.g., Zaytsev et al., 2019a). For example, rapid switching between iodide and the acid-selective acetate reagent-ion informs detection of organic acids with iodide (e.g., Brophy and Farmer, 2015). Switching between NH\textsubscript{4}\textsuperscript{+} and H\textsubscript{3}O\textsuperscript{+} has benefits for measuring both reduced VOCs and their early generation oxidation products (Zaytsev et al., 2019a, b), while also allowing a direct comparison between the
subsets of ROC detected by each reagent-ion without the complications associated with differing instrument and inlet design (e.g., Riva et al., 2019).

Ambient atmospheric observations with NH$_4^+$ adduct ionization CIMS have focused primarily on urban environments, where NH$_4^+$ ion chemistry allows detection of oxygenated VOCs from volatile chemical products (Xu et al., 2022; Khare et al., 2022). NH$_4^+$/$H_3O^+$ reagent-ion switching has so far been limited to laboratory experiments demonstrating feasibility of switching (Muller et al., 2020) and application following laboratory oxidation of VOCs and oxygenated VOCs (Zaytsev et al., 2019a, b).

We characterize NH$_4^+$/$H_3O^+$ reagent-ion switching using a Vocus Chemical Ionization Time-of-Flight Mass Spectrometer (Vocus-CI-ToFMS) using both laboratory standards and deployment at a rural forested site. We describe selection of ideal IMR conditions for NH$_4^+$/$H_3O^+$ reagent-ion switching, at the same temperature, with a focus on sensitivity, fragmentation, and prominence of competing ionization pathways. Using ambient reagent-ion switching data, we describe an approach to filter periods of impure ion chemistry, and once filtered, ambient observations allow us to directly compare the fractions of ambient ROC detected by $H_3O^+$ and NH$_4^+$. Our observations demonstrate that NH$_4^+$ is able to detect oxygenated and multi-functional biogenic ROC with both reduced fragmentation and higher selectivity compared to $H_3O^+$, illustrating a highly complimentary set of CIMS reagent-ions.

2 Methods and field site description

2.1 Instrument description

The Vocus-CI-ToFMS (Tofwerk AG and Aerodyne Research Inc.) is described in detail elsewhere (Krechmer et al., 2018), with a brief description supplied here. Two features differentiate the Vocus-CI-ToFMS from other chemical ionization or proton transfer reaction time-of-flight mass spectrometers. First, the Vocus-CI-ToFMS is equipped with a focusing ion-molecule reactor (fIMR) which consists of a radio-frequency only quadrupole oriented around a 10 cm long resistive glass tube (Krechmer et al., 2018). The fIMR focuses ions toward the center-line, reducing ion losses to the walls and promoting ion transmission into a quadrupole high pass mass filter (BSQ). Second, polyether ether ketone (PEEK) tubing is used to establish flow restriction between ambient pressure and the fIMR. The use of PEEK at the instrument inlet reduces interactions between sampled air and more absorptive surfaces which impact transmission of S/IVOCs into the fIMR (Deming et al., 2019). These modifications to the Vocus-CI-ToFMS improve the ability to detect both reduced and oxidized ROC (Riva et al., 2019). The Vocus-CI-ToFMS used in this study has a mass resolving power of $\sim$5000 m dm$^{-1}$, a mass range of $\sim$50-500 m/z, with a 25 kHz ToF extraction frequency and is equipped with a multi-port reagent-ion injection, current-regulated discharge ion source.

2.2 Reactor pressure and voltage gradient

The fIMR collision energy can be controlled in part by adjusting the conditions that impact the velocity, free path, and thermal energy of ions; axial voltage gradient, pressure, and temperature. The temperature must remain constant during reagent-ion switching to allow for switching on 15-minute timescales. This restricts control of collisional energy to adjustments of the
fIMR voltage gradient and pressure. To understand the impact that these parameters have on ion chemistry, we introduce a constant flow of dilute calibration standard while systematically changing the fIMR voltage gradient and pressure. We change the fIMR pressure in 0.1 mbar increments and hold it constant while we increase the fIMR front voltage by 10 V steps.

2.3 Sensitivity, detection limit, and fragmentation with standards

We calibrated 23 analytes from multi-component standardized gas cylinders (Apel-Riemer Environmental Inc.) to report sensitivities (counts s$^{-1}$ ppt$^{-1}$) and detection limits (3σ of the background with 1s integration). Backgrounds were obtained using a zero air generator (Sabio Model 1001). We investigate fragmentation of molecular ions using single component samples of trans-2-hexen-1-ol (96.5 %, Acros Organics, Lot: A0340603), β-cyclocitral (92.3 %, ThermoFisher, Lot: 10237632), 2-hexenal (97.5 %, Oakwood Products Inc., Lot: 098868J071), 2-hexanone (100 %, Oakwood Products Inc., Lot: 098350R22K), and 2-methyl-3-buten-2-ol (99.5 %, Oakwood Products Inc., Lot: 051281K14H). To calculate a molecular ion fraction, we average 15 s of 2 Hz data and fit peaks corresponding to molecular ions (i.e., $A \cdot H^+$ for $H_3O^+$ and $A \cdot NH^+_4$ for $NH^+_4$), identified fragments, and clusters then divide the molecular ion signal by the sum of all related peaks. fIMR conditions for $H_3O^+$ ionization during these experiments were 2.2 mbar, 60 °C, with a voltage gradient of 67.5 V cm$^{-1}$ and 3.1 mbar, 60 °C, with a voltage gradient of 60 V cm$^{-1}$ for $NH^+_4$.

2.4 Signal response to ambient relative humidity

To test the effect of relative humidity on sensitivity we varied the ratio of wet and dry flows (controlled with mass flow controllers, MKS Instruments Model 1179C Mass-Flo) to achieve a range of relative humidities. The relative humidity was measured inline (Omega Engineering Model HX71-V1). Downstream of the relative humidity measurement 10 cm$^3$ min$^{-1}$ (STP) of a certified gas standard (Apel-Riemer Environmental Inc. and Airgas for dimethyl sulfide) was added to the humidified flow before being sampled to the Vocus-CI-ToFMS. Measurements alternated between elevated relative humidity and dry conditions, such that each measurement at elevated humidity could be directly compared to a dry (0 % RH) measurement immediately before.

