Response to Reviewers Comments:

Below, please find our responses to the reviewers second round of comments:

One question in reading the revised manuscript: lines 298-299 mentions that the [M+32]+ peak is reduced by sampling in N2. Is the same observed for the [M-H]+ peak that the authors speculate could be formed via oxidation of the [M+1]+ ion? If not, can the authors provide a different explanation for the [M-H]+ peak?

Yes, the $[M-1]^+$ peak intensity is also reduced to near zero when sampling N₂. This has been noted on line 298 in the revised manuscript.

Figure 9: The symbols in the figure do not match the description in the text.

This has been edited.

Figure 5 on page 26 should be figure 12. The caption doesn't match the symbols used.

This has been edited.

Figure 6 on page 27 should be figure 13

This has been edited.

1 The sensitivity of benzene cluster cation chemical ionization mass spectrometry to select

- 2 biogenic terpenes
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- 9 10 Abstract

11 Benzene cluster cations are a sensitive and selective reagent ion for chemical ionization of select biogenic volatile organic compounds. We have previously reported the sensitivity of a field 12 13 deployable chemical ionization time-of-flight mass spectrometer (CI-ToFMS), using benzene 14 cluster cation ion chemistry, for detection of dimethyl sulfide, isoprene and α -pinene. Here, we 15 present laboratory measurements of the sensitivity of the same instrument to a series of terpenes, 16 including isoprene, α -pinene, β -pinene, D-limonene, ocimene, β -myrcene, farnesene, α -17 humulene, β -caryophyllene and isolongifolene at atmospherically relevant mixing ratios (< 100 18 pptv). In addition, we determine the dependence of CI-ToFMS sensitivity on the reagent ion 19 neutral delivery concentration and water vapor concentration. We show that isoprene is primarily detected as an adduct ($C_5H_8 \cdot C_6H_6^+$) with a sensitivity ranging between 4-10 ncps ppt⁻¹, that 20 21 depends strongly on the reagent ion precursor concentration, de-clustering voltages, and specific 22 humidity (SH). Monoterpenes are detected primarily as the molecular ion $(C_{10}H_{16}^+)$ with an 23 average sensitivity, across the five measured compounds, of 14 ± 3 ncps ppt⁻¹ for SH between 7 24 and 14 g kg⁻¹, typical of the boreal forest during summer. Sesquiterpenes are detected primarily as 25 the molecular ion $(C_{15}H_{24}^{+})$ with an average sensitivity, across the four measured compounds, of 26 9.6 ± 2.3 ncps ppt⁻¹ that is also independent of specific humidity. Comparable sensitivities across 27 broad classes of terpenes (e.g., monoterpenes and sesquiterpenes), coupled to the limited 28 dependence on specific humidity, suggests that benzene cluster cation CI-ToFMS is suitable for 29 field studies of biosphere-atmosphere interactions.

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32 1. Introduction

33 The annual global emission of biogenic volatile organic compounds (BVOCs) is estimated at 1000 TgC yr⁻¹ and exceeds the total VOC emissions from anthropogenic activities (Guenther et al., 34 35 2012; IPCC). Foliage emissions account for 90% of global BVOC emissions, of which isoprene (C_5H_8) , monoterpenes (MTs; $C_{10}H_{16}$) and sesquiterpenes (SQTs; $C_{15}H_{24}$) are the primary 36 37 constituents (Guenther et al., 1995). The emission rate and the chemical composition of emitted 38 BVOCs is a complex function of the vegetation species and the wide array of stress factors that it 39 is exposed to (Hallquist et al., 2009; Lang-Yona et al., 2010; Zhao et al., 2017). Atmospheric 40 oxidation of BVOCs results in the formation of low volatility compounds that can lead to new 41 particle formation (Jokinen et al., 2015; Kirkby et al., 2016) and particle growth through secondary organic aerosol formation (Allan et al., 2006; Wiedensohler et al., 2009). Both of these processes 42 43 impact Earth's radiative budget by scattering solar radiation and/or altering cloud formation and 44 precipitation (Chung et al., 2012). The contribution of different types of BVOCs (e.g., isoprene, MTs and SQTs) to secondary organic aerosols (SOA) differ significantly (Zhao et al., 2017). 45 46 Therefore, uncertainties in BVOCs emissions present significant issues in estimating net climate 47 forcing (Kerminen et al., 2005; Kulmala et al., 2004). Identification of the chemical composition of the emitted BVOCs and quantification of the surface exchange rates of these compounds are 48 49 essential for understanding complex and non-linear biosphere-atmosphere interactions.

