LETTERS
PUBLISHED ONLINE: 18 JANUARY 2009 | DOI: 10.1038/NGEO415

nature geoscience

Exhibit 38

Rapid photochemical production of ozone at high concentrations in a rural site during winter

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Ozone is an air pollutant that can cause severe respiratory health effects. Photochemical ozone production near the Earth's surface is considered a summertime, urban phenomenon[1–3], where hourly average ozone concentrations can exceed 150 p.p.b., compared with background values of about 50 p.p.b., and wintertime ozone concentrations in the US are usually in the range of 35–50 p.p.b. (refs 1–3). Here we report rapid, diurnal photochemical production of ozone during air temperatures as low as −17 °C, in the rural Upper Green River Basin, Wyoming, in the vicinity of the Jonah–Pinedale Anticline natural gas field. We find that hourly average ozone concentrations rise from 10–30 p.p.b. at night to more than 140 p.p.b. shortly after solar noon, under the influence of a stagnant, high-pressure system that promotes cold temperatures, low wind speeds and limited cloudiness. Under these conditions, an intense, shallow temperature inversion develops in the lowest 100 m of the atmosphere, which traps high concentrations of ozone precursors at night. During daytime, photolytic ozone production then leads to the observed high concentrations. We suggest that similar ozone production during wintertime is probably occurring around the world under comparable industrial and meteorological conditions.

Ozone air pollution is generally considered to be produced photochemically at levels above health-based standards only in urban areas in the summertime. As such, ozone monitoring is generally not required in the winter in the US. In February 2008, hourly average ozone concentrations above 140 p.p.b. (8 h average of 122 p.p.b.) were recorded in rural Wyoming, near the 400 km^2 Jonah–Pinedale Anticline (JPA) natural gas field. The US Environmental Protection Agency averaging time of 8 h at 75 p.p.b. (ref. 4) was exceeded on 14 days and resulted in the first ever wintertime ozone advisories in Wyoming[5].

Year-round air-quality measurements have been conducted in the JPA gas-field area (42.50° N, 109.71° W) at three sites since 2005 and an additional eight sites for 2 months in the winter of 2008 (ref. 6). Rapid ozone-production events with hourly average ozone concentrations greater than 75 p.p.b. were first observed in January–March 2005 (http://www.esrl.noaa.gov/gmd/obop/Wyoming_Ozone_Long.pdf). In 2007 there were few events, coincident with low snow cover in the Upper Green River Basin (UGRB) (∼75 km × 75 km centred on 42.5° N, 110° W); the snow and ozone-production relationship is discussed later. In January–March 2008 balloon-borne ozonesonde measurements were conducted in the JPA region. This paper focuses on 2008 because of the availability of the ozonesonde and ancillary data, and on the Jonah site.

In 2007 the JPA field produced ∼20 million m^3 yr^{-1} (∼2 billion cubic feet per day) of natural gas[7–9], enough to supply the natural-gas needs of 17 million US homes and valued at ∼$4 billion. Drilling rigs and pipeline compressors are powered by diesel/natural-gas engines operating 24 h per day. We calculate there was ∼200,000 hp (150 million watts) of engine power operating at any one time in the JPA gas field in February 2008. In 2008 there were ∼2,200 wells in operation in the Jonah field; wells are expected to number 10,000 by 2020 (ref. 9).

Hourly average ozone, solar radiation and NO_x (precursor for ozone production) levels for a typical ozone production event (18–25 February 2008) are presented in Fig. 1 for the Jonah site (42.42° N, 109.68° W; 2,027 m above sea level) at the southern edge of the gas field. From this figure it may be observed that ozone concentrations track solar radiation with a 1–2 h time lag. On 22 February, hourly average ozone concentrations at Jonah increased to 120 p.p.b. by 14:30 MST from 37 p.p.b. 4 h earlier. Ozone precursor NO_x concentrations (Fig. 1b) show high anticorrelation with ozone and attained maximum concentrations of ∼200 p.p.b. during the morning of 21 February, when much of the NO_x was in the form of NO_2 (measured along with NO, but not plotted). Later in the day NO_x concentrations dropped below 15 p.p.b. as the NO_2 photolysed to NO, which is recycled through the reaction with peroxy radicals and ensuing ozone formation (discussed later).