2.5 Manitou experimental forest observatory

We deployed a Vocus-CI-ToFMS in Manitou Experimental Forest Observatory (MEFO) from September 3rd to September 24th of 2021. MEFO is a rural ponderosa pine forest at middle elevation (∼2,300 m) located ∼40 km northwest of Colorado Springs and ∼70 km southwest of Denver (39.1006°N, 105.0942°W). The ROC composition at this site is well characterized with emissions dominated by local biogenic sources (Hunter et al., 2017; Vermeuel et al., 2023a; Riches et al., 2024; Link et al., 2024). A full description of the field site can be found in Ortega et al. (2014). The Vocus-CI-ToFMS sample inlet was ∼4 m of 0.25 inch outer diameter perfluoroalkoxy (PFA) tubing situated ∼4 m above ground. The inlet flow was ∼3.8 L min$^{-1}$ (i.e., 2.9 L min$^{-1}$ (STP)) pulled by a flow restricted bypass pump resulting in a laminar flow inlet (Reynolds number of ∼1150) corresponding to a residence time of ∼0.7 s. The Vocus-CI-ToFMS sub-sampled 93-100 cm$^3$ min$^{-1}$ (i.e., 71 - 77 cm$^3$ min$^{-1}$
(STP)) perpendicular to the main inlet flow which helps prevent ambient aerosol clogging the capillary inlet interface compared to a linear sub-sampling assembly (Jensen et al., 2023). We performed bi-hourly, 3 minute instrument backgrounds with ultra zero air (Airgas, UZA grade) followed by a 1 minute, single-point calibration with a certified calibrant mixture (Apel-Riemer Environmental Inc.) for both reagent-ions.

### 2.5.1 $\text{NH}_4^+$ and $\text{H}_3\text{O}^+$ instrument conditions

The Vocus-CI-ToFMS switched between $\text{NH}_4^+$ and $\text{H}_3\text{O}^+$ ionization on 15-minute time intervals during the deployment in MEFO. fIMR conditions for $\text{H}_3\text{O}^+$ ionization were 2.5 mbar, 60 °C, with a voltage gradient of 62 V cm$^{-1}$; and for $\text{NH}_4^+$ ionization were 3.1 mbar, 60 °C, with a voltage gradient of 65 V cm$^{-1}$. The fIMR settings correspond to $E/N$ values of 114 Td and 96 Td for $\text{H}_3\text{O}^+$ and $\text{NH}_4^+$ respectively. fIMR parameters for both reagent-ions were informed by experiments detailed in Sect. 3.1.

When using $\text{H}_3\text{O}^+$ ionization, we inject 20 cm$^3$ min$^{-1}$ (STP) from the head-space above ultra high purity water (Millipore-Sigma, OmniSolv LC-MS) under vacuum into the discharge ion source. When switching to $\text{NH}_4^+$ ionization, we further add a flow from the head-space above a $\sim$1 w/w% solution of ammonium hydroxide (Oakwood Products Inc., Trace Metals Grade) in water to the ion source. Additionally, when switching between reagent-ions the voltages and pressure in the fIMR and the ion optics are adjusted to compliment each reagent-ion, taking into account sensitivity, fragmentation, and purity of ionization chemistry; this is discussed in Sect. 3.1. A change between ionization modes results in hysteresis, where the ion chemistry is impure, the filtering of hysteretic periods is discussed in Sect. 3.4.

### 2.6 Data analysis

Raw mass spectra data were collected with Acquility (version 2.3.18) and ToFDAQ (version 1.99) (Tofwerk AG) and processed in Tofware (version 3.2.5, Tofwerk AG and Aerodyne Research Inc.). For MEFO data, the time resolution was pre-averaged from 1 Hz to 0.1 Hz. All data was mass calibrated, baseline subtracted, and peak fit in Tofware. Time-integrated high resolution ion signals were exported for further analysis in python (version 3.9.12). Responses in the $E/N$ scans in Sect. 3.1 were interpolated using a linear interpolation on a triangular grid (using matplotlib.tri.LinearTriInterpolator). $C^*$ values are estimated using EPI Suite (US EPA).
Figure 1. (a-d) Contour plots of fIMR pressure and voltage gradient scans with a constant concentration of analyte (10 ppb) introduced into the Vocus-CI-ToFMS. Normalized signal intensity for (a) methyl ethyl ketone measured with NH$_4^+$(C$_4$H$_8$O·NH$_4^+$) and (b) α-pinene measured with H$_3$O$^+$(C$_{10}$H$_{16}$·H$^+$). (c) Fractional contribution of the NH$_4^+$ molecular ion (C$_{10}$H$_{16}$·NH$_4^+$) to the total α-pinene signal (i.e., the sum of the proton transfer product (C$_{10}$H$_{16}$·H$^+$) and the molecular ion). (d) Fractional contribution of the H$_3$O$^+$ molecular ion (C$_{10}$H$_{16}$·H$^+$) to the total α-pinene signal (i.e., the sum of the α-pinene fragment (C$_6$H$_8$·H$^+$) and the molecular ion). Contour plots of calculated $E/N$ values over the scanned space for both (e) NH$_4^+$ and (f) H$_3$O$^+$. 
3 Results and discussion

3.1 Ion-molecule reactor pressure and voltage gradient

$\text{H}_3\text{O}^+$ and $\text{NH}_4^+$ ionization operate optimally at differing combinations of fIMR pressure, voltage gradient, and temperature (Xu et al., 2022; Gouw and Warneke, 2007), all of which impact the reduced electric field ($E/N$) of the fIMR:

$$E/N = \frac{T \times \Delta V \times k_B}{l_{imr} \times p}$$

(1)

Where $T$ is the temperature (kelvin), $\Delta V$ is the difference between the front and back voltage (volts), $l_{imr}$ is the fIMR length (meters), $k_B$ is the Boltzmann constant (joules per kelvin), and $p$ is pressure (pascals or joules per cubic meter). $E/N$ has units of townseonds (Td, $1 \text{Td} = 1 \times 10^{-17} \text{V cm}^2$) and describes ion velocity and collisional energy. High $E/N$ values promote increased fragmentation and reduced clustering while low $E/N$ values promote cluster formation and reduced fragmentation. We analyzed relative sensitivity, fragmentation, and prevalence of ionization pathways, while varying the fIMR pressure and voltage gradient with a constant temperature of 60°C (Fig. 1) to inform our selection of fIMR settings.

