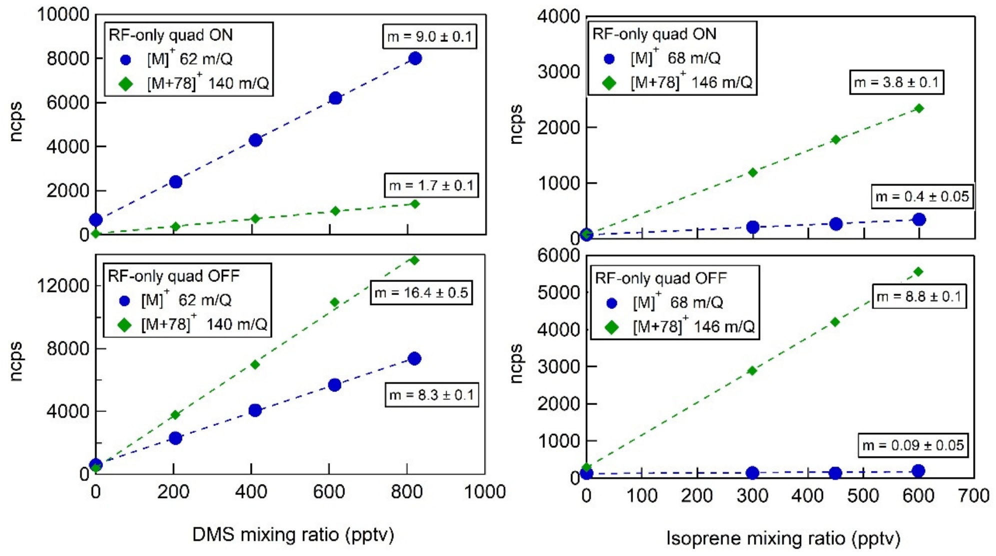
Below, please find our detailed response and a short description of how the manuscript was revised in response to each of the reviewer's comments.

Reviewer 2

1) The manuscript states that a "new set of applied voltages with softer de-clustering power" (line 118) is used here, however there is no information given on what the voltages are or how the voltages compare to those used by the group previously (other than the above vague remark). For instance, there is no discussion about how the relative intensity of the $C_6H_6^+$ and $(C_6H_6)^+(C_6H_6)$ compare. Given the current emphasis on voltage scanning within the community (Brophy and Farmer, 2016; Lopez-Hilfiker et al., 2016), I am surprised that such experiments were not carried out here. I think that the inclusion of such experiments would be an asset to the manuscript as it may help provide (at least a basic) explanation of some of the peculiarities that are occurring with isoprene. I am not suggesting that the declustering experiments be performed for all the compounds investigated here; however, the inclusion of a select few would improve the impact of the manuscript. Currently, the only change in the declustering voltages is by turning off the voltages in the first RF-only quadrupole and these results are only shown for sampling zero air (no analyte; Figure 3). While this provides some insight, it is limited given the large drop in ion transmission and the lack of measurement of an analyte. It would be interesting to see how the distribution of $[M-1]^+$, M^+, and $[M+32]^+$ changed as a function of voltage scanning for the monoterpenes and sesquiterpenes. I think it is also an overstatement to say in the abstract (lines 19 & 22) and conclusion (line 328) that the effect of declustering voltages was studied given the limited investigation into this effect.

The reviewer raises an important point that highlights we need to further clarify our intent regarding voltage settings. In Bertram et al. [2011], we described the utility of voltage tuning of the exit lenses of the RF-only octupoles to vary cluster distributions while maintaining high transmission. The operational voltages used here have essentially the same field strengths at the "weak field" described in Bertram et al. [2011]. The only deviation is that we start from 0V on the front end of the IMR for practical considerations.

To reduce field strengths even further, in an attempt to probe the cluster distributions of the IMR, we turned off the RF-only quadrupoles completely. This is not meant as an operational configuration, as ion transmission is sacrificed (as the reviewer notes). However, it gives us the best insight into the cluster distribution in the IMR and hence the ion-molecule reaction mechanism. Below, we show the impact of the RF-only quadrupole on analyte-cluster distributions for DMS and isoprene.



As shown above, reduction in the field strength favors the M+78 cluster in the case of DMS, as expected. In the case of isoprene, with the focusing RF quad on, we observe a small percentage of isoprene as the bare ion (ca. 10%). We expect that this is due to declustering of the isoprene-benzene cluster at a point when a sufficient amount of positive charge is on the isoprene in the cluster. Following declustering, there are few collisions of the bare isoprene ion with benzene and the molecular ion is transferred to the mass analyzer. With the RF-only quad off, we do not observe statistically significant amounts of the bare ion. This suggests that the isoprene is found exclusively as the cluster in the IMR.

The manuscript has been edited in the following locations to address these points:

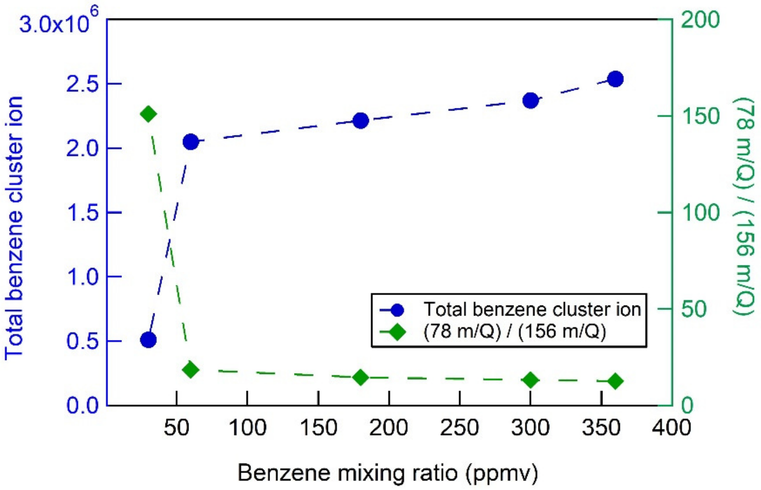
Line 18: In addition, we determine the dependence of CI-ToFMS sensitivity on the reagent ion neutral delivery concentration and water vapor concentration.

We have also removed the phrase “declustering voltages” from line 328 as the reviewer is correct that we adjusted the field strength to learn about the ionization mechanism, but not to develop new operational configurations for sampling.

Line 118: This line has been edited to now read: “We also examine the de-clustering power of the RF only quadrupole to better determine the cluster distribution present in the ion molecule reaction chamber.”

2) Sections 3.1 & 3.2: How does the abundance and ratio between $C_6H_6^+$ and $(C_6H_6)^+(C_6H_6)$ change as the concentration of neutral benzene is increased? Does this provide any insight into the isoprene results?

We expect that at higher benzene neutral concentrations, larger benzene cluster cations ($(C_6H_6)^+(C_6H_6)_n$, n>1) are favored. However, we do not have evidence for this as clusters larger than n=1 have very weak binding enthalpies, prohibiting their efficient transmission in the mass spectrometer. As noted in the manuscript, even with the RF-only quadrupole off, we do not observe clusters larger than n=1. As a result, there is only a small change in the cluster distribution observed in the mass spectra. The effect of benzene neutral concentration on the observed cluster distribution and the total benzene cluster ion concentration are shown below. We note that at low benzene neutral concentrations, a significant fraction of total ion current can be found as protonated water clusters or O_2^+. We caution over interpretation of the reduction in total benzene cluster ion signal intensity at low benzene neutral concentrations (< 50 ppm) shown here as this experiment was not designed to assess the low concentration regime.



3) I do not see where the text references the tables. Including a reference to the table in the text would be beneficial since the tables show that the M+, $[M-1]^+$, and $[M+32]^+$ ions were investigated for all the compounds and not just those discussed in depth in the text.

We have added references to the tables in the text.

The manuscript has been edited in the following locations to address these points:

Table 1 is now referenced in line 113: "We discuss the sensitivity of benzene cluster cation chemistry to a select number of terpenes (Table 1) at atmospherically relevant mixing ratios (<500 pptv)."

Table 1 is now referenced in line 304: "The reported sensitivities, product ions, and dependence on ambient water concentrations and neutral benzene concentration for select monoterpenes are shown in Table 2."

