Deployment and evaluation of an NH_4^+/H_3O^+ 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_3O^+ in a Vocus chemical

5   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_3O^+ 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 ~ 5 counts s^{-1} ppt_v^{-1}) with detection limits on the order of 1-10 s of ppt_v. We deploy NH_4^+/H_3O^+ reagent-ion switching in a rural pine forest in central

10   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_3O^+ in the same instrument, without interferences from variation in instrument and inlet designs. We find that H_3O^+ 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_3O^+.

15   # 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

20   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 3×10^6 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,

25   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

30   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.,

35   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 ($I^-/(H_2O)_n \cdot I^-$) (Lee et al., 2018, 2014), acetate ($CH_3O_2^-$) (Brophy and Farmer, 2015; Roberts et al., 2010), CF_3O^- (Crounse et al., 2013, 2006), sulfur hexafluoride (SF_6^-) (Nah et al., 2018; Huey, 2007), nitrate (NO_3^-) and bromide (Br^-) (Rissanen et al., 2019; Bianchi et al., 2019) reagent-ions. Highly oxygenated organic species (with $C^* < 0.3 \times 10^6$ µg m^{-3}), together with low volatility inorganic species (e.g.,

40   H_2SO_4), can be detected with nitrate and bromide ionization at ambient pressure (Bianchi et al., 2019; Rissanen et al., 2019; Riva et al., 2019). CF_3O^- effectively detects organic peroxides (Crounse et al., 2013, 2006), while I^-, Br^-, NO_3^- and SF_6^- 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 (H_3O^+) reagent-ions (e.g., Kilgour et al., 2022; Pagonis

45   et al., 2019; Krechmer et al., 2018; Yuan et al., 2017). NO^+ and O_2^+ allow detection of reduced VOCs, with proton affinities below that of water, that are generally not detectable with H_3O^+ (Jordan et al., 2009; Smith and Spanel, 2005). While H_3O^+ 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 H_3O^+ ionization, fast separation techniques have been coupled to proton-transfer instru-

50   ments (Claflin 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 ($C_6H_6^+$) reagent-ions detect dimethyl sulfide, monoterpenes and sesquiterpenes with reduced fragmentation and higher selectivity compared to H_3O^+ (Kim et al., 2016). Water clusters (i.e., $(H_2O)_nH^+$) can detect a small subset of species detected by H_3O^+, such as dimethyl sulfide, with high selectivity (Blomquist et al., 2010). An array of oxygenated, multi-functional compounds in the intermediate to semi-volatile

55   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 CF_3O^-.

    Compared to other positive polarity reagent-ions, ammonium (NH_4^+) adduction ionization is selective toward a wider range of multi-functional oxygenated compounds, such as carbonyls, alcohols, ethers, furans, and siloxanes (Xu et al., 2022; Khare et al., 2022; Muller et al., 2020; Zhang et al., 2019; Zaytsev et al., 2019a; Berndt et al., 2019). Ambient observations have

60 recently shown that NH_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_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

65 compounds and associated sensitivity. Possible reagent-ions include $NH_4 \cdot X_n^+$ (where X = H_2O or NH_3 and n = 0, 1, 2, ...). In practice, multiple reagent-ions can be present, with $NH_4 \cdot H_2O^+$ 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_4^+ alone (i.e., n = 0) (Xu et al., 2022; Canaval et al., 2019; Adams et al., 2003).

70 $$NH_4 \cdot X^+ + A^+ \rightarrow A \cdot NH_4^+ + X \qquad\qquad (R1)$$

Given an analyte, A, with larger NH_4^+ affinity (i.e., the negative enthalpy of the reaction: $NH_4^+ + A \rightarrow A \cdot NH_4^+$; e.g., Xu et al. (2022)) than X, the ionization reaction (R1) is exothermic (Adams et al., 2003). Therefore, $NH_4 \cdot X^+$ 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

75 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

80 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_3O^+ and NO^+/O_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

85 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

90 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_4^+ and H_3O^+ 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
95 (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).
100 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
105 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

110 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
115 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 ~ 5000 m dm^{-1}, a mass range of $\sim$50-500 m/z, with a 25 kHz ToF extraction
120 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

125 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 sensi-
130 tivities ($counts\ s^{-1}\ ppt_v^{-1}$) and detection limits ($3\sigma$ 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: 098868J07I), 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
135 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 Vcm^{-1} and 3.1 mbar, 60 °C, with a voltage gradient of 60 Vcm^{-1} for NH_4^+.

2.4 Signal response to ambient relative humidity

140 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
145 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 ($\sim$2,300 m) located $\sim$40 km northwest of Colorado
150 Springs and $\sim$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 $\sim$4 m of 0.25 inch outer diameter perfluoroalkoxy (PFA) tubing situated $\sim$4 m above ground. The inlet flow was $\sim$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 $\sim$1150)
155 corresponding to a residence time of $\sim$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 NH_4^+ and H_3O^+ instrument conditions

The Vocus-CI-ToFMS switched between NH_4^+ and H_3O^+ ionization on 15-minute time intervals during the deployment in MEFO. fIMR conditions for H_3O^+ ionization were 2.5 mbar, 60 °C, with a voltage gradient of 62 Vcm^{-1}; and for NH_4^+ ionization were 3.1 mbar, 60 °C, with a voltage gradient of 65 Vcm^{-1}. The fIMR settings correspond to E/N values of 114 Td and 96 Td for H_3O^+ and NH_4^+ respectively. fIMR parameters for both reagent-ions were informed by experiments detailed in Sect. 3.1.

