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Atmospheric Chemistry and Physics Discussions

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

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Reply to Comment

We appreciate the important comments made by James M. Roberts and David D. Parrish. Here we will provide some replies

The observation of high ozone during stable wintertime conditions in areas heavily impacted by emissions from oil and gas production is an intriguing problem in atmospheric chemistry. Based upon their daytime nitrous acid (HONO) data, Rappenglück et al. conclude that HONO, largely produced from reactions within the surface snow cover, is the dominant source of photochemical radicals during such periods in the Upper Green River Basin (UGRB) in Wyoming. This is potentially an interesting find-

ing, but several questions must be answered before this conclusion can be considered definitive.

First, measurement of HONO in the atmosphere is difficult. Comparisons between measurements made by different techniques often disagree, and measurement artifacts are common. The technique used in this study must be shown to be accurate and free from such artifacts. This is particularly important in the cold wintertime environment of the UGRB when unusual oxidized nitrogen species such as peroxynitric acid may be present at high concentrations. Further, photochemical modeling of the high ozone events over-predicts ozone if the high HONO concentrations reported by Rappenglück et al. are included [Carter and Seinfeld, 2012]. so this inconsistency between the model and measurements requires consideration of whether there could be problems with the measurement.

Answer: We added some further information in the section "2 Methods": "The LOPAP® instrument has been tested against DOAS measurements both in smog chamber studies as well as in field campaigns (Kleffmann et al., 2006). Excellent agreement was obtained between these techniques during daytime as well as nighttime. The UH LOPAP instrument recently participated in a large intercomparison chamber instrument (Ródenas et al., 2011) and in a recent field intercomparison (Pinto et al., 2013). So far, interferences were found to be negligible in most atmospheric air masses (Heland et al., 2001; Kleffmann et al., 2002). Some interferences were found for nitrites (Ródenas et al, 2013), however at nitrite levels orders of magnitude above atmospheric concentrations. The instrument has been tested under polar conditions (Kleffmann and Wiesen, 2008; Villena et al., 2011). Interferences with peroxynitric acid (HO2NO2) were found to be less than 0.5% (Ammann, 2013)."

We added some further information in the section "3.4. NMHC versus NOx limitation of ozone production: "Carter and Seinfeld (2012) found that regimes sensitive to VOC or NOx 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

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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 NOx 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."

Ammann, M.: priv. comm., Paul Scherrer Institute (PSI), Villigen, Switzerland, 2013. Carter, W.P.L., and Seinfeld, J.H.: Winter ozone formation and VOC incremental reactivities in the Upper Green River Basin of Wyoming, Atmos. Environ., 50, 255-266, doi:10.1016/j.atmosenv.2011.12.025, 2012 Heland, J., Kleffmann, J., Kurtenbach, R., and Wiesen, P.: A new instrument to measure gaseous nitrous acid (HONO) in the atmosphere, Environ. Sci. Technol., 35, 3207-3212, 2001. Kleffmann, J., and Wiesen, P.: Technical Note: Quantification of interferences of wet chemical HONO LOPAP measurements under simulated polar conditions, Atmos. Chem. Phys., 8, 6813-6822, 2008. Kleffmann, J., Heland, J., Kurtenbach, R., Lörzer, J.C., and Wiesen, P.: A new instrument (LOPAP) for the detection of nitrous acid (HONO), Environ. Sci. Pollut. Res., 9, 48-54, 2002. Kleffmann, J., Lörzer, J.C., Wiesen, P., Kern, C., Trick, S., Volkamer, R., Ródenas, M., and Wirtz, K.: Intercomparison of the DOAS and LOPAP techniques for the detection of nitrous acid (HONO), Atmos. Environ., 40, 3640-3652, 2006. Pinto J., Dibb J., Lee B., Rappenglück B., Wood E., Zhang R., Lefer B., Ren X., Stutz J., Ackermann L., Golovko J., Herndon S., Levi M., Meng Q., Munger J., Zhaniser M., Zheng J.: Intercomparison of Field Measurements of Nitrous Acid (HONO) during the SHARP Campaign, J. Geophys. Res., submitted, 2013. Ródenas, M., Munoz, A., Alacreu, F., Brauers, T., Dorn, H.-P., Kleffmann, J., and Bloss, W.: Assessment of HONO Measurements: the FIONA Campaign at EUPHORE in Disposal of Dangerous Chemicals in Urban Areas and Mega Cities, I. Barnes and K.J. Rudzinski (eds.), NATO Science for Peace and Security Series C: Environmental Security, DOI 10.1007/978-94-007-5034-0_4, 2013. Ródenas, M., Muñoz, A., Alacreu, F., Dorn, H-P., Brauers, T., Kleffmann, J.,