Table 1 is now referenced in line 323: "The reported sensitivities, product ions, and dependence on ambient water concentrations and neutral benzene concentration for select sesquiterpenes are shown in Table 3."

4) Line 14: replace alpha with the correct symbol

This has been corrected.

5) Line 57-58: The references for NO^+ and H_3O^+ seem a bit strange as the references refer only to early work and not more recent work, while the references for other ionization mechanisms contains more recent work. For instance, the absence of Koss et al. (2016).

References to Karl et al., 2012, Mochalski et al., 2014, and Koss et al., 2016 have been added.

6) Line 185: "error bars are the standard deviation of repeated triplicate measurements" but caption of figure 2 "error bars represent the standard deviation of the 1 Hz measurements."

The figure caption has been revised. The error bars represent the standard deviation of the triplicate calibrations.

7) Line 209: "Without the first RF-only quadrupole" Is it removed or just the voltages turned off. If the voltages was it all the voltages or just the RF component?

The manuscript has been revised to read: " … but without the RF and voltage bias applied to the first quadrupole ion guide."

8) Line 330-331: The wording here makes it appear like a recommendation to only use $C_{10}H_{16}^+$ for quantification of monoterpenes. However, the average sensitivity appears to be that obtained using the M^+, $[M-1]^+$, and $[M+32]^+$ ions (Figure 10) and not just the M^+ ion (Figure 7). What recommendation do the authors provide for quantification of monoterpenes?

As shown in Table 2 (and 3), for most monoterpenes and sesquiterpenes measured, the majority of the measured signal is as the molecular ion. However, select monoterpenese (and sesquiterpenes) such as D-limonene have a significant amount of signal at [M-1] and [M+32]. For these reasons, we would recommend including signal intensity at these masses in the overall measurement of monoterpenes (and sesquiterpenes).

The manuscript has been revised (line 337) to read: "Given that signal intensity was observed at ($[M-1]^+$ and ($[M+32]^+$, for a few select terpenes (e.g., D-limonene) we recommend that future measurements of total monoterpenes utilize all three product ions."

9) Lines 333-334: Same comment as above expect for sesquiterpenes.

See response to comment #8.

10) Table 1: I don't find this particularly useful since there is no in depth exploration of how structure might relate to the different observed sensitivities. To be clear, I am not suggesting that such an explanation be incorporated; I do not think it would be appropriate given the extent of the data.

While we did not make tangible connections between terpene structure and sensitivity, we think the table is helpful to the reader that may not be directly familiar with terpene structure.

11) Figure 3: The peak at m/z 156 should be labeled $(C_6H_6)^+$ (C_6H_6)

Thank you for catching this error. The figure has been revised.

Reviewer 3

1) Page 6 line 161-163: Chloroform is unlikely to be ionized by benzene dimer cation given its higher ionization energy. Where would the chloroform fragment come from, i.e. how is the parent chloroform ion generated?

We expect that the chloroform fragment is generated from trace O_2^+ in the instrument. The sensitivity is extremely small (ca. 100 Hz for 180 ppm).

2) Page 9 line 237-241: For the unclear benzene cation reaction mechanism with isoprene, can you approach it through relationship between sharing pi electrons and reaction enthalpy? Presumably, the isoprene molecule shares its pi electrons with the benzene cation. For bigger benzene cation clusters, they have bigger pi system and more pi electrons, and isoprene needs to share "less" of its pi electrons with the benzene cation. It seems reasonable this trend with increasing benzene concentrations was observed.

This is possible. We decided not to speculate on the dependence of the isoprene sensitivity on the concentration of neutral benzene in the manuscript. We expect, although do not have evidence, that the benzene clusters are larger for higher neutral benzene concentrations. It is possible that for larger benzene clusters a larger fraction of the charge is on isoprene at the point of collisional declustering as the reviewer suggests. This would translate to a larger sensitivity at higher benzene concentration. We are working on a subsequent paper that focuses on quantum calculations of these benzene adducts and elect not to speculate on the cause in this manuscript.

3) Page 10 line 268-271: The cited work by Ibrahim et al. (2005) does not contain any IR spectrum. It is also hard to imagine a 3-body deprotonation process that involves benzene, water cluster and isoprene, as proposed by the paper. Could m/z 73 be an isobaric ion of water tetramer ion? Does the ToF have the resolution to determine the exact mass and identify the chemical formula? Also, given this high intensity of protonated water clusters (~9E4 Hz water ion in Figure 6, comparable to 2E5 Hz benzene ion in Figure 5), could BVOC also undergo proton transfer reaction in the IMR?

We thank the reviewer for catching this citation error. As the reviewer notes, the Ibrahim paper did not contain the IR spectra; it only presented the hydration path of ionized benzene via the arrival time distributions of $C_6H_6\text{-}(H_2O)_n^+$ clusters and supporting quantum calculations. The publication the authors should have also cited is Miyazaki et al. (2004). Miyazaki et al. presents IR spectra of $C_6H_6\text{-}(H_2O)_n^+$ clusters up to n=23. Figures 1 & 3 show that the IR spectra of $C_6H_6\text{-}(H_2O)_n^+$ clusters resemble $H^+(H_2O)_n$ starting at $n \geq 4$. Figure 2 of Miyazaki et al. shows the hydrogen bonded H_2O networks required to deprotonate a $C_6H_6^+$. We are speculating that we see the effects of a proton-transfer from a $C_6H_6 \cdot C_5H_8^+$ cluster to a network of H_2O. At this time we cannot definitively comment on what the structure of that network is exactly but the end product is that of a protonated water tetramer. Our own computational studies have so far shown that a key component of sensitivity in benzene CIMS is through charge migration within a given benzene adduct. The influence of a water environment on that charge migration varies depending on the species in that adduct. We have performed quantum mechanical calculations of charged benzene adducts in the presence of varying $(H_2O)_n$ with water network structures of both those in Ibrahim et al. and Miyazaki et al. and have found that in the case of a $C_6H_6\text{-}C_5H_8^+$ adduct, the positive charge starts to migrate towards a $(H_2O)_5$ cluster. Our group is working on more calculations to prepare a separate paper explaining charge distribution with respect to detection *via* benzene CIMS so we chose not to comment further on this at this time.

We cannot rule out an isobaric ion at m/z 73 with the mass resolution of our ToFMS. However, the sensitivity to the isobaric ion would need to be dependent on water and stem from the isoprene source (to be consistent with Fig. 5 and 6). It is possible that this is due to a proton transfer as total water cluster intensity will increase with SH, but total water cluster signal even at 14 g kg^{-1} SH is only 3.7E4 Hz, compared with 9.8E5 Hz for benzene clusters. In addition, this would not explain the observed anti-correlation in signal intensity at 73 and 146 m/Q which would be explained by our proposed mechanism.

The reference on line 267 has been changed from Ibrahim et al. (2005) to Miyazaki et al. (2004). We think this sufficiently addresses the reviewer's concerns.

Reference: Miyazaki et al., Infrared Spectroscopy of Size-Selected Benzene-Water Cluster Cations [C6H6-(H2O)*n*]+(*n*) 1-23): Hydrogen Bond Network Evolution and Microscopic Hydrophobicity, *J. Phys. Chem. A* 2004, *108,* 10656-10660

4) Page 10 line 280: It is not self-explanatory how instrument operational configuration (benzene concentration and electric field) would cause the inconsistency between current work and Kim et al. (2016). More clarifications are needed here.

The inconsistency between Kim et al and this paper is in the SH dependence of the α-pinene sensitivity. In Kim et al., we observed an increase in sensitivity with SH. Here, we observe a very slight decrease. We think the difference in benzene neutral concentration is key here. The increase in sensitivity with SH (Kim et al) was observed using three different mass spectrometers for both laboratory calibrations and in field standard additions. All operating with 10 ppm neutral C_6H_6 concentrations. The slight decrease in sensitivity with SH was replicated over a comprehensive 6 month evaluation of monoterpene sensitivity (this study), at high benzene concentration (>300 ppm).

