

# Winter Photochemical Ozone Events in the Upper Green River Basin

## Extended Abstract # 96

**John V. Molenaar**

Air Resource Specialists, Inc., 1901 Sharp Point Drive, Suite E, Fort Collins, CO 80525

## INTRODUCTION

Ozone is an air pollutant that can cause severe respiratory health effects, especially in children and the elderly. Traditionally, photochemical ozone production has been considered a summertime, urban phenomenon where hourly average ozone concentrations may exceed 150 ppb compared to background values of ~50 ppb. Wintertime U.S. ozone concentrations are generally 35-50 ppb. However, in February, 2005 routine air quality monitoring in rural Upper Green River Basin, Wyoming, in the vicinity of the Jonah-Pinedale Anticline (JPA) natural gas field, measured hourly ozone concentration greater than 120 ppb at air temperatures as low as -17°C. After verifying the validity of the ozone data, investigations lead to the realization that these winter ozone production events were occurring in the Oil and Gas development area during very specific conditions: under stagnant, cold, high pressure meteorological systems typified by low surface wind speeds; snow cover; and limited cloudiness, surface based temperature inversions trap high concentrations of ozone precursors emitted by Oil and Gas activities at night followed by rapid daytime photolytic ozone production with hourly average ozone concentrations rising from 10-30 ppb (night) to >140 ppb (shortly after solar noon). Similar wintertime ozone production is probably occurring around the world under comparable industrial and meteorological conditions.<sup>1</sup>

## ANALYSES

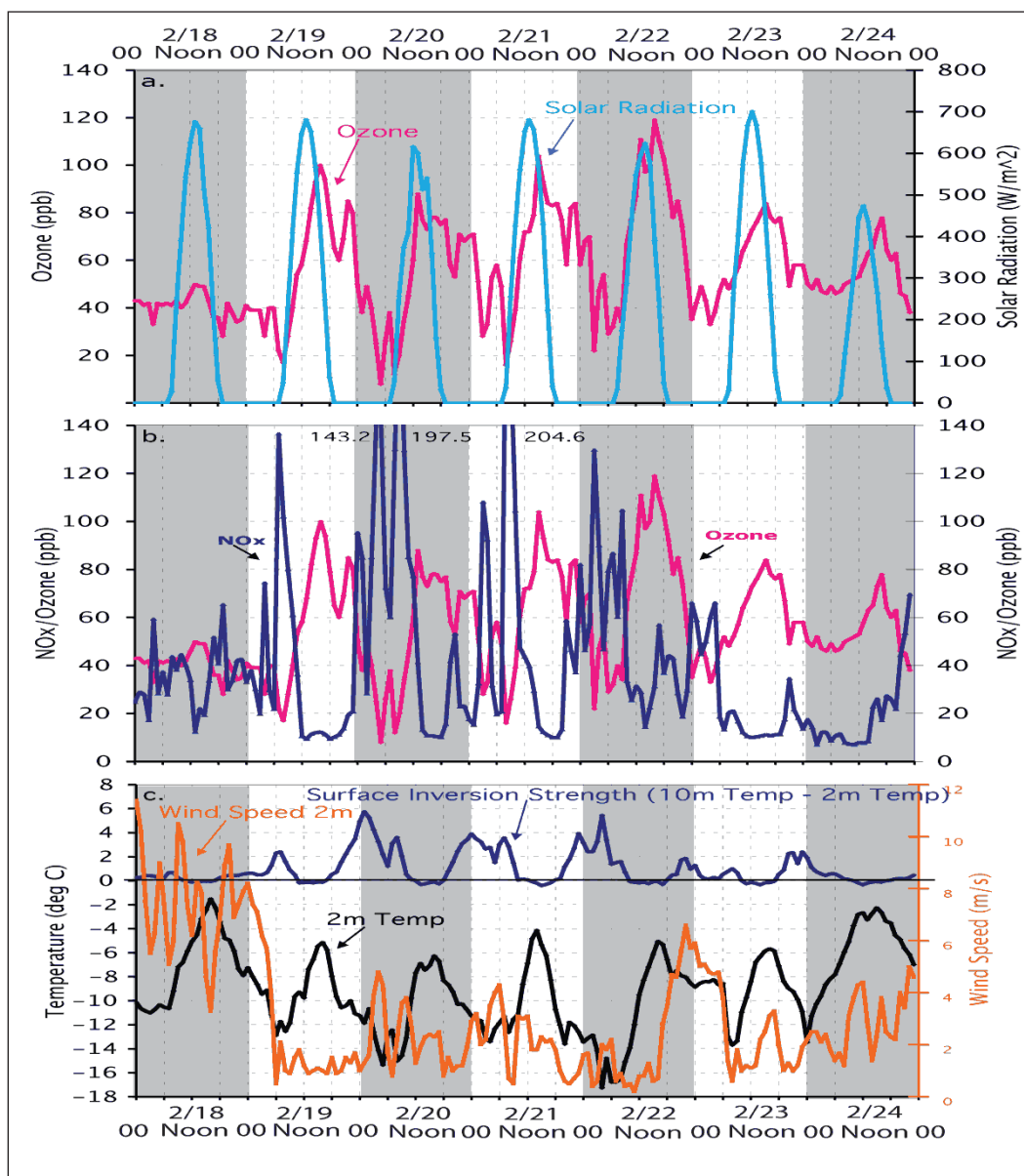
Ozone pollution is generally considered to be only produced photochemically at levels above health based standards in urban areas in the summertime. As such, ozone monitoring is generally not required in the winter in the U.S. Year around air quality measurements have been conducted in Jonah/Pinedale Anticline gas field area at three sites since 2005. In 2005 the JPA field produced ~600 million cubic feet of natural gas—enough to supply the energy needs of 3 million US homes and valued at ~\$6 billion. Drilling rigs and pipeline compressors are powered by diesel/natural gas engines operating 24 hours per day. There was ~200,000 hp (150 million watts) of engine power operating at any one time in the JPA gas field in Feb 2005. In 2008 there are ~1,500 wells in operation in the Jonah field with wells expected to triple by 2012.

