

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

B. Rappenglück et al.

brappenglueck@uh.edu

Received and published: 24 October 2013

Reply to Referee #1

We appreciate the important comments made by the reviewer and we hope that our manuscript has improved.

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 HNO₃ 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

C8417

data from this study cannot identify the “missing” daytime HONO source mechanism during these wintertime O₃ 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 HNO₃ 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(HNO₃)? 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.

Answer: We added additional sections:

Chapter 3.2.4 "The plot contains all data of the 2/28-3/16/2011 period, as segregation into IOP and non-IOP days would have resulted into patchier time series with larger intermittent data gaps. To some extent S8 may provide some general characterization." and "...the observed maximum at 1.80 m may be due to transport of HONO rather than a surface source most likely due to the stratified properties of the planetary boundary layer (PBL) with suppressed vertical mixing during these times (see chapter 3.6),..."

Chapter 3.6 (and corresponding figures 14, S14 and S15) "Figure S14 shows that generally the HONO extra source, which balances the OH production rate due to HONO photolysis (dOH/dt -HONO; see Figure 13) correlates better with JO(1D) (=0.86; =0.85) and JHNO₃ (=0.82; =0.88) than with JNO₂ (=0.71; =0.85). According to Villena et al. (2010) and Elshorbany et al. (2012) a better correlation of the daytime HONO extra source with JO(1D) would point to photolysis of HNO₃ as a potential

C8418

HONO source, whereas a better correlation with JNO₂ would point to photosensitized conversion of NO₂ on humic acid surfaces. Following the approach by Villena et al. (2010) we determined the correlation of the HONO extra source with photolysis rates for each day. In our case we used photolysis rates based on TUV calculation. In Figure S15 the slopes m of each daily correlation of the HONO extra source versus JNO₂ (m JNO₂) are plotted against median daytime NO₂ mixing ratios for the same time periods. For these plots any days with daily median NO mixing ratios > 500 pptv were excluded to avoid potential bias due to freshly polluted air masses. The results are segregated for IOP and non-IOP days. A similar approach is shown for m JHNO₃ against median daytime HNO₃ mixing ratios. Following observations can be deduced: (i) in both cases IOP days show higher m J NO₂, HNO₃ values, (ii) the slopes of m J NO₂, HNO₃ are steeper on IOP days than on non-IOP days, and (iii) correlation coefficients R^2 of m JNO₂, HNO₃ versus NO₂ and HNO₃, respectively, are higher on IOP than non-IOP days. While this indicates photo-enhanced HONO formation on IOP days, the stronger correlation coefficients in the case of m JHNO₃ versus HNO₃ mixing ratios ($=0.97$; $=0.89$) compared with the case of m JNO₂ versus NO₂ mixing ratios ($=0.84$; $=0.39$) would indicate that photolysis of HNO₃ may play an important role for HONO formation. According to Villena et al. (2010) the correlation of m JNO₂ against the product of $[NO_2] \times 1/v$ (v being the horizontal windspeed) used as an indication for turbulent vertical mixing, was even stronger, suggesting a ground surface source. In our study, correlations of m JHNO₃ versus HNO₃ mixing ratios ($=0.98$; $=0.97$) as well as m JNO₂ versus NO₂ mixing ratios ($=0.95$; $=0.85$) also became stronger when windspeed was included."

and

"Figure 14 indicates that on IOP days most of the time the PBL is stable and behaves like a laminar stratified flow. This likely explains why figure S8 does not indicate a vertical gradient of HONO mixing ratios and that the layers seem to be decoupled from each other. It is only during the time frame 11:00-16:00 MST the PBL becomes

C8419

turbulent. During this time frame also the mixing layer height tends to increase, albeit slightly, until the maximum atmospheric instability is reached. More importantly, this time frame also coincides with the time period of maximum OH mixing ratios as shown in Figure 14 and the development of a vertical gradient in HONO mixing ratios as indicated in Figure S8. This is the time frame when vertical exchange processes from the surface may occur. During other times of the day these processes are largely suppressed."

and

"As mentioned earlier Figure S8 provides some general characterization of HONO mixing ratios obtained at 1.80 m above the ground versus HONO mixing ratios obtained 10 cm above the ground. -Quantitative flux measurements were not performed based on the small tower measurements. However, some additional estimates on PBL properties can be deduced based on meteorological measurements obtained at the Tall Tower site located about 10 km Southeast of the Boulder site (2,149 m; 42.4241°N; -109.5609°W; see Figure 1)."