The synoptic-scale meteorological condition controlling the high-ozone-production event is the movement of high pressure into western Wyoming on 19 February, bringing colder temperatures and lower wind speeds over the UGRB (Fig. 1c). Snow had fallen earlier across the basin. The falling air temperatures (to a low of −17 °C on 22 February), 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 becomes warmer with increasing height. In a well mixed atmosphere, the air temperature decreases (that is, becomes colder) on average by 6.5 °C for every 1,000 m increase in altitude. At the Jonah site air temperature is monitored at 2 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. 1c, where the temperature difference between 10 and 2 m is plotted. Positive values show that on the nights of 20 and 22 February the temperature was up to 6 °C higher at 10 m than at 2 m. This exceptional thermal stratification serves to curtail vertical mixing and subsequent dilution of volatile organic compounds (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. 1c), but the solar heating is insufficient to erode the

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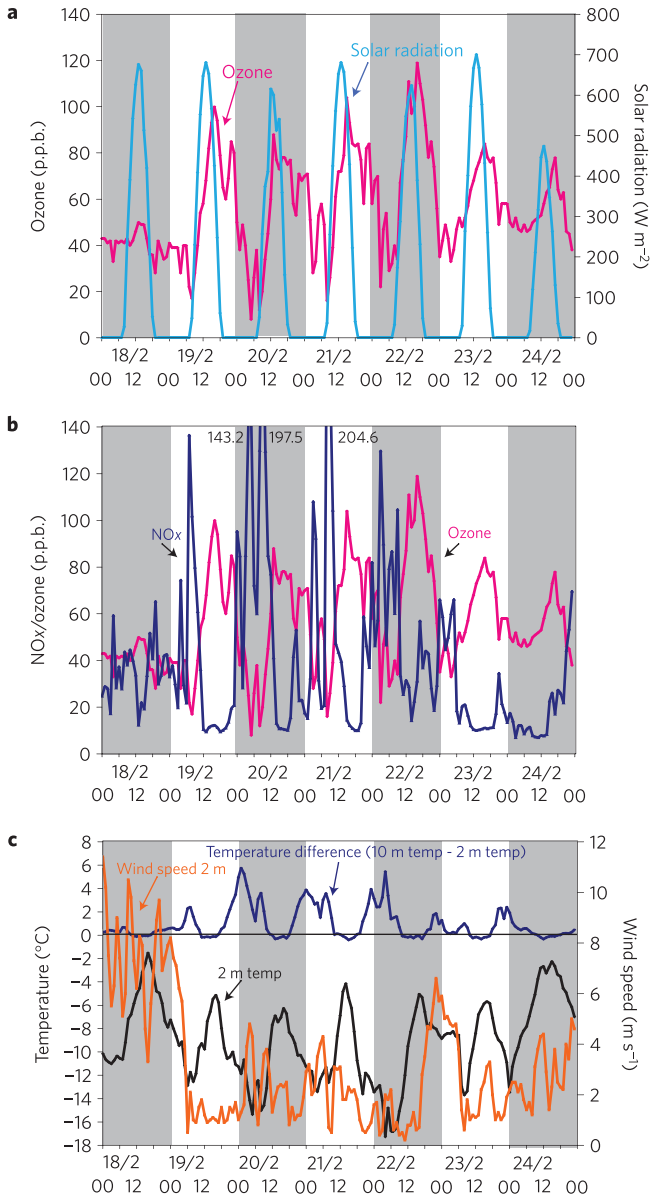

Figure 1 | Hourly average solar radiation, ozone, NO_x and temperature data for the Jonah air-quality-monitoring site, 18–25 February 2008. **a**, Rapid production and elevated concentrations of ozone closely track solar radiation with a 1–2 h time lag. **b**, Ozone and NO_x at Jonah showing high anticorrelation during the enhanced-ozone-formation period (19–23 February), at below-freezing temperatures. **c**, Ambient air temperature and wind speed at 2 m above the ground surface, and temperature difference between 2 and 10 m above ground level.