In Kim et al., we operated at low C_6H_6 concentrations due to contaminants in the benzene compressed gas source. Unfortunately, this led to an increase in the percentage of protonated water clusters as SH increases. This has a few implications. The most notable is that proper normalization to the primary ion becomes challenging at high SH as the observed signal of benzene cluster cations is small. In Kim et al., we normalized only to the sum of the benzene cluster cations, which may have overestimated the dependence of sensitivity on SH when compared to the current study where the sum of the benzene cluster cation signal is small. We note that this does not impact the conclusions drawn from the analyses of Kim et al. 2016 or 2017, as the normalization method was consistent. However, we strongly recommend that future studies use higher benzene neutral concentrations to avoid these issues.

The manuscript has been revised to state:

Line 279: "This is attributed to the different instrument operational configuration used here (e.g., high concentration and purity benzene reagent ion precursor). More specifically, high neutral benzene concentrations (300 ppmv) suppress the formation of protonated water clusters at high specific humidity. As a result, the benzene cluster cations account for greater than 90% of total ion current under all conditions. This reduces complications surrounding the normalization of analyte signals."

5) Page 10 line 292-294: If limonene is ionized through charge transfer followed by isomerization, how to rationalize the fact the stronger C-H bond is broken, instead of the weaker C-C bond? What hydride abstraction reactions for alkenes have been reported in literature that can be related to this work?

A suggested path would require oxidation of an $[M+1]^+$ ion to form a hydroperoxide followed by HOOH elimination. The presence of water clusters in our system should suggest some proton transfer reactions to limonene to make an $[M+1]^+$. It is known that the autoxidation of *d*-limonene results in the allergens *cis*- and *trans*-limonene-2-hydroperoxides. A hydrogen abstraction can occur following the departure of the hydroperoxyl radical from one of these peroxides. Given the abundance of limonene hydroperoxides from autoxidation in nature, the absence of $[M+1]^+$, and our sensitivity to the $[M+32]^+$ ion, an oxidation product ion, this would make the most sense. This value may decrease with increasing specific humidity due to the change in water cluster size distribution to larger water networks, inhibiting proton donation.

The manuscript has been revised to state:

Line 291: “The peak at 135 *m/Q* $(C_{10}H_{15})^+$ represents the $[M-1]^+$ product, perhaps due to oxidation of an $[M+1]^+$ ion followed by departure of HOOH (Karlberg et al., 1994).”

Reference: Karlberg et al., *Hydroperoxides in oxidized d-limonene identified as potent contact allergens*, Arch Dermatol Res (1994) 286:97 103

6) Figure 3 caption line 370-371: “...using a liquid reagent ion delivery...” should be “liquid reagent ion precursor delivery”. “...the first RF-only octupole...” I assume it is RF-only quadrupole here. Also in both panels in figure 3, the peak at m/z 156 should be (C6H6)+(C6H6), not the trimer.

This has been changed.

7) Table 2 and Table 3: The manuscript does not have clear reference to what f(H2O) and f(C6H6) are.

Line 304 and 323 have been edited to include these definitions: “The reported sensitivities, product ions, and dependence on ambient water concentrations, $f(H_2O)$, and neutral benzene concentration, $f(C_6H_6)$, for select monoterpenes are shown in Table 2.”

8) Table 3: The first two ratios under SH=6.9 look like typos.

Thank you, this has been updated.

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

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Abstract

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 deployable chemical ionization time-of-flight mass spectrometer (CI-ToFMS), using benzene cluster cation ion chemistry, for detection of dimethyl sulfide, isoprene and α-~~alpha~~ pinene. Here, we present laboratory measurements of the sensitivity of the same instrument 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). In addition, we determine the dependence of CI-ToFMS sensitivity on the reagent ion neutral delivery concentration~~, the instrument electric field strength~~ 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 depends strongly on the reagent ion precursor concentration, de-clustering voltages, and specific humidity (SH). Monoterpenes are detected primarily 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 of the boreal forest during summer. Sesquiterpenes are detected primarily as the molecular ion ($C_{15}H_{24}^+$) with an average sensitivity, across the four measured compounds, of 9.6 ± 2.3 ncps ppt^{-1} that is also independent of specific humidity. Comparable sensitivities across broad classes of terpenes (e.g., monoterpenes and sesquiterpenes), coupled to the limited dependence on specific humidity, suggests that benzene cluster cation CI-ToFMS is suitable for field studies of biosphere-atmosphere interactions.

1. Introduction

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., 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 constituents (Guenther et al., 1995). The emission rate and the chemical composition of emitted BVOCs is a complex function of the vegetation species and the wide array of stress factors that it is exposed to (Hallquist et al., 2009; Lang-Yona et al., 2010; Zhao et al., 2017). Atmospheric oxidation of BVOCs results in the formation of low volatility compounds that can lead to new 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 impact Earth's radiative budget by scattering solar radiation and/or altering cloud formation and 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). Therefore, uncertainties in BVOCs emissions present significant issues in estimating net climate 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 essential for understanding complex and non-linear biosphere-atmosphere interactions.

Chemical ionization mass spectrometry (CIMS) is a commonly utilized selective and sensitive method for *in situ* detection of trace gases (Huey, 2007). The sensitivity and selectivity towards a specific compound or class of compounds having similar functional groups rely on the selection of an appropriate ion (i.e. reagent ion) that reacts with and ionizes the analyte *via* an ion-molecule reaction. For example, iodide ions have been used to measure reactive nitrogen compounds, halogen containing species and oxygenated VOCs (Lopez-Hilfiker et al., 2015; Riedel et al., 2012; Thornton et al., 2010), CF_3O^- has been used for the detection of peroxides and organic nitrates (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 et al., 2014), H_3O^+ for VOCs and their oxygenated products (Lindinger et al., 1998) and benzene cluster cations for dimethyl sulfide (DMS), isoprene, and terpenes (Kim et al., 2016; Leibrock and Huey, 2000).

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

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

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

$$(C_6H_6)_2^+ + M \rightarrow M^+\cdot(C_6H_6)_2 \qquad (R2)$$

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

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 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).

The field deployable CIMS that utilizes a time-of-flight mass analyzer (ToFMS), previously described by Kim et al. combines the efficient production and transmission of ions at high pressure (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 spectra (10-800 *m/Q*) at rates higher than 10 Hz (Bertram et al., 2011). These benefits make CI-ToFMS highly applicable for studying atmospheric exchange processes of trace gases at the air-ocean interface that require fast response rates (Kim et al., 2014). However, at these pressures, the distribution of benzene clusters and their associate ion-molecule reactions times are not well constrained. Unlike PTR-MS, it is not possible to directly derive the analyte mixing ratio from laboratory studies of the ion-molecule kinetics (reaction rates) that are conducted at lower pressure in which both the reaction times and cluster distribution have been previously determined. As such, quantitative analysis of atmospheric trace gases using high pressure CIMS necessitates either a direct or empirical calibration for each analyte as a function of the atmospheric conditions (e.g. 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, D-limonene, β-myrcene, ocimene, farnesene, isolongifolene, α-humulene and β-caryophyllene). We ~~demonstrate the effect of a new set of applied voltages with softer~~also examine the de-clustering power ~~on the observed cluster distribution in the instrument and discuss the effects~~ of the RF only quadrupole to better determine the cluster distribution present in the ion molecule reaction chamber. ~~on ion transmission and its contribution to the de-clustering power of the instrument~~.

2. Experimental

2.1 Materials

The following analytes were purchased from Sigma-Aldrich and used with no further purification: isoprene, α-pinene, β-pinene, D-limonene (≥99%), β-myrcene (96.2%), ocimene (97.0%, as a mixture of isomers), farnesene (>90.0%, as a mixture of isomers) α-humulene (>96.5%), β-caryophyllene (≥98.5%), isolongifolene (≥98.0%, as a mixture of isomers), benzene (≥99.5%) and chloroform-d (99.8 atom % D). A compressed gas cylinder of 0.184 ppm of DMS-d_3 in N_2 was purchased from Praxair, USA. Water was supplied from a Milli-Q system at 18.2 MΩ·cm. Nitrogen was used from a UHP liquid N_2 dewar (Airgas). UHP (99.999%) oxygen cylinders were purchased from Airgas.

