1.0 PREFACE, CONTRIBUTORS AND ACKNOWLEDGEMENTS

1.1 Preface

This report supersedes the UBOS 2012 report and includes most of the relevant background information and results from the 2012 study. While some references to specific material in the 2012 study are retained, this is intended to be a stand-alone report presenting findings from both the UBOS 2012 and 2013 studies.

1.2 Contributors

This report represents the contributions of a large number of dedicated scientists from federal and state government departments and agencies as well as several research universities. Primary authors are listed by section below. In most cases, a number of other UBOS participants provided detailed and helpful comments which greatly improved the initial drafts prepared by the primary authors. Affiliations of all authors are listed in the author list at the beginning of Sections 2 - 10.

Executive Summary: Till Stoeckenius, Brock LeBaron, Gail Tonnesen and Jim Roberts.

1.0 Preface, Contributors and Acknowledgements: Till Stoeckenius.

2.0 Synthesis of Results: Till Stoeckenius and Dennis McNally (parts of Section 2.1 contributed by Seth Lyman and Howard Shorthill).

3.0 Long-Term and Distributed Monitoring of Ozone, Precursors and Meteorology:

> Sections 3.1 and 3.4: Seth Lyman, Marc Mansfield, Howard Shorthill, Randy Anderson, Chad Mangum, Jordan Evans, and Tate Shorthill;
>
> Section 3.2: John Horel, Erik Crosman, and Erik Neemann;
>
> Section 3.3: Michael Christiansen, Trevor O'Neil, and Seth Lyman.

4.0 Aircraft Observations: Anna Karion, Sam Oltmans, Gaby Petron, Colm Sweeney and Russ Schnell.

5.0 Intensive Chemical Measurements at Horsepool: James M. Roberts, Patrick R. Veres, Bin Yuan, Carsten Warneke, Felix Geiger, Peter M. Edwards, Robert Wild, William Dube, Gabrielle Petron, Jonathan Kofler, Andreas Zahn, Steven S. Brown, Martin Graus, Jessica Gilman, Brian Lerner, Jeff Peischl, Joost A. de Gouw, Rui Li, Timothy Bates, Patricia Quinn, Abigail Koss, Shao-Meng Li, David D. Parrish, Christoph J. Senff, Andrew O. Langford, Robert Banta, Randall Martin, Robert Zamora, Shane Murphy, Jeff Soltis, Robert Field.

6.0 Balloon-Borne Vertical Profiles of Ozone, Methane, Non-Methane Hydrocarbons, Nitrogen Oxides and Meteorological Parameters: Detlev Helmig, Chelsea Stephens, Jeong-Hoo Park, Jacques Hueber, Patrick Boylan, Jason Evans.

7.0 Ozone Deposition Velocity During Snow-Covered and Non-Snow-Covered Periods by Eddy Covariance: Detlev Helmig, Chelsea Stephens, Jeong-Hoo Park, Jacques Hueber, Patrick Boylan, Jason Evans.

8.0 Tethered Ozonesonde and Surface Ozone Measurements in the Uinta Basin, Winter 2013: Russ Schnell, Bryan Johnson, Patrick Cullis, Chance Sterling, Emrys Hall, Rob Albee, Allen Jordan, Jim Wendell, Samuel Oltmans, Gabrielle Petron and Colm Sweeney.

9.0 Ozone Precursor Emissions in the Uinta Basin:

- 9.1 Uinta Basin Emissions Inventory: Patrick Barickman;
- 9.2 Wintertime Emissions of Hydrocarbons from Produced Water Evaporation Facilities: Seth Lyman, Marc Mansfield, Howard Shorthill, Randy Anderson, Jordan Evans, Chad Mangum, Tate Shorthill;

10.0 Numerical Modeling of a Thermal Inversion in the Uinta Basin, Utah, January 26-30, 2013: Trang Tran, Marc Mansfield, Seth Lyman.

1.3 Acknowledgements: Funding Agencies

The Uinta Basin Ozone Studies for 2012 and 2013 were made possible by the combined contributions of several private and public sector organizations. The 2013 study was funded by and provided in-kind support by the: Uintah Impact Mitigation Special Service District (UIMSSD), Western Energy Alliance, QEP Resources, Inc., Bureau of Land Management (BLM), National Oceanic and Atmospheric Administration (NOAA), Environmental Protection Agency (EPA), Utah Department of Environmental Quality (UDEQ) and Utah Science Technology and Research Initiative (USTAR), and Utah School and Institutional Trust Lands Administration (SITLA).