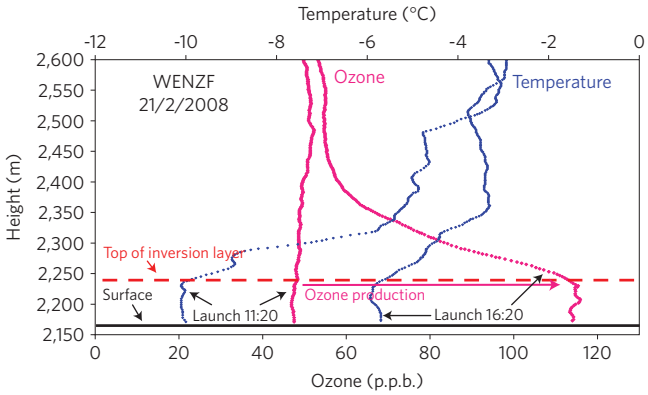

Figure 2 | Ozonesonde profile 10 km north of the gas field showing ozone and temperature profiles, surface to 2,600 m, 21 February 2008. Balloon-borne ozonesondes were launched at 11:20 and 16:20 MST and passed through 2,600 m (top of graph) ~30 min later. The top of the ozone production zone at 100 m corresponds to the top of the temperature-inversion layer (red line), and even though the boundary-layer air warmed during the day the 'chemical retort' bounded by the ground surface and the top of the inversion layer remained intact throughout the day.

entire depth of the strong inversions, especially when the ground is snow covered[10,11]. By 23 February the cold air moved southeast from the UGRB, temperatures warmed, inversion strength decreased, mixing increased and rapid diurnal ozone production was lowered.

In Fig. 2 are presented vertical profiles of ozone and temperature obtained from balloon-borne ozonesondes launched at 11:20 and 16:20 MST on 21 February, 35 km north of the Jonah monitoring site and ~10 km beyond the northern edge of the gas field. The stable atmospheric boundary layer was ~100 m deep throughout the day, as shown in the temperature and ozone profiles. Ozone was relatively constant at around 45 p.p.b. throughout the 11:20 profile. By 16:20, ozone concentrations had increased to around 117 p.p.b. throughout the boundary layer. We interpret the lack of ozone formation in the 11:20 sounding compared with Jonah, where ozone had increased from a nocturnal average of ~30–80 p.p.b. by the same time, as being due to wind flow that had not yet brought ozone precursors and ozone from the gas field to the ozonesonde site. A similar pattern has been observed at other monitoring sites located outside the boundaries of the gas field; the presence of elevated ozone outside the gas field is predicated on wind direction over the previous 3–6 h transporting ozone precursors or ozone-enriched air to the remote sites. The two primary photolytic reactions in the photochemical ozone production cycle[12] are the photolysis of NO_2 to form NO and atomic O, and the combination of O_2 with the O atom to form ozone (see the Methods section). 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 NO_2 must be produced from NO—either directly emitted, or produced from 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 $O(^1D)$ with a water molecule to yield two OH radicals. However, at the very low temperatures found in these wintertime situations, the concentration of water vapour is very low, and it is expected that nearly all $O(^1D)$ will simply be collisionally quenched to $O(^3P)$, 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 owing to direct emissions from the combustion sources responsible for the observed high concentrations of NO_x and VOCs. HONO is produced from the heterogeneous reaction of NO_2 with water on moist surfaces, such as snow cover or atmospheric aerosols. Future research should be directed towards 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

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these photolysis rates are dramatically reduced compared with mid-summer rates owing 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)[13] 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 modelled, 22 February 2008, a high-ozone-production day with snow on the ground, and 21 June (a day with the highest solar-zenith angle). For 22 February, satellite-measured total-column vertical ozone of 339 Dobson units was measured over the UGRB (ref. 14) and surface albedo was 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 21 June. The resulting modelled peak photolysis rate for NO_2 is ~50% greater on 22 February than 21 June, emphasizing the role of fresh snow cover as a factor in the UGRB ozone-formation process (see the Methods section).

We suggest that the exceptionally high photochemical ozone production observed in the UGRB in winter is the result of NO_x 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 and are then rapidly converted photochemically to ozone, which in turn is also trapped in the shallow, stable boundary layer.