2.2 Chemical Ionization Mass Spectrometer

The detailed description of the CI-ToFMS (Tofwerk AG, Switzerland and Aerodyne Research Inc., USA) and its performance are discussed in Bertram et. al.(Bertram et al., 2011) In brief, reagent ions are generated by passing 10 sccm of UHP N_2 over the headspace of a liquid benzene reservoir contained in a stainless steel bottle. Benzene vapor is diluted with 2.2 slpm of N_2, prior to delivery to the ^{210}Po source. The benzene vapor mixing ratio is estimated from the dilution ratio and benzene vapor pressure. In the experiments discussed here, we varied the benzene concentration between 60 and 360 ppm. A combination of stainless steel and Teflon tubing was used to transfer benzene vapors to minimize extraction of organic compounds from the tubing. Following dilution, benzene vapor flows through a 10 mCi α emitting radioactive ^{210}Po source (NRD 2021–1000). The collision of α-particles with N_2 results in the formation of N_2^+ ions that ionize the benzene clusters (Dondes et al., 1966). The analyte sample is mixed with the formed benzene cluster cations at the ion-molecule reactor (IMR) held at 75mbar. At this pressure, the estimated analyte residence time in the IMR is 100 ms. The reagent and product ions are 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}

mbar) in which a second RF-only quadrupole is used to focus the ion beam. The ion beam is then guided by a further set of ion optics to the entrance point of the extraction region of the compact time of flight mass analyzer (Tofwerk AG, Switzerland).

2.3 Liquid Calibration Unit

A custom liquid calibration system was developed to deliver known, atmospherically relevant mixing ratios (< 500 pptv) of gas-phase terpenes to the CI-ToFMS. The liquid calibration system uses a syringe pump to continuously evaporate known quantities of solution into a heated carrier gas flow, generating known mixing ratios of select terpenes. To produce trace concentrations of each analyte, the standard liquid material was diluted in-series with chloroform-d using a set of calibrated auto pipettes. Chloroform-d was chosen due to its solvent properties and low boiling point (61°C) that enhances the evaporation of the analyte. Due to its ionization energy (IE > 11 eV (Bieri et al., 1981)), higher than that of benzene cation clusters, it was expected that chloroform would not be ionized and would have negligible impact on the benzene cluster cation ionization mechanisms. To assess this, mass spectra were recorded for solutions containing solely deuterated chloroform for a variety of different pump flows from 0 to 5µl min^{-1}. We did not observe the molecular cation of chloroform-d ($CDCl_3^+$, 120 *m/Q*) and only very small signatures of the fragments (at 48, 84 or 86 *m/Q*) were observed (Figure 1), consistent with the IE of chloroform-d being higher than that of the reagent ions (11.37 ± 0.02 eV compared with 8.69 eV) (Grover et al., 1987) (Werner et al., 1974). It was also determined that concentration of deuterated chloroform did not interfere with reagent ion or water cluster signal intensities.

To evaporate the analyte solution, a controlled amount (0-5µl min^{-1}) of the analyte solution was delivered by a syringe pump (Harvard Apparatus, model 11) *via* PEEK tubing (Upchurch scientific) into a heated carrier stream resulting in $CDCl_3$ mixing ratios from 60-300 ppmv. A synthetic 80:20 N_2:O_2 mixture was used as zero air and heated by an in-line gas heater (Omega, AHP-3741). The temperature of the zero air flow at the point of intersection with the PEEK tubing was kept at 80°C via a PID temperature controller (Omega, CN9300). Excess zero air flow was used to ensure an overflow of the CIMS inlet. The trace concentration of the evaporated analytes and the elevated temperature in front of the inlet (ca. 50°C) helped to prevent re-condensation of the analyte on the inlet tubing. Humidified zero air was generated by passing a fraction of the total flow through the head space of a water reservoir. The relative humidity (RH) of the total air flow was measured using a relative humidity sensor (Vaisala, HMP110), calibrated using the procedure described in Greenspan (1977).

The sensitivities reported in this paper are presented in normalized counts per second per pptv (ncps·pptv^{-1}). We normalized the analyte ion count-rates by the sum of the benzene cation monomer (78 *m/Q*) and dimer (156 *m/Q*) count rates to a reference of 1×10^6 counts per second of total reagent ion signal in order to account for changes in ion transmission and generation over time. Sensitivities are calculated as the slope of the linear fit of each calibration curve of 5-7 steps (Figure 2~~Figure 2~~). Error bars are the standard deviation of repeated triplicate measurements. The performance of the liquid evaporation technique was validated by comparing the sensitivity to dimethyl-1,1,1-d$_3$ sulfide (Praxair certified compressed gas standard, 0.184 ppm ±10%) diluted by zero air to a desired mixing ratio, with that of a diluted nebulized solution of DMS. The slope of the linear fit for calibration measurements from the pressurized cylinder (DMS-d3, 65 *m/Q*) and the solution (DMS, 62 *m/Q*) agreed to better than 10%.

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3. Results and Discussion

3.1 Benzene Cluster Cation Mass Spectra

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

Talebpour et al., 2000). For comparison, a similar spectrum is shown in Figure 3b, using the same benzene neutral concentration and operating voltages, but without the RF and voltage bias applied to the first ~~RF-only~~ quadrupole ion guide. In this mode of operation, the total ion current is reduced by over 95%, and $C_6H_6^+$ and $C_6H_6^+{\cdot}(C_6H_6)$ are nearly equal in intensity, highlighting that benzene cluster collisional dissociation is occurring within this region. Even with the first RF-only quadrupole electronics turned off, the n=2 cluster ($C_6H_6^+{\cdot}(C_6H_6)_2$; 234 *m/Q*) was not observed. Of notable absence (< 1% TIC) in both Figures 3a and 3b are the organic contaminants (92, 106, and 120 *m/Q*) previously attributed to alkyl substituted benzene and protonated water clusters ($H_3O^+{\cdot}(H_2O)_n$; 19, 37, 55, and 73 *m/Q*) that were present at high abundance (>10% of TIC) in Kim et al. (2016). It was postulated in Kim et al., that the source of the organic contaminants was the benzene compressed gas cylinder, as their combined contribution to TIC scaled with the neutral benzene concentration. It was also noted that low benzene neutral concentrations led to elevated water cluster abundance. This resulted in an optimum benzene neutral concentration of 10 ppm, to balance the contributions from organic contaminants and water clusters. Here, we eliminate the organic contaminants through the use of a high purity benzene liquid source permitting operation at higher neutral benzene concentrations (> 300 ppm). As discussed in section 3.2, this has critical advantages for the detection of analytes such as isoprene, and effectively eliminates competing ion 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 3.2) and water vapor concentration (section 3.3).

3.2 Impact of Benzene Neutral Concentration on Terpene Sensitivity

We examined the impact of the benzene reagent ion precursor concentration on terpene sensitivity in nominally dry zero air for benzene neutral concentrations between 60-300 ppm. For the selection of monoterpenes and sesquiterpenes studied here, there was no indication that instrument sensitivity was dependent on the neutral benzene reagent ion precursor concentration between 60–300 ppm (Figure 4~~Figure 4~~ a-b). In Figure 4a-c, the reported sensitivity for each terpene is 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 ($C_6H_6^+ \cdot C_5H_8$; 146 *m/Q*) strongly depends on the benzene concentration below 200 ppm (Figure 4~~Figure 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 $C_6H_6^+ \cdot C_5H_8$ 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.

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3.3 Impact of Specific Humidity on Sensitivity

3.3.1 Isoprene

In these experiments, the specific humidity (SH) was varied between 0 and 14 g kg^{-1}, equivalent to 0-80% RH at 23℃, to assess its effect on the sensitivity. Our reported “nominally dry” cases correspond to 0.7% RH or ca. 0.01 g kg^{-1} SH. As shown in Figure 5, the sensitivity of the CI-ToFMS to isoprene ($C_6H_6^+ \cdot C_5H_8$; 146 *m/Q*) displays a strong, non-linear dependence on SH. Instrument sensitivity increases with increasing SH, reaching a maximum value of 10 ncps·ppt^{-1} at 4 g kg^{-1} (25% RH at 23°C), then decreases significantly at higher humidity. Surprisingly, we observed a linear correlation ($R^2 > 0.95$) between the protonated water tetramer signal (73 *m/Q*) and the delivered isoprene mixing ratio at constant SH that was not observed for smaller protonated water clusters (Figure 6). The apparent sensitivity, derived from the slope of the linear-least squares fit of the observed water tetramer signal *vs.* delivered isoprene concentration, increases with increasing specific humidity above 2 g kg^{-1} (Figure 5). We reiterate that Figure 5 does not show the protonated tetramer signal as a function of SH, but the *sensitivity* of the 73 *m/Q* signal to the delivered isoprene mixing ratio as shown in Figure 6. The decreased sensitivity to isoprene adduct and increase in water tetramer signal with isoprene mixing ratio are unlikely the result of the formation of water protonated clusters *via* charge transfer reaction with benzene cations since the IE of water is significantly higher than that of the benzene dimer (12.62 and 8.69 eV respectively) (Chan et al., 1993; Grover et al., 1987). Since the formation of water tetramer clusters 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 isoprene-adduct to the water tetramer in a similar way that was previously described between benzene cation and water clusters. For example, Miyazaki *et al.* (2004) ~~Ibrahim *et al.* (2005)~~

showed that the IR spectra of benzene-water ion clusters $[(H_2O)_n{\cdot}C_6H_6]^+$ where ($n \geq 4$) 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.

