

Interactive comment on “Peroxynitric acid (HO₂NO₂) measurements during the UBWOS 2013 and 2014 studies using iodide ion chemical ionization mass spectrometry” by P. R. Veres et al.

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Veres et al present details of the use of I(H₂O)- for chemical ionization mass spectrometry measurements of HO₂NO₂ in the ambient atmosphere. Two inlet set-ups, “cold” and “hot”, are discussed, as well as the detection of several product ions, including IHO₂-, NO₃-, and IHO₂NO₂-. Results of ambient measurements and modeling for HO₂NO₂ during the 2013 and 2014 Uintah Basin Wintertime Ozone Study is presented. Most of the manuscript is dedicated to the description and calibration of the technique (12 pages) with only 5 pages discussing the science of the ambient measurements. Since the discussion of the ambient results is minimal in comparison, it

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might be more appropriate for this manuscript to be published in Atmos. Meas. Technol. Regardless, the manuscript is well-written and is an important contribution.

We can see the reviewer’s viewpoint on the balance of the manuscript and its potential suitability for publication in Atmos. Meas. Technol. We ourselves initially considered this an option for this work, however feel the scientific discussion on the impacts of HO₂NO₂ in this region to be a major focal point of this manuscript. I shall refer to the statements of Reviewer 1 as they have very succinctly conveyed what we feel is the largest contribution of this work “This paper has several scientific merits such as . . . highlighting potential importance of HO₂NO₂ in boundary layer photochemistry in the mid latitude region during the winter time that has been considered only important in the free troposphere or the polar regions.” Additionally it was considered to separate this work into two manuscripts, however we felt that while there are many benefits in having two shorter works, a single publication containing all of the details of this work would be more impactful and beneficial to the broader community. In light of this, we remain certain the ACP is the most appropriate venue for publication when considered as a whole body of work. We note that this paper will be part of a joint special issue between ACP and AMT that has been set up for the results of the Uintah Basin Winter Ozone Studies.

The discussions portion of the manuscript that the reviewer is referring to has been reorganized slightly to separate the sections in question. Briefly the laboratory work and field results have been separated within the discussions section. Please see the response to reviewer #1 for a detailed explanation.

Additionally, section 3.2 is labeled “UBWOS observations”, but the first three paragraphs discuss the method rather than the science. Perhaps this should be labeled differently from the discussion of the ambient data in the subsequent paragraphs. Characterization of the method is stated as “laboratory results”, which can be confusing.

As to the differentiation between the method and science the reviewer is referring to

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in the UBWOS observations, we feel that the information presented here are observations about the measurement technique concluded from the field measurements. This information pertains directly to the field observations and our ability to interpret and understand the measurements. As such we feel that these paragraphs are appropriately placed at the beginning of the field observations section as results from that work.

In terms of the science, the authors should address the near-surface production of HO₂NO₂ from snowpack photochemistry (e.g. NO_x emission – a well-known phenomenon). Additional suggestions are noted below.

We will address this aspect of the review, which has come up several times in both reviewers comments and our responses to these will be discussed in the many highlighted comments below.

Abstract: The first half of the abstract is very technical. I suggest removing sensitivities and added an explanation of the importance of HO₂NO₂ at the beginning of the abstract.

We agree with the reviewer and appreciate the suggestion to include a more focused abstract with less technical details. We have edited the abstract keeping in mind this suggestion.

Section 2.2: Were snow samples collected during the UBWOS 2014 study?

Snow samples we collected during the 2014 study and the 2013 study and we thank the review for pointing out our failure to mention the 2014 measurements. We have added mention of the 2014 snow samples to section 2.2.

Section 3.2, 4th paragraph: Discuss the concentrations of HO₂NO₂ so that the reader isn't required to look at the figure.

The text has been edited to better describe the observed concentration during the 2013 and 2014 studies presented in figure 4. The 4th paragraph now reads: "Figure 4a shows the diurnal average of 2013 I- CIMS observations of PNA for the entire study.

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While the average diurnal mixing ratio peaks at 0.5 ppbv, mixing ratios up to 1.5 ppbv were observed during the 2013 study and can be explained by the coincidence of high daytime levels of NO₂ with the low temperatures in the Uintah basin. Similarly to the 2014 measurements, also included in Figure 4a, PNA reaches a peak after solar maximum (~ 15:00 MST) with a minimum observed throughout the night. Concentrations of HO₂NO₂ observed during the 2014 study were significantly lower relative to the 2013 study with a maximum average mixing ratio of 0.1 ppbv. During the 2013 and 2014 study, N₂O₅, a nighttime species and potential interference on the NO₃- ion, was not observed to contribute to the observed daytime signal."

Figure 5 is a great contribution to the paper. It would be good to expand the discussion and implications of this figure, including where HO₂NO₂ chemistry will matter and what the impact of oil activities in the region have on the chemistry in terms of this figure.

The following has been added to the paragraph discussing Figure 5 to give the reader a better idea of why this wintertime measurements in this region yield higher HO₂NO₂ mixing ratios than one may initially expect. "The Uintah basin provided a unique atmosphere that promotes the formation of PNA for several reasons (1) a strong inversion during the wintertime allows concentrations to build up in the boundary layer over several day periods (e.g. NO₂) (2) low ambient temperatures favoring the formation of HO₂NO₂ over thermal decomposition, and (3) radical species propagation, e.g. HO₂ formation, is enhanced due to the active chemistry observed during ozone formation events (Edwards et al., 2014). Lastly, as will be discussed later, the snow surface acts as an important interface serving as both a source and a sink of HO₂NO₂."

Page 3647, lines 11-13: Move to previous paragraph or integrate paragraphs.

This section has been incorporated into the previous paragraph.