50 Chemical ionization mass spectrometry (CIMS) is a commonly utilized selective and sensitive 51 method for in situ detection of trace gases (Huey, 2007). The sensitivity and selectivity towards a 52 specific compound or class of compounds having similar functional groups rely on the selection 53 of an appropriate ion (i.e. reagent ion) that reacts with and ionizes the analyte via an ion-molecule 54 reaction. For example, iodide ions have been used to measure reactive nitrogen compounds, 55 halogen containing species and oxygenated VOCs (Lopez-Hilfiker et al., 2015; Riedel et al., 2012; 56 Thornton et al., 2010), CF_3O^- has been used for the detection of peroxides and organic nitrates 57 (Crounse et al., 2006), NO⁺ has been used for the selective detection of primary alcohols and alkenes (Hunt and Harvey, 1975; Hunt et al., 1982; Karl et al., 2012; Koss et al., 2016; Mochalski 58 59 et al., 2014), H₃O⁺ for VOCs and their oxygenated products (Lindinger et al., 1998) and benzene 60 cluster cations for dimethyl sulfide (DMS), isoprene, and terpenes (Kim et al., 2016; Leibrock and

61 Huey, 2000).

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62 The benzene cation clusters spontaneously with neutral benzene via attractive, non-covalent 63 interactions (Chipot et al., 1996; Grover et al., 1987). Leibrock and Huey (2000) and recently Kim 64 et al. (2016) demonstrated that select VOCs including isoprene, MTs, SQTs and aromatic 65 compounds can be ionized by benzene cation clusters. Kim et al. studied the parameters that control the benzene cation cluster distribution $(C_6H_6)^+$ $(C_6H_6)_n$ at the operational conditions of the 66 67 CI-ToFMS, concluding that, for the specific operating conditions used, the reagent ion within the 68 ion-molecule reaction chamber was primarily in the form of the benzene dimer or larger clusters 69 (Kim et al., 2016). This conclusion is in agreement with studies showing that the dissociation 70 energy of the benzene cation dimer is significantly higher than that of the trimer or larger benzene 71 cation clusters (Krause et al., 1991), suggesting that ionization in the CI-ToFMS by benzene cluster 72 cations proceeds primarily through clusters that are at least the size of the benzene cation dimer.

73 The ionization mechanism for a given analyte (M) with the benzene cation dimer, depends on the 74 ionization energy (IE) of the analyte. Charge transfer (R1) is expected to be the dominant reaction 75 for analytes having ionization energies smaller than the benzene dimer (8.69 eV) (Grover et al., 76 1987). In cases when the analyte IE is higher than that of benzene cation dimer, charge transfer is 77 thermodynamically unfavored and adduct formation (R2) or ligand exchange (R3) are the sole 78 modes of ionization. The ligand exchange product (R3) was previously reported for isoprene, 79 dimethyl sulfide and select alkenes, however the reaction pathway is not known (Kim et al., 2016; 80 Leibrock and Huey, 2000).

81	$(C_6H_6)_2^+ + M \rightarrow M^+ + 2C_6H_6$	(R1)
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(R2)

83
$$(C_6H_6)_2^+ + M \rightarrow M^+ \cdot (C_6H_6) + C_6H_6$$
 (R3)

The low IE of benzene clusters (8.69 eV for the dimer and even smaller for larger benzene cation
clusters) (Grover et al., 1987; Shinohara and Nishi, 1989) is a major advantage in the quantification
of monoterpenes or larger volatile organic compounds such as sesquiterpenes. The IE of these
compounds is slightly smaller than that of the benzene dimer (e.g. 8.3 eV for β-caryophyllene
(Novak et al., 2001)) and the minimal excess energy in charge transfer reactions results in limited
fragmentation. For example, approximately 60% of β- caryophyllene was detected in its molecular

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ionic form (M⁺) in comparison to significant fragmentation observed by proton transfer reaction
mass spectrometry (PTR-MS) (Kim et al., 2014; Kim et al., 2009).

92 The field deployable CIMS that utilizes a time-of-flight mass analyzer (ToFMS), previously 93 described by Kim et al. combines the efficient production and transmission of ions at high pressure 94 (e.g. 75 mbar) with the high ion duty cycle of orthogonal extraction ToFMS (Bertram et al., 2011). This instrument configuration is highly sensitive and capable of measuring and logging mass 95 96 spectra (10-800 m/Q) at rates higher than 10 Hz (Bertram et al., 2011). These benefits make CI-97 ToFMS highly applicable for studying atmospheric exchange processes of trace gases at the air-98 ocean interface that require fast response rates (Kim et al., 2014). However, at these pressures, the 99 distribution of benzene clusters and their associate ion-molecule reactions times are not well 100 constrained. Unlike PTR-MS, it is not possible to directly derive the analyte mixing ratio from 101 laboratory studies of the ion-molecule kinetics (reaction rates) that are conducted at lower pressure 102 in which both the reaction times and cluster distribution have been previously determined. As such, 103 quantitative analysis of atmospheric trace gases using high pressure CIMS necessitates either a 104 direct or empirical calibration for each analyte as a function of the atmospheric conditions (e.g. 105 humidity or temperature).

In what follows, we build on earlier studies in our group (Kim et al., 2016), which described the use of benzene cluster cations as a reagent ion for the detection and quantification of dimethyl sulfide, isoprene, and α -pinene. At the time of Kim et al. (2016), it was not known if: 1) $C_6H_6\cdot(C_6H_6)_n^+$ ion chemistry was equally sensitive to all monoterpene compounds, 2) the dependence of CI-ToFMS sensitivity on specific humidity for a broad range of monoterpenes and sesquiterpenes, and 3) the source of organic impurities in the reagent ion delivery. Here, we address each of these topics.