3.3.2 Monoterpenes

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

The humidity dependent sensitivity of D-limonene is anomalous compared with the other monoterpenes studied, where the CI-ToFMS sensitivity to D-limonene decreases by a factor of 4 over the studied humidity range. The gradual and systematic decrease of the sensitivity suggests that the ionization of D-limonene by charge transfer is not the only ionization mechanism and/or that the D-limonene cation is subjected to subsequent reactions which results in the formation of other detectable ions. We calculated the calibration curves of each of the recorded mass-to-charge ratios to identify product ions that showed: 1) high correlation with the delivered D-limonene 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 *m/Q*) that met these criteria is presented in Figure 8. The peak at 168 *m/Q* ($C_{10}H_{16}O_2^+$) is attributed to either a D-limonene-O_2 adduct or a D-limonene oxidation product (e.g. limonene epoxide). The peak at 135 *m/Q* $(C_{10}H_{15})^+$ represents the $[M-1]^+$ product. We speculate that this product ~~,~~ ~~perhaps~~could be formed following the~~ due to~~ oxidation of an $[M+1]^+$ ion, formed *via* proton transfer, ~~followed by~~and the subsequent departure of HOOH (Karlberg et al., 1994). ~~(Karlberg et al., 1994).~~ ~~The peak at 135 *m/Q* ($C_{10}H_{15}^+$) represent the $[M-1]^+$ product, perhaps due to rearrangements of the molecular ion.~~ The purity of the primary standard was confirmed *via* GC-MS, and comparable peak ratios were measured when sampling the standard directly, ruling out the potential for the nebulization process to alter the MS peak ratios. Finally, the $[M+32]^+$ peak intensity is reduced to baseline by sampling the terpene in nitrogen, suggesting that the $[M+32]^+$ peak is a result of secondary ion chemistry involving O_2. The normalized sensitivity of each of these three peaks decreases with increasing SH (Figure 9), suggesting that water clusters compete or suppress the charge transfer to the contributing ions. The humidity dependent sensitivity of all the studied MTs, calculated as the sum of all their contributing ions, shows lower variability, mostly due to the higher sensitivity to D-limonene when all product ions are accounted for (Figure 10). The variations in the sensitivities between different monoterpenes is small (14 ± 3 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). The reported sensitivities, product ions, and dependence on ambient water concentrations and neutral benzene concentration for select monoterpenes are shown in Table 2.

3.3.3 Sesquiterpenes

The sensitivities of the CI-ToFMS toward SQTs, detected as the charge transfer product at 204 *m/Q*, show minimal dependence on SH between nominally dry conditions and 14 g kg^{-1} (Figure 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* ($C_{15}H_{23}^+$ and $C_{15}H_{24}O_2^+$) also contributed to product ion intensity.

The response of the farnesene and isolongifolene molecular ions and their related contributing ions are presented as examples of SQTs dependence on SH (Figure 12). All three major ions were observed at all measured SHs and in the case of isolongifolene, the normalized response of 203 *m/Q* ($C_{15}H_{23}^+$) was higher than the molecular ion (204 *m/Q*, $C_{15}H_{24}^+$) over the entire SH range including at nominally dry conditions (Figure 12). At present, we don't have a definitive mechanism for the product ion distribution, but the presence of similar products (i.e. ($[M-1]^+$ and ($[M+32]^+$) and their humidity dependence suggest that the molecular ions of sesquiterpenes are subjected to similar reactions as MTs which results in a lower signal of the molecular ion. Similar to MTs, the humidity dependent sensitivities of sesquiterpenes calculated as the sum of all contributing ions, lowers the variability in calculated sensitivities (Figure 13). Since the sensitivity is independent of the humidity a general sensitivity to all SQTs of 9.6 ± 2.3 ncps $pptv^{-1}$ can be further used for quantification of ambient SQTs. The reported sensitivities, product ions, and dependence on ambient water concentrations and neutral benzene concentration for select sesquiterpenes are shown in Table 3.

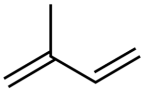
4. Conclusions

We show that benzene cluster cations are a sensitive reagent ion for chemical ionization of select biogenic volatile organic compounds. We demonstrate 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 depends strongly on the reagent ion precursor concentration~~, de-clustering voltages,~~ and specific humidity (SH). This highlights the importance of continuous infield calibrations for isoprene concentration measurements. We show that 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 of the boreal forest during summer. Sesquiterpenes are detected primarily as the molecular ion ($C_{15}H_{24}^+$) 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]$^+$ and ([M+32]$^+$, for a few select terpenes (e.g., D-limonene) we recommend that future measurements of total monoterpenes utilize all three product ions. We suggest that future studies that utilize benzene cluster cation chemistry use high purity liquid reservoirs and benzene neutral concentrations at or above 300 ppmv.

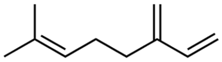
Acknowledgements

This work was supported by a National Science Foundation (NSF) CAREER Award (Grant No. AGS-1151430) and the Office of Science (Office of Biological and Environmental Research), U.S. Department of Energy (Grant No. DE-SC0006431). A.L. gratefully acknowledges support from the Dreyfus Foundation Environmental Chemistry Postdoctoral Fellowship Program.

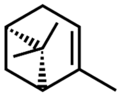
Table 1. Molecular structures for the terpenes characterized in this study.



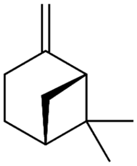
isoprene



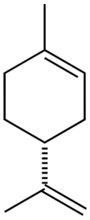
β-myrcen~~e~~e



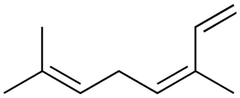
α-pinene



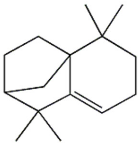
β-pinene



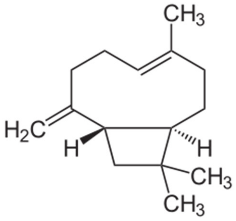
D~~d~~-limonene



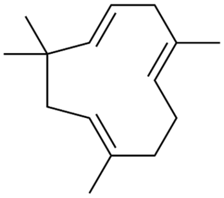
ocimene



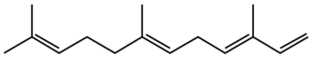
isolongifolene



β-caryophyllene



α-humulene



farnesene

Table 2. Monoterpene 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_2O)**	**f(C_6H_6)**
α-pinene	17.9	23.9:0.64:0.35	17.4:0.21:0.25	Y	N
β-pinene	18.4	14.9:0.28:0.33	17.6:0.33:0.39	N	N
D-limonene	13.6	5.4:3.4:8.0	3.7:3.0:6.9	Y	N
β-myrcene	11.5	4.6:0.56:0.94	8.7:1.1:1.7	Y	N
ocimene	13.2	13.1:1.50:0.29	12.4:0.42:0.36	N	N

[†] 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.

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

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_2O)**	**f(C_6H_6)**
farnesene	10.4	7.8:1.3:1.6	7.8:1~~:~~.1:1.5	Y	N
α-humulene	8.6	5.2:2.6:0.63	~~1:~~5.3~~.3~~:2.8:0.54	N	N
β-caryophellene	6.9	4.6:1.4:2.2	4.0:1.1:1.9	Y	N
isolongifolene	12.3	3.1:7.7:1.2	3.4:8.8:0.15	Y	N

[†] 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.