2.0 SYNTHESIS OF RESULTS

2.1 Introduction

Background

The Uinta Basin is an enclosed basin that lies in the northeast corner of Utah and is part of a larger area known as the Colorado Plateau. The Basin is bounded on the north by the Uinta Mountain range, on the south by the Book and Roan Cliffs, on the west by the Wasatch Range and on the east by elevated terrain separating it from the Piceance Basin in Colorado. The Green River runs through the Basin from northeast to southwest, exiting through the Book Cliffs via Desolation Canyon. The floor of the Basin is at approximately 4800 feet above sea level with significant local topography on the order of tens to hundreds of feet.

Duchesne and Uintah Counties make up essentially the entire Basin. The Uintah and Ouray Indian Reservations cover a significant portion of the Basin (Figure 2-1). EPA and the Ute Tribe have jurisdiction over air quality management on the reservations and in Indian Country.

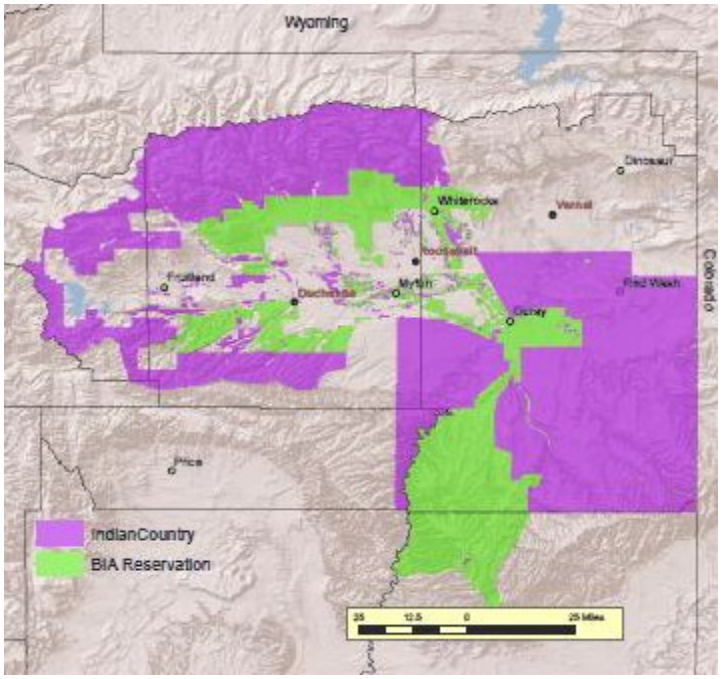


Figure 2-1. Uinta Basin and surrounding region.

The Basin is rural with a population of about fifty thousand people primarily located in three main towns (Duchesne, Roosevelt, and Vernal) which lie along the east-west State Highway 40 corridor. The economy of the Basin is driven by energy production from vast petroleum resources. Oil and gas development (approximately 10,000 producing wells) is widely scattered throughout the Basin (Figure 2-2) with associated drilling, processing, compression and pipeline facilities. A 500 megawatt coal fired power plant (Bonanza) operates in the Basin. There is also

some agricultural production in the Basin, primarily alfalfa and corn along with other hay and grain crops.

