Answers to Anonymous Referee #2

We thank the reviewer for the interesting comments which we tried to incorporate in the revised version as much as possible.

Comment: Rimetz-Planchon et al present the fragmentation patterns of multiple SQT species by applying MS/MS techniques with H3O+ and NO+ reagent ion. They also provide an excellent summary of previous studies on analytical characteristics of SQT using CIMS instrumentation. Based on the experiment results, they discuss how to identify specific SQT isomers by using notable fragment ions. Considering the importance of SQT in photochemistry and SOA formation in tropospheric chemistry, this research will be beneficial to researchers, who need to quantify SQT in the atmosphere. The quality of this work, also, is excellent that satisfies aims of this journal. Therefore, I recommend to publish this article to AMT after authors' considerations of following comments that I would like to see some clarification and corrections.

Major Concerns

It is great discussion to apply laboratory observations to ambient measurement of SQT, potentially a complicated mixture of multiple SQT isomers. In that aspects, the triple quad application should be a perfect application for the measurement. However, in consideration of relatively low concentration of SQT in the ambient air, quantitative discussion on possible lower limit of detection would be preferable. There is some discussion in conclusion but I would like to see this appearing in the main discussion section and becoming more comprehensive discussion. Especially this is because, the triple quad system may have lower ion throughput than the single quad system. Any discussion in this perspective will make this paper more comprehensive.

Reply: The major objective of the present work was to investigate, through laboratory measurements, whether break-up of protonated sesquiterpene ions or sesquiterpene molecular ions, produced by chemical ionization of sesquiterpenes by H_3O^+ or NO^+, respectively, in a flow or drift tube reactor, results in tracer fragment ions which may be useful for selective on-line detection of specific sesquiterpenes in CIMS instrumentation. Since the laboratory FA-TMS instrument is not optimized for sensitive detection of trace gases, we did not focus on detection sensitivity. However, the reviewer is right that this is an important issue and therefore, as suggested, we will add an additional paragraph (3.5) to the main section of the paper. This new paragraph will be entitled "Considerations about the sensitivity of CI/MS/MS using NO^+ reagent ions for selective sesquiterpene detection", and its content is given below.

New paragraph:

"In its present configuration the laboratory FA-TMS instrument is not sufficiently sensitive for selective detection of sesquiterpenes at low concentrations. This lack of sensitivity is mainly due to a limited reagent ion production and inefficient ion optics for guiding the ions from the sampling orifice to the ion deflector in front of the QoQ probe. In order to allow selective detection of sesquiterpenes in ambient conditions, the instrument might well benefit from a replacement of the FA reactor by a drift tube reactor equipped with a highly efficient hollow cathode NO^+ ion source as in the commercial PTR+SRI-MS instrument (Jordan et al., 2009). In order to evaluate the usefulness of the CI/MS/MS technique for ambient selective sesquiterpene detection, we estimated the sensitivity and detection limit (LOD) of such a hypothetical instrument in which the quadrupole mass filter of a PTR+SRI-MS was replaced by the QoQ tandem mass spectrometer probe. Sensitivity values (expressed in counts per second per ppbv) were calculated for the different sesquiterpenes based on their CID tracer fragment ion intensities. These calculations were based on realistic values for the production and transmission of sesquiterpene molecular ions in a PTR+SRI-MS instrument in typical NO^+ operating conditions (E/N = 100 Td, 40 Mcps NO^+, $T_{reactor}$ = 333 K) and on experimental values of E_{CID} and the fragmentation fraction (FF) of the tracer fragment ions