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

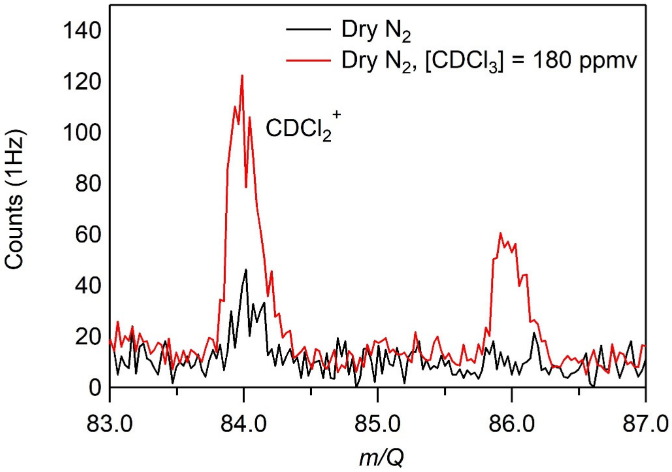


Figure 1. CI-ToFMS mass spectrum acquired when overflowing the inlet with excess nitrogen (black) and for a nebulized solution of chloroform-d at a flow rate of 3µl min^{-1} in a nitrogen carrier gas (red), where the resulting [$CDCl_3$] = 180 ppmv. No signal was observed above the baseline for any other fragments or the parent ($CDCl_3^+$, 120 *m/Q*).

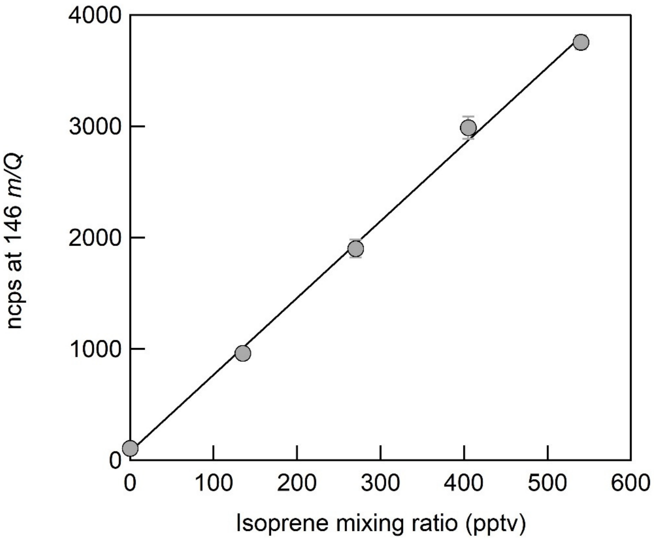


Figure 2. CI-ToFMS calibration curve for isoprene, detected as $C_6H_6^+ \cdot C_5H_8$ at 146 *m/Q*. The sensitivity (slope) is 7 ncps, R^2=0.99. Error bars represent the standard deviation of the triplicate calibrations.~~Error bars represents the standard deviation of the 1Hz measurements.~~

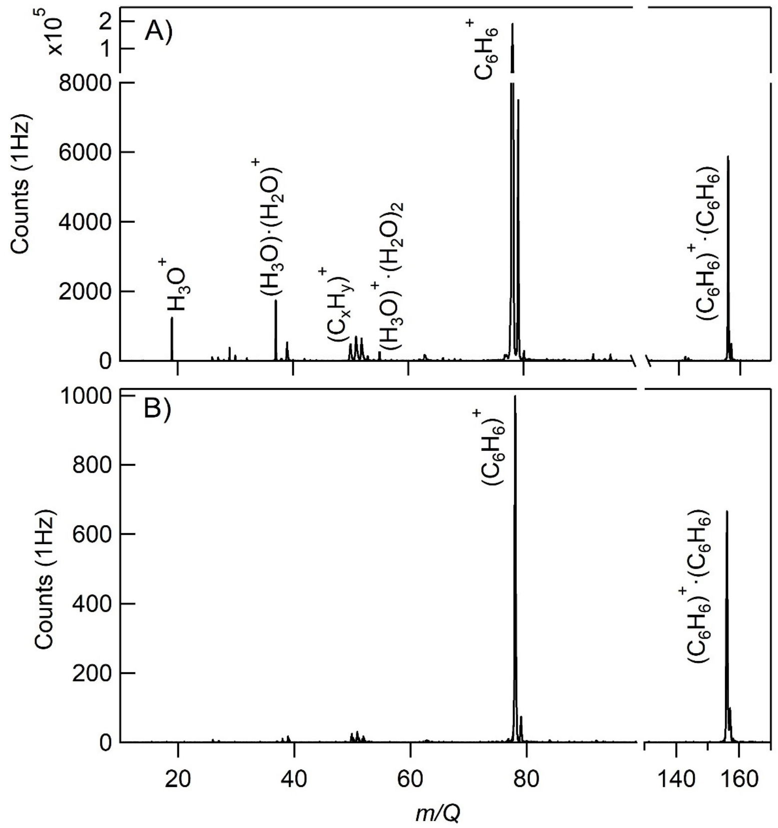


Figure 3. a) CI-ToFMS mass spectrum acquired when overflowing the inlet with nominally dry zero air for a benzene neutral concentration of 300 ppm using a liquid reagent ion delivery and b) same as in a, but with the first RF-only octupole ion guide turned off, resulting in a much weaker electric field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

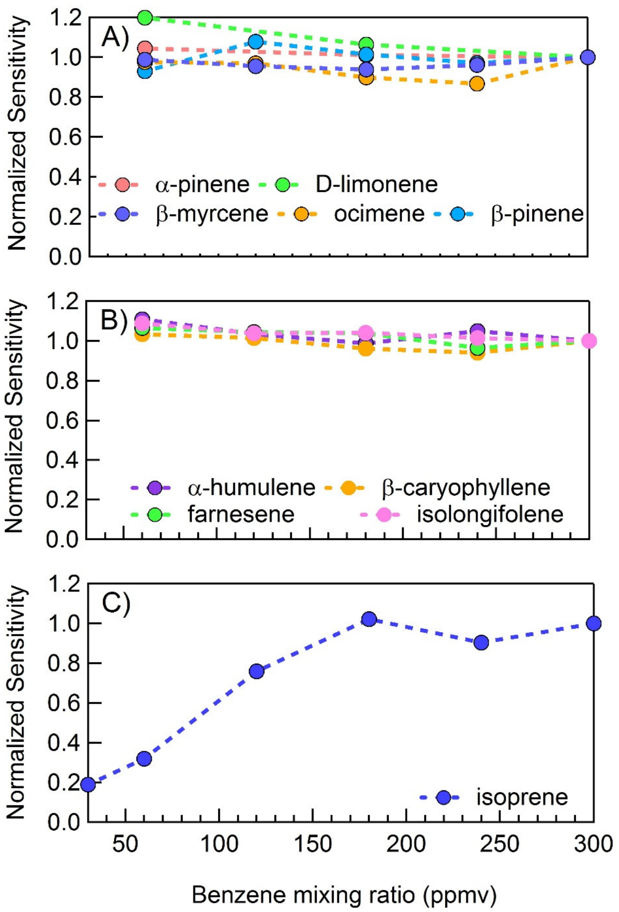


Figure 4. CI-ToFMS sensitivity to: a) monoterpenes ($C_{10}H_{15}^+$; 136 *m/Q*), b) sesquiterpenes ($C_{15}H_{24}^+$; 204 *m/Q*), and c) isoprene ($C_6H_6^+ \cdot C_5H_8$; 146 *m/Q*) as a function of benzene neutral concentration normalized to the sensitivity at 300 ppmv neutral benzene. Measurements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