and

"HONO measurements were taken at 10 cm and 1.80 m above the ground, which translates into turbulent diffusion times from the ground of 0.15 s and 46.5 s, respectively. During the time frame 11-13:00 MST of Figure S8 a vertical HONO gradient is visible. The average HONO photolysis rate during that time frame is $3.44 \times 10^{-3} \text{ s}^{-1}$. Considering an average HONO mixing ratio at 10 cm of ~ 700 pptv and a vertical turbulent diffusion time of 46.35 s from the bottom sampling location to the 1.80 m sampling location an average HONO mixing ratio of ~ 600 pptv at the 1.80 m level would be expected, a decrease of $\sim 14\%$. The data of S8 indicates an average HONO mixing ratio of ~ 500 pptv, which would imply a doublefold decrease. Given the uncertainties and limitations in our assumptions on the atmospheric stability as retrieved from the "Tall Tower" site, the HONO small tower observations at the Boulder site, and the TUV

C8420

calculated HONO photolysis rate, the results are reasonable."

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 between the IOP and non-IOP days that could potentially increase HONO production, such as increased HNO₃ concentrations and increased oxidation of NO_x 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 O₃ 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.

Answer: In the revised version we calculated OH concentrations. Based on the calculated OH concentrations we determined the photostationary state concentration of HONO, [HONO]_{PSS}. We now focus on the "HONO extra source" which only considers the net HONO concentration by subtracting [HONO]_{PSS}.

We added additional information in chapter 3.6 and corresponding figures S14 and S15: "Figure S14 shows that generally the HONO extra source, which balances the OH production rate due to HONO photolysis (dOH/dt -HONO; see Figure 13) correlates better with JO(1D) (=0.86; =0.85) and JHNO₃ (=0.82; =0.88) than with JNO₂ (

C8421

=0.71; =0.85). According to Villena et al. (2010) and Elshorbany et al. (2012) a better correlation of the daytime HONO extra source with JO(1D) would point to photolysis of HNO₃ as a potential HONO source, whereas a better correlation with JNO₂ would point to photosensitized conversion of NO₂ on humic acid surfaces. Following the approach by Villena et al. (2010) we determined the correlation of the HONO extra source with photolysis rates for each day. In our case we used photolysis rates based on TUV calculation. In Figure S15 the slopes *m* of each daily correlation of the HONO extra source versus JNO₂ (mJNO₂) are plotted against median daytime NO₂ mixing ratios for the same time periods. For these plots any days with daily median NO mixing ratios > 500 pptv were excluded to avoid potential bias due to freshly polluted air masses. The results are segregated for IOP and non-IOP days. A similar approach is shown for mJHNO₃ against median daytime HNO₃ mixing ratios. Following observations can be deduced: (i) in both cases IOP days show higher mJ NO₂, HNO₃ values, (ii) the slopes of mJ NO₂, HNO₃ are steeper on IOP days than on non-IOP days, and (iii) correlation coefficients R² of mJNO₂, HNO₃ versus NO₂ and HNO₃, respectively, are higher on IOP than non-IOP days. While this indicates photo-enhanced HONO formation on IOP days, the stronger correlation coefficients in the case of mJHNO₃ versus HNO₃ mixing ratios (=0.97; =0.89) compared with the case of mJNO₂ versus NO₂ mixing ratios (=0.84; =0.39) would indicate that photolysis of HNO₃ may play an important role for HONO formation. According to Villena et al. (2010) the correlation of mJNO₂ against the product of [NO₂]×1/*v* (*v* being the horizontal windspeed) used as an indication for turbulent vertical mixing, was even stronger, suggesting a ground surface source. In our study, correlations of mJHNO₃ versus HNO₃ mixing ratios (=0.98; =0.97) as well as mJNO₂ versus NO₂ mixing ratios (=0.95; =0.85) also became stronger when windspeed was included."