at the specified E_{CM} values. The contribution of the sesquiterpene molecular ions to the NO^+/sesquiterpene product ion distribution in the PTR+SRI reactor was considered to be similar as in SIFT conditions, as was the case for protonated sesquiterpenes in the $H_3O^+.(H_2O)_n$/sesquiterpene product ion distribution (Demarcke et al., 2009) for an *E/N* of 100 Td. Tests performed on the TMS probe by the manufacturer (Extrel CMS, Pittsburgh, USA) showed a transmission loss of about 80 % for ions at *m/z* 219 (an EI fragment of perfluorotributylamine) when switching from a single quadrupole configuration to a QoQ configuration without introducing collision gas in the octupole collision cell. Given the proximity of this *m/z* ratio to the one of the sesquiterpene molecular ion, a similar transmission loss is taken into account for the latter ion species. The tracer fragment ion signal in the presence of collision gas will only be a fraction, equal to $E_{CID} \times FF$, of the ion signal at m/z 204 in the absence of collision gas. The unfavourable effects of reduced ion transmission in the tandem probe and incomplete fragmentation of the precursor ions in the collision cell (E_f varies between 5 and 75 %) on the detection limit of the individual sesquiterpenes are partly compensated by the very low TMS background signal at the *m/z* values of the tracer fragment ions (no contributions from ionization of interfering compounds in the PTR+SRI reactor), which is lower than 0.05 cps for an integration time of 20 s, resulting in acceptable detection limits for most sesquiterpenes. Estimations of the sensitivity and LOD (for a 20 s dwell time) of the hypothetical instrument for detection of individual sesquiterpenes based on tracer fragment ions at specific E_{CM} conditions are given in Table 4. These LOD values can be considered as conservative upper limits as the upper limit for the background signal (0.05 cps for a 20 s integration period) was taken as the standard deviation on the background signal. Presently the octupole guide in the collision cell of the tandem probe is operated at an RF-frequency of 2.1 MHz. Performance tests on the QoQ probe by the manufacturer (Extrel CMS, Pittsburgh, USA) have shown that increasing this frequency to 2.9 MHz results in a significant increase in the transmission and fragmentation efficiencies (K. Kuchta and J. Wei, Extrel Application note GA-380C). Estimated sensitivities and detection limits taking into account the performance of a 2.9 MHz octupole guide are given in Table 4 as well."

Table 4 originally contained those fragment ions which can be used as tracers for a specific SQT when considering a mixture containing the seven SQTs studied. A tracer fragment ion for a specific SQT was defined as one having a fragmentation fraction (FF) which is at least 10 times higher than the one for the other six SQTs. When using this criterion, no tracer fragment ions were found for aromadendrene, isolongifolene and β-caryophyllene. Within a subset of the SQTs studied, however, tracer fragment ions at specific E_{CM} values could still be found for these three sesquiterpenes. This information will also be included in Table 4 and an additional paragraph will be added to section 3.4:

"No tracers were found for the other three SQTs when considering the set of seven SQTs studied. However, when reducing this set, specific tracer fragment ions could still be found for aromadendrene at *m/z* 120 at 4.8 eV, isolongifolene at *m/z* 175 at 4.5 eV and β-caryophyllene at *m/z* 133 at 3.2 eV (Table 4).
Although the fragment ion at *m/z* 131 (at 0.7 eV) is a tracer for α-humulene within the set of the seven SQTs studied, its applicability for sensitive detection is restricted by its low fragmentation fraction and the low CID efficiency of the SQT molecular ion at 0.7 eV. A different fragment ion, allowing more sensitive detection of α-humulene albeit within a reduced set of SQTs, was found at *m/z* 147 at 2.8 eV."

