

## ***Interactive comment on “Selective measurements of isoprene and 2-methyl-3-buten-2-ol based on NO<sup>+</sup> ionization mass spectrometry” by T. Karl et al.***

**Anonymous Referee #3**

Received and published: 17 October 2012

The manuscript describes the investigation and deployment of a PTR-TOF-MS instrument operating with NO<sup>+</sup> reagent ions for the interference free detection of both isoprene and 2-methyl-3-buten-2-ol. The paper goes into excellent detail on the laboratory experiments performed as well as the field measurements used to validate this chemistry. This is a great example of the types of manuscripts that are necessary in order to push PTR or more generally CIMS in the right direction. The paper is organized well and written in a clear and concise manner and is highly suitable for publication. My only comment is that from the content it seems that it would be more suitable for publication in a journal such as IJMS or even more appropriately AMT. There is not much content on the chemistry of these two species aside from observing their co-emissions

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and postulation of an additional source of isoprene.

General comments to the manuscript

I believe a brief discussion or citation on how the interference affects the previous measurements of isoprene utilizing PTR is necessary. You show that you can differentiate the species in this work but what does that mean for previous measurements. An explicit statement of the magnitude of the interference would be beneficial.

While you mention that 232 MBO is traditionally detected as an interference with PTR chemistry you do not explicitly show the reaction or mention how the fragmentation occurs. It is a bit of a petty desire, but I think that it will help readers to better understand the importance of this work and better follow the discussions included to see this reaction explicitly stated in this manuscript written as a chemical reaction.

On page 19356 and first sentence on pg 19357, these two places referring to Figure 1 state the mass spectra are shown in the figure as evidence for no significant fragmentation. Two things are wrong with this the way it is written. Figure one does not show mass spectra but a portion of a mass spectrum including only the primary ions that are expected. I just suggest tightening up the wording of this section so as to not be misleading. Alternatively you could add a full mass spectrum showing the absence of fragmentations but that would lead to far more questions and require a lengthy discussion to describe the modified figure.

After introducing Figure 3 and commenting on the regression lines you completely neglect to go into details on the dotted/dashed lines that are also present on the figure. They require some explanation, as the results are significant. The details given in the figure caption are not sufficient enough to explain their presence.

Specific Comments

Abstract:

pg 19350, line 3: suggest adding “a” in “NO<sup>+</sup> as a primary ion”

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pg 19350, line 5: The way this sentence reads in using the wording “NO+... was achieved... using PTR-TOF-MS” is grammatically misleading. I believe replacing the word achieving with something like utilized would make the statement clearer.

pg 19350, line 18: the concentration range stated (90 – 250 pptv) as used in the containing sentence implies an upper limit to this chemistry without observing interference. It should be made clear that this is the range observed in this study and not the absolute operable range of concentrations.

Introduction:

pg 19351, line 11: place the phrase “along with other VOCs” between commas.

pg 19351: in the first paragraph on this page you do a good job of introducing the importance of isoprene in the chemistry of the atmosphere. However you follow that paragraph by introducing 232 MBO without commenting on the chemistry of this species. How different from isoprene is the chemistry of 232 MBO. Are their chemistries so different that counting 232 MBO as isoprene signal with the H<sub>3</sub>O<sup>+</sup> ion chemistry would cause a significant misunderstanding of local atmospheric chemistry in this or other forest ecosystems?

Section 2:

pg 19352, line 24: heated or unheated inlet line were used?

pg 19354, line 12: comma in the number 174,499?

Section 3:

Pg 19357, line 17: please explicitly indicate which primary ion you are talking about. This whole section throws around a lot of sensitivities and it is hard to follow which chemistries are being discussed. His section would benefit from more explicit naming of the ions in several places.

Pg 19358, line 28: insert comma after “Kaser et al., 2012),”

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Pg 19359, line 18: change assessing to assess

Figure 1: more detailed figure caption so that it can stand a bit more independent from the paper.

Figure 3: the dashed dotted line is a very difficult to distinguish from the dashed line of the same color.

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Interactive comment on Atmos. Chem. Phys. Discuss., 12, 19349, 2012.

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