In this paper, we describe a high purity liquid benzene source, which permits operation of the CI-ToFMS at higher reagent ion concentrations. We discuss the sensitivity of benzene cluster cation chemistry to a select number of terpenes (Table 1) at atmospherically relevant mixing ratios (<500 pptv). We report on the effect of atmospheric water vapor and the neutral benzene reagent ion precursor concentration on CI-ToFMS sensitivity to select terpenes (isoprene, α - and β -pinene, Dlimonene, β -myrcene, ocimene, farnesene, isolongifolene, α -humulene and β -caryophyllene). We

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also examine the de-clustering power of the RF only quadrupole to better determine the cluster

120 distribution present in the ion molecule reaction chamber..

121 2. Experimental

122 2.1 Materials

123 The following analytes were purchased from Sigma-Aldrich and used with no further purification: 124 isoprene, α -pinene, β -pinene, D-limonene (\geq 99%), β -myrcene (96.2%), ocimene (97.0%, as a 125 mixture of isomers), farnesene (>90.0%, as a mixture of isomers) α -humulene (>96.5%), β -126 caryophyllene (\geq 98.5%), isolongifolene (\geq 98.0%, as a mixture of isomers), benzene (\geq 99.5%) and 127 chloroform-d (99.8 atom % D). A compressed gas cylinder of 0.184 ppm of DMS-d3 in N2 was 128 purchased from Praxair, USA. Water was supplied from a Milli-Q system at 18.2 M Ω ·cm. 129 Nitrogen was used from a UHP liquid N₂ dewar (Airgas). UHP (99.999%) oxygen cylinders were 130 purchased from Airgas.

150 purchased from Airgas.

131 2.2 Chemical Ionization Mass Spectrometer

The detailed description of the CI-ToFMS (Tofwerk AG, Switzerland and Aerodyne Research 132 133 Inc., USA) and its performance are discussed in Bertram et. al.(Bertram et al., 2011) In brief, 134 reagent ions are generated by passing 10 sccm of UHP N2 over the headspace of a liquid benzene reservoir contained in a stainless steel bottle. Benzene vapor is diluted with 2.2 slpm of N₂, prior 135 to delivery to the ²¹⁰Po source. The benzene vapor mixing ratio is estimated from the dilution ratio 136 137 and benzene vapor pressure. In the experiments discussed here, we varied the benzene 138 concentration between 60 and 360 ppm. A combination of stainless steel and Teflon tubing was 139 used to transfer benzene vapors to minimize extraction of organic compounds from the tubing. 140 Following dilution, benzene vapor flows through a 10 mCi α emitting radioactive ²¹⁰Po source 141 (NRD 2021–1000). The collision of α -particles with N₂ results in the formation of N₂⁺ ions that 142 ionize the benzene clusters (Dondes et al., 1966). The analyte sample is mixed with the formed 143 benzene cluster cations at the ion-molecule reactor (IMR) held at 75mbar. At this pressure, the 144 estimated analyte residence time in the IMR is 100 ms. The reagent and product ions are 145 transmitted from the IMR chamber into a collisional dissociation chamber (CDC, P=2 mbar) equipped with a RF only ion-guide quadrupole, followed by a subsequent chamber (P=1.4 x 10^{-2} 146 147 mbar) in which a second RF-only quadrupole is used to focus the ion beam. The ion beam is then

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guided by a further set of ion optics to the entrance point of the extraction region of the compact

- 149 time of flight mass analyzer (Tofwerk AG, Switzerland).
- 150 2.3 Liquid Calibration Unit

151 A custom liquid calibration system was developed to deliver known, atmospherically relevant 152 mixing ratios (< 500 pptv) of gas-phase terpenes to the CI-ToFMS. The liquid calibration system 153 uses a syringe pump to continuously evaporate known quantities of solution into a heated carrier 154 gas flow, generating known mixing ratios of select terpenes. To produce trace concentrations of 155 each analyte, the standard liquid material was diluted in-series with chloroform-d using a set of 156 calibrated auto pipettes. Chloroform-d was chosen due to its solvent properties and low boiling 157 point (61°C) that enhances the evaporation of the analyte. Due to its ionization energy (IE > 11 eV 158 (Bieri et al., 1981)), higher than that of benzene cation clusters, it was expected that chloroform 159 would not be ionized and would have negligible impact on the benzene cluster cation ionization 160 mechanisms. To assess this, mass spectra were recorded for solutions containing solely deuterated 161 chloroform for a variety of different pump flows from 0 to 5μ l min⁻¹. We did not observe the 162 molecular cation of chloroform-d (CDCl₃⁺, 120 m/Q) and only very small signatures of the 163 fragments (at 48, 84 or 86 m/Q) were observed (Figure 1), consistent with the IE of chloroform-d 164 being higher than that of the reagent ions $(11.37 \pm 0.02 \text{ eV} \text{ compared with } 8.69 \text{ eV})$ (Grover et al., 165 1987) (Werner et al., 1974). It was also determined that concentration of deuterated chloroform 166 did not interfere with reagent ion or water cluster signal intensities.