Selecting $\text{H}_3\text{O}^+$ ionization fIMR parameters requires balancing fragmentation and sensitivity. We observe a large increase (>60 % at 2.4 mbar) in the sensitivity to the molecular ion ($\text{C}_{10}\text{H}_{16} \cdot \text{H}^+$) with increased fIMR voltage gradient (Fig. 1b) which arises from three main factors. First, reduced residence time with increased voltage gradient (163 µs or 113 µs at 45 V cm$^{-1}$ or 65 V cm$^{-1}$ respectively with pressure and temperature of 2.4 mbar and 333.15 K) could increase ion transmission through the fIMR. Second, at low $E/N$ protonated water clusters contribute to ionization of $\alpha$-pinene, evident from the reduced benzene sensitivity at lower $E/N$ (Fig. A1) (Gouw and Warneke, 2007). Water clusters have a higher proton affinity (i.e., the negative enthalpy of the reaction: $\text{H}^+ + \text{A} \rightarrow \text{A} \cdot \text{H}^+$) compared to water (Hunter and Lias, 1998), and $\alpha$-pinene has a higher proton affinity than both water and the first water cluster (i.e., (H$_2$O)$_2$), making ionization reactions with both exothermic. In contrast, benzene has a proton affinity higher than water but lower than the first cluster, making the ionization reaction of benzene with (H$_2$O)$_2$H$^+$ endothermic and unlikely. Therefore the formation of water clusters will reduce the sensitivity to benzene while increasing the sensitivity to $\alpha$-pinene. Third, the known $\text{H}_3\text{O}^+$ $\alpha$-pinene fragment, $\text{C}_6\text{H}_8 \cdot \text{H}^+$ has a larger contribution to the total $\alpha$-pinene signal at higher $E/N$ (Fig. 1d) which suggests that part of the increased sensitivity to $\text{C}_{10}\text{H}_{16} \cdot \text{H}^+$ at higher pressures is also attributable to reduced loss to fragmentation. The combined responses of transmission, fragmentation, and proton affinity to changes in voltage and pressure with $\text{H}_3\text{O}^+$ ionization result in a sensitivity that does not follow $E/N$ directly (Fig. 1b & 1f).

Selecting $\text{NH}_4^+$ ionization fIMR parameters requires balancing between signal intensity and purity of ion chemistry. Similar to $\text{H}_3\text{O}^+$, with $\text{NH}_4^+$ we observe increased signal intensity of the methyl ethyl ketone molecular ion ($\text{C}_4\text{H}_8\text{O} \cdot \text{NH}_4^+$) at higher voltage gradients (Fig. 1a). In contrast to $\alpha$-pinene detection with $\text{H}_3\text{O}^+$, sensitivity to $\text{C}_4\text{H}_8\text{O} \cdot \text{NH}_4^+$ is not impacted by fragmentation and changing reagent-ion proton affinity across the range in voltage gradient. The sensitivity to the $\text{C}_4\text{H}_8\text{O} \cdot \text{NH}_4^+$ ion is highest at high $E/N$, but the change in sensitivity is mostly dependent on the voltage gradient and is less impacted by the fIMR pressure (Fig. 1a). We observe a similar trend for other oxygenated ROC species (Fig. A2). The vertical contours in the $\text{NH}_4^+$ sensitivity contrasted with the L-shaped contouring in the $\text{H}_3\text{O}^+$ sensitivity (Fig. 1a & 1b) supports the
three-factor dependence for $\text{H}_3\text{O}^+$ on transmission, fragmentation, and proton affinity, and points to transmission as the major factor impacting sensitivity with $\text{NH}_4^+$ ionization. However, at high $E/N$ we observe impurities in the ionization chemistry (i.e., proton transfer products ($\text{A} \cdot \text{H}^+$) occurring for $\alpha$-pinene) with $\text{NH}_4^+$ ionization (Fig. 1c). Proton transfer ionization under $\text{NH}_4^+$ is undesirable because it provides lower selectivity, leads to higher fragmentation rates compared to the ligand-switching mechanism, and complicates interpretation of the mass spectrum. $\alpha$-pinene has a lower ammonium affinity than $\text{H}_2\text{O}$ (Canaval et al., 2019) which makes the ligand switching reaction (R1) endothermic and thus dependent on increased collisional energy at higher voltage gradients (Xu et al., 2022). We observe a larger contribution of the proton transfer product at higher $E/N$, which is consistent with electric field-induced production of $\text{C}_{10}\text{H}_{16} \cdot \text{H}^+$ through internal proton transfer (Xu et al., 2022). Alternatively, it is also possible that $\text{C}_{10}\text{H}_{16} \cdot \text{H}^+$ production is enhanced by declustering of the $\text{NH}_4^+ \cdot \text{H}_2\text{O}$ ions to form $\text{NH}_4^+$ which is more likely to undergo proton transfer reactions directly, without the need for internal proton transfer, due to the lower proton affinity of $\text{NH}_3$ compared to $\alpha$-pinene (Canaval et al., 2019). Regardless of the mechanism, formation of proton transfer products is ideally avoided and we find that their production is minimized at low $E/N$ (Fig. 1c). We note that the formation of secondary clusters (i.e., $\text{NH}_4 \cdot \text{H}_2\text{O} \cdot \text{A}^+$ and $\text{NH}_4 \cdot \text{NH}_3 \cdot \text{A}^+$) is negligible over the entire investigated $E/N$ space (Fig. S1 & S2). The sensitivity to methyl ethyl ketone, and prevalence of undesirable reaction products ($\text{C}_{10}\text{H}_{16} \cdot \text{H}^+$) are optimal under opposing conditions in the voltage gradient-pressure space, such that optimal fIMR parameters for $\text{NH}_4^+$ require a compromise between sensitivity and purity of ionization chemistry.
Figure 2. Sensitivities (bottom) and detection limits (top, log y-axis) for the Vocus-CI-ToFMS with NH$_4^+$ ionization (orange) and H$_3$O$^+$ ionization (blue) for 23 analytes from standardized gas cylinders, grouped by functional group/compound type. Sensitivities and detection limits (DLs) are calculated for the molecular ion only (i.e., $A \cdot$ NH$_4^+$ for NH$_4^+$, or $A \cdot$ H$^+$ for H$_3$O$^+$), and mass spectral fragments are not included. DL are calculated as 3 $\sigma$ over a 600 second background at 1 Hz.
Figure 3. Molecular ion fraction and the contribution of various non-molecular ions for 5 analytes using $\text{H}_3\text{O}^+$ ionization (blue/left) and $\text{NH}_4^+$ ionization (orange/right). The contribution of the molecular ion is highlighted with a scatter plot and uncertainty bars are standard deviation across 30 mass spectra at 2 Hz.
3.2 Sensitivities, detection limits, and fragmentation