When using H_3O^+ 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 NH_4^+ ionization, we further add a flow from the head-space above a ∼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).
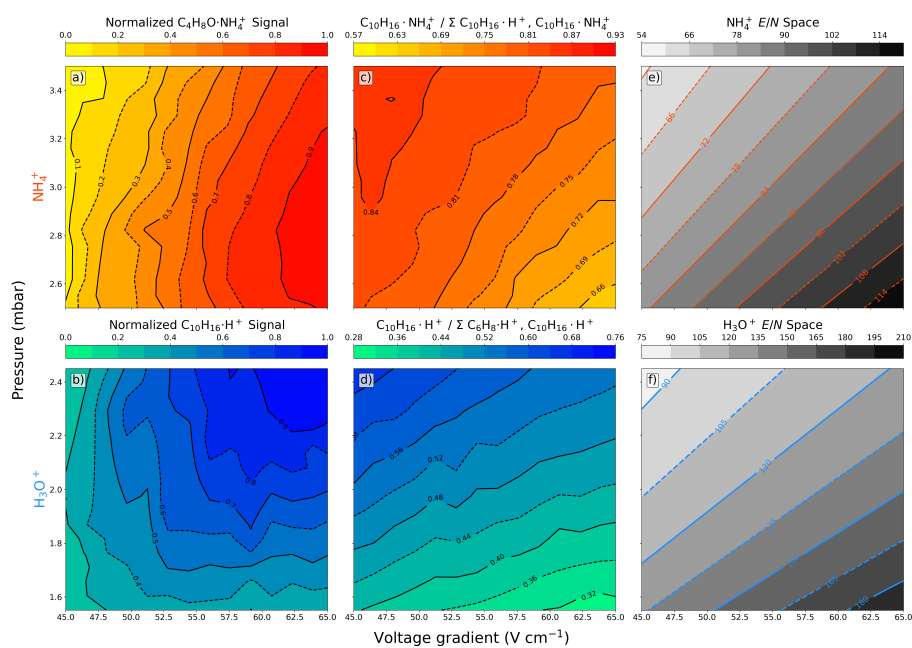
Figure 1. (a-d) Contour plots of fIMR pressure and voltage gradient scans with a constant concentration of analyte ($10\ \mathrm{ppb_v}$) introduced into the Vocus-CI-ToFMS. Normalized signal intensity for (a) methyl ethyl ketone measured with $\mathrm{NH_4^+}$ ($\mathrm{C_4H_8O \cdot NH_4^+}$) and (b) α-pinene measured with $\mathrm{H_3O^+}$ ($\mathrm{C_{10}H_{16} \cdot H^+}$). (c) Fractional contribution of the $\mathrm{NH_4^+}$ molecular ion ($\mathrm{C_{10}H_{16} \cdot NH_4^+}$) to the total α-pinene signal (i.e., the sum of the proton transfer product ($\mathrm{C_{10}H_{16} \cdot H^+}$) and the molecular ion). (d) Fractional contribution of the $\mathrm{H_3O^+}$ molecular ion ($\mathrm{C_{10}H_{16} \cdot H^+}$) to the total α-pinene signal (i.e. the sum of the α-pinene fragment ($\mathrm{C_6H_8 \cdot H^+}$) and the molecular ion). Contour plots of calculated E/N values over the scanned space for both (e) $\mathrm{NH_4^+}$ and (f) $\mathrm{H_3O^+}$.

3 Results and discussion

3.1 Ion-molecule reactor pressure and voltage gradient

H_3O^+ and 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:

$$E/N = \frac{T \times \Delta V \times k_B}{l_{imr} \times p} \tag{1}$$

Where T is the temperature (kelvin), ΔV 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 townsends (Td, 1 Td = 1×10^{-17} Vcm^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 H_3O^+ 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 ($C_{10}H_{16} \cdot H^+$) 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 Vcm^{-1} or 65 Vcm^{-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 α-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: $H^+ + A \rightarrow A \cdot H^+$) compared to water (Hunter and Lias, 1998), and α-pinene has a higher proton affinity than both water and the first water cluster (i.e., $(H_2O)_2$), 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 $(H_2O)_2H^+$ endothermic and unlikely. Therefore the formation of water clusters will reduce the sensitivity to benzene while increasing the sensitivity to α-pinene. Third, the known H_3O^+ α-pinene fragment, $C_6H_8 \cdot H^+$ has a larger contribution to the total α-pinene signal at higher E/N (Fig. 1d) which suggests that part of the increased sensitivity to $C_{10}H_{16} \cdot H^+$ 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 H_3O^+ ionization result in a sensitivity that does not follow E/N directly (Fig. 1b & 1f).

