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## ***Interactive comment on* “Strong wintertime ozone events in the Upper Green River Basin, Wyoming” by B. Rappenglück et al.**

**Anonymous Referee #1**

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In recent years, wintertime ozone pollution events have been observed in several locations in the mountainous Western US. In all of these regions there has been rapid development of oil and gas extraction over the past decade. Ozone pollution is usually considered an urban summertime issue, and hence these wintertime pollution episodes, in regions of low population density, are an interesting phenomenon, which have been linked to emissions from oil and gas extraction processes. This paper presents an analysis of observations of ozone precursor species in the Upper Green River Basin (UGRB), Wyoming, during several high ozone days in early 2011, with the aim of improving understanding of the chemistry driving these winter ozone pollution events.

High mixing ratios of non-methane hydrocarbons (NMHCs) (>1 ppmv) and NO<sub>x</sub> (> 20 C6244

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ppbv) were observed during periods when high ozone concentrations were observed (referred to in this work as Intensive Operation Periods, IOP), when emissions were confined to a low mixing height with low wind speeds. These high ozone precursor concentrations have been observed previously in regions of oil and gas development (e.g. Katzenstein et al. 2003, Carter and Seinfeld 2012, Gilman et al. 2013, Edwards et al. 2013), but do not provide all of the information necessary to explain the drivers for ozone production without an understanding of the local radical budget. Unfortunately radical measurements (e.g. OH, HO<sub>2</sub>, RO<sub>2</sub>) were not made during this study, however, the radical precursor species, HCHO and HONO, were measured and used to help estimate the dominant radical sources in this environment. The most surprising result of this work is the very large HONO mixing ratios observed (average diurnal maximum on IOP days of > 1 ppbv) and the unusual diurnal pattern, with peak [HONO] observed in the middle of the day. Using this observed HONO data, the calculated OH production in the UGRB on IOP days was dominated by HONO photolysis, accounting for 74–98% of the calculated OH production before noon and approximately 50% after noon. These large HONO concentrations are difficult to explain with current understanding of gas phase tropospheric photochemistry, as the short lifetime of HONO with respect to photolysis means a midday peak of the magnitude observed requires a very large photolytic source of HONO (2900 pptv h<sup>-1</sup>). The authors investigate some potential mechanisms to achieve this required number, in particular the role of photo-enhanced heterogeneous conversion of HNO<sub>3</sub> to HONO on the snow surface.

After presenting the observations, the authors use several different indicator ratios (proposed in Sillman and He, 2002) to assess the NO<sub>x</sub> vs. VOC sensitivity of the O<sub>3</sub> production chemistry in this environment. This is an important part of the paper, as it is this information that will be used in future mitigation strategies in the UGRB.

This paper is a valuable contribution to the currently limited data available on wintertime ozone pollution episodes associated with oil and gas production. However, before publication several of the conclusions drawn in the paper need to be better supported by

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the data analysis, and the paper should therefore be published only after the following major comments have been addressed.

Major comments:

The first major concern that needs to be addressed in this work relates to the strength of the observational evidence for a strong surface HONO source from heterogeneous HNO<sub>3</sub> reactions. The following comments identify specific sections of the work where the conclusions require further justification. The authors should attempt to either better display their evidence for the proposed surface source and mechanism or acknowledge that, although several daytime HONO sources have been proposed in the literature, the data from this study cannot identify the “missing” daytime HONO source mechanism during these wintertime O<sub>3</sub> pollution events in the UGRB.

1) Although the surface HONO data in Figure S8 shows spikes higher than that at a height of 1.8 m between the hours of 10:00 and 13:00, this is not the case throughout the rest of the day. This is especially true in the afternoon when the 1.8 m data appears higher than at the surface. This plot alone does not seem to support the hypothesis that the snow surface is the major source of daytime HONO, and instead implies that for large parts of the day HONO deposition is occurring at the surface. If, as suggested on pages 17980-17981, the emission of HONO from HNO<sub>3</sub> photolysis on the surface accounts for almost 80% of the total noontime HONO source should the gradient not be more apparent and have a diurnal profile following J(HNO<sub>3</sub>)? Maybe an analysis of the time series of individual days would better show the difference between the two measurement heights, as the high degree of variability in this average diurnal plot makes comparison difficult.

2) Pg 17977 “Data in Fig. 14 shows that HONO increases as incoming UV radiation increases.” This statement implies causality in the higher observed HONO concentrations due to increased photolysis during IOP days. This however is not apparent from the data shown in this paper, and there are many other more significant changes

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between the IOP and non-IOP days that could potentially increase HONO production, such as increased HNO<sub>3</sub> concentrations and increased oxidation of NO<sub>x</sub> species. As increased photolysis will also increase the loss rate for HONO, some attempt to separate the observed variability in HONO due to photolysis may strengthen the argument for photolytic HONO production. The data in Fig. 14 appears to show that UV radiation on non-IOP days still has the same maximum values, but shows a greater degree of variability. This, one assumes, is because in order for O<sub>3</sub> pollution events to occur stable meteorology is required to allow the formation of temperature inversions. As cloud cover is associated with unstable meteorology, non-IOP days are more likely to show decreases in UV radiation than IOP days, which will show much less variability from clear skies photolysis. The authors need to either provide some form of correlation plot as strong evidence of the direct link between photolysis and HONO production, or rephrase this statement to acknowledge that photolysis and HONO mixing ratios are two of many things that change between IOP and non-IOP days, and are not necessarily directly linked.