TABLE 4

SQT	m/z 162 0.68 eV	m/z 119 0.68 eV	m/z 131 0.68 eV	m/z 137 3.2 eV	m/z 83 6.1 eV	m/z 147 2.8 eV	m/z 133 3.2 eV	m/z 175 4.5 eV	m/z 120 4.8 eV	%PID m/z 204 (*)
Aromadendrene	3.9 ± 0.2	2.4 ± 0.2	N.O.	N.O.	0.49 ± 0.05	5.0 ± 0.2	6.4 ± 0.2	1.6 ± 0.1	**5.0 ± 0.2**	94
α-cedrene	N.O.	**24.5 ± 0.8**	0.24 ± 0.04	N.O.	0.40 ± 0.03	9.7 ± 0.2	1.27 ± 0.04	0.91 ± 0.02	2.6 ± 0.1	98
longifolene	N.O.	0.57 ± 0.04	N.O.	**4.7 ± 0.1**	N.O.	3.6 ± 0.1	15.8 ± 0.3	2.6 ± 0.1	2.4 ± 0.1	93
δ-neoclovene	**71 ± 1**	0.97 ± 0.05	N.O.	N.O.	**9.3 ± 0.2**	3.3 ± 0.1	2.0 ± 0.1	0.64 ± 0.03	4.9 ± 0.1	94
isolongifolene	N.O.	1.3 ± 0.2	N.O.	N.O.	0.44 ± 0.04	24.2 ± 0.4	3.7 ± 0.1	**9.8 ± 0.2**	0.28 ± 0.02	99
α-humulene	0.96 ± 0.08	1.7 ± 0.1	**3.8 ± 0.2**	N.O.	0.17 ± 0.02	**44.2 ± 0.7**	1.6 ± 0.1	0.80 ± 0.04	1.5 ± 0.1	77
β-caryophyllene	N.O.	0.47 ± 0.05	N.O.	N.O.	0.33 ± 0.03	6.3 ± 0.2	**16.1 ± 0.4**	3.4 ± 0.1	3.1 ± 0.1	59
$S_{est, 2.1\,MHz}$ (cps/ppbv)	3.52	0.24	0.03	0.26	1.22	1.97	0.48	0.67	0.32	
$LOD_{est, 2.1\,MHz}$ (pptv)	43	630	5600	580	120	76	320	240	470	
$S_{est, 2.9\,MHz}$ (cps/ppbv)	47.9	2.07	0.27	2.75	13.1	23.4	4.89	10.0	2.77	
$LOD_{est, 2.9\,MHz}$ (pptv)	3	47	410	43	9	6	23	18	35	

Caption: Fragmentation fractions (FF) for SQT^+ fragment ions. Values shown in bold are associated to SQTs for which the corresponding fragment ion at the specified E_{CM} value can be considered as a tracer when analyzing mixtures containing the seven SQTs studied. Tracer fragment ions for aromadendrene, β-caryophyllene and isolongifolene were only found for restricted sets of SQTs, which do not comprise those compounds for which the FF value is shown against a grey background. Results are not corrected for mass discrimination effects. Also shown is the estimated sensitivity and LOD (based on a 20 s dwell time) of a hypothetical PTR-SRI-TMS instrument for the detection of individual SQTs (associated to FF values in bold) by monitoring the corresponding tracer fragment ions. The estimated sensitivity and LOD values are given for two distinct values of the RF frequency (2.1 and 2.9 MHz) of the voltages on the collision cell octupole rods (see text). N.O.: fragment ion not observed. (*) Relative contribution (%) of the SQT^+ ion in the NO^+/SQT product ion distribution as obtained from SIFT-MS experiments (Dhooghe *et al.*, 2008).

Comment: More comprehensive discussion on differences between NO+ and H3O+ ion chemistry is preferable. Discussion on the both ion chemistry in the perspective of why two applications can provide unique signatures to identify complex structure molecules in thermodynamical and kinetics perspectives can provide useful information to readers.

Reply: For a discussion on NO^+/sesquiterpene and H_3O^+/sesquiterpene ion chemistry we refer to the paper of Dhooghe et al. (INT J MASS SPECTROM, 272, 137-148, 2008) which deals with the study of these reactions in a SIFT instrument. It would indeed be interesting to unravel the different pathways leading to the CID fragment ions of protonated sesquiterpenes and molecular sesquiterpene ions, and especially those leading to tracer fragment ions. However, given the complexity of the molecules and the lack of available thermochemical data, elucidation of the fragmentation pathways will demand complex quantumchemical calculations which are beyond the scope of the present paper.

Comment: Minor concerns
P 4287 Line 9 Hoffmann et al. J Atmos Chem 1997 argued that the SOA yield from bcaryophyllene is 100%. You also should note the specific SQT species for the SOA yields in the text.