Selecting NH_4^+ ionization fIMR parameters requires balancing between signal intensity and purity of ion chemistry. Similar to H_3O^+, with NH_4^+ we observe increased signal intensity of the methyl ethyl ketone molecular ion ($C_4H_8O \cdot NH_4^+$) at higher voltage gradients (Fig. 1a). In contrast to α-pinene detection with H_3O^+, sensitivity to $C_4H_8O \cdot NH_4^+$ is not impacted by fragmentation and changing reagent-ion proton affinity across the range in voltage gradient. The sensitivity to the $C_4H_8O \cdot NH_4^+$ 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 NH_4^+ sensitivity contrasted with the L-shaped contouring in the H_3O^+ sensitivity (Fig. 1a & 1b) supports the

three-factor dependence for H_3O^+ on transmission, fragmentation, and proton affinity, and points to transmission as the major factor impacting sensitivity with NH_4^+ ionization. However, at high E/N we observe impurities in the ionization chemistry

215 (i.e., proton transfer products ($A \cdot H^+$) occurring for α-pinene) with NH_4^+ ionization (Fig. 1c). Proton transfer ionization under 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. α-pinene has a lower ammonium affinity than H_2O (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,

220 which is consistent with electric field-induced production of $C_{10}H_{16} \cdot H^+$ through internal proton transfer (Xu et al., 2022). Alternatively, it is also possible that $C_{10}H_{16} \cdot H^+$ production is enhanced by declustering of the $NH_4^+ \cdot H_2O$ ions to form 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 NH_3 compared to α-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

225 secondary clusters (i.e., $NH_4 \cdot H_2O \cdot A^+$ and $NH_4 \cdot NH_3 \cdot A^+$) is negligible over the entire investigated E/N space (Fig. S1 & S2). The sensitivity to methyl ethyl ketone, and prevalence of undesirable reaction products ($C_{10}H_{16} \cdot H^+$) are optimal under opposing conditions in the voltage gradient-pressure space, such that optimal fIMR parameters for NH_4^+ require a compromise between sensitivity and purity of ionization chemistry.
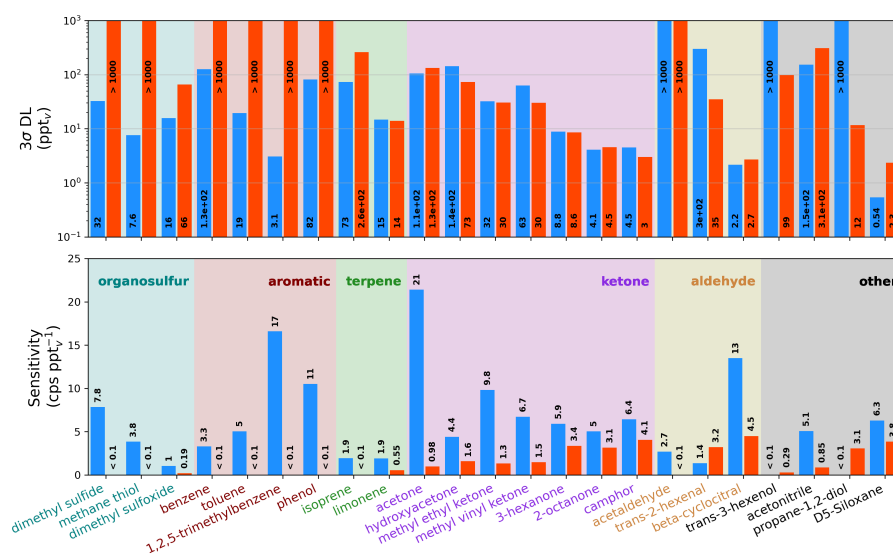
Figure 2. Sensitivities (bottom) and detection limits (top, log y-axis) for the Vocus-CI-ToFMS with NH_4^+ ionization (orange) and H_3O^+ ionization (blue) for 23 analytes from standardized gas cylinders, grouped by functional group/compound type. Sensitivities and detection limits (DLs) are calculated for the molecular ion only (i.e., $A \cdot NH_4^+$ for NH_4^+, or $A \cdot H^+$ for H_3O^+), and mass spectral fragments are not included. DL are calculated as $3\,\sigma$ over a 600 second background at 1 Hz.
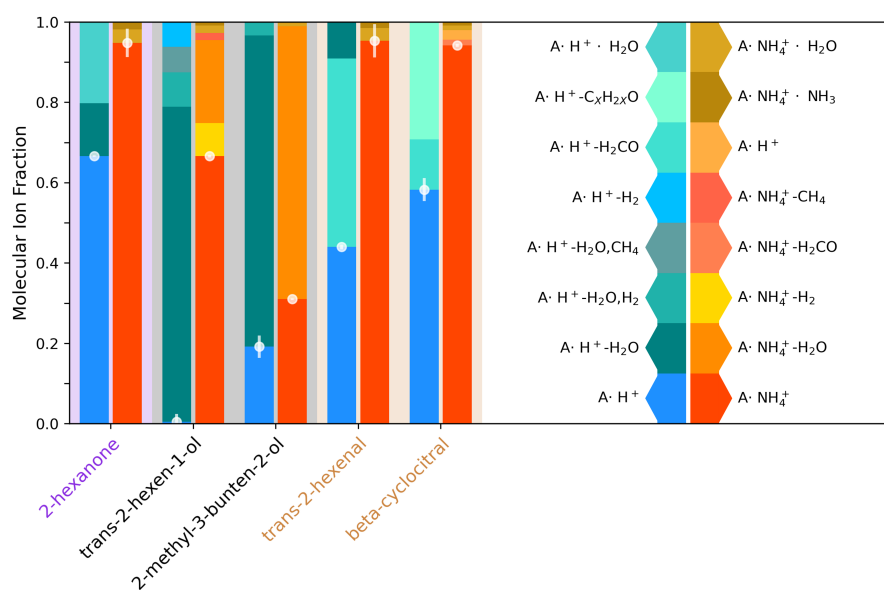
Figure 3. Molecular ion fraction and the contribution of various non-molecular ions for 5 analytes using H_3O^+ ionization (blue/left) and NH_4^+ ionization (orange/right). The contribution of the molecular ion is highlighted with a scatter plot and uncertainty bars are standard deviation across 30 mass spectra at 2 Hz.

