

We thank all three reviewers for their constructive comments which help to improve the manuscript. Below is our response to individual comments:

Reviewer 1:

- (1) We specify the inner diameter of the Teflon tubing.
- (2) As indicated on page 19354, the residual water concentration in the drift tube was small, typically only a couple (e.g. 1-2) %. Thus the upper limit of the isoprene + H<sub>3</sub>O<sup>+</sup> signal on m/z 69 is 1-2 % in NO<sup>+</sup> mode. For ambient measurement this means that the interference was less than 0.2 %.
- (3) Figure 1: we believe that showing the normalized signals presents a clearer picture; due to different concentrations between laboratory and field measurements we would need to introduce a secondary axis or more panels, if we were to show absolute signals.

Reviewer 2:

- (1) General comment: While the manuscript would fit in AMT, we believe there is enough overlap with future publications to be submitted to the joint BEACHON-ROCS / BEACHON-ROMBAS special issue. The issue of isoprene concentrations in this ecosystem should be of particular interest to the BEACHON special issue.
- (2) We will change the terminology to SRI-MS (for selective reagent ionization ms).
- (3) We will change this to normalized sensitivities
- (4) We will change the reference and mention the 1965 paper
- (5) Similarly to a pH stat, the phrase was coined to describe the biochemistry of plant metabolites and chemical intermediates stationary.
- (6) The reaction sequence is reduced to the basic equations to keep it simple. Generally charged ions are produced via electron impact ionization (e.g.  $e^- + N_2 \rightarrow N^+ + N + 2 e^-$ ; or  $e^- + N_2 \rightarrow N_2^+ + 2 e^-$ ). Further neutral reactions can be complex involving recombination and photochemical reactions leading to NO.
- (7) The unit Th stands for Thomson and is actually used without a decimal point. We will correct this.
- (8) We do not observe any clusters for isoprene and MBO. NO<sup>+</sup> ionization chemistry in a SIFDT can be very selective and generally does not lead to significant clustering. The association reaction 2d is completely suppressed in the current case. We mentioned the reaction for completeness listing all possible reaction paths, however note that it is generally not a significant path in a SIFDT instrument. The main reason that clustering is not significant is the electric field applied across the drift tube. We added a new figure showing the mass range between 35 and 70 amu. The range between 27 and 33 is dominated by primary ion peaks related to NO<sup>+</sup> and not shown.
- (9) We could not identify the contamination compound; the compound was likely an impurity that contaminated the system for some period at the field site, when the mass spectrometer had to be shut down and was restarted after transport. It could have been caused by indoor trailer air impurities at the field site and we observed that the compound slowly degraded over the period of the campaign.

- (10) Typical E/N dependencies of the fragmentation pattern of 232 MBO + H<sub>3</sub>O<sup>+</sup> suggest that the fragmentation is definitely influenced by collisional dissociation, however dehydration due to excess energy during the Proton Transfer can not be ruled out. We have revised this statement.
- (11) We will fix references in a revised manuscript

Reviewer 3:

- (1) As to choosing another journal we believe that the content fits in ACP due to the BEACHON-ROMBAS/ROCS special issue (see response to reviewer 2).
- (2) In PTR-MS 232 MBO undergoes collisional dissociation and a hydration reaction leading to a dominant ion fragment m/z 69+ (losing an H<sub>2</sub>O group); typically about 25% remains on the parent ion (m/z 87+). It is therefore theoretically possible to distinguish 232MBO and isoprene, as long as a significant portion of both compounds enables investigating the ratio of both ions (isoprene would only be detected on m/z 69+). However this exercise becomes increasingly difficult when isoprene concentrations are low (e.g. <30%); thus a more common scenario is that 232MBO measurements could suffer from an interference of low levels of isoprene (e.g. up to 30% relative to MBO), both being detected on m/z 69+. Generally speaking though it is correct that isoprene concentration measurements could be biased too, if the 232 MBO fragment is not subtracted out from m/z 69+. We will expand on this issue in the introduction of the revised manuscript.
- (3) We will rephrase this section and will add a new figure showing the entire portion of the mass spectrum of interest as suggested by reviewer 2.
- (4) We will add more explanation in the main body of the text. Briefly the dotted and dash-dotted lines for 232 MBO represent two cases: (1) the reaction rate coefficient was held constant and (2) the reaction rate constant was varied according to a functional dependence reported by Cappellin et al., ES&T 2012, who found a varying rate coefficient for 232 MBO for proton transfer reactions.
- (5) Pg 19350, line 3: ok
- (6) Pg 19350, line 5: ok replaced by utilized
- (7) Pg 19350, line 18: ok
- (8) Pg 19351, line 11: ok
- (9) Generally MBO is thought to play a minor role in isoprene dominated ecosystems; in addition due to its lower reactivity the impact on chemistry will be even smaller. However whenever there is a significant fraction of MBO, the chemistry should of course be dominated by it. In this case trace amounts of isoprene might be more important for accurately understanding the impact on chemistry due to the higher reactivity of isoprene. In the past the presence and interference of isoprene at these sites could be assessed using conventional PTR-MS as long as isoprene was present in significant amounts (e.g. >50%), which would become evident in the m/z 69 to m/z 87 ratio (about 25% of 232MBO does not fragment and the relative amounts of m/z 87 to m/z 69 can give a hint on the presence of isoprene).
- (10) Pg 19352, line 24: unheated lines

- (11) Pg 19354, line 12: no the TOF-MS was measuring 174499 channels (or bins)
- (12) Pg 19357, line17: Most of the section deals with NO+ chemistry, but we will clarify this issue in a revised manuscript.
- (13) Pg 19358, line 28: ok
- (14)Pg 19359, line 18: ok
- (15)Figure 1: the mass spectral figures will be modified including a new figure
- (16) Color will be changed.