Direct calibrations demonstrate the selectivity of NH$_4^+$ relative to H$_3$O$^+$ ionization for a range of carbonyls, hydrocarbons, alcohols, and organic sulfur compounds (Fig. 2). We observe that H$_3$O$^+$ is capable of detecting nearly every compound in this set of analytes from standardized gas cylinders at the molecular ion, which demonstrates the utility of H$_3$O$^+$ as a general reagent-ion that allows for detection of reduced and some oxidized species. In contrast, NH$_4^+$ ionization is more selective toward oxygenates, including saturated and unsaturated ketones, unsaturated aldehydes, and the multi-functional propane-1,2-diol. NH$_4^+$'s selectivity toward oxygenates demonstrates its utility for expanding the range of compounds detectable with a single instrument, and supporting identification of molecular ions and fragments detected simultaneously with H$_3$O$^+$. In addition, NH$_4^+$ does not detect aromatics, small alkenes, and reduced sulfur compounds that H$_3$O$^+$ detects well, demonstrating the complimentary nature of these reagent-ions. While Fig. 2 suggests that H$_3$O$^+$ detects dimethyl sulfoxide (DMSO), an oxidation product of dimethyl sulfide (Barnes et al., 2006), with a detection limit (DL) of 16 ppt,v, this DL is optimistic because DMSO peak separation is hindered by isobaric ions of protonated benzene and a protonated water cluster of acetic acid. We therefore expect that DMSO cannot be detected with H$_3$O$^+$ in the Vocus-CI-ToFMS at concentrations relevant to the marine boundary layer (i.e., <100 ppt,v, Putaud et al. (1999); Sciare et al. (2000); Legrand et al. (2001); Nowak et al. (2001)).

For the compounds detected with both ionization modes, sensitivities and detection limits for H$_3$O$^+$ and NH$_4^+$ are broadly comparable (Fig. 2 & A3). NH$_4^+$ detects the subset of ketones and the unsaturated aldehydes shown in Fig. 2 with a lower or similar DL to H$_3$O$^+$. Propane-1,2-diol, trans-3-hexenol, and D5-siloxane suggest that NH$_4^+$ has a greater ability than H$_3$O$^+$ to detect oxygenated and functionalized compounds, but this is not broadly apparent across the families of compounds we calibrated directly (Fig. 2). This likely arises because the analytes shown in Fig. 2 are limited to compounds amendable to gas cylinder calibration, and are therefore biased toward VOCs and S/IVOCs with minimal oxygenation and relatively high volatility (i.e., $C^*$ > 9 × 10$^4$ µg m$^{-3}$; Table S2). Despite the compromises in the FMR temperature made to allow for the switching system (Sect. 3.1) the sensitivities for NH$_4^+$ ionization reported here are similar to the sensitivities reported in recent NH$_4^+$ literature (Khare et al., 2022; Xu et al., 2022) (Table S3).

Compared to H$_3$O$^+$ ionization, NH$_4^+$ ionization reduces molecular ion fragmentation for functionalized compounds (Fig. 3). We use a molecular ion fraction (Fig. 3; ratio of the molecular ion signal to the total signal from the molecular ion, fragments, and clusters) to analyze the contributions of molecular ions and mass spectral fragments from both NH$_4^+$ and H$_3$O$^+$ ionization for a series of analytes complimentary to those calibrated with standardized gas cylinders (Fig. 2). Alcohols fragment substantially using both reagent-ions; with H$_3$O$^+$, trans-2-hexenol fragments almost completely away from the molecular ion resulting in a near zero molecular ion fraction. This is consistent with the negligible sensitivity to the similarly structured trans-3-hexenol molecular ion (Fig. 2) with H$_3$O$^+$ owing to fragmentation (e.g., Pagonis et al., 2019). In contrast, NH$_4^+$ ionization detects trans-2-hexenol with a molecular ion fraction of 0.67. For the tertiary alcohol, 2-methyl-3-buten-2-ol, (2,3,2-MBO), we observe substantial fragmentation with both ionization modes, but a higher molecular ion fraction under NH$_4^+$ (i.e., 0.31 with NH$_4^+$ and 0.19 with H$_3$O$^+$). The ketone and aldehydes sampled only fragmented substantially under H$_3$O$^+$ ionization, while NH$_4^+$ retains the molecular structure leading to high molecular ion fraction. This is consistent with the lower NH$_4^+$
detection limit for the majority of ketones we examined (with the exception of 2-octanone) and the aldehyde trans-2-hexenal (Fig. 2). Our observations suggest that reduced fragmentation has a larger impact on sensitivity between the two reagent-ions for more highly oxidized compounds with multiple functional groups. This is observed for propane-1,2-diol which is readily detected with NH$_4^+$ but not with H$_3$O$^+$. Overall, these observations demonstrate the high selectivity of NH$_4^+$ ionization for oxygenates and the benefits of reduced fragmentation with NH$_4^+$. Coupling the detection of reduced ROC and organic sulfur from H$_3$O$^+$ with the detection of oxygenates from NH$_4^+$ expands the fraction of atmospheric ROC that we can detect with a single instrument.
Figure 4. Signal dependence on sample relative humidity for NH$_4^+$ (top, orange), and H$_3$O$^+$ (bottom, blue). Measurements were made at relative humidities of 15, 30, 50, 70, and 85 %; points are offset from these values for visibility. Ethanol, benzene, m-xylene, and 1,2,4-trimethylbenzene are excluded for NH$_4^+$ due to low signal. Acetonitrile and ethanol are omitted for H$_3$O$^+$ due to low transmission through the BSQ. Methyl ethyl ketone is omitted for H$_3$O$^+$ due to interference of the reagent-ion cluster (H$_2$O)$_3$·H$^+$. The error bars represent propagated relative deviations in dry and humidified signals.
3.3 Impact of sample relative humidity