3.2 Sensitivities, detection limits, and fragmentation

230   Direct calibrations demonstrate the selectivity of NH_4^+ relative to H_3O^+ ionization for a range of carbonyls, hydrocarbons, alcohols, and organic sulfur compounds (Fig. 2). We observe that H_3O^+ 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_3O^+ 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-

235   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_3O^+. In addition, NH_4^+ does not detect aromatics, small alkenes, and reduced sulfur compounds that H_3O^+ detects well, demonstrating the complimentary nature of these reagent-ions. While Fig. 2 suggests that H_3O^+ 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

240   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_3O^+ 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_3O^+ 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

245   similar DL to H_3O^+. Propane-1,2-diol, trans-3-hexenol, and D5-siloxane suggest that NH_4^+ has a greater ability than H_3O^+ 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., $C^* > 9 \times 10^4$ µg m^{-3}; Table S2). Despite the compromises in the fIMR temperature made to allow for the

250   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_3O^+ 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_3O^+

255   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_3O^+, 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_3O^+ 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),

260   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_3O^+). The ketone and aldehydes sampled only fragmented substantially under H_3O^+ 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
265   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_3O^+. 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_3O^+ with the detection of oxygenates from NH_4^+ expands the fraction of atmospheric ROC that we can detect with a
single instrument.
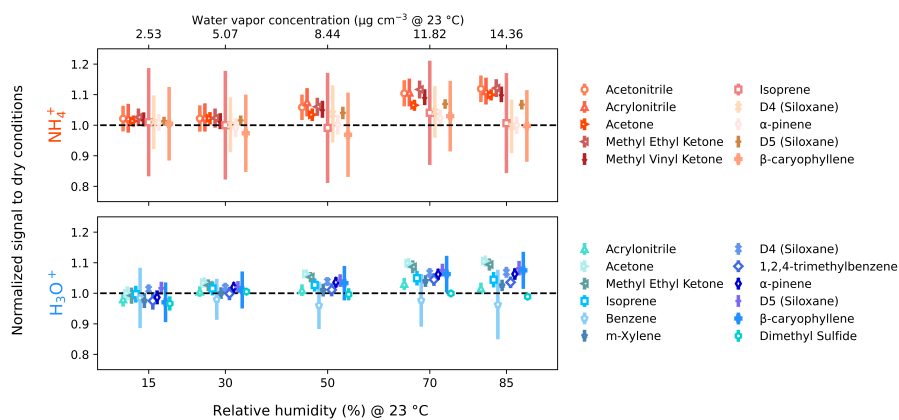
Figure 4. Signal dependence on sample relative humidity for NH_4^+ (top, orange), and H_3O^+ (bottom, blue). Measurements were made at relative humidities of 15, 30, 50, 70, and 85 %; points are offset from these values for visibility. Ethanol, benzene, m-xylene, and 1,2,4-trimethylbenzene are excluded for NH_4^+ due to low signal. Acetonitrile and ethanol are omitted for H_3O^+ due to low transmission through the BSQ. Methyl ethyl ketone is omitted for H_3O^+ due to interference of the reagent-ion cluster $(H_2O)_3 \cdot H^+$. The error bars represent propagated relative deviations in dry and humidified signals.

3.3 Impact of sample relative humidity

270

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., $20\,\mathrm{cm^3\,min^{-1}}$ (STP)) injected into the ion source (Krechmer et al.,

275 2018; Khare et al., 2022). Varying sample humidity with constant analyte concentration demonstrates humidity independence with both NH_4^+ and H_3O^+ ionization across a range of reduced and oxygenated ROC (Fig. 4). Humidity independence of the Vocus-CI-ToFMS has been demonstrated previously for H_3O^+ 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