Other possible explanations for the rapid, diurnal ozone production such as stratospheric ozone intrusions seem unlikely, as the presence of a high-pressure system over the region essentially precludes stratospheric air reaching the surface[15]. Vorticity cross-sections (measure of ozone-rich stratospheric air entering the troposphere) centred on the JPA gas field during days of elevated surface ozone production showed no evidence of stratospheric air contributing to the high surface ozone levels. This is reinforced by ozonesonde profiles in which elevated ozone was confined to a shallow layer near the surface with no enhancements at higher altitudes, nor was ozone excessive at the Pinedale CASTNET site 20 km north and 221 m higher in elevation than the Jonah site (~100 m above the top of the inversion). Finally, the strong, repeated diurnal ozone production correlated with solar insolation does not follow the pattern of ozone input from the stratosphere[14].

We conclude by noting that similar low-temperature ozone formation is probably occurring in other regions of the western US, 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 non-existent.

Methods

This study was carried out on data provided by the Wyoming Department of Environmental Quality (WDEQ) collected in a large air-quality programme in the UGRB. All these data are quality controlled to US Environmental Protection Agency procedures 40 CFR 50 and 58. Synoptic-scale meteorological data were accessed at <http://www.hpc.ncep.noaa.gov/dailywxmap/ >. Snow-coverage data were available from multiple web cameras located at the air-quality monitoring stations accessed through the WDEQ site. Basic data analysis was carried out by plotting and comparing the time series of the chemical and meteorological parameters. This analysis revealed a consistent pattern of strong coherence in each of the events that was studied, over multiple years, reinforcing the robustness of the results.

To examine the effects of reduced vertical ozone and increased surface albedo on the ozone-production reactions ((1)–(4) below)

$$NO_2 + h\nu \rightarrow NO + O(^3P) \quad (1)$$

$$O_3 + h\nu \rightarrow O_2 + O(^1D) \quad (2)$$

$$HCHO + h\nu \rightarrow H_2 + CO \quad (3)$$

$$HCHO + h\nu \rightarrow H^* + HC^*O \quad (4)$$

the TUV radiative-transfer model was used to calculate photolysis rates. TUV outputs actinic flux and spectral photolysis rates for all important atmospheric photolysis reactions. Normalization was done by dividing all hourly rates by the peak 21 June rate for each reaction. As expected, using average total vertical ozone of 350 Dobson units and a dark surface (albedo = 0.1), the 22 February peak rates are significantly lower than on 21 June, supporting the conventional wisdom of suppressed photochemistry during winter months. Decreasing the total vertical ozone by 100 Dobson units almost doubles the peak rate for O_3 photolysis but the increases in NO_2 and CH_2O photolytic rates are minor at best. This is because the actinic flux for NO_2 and CH_2O photolysis is driven by wavelengths that are not absorbed by ozone, thus varying total vertical ozone will have little effect. Increased O_3 photolysis rate without a simultaneous increase in NO_2 and CH_2O photolytic rates will probably not support enhanced photochemistry. However, very large increases in the peak photolytic rates (>50%) are seen for all reactions when a snow-covered surface (albedo = 0.9) is used. The peak photolytic rate is not the only factor determining the extent of the ozone production. The duration of actual photolysis must also be considered. This is done by stating the integrated reaction rates for 22 February simulations as a percentage of the integrated 21 June rates.

Received 27 October 2008; accepted 18 December 2008; published online 18 January 2009

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Acknowledgements

This research was supported by the NOAA, Earth System Research Laboratory, Boulder, Colorado. Data were provided by the Wyoming Department of Environmental Quality, Cheyenne, Wyoming. P. J. Crutzen, Max-Planck Institute, Mainz, Germany, and D. D. Parrish and J. A. deGouw, NOAA Earth System Research Laboratory, Boulder, Colorado, provided helpful suggestions on ozone formation chemistry.

Author contributions

R.C.S., S.J.O., R.R.N., J.V.M. and A.B.W. conducted the data analysis; J.V.M. assisted in field data collection and ran the TUV model; M.S.E. brought the ozone-production phenomenon to our attention and facilitated access to the data. Conclusions expressed should be considered those of the NOAA authors.

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