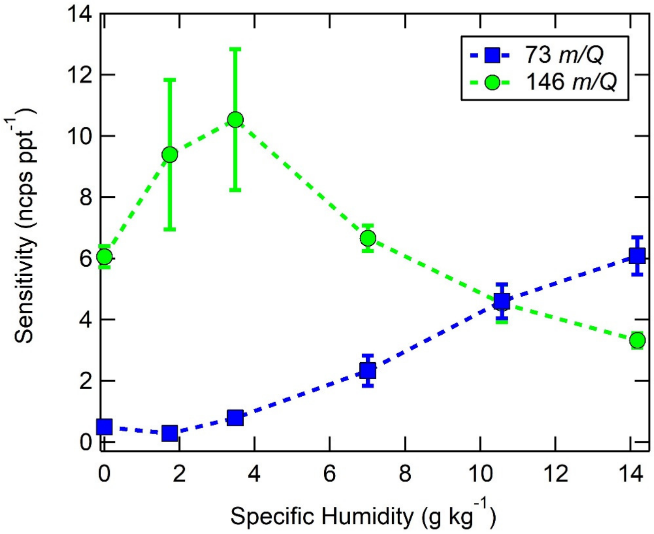


Figure 5. Humidity dependent CI-ToFMS sensitivities to isoprene (green circles, $C_6H_6^+ \cdot C_5H_8$, 146 *m/Q*), and the protonated water tetramer (blue squares, $H_3O^+ \cdot (H_2O)_3$, 73 *m/Q*), derived from calibration curves such as those shown in Figure 6. The reported sensitivities are the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

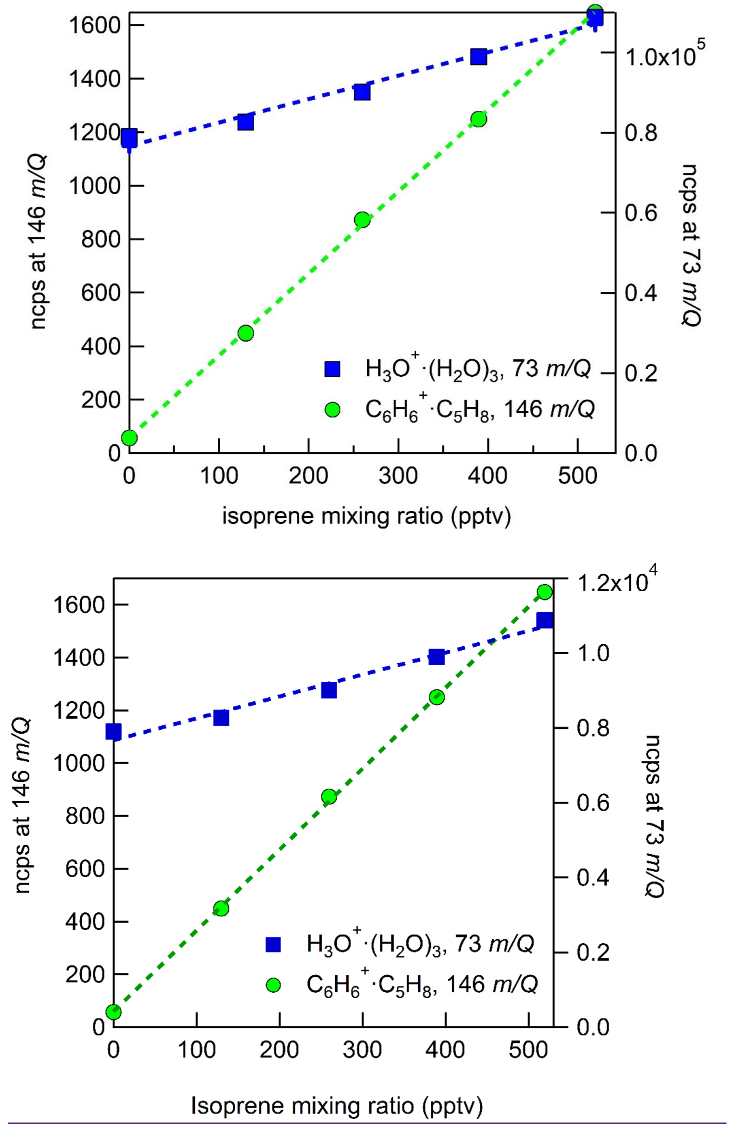


Figure 6. CI-ToFMS sensitivity to isoprene, observed as the isoprene-benzene cluster (green circles, $C_6H_6^+{\cdot}C_5H_8$, 146 *m/Q*) and water protonated tetramer (blue squares, $H_3O^+{\cdot}(H_2O)_3$, 73 *m/Q*). Dashed lines are the least square best fit lines (R^2>0.98). Calibration was performed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

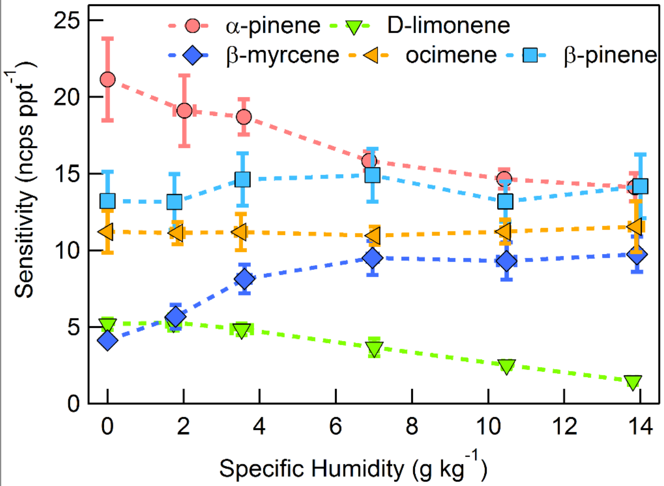


Figure 7. Humidity dependent sensitivities to select MTs detected as M$^+$ ($C_{10}H_{16}^+$, 136 *m/Q*). Error bars indicate the standard deviation of triplicate measurements. All calibrations were conducted in zero air. Error bars represent the standard deviation of the triplicate calibrations. All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

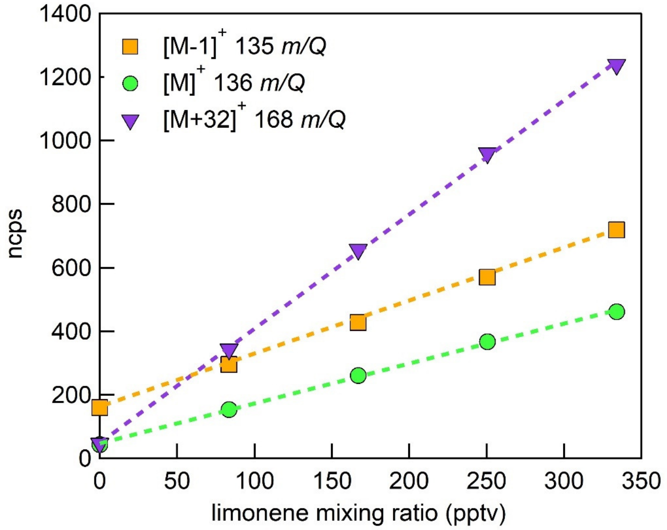


Figure 8. Normalized calibration of D-limonene for all major product ions ($C_{10}H_{16}^+$, 136 *m/Q*, green circles), ($C_{10}H_{15}^+$, 135 *m/Q*, orange squares), and ($C_{10}H_{16}O_2^+$, 168 *m/Q*, purple triangles). Calibration was performed in zero air at 14 g kg^{-1} specific humidity (80% RH at 23℃). Dashed lines are least squares best fit lines (all R^2>0.99).