Previous studies have characterized the significant humidity dependence of sensitivity in various CIMS instruments to understand and correct for changing ambient humidity (e.g., Warneke et al., 2001; Gouw and Warneke, 2007; Kari et al., 2018; Zaytsev et al., 2019a). Humidity-driven changes in reagent-ion chemistry, and therefore sensitivity, are generally small in the Vocus-CI-ToFMS due to the large flow of water vapor (i.e., 20 cm$^3$ min$^{-1}$ (STP)) injected into the ion source (Krechmer et al., 2018; Khare et al., 2022). Varying sample humidity with constant analyte concentration demonstrates humidity independence with both NH$_4^+$ and H$_3$O$^+$ ionization across a range of reduced and oxygenated ROC (Fig. 4). Humidity independence of the Vocus-CI-ToFMS has been demonstrated previously for H$_3$O$^+$ for a variety of analytes (Krechmer et al., 2018; Kilgour et al., 2022; Li et al., 2024) and for a select number of small oxygenates, alkenes, and acetonitrile with NH$_4^+$ (Khare et al., 2022; Xu et al., 2022). We demonstrate humidity-independent sensitivity with NH$_4^+$ ionization under different instrumental conditions and for a selection of analytes including oxygenated alkenes and siloxanes (Fig. 4).
Figure 5. Ion signal after a reagent-ion switch for (a & b) \( \text{H}_3\text{O}^+ \) and (c & d) \( \text{NH}_4^+ \). We grouped ion signals by the time after a switch and normalized the mean of each group by the maximum, and normalized means were fit with a bi-exponential function. The derivative of the fit \( \delta_n \) is displayed on the right axes for (a-d) and used as a metric to filter reagent-ion hysteresis. (e) The number of seconds removed after a switch as a function of \( \delta_n \) threshold for various ions.
3.4 Removal of reagent-ion hysteresis from switching

Reagent-ion chemistry does not stabilize immediately upon switching between \( \text{NH}_4^+ \) and \( \text{H}_3\text{O}^+ \) ionization. This reagent-ion switch requires adjustment of instrument conditions that impact ion chemistry; these include the reagents introduced into the ion source, the fIMR pressure and voltage gradient, and downstream ion optic voltages. However, instrument conditions for each reagent-ion (Sect. 3.1) are such that analyte detection through the alternate ionization pathway is possible with both \( \text{NH}_4^+ \) and \( \text{H}_3\text{O}^+ \) ionization (e.g., Zaytsev et al., 2019a). This is in contrast to some other reagent-ion pairs (e.g., \( \text{CH}_3\text{O}_2^- \) and \( \text{I}^- \)) where instrument conditions differ drastically, and so hysteresis is not observed (e.g., Brophy and Farmer, 2015). As a result, when \( \text{NH}_4^+ \) and \( \text{H}_3\text{O}^+ \) are paired in a single instrument we observe a distinct transitional period of reagent-ion hysteresis following each reagent-ion switch. The hysteretic period arises from: (1) changes in ion transmission due to instrument conditions, such as ion optics and fIMR settings, which are fast (ones to tens of seconds), and (2) changes in the reagent-ion speciation due to the presence/absence of \( \text{NH}_3(g) \), which is slower (tens of seconds to minutes). Periods of hysteresis must be characterized and removed to ensure stable and consistent measurements without drifting sensitivities over the course of each 15-minute measurement period. We accomplish this by monitoring ion stability over a large number of repeated switches.

We compare the use of a reagent-ion signal and an \( \text{NH}_4^+ \)-analyte molecular ion signal as markers to quantify reagent-ion switching hysteresis (Fig. 5). We selected ions primarily measured with \( \text{NH}_4^+ \) ionization because the influence of \( \text{NH}_3(g) \) is observed under both \( \text{H}_3\text{O}^+ \) and \( \text{NH}_4^+ \) ionization modes, whereas the influence of \( \text{H}_2\text{O}(g) \) reagent-ions are not observed in \( \text{NH}_4^+ \) mode. This arises because \( \text{NH}_3(g) \) has a higher proton affinity than \( \text{H}_2\text{O}(g) \) (Hunter and Lias, 1998) which causes any \( \text{NH}_3(g) \) present in the ion source and fIMR to readily form \( \text{NH}_4^+ \) or \( \text{NH}_4 \cdot \text{H}_2\text{O}^+ \) at the expense of \( \text{H}_3\text{O}^+ \) formation. We follow \( \text{NH}_3(g) \) presence and stability by monitoring \( \text{NH}_4 \cdot \text{H}_2\text{O}^+ \) (i.e., the prominent ammonium reagent-ion signal) and \( \text{C}_3\text{H}_6\text{O} \cdot \text{NH}_4^+ \) (i.e., a ubiquitous analyte-ammonium molecular ion) under both ionization methods. Both \( \text{NH}_4 \cdot \text{H}_2\text{O}^+ \) and \( \text{C}_3\text{H}_6\text{O} \cdot \text{NH}_4^+ \) decay after switching to \( \text{H}_3\text{O}^+ \) ionization (Fig. 5a, b; \( \text{NH}_3(g) \) depletion in the fIMR) and intensify after switching to \( \text{NH}_4^+ \) ionization (Fig. 5c, d; \( \text{NH}_3(g) \) accumulation in the fIMR).