Reply: The suggestion of the referee will be incorporated in the text.

Comment: Line 14 Provide brief information about "carbon sequestration"

Reply: To avoid possible misunderstandings, the term "Carbon sequestration" will be replaced by "the carbon cycle". Accurate emissions of BVOCs (and amongst them sesquiterpenes) are necessary to be able to quantify which fraction of assimilated carbon is re-emitted into the atmosphere.

Comment: Line 19 There are a few more updated publications on GC applications on SQT measurement. See Bouvier-Brown et al (2009) ACP and references therein

Reply: A reference to the publication of Bouvier-Brown et al. 2009 will be added in the revised manuscript.

Comment: P4288 Line 1 No mass discrimination in higher mass ions is an obvious advantage of PTR-ToF-MS for quantifying higher mass species. Briefly discuss about it.

Reply: The sentence concerning PTR-ToF-MS will be adapted in order to mention the advantage of the absence of mass discrimination in higher mass ions:

"Even if the recent development of the high resolution Proton Transfer Reaction-Time of Flight-Mass Spectrometer (PTR-ToF-MS) (Blake et al., 2004; Jordan et al., 2009; Graus et al., 2010) opens the possibility of distinguishing nominally isobaric compounds on the basis of their accurate masses and with high sensitivity due to the absence of mass discrimination for higher mass ions, the distinction of isomers remains difficult."

Comment: P 4289 Line 17 Specify "medium pressure"

Reply: The term "medium pressure" is used to differentiate between low pressure chemical ionization (as is f.i. used in Ion Cyclotron Resonance (ICR) instrumentation, medium pressure chemical ionization (at pressures of a few mbars up to a few tens of mbars) and Atmospheric Pressure Chemical Ionization (APCI). In the techniques to which we refer in P 4289, Line 17, the operating pressure is a few mbar and this will be added between brackets.

Comment: P 4290 2.1 I am with authors for having brief description of the FA-TMS method because it has been already thoroughly described elsewhere. However, adding the schematic diagram of FA-TMS would help for readers to understand analytical technique.

Reply: An additional figure showing a schematic representation of the FA-TMS instrument will be added.
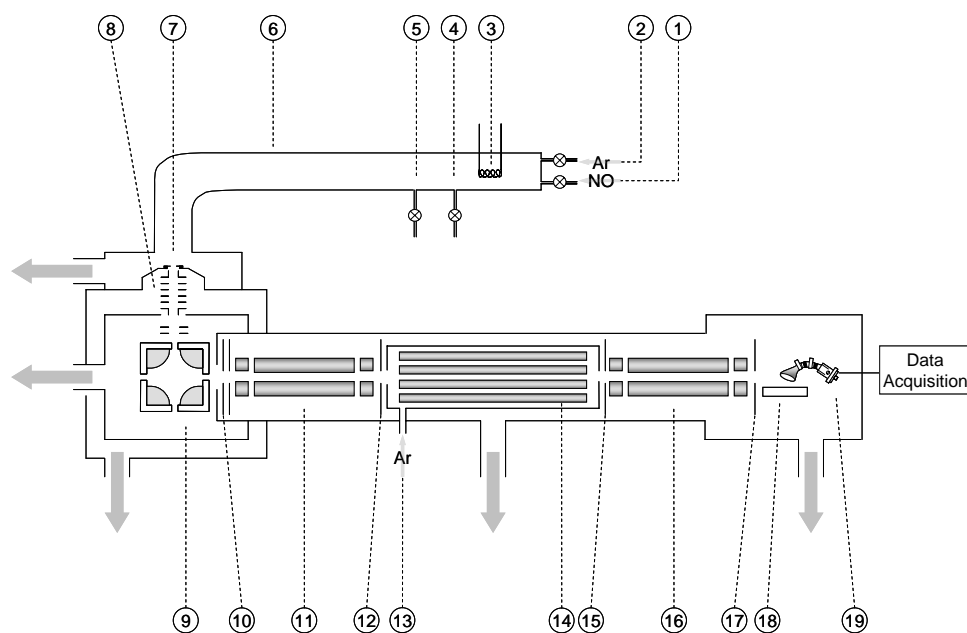
Caption: Schematic representation of the FA-TMS instrument. Light grey arrows indicate regulated gas flows entering the instrument, dark grey arrows indicate gas flows exiting the instrument towards the pumping systems. (1) NO inlet, (2) Argon inlet, (3) electron emitting filament, (4-5) neutral inlets (H$_2$O, SQT), (6) flow tube (FT), (7) interface plate, (8) lens system, (9) ion deflector, (10) entrance lens to first quadrupole, (11) first quadrupole with pre- and post filter, (12) lens between first quadrupole and octupole, (13) argon collision gas inlet (14), octupole collision cell, (15) lens between octupole and second quadrupole, (16) second quadrupole with pre- and post filter, (17) exit lens, (18) discrete dynode, (19) electron multiplier.

Comment: P 4291 Line 13 It would be helpful to have a table, summarizing molecular structure of investigated molecules and their reaction constants towards OH and ozone

Reply: We will add a figure showing the molecular structures of the investigated sesquiterpenes (see below). However, given the fact that the present paper is not dealing with the atmospheric fate of sesquiterpenes, we believe that adding a table with rate constants of sesquiterpenes with the main atmospheric oxidants is not really required.
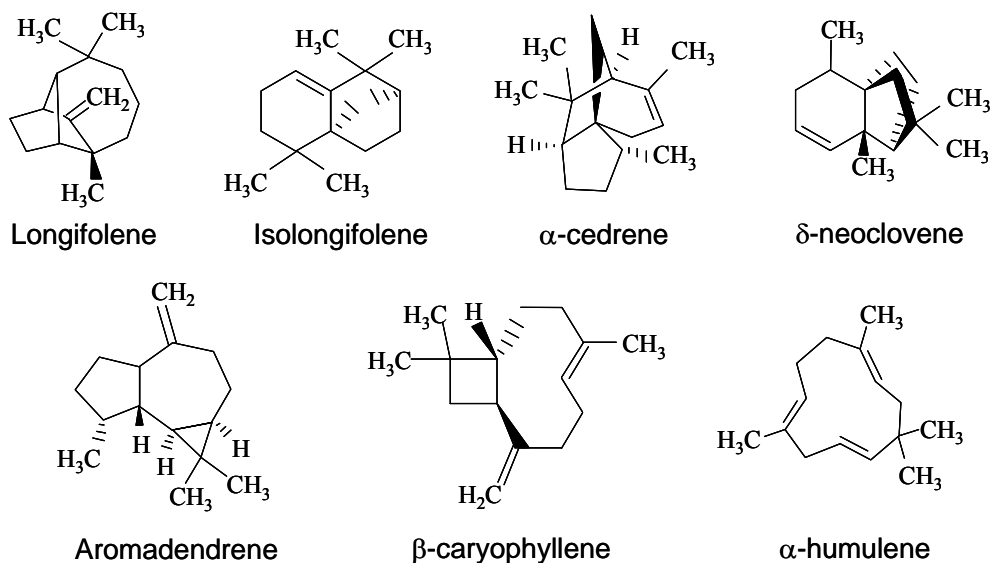
Caption: Molecular structures of the seven sesquiterpenes studied.

Comment: P4294 Line 19 The mass discrimination pattern of Ionicon PTR-MS have been studied and seems relatively well established (Taipale et al., 2008 ACP and Kim et al., 2009). Discuss accordingly.

Reply: "Former" in this sentence does not refer to PTR-MS, for which mass discrimination can indeed relatively well be established, but to FA-TMS, for which it is very difficult to determine mass discrimination. In order to avoid misunderstandings, the sentence will be modified as follows: "It needs to be stressed, however, that one should be cautious when comparing quantitatively branching ratios obtained by FA-TMS with those obtained by PTR-MS and SIFT-MS since mass discrimination of the FA-TMS instrument is not known."