280 and for a selection of analytes including oxygenated alkenes and siloxanes (Fig. 4).
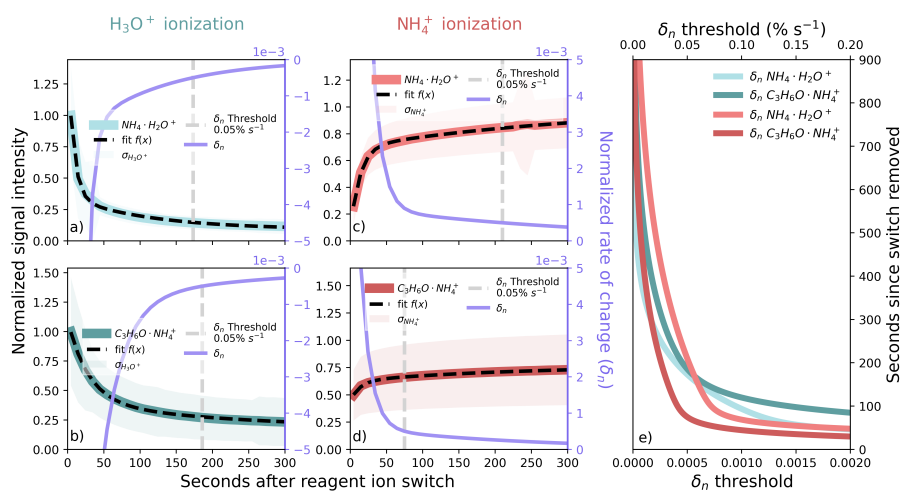
Figure 5. Ion signal after a reagent-ion switch for (a & b) H_3O^+ and (c & d) NH_4^+. We grouped ion signals by the time after a switch and normalized the mean of each group by the maximum, and normalized means were fit with a bi-exponential function. The derivative of the fit (δ_n) is displayed on 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 δ_n threshold for various ions.

3.4 Removal of reagent-ion hysteresis from switching

reagent-ion chemistry does not stabilize immediately upon switching between NH_4^+ and H_3O^+ 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

285 reagent-ion (Sect. 3.1) are such that analyte detection through the alternate ionization pathway is possible with both NH_4^+ and H_3O^+ ionization (e.g., Zaytsev et al., 2019a). This is in contrast to some other reagent-ion pairs (e.g., $CH_3O_2^-$ and I^-) where instrument conditions differ drastically, and so hysteresis is not observed (e.g., Brophy and Farmer, 2015). As a result, when NH_4^+ and H_3O^+ 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

290 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 $NH_3(g)$, 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 NH_4^+-analyte molecular ion signal as markers to quantify reagent-ion

295 switching hysteresis (Fig. 5). We selected ions primarily measured with NH_4^+ ionization because the influence of $NH_3(g)$ is observed under both H_3O^+ and NH_4^+ ionization modes, whereas the influence of $H_2O(g)$ reagent-ions are not observed in NH_4^+ mode. This arises because $NH_3(g)$ has a higher proton affinity than $H_2O(g)$ (Hunter and Lias, 1998) which causes any $NH_3(g)$ present in the ion source and fIMR to readily form NH_4^+ or $NH_4 \cdot H_2O^+$ at the expense of H_3O^+ formation. We follow $NH_3(g)$ presence and stability by monitoring $NH_4 \cdot H_2O^+$ (i.e., the prominent ammonium reagent-ion signal)

300 and $C_3H_6O \cdot NH_4^+$ (i.e., a ubiquitous analyte-ammonium molecular ion) under both ionization methods. Both $NH_4 \cdot H_2O^+$ and $C_3H_6O \cdot NH_4^+$ decay after switching to H_3O^+ ionization (Fig. 5a, b; $NH_3(g)$ depletion in the fIMR) and intensify after switching to NH_4^+ ionization (Fig. 5c, d; $NH_3(g)$ accumulation in the fIMR).

To compare the utility of $NH_4 \cdot H_2O^+$ and $C_3H_6O \cdot NH_4^+$ signals for filtering reagent-ion hysteresis, we grouped a total of 558 hours of ambient NH_4^+/H_3O^+ 15-minute reagent-ion switching observations (Sect. 2.5) by time after a reagent-ion

305 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 $NH_3(g)$ in the ion source and fIMR that drives reagent-ion chemical speciation (slow). We use the derivative of this decay function (δ_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 δ_n to set a threshold for filtering hysteresis, removing data before

310 δ_n reaches the set threshold. δ_n changes rapidly in the first ~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 $NH_3(g)$ equilibration with instrument surfaces.

Monitoring $NH_4 \cdot H_2O^+$ δ_n has the benefit of being directly related to the abundance of reagent-ion; however, both the decay of $NH_4 \cdot H_2O^+$ in H_3O^+ ionization mode and its initial increase in NH_4^+ ionization mode is driven largely by changes

315 in the BSQ mass range. We are able to avoid the impacts of changing BSQ mass range by monitoring an ion with higher $\mathrm{m/z}$. Additionally, using an analyte for filtering reagent-ion hysteresis means that we are using a direct measurement of the formation of analyte ions for $\mathrm{NH_4^+}$ ionization and a direct measurement of contamination from other reagent-ion chemistry with $\mathrm{H_3O^+}$ ionization. For these reasons we decided to use the persistent ion $\mathrm{C_3H_6O \cdot NH_4^+}$ to monitor hysteresis. We acknowledge this choice brings the complication of varying ambient concentrations in time; however, due to the substantial averaging over