167 To evaporate the analyte solution, a controlled amount $(0.5\mu l min^{-1})$ of the analyte solution was 168 delivered by a syringe pump (Harvard Apparatus, model 11) via PEEK tubing (Upchurch 169 scientific) into a heated carrier stream resulting in CDCl₃ mixing ratios from 60-300 ppmv. A 170 synthetic 80:20 N₂:O₂ mixture was used as zero air and heated by an in-line gas heater (Omega, 171 AHP-3741). The temperature of the zero air flow at the point of intersection with the PEEK tubing 172 was kept at 80°C via a PID temperature controller (Omega, CN9300). Excess zero air flow was 173 used to ensure an overflow of the CIMS inlet. The trace concentration of the evaporated analytes 174 and the elevated temperature in front of the inlet (ca. 50° C) helped to prevent re-condensation of 175 the analyte on the inlet tubing. Humidified zero air was generated by passing a fraction of the total 176 flow through the head space of a water reservoir. The relative humidity (RH) of the total air flow

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177 was measured using a relative humidity sensor (Vaisala, HMP110), calibrated using the procedure

178 described in Greenspan (1977).

179 The sensitivities reported in this paper are presented in normalized counts per second per pptv+

180 (ncps·pptv⁻¹). We normalized the analyte ion count-rates by the sum of the benzene cation 181 monomer (78 m/Q) and dimer (156 m/Q) count rates to a reference of 1×10⁶ counts per second of 182 total reagent ion signal in order to account for changes in ion transmission and generation over 183 time. Sensitivities are calculated as the slope of the linear fit of each calibration curve of 5-7 steps

184 (185 Figure 2Figure 2). Error bars are the standard deviation of repeated triplicate measurements. The 186 performance of the liquid evaporation technique was validated by comparing the sensitivity to 187 dimethyl-1,1,1-d₃ sulfide (Praxair certified compressed gas standard, 0.184 ppm $\pm 10\%$) diluted by 188 zero air to a desired mixing ratio, with that of a diluted nebulized solution of DMS. The slope of 189 the linear fit for calibration measurements from the pressurized cylinder (DMS-d3, 65 *m/Q*) and 190 the solution (DMS, 62 *m/Q*) agreed to better than 10%.

191

192 3. Results and Discussion

193 3.1 Benzene Cluster Cation Mass Spectra

194 The CI-ToFMS mass spectra, obtained while overflowing the inlet with nominally dry zero air is 195 shown in Figure 3a. To maximize the transmission of weakly bound ion-molecule adducts, we 196 operated the instrument in all of the experiments described here with a minimal applied electric 197 field between the instrument inlet and the entrance of the second RF-only quadrupole ion guide. 198 The two primary peaks in the mass spectrum correspond to the benzene cation ($C_6H_6^+$; 78 m/Q) 199 and the benzene cation clustered to a single, neutral benzene $(C_6H_6^+, (C_6H_6); 156 m/Q)$, where 200 $C_6H_6^+$ and $C_6H_6^+$ (C_6H_6) combined account over 90% of the total ion current (TIC) for a benzene 201 neutral concentration of 300 ppm. Benzene cation clusters larger than the dimer were not observed, 202 as expected from their dissociation enthalpy, which is significantly smaller than that of the benzene 203 cation clustered with a single neutral benzene molecule (Krause et al., 1991). The observed mass 204 spectrum indicates significant ion intensity at 39, 50, 51, and 52 m/Q that are attributed to the 205 dissociation of the molecular ($C_6H_6^+$) ion into its fragments $C_3H_3^+$, $C_4H_2^+$, $C_4H_3^+$, and $C_4H_4^+$, 206 accounting for ca. 5% of TIC. The fragmentation may result from the interaction of N_2^+ , α -particles 207 or electrons with benzene clusters in the ion molecule reaction region (Lifshitz and Reuben, 1969;