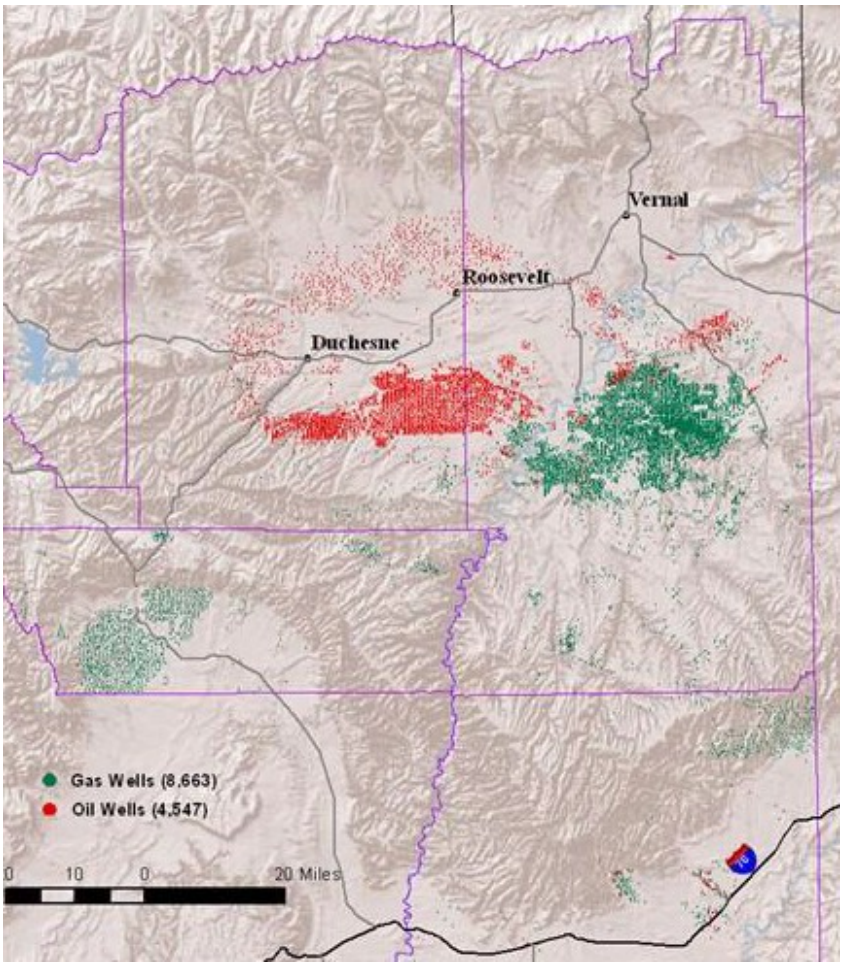


Figure 2-2. Oil and gas well sites in Utah as of 2010.

Air quality monitoring in the Basin began in 2006 when the Utah Department of Air Quality (UDAQ) installed monitors in Vernal to measure fine particulate ($PM_{2.5}$), ozone (O_3) and oxides of nitrogen (NO_x). Data were collected from February 2006 through December 2007. Highest 8-hour ozone averages reaching 81 ppb were found in the summer. No concentrations exceeding the 85 ppb National Ambient Air Quality Standard (NAAQS) then in affect were recorded and no elevated ozone was noted in the winter months. Two additional special studies were conducted during the winters of 2007-08 and 2008-09, but these were focused on $PM_{2.5}$ since no elevated winter ozone values had been observed in 2006-2007.

In the spring of 2009, EPA used consent decree funding to establish two monitoring sites at Ouray and Redwash in the oil and gas production area of the Basin. These sites were instrumented to measure $PM_{2.5}$, NO_x, O_3, and meteorological parameters year-round. In sharp contrast to the low ozone values found in the winter of 2006-2007, the winter of 2009-10

experienced very high ozone levels, with the highest 8-hour average of 124 ppb being measured at the Ouray site.

Utah State University (USU) conducted a special study in the winter of 2010-11 to confirm the presence of high winter ozone concentrations and map out the spatial extent of elevated ozone levels. Results from the 2010-11 study showed that ozone values were elevated throughout the Basin, with the highest concentrations tending to occur at lower elevations in the center of the Basin. The highest 8-hour ozone value measured at Ouray was 139 ppb. The data also showed that elevated ozone correlated highly with the presence of snow-covered ground and a strong temperature inversion, and that elevated ozone values did not occur absent of these conditions. A full report on results of the 2010-2011 study is available (Martin et al., 2011) and can be found at http://rd.usu.edu/files/uploads/edl_2010-11_report_ozone_final.pdf.

2011 – 2012 Uinta Basin Ozone Study

A full field campaign was mounted in the winter of 2011-12 to gain a more complete understanding of factors contributing to high wintertime ozone in the Basin. This campaign was part of a multi-phased study designed to identify the emissions sources and potentially unique photochemical processes that produce elevated winter ozone concentrations and assist in determining the most effective mitigation strategies. The Uinta Basin Ozone Study for the 2011-2012 winter season (UBOS 2012) consisted of six components carried out by several research organizations. Key results from each research group's work were presented at a meeting of study participants held 3 - 4 June 2012 in Vernal. A full report of the study results obtained by each research group along with a synthesis of results across all groups and a unified set of key results and conclusions accessible to a wider audience was subsequently prepared and made publically available (Lyman and Shorthill, 2013; referred to hereafter as the 2012 Synthesis Report or 2012SR).

