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Surface ozone pollution in winter

TOXIC TRANSPORT
Microbial mercury uptake

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Thermal runaway

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 phenomenon¹⁻³, 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 km² 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 Wyoming⁵.

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) ($\sim 75\text{ km} \times 75\text{ km}$ 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 m³ yr⁻¹ (~ 2 billion cubic feet per day) of natural gas⁷⁻⁹, enough to supply the natural-gas needs of 17 million US homes and valued at $\sim \$4$ billion. Drilling rigs and pipeline compressors are powered by diesel/natural-gas engines operating 24 h per day. We calculate there was $\sim 200,000$ hp (150 million watts) of engine power operating at any one time in the JPA gas field in February 2008. In 2008 there were $\sim 2,200$ 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 NO₂ (measured along with NO, but not plotted). Later in the day NO_x concentrations dropped below 15 p.p.b. as the NO₂ 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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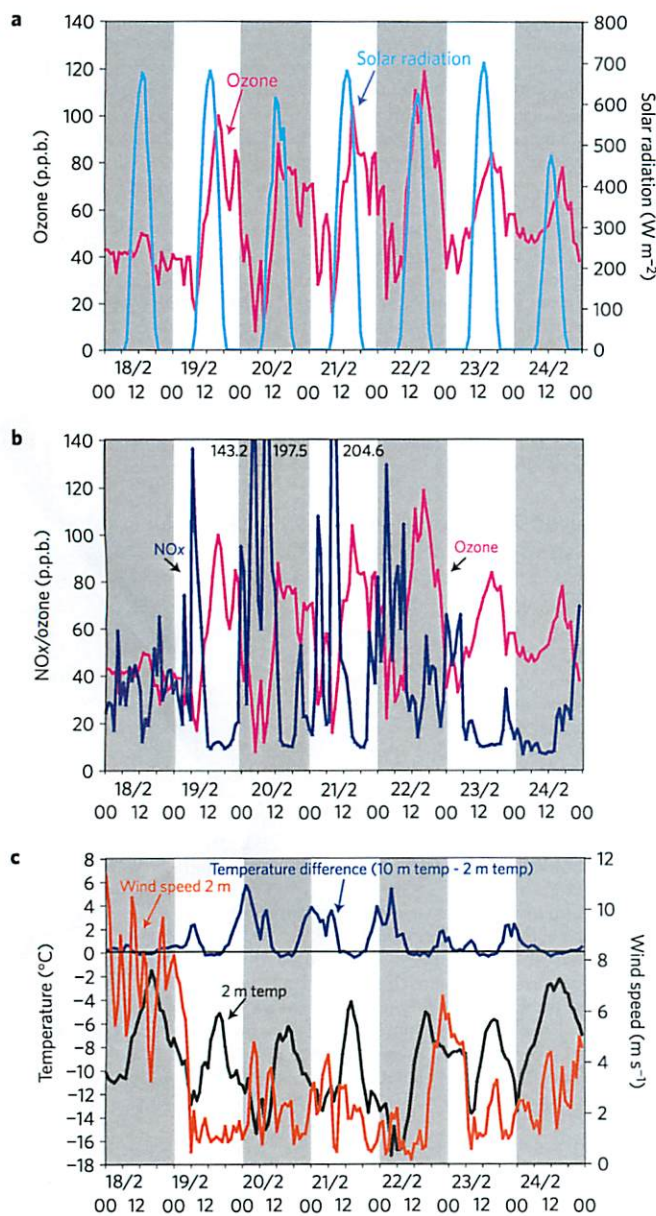


Figure 1 | Hourly average solar radiation, ozone, NO_x and temperature data for the Jonah air-quality-monitoring site, 18–25 February 2008.

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.