Rapid ozone production events with hourly average ozone concentrations greater than 120ppb were first observed in JPA in Jan-Mar, 2005. These events reoccurred during mid-winter in 2005, 6, 8, & 10 The U.S. EPA averaging time of 8-hours at 75 ppb, was exceeded on many days and resulted in the first ever wintertime ozone advisories in the United States.

Possible explanations for the rapid, diurnal ozone production such as instrument malfunction, interferences from some other gas, long range transport, and stratospheric ozone intrusions were all extensively examined and dismissed.

Hourly average ozone, solar radiation and NO<sub>x</sub> (precursor for ozone production) for a typical ozone production event (Feb 18-25, 2008) are presented in Fig.1 for the Jonah site at the southern edge of the gas field.

Figure 1. Hourly average solar radiation, ozone, NO<sub>x</sub> and temperature data for the Jonah air quality monitoring site, Feb 18-25, 2008.



From this figure it may be observed that ozone concentrations track solar radiation with a 1-2 hour time lag. On Feb. 22, hourly average ozone concentrations at Jonah increased to 120 ppb

by 1430 MST from 37 ppb 4 hours earlier. Ozone precursor  $\text{NO}_x$  concentrations (panel b) exhibit high anti-correlation with ozone and attained maximum concentrations of  $\sim 200$  ppb during the morning of Feb. 21 when much of the  $\text{NO}_x$  is in the form of  $\text{NO}_2$  (measured along with NO, but not plotted). Later in the day  $\text{NO}_x$  concentrations drop below 15 ppb as the  $\text{NO}_2$  photolyzes to NO that is recycled through the reaction with peroxy radicals and ensuing ozone formation. The synoptic scale meteorological condition controlling the high ozone production event is the movement of high pressure into western Wyoming Feb. 19 bringing colder temperatures and lower wind speeds over the UGRB, Fig. 1, (panel c). Snow had fallen earlier across the basin. The falling air temperatures (to a low of  $-17^\circ\text{C}$  on Feb 22), low wind speeds, clear nights and snow cover combined to produce exceptionally strong temperature inversions, a meteorological condition in which the temperature of the air above the surface is warmer with increasing height. In a well mixed atmosphere, the air temperature decreases (i.e. becomes colder) on average by  $6.5^\circ\text{C}$  for every 1000 m increase in altitude. At the Jonah site air temperature is monitored at 2 m and 10 m above ground level. A measure of the highly stable lapse rate present at low altitude during the ozone production period is presented in Fig. 1 (panel c) where the temperature difference between 10 m and 2 m is plotted. Positive values show that on the nights of Feb 20 and 22 the temperature at 10 m was up to  $6^\circ\text{C}$  warmer than at 2 m. This exceptional thermal stratification serves to curtail vertical mixing and subsequent dilution of VOCs, NO and other gaseous effluents emitted near the surface constraining them into a de facto “chemical retort.” During the day, the air near the surface warms, reducing the low level temperature gradient (Fig 1, panel c), but the solar heating is insufficient to erode the entire depth of the strong inversions, especially when the ground is snow covered. By Feb 23 the cold air moved south-east from the UGRB, temperatures warmed, inversion strength decreased, mixing increased and rapid diurnal ozone production was lowered.

