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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Peroxynitric acid (HO_2NO_2) 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. described a new analytical technique to quantify peroxynitric acid (HO2NO2) and hydroperoxyl radical (HO2) 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 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. 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-HO2NO2, I-HO2). 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

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has been edited to include the following sentence. “This was achieved by flowing $\sim$ 10 sccm N2 bubbled through water directly into the flow tube at a pressure of 30 torr.”

2) The standard generation methods for HO2NO2, HO2, 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 HO2NO2 we describe the wet chemical synthesis methods in terms of the reagents used and details of the resulting solution. The explicit method for synthesizing HO2NO2 (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 HO2NO2 is the only source for nitrite to the snowpack?

It was certainly not our intention to suggest that HO2NO2 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. HNO3 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

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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 HO2 and HO2 from HO2NO2. 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 HO2NO2 detected as I-HO2 and the sensitivity of HO2 detected as I-HO2. In this case, a lower sensitivity is observed for HO2NO2 detected as I-HO2, likely as a result of either a thermal dissociation efficiency of less than unity, recombination of HO2 and NO2 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 HO2 detection, these experiments will be conducted and the results conveyed in later works specifically focused on the measurement of HO2, 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 assign-

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ment 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 Atmos. Chem. Phys. Discuss., 15, 3629, 2015.