

Interactive
Comment

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

J. Roberts

james.m.roberts@noaa.gov

Received and published: 19 September 2013

This is a joint comment by James M. Roberts and David D. Parrish, both of the Chemical Sciences Division of the NOAA Earth System Research Laboratory.

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 finding, but several questions must be answered before this conclusion can be considered

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



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 peroxyacetic 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.

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.

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.

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 plane-

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



tary boundary layer in the UGRB. A significant gradient below 1.8m may imply greater stability than can be reasonably expected.

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.

Carter, W. P. L., and J. H. Seinfeld (2012), 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.

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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