2012-2013 Uinta Basin Ozone Study

Motivated by the lack of ozone conducive conditions during the 2011-2012 study, a second round of field monitoring was undertaken in the Uinta Basin during January – March 2013. Recognizing the possibility that the 2012-2013 winter could also turn out to have minimal snow and no ozone episodes, UBOS 2013 was designed to minimize upfront investment of labor and materials required to conduct an intensive measurement program unless and until such time as there was a reasonable certainty that snow cover sufficient to produce ozone conducive conditions would occur during the January – February study window. As it turned out, storms during December and early January produced a good snow pack in the Basin, and by mid-January it was obvious that conditions during UBOS 2013 would be favorable for ozone formation, prompting the decision to proceed with the intensive measurement program. Numerous exceedances of the NAAQS were subsequently observed as detailed in this report. As in the 2011-2012 study, researchers from the National Oceanic and Atmospheric Administration (NOAA) and several universities conducted extensive ground-based and airborne measurements of ozone and other key air quality and meteorological parameters and the Horsepool site was again chosen as the location to conduct a series of intensive

measurements of meteorology, ozone, ozone precursors and particulate matter. Instrumentation in 2013 differed somewhat from that used in 2012: some measurements were not available but a new set of measurements were added in 2013 to examine ozone deposition to the snow surface and chemical reactions within the snow pack which may play a role in winter ozone formation.

Organization of the UBOS 2013 Synthesis Report

In this *Synthesis of Results* section, we present an update to the 2011-2012 field study final report which reflects the significant amount of new information obtained from the 2013 study. As such, it represents a melding of the findings and conclusions from both the 2011-2012 and 2013 studies. Relevant material from the 2011-2012 report is carried over into this update and new or revised findings and conclusions are described.

As was the case for the 2011-2012 study, each research group participating in the 2013 winter field study prepared a final report describing in detail their individual data collection and analysis methods. These reports are included here in Sections 3 – 10 as listed in Table 2-1. Researcher's results from the 2011-2012 studies were included in the UBOS 2012 Synthesis Report (2012SR; Lyman and Shorthill, 2013). While relevant results, summaries, and conclusions from the 2012SR are included in this report, frequent references are made to the 2012SR to avoid unnecessary duplication of material and improve readability. A copy of the 2012SR is available for download at http://www.deq.utah.gov/locations/uintahbasin/docs/2014/03Mar/ubos_2011-12_final_report.pdf.

Table 2-1. UBOS 2013 Study Components, associated research groups and the section of this report in which the final report(s) for the Study Component can be found.

Study Component	Research Group (Principal Investigator)	Summary Report in Section
Long-Term and Distributed Monitoring of Ozone, Precursors and Meteorology	Utah State Univ. (S. Lyman)	3
Aircraft Observations	NOAA/GMD	4
Intensive Chemical Measurements at Horsepool	NOAA/CIRES (J. Roberts)	5
Balloon-Borne Vertical Profiles of Ozone, Methane, Non-Methane Hydrocarbons, Nitrogen Oxides and Meteorological Parameters	Univ. Colorado, Boulder (D. Helmig)	6
Ozone Deposition Velocity During Snow-Covered and Non-Snow-Covered Periods by Eddy Covariance	Univ. Colorado, Boulder (D. Helmig)	7
Tethered Ozonesonde and Surface Ozone Measurements in the Uinta Basin, Winter 2013	NOAA GMD (R. Schnell)	8
Ozone Precursor Emissions: Uinta Basin Emissions Inventory	P. Barickman	9.1
Ozone Precursor Emissions: Produced Water Evaporation Facilities	S. Lyman	9.2
Numerical Modeling of a Thermal Inversion in the Uinta Basin	M. Mansfield	10

To present the synthesis of results in an efficient manner, this section has been written as a series of relatively short responses to a set of key questions focused on the ultimate study objectives as listed below. For each response, a brief background discussion explaining the significance of the question is provided along with a list of the field study elements that are used to address the question. This is followed by a set of *findings* that answer the question in different ways. Each response ends with a short conclusion summarizing the main points of the *findings*. Questions are grouped as to subject area as follows:

A. Physical Characteristics

A.1: What are the key characteristics of meteorological conditions associated with ozone exceedances in the Basin?