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

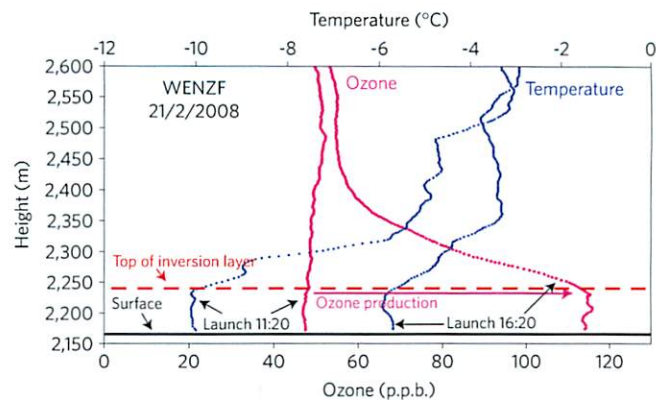


Figure 2 | Ozonesonde profile 10 km north of the gas field showing ozone and temperature profiles, surface to 2,600 m, 21 February 2008.

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.

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 cycle¹² are the photolysis of NO₂ to form NO and atomic O, and the combination of O₂ 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 NO₂ must be produced from NO—either directly emitted, or produced from NO₂ 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 NO₂ 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

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 NO₂ 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.

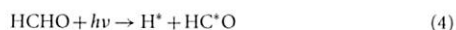
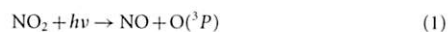
Other possible explanations for the rapid, diurnal ozone production such as stratospheric ozone intrusions seem unlikely, as the presence of a high-pressure system over the region essentially precludes stratospheric air reaching the surface¹⁵. Vorticity cross-sections (measure of ozone-rich stratospheric 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 stratosphere¹⁴.

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)



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 O₃ photolysis but the increases in NO₂ and CH₂O photolytic rates are minor at best. This is because the actinic flux for NO₂ and CH₂O photolysis is driven by wavelengths that are not absorbed by ozone, thus varying total vertical ozone will have little effect. Increased O₃ photolysis rate without a simultaneous increase in NO₂ and CH₂O 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.

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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.

Additional information

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Wyoming winter smog

Surface ozone levels are expected to be high in polluted regions during summer months. Observations from Wyoming in February 2008 indicate that equally high concentrations of ozone can be produced during winter.

Joseph Pinto

Ozone levels of concern for human health are expected to occur near the Earth's surface mostly in the warmer months of the year. In many areas of the United States, the 'ozone season', a period when temperatures reach well-below freezing point, and the sun is low in the sky. Yet, on page 120 of this issue, Schnell and colleagues² report ozone concentrations in February, near the Wyoming natural gas fields, which are three to four times larger than typical winter concentrations in the region (Fig. 1).

Ozone is produced near the Earth's surface when its atmospheric precursors, notably nitrogen oxides (nitric oxide and nitrogen dioxide) and reactive volatile organic compounds, mainly small alkenes and aldehydes, undergo photochemical transformation. Ultraviolet radiation from the sun provides the necessary energy influx to trigger this process, and high temperatures speed-up chemical reactions. Typical conditions during the summer months, when the air is warm and the sun is high in the sky, are therefore particularly conducive to the formation of ozone and photochemical smog. By contrast, in southwestern Wyoming in February, with temperatures as low as $-17\text{ }^{\circ}\text{C}$ and the sun much lower in the sky, expectations for ozone production are low.

Schnell and colleagues², however, report 8-hour average ozone concentrations of 120 ppbv (parts per billion by volume) during February 2008 near Wyoming's natural gas fields. For context, ozone concentrations in the gas fields typically lie between 30 and 40 ppbv during winter. May to September daily maximum concentrations, averaged over 8 hours, range from approximately 50 to 55 ppbv for the United States^{1,3}, with peak summer values of up to about 140 ppbv reported in 2007.

The Wyoming results cannot be explained by measurement artefacts — the high values were observed with two entirely independent techniques: electrochemical ozonesondes that measured the vertical profile of ozone concentrations, and ultraviolet photometry. The unusual ozone concentrations are almost certainly not associated with intrusions of stratospheric air (one of the main sources of winter ozone in this part of the US, together with air transport from polluted areas⁴), as the vertical profiles of ozone concentrations showed that high values occurred only in the lowermost atmosphere, within about 100 m of the Earth's surface.