To compare the utility of \( \text{NH}_4 \cdot \text{H}_2\text{O}^+ \) and \( \text{C}_3\text{H}_6\text{O} \cdot \text{NH}_4^+ \) signals for filtering reagent-ion hysteresis, we grouped a total of 558 hours of ambient \( \text{NH}_4^+/\text{H}_3\text{O}^+ \) 15-minute reagent-ion switching observations (Sect. 2.5) by time after a reagent-ion switch. We normalized the mean signal (in 10 second intervals starting at 5 seconds into a switch) to the maximum and fit the normalized data with a bi-exponential function (Fig. 5). The bi-exponential function describes changes in both instrument conditions (fast) and equilibration of \( \text{NH}_3(g) \) in the ion source and fIMR that drives reagent-ion chemical speciation (slow). We use the derivative of this decay function (\( \delta_n \)) to quantify a normalized rate of change in the ion signal as a function of the time after a switch (Purple lines in Fig. 5a-d). We use \( \delta_n \) to set a threshold for filtering hysteresis, removing data before \( \delta_n \) reaches the set threshold. \( \delta_n \) changes rapidly in the first \( \sim 100 \) s after a reagent-ion switch and slowly approaches but does not reach zero on the measurement timescale (900 s), likely due to the time scale for complete \( \text{NH}_3(g) \) equilibration with instrument surfaces.

Monitoring \( \text{NH}_4 \cdot \text{H}_2\text{O}^+ \) \( \delta_n \) has the benefit of being directly related to the abundance of reagent-ion; however, both the decay of \( \text{NH}_4 \cdot \text{H}_2\text{O}^+ \) in \( \text{H}_3\text{O}^+ \) ionization mode and its initial increase in \( \text{NH}_4^+ \) ionization mode is driven largely by changes...
in the BSQ mass range. We are able to avoid the impacts of changing BSQ mass range by monitoring an ion with higher m/z. Additionally, using an analyte for filtering reagent-ion hysteresis means that we are using a direct measurement of the formation of analyte ions for NH$_4^+$ ionization and a direct measurement of contamination from other reagent-ion chemistry with H$_3$O$^+$ ionization. For these reasons we decided to use the persistent ion C$_3$H$_6$O·NH$_4^+$ to monitor hysteresis. We acknowledge this choice brings the complication of varying ambient concentrations in time; however, due to the substantial averaging over a multi-week measurement period, normalized mean time variation over the 15-minute (900 s) acquisition time should be mainly due to changes in reagent-ion chemistry. Despite this, future iterations of this approach would benefit from applying our method on the signal from an internal standard infused into the sampling inlet.

The choice of $\delta_n$ threshold represents a compromise between ion chemistry stability and data loss. For both reagent and analyte ions, the amount of data removed becomes very sensitive to a small decrease in the $\delta_n$ threshold below $\sim$0.05 % s$^{-1}$ (Fig. 5e). A 0.05 % s$^{-1}$ threshold applied to C$_3$H$_6$O·NH$_4^+$ results in the loss of $\sim$185 s and $\sim$75 s of data per switch with H$_3$O$^+$ and NH$_4^+$ ionization, respectively. For 15-minute reagent-ion switching (Sect. 2.5.1), this corresponds to $\sim$14 % of all data being removed. This result is qualitatively similar to that suggested by Zaytsev et al. (2019a) for NH$_4^+$ and H$_3$O$^+$ switching in an Ionicon PTR3: $\sim$120 s and $\sim$60 s of data removed after switching to H$_3$O$^+$ and NH$_4^+$ ionization, respectively. The approach we describe here can be applied easily to other instruments and at different instrument conditions (e.g., fIMR temperature and pressure) to best balance the need for both measurement stability and data coverage.
Figure 6. Campaign mean mass defect plots for NH$_4^+$ and H$_3$O$^+$ ionization from deployment in MEFO. The NH$_4^+$ mass spectrum is displayed as a left half-circle and the H$_3$O$^+$ is displayed as a right half-circle. Points are sized by the average signal across the campaign divided by the detection limit signal (DL: 3σ of campaign zero air background). The reagent-ion masses have been removed from the ion molecular mass. The top 100 ions in terms of signal-to-DL ratio for both reagent-ions have been colored according to their molecular formulae with periods of reagent-ion hysteresis removed (Sect. 3.4).
Figure 7. Selected campaign average high resolution mass spectra for (a & b) monoterpene (C$_{10}$H$_{16}$) and (c & d) monoterpene oxygenate (C$_{10}$H$_{16}$O$_{3}$) molecular ions detected with NH$_4^+$ (a & c, orange) and H$_3$O$^+$ (b & d, blue).
3.5 reagent-ion comparison from ambient measurements