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208 Talebpour et al., 2000). For comparison, a similar spectrum is shown in Figure 3b, using the same 209 benzene neutral concentration and operating voltages, but without the RF and voltage bias applied 210 to the first quadrupole ion guide. In this mode of operation, the total ion current is reduced by over 211 95%, and $C_6H_6^+$ and $C_6H_6^+$ (C_6H_6) are nearly equal in intensity, highlighting that benzene cluster 212 collisional dissociation is occurring within this region. Even with the first RF-only quadrupole 213 electronics turned off, the n=2 cluster $(C_6H_6^+, (C_6H_6)_2; 234 m/Q)$ was not observed. Of notable 214 absence (< 1% TIC) in both Figures 3a and 3b are the organic contaminants (92, 106, and 120 215 m/Q) previously attributed to alkyl substituted benzene and protonated water clusters 216 $(H_3O^+, (H_2O)_n; 19, 37, 55, and 73 m/Q)$ that were present at high abundance (>10% of TIC) in Kim 217 et al. (2016). It was postulated in Kim et al., that the source of the organic contaminants was the 218 benzene compressed gas cylinder, as their combined contribution to TIC scaled with the neutral 219 benzene concentration. It was also noted that low benzene neutral concentrations led to elevated 220 water cluster abundance. This resulted in an optimum benzene neutral concentration of 10 ppm, to 221 balance the contributions from organic contaminants and water clusters. Here, we eliminate the 222 organic contaminants through the use of a high purity benzene liquid source permitting operation 223 at higher neutral benzene concentrations (> 300 ppm). As discussed in section 3.2, this has critical 224 advantages for the detection of analytes such as isoprene, and effectively eliminates competing ion 225 chemistry stemming from protonated water clusters.

It what follows we assess the CI-ToFMS sensitivity to a series of terpenes, including isoprene, α pinene, β -pinene, D-limonene, ocimene, β -myrcene, farnesene, α -humulene, β -caryophyllene, and isolongifolene at atmospherically relevant mixing ratios (< 100 pptv) and determine the dependence of CI-ToFMS sensitivity on the reagent ion neutral delivery concentration (section

230 3.2) and water vapor concentration (section 3.3).

231 3.2 Impact of Benzene Neutral Concentration on Terpene Sensitivity

232 We examined the impact of the benzene reagent ion precursor concentration on terpene sensitivity

233 in nominally dry zero air for benzene neutral concentrations between 60-300 ppm. For the selection

234 of monoterpenes and sesquiterpenes studied here, there was no indication that instrument

235 sensitivity was dependent on the neutral benzene reagent ion precursor concentration between 60-

236 300 ppm (Figure 4 Figure 4 a-b). In Figure 4a-c, the reported sensitivity for each terpene is

237 normalized to that measured at a benzene neutral concentration of 300 ppm. Unlike MTs and

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SQTs, the sensitivity of the isoprene benzene adduct ($C_6H_6^+$ · C_5H_8 ; 146 *m/Q*) strongly depends on the benzene concentration below 200 ppm (Figure 4Figure 4 c) and therefore all the measurements in this study, were conducted at 300 ppm benzene. The cause for this dependence in benzene concentration is unclear as the exact mechanism for $C_6H_6^+$ · C_5H_8 formation is unknown. It should also be noted that the sensitivity to DMS is independent of benzene concentration. Based on these analyses, we suggest that future studies utilizing benzene ion chemistry operate at neutral benzene reagent ion precursor concentrations of 300 ppm, generated from a high purity liquid source.

245

246 3.3 Impact of Specific Humidity on Sensitivity

247 3.3.1 Isoprene

In these experiments, the specific humidity (SH) was varied between 0 and 14 g kg⁻¹, equivalent 248 249 to 0-80% RH at 23 °C, to assess its effect on the sensitivity. Our reported "nominally dry" cases 250 correspond to 0.7% RH or ca. 0.01 g kg⁻¹ SH. As shown in Figure 5, the sensitivity of the CI-251 ToFMS to isoprene ($C_6H_6^+$, C_5H_8 ; 146 m/Q) displays a strong, non-linear dependence on SH. 252 Instrument sensitivity increases with increasing SH, reaching a maximum value of 10 $ncps \cdot ppt^{-1}$ at 4 g kg⁻¹ (25% RH at 23°C), then decreases significantly at higher humidity. Surprisingly, we 253 254 observed a linear correlation ($R^2 > 0.95$) between the protonated water tetramer signal (73 m/Q) 255 and the delivered isoprene mixing ratio at constant SH that was not observed for smaller protonated 256 water clusters (Figure 6). The apparent sensitivity, derived from the slope of the linear-least 257 squares fit of the observed water tetramer signal vs. delivered isoprene concentration, increases 258 with increasing specific humidity above 2 g kg⁻¹ (Figure 5). We reiterate that Figure 5 does not 259 show the protonated tetramer signal as a function of SH, but the sensitivity of the 73 m/Q signal to 260 the delivered isoprene mixing ratio as shown in Figure 6. The decreased sensitivity to isoprene 261 adduct and increase in water tetramer signal with isoprene mixing ratio are unlikely the result of 262 the formation of water protonated clusters via charge transfer reaction with benzene cations since 263 the IE of water is significantly higher than that of the benzene dimer (12.62 and 8.69 eV 264 respectively) (Chan et al., 1993; Grover et al., 1987). Since the formation of water tetramer clusters 265 increases with isoprene mixing ratio and humidity, it is suggested that the interaction between water clusters and isoprene-benzene adducts in the IMR results in a charge exchange from the 266 267 isoprene-adduct to the water tetramer in a similar way that was previously described between 268 benzene cation and water clusters. For example, Miyazaki et al. (2004) showed that the IR spectra

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of benzene-water ion clusters $[(H_2O)_n C_6H_6]^+$ where $(n \ge 4)$ resembles that of protonated water clusters and suggested that the charge is held by the water molecules, such clusters that are likely to be formed in the IMR are expected to be broken apart in the ion optics. It is likely that the observed trends of the humidity dependent sensitivity of isoprene and water tetramer signal also results from a similar formation and de-clustering in our CI-ToFMS.