Indeed, the shallowness of the high-ozone area gives an indication of one potentially important factor in its generation: weak vertical mixing. Schnell and colleagues measured an exceptionally strong temperature inversion (whereby warmer air overlies cold surface air

during which ozone monitoring is required, lasts from May to September. During these warm months, the daily maximum ozone concentration (averaged over moving windows of 8 h) is well-correlated with

the daily maximum temperature¹, because warmth and solar ultraviolet radiation facilitate the formation of ozone from its atmospheric precursors. Much lower levels of photochemical activity are expected



JENNIFER FRAZIER, WDEQ

Figure 1 | The Jonah-Pinedale Anticline natural gas field in Wyoming. Here in February 2008, a strong temperature inversion trapped ozone precursors released from the gas fields at the Earth's surface, resulting in a build-up of surface ozone, according to Schnell and colleagues².

and acts as a lid, trapping emissions from the gas field close to the surface). Indeed, during the high ozone period, morning concentrations of the ozone precursors nitric oxide and nitrogen dioxide exceeded 200 ppbv. Later in the day, ozone precursor concentrations declined, while ozone concentrations rose. As the gas fields are not affected by winds from extensive urban areas, the ozone precursors were probably emitted by activities related to the exploration of the gas fields.

A second factor that probably contributed to the ozone production is the snow cover observed by Schnell and colleagues. The availability of solar photons is crucial for driving photochemical reactions. The reflectivity of a surface that is freshly covered with snow is much higher than that of bare ground⁵. The spherically integrated solar fluxes that drive photochemistry in the ultraviolet spectrum are about twice as large over snow-covered surfaces than over bare ground at this time of year⁶. Despite this fact, very high ozone levels are not normally found over snow or ice-covered surfaces — at Camp Summit in Greenland at summer solstice, when the sun is higher and the days are much longer than in Wyoming in February, ozone is usually less than half that observed in the gas fields⁷. However, taken together, the snow cover, combined with the high concentrations of ozone precursors trapped within a relatively small volume of air, could have been the cause of the observed ozone levels.

Unfortunately, Schnell *et al.* did not measure the concentrations of various reactive volatile organic compounds, carbon monoxide and other chemical constituents that could clarify the chemical processes involved in ozone production were not measured. For example, it is unclear how the abundance of free radicals such as hydroxyl or hydroperoxyl — essential for ozone production — can be maintained in Wyoming during winter. Under warm and sunny conditions, reactions of organic compounds facilitate the release of free radicals, but the reaction rates of the relevant chemical processes would be much reduced at the observed temperatures of $-17\text{ }^{\circ}\text{C}$. Moreover, as Schnell *et al.* note, reactions involving water vapour are not likely to initiate photochemical cycles that produce ozone because the abundance of water is so low.

One possibility is that formaldehyde, which is probably emitted from the gas fields, formed free radicals through photodissociation. Alternatively, nitrous acid could have formed through interactions of gas-field emissions with aerosol surfaces or snow. A rather thick haze, as well as snow, was present when the ozone observations were made, and heterogeneous reactions forming nitrous acid are known to occur on the surface of carbon-containing aerosols⁸ and on snow or ice surfaces⁹.

The importance of heterogeneous chemistry in destroying high-level, stratospheric ozone in the polar regions

during winter, and surface ozone at high northern latitudes during the onset of spring, has long been recognized; whether heterogeneous reactions are also important in the production of ozone during winter at mid-latitudes is less clear. Although the haze suggests that the photochemistry might result in the formation of secondary organic aerosols in the smog.

Of course, the high levels of ozone measured by Schnell and colleagues² could be specific to the local environment, given the restrictions in our understanding of the processes responsible for the findings. Nevertheless,

the number of wells in the Wyoming gas field measured by Schnell and colleagues² are expected to triple by 2010 with respect to their number in 2008, with unknown consequences for the future probability of local ozone pollution.