We compare the capabilities of NH$_4^+$ and H$_3$O$^+$ reagent-ions in a single instrument using ambient observations from MEFO (Sect. 2.5.1). Switching between H$_3$O$^+$ and NH$_4^+$ on a 15-minute timescale over the 21-day deployment allows us to directly compare the two reagent-ions in a predominantly biogenic environment (Hunter et al., 2017; Vermeuel et al., 2023a; Riches et al., 2024; Link et al., 2024). A single instrument approach avoids inlet and instrument design influences on detection that would otherwise complicate a direct reagent-ion comparison (e.g., Riva et al., 2019). Previously Zaytsev et al. (2019a) used a switching NH$_4^+/H_3O^+$ Ionicon PTR3 with a modified helical tripole reaction chamber to measure products from the ·OH initiated oxidation of 3-methylecatecol. This chamber study demonstrated the sets of compounds detected by each reagent-ion and concluded that NH$_4^+$ is able to detect larger, more functionalized molecules, while H$_3$O$^+$ is able to detect smaller organic molecules (Zaytsev et al., 2019a). To facilitate a direct and quantitative reagent-ion comparison, we use the ratio of campaign average ambient signal to detection limit signal (i.e., 3σ of the background) for each ion as a measure of the signal-to-noise ratio (Fig. 6). With the assumption that ambient concentrations measured with each reagent-ion over the campaign mean are equivalent, a higher signal-to-DL ratio also implies a lower detection limit. This analysis allows us to evaluate the relative capability of each reagent-ion without direct calibrations for multifunctional biogenic organic compounds (e.g., Hunter et al., 2017; Vermeuel et al., 2023a; Link et al., 2024).

NH$_4^+$ ionization detects oxygen-containing species with a higher signal-to-noise ratio than H$_3$O$^+$. At MEFO, four series of C$_n$H$_{2n}$O$_n$ ions dominate our mass spectrum (highlighted in Fig. 6): C$_{10}$H$_{16}$O$_n$, C$_{10}$H$_{14}$O$_n$, C$_{10}$H$_{18}$O$_n$, and C$_{5}$H$_8$O$_n$ which represent a mixture of biogenic terpenoid compounds and their early generation oxidation products. The C$_{10}$H$_{16}$O$_n$ and C$_{10}$H$_{14}$O$_n$ series suggest a mixture of primary emissions, such as citral (C$_{10}$H$_{16}$O; C$^*$ = 1 × 10$^6$ µg m$^{-3}$) and thymol or carvone (C$_{10}$H$_{14}$O; C$^*$ = 1 – 9 × 10$^5$ µg m$^{-3}$) (McKinney et al., 2011; Kaser et al., 2013; Vermeuel et al., 2023a), and oxidation products of other terpenoids. H$_3$O$^+$ detects the reduced C$_{10}$H$_{14}$ species with higher signal-to-noise compared to NH$_4^+$, with signal-to-DL ratios of 10.5 and 6.00, respectively. Similarly, H$_3$O$^+$ detects C$_{10}$H$_{16}$ with a signal-to-DL ratio of 23.5, compared to 14.3 for NH$_4^+$. Following this C$_{10}$H$_{16}$O$_n$ series, the n = 1 ion is detected with a signal-to-DL ratio of 6.31 with H$_3$O$^+$ and 10.8 with NH$_4^+$. The tendency toward increased signal-to-noise with oxygenation for NH$_4^+$ ionization continues in the C$_{10}$H$_{14}$O$_{12}$ series up to C$_{10}$H$_{14}$O$_3$ (with C$^*$ between 4 × 10$^2$ and 9 × 10$^3$ µg m$^{-3}$, Table S4). The C$_{10}$H$_{18}$O$_n$ series lacks a C$_{10}$H$_{18}$ ion and the distribution in the x-y scatter between the C$_{10}$H$_{16}$ and C$_{10}$H$_{18}$O peaks is bi-modal (Fig. S3), which suggests multiple paths to form C$_{10}$H$_{18}$O ions. These paths are likely (1) primary emissions of C$_{10}$H$_{18}$O terpenoid compounds with similar emission profiles to monoterpines and (2) water clusters formed with monoterpines (C$_{10}$H$_{18}$ · H$_2$O · H$^+$ and C$_{10}$H$_{18}$ · H$_2$O · NH$_4^+$). The C$_5$H$_8$O$_n$ series represents a combination of fragments, primary emissions and oxidation products.

The C$_5$H$_8$ ion is likely a mixture of isoprene and fragments from larger oxygenates and 2,3,2-MBO with both reagent-ions (e.g., Kilgour et al., 2024). Within the C$_5$H$_8$O$_n$ series, the C$_5$H$_8$ signal-to-DL ratio is larger than expected with NH$_4^+$ ionization; we suspect that this is due partly to fragmentation of other compounds into the C$_5$H$_8$ mass. The NH$_4^+$ sensitivity to isoprene is very low; however 2,3,2-MBO fragments substantially into C$_5$H$_8$ through dehydration of the tertiary alcohol group (Fig. 3). Fragmentation into C$_5$H$_8$ combined with a low background (Fig. A3 & S4) leads to a very large signal-to-DL ratio.
(Fig. 6). The C₅H₈O₃ and C₅H₈O₄ peaks are likely oxidation products of isoprene and 2,3,2-MBO, while C₅H₈O₂ is likely an isoprene oxidation product (Saunders et al., 2003; Jenkin et al., 2015).

NH₄⁺ can detect organic nitrates that easily fragment with H₃O⁺ (Aoki et al., 2007; Duncianu et al., 2017) and so often go undetected in ambient measurements with H₃O⁺ ionization (Fig. 6). Organic nitrates ionized with H₃O⁺ fragment to form nitric acid (HNO₃) or nitronium ions (NO₂⁺), where the loss of HNO₃ results in fragmentation into the masses for other oxygenates (Aoki et al., 2007). The two predominant series of organic nitrate ions (C₁₀H₁₅NO₄ and C₁₀H₁₇NO₅ with C⁺ down to 10s of µg m⁻³; Table S4) are generally detected with a higher signal-to-DL ratio with NH₄⁺ ionization compared to H₃O⁺ ionization, if the ion is detected with H₃O⁺ at all (Fig. 6). The exception is C₁₀H₁₅NO₃ which is detected at higher signal-to-DL (2.13) with H₃O⁺ ionization compared to NH₄⁺ (0.774); though this ion may arise from dehydration of hydroxy nitrates (i.e., C₁₀H₁₇NO₄·H₂O) and that H₃O⁺ is fragmenting larger organic nitrates into the C₁₀H₁₅NO₃ ion. The nitrates we observe are potentially a mixture of carbonyl, hydroxy, and peroxy nitrates derived from the oxidation of monoterpenes (C₁₀H₁₆) and potentially other terpenoid (C₁₀H₁₆O/C₁₀H₁₄O) precursors (Table S5, Fry et al., 2013; Jenkin et al., 2015; Faxon et al., 2018; Bates et al., 2022). Additionally, C₅H₁₁NO₅ and C₅H₉NO₅ are detected using both reagent-ions but both with higher signal-to-DL ratio with NH₄⁺. C₅H₁₁NO₅ is likely a nitrate from the oxidation 2,3,2-MBO while both 2,3,2-MBO and isoprene could form the C₅H₉NO₅ ion (Link et al., 2024).