274 3.3.2 Monoterpenes

275 The dependence of monoterpene sensitivity on SH is shown in Figure 7 for the molecular ion 276 ($C_{10}H_{16}^+$; 136 *m/Q*). Instrument sensitivity under nominally dry conditions displays a wide range 277 of sensitivities, that are species dependent (4.8 to 21.0 ncps·ppt⁻¹). At high specific humidity, 278 sensitivities converge significantly (9.5 to 15.0 ncps·ppt⁻¹). The observed dependence in the α -279 pinene sensitivity on SH reported here is counter to that previously reported by our group in Kim 280 et al. (2016). This is attributed to the different instrument operational configuration used here (e.g., 281 high concentration and purity benzene reagent ion precursor and low electric field strengths).

282 The humidity dependent sensitivity of D-limonene is anomalous compared with the other 283 monoterpenes studied, where the CI-ToFMS sensitivity to D-limonene decreases by a factor of 4 284 over the studied humidity range. The gradual and systematic decrease of the sensitivity suggests 285 that the ionization of D-limonene by charge transfer is not the only ionization mechanism and/or 286 that the D-limonene cation is subjected to subsequent reactions which results in the formation of 287 other detectable ions. We calculated the calibration curves of each of the recorded mass-to-charge 288 ratios to identify product ions that showed: 1) high correlation with the delivered D-limonene 289 mixing ratio ($R^2 > 0.98$) and 2) the contribution to the total sensitivity (i.e. slope) was higher than 1 ncps ppt⁻¹. A representative normalized calibration curve of the three ions (135, 136, and 168 290 291 m/Q) that met these criteria is presented in Figure 8. The peak at 168 m/Q (C₁₀H₁₆O₂⁺) is attributed 292 to either a D-limonene-O₂ adduct or a D-limonene oxidation product (e.g. limonene epoxide). The 293 peak at 135 m/Q (C₁₀H₁₅)⁺ represents the [M-1]⁺ product. We speculate that this product could be 294 formed following the oxidation of an $[M+1]^+$ ion, formed via proton transfer, and the subsequent 295 departure of HOOH (Karlberg et al., 1994). The purity of the primary standard was confirmed via 296 GC-MS, and comparable peak ratios were measured when sampling the standard directly, ruling 297 out the potential for the nebulization process to alter the MS peak ratios. Finally, the $[M+32]^+$ and 298 [M-1]⁺ peak intensity intensities is are reduced to baseline by sampling the terpene in nitrogen,

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suggesting that the [M+32]⁺these peaks is are a result of secondary ion chemistry involving O₂. 299 300 The normalized sensitivity of each of these three peaks decreases with increasing SH (Figure 9), 301 suggesting that water clusters compete or suppress the charge transfer to the contributing ions. The 302 humidity dependent sensitivity of all the studied MTs, calculated as the sum of all their 303 contributing ions, shows lower variability, mostly due to the higher sensitivity to D-limonene when 304 all product ions are accounted for (Figure 10). The variations in the sensitivities between different 305 monoterpenes is small $(14 \pm 3 \text{ ncps ppt}^{-1})$ and instrumental response is largely independent on SH from 4 to 14 g kg⁻¹. This range is typical at boreal forests during the summer (Suni et al., 2003). 306 307 The reported sensitivities, product ions, and dependence on ambient water concentrations and 308 neutral benzene concentration for select monoterpenes are shown in Table 2.

309 3.3.3 Sesquiterpenes

310 The sensitivities of the CI-ToFMS toward SQTs, detected as the charge transfer product at 204

311 m/Q, show minimal dependence on SH between nominally dry conditions and 14 g kg⁻¹ (Figure

312 11). Using the same process discussed in section 3.3.2 for identifying other product ions, it was

found that 203 and 236 m/Q (C₁₅H₂₃⁺ and C₁₅H₂₄O₂⁺) also contributed to product ion intensity.

314 The response of the farnesene and isolongifolene molecular ions and their related contributing ions 315 are presented as examples of SQTs dependence on SH (Figure 12). All three major ions were 316 observed at all measured SHs and in the case of isolongifolene, the normalized response of 203 317 m/Q (C₁₅H₂₃⁺) was higher than the molecular ion (204 m/Q, C₁₅H₂₄⁺) over the entire SH range 318 including at nominally dry conditions (Figure 12). At present, we don't have a definitive 319 mechanism for the product ion distribution, but the presence of similar products (i.e. ([M-1]⁺ and 320 $([M+32]^+)$ and their humidity dependence suggest that the molecular ions of sesquite penes are 321 subjected to similar reactions as MTs which results in a lower signal of the molecular ion. Similar 322 to MTs, the humidity dependent sensitivities of sesquiterpenes calculated as the sum of all 323 contributing ions, lowers the variability in calculated sensitivities (Figure 13). Since the sensitivity 324 is independent of the humidity a general sensitivity to all SQTs of 9.6 \pm 2.3 ncps pptv⁻¹ can be 325 further used for quantification of ambient SQTs. The reported sensitivities, product ions, and 326 dependence on ambient water concentrations and neutral benzene concentration for select 327 sesquiterpenes are shown in Table 3.