A.2: Were the high levels of wintertime ozone observed during the winters of 2009-2010, 2010-2011, and 2012-2013 a result of meteorology or changes in precursor emissions?A.3: What is the climatological frequency of meteorological conditions that are conducive to ozone formation in the Uinta Basin?

A.4: What role does transport of ozone or ozone precursors into the Basin play in generating elevated ozone concentrations?

A.5: What similarities and differences are there between the Uinta Basin and the Upper Green River Basin in Wyoming?

A.6: Is there significant vertical stratification of precursors and if so, what role does this play in ozone formation?

B. Atmospheric Chemistry of Ozone Formation

B.1: Do VOC speciation and reactivity in the Basin have unique characteristics that contribute to wintertime ozone production?

B.2: Do pathways for ozone production exist that are unique to wintertime ozone events?

C. Sources of Ozone Precursor Emissions

C.1: What are the primary sources of ozone precursor emissions in the Basin? What is the spatial distribution of precursor sources?

C.2: Do ambient measurements and emission inventories agree for ozone precursor emissions in the Basin?

D. Mitigation Strategies

D.1: What possible mitigation strategies should be considered for adoption in the Uinta Basin?

E. Additional Information Needs and Modeling Issues

E.1: What special challenges does the basin pose for meteorological modeling?

E.2: Can the formulation of existing 1-D box and more complex transport and chemical models represent the observed phenomena in the Basin? If not, what are the most urgent measurement needs for improving the model representation?

E.3: What are the main issues regarding winter ozone formation that should be the focus of future studies?

2.2 Part A: Physical Characteristics and Meteorology

A.1: What are the key characteristics of meteorological conditions associated with ozone exceedances in the Basin?

Background

Ozone levels in excess of the EPA 75 ppb 8-hour standard were observed in the Uinta Basin during the winters of 2009-2010, 2010-2011 and 2012-2013 but not during 2011-2012. Results from these four winter monitoring periods provide key insights into the meteorological conditions associated with the presence (or absence) of high winter ozone concentrations. Additional insight is provided by data collected in the Upper Green River Basin (UGRB) of southwestern Wyoming where exceedances of the ozone standard were first observed in February, 2005. The UGRB is a large oil and gas producing mountain basin located 250 km north of the Uinta Basin. Climatological conditions in the two basins are similar although the Upper Green River basin is higher in elevation (see Question A.5 below). Analyses of data from the Upper Green River Winter Ozone Study (UGWOS) indicated that ozone episodes occurred under clear skies during strong temperature inversions and in the presence of extensive snow cover (ENVIRON, 2008; Schnell et al., 2009; Stoeckenius and Ma, 2010). Comparisons of data collected in the UGRB during different winter seasons in which snow cover was and was not present indicate that snow cover is the key requirement for ozone formation. Box modeling of a winter ozone event based on UGWOS data (Nopmongcol et al., 2010; Carter and Seinfeld, 2012) indicate that the high UV albedo of the snow is one of the key drivers of ozone formation. In addition, it is hypothesized that snow cover promotes retention of the strong nocturnal surface temperature inversion during the day, thus trapping pollutants near the surface and increasing ozone precursor concentrations and ozone production rates. The snow surface could also influence the production and loss of chemical radical species necessary for ozone formation.

Finding A.1.1: Snow cover and strong inversions with low mixed layer heights are required for formation of elevated winter ozone concentrations in the Uinta Basin. Meteorological conditions during the low ozone 2012 UBOS period differed from those in the previous two winters and during the 2013 UBOS period (all of which had high ozone) in that snow cover was not present.

