Interactive comment on "MS/MS studies on the selective on-line detection of sesquiterpenes using a flowing afterglow-tandem mass spectrometer" *by* J. Rimetz-Planchon et al.

Anonymous Referee #1

Received and published: 13 December 2010

This is an interesting and well written article that demonstrates approaches for an ambient real-time Sesquiterpene differentiation using mass spectrometry. The authors clearly present the abilities as well as the limitations of collision induced dissociation by prior chemical ionization of Sesquiterpenes, either by proton transfer reaction (H_3O+) or charge transfer ($NO+$). The experimental studies are carefully conducted and detailed information is provided. I want to encourage the authors to the instrumental improvements, as stated in the conclusion, that might allow a quantitative analysis at (or close to) ambient levels.

Specific comments:

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 Line 5: the exact (ionic) m/z ratio of $C_{15}H_{25}+$ is 205.1951 instead of 215.1956.

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).

Page 4291, line 9: comma is missing

Page 4292, lines 8-17: How representative are the values for Ec, Ef, and ECID without taking transmission effects (page 4294, line 17) into account?

Page 4295: Line 2: 12 V UCC instead of 12cc 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 H_3O+. Please consider adding some fragmentation information for the molecular and the protonated SQTs without CID!

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

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

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.