329 4. Conclusions

330 We show that benzene cluster cations are a sensitive reagent ion for chemical ionization of select 331 biogenic volatile organic compounds. We demonstrate that isoprene is primarily detected as an 332 adduct ($C_5H_8 \cdot C_6H_6^+$) with a sensitivity ranging between 4-10 ncps ppt⁻¹, that depends strongly on 333 the reagent ion precursor concentration and specific humidity (SH). This highlights the importance 334 of continuous infield calibrations for isoprene concentration measurements. We show that 335 monoterpenes are primarily detected as the molecular ion $(C_{10}H_{16}^+)$ with an average sensitivity, across the five measured compounds, of 14 ± 3 ncps ppt⁻¹ for SH between 7 and 14 g kg⁻¹, typical 336 of the boreal forest during summer. Sesquiterpenes are detected primarily as the molecular ion 337 338 $(C_{15}H_{24}^{+})$ with an average sensitivity, across the four measured compounds, of 9.6 ± 2.3 ncps ppt ¹ that is also independent of specific humidity. Given that signal intensity was observed at ([M-1]⁺ 339 340 and ([M+32]⁺, for a few select terpenes (e.g., D-limonene) we recommend that future 341 measurements of total monoterpenes utilize all three product ions. We suggest that future studies 342 that utilize benzene cluster cation chemistry use high purity liquid reservoirs and benzene neutral concentrations at or above 300 ppmv. 343

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349 Table 1. Molecular structures for the terpenes characterized in this study.





352 Table 2. Monoterpene sensitivities and dependence on operating and sampling condi	tions.
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Compound	Sensitivity [†] (ncps pptv ⁻¹) (SH = 6.9 g kg ¹)	M ⁺ :[M-1] ⁺ :[M+32] ⁺ (SH = 0.01 g kg ⁻¹) [‡]	M ⁺ :[M-1] ⁺ :[M+32] ⁺ (SH = 6.9 g kg ⁻¹) [‡]	f(H ₂ O)	f(C ₆ H ₆)
α-pinene	17.9	23.9:0.64:0.35	17.4:0.21:0.25	Y	Ν
β-pinene	18.4	14.9:0.28:0.33	17.6:0.33:0.39	Ν	Ν
D-limonene	13.6	5.4:3.4:8.0	3.7:3.0:6.9	Y	Ν
β-myrcene	11.5	4.6:0.56:0.94	8.7:1.1:1.7	Y	Ν
ocimene	13.2	13.1:1.50:0.29	12.4:0.42:0.36	Ν	Ν

 † SH = 6.9 g kg⁻¹ corresponds to 65 % RH at 15 °C, representative of Boreal regions. The reported sensitivity includes the contributions from the M⁺, M-1⁺, and M+32⁺ ions.

 $^{\pm}$ Sensitivities (ncps pptv⁻¹) at M⁺, M-1⁺, and M+32⁺, is reported for SH = 0.01 and 6.9 g kg⁻¹.

356

357 Table 3. Sesquiterpene sensitivities and dependence on operating and sampling conditions.

Compound	Sensitivity [†] (ncps pptv ⁻¹) (SH = 6.9 g kg ⁻¹)	M ⁺ :[M-1] ⁺ :[M+32] ⁺ (SH = 0.01 g kg ⁻¹) [‡]	M ⁺ :[M-1] ⁺ :[M+32] ⁺ (SH = 6.9 g kg ⁻¹) [‡]	f(H ₂ O)	f(C ₆ H ₆)
farnesene	10.4	7.8:1.3:1.6	7.8:1.1:1.5	Y	Ν
α-humulene	8.6	5.2:2.6:0.63	5.3:2.8:0.5	Ν	Ν
β -caryophellene	6.9	4.6:1.4:2.2	4.0:1.1:1.9	Y	Ν
isolongifolene	12.3	3.1:7.7:1.2	3.4:8.8:0.15	Y	Ν

 ${}^{\dagger}SH = 6.9 \text{ g kg}^{-1}$ corresponds to 65 % RH at 15 °C, representative of Boreal regions. The reported sensitivity includes the contributions from the M⁺, M-1⁺, and M+32⁺ ions.

360 *Sensitivities (ncps pptv⁻¹) at M⁺, M-1⁺, and M+32⁺, is reported for SH = 0.01 and 6.9 g kg⁻¹.



Figure 1. CI-ToFMS mass spectrum acquired when overflowing the inlet with excess nitrogen (black) and for a nebulized solution of chloroform-d at a flow rate of 3μ l min⁻¹ in a nitrogen carrier gas (red), where the resulting [CDCl₃] = 180 ppmv. No signal was observed above the baseline for any other fragments or the parent (CDCl₃⁺, 120 m/Q).