Ozone monitoring in the Uinta Basin first began during the 2009-2010 winter season and levels of ozone exceeding the 75 ppb 8-hour National Ambient Air Quality Standard were observed. Ozone exceedances were again recorded during January - March 2011 (Martin et al., 2011). In all cases, the ozone exceedances occurred during so-called “cold pool” events when stagnant weather conditions combined with extensive snow cover resulted in an extremely shallow

temperature inversion over the Basin which trapped pollutants near the surface (*ibid*). Similar conditions were observed during January – March 2013: several cold pool events with snow cover occurred during this period and these events coincided with strong temperature inversions and elevated ozone levels. Daily maximum 8-hour average ozone concentrations in the Basin during the 2013 UBOS period reached as high as 142 ppb at the Ouray monitor (which has among the highest readings in the Basin) as described in Section 3 below. In contrast, snow cover was nearly absent during the 2012 UBOS period, no exceedances of the 8-hour ozone NAAQS were observed and daily maximum 8-hour average ozone concentrations ranged from 47 to 63 ppb (2012SR, Figure 3). A comparison of ozone concentration, snow cover, and surface temperature and wind speed for January – March 2012 with the same period in 2013 shows the marked difference between these two years (Figure 2-3).

Mansfield and Hall (2012SR, Ch. VII) constructed pseudo temperature profiles by examining surface temperature readings from stations within and along the edge of the Basin located at different altitudes. This analysis showed that inversion conditions which occurred during 2011 were not present in 2012. Mansfield and Hall also performed a regression analysis based on ozone and meteorological data from 2009 – 2012 which confirmed the role of temperature inversions and snow depth in ozone formation. Their model also showed the influence of overnight carryover of ozone and ozone precursors: longer multi-day periods with inversions and snow cover are characterized by higher ozone levels than shorter periods. This is consistent with the build-up of ozone over multi-day episodes observed in 2013 (see Section 3, Figure 3-1).

Finding A.1.2: High ozone episodes typically occur between January and March, with episodes occurring most frequently during February.

Analysis of the 2009 – 2012 data by Mansfield and Hall (2012SR, Ch. VII) shows that, while the frequency and strength of temperature inversions in the Basin peaks in January, high ozone episodes appear to be most common in February (based on the limited observational record). Measurements made 1 November – 15 March 2013 are consistent with this pattern with no exceedance days prior to 7 January, 18 days exceeding the 8-hour standard at one or more sites in January vs. 22 days in February and 7 days in March. Mansfield and Hall hypothesize that this pattern is due to the rapid decrease in noon solar zenith angles following the winter solstice; angles do not become small enough to strongly drive the photochemical reactions until February. A similar effect was noted in the UGRB by Stoeckenius and Ma (2010). It should be noted, however, that preliminary data from winter 2013-14 show exceedances of the ozone standard at several monitors throughout the second half of December, indicating that high ozone levels can occur even when the solar zenith angle approaches its maximum at the winter solstice, so long as conditions are otherwise favorable. Analyses of indicator species ratios and other data show a trend towards higher ozone formation efficiency from December to March as solar zenith angles decrease and hours of daylight increase. This can impact total ozone production and the effectiveness of different emissions control strategies, as described in Section 3.1.3.5

Conclusions

Observations made during January – March in 2011, 2012 and 2013 clearly demonstrate that snow cover is a necessary condition for formation of winter ozone episodes in the Uinta Basin. Data from the 2011 and 2013 high ozone episodes and data from studies performed in the Upper Green River Basin show that ozone episodes are associated with snow cover, light winds, and strong temperature inversions, and are most common in February when the noon solar zenith angle has decreased sufficiently from its winter solstice maximum but snow cover is still more likely to be present.

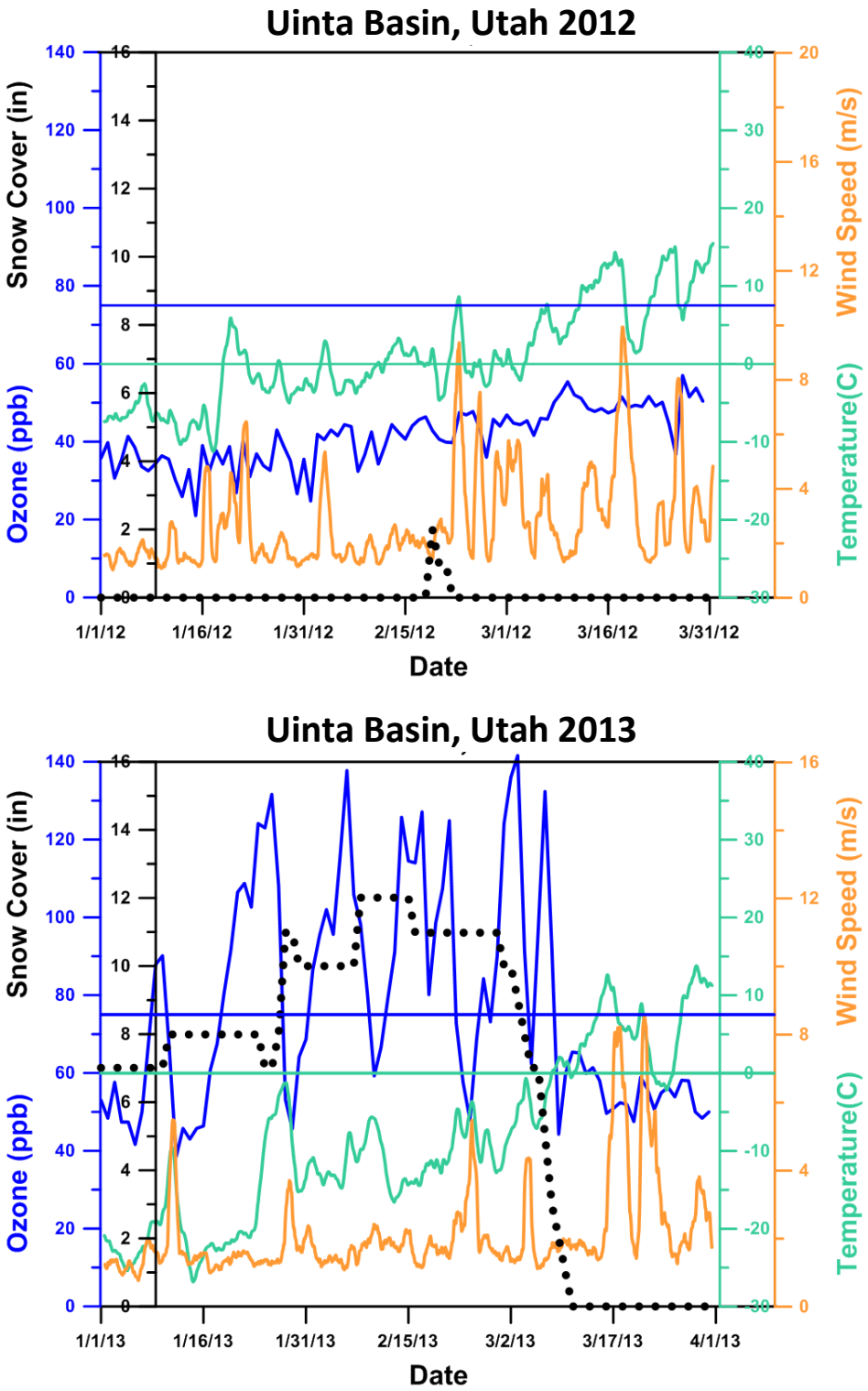


Figure 2-3. Comparison of maximum daily 8-hr average ozone mixing ratio (MDA8) in ppb (blue), smoothed temperature (green) and wind speed (orange), and daily snow depth (black dots) from the EPA monitoring site at Ouray, Uinta Basin for January – March: 2012 (top) and 2013 (bottom); horizontal blue line represents 75 ppb ozone; horizontal green line represents 0 deg. C (Section 8).

A.2: Were the high levels of wintertime ozone observed during the winters of 2009-2010, 2010-2011 and 2012-2013 a result of meteorology or changes in precursor emissions?

Background

Day-to-day variations of ozone concentrations in most urban air basins have been shown to be dominated by meteorological factors (e.g., Solomon et al., 2000; NRC, 1991). Large oil and gas production areas such as exist in the Uinta basin consist of thousands of wells, all in varying phases of the production cycle (well pad construction, drilling, completion, production, recompletion, closure), each of which involve release of ozone precursor emissions that go on more or less regardless of meteorological conditions (aside from seasonal use of heaters and methanol to avoid freeze-ups). Thus, on a basin-wide level, day-to-day variations in emissions are expected to be small (with some important exceptions) and, as in the more extensively studied urban air basins, day to day variations in ozone concentrations are driven by meteorological conditions.

In rural areas where precursor emissions are dominated by oil and gas production and exploration activities, the level of certain key oil and gas production activities (most notably drilling and completions) can vary significantly from one year to the next in response to market forces. This can create significant fluctuations in precursor emissions and potentially lead to variations in ozