

**Interactive comment on “Peroxynitric acid ( $\text{HO}_2\text{NO}_2$ ) measurements during the UBWOS 2013 and 2014 studies using iodide ion chemical ionization mass spectrometry” by P. R. Veres et al.**

**Anonymous Referee #1**

**Received and published: 11 March 2015**

**Veres et al. described a new analytical technique to quantify peroxynitric acid ( $\text{HO}_2\text{NO}_2$ ) and hydroperoxyl radical ( $\text{HO}_2$ ) using a chemical ionization mass spectrometer with iodine negative ion chemistry. The authors presented laboratory experimental results and field observational datasets from winter field campaigns. This paper has several scientific merits such as 1) Introducing a new analytical technique for the rarely observed reactive species and 2) highlighting potential importance of  $\text{HO}_2\text{NO}_2$  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. As a number of researchers is using the iodine negative ion chemistry application, the publication of the presented research outcomes will be highly beneficial to the research community. In this sense, some additional information on the analytical techniques are urged.**

We thank the reviewer for pointing out many of the strengths of this work. Additionally, we would like to commend the reviewer for making the simple but impactful observation of the relevancy of this manuscript considering the increasing growth of researchers using iodide ion CIMS. In the following sections we will do our best to address the concerns of the reviewer, where our responses to the reviewers questions (bold text) will be given in plain text following the comment.

**The specifics are;**

**1) A diagram of the CIMS system would be helpful for readers to follow. In the text, it is not clear whether the sample was humidified by water vapor addition.**

We appreciate the suggestion about the CIMS diagram, however we would only include a figure nearly identical to that shown in Slusher et al. 2004. It is important to note that while this instrument is highly specialized, various versions of this type of CIMS instrument exist all of which would be suitable for pairing with the ion chemistry detailed in this work. On this note, we choose not to go into too many instrumental details, which would otherwise complicate the description of this method, and lengthen the manuscript. We do however thank the reviewer for pointing out our failure to include adequate information on the humidification of the sample. In all cases, water was added to the flow tube to promote the softer ion cluster chemistry necessary for the detection schemes used (I-HONO, I- $\text{HO}_2\text{NO}_2$ , I- $\text{HO}_2$ ). We have added a citation to the Lee et al. 2014 ES&T paper that includes a rather detailed discussion of iodide ion water clustering dynamics in the supplemental material. To clarify this to the reader the manuscript has been edited to include a description of the humidification method used. The portion of the text in

section 2.1.1. that mentions the humidification of the flow tube has been edited to include the following sentence. “This was achieved by flowing ~ 10 sccm N<sub>2</sub> bubbled through water directly into the flow tube at a pressure of 30 torr.”

**2) The standard generation methods for HO<sub>2</sub>NO<sub>2</sub>, HO<sub>2</sub>, and HONO may be better situated in the method section rather than in the results and discussion section. It is understandable that the authors try to balance between laboratory and field studies so that the manuscript is not overwhelmingly extended. However, more specific descriptions on standard generation methods in the manuscript rather than referring previous studies would be better for reader to grasp the described analytical techniques.**

We appreciate the reviewer’s suggestion about the reorganization of the manuscript with respect to the calibration methods. We agree with the reviewer and have decided to rearrange these sections slightly. Specifically we separated the results into section “3 Laboratory Results” and section “4 Uintah Basin Wintertime Ozone Study (UBWOS) Observations”. Considering the request for additional details on the standard generation methods, we have reread the sections describing these sources and feel that ample detail has been given in the manuscript in the current version. For example in the case of HO<sub>2</sub>NO<sub>2</sub> we describe the wet chemical synthesis methods in terms of the reagents used and details of the resulting solution. The explicit method for synthesizing HO<sub>2</sub>NO<sub>2</sub> (e.g. what to mix, how, and when) from there is presented in full in the Appelman and Gosztola 1995 reference, which we follow to precisely. In order to keep the manuscript as succinct as possible we describe only the details necessary that are not presented in full in references cited for each standard generation procedure.

**3) Is HO<sub>2</sub>NO<sub>2</sub> is the only source for nitrite to the snowpack?**

It was certainly not our intention to suggest that HO<sub>2</sub>NO<sub>2</sub> is the only source of nitrite to the snowpack. We also acknowledge there is established chemistry known to be sources of nitrite to snow surfaces (e.g. HNO<sub>3</sub> deposition and subsequent photo-induced reaction, as well as uptake of HONO from the gas phase). This topic has come up in both of the reviewer’s comments and as such we recognize this are one of the weaker area of discussion. We have chosen to expound on the ideas included on snow surface chemistry and sources of nitrite. These changes are reflected in the updated manuscript and are somewhat detailed in the responses to the comments of reviewer 2 that were on a similar theme with more specific comments to focus the changes.

**4) Line 22. If there is a systematic sensitivity difference between ambient HO<sub>2</sub> and HO<sub>2</sub> from HO<sub>2</sub>NO<sub>2</sub>. Wouldn’t you be able to determine it from laboratory calibration datasets? Further empirical and theoretical explanations are required rather than just a simple speculation.**

Unfortunately, the reviewer has not provided a page number with the line number to

direct us to exact statement to invoke this response. However, we will assume the reviewer is commenting on the difference in sensitivities reported between HO<sub>2</sub>NO<sub>2</sub> detected as I-HO<sub>2</sub> and the sensitivity of HO<sub>2</sub> detected as I-HO<sub>2</sub>. In this case, a lower sensitivity is observed for HO<sub>2</sub>NO<sub>2</sub> detected as I-HO<sub>2</sub>, likely as a result of either a thermal dissociation efficiency of less than unity, recombination of HO<sub>2</sub> and NO<sub>2</sub> prior to detection in the ion flow tube, or very likely a combination of both processes. Elucidation of the exact reason would require calibration experiments involving perturbation of the inlet temperature, length, and pressure that we have not performed at this point. As additional work is performed to improve this method for ambient HO<sub>2</sub> detection, these experiments will be conducted and the results conveyed in later works specifically focused on the measurement of HO<sub>2</sub>, which we believe is a better forum for those details.

### **Specifics**

**Figure 4b. It seems that the discussion is based on the minuscule concentration differences. Further statistical justification on whether the reported differences are meaningful. There is no figure caption for Figure 4b.**

First we would like to acknowledge that the figure caption was incorrect on the assignment of the year to the data in 4b, which presents the data collected during 2014. We agree with the reviewer that the concentration differences presented in figure 4 are small changes; however we point out that a change in 20ppt represents approximately a 20% change in the average ambient concentration during 2014. The data in this figure also represents the average over the entire six-week measurement period, where the shaded areas represent one standard deviation on the measurement. The standard deviation has been included to allow the reader to understand the significance of the reported differences. There are periods where the differences between measurement heights are far more significant however; we choose to report this as the average of all observations to be more representative of typical conditions. The following text has been added to the discussion of Figure 4: “It is important to note that this data represents a 1-hour average over the entire measurement period, and while the overall magnitude shown here is small observed ΔPNA values ranged from -150 pptv to 150 pptv.”

**The authors use both “Figure” and “Fig” for the figure references in the manuscript. Please be consistent.**

We appreciate the reviewer for pointing out this inconsistency and have changed all figure reference to the consistent form “Figure X”.

**Interactive comment on “Peroxynitric acid (HO<sub>2</sub>NO<sub>2</sub>) measurements during the UBWOS 2013 and 2014 studies using iodide ion chemical ionization mass spectrometry” by P. R. Veres et al.**

**Anonymous Referee #2**

**Received and published: 16 March 2015**

**Veres et al present details of the use of I(H<sub>2</sub>O)- for chemical ionization mass spectrometry measurements of HO<sub>2</sub>NO<sub>2</sub> in the ambient atmosphere. Two inlet set-ups, “cold” and “hot”, are discussed, as well as the detection of several product ions, including IHO<sub>2</sub>-, NO<sub>3</sub>-, and IHO<sub>2</sub>NO<sub>2</sub>-. Results of ambient measurements and modeling for HO<sub>2</sub>NO<sub>2</sub> 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 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 HO<sub>2</sub>NO<sub>2</sub> 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 HO<sub>2</sub>NO<sub>2</sub> 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 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 HO<sub>2</sub>NO<sub>2</sub> from snowpack photochemistry (e.g. NO<sub>x</sub> 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 HO<sub>2</sub>NO<sub>2</sub> 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 HO<sub>2</sub>NO<sub>2</sub> 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. 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 NO<sub>2</sub> 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 HO<sub>2</sub>NO<sub>2</sub> 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, N<sub>2</sub>O<sub>5</sub>, a nighttime species and potential interference on the NO<sub>3</sub><sup>-</sup> 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 HO<sub>2</sub>NO<sub>2</sub> 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 HO<sub>2</sub>NO<sub>2</sub> 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. NO<sub>2</sub>) (2) low ambient temperatures favoring the formation of HO<sub>2</sub>NO<sub>2</sub> over thermal decomposition, and (3) radical species propagation, e.g. HO<sub>2</sub> 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 HO<sub>2</sub>NO<sub>2</sub>.”*

**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.**

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 HO<sub>2</sub> from the snow surface we cannot determine the driving force behind the apparent daytime emissions of HO<sub>2</sub>NO<sub>2</sub>. 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 HO<sub>2</sub>NO<sub>2</sub> can contribute to the net flux of nitrite at the snow surface other species such as HNO<sub>3</sub> 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<sub>x</sub> from the snow surface in the form of NO<sub>2</sub> 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 HO<sub>2</sub>NO<sub>2</sub>. In this case, a surface depletion of HO<sub>2</sub> radicals would be expected, however; measurements of HO<sub>2</sub> 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 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<sub>x</sub> mixing ratios and higher ambient temperatures during the 2014 study thereby favored thermal dissociation of HO<sub>2</sub>NO<sub>2</sub> and led to lower ambient mixing ratios than observed during the 2013 study. In addition, limited snow cover and reduced deposition of NO<sub>y</sub> 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 HO<sub>2</sub>NO<sub>2</sub> 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 HO<sub>2</sub>NO<sub>2</sub> 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<sub>x</sub> production from snow, potentially resulting in more HO<sub>2</sub>NO<sub>2</sub> 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 HO<sub>2</sub>NO<sub>2</sub> can contribute to the net flux of nitrite at the snow surface other species such as HNO<sub>3</sub> 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<sub>x</sub> from the snow surface in the form of NO<sub>2</sub> 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 HO<sub>2</sub>NO<sub>2</sub>. In this case, a surface depletion of HO<sub>2</sub> radicals would be expected, however; measurements of HO<sub>2</sub> were not made during the 2013 and 2014 studies.*”

**Page 3651: The snow as a sink of HO<sub>2</sub>NO<sub>2</sub> is discussed; however, the surface snowpack 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 HO<sub>2</sub>NO<sub>2</sub>, see Figure 4. From this figure the largest impact of the snow surface is to serve as a sink of HO<sub>2</sub>NO<sub>2</sub>, 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 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.