The two primary photolytic reactions in the photochemical ozone production cycle are the photolysis of  $\text{NO}_2$  to form NO and atomic O, and the combination of  $\text{O}_2$  with the O atom to form ozone. In these cold wintertime conditions the relative importance of the radical sources that are the other primary drivers of local photochemical ozone production is not well understood. However, for net ozone production, the  $\text{NO}_2$  must be produced from NO - either directly emitted, or produced from  $\text{NO}_2$  without consuming ozone in the process. This conversion process is accomplished in the atmosphere when NO reacts with peroxy radicals. These peroxy radicals are produced when VOCs are oxidized by the hydroxyl radical, OH. Generally, the most important source of OH is the reaction of the  $\text{O}(^1\text{D})$  with a water molecule to yield 2 OH radicals. However, at the very low temperatures found in these wintertime situations, the concentration of water vapor is very low, and it is expected that nearly all  $\text{O}(^1\text{D})$  will simply be collisionally quenched to  $\text{O}(^3\text{P})$ , followed by reformation of ozone. It is possible that still undetermined processes dominate the OH production, especially in the hours immediately after sunrise when it is difficult to initiate the photochemistry. Alternative OH production processes include direct formation through photolysis of formaldehyde or nitrous acid, HONO. Formaldehyde may accumulate overnight due to direct emissions from the combustion sources responsible for the observed high concentrations of  $\text{NO}_x$  and VOCs. HONO is produced from the heterogeneous reaction of  $\text{NO}_2$  with water on moist surfaces, such as snow cover or atmospheric aerosols. Future research should be directed toward investigating the relative importance of these and other OH radical formation processes.

The spectral photolysis rates of these reactions depend solely on the actinic flux, absorption cross section, and quantum yield for disassociation and are independent of temperature. Conventional thought is that during the northern hemisphere winter these photolysis rates are dramatically reduced compared to mid-summer rates due to the low solar zenith angles. To examine the effects of reduced columnar ozone and high surface albedo, the Tropospheric Ultraviolet and Visible radiation model (TUV) was used to calculate hourly actinic flux and spectral photolysis rates for all important atmospheric photolytic reactions in wintertime in the JPA field. Two days were modeled, Feb 22, 2008, a high ozone production day with snow on the ground, and June 21 (a day with the highest solar zenith angle). For Feb 22, satellite measured total column vertical ozone of 339 Dobson units was measured over the UGRB and surface albedo set at 0.9 for the freshly snow covered surface. Total vertical columnar ozone of 350 Dobson units, and a surface albedo of 0.1 were input for June 21. The resulting modeled peak photolysis rate for NO<sub>2</sub> is ~50% greater on Feb 22 than June 21 emphasizing the role of fresh snow cover as a factor in the UGRB ozone formation process.

## **SUMMARY**

Measurements and analyses have shown that the exceptionally high photochemical ozone production observed in the UGRB in winter is the result of NO<sub>x</sub> and VOC effluents released in the production of natural gas in the area. These effluents become contained within a relatively shallow stagnant, stable air layer near the surface. When there is extensive snow cover and clear skies, these emissions are rapidly converted photochemically to ozone which is in turn also trapped in the shallow, stable boundary layer. We conclude by noting that similar cold temperature ozone formation is probably occurring in other regions of the western U.S., and in Canada, Russia, Kazakhstan, Mongolia and China where fossil fuel extraction occurs in similar terrain and under similar meteorological conditions. At present, ozone measurements in most of these regions in winter are limited to non-existent.

## **REFERENCES**

1. Schnell, R. C., Oltmans, S. J., Neely, R. R., Endres, M. S., Molenar, J. V., and White, A. B. "Rapid photochemical production of ozone at high concentrations in a rural site during winter", *Nature Geoscience*, 2009, 2, 120-122

## **KEYWORDS**

ozone, winter, photochemical, oil & gas