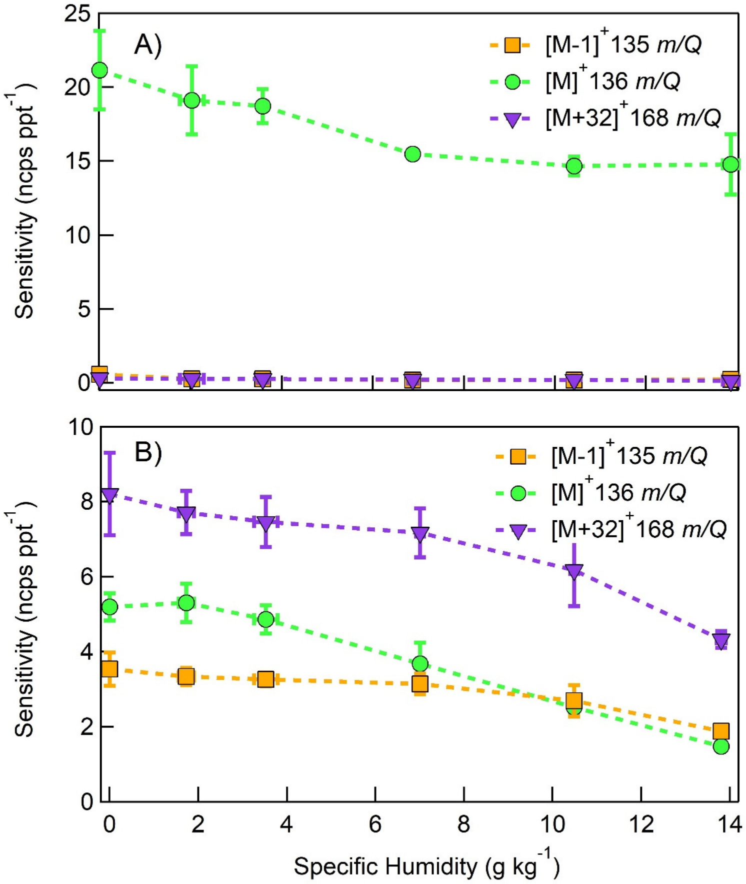


Figure 9. Humidity dependent, normalized sensitivities to a) α-pinene b) D-limonene for all major product ions ($C_{10}H_{16}^+$, 136 *m/Q*, blue circles), ($C_{10}H_{15}^+$, 135 *m/Q*, green squares), and ($C_{10}H_{16}O_2^+$, 168 *m/Q*, red triangles). Error bars represent the standard deviation of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

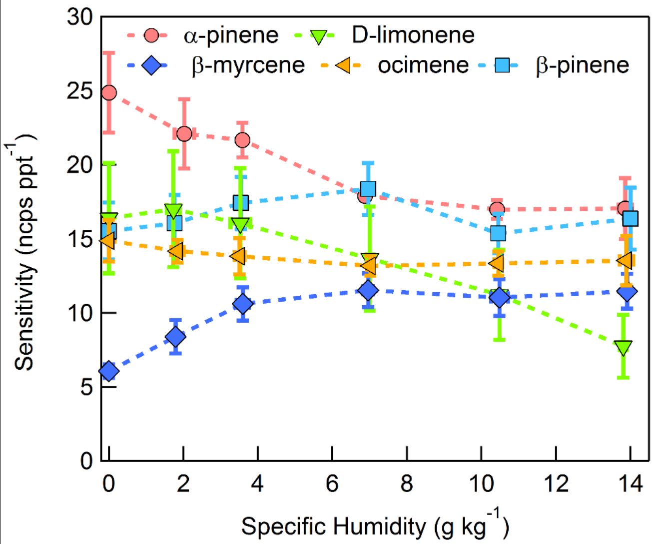


Figure 10. Humidity dependent, CI-ToFMS monoterpene sensitivities reported as the sum of all detected masses (135, 136, and 168 *m/Q*). Error bars represent the standard deviation of the triplicate calibrations. All calibrations were performed in zero air.

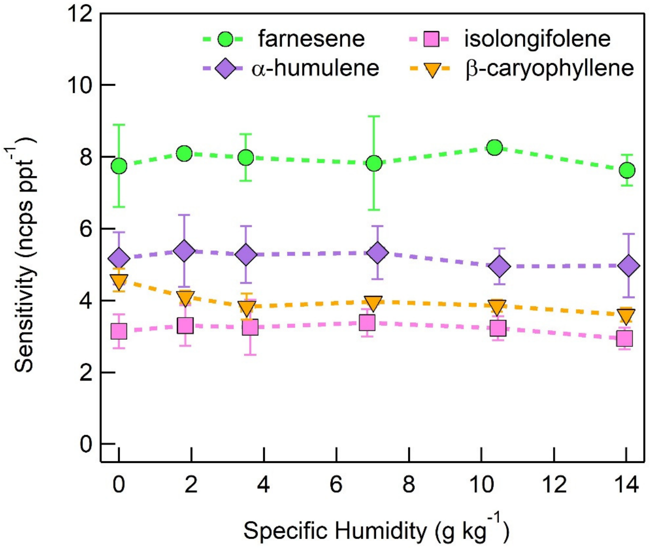


Figure 11. Humidity dependent sensitivities of SQTs detected as $C_{15}H_{24}$ (204 *m/Q*). Error bars represent the standard deviation of triplicate measurements. All calibrations were performed in zero air.

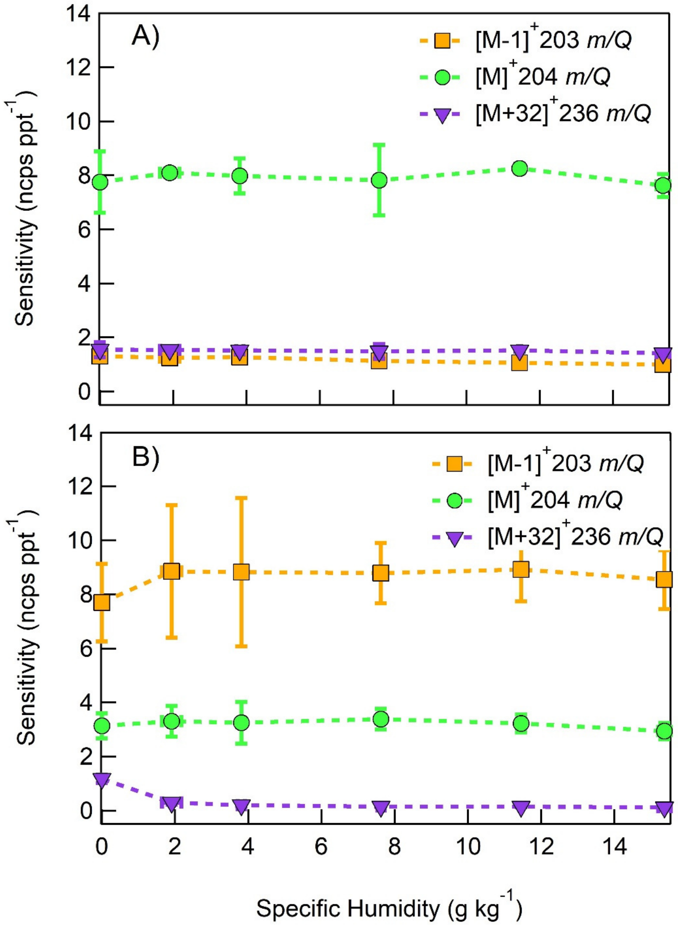


Figure 5~~12~~. Humidity dependent, normalized sensitivities to a) farnesene and b) isolongifolene for all major product ions ($C_{15}H_{23}^+$, 203 *m/Q*, blue circles), ($C_{15}H_{24}^+$, 204 *m/Q*, gray squares), and ($C_{15}H_{24}O_2^+$, 236 *m/Q*, red diamonds). Error bars represent the standard deviation of the triplicate measurement.

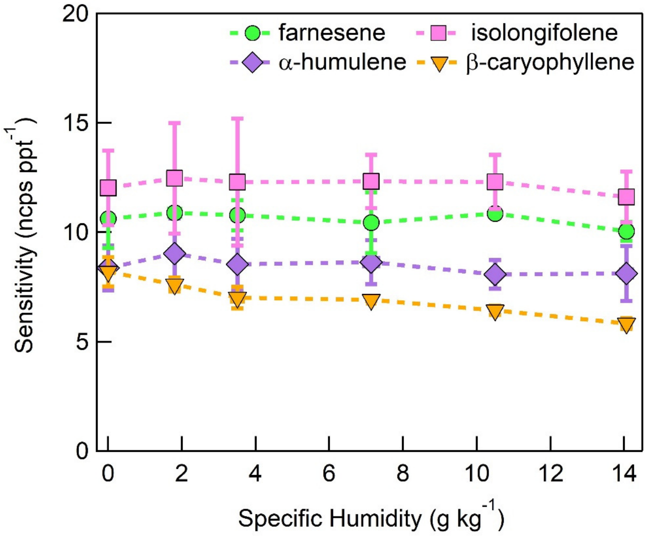


Figure 6~~13~~. Humidity dependent, normalized sensitivities to sesquiterpenes, reported as the sum of the major product ions ($C_{15}H_{23}^+$, 203 *m/Q*), ($C_{15}H_{24}^+$, 204 *m/Q*), and ($C_{15}H_{24}O_2^+$, 236 *m/Q*). Error bars represent the standard deviation of triplicate measurements.

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