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 NO₂ 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

C8422

coincides with the time of strongest O₃ production and the peak in observed O₃ concentrations. Could the decrease in observed NO be instead due to faster photochemistry resulting in more rapid NO_x oxidation, as indicated by the increase in observed HNO₃ and high NO_y concentrations during this period, or by NO titration by O₃? 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 O₃ production and NO_x oxidation. If the dominant daytime HONO production mechanism that is favored in this work (i.e. gas phase HNO₃ 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 peak HONO emission time period? As HNO₃ deposition to the snow occurs throughout the day, albeit faster during the day when HNO₃ 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⁻¹, must be matched by a stoichiometric production of NO. Can this NO_x 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 NO₂.

Answer: We inserted some additional clarifications in Chapter 6 and rewrote part of that chapter:

1) Minor issue: there might have been a typo: by saying "nitrogen oxides" we wanted to refer to NO_x, not only to NO. So we replaced the term "nitrogen oxides" by "NO_x" to make this statement less ambiguous.

2) We inserted following statements: "According to Villena et al. (2011) the magnitude of the HONO/NO_x ratio is similar to the magnitude of the ratio of the corresponding atmospheric lifetimes. Based on the calculated JHONO photolysis rates an atmospheric lifetime for HONO of about 5-7 min between 11:30-15:30 MST on IOP days can be deduced. Using the calculated OH concentrations and temperature dependant reaction

C8423

rates for reactions with OH and O₃ a corresponding atmospheric lifetime of ~19 min for NO₂ can be retrieved, which translates into a ratio of both lifetimes in the order of ~26, which is close to the observed average median HONO/NO_x ratios for that time period, which is ~21. On non-IOP days, the atmospheric lifetime of NO_x is much longer (almost 1 hr), the ratio of the HONO and NO_x lifetimes is ~12, the observed HONO/NO_x ratio is ~9. This indicates that more HONO is being formed in photochemical processes, most likely through NO₂ conversion, on IOP days during these time periods. At the same time, NO_x levels decrease (Figure 3a). As meteorological conditions (PBL height; SW wind flow) do not vary much during this time of the day on IOP days, and NO_x deposition velocity onto snow surfaces is low (Hauglustaine et al., 1994), rapid oxidation of NO_x leads to a decrease in NO_x mixing ratios. Reactions of NO₂ with OH and O₃ will lead to the formation of HNO₃ accelerated through the enhanced availability of radicals due to the strong HONO photolysis source. This decrease in ambient NO_x levels indicate that these removal processes exceed other sources for NO_x, e.g. through photolysis of HONO."

The second major comment relates to Sect. 3.4 and the use of the photochemical indicators to assess VOC or NO_x limited O₃ production. These observable ratios have been used in many urban and rural environments to assess the sensitivity of the local O₃ production chemistry to its main precursor species. As discussed in Sillman and He (2002) however, the transition point between NO_x and VOC limited for these ratios of observed species can vary depending on the chemical environment, in particular the O₃/NO_z 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 O₃ 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 O₃ production. This uncertainty needs to be acknowledged and the discrepancies with previous work discussed.

C8424

Answer: Thank you for pointing this out! 1) The section 3.4 has been rewritten to address the photochemical indicators more appropriately. The general finding (VOC limitation in the morning; NO_x limitation in the afternoon; passing the transitional regime in between) is still being supported.

1) We now have included a discussion of our results with the findings by Carter and Seinfeld (2012). "Carter and Seinfeld (2012) found that regimes sensitive to VOC or NO_x may vary from year to year and depend on the specific location in the UGRB. For the Boulder site in 2011 they determined a VOC sensitive regime, which largely agrees with our analysis for the morning hours on IOP days. Carter and Seinfeld also state that under such conditions additional OH generated by an increased level of HONO would favor O₃ formation, while NO_x saturation would also have the potential to cause additional HONO formation. Carter and Seinfeld (2012) modeled the Boulder 2011 case based on the HONO data presented in this paper and found much better simulations of O₃ compared to the baseline scenario, when HONO was added, which is very encouraging. In addition to the Carter and Seinfeld analysis our paper also considers diurnal variations of the NMHC/NO_x ratio, including any fluctuations in the NMHC mix, which is also subject to wind directional changes, at least for the Boulder site. As mentioned above, our data shows that there is likely a transition phase after the morning NO_x saturation conditions towards a VOC saturation regime, which is not described by Carter and Seinfeld and would require diversified speciated regulatory mitigation strategies."