320 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 δ_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 δ_n threshold below $\sim$0.05 % s^{-1}

325 (Fig. 5e). A 0.05 % s^{-1} threshold applied to $\mathrm{C_3H_6O \cdot NH_4^+}$ results in the loss of $\sim$185 s and $\sim$75 s of data per switch with $\mathrm{H_3O^+}$ and $\mathrm{NH_4^+}$ 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 $\mathrm{NH_4^+}$ and $\mathrm{H_3O^+}$ switching in an Ionicon PTR3: $\sim$120 s and $\sim$60 s of data removed after switching to $\mathrm{H_3O^+}$ and $\mathrm{NH_4^+}$ ionization, respectively. The approach we describe here can be applied easily to other instruments and at different instrument conditions (e.g., fIMR

330 temperature and pressure) to best balance the need for both measurement stability and data coverage.
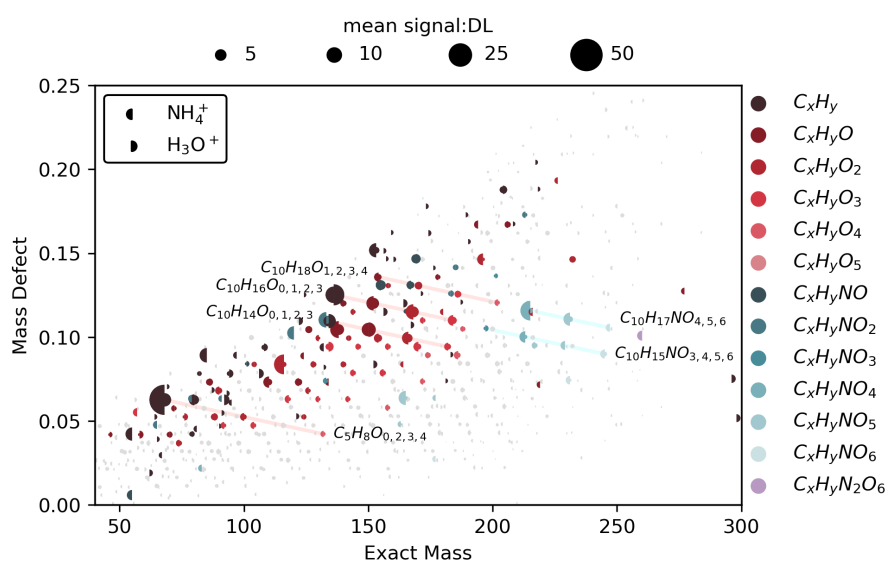
Figure 6. Campaign mean mass defect plots for NH_4^+ and H_3O^+ ionization from deployment in MEFO. The NH_4^+ mass spectrum is displayed as a left half-circle and the H_3O^+ is displayed as a right half-circle. Points are sized by the average signal across the campaign divided by the detection limit 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).
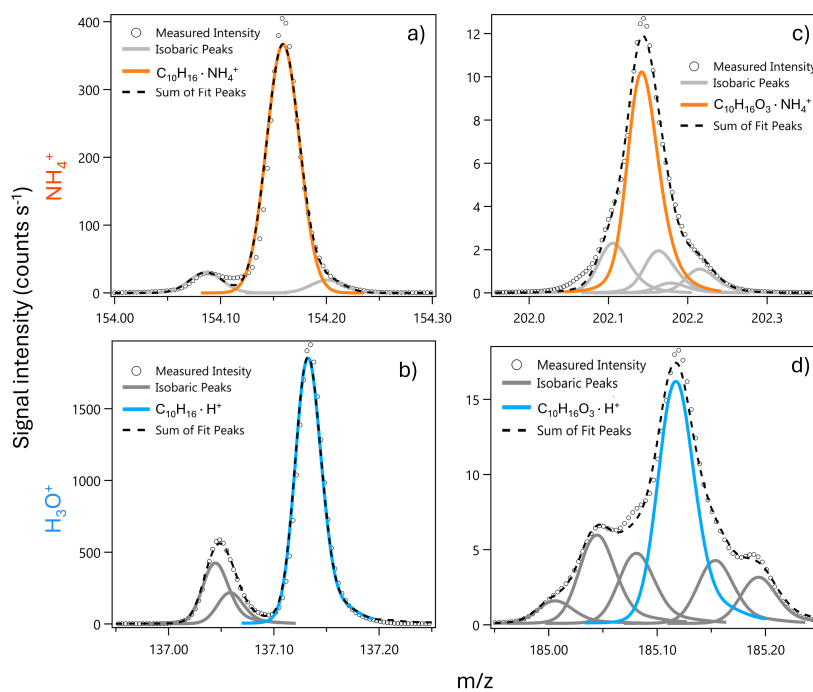
Figure 7. Selected campaign average high resolution mass spectra for (a & b) monoterpene ($C_{10}H_{16}$) and (c & d) monoterpene oxygenate ($C_{10}H_{16}O_3$) molecular ions detected with NH_4^+ (a & c, orange) and H_3O^+ (b & d, blue).