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backstory : Cold case

■ What was the objective of the work?

In the upper atmosphere, primarily between 10 and 30 km, ozone acts as a shield against damaging ultraviolet radiation. However, in the lower atmosphere — particularly at the Earth's surface — ozone is a significant pollutant, harmful to human health and ecosystems. Until now, the formation of surface ozone was considered to be a summer phenomenon, resulting from the action of bright sunlight on ozone precursors. For this reason, regulatory measurements in the US have been confined to the summer months between April and October, when ozone is most likely to exceed regulatory threshold levels. So, when a member of staff at the Wyoming Department of Environmental Quality (WDEQ) asked us what might be behind anomalously high levels of surface ozone observed in winter in rural Wyoming (near natural gas fields), that neither gas production companies, consultants nor WDEQ staff could adequately explain, we were hooked and went in search of an answer.

■ Why did you choose this particular location for the fieldwork?

We found this field location by chance. The ozone data were collected by WDEQ contractors and staff in winter near the Jonah–Pinedale Anticline natural gas field in Wyoming. One of the staff members mentioned the difficulties they were having in explaining the data to her brother, who happened to work at our observatory in Barrow, Alaska; he pointed them in our direction, and the rest is history.

■ What sorts of data did you use?

The WDEQ had high-quality environmental and air chemistry data from continuous monitoring stations

in and around the natural gas field in Wyoming where the anomalously high ozone levels were observed. We had access to an array of meteorological data connected to the problem,



JENNIFER FRAZIER, WDEQ

Balloon-borne ozonesonde used to measure vertical profiles of near-surface ozone during winter production events.

including balloon-borne, air trajectory and satellite measurements, through the National Weather Service, the National Environmental Satellite and Information Service and NASA. Indeed, data supply was not a problem; it was finding the pieces relevant to the puzzle that was the hard part.

■ Did you encounter any difficulties?

Within three days of initiating the project we basically understood the cause of the exceptionally high ozone levels. As outlined in the paper: standard ozone photochemistry and unusual meteorological circumstances in a mountain basin produced a natural 'chemical retort'. Specifically, ozone precursors released from the gas field became trapped at the surface due to strong temperature inversions, and the build-up of precursors with nowhere to go resulted in high levels of ozone production. However, it took another year to acquire and analyse the supporting ancillary data, and to have our findings vetted and accepted by immediate colleagues. Initially, some fellow scientists said that the data could not be correct as ozone production in winter was not possible,

but after we presented our analyses from different years and different sites within the gas field, they began to get excited too.

■ Any lowpoints?

During the preparation of the paper for publication, writing was interrupted when one of the main authors, key to preparing the final stages of the manuscript, was hospitalized for nearly two months with a severe internal infection — probably the result of eating a local delicacy during a recent trip to Asia-Pacific. He had been hosted by a group of mountain aborigines while setting up an air sampling site on their land — the meal, a tree-top marsupial, was one reserved for honoured guests.

■ Any economic implications?

The gas field at the centre of this study brings in an excess of \$3.6 billion per year in gas sales, and production is scheduled to triple by 2020, with revenues expected to reach \$12 billion per year. In 2008, gas production companies spent in excess of \$100 million on the mitigation of fugitive emissions from natural gas processing and from combustion related to drilling and transportation. The state of Wyoming collects around \$100 million per year in taxes from and related to this particular gas field. The discovery that the emission of ozone precursors from this gas field, when combined with the right meteorological conditions, generates toxic levels of ozone in the winter may mean that gas companies have to curtail some winter operations, at a huge cost to the companies and the state of Wyoming.

■ Did this work give you any ideas for future research projects?

We believe that there are other areas round the world with similar winter ozone production, and we expect that publication of this paper will bring them to light. We are also looking for a 'mystery ingredient' or process that helps to fire-up ozone production as the sun rises. At present, there are questions as to what the ignition 'spark' may be.

This is the Backstory to the work by Russell Schnell and colleagues, published on page 120 of this issue.