Minor comments:

Pg 17961, line 3 – The low temperatures and high NO₂ concentrations experienced during the study would also favor N₂O₅ over NO₃.

Answer: Added to this statement.

Pg 17961-17962 - The increased photochemistry that results in O₃ production should also increase the NO_z/NO_y ratio, as the emitted NO_x is more rapidly oxidized. As

C8425

several components of NO_z have not been measured during this study, such as PAN and organic nitrates, one would expect there to be a larger "missing" NO_y fraction during IOP days compared with non-IOP days. However, Fig. S3 provides evidence against this, likely due to the increased NO_y fraction attributed to the observed HONO. Insight into the local photochemistry might be gained by looking at the diurnal variation of the "missing" NO_y 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 O₃ concentrations.

Answer: Unfortunately, we do not have a conclusive answer on why the "missing" NO_y fraction is slightly larger on non-IOP versus IOP days. It seems that while the "missing" NO_y fraction is largest during the day on IOP and non-IOP days, albeit slightly larger on non-IOP days, indicating some "missing" NO_z. More importantly, on non-IOP days during the early morning hours (i.e. 00:00-06:00 MST) the "missing" NO_y is larger than on IOP days.

With regard to the PAN data we included some additional statement: "The results showed up to 1 ppbv PAN during daytime and up to 400 pptv as an estimated 24 hour average, while corresponding ozone values were 85 ppbv and 51 ppbv, respectively, i.e. PAN was ~1% of the ozone mixing ratios, which lies in the range observed in areas (e.g. Rappenglück et al., 2003). Most important precursor candidates for PAN in the UGRB will be ethane, toluene and xylenes."

Pg 17962, line 17 - PAN also acts as a radical reservoir and can transport radicals in addition to NO_x out of the UGRB.

Answer: Sentence modified. It now reads: "However, it can serve as a reservoir for NO_x and radicals and remove NO_x and radicals out of the UGRB."

Pg 17963, line 20 - Although the potential primary emission sources of HCHO, HONO

C8426

and HNO₃ 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.

Answer: This section was rewritten partly and information about emission sources for HCHO and HONO provided. It now reads: "NO_y, HNO₃, HONO, and HCHO (S4b) largely follow the same directional pattern as NO_x and hydrocarbons (S4a). However, contrary to the primarily emitted pollutants NO_x, NMHC, and CH₄, species, which may be formed secondarily, i.e. HNO₃, HONO, and HCHO, generally show higher values during daytimes. It is known that HCHO may be emitted primarily from incomplete combustion in either mobile or stationary sources (Zweidinger et al., 1988; Altshuler, 1993; Chen et al., 2004; Dasgupta et al., 2005; Rappenglück et al., 2013). Also, HONO can be emitted primarily from various combustion processes (Kirchstetter et al., 1996; Kurtenbach et al., 2001; Rappenglück et al., 2013) with traffic emissions being an important contribution to ambient HONO (Sarwar et al., 2008)."

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

Answer: We added the following statement: "...(~6-7 hrs for HCHO vs. ~5-7 min for HONO at local noontime conditions during the UGRB study)..."

Sect. 3.4 – At the end of this section it would be useful to compare the findings of NO_x vs. NMHC limited O₃ 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 O₃ pollution events in the UGRB in early 2011, would benefit the conclusions of this section of the paper.

Answer: We inserted additional statements. Please see also above our reply to the "second major comment relates to Sect. 3.4."

Pg 17981 – "We assume that these emissions may be transported to the Boulder site

C8427

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

Answer: We added the following statement: Given an average windspeed of 1.4 m s⁻¹ between 11:00-16:00 MST on IOP days and a distance of about 3-5 km between the Boulder site and most local sources we estimate that photolysis will have removed 85% (for the closest sources) and up to 90% (for the most distant sources) of ambient HONO by the time air masses would reach the Boulder site. based on a HONO lifetime of ~5-7 min during the same time period Thus during the transport HONO photolysis may likely have contributed to radical formation. At the Boulder site an estimated HONO production of 70 pptv/hr would still be due combustion related HONO emissions.

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

Answer: Corrected

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

Answer: Axis labels were enlarged

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

Answer: Yes, S2 lists HONO data at 1.8 m. We included corresponding additional information in the Chapter 2 Methods.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/13/C8417/2013/acpd-13-C8417-2013-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 17953, 2013.

C8428