3) Also on Pg 17977, the statement “During the same time periods, nitrogen oxide levels decrease (Fig. 3a). This indicates that more HONO is being formed through NO<sub>2</sub> conversion” does not explain how the authors come to this conclusion. Fig. 3a does show that NO concentrations drop between 11:00-16:00 on IOP days, however, this coincides with the time of strongest O<sub>3</sub> production and the peak in observed O<sub>3</sub> concentrations. Could the decrease in observed NO be instead due to faster photochemistry resulting in more rapid NO<sub>x</sub> oxidation, as indicated by the increase in observed HNO<sub>3</sub> and high NO<sub>y</sub> concentrations during this period, or by NO titration by O<sub>3</sub>? An increased HONO source, of the magnitude implied here, at this time of day will definitely create a surge in radical concentrations, which in turn will increase both O<sub>3</sub> production and NO<sub>x</sub> oxidation. If the dominant daytime HONO production mechanism that is favored in this work (i.e. gas phase HNO<sub>3</sub> deposited to the snow surface and subsequently undergoing photo-enhanced heterogeneous conversion to HONO) is correct, would you expect to see a decrease in the gas phase NO concentrations during the

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peak HONO emission time period? As HNO<sub>3</sub> deposition to the snow occurs throughout the day, albeit faster during the day when HNO<sub>3</sub> concentrations are highest, would it not seem reasonable to expect an increase in observed NO concentration instead of a decrease? As the calculated radical source from the photolysis of the observed HONO, of 2.9 ppbv h<sup>-1</sup>, must be matched by a stoichiometric production of NO. Can this NO<sub>x</sub> source be seen in the observations? The authors should make it clear how they came to the conclusion that a reduction in observed NO concentration “indicates” that this is due to HONO formation from NO<sub>2</sub>.

The second major comment relates to Sect. 3.4 and the use of the photochemical indicators to assess VOC or NO<sub>x</sub> limited O<sub>3</sub> production. These observable ratios have been used in many urban and rural environments to assess the sensitivity of the local O<sub>3</sub> production chemistry to its main precursor species. As discussed in Sillman and He (2002) however, the transition point between NO<sub>x</sub> and VOC limited for these ratios of observed species can vary depending on the chemical environment, in particular the O<sub>3</sub>/NO<sub>z</sub> ratio. It is also uncertain as to how these observed ratios respond in environments where unconventional radical sources, such as HONO, dominate as these ratios were developed for systems where O<sub>3</sub> photolysis was the dominant radical source. This uncertainty is not discussed by the authors, nor are the differences in the findings of this work and that by Carter and Seinfeld (2012) who carried out a modeling study using the data from the 2011 UGRB study to look at the sensitivity of O<sub>3</sub> production. This uncertainty needs to be acknowledged and the discrepancies with previous work discussed.

Minor comments:

Pg 17961, line 3 – The low temperatures and high NO<sub>2</sub> concentrations experienced during the study would also favor N<sub>2</sub>O<sub>5</sub> over NO<sub>3</sub>.

Pg 17961-17962 - The increased photochemistry that results in O<sub>3</sub> production should also increase the NO<sub>z</sub>/NO<sub>y</sub> ratio, as the emitted NO<sub>x</sub> is more rapidly oxidized. As

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several components of NO<sub>z</sub> have not been measured during this study, such as PAN and organic nitrates, one would expect there to be a larger “missing” NO<sub>y</sub> fraction during IOP days compared with non-IOP days. However, Fig. S3 provides evidence against this, likely due to the increased NO<sub>y</sub> fraction attributed to the observed HONO. Insight into the local photochemistry might be gained by looking at the diurnal variation of the “missing” NO<sub>y</sub> fraction. The authors should comment on why this fraction is larger on non-IOP days than IOP days. This also has implications for the assumed PAN mixing ratio of 400 pptv based on previous observations in the UGRB. The authors should state if these PAN observations were made during periods of high or low O<sub>3</sub> concentrations.

Pg 17962, line 17 - PAN also acts as a radical reservoir and can transport radicals in addition to NO<sub>x</sub> out of the UGRB.

Pg 17963, line 20 - Although the potential primary emission sources of HCHO, HONO and HNO<sub>3</sub> are discussed later in the paper, it would help the reader if the potential primary sources of these species were mentioned here, or at least forward referenced to where this is discussed within the paper.

Pg 17970, line 2 – Estimated photolysis lifetimes of HONO and HCHO during the observational period would be useful for the reader.

Sect. 3.4 – At the end of this section it would be useful to compare the findings of NO<sub>x</sub> vs. NMHC limited O<sub>3</sub> production with other work in this type of environment. In particular a contrast with the findings of Carter and Seinfeld (2012), which looked at the same O<sub>3</sub> pollution events in the UGRB in early 2011, would benefit the conclusions of this section of the paper.

Pg 17981 – “We assume that these emissions may be transported to the Boulder site and that removal processes may be negligible.” The authors should make some comment on the distance between the measurement site and the local sources as well as HONO lifetime, as during the day HONO photolysis will likely result in a lifetime of less

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than 1 h, and the assumption of negligible losses might be brought into question.

Pg 17981, line 23 - "Intensive During the IOPs" Typo?

Fig 3 and Fig. 14 – Larger axis labels would make figure easier to read.

S2 - Is the HONO reported here at the surface or 1.8 m or all data?

## References

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