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Second, the LOPAP instruments detailed in the literature have time constants that range from 4 to 7 minutes, due primarily to the time constants associated with the liquid flow system. A LOPAP instrument was used by Rappenglück et al. in this work; it must be demonstrated that the time constant was adequately accounted for when the HONO data were separated into the inlet up (1.8m) and inlet down (10cm) observations.

Answer: We added some further information in the section "2 Methods": "The sampling time is 30 s. The response time, i.e. the time it takes for the signal to go from 100% to 10% of the initial value or from 0% to 90% of the final value, changes every time a new set of peristaltic pump tubing is installed, yet is stable for any given set of tubings. The response time was determined for each set of tubing and ranged between 3.45 - 6.15 min. The time correction used to create the time stamp reported was equal to the sum of the time delay and half the response time, which ranged accordingly between 6.67 - 10.08 min. This time stamp was used to properly allocate air samples to the bottom or

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up position of the small tower."

Third, the authors derive their reported HONO gradient from a comparison of an average of all the up-inlet measurements with an average of all the down-inlet measurements. It is critical to demonstrate that this difference between the two inlet heights is statistically significant, and that analyses on shorter time scales (e.g., hourly, daily) are consistent with the analysis of the total data set. This latter issue is particularly important given the episodic variability of the reported HONO concentrations, so that one day cannot be simply compared to another since the gas phase and snow conditions are likely different.

Answer: Unfortunately, the small tower data was too patchy. Due to these limitations it is not our intention to overinterpret plot S8 and prefer using it as a conceptual figure. Conclusions drawn in the paper can also be established without plot S8.

We added some further information in the section "3.2.4 HONO and relationships with radiation and relative humidity": "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."

We added some further information in the section "3.6 Role of HONO" "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."

Fourth, it must be shown that the reported HONO gradient is consistent with the range of eddy diffusivities and photolysis rates expected to apply to the wintertime planetary boundary layer in the UGRB. A significant gradient below 1.8m may imply greater stability than can be reasonably expected.

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Answer: In the section "3.6 Role of HONO" we added some further information about eddy diffusivities, turbulent mixing time versus photolytic lifetime of HONO and the development of HONO gradients within the PBL.

Fifth, if the above questions can be adequately answered, then the contribution of HONO to photochemical radical production must properly account for the HONO gradient within the planetary boundary layer (PBL), since the average through the depth of the PBL will be significantly smaller than that measured at 1.8m.

Answer: Based on our calculations of eddy diffusivities, which are of the same magnitude as found in Alert (Zhou et al., 2001) we estimate that HONO will be removed by its photolysis, which is likely stronger than observed in Alert, as UV radiation at Boulder is stronger by at least a factor 2 than in Alert (Zhou et al., 2001) within the lowermost 10 m of the PBL. We only consider radical production at the sampling height 1.80 m, not as an integrated quantity throughout the PBL, as this would require additional information about the vertical distribution of the photostationary state concentration of HONO within the lowermost 10 m of the PBL. Corresponding discussions have been added to chapter "3.6 Role of HONO".

Zhou, X., Beine, H.J., Honrath, R.E., Fuentes, J.D., Simpson, W., Shepson, P.B., and Bottenheim, J.W.: Snowpack photochemical production of HONO: a major source of OH in the arctic boundary layer in springtime, Geophys. Res. Lett., 28 (21), 4087-4090, 2001.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/13/C8433/2013/acpd-13-C8433-2013-supplement.pdf

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