3.5 reagent-ion comparison from ambient measurements

We compare the capabilities of NH_4^+ and H_3O^+ reagent-ions in a single instrument using ambient observations from MEFO (Sect. 2.5.1). Switching between H_3O^+ 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-methylcatecol. 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_3O^+ 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_3O^+. At MEFO, four series of $C_xH_yO_z$ 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 $C_5H_8O_n$ 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 ($C_{10}H_{16}O$; $C^* = 1 \times 10^6$ µg m^{-3}) and thymol or carvone ($C_{10}H_{14}O$; $C^* = 1-9 \times 10^5$ µg m^{-3}) (McKinney et al., 2011; Kaser et al., 2013; Vermeuel et al., 2023a), and oxidation products of other terpenoids. H_3O^+ 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_3O^+ 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_3O^+ and 10.8 with NH_4^+. The tendency toward increased signal-to-noise with oxygenation for NH_4^+ ionization continues in the $C_{10}H_{14,16}O_n$ series up to $C_{10}H_{14,16}O_3$ (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 monoterpenes and (2) water clusters formed with monoterpenes ($C_{10}H_{18} \cdot H_2O \cdot H^+$ and $C_{10}H_{18} \cdot H_2O \cdot NH_4^+$). The $C_5H_8O_n$ series represents a combination of fragments, primary emissions and oxidation products. The C_5H_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 $C_5H_8O_n$ series, the C_5H_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_5H_8 mass. The NH_4^+ sensitivity to isoprene is very low; however 2,3,2-MBO fragments substantially into C_5H_8 through dehydration of the tertiary alcohol group (Fig. 3). Fragmentation into C_5H_8 combined with a low background (Fig. A3 & S4) leads to a very large signal-to-DL ratio

365   (Fig. 6). The $C_5H_8O_3$ and $C_5H_8O_4$ peaks are likely oxidation products of isoprene and 2,3,2-MBO, while $C_5H_8O_2$ is likely an isoprene oxidation product (Saunders et al., 2003; Jenkin et al., 2015).

NH_4^+ can detect organic nitrates that easily fragment with H_3O^+ (Aoki et al., 2007; Duncianu et al., 2017) and so often go undetected in ambient measurements with H_3O^+ ionization (Fig. 6). Organic nitrates ionized with H_3O^+ fragment to form nitric acid (HNO_3) or nitronium ions (NO_2^+), where the loss of HNO_3 results in fragmentation into the masses for other

370   oxygenates (Aoki et al., 2007). The two predominant series of organic nitrate ions ($C_{10}H_{15}NO_n$ and $C_{10}H_{17}NO_n$ with C^* down to 10s of µg m^{-3}; Table S4) are generally detected with a higher signal-to-DL ratio with NH_4^+ ionization compared to H_3O^+ ionization, if the ion is detected with H_3O^+ at all (Fig. 6). The exception is $C_{10}H_{15}NO_3$ which is detected at higher signal-to-DL (2.13) with H_3O^+ ionization compared to NH_4^+ (0.774); though this ion may arise from dehydration of hydroxy nitrates (i.e., $C_{10}H_{17}NO_4$-H_2O) and that H_3O^+ is fragmenting larger organic nitrates into the $C_{10}H_{15}NO_3$ ion. The nitrates

375   we observe are potentially a mixture of carbonyl, hydroxy, and peroxy nitrates derived from the oxidation of monoterpenes ($C_{10}H_{16}$) and potentially other terpenoid ($C_{10}H_{16}O$/$C_{10}H_{14}O$) precursors (Table S5, Fry et al., 2013; Jenkin et al., 2015; Faxon et al., 2018; Bates et al., 2022). Additionally, $C_5H_{11}NO_5$ and $C_5H_9NO_5$ are detected using both reagent-ions but both with higher signal-to-DL ratio with NH_4^+. $C_5H_{11}NO_5$ is likely a nitrate from the oxidation 2,3,2-MBO while both 2,3,2-MBO and isoprene could form the $C_5H_9NO_5$ ion (Link et al., 2024).

380   NH_4^+ ionization's ability to detect oxygenated compounds with higher signal-to-noise ratio and lower detection limits than H_3O^+ arises from two main factors. First, NH_4^+ is a softer ionization method compared to H_3O^+, resulting in less molecular ion fragmentation (Sect. 3.2). This is evident in our ambient data for the known H_3O^+ monoterpene fragment, $C_6H_8 \cdot H^+$ compared to the analogous fragment with NH_4^+ ionization, $C_6H_8 \cdot NH_4^+$. The fragment is present in NH_4^+ ionization mode at a 1:10 fragment-to-molecular-ion ratio, compared to a 1:1 ratio with H_3O^+ under our fIMR conditions (Fig. S3). Second,

385   NH_4^+ has higher selectivity toward oxygenates compared to H_3O^+ (Sect. 3.2). Our ambient reagent-ion switching observations further demonstrate this selectivity (Fig. 7 & A3). The monoterpenes ($C_{10}H_{16}$) are easily distinguished from isobaric ions with both H_3O^+ and NH_4^+, but oxygenates ($C_{10}H_{16}O_3$) have multiple isobaric interferences with H_3O^+ (Fig. 7). Both higher selectivity and reduced fragmentation contribute to fewer isobaric ions with NH_4^+. While our observations demonstrate the utility of NH_4^+ for detecting oxidized species that H_3O^+ ionization struggles to detect (e.g., Yuan et al., 2017; Riva et al.,