368 369 370 Figure 2. CI-ToFMS calibration curve for isoprene, detected as $C_6H_6^+$ · C_5H_8 at 146 m/Q. The 371 372 373 sensitivity (slope) is 7 ncps, R²=0.99. Error bars represent the standard deviation of the triplicate calibrations.



377 Figure 3. a) CI-ToFMS mass spectrum acquired when overflowing the inlet with nominally dry 378 zero air for a benzene neutral concentration of 300 ppm using a liquid reagent ion delivery and b) 379 same as in a, but with the first RF-only octupole ion guide turned off, resulting in a much weaker 380 381 electric field strength.

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Figure 4. CI-ToFMS sensitivity to: a) monoterpenes $(C_{10}H_{15}^+; 136 m/Q)$, b) sesquiterpenes $(C_{15}H_{24}^+; 204 m/Q)$, and c) isoprene $(C_6H_6^+\cdot C_5H_8; 146 m/Q)$ as a function of benzene neutral concentration normalized to the sensitivity at 300 ppmv neutral benzene. Measurements were conducted in nominally dry zero air.

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Figure 5. Humidity dependent CI-ToFMS sensitivities to isoprene (green circles, $C_6H_6^+\cdot C_5H_8$, 146 *m/Q*), and the protonated water tetramer (blue squares, $H_3O^+\cdot(H_2O)_3$, 73 *m/Q*), derived from calibration curves such as those shown in Figure 6. The reported sensitivities are the average of triplicate calibration curves with all linear best fits having $R^2 > 0.98$. Error bars represent the

393 standard deviation of the triplicate calibrations. All calibrations were performed in zero air.



Isoprene mixing ratio (pptv)

395 396 Figure 6. CI-ToFMS sensitivity to isoprene, observed as the isoprene-benzene cluster (green 397 circles, $C_6H_6^+C_5H_8$, 146 m/Q) and water protonated tetramer (blue squares, $H_3O^+(H_2O)_3$, 73 m/Q). 398 Dashed lines are the least square best fit lines (R^2 >0.98). Calibration was performed at SH of 14 g 399 kg⁻¹ in zero air.





402 **Figure 7.** Humidity dependent sensitivities to select MTs detected as $M^+(C_{10}H_{16}^+, 136 m/Q)$. Error 403 bars indicate the standard deviation of triplicate measurements. All calibrations were conducted in 404 zero air. Error bars represent the standard deviation of the triplicate calibrations. All calibrations 405 were performed in zero air.





409 **Figure 8.** Normalized calibration of D-limonene for all major product ions ($C_{10}H_{16}^+$, 136 m/Q,

410 green circles), $(C_{10}H_{15}^+, 135 \text{ m/Q}, \text{ orange squares})$, and $(C_{10}H_{16}O_2^+, 168 \text{ m/Q}, \text{ purple triangles})$. 411 Calibration was performed in zero air at 14 g kg⁻¹ specific humidity (80% RH at 23 °C). Dashed 412 lines are least squares best fit lines (all R²>0.99).



415 **Figure 9.** Humidity dependent, normalized sensitivities to a) α-pinene b) D-limonene for all major 416 product ions ($C_{10}H_{16}^+$, 136 *m/Q*, blue-green circles), ($C_{10}H_{15}^+$, 135 *m/Q*, green-orange squares), 417 and ($C_{10}H_{16}O_2^+$, 168 *m/Q*, red-purple triangles). Error bars represent the standard deviation of the 418 triplicate calibrations. All calibrations were performed in zero air.



421

422 423 Figure 10. Humidity dependent, CI-ToFMS monoterpene sensitivities reported as the sum of all detected masses (135, 136, and 168 m/Q). Error bars represent the standard deviation of the

424 425 triplicate calibrations. All calibrations were performed in zero air.



427 **Figure 11.** Humidity dependent sensitivities of SQTs detected as $C_{15}H_{24}$ (204 *m/Q*). Error bars 428 represent the standard deviation of triplicate measurements. All calibrations were performed in 429 zero air.



431 432

Figure 12. Humidity dependent, normalized sensitivities to a) farnesene and b) isolongifolene for all major product ions ($C_{15}H_{23}^+$, 203 m/Q, blue circlesorange squares), ($C_{15}H_{24}^+$, 204 m/Q, gray squaresgreen circles), and ($C_{15}H_{24}O_2^+$, 236 m/Q, red diamondspurple triangles). Error bars represent the standard deviation of the triplicate measurement.





440 **Figure 13.** Humidity dependent, normalized sensitivities to sesquiterpenes, reported as the sum of

- 441 the major product ions $(C_{15}H_{23}^+, 203 m/Q)$, $(C_{15}H_{24}^+, 204 m/Q)$, and $(C_{15}H_{24}O_2^+, 236 m/Q)$. Error
- 442 bars represent the standard deviation of triplicate measurements.

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