Page 3647, lines 16-21: These sentences describe the figure but not the observed result, as would be helpful.

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This section has been expanded upon to include a better description of data contained within the figure. Additionally the figure legend should be in concentrations of pptv, not ppbv, and has been corrected.

Page 3647, lines 21-23: Why is the emission of precursors from snow photochemistry not discussed?

The author is correct to point out that the snow surface could serve as a source of precursors. As we did not measure fluxes of nitrogen containing species or HO₂ from the snow surface we cannot determine the driving force behind the apparent daytime emissions of HO₂NO₂. Therefore the manuscript is in need of additional discussion on this point. The following has been added to the manuscript to draw the reader's attention to this possibility. "While the deposition and potential volatilization of HO₂NO₂ can contribute to the net flux of nitrite at the snow surface other species such as HNO₃ and HONO are also known to deposit to snow surfaces and should also be considered as part of the net surface nitrogen budget. Furthermore, release of NO_x from the snow surface in the form of NO₂ could also result in a net apparent surface source as it would shift the gas phase equilibrium, reactions (1) and (2), towards the formation of HO₂NO₂. In this case, a surface depletion of HO₂ radicals would be expected, however; measurements of HO₂ were not made during the 2013 and 2014 studies."

Section 3.2: It would be useful to add discussion of the differences between the magnitude of the 2013 and 2014 results in Figure 4. Alternatively, just 2014 could be shown to illustrate the vertical profile conclusions. In general, more discussion of the results would be useful.

We would like to thank the reviewer for pointing out this potential to discuss the causes for the largely different ambient mixing ratios observed in the 2013 and 2014 seasons. We have edited the manuscript to include a paragraph on the differences and the reason for the larger concentrations observed during the 2013 study, particularly as they relate to the data presented in figure 5. The following has been added to the

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latest version of the manuscript: "The conditions encountered in the basin between the 2013 and 2014 season can be used to explain the large difference in the observed PNA ambient mixing ratios, shown in Figure 4a. Mainly during the 2013 study we observed strong inversions over multi-day periods allowing the buildup of primary and secondary pollutants, a phenomenon driven by snow surface cover and meteorological conditions encountered during the 2013 study (Ahmadov et al., 2015; Edwards et al., 2014). In contrast, relatively low snow cover during the 2014 season limited the formation of multi-day inversions yielding lower ambient mixing ratios of both primary and secondary pollutants. The resulting combination of lower NO_x mixing ratios and higher ambient temperatures during the 2014 study thereby favored thermal dissociation of HO₂NO₂ and led to lower ambient mixing ratios than observed during the 2013 study. In addition, limited snow cover and reduced deposition of NO_y species to the snow surface, as a result of lower ambient mixing ratios, likely reduced the role of the snow surface as a source of HO₂NO₂ in 2014."

Page 3648, lines 1-9: This paragraph would be more well-suited in the methods section.

While this paragraph could fit well into the methods section, we choose to keep this model description directly preceding the discussion of the model results. In this manner the details are fresh in the readers mind when the results are discussed.

Page 3650, line 1: Zhang et al refers to an experiment with sulfuric acid solution, which is quite different from the snow surface.

We do not disagree with this statement; unfortunately there are a limited number of studies investigating the uptake of HO₂NO₂ onto snow-like systems. In this case, we are explicitly stating that the work shows reversible uptake to highly acidic surfaces, therefore we do not feel we are misleading the reader and feel that no change to the manuscript is necessary.

Page 3650 discussion: Couldn't increasing nitrite levels increase NO_x production from

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snow, potentially resulting in more HO₂NO₂ production?

We thank the review for pointing out this mechanism that we have failed to discuss in the first version of the manuscript. Among the additional discussion included on the snow surface chemistry the following paragraph has been added to the manuscript. "While the deposition and potential volatilization of HO₂NO₂ can contribute to the net flux of nitrite at the snow surface other species such as HNO₃ and HONO are also known to deposit to snow surfaces and should also be considered as part of the net surface nitrogen budget. Furthermore, release of NO_x from the snow surface in the form of NO₂ could also result in a net apparent surface source as it would shift the gas phase equilibrium, reactions (1) and (2), towards the formation of HO₂NO₂. In this case, a surface depletion of HO₂ radicals would be expected, however; measurements of HO₂ were not made during the 2013 and 2014 studies."

Page 3651: The snow as a sink of HO₂NO₂ is discussed; however, the surface snow-pack as a source should also be discussed.

We thank the reviewer for this comment, and have certainly meant to present the snow surface as both a source and sink of HO₂NO₂, see Figure 4. From this figure the largest impact of the snow surface is to serve as a sink of HO₂NO₂, as such we have focused on this aspect of the surface with only a few comments on the surface as a source. We believe that the additional discussion in the manuscript, see responses above, along with the original material presented now gets this point across more clearly.

Figure 4: Is the shaded area campaign variability or uncertainty? This impacts interpretation of the results.

The shaded area is the standard deviation on the 1-hour measurement throughout the entire study. This information has been added to the description of the figure in the edited text. The following sentence has been added "Figure 4b shows the result of the difference of the 1m minus the 30m PNA measurements where the shaded region

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represents one standard deviation on the average for the entire study."

Technical Corrections:

Page 3638, line 10: Fix typo

This section has been reorganized and we believe the reviewer will find that while we could not find a typo in the line pointed out, we have improved the readability of this section. These particular changes have been discussed in the above responses to the reviewer's comments.

Page 3642, line 9-13: Remove repeated sentence.

The repetition was a typesetting error that was not caught, thank you for pointing this out. The issue will be corrected in the revised manuscript.

Figures 1 & 7: Increase font size in figure.

The font size in figure 1 and 7 has been increased.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 3629, 2015.

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