390   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 NH_4^+ is complementary to H_3O^+, 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

395   To expand the range of ROC detectable with a single chemical ionization instrument, we present an approach to combine two positive reagent-ions, NH_4^+ and H_3O^+, 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_3O^+ to detect a range of reduced and oxygenated VOCs and S/IVOCs through analysis of laboratory standards and find that H_3O^+ detects reduced species well and fragments function-

400   alized 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, $C_3H_6O \cdot NH_4^+$. 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),

405   corresponding to ~ 86 % data retention for 15-minute switching intervals. We deploy our NH_4^+/H_3O^+ 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_3O^+ does not detect, while H_3O^+ detects reduced species that are undetectable with NH_4^+. NH_4^+/H_3O^+ reagent-ion switching takes advantage of the complimentary nature of the two reagent-ions to expand the range

410   of ROC detectable with a single instrument.

Appendix A
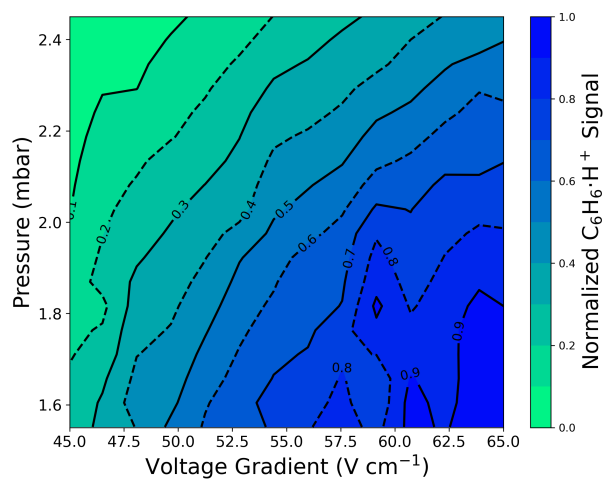
Figure A1. Normalized signal intensity for benzene measured with H_3O^+ ($C_6H_6 \cdot H^+$) from pressure-voltage gradient scans.
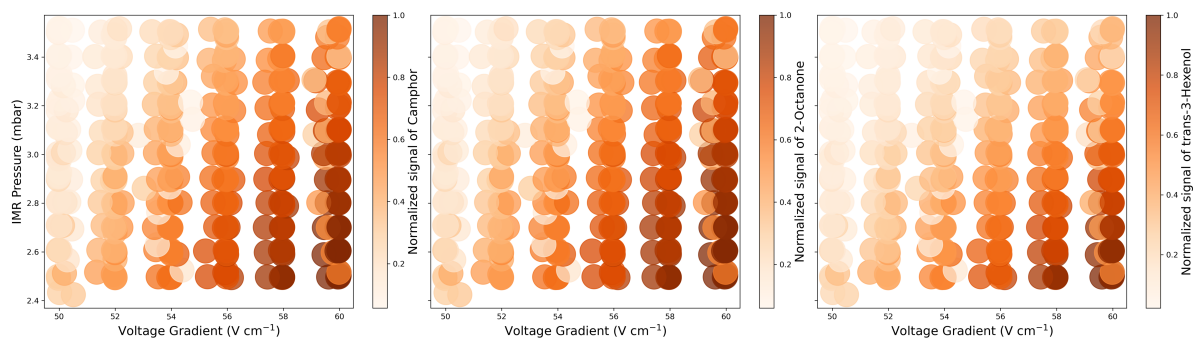
Figure A2. Normalized signal intensity for camphor (left), 2-octanone (middle), and trans-3-hexenol (right) measured with NH_4^+ ($C_{10}H_{16}O \cdot NH_4^+$, $C_8H_{16}O \cdot NH_4^+$, and $C_6H_{12}O \cdot NH_4^+$ respectively).
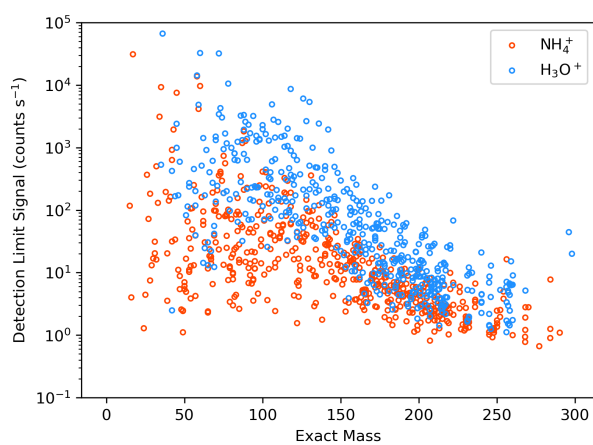
Figure A3. Mass dependent campaign average detection limit signal for ions detected with NH_4^+ (orange) and H_3O^+ (blue). The reagent-ion masses have been removed from ion exact masses.

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
415 (Zang and Willis, 2024).

Competing interests. The authors declare no competing interests.

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