NH₄⁺ ionization’s ability to detect oxygenated compounds with higher signal-to-noise ratio and lower detection limits than H₃O⁺ arises from two main factors. First, NH₄⁺ is a softer ionization method compared to H₃O⁺, resulting in less molecular ion fragmentation (Sect. 3.2). This is evident in our ambient data for the known H₃O⁺ monoterpane fragment, C₆H₈·H⁺ compared to the analogous fragment with NH₄⁺ ionization, C₆H₈·NH₄⁺. The fragment is present in NH₄⁺ ionization mode at a 1:10 fragment-to-molecular-ion ratio, compared to a 1:1 ratio with H₃O⁺ under our fIMR conditions (Fig. S3). Second, NH₄⁺ has higher selectivity toward oxygenates compared to H₃O⁺ (Sect. 3.2). Our ambient reagent-ion switching observations further demonstrate this selectivity (Fig. 7 & A3). The monoterpenes (C₁₀H₁₆) are easily distinguished from isobaric ions with both H₃O⁺ and NH₄⁺, but oxygenates (C₁₀H₁₆O₃) have multiple isobaric interferences with H₃O⁺ (Fig. 7). Both higher selectivity and reduced fragmentation contribute to fewer isobaric ions with NH₄⁺. While our observations demonstrate the utility of NH₄⁺ for detecting oxidized species that H₃O⁺ ionization struggles to detect (e.g., Yuan et al., 2017; Riva et al., 2019; Pagonis et al., 2019; Coggon et al., 2024), the extent of fragmentation for specific compounds is difficult to diagnose in ambient, and complex laboratory, mass spectra. Overall, our ambient reagent-ion comparison demonstrates quantitatively that NH₄⁺ is complementary to H₃O⁺, and together these two reagent-ions allow improved detection and identification of a range of biogenic reactive organic carbon compounds and their early generation oxidation products.

4 Conclusions

To expand the range of ROC detectable with a single chemical ionization instrument, we present an approach to combine two positive reagent-ions, NH₄⁺ and H₃O⁺, in a Vocus-CI-ToFMS. To accommodate the need for a constant ion-molecule reactor temperature during switching, we apply an E/N space scanning approach to select fIMR conditions compatible with
both reagent-ions. We characterize the ability of NH$_4^+$ and H$_3$O$^+$ to detect a range of reduced and oxygenated VOCs and S/IVOCs through analysis of laboratory standards and find that H$_3$O$^+$ detects reduced species well and fragments functionalized oxygenates away from the molecular ion, while NH$_4^+$ retains the molecular ion and allows for improved detection of oxygenates. We find that fragmentation generally correlated with $E/N$, while sensitivity is impacted by a combination of ion transmission, competing ionization pathways, and molecular ion fragmentation. Switching between reagent-ions results in a period of hysteresis which we characterize and filter using a ubiquitous analyte ion, C$_3$H$_6$O·NH$_4^+$. Optimizing ion chemistry stability, while preserving data coverage results in the loss of ~260 s of data on a reagent switching full cycle (1800 s), corresponding to ~86 % data retention for 15-minute switching intervals. We deploy our NH$_4^+/H_3$O$^+$ reagent-ion switching Vocus-CI-ToFMS during a 3-week period at a rural pine forest to facilitate a direct and quantitative comparison of the reagent-ions. Our ambient observations demonstrate that NH$_4^+$ detects oxygenated ROC with higher signal-to-noise and lower DL, including organic nitrates that H$_3$O$^+$ does not detect, while H$_3$O$^+$ detects reduced species that are undetectable with NH$_4^+$. NH$_4^+/H_3$O$^+$ reagent-ion switching takes advantage of the complimentary nature of the two reagent-ions to expand the range of ROC detectable with a single instrument.
Appendix A

![Normalized signal intensity for benzene measured with $\text{H}_3\text{O}^+ \cdot (\text{C}_6\text{H}_6 \cdot \text{H}^+)$ from pressure-voltage gradient scans.](https://doi.org/10.5194/egusphere-2024-1738)

**Figure A1.** Normalized signal intensity for benzene measured with $\text{H}_3\text{O}^+ \cdot (\text{C}_6\text{H}_6 \cdot \text{H}^+)$ from pressure-voltage gradient scans.
Figure A2. Normalized signal intensity for camphor (left), 2-octanone (middle), and trans-3-hexenol (right) measured with NH$_4^+$ (C$_{10}$H$_{16}$O·NH$_4^+$, C$_8$H$_{16}$O·NH$_4^+$, and C$_6$H$_{12}$O·NH$_4^+$ respectively).
Figure A3. Mass dependent campaign average detection limit signal for ions detected with NH$_4^+$ (orange) and H$_3$O$^+$ (blue). The reagent-ion masses have been removed from ion exact masses.
Author contributions. CLZ & MDW designed research, CLZ collected and analyzed field and laboratory data with significant input from MDW, CLZ & MDW wrote the manuscript.

Code and data availability. Data and python code required to regenerate figures are available at https://doi.org/10.7910/DVN/FL0CZM (Zang and Willis, 2024).

Competing interests. The authors declare no competing interests.

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