

Answers to Anonymous Referee #1

The Authors would like to thank the referee for his/her constructive remarks.

Comment: Page 4288: Line 1: consider adding Graus et al. 2010; JASMS, V21m, I6, June 2010, p 1037 – 1044: High resolution PTR-TOF: quantification and formula confirmation of VOC in real time

Reply: This reference will be added in the corrected manuscript.

Comment: Line 5: the exact (ionic) m/z ratio of C₁₅H₂₅⁺ is 205.1951 instead of 215.1956.

Reply: This mistake will be corrected.

Comment: Page 4290, lines 1-3: please consider in this statement, that at ambient measurements isobaric interferences of oxygenated species are very likely (especially for measurements at pptv levels).

Reply: The referee refers to the general statement that NO⁺ is clearly not the perfect reactant ion for VOC detection with CIMS instrumentation since it generally results in a higher degree of fragmentation of the nascent excited VOC^{+*} product ions. Although reactions of NO⁺ with isobaric species of some classes of chemical compounds (e.g. ketones and aldehydes) are characterized by different reaction mechanisms and may result in product ions at different m/z values, the reviewer is right that at ambient measurements isobaric interferences of oxygenated species are still very likely. We will therefore add the following sentence to the manuscript:

“Moreover, it is expected that at ambient measurements isobaric interferences of oxygenated species are very likely when using NO⁺ reactant ions.”

Comment: Page 4291, line 9: comma is missing

Reply: A comma will be added.

Comment: Page 4292, lines 8-17: How representative are the values for E_c, E_f, and E_{CID} without taking transmission effects (page 4294, line 17) into account?

Reply: Even if mass discrimination of our instrument would be well-known and taken into account, it needs to be stressed that the values of E_c, E_f and E_{CID} can not directly be applied to other tandem MS instrumentation as next to the collision energy and the type and number density of collision gas used, these values are also dependent on instrumental parameters. However, the main purpose of this work was not to compare fragmentation efficiencies with other studies but to illustrate that, within specific ranges of the collision energy, selective detection of some SQT can be possible. Since the measurements of all sesquiterpenes were carried out at the same experimental conditions, values of E_c, E_f and E_{CID} can be compared within this study and were found to be useful parameters for the comparison of fragmentation fractions among sesquiterpenes, even without taking into account mass discrimination.

Comment: Page 4295: Line 2: 12 V UCC instead of 12cc

Reply: This mistake will be corrected.

Comment: Lines 5 – 27: The authors observe, as expected, much less fragmentation for chemical ionization with NO⁺ compared to 70 eV EI ionization. Nevertheless, I couldn't find any information about the relative fragmentation pattern of the Sesquiterpens due to ionization. A low amount of fragmentation is very important for the low ambient concentrations, especially because specific differences are only visible for the molecular and the protonated SQTs.

At page 4289, line 28, it is written, that by CI by NO⁺ a greater degree of fragmentation is observed compared to H₃O⁺. Please consider adding some fragmentation information for the molecular and the protonated SQTs without CID!

Reply: A low amount of fragmentation by direct chemical ionization by H₃O⁺ or NO⁺ is indeed important to measure low ambient concentration of SQTs. Ion/molecule reaction measurements at thermal conditions in our laboratory SIFT instrument have revealed high contributions of the molecular ion and the protonated molecule for NO⁺/sesquiterpene and H₃O⁺/sesquiterpene reactions, respectively. This information can be found in the paper of Dhooche et al. (INT J MASS SPECTROM, 272, 137-148, 2008), to which we referred in the manuscript. In contrast to what is found for many VOCs, the NO⁺/sesquiterpene reaction results in less fragmentation than the H₃O⁺/sesquiterpene reaction, probably because the ionization potential of sesquiterpenes is close to that of NO (9.26 eV). As the information can be found in the literature, we don't feel the necessity to add a supplementary table to the revised manuscript. Nevertheless, a table showing the yields of MH⁺ and M⁺ for CI by H₃O⁺ and NO⁺, respectively, for the studied sesquiterpenes can be found below.

Compound (M)	H ₃ O ⁺ (MH ⁺) (%)	NO ⁺ (M ⁺) (%)
Beta-caryophyllene	30	59
Aromadendrene	80	94
α -cedrene	94	98
α -humulene	54	77
Isolongifolene	97	99
Longifolene	83	93
δ -neoclovene	79	94

Comment: Fig. 2: consider adding m205 (Ip) to the graphs. According to fig. 1 between 10 and 40% of Ip should be remaining.

Reply: The contribution of the precursor ion at m/z 205 to the sum of the remaining precursor ion and the fragment ions ($I_p/(I_p + \sum I_{fi})$) in Fig. 2d ($E_{CID} = 0.68$ eV), Fig. 2e (5.1 eV) and Fig. 2f (6.4 eV) equals 95.1, 30.3 and 29.9 %, respectively, and corresponds to $E_f (= \sum I_{fi}/(I_p + \sum I_{fi}))$ values of 4.9, 69.7 and 70.1 %, respectively, in agreement with the data from Figure 1 obtained for α -cedrene. Because Figure 2 focuses on the comparison of fragmentation spectra (relative contributions of the CID fragments in different instrumental configurations) we preferred not to add the remaining precursor ion to these graphs. However, in order to meet the request of the reviewer, we added the explicit values for the contribution of the precursor ion to the sum of the remaining precursor and the sum of fragments for each of the graphs in Figure 2 in the caption of this Figure.

Comment: Fig. 3: m/z 105 is depicted as _ and *. Consider unifying it.

Reply: Figure 3 and its corresponding caption will be modified to take into account this remark. Furthermore colored symbols will be used for clarity.

Comment: Fig. 4: Is there a reason why 6 different ECM are selected to display the 6 different ratios? For fast mixture analysis a low amount of different ECM values would be preferable due to detection and time limitations.

Reply: Values of fragment ion intensity ratios for a given SQT vary with E_{CM} . The E_{CM} values chosen in figure 4 (4.8 eV, 1.2 eV, 6.1 eV, 1.8 eV, 5.1 eV and 3.8 eV) allow to distinguish individual SQT. To give an example, the following figure presents intensity ratios I_{81}/I_{93} at 1.2 eV (E_{CM} chosen in Figure 4) and at 4.8 eV. At this last collision energy, I_{81}/I_{93} does not allow to distinguish SQT. With respect to time limitation, it should be noted that changing between E_{CM} values can be done quasi instantaneously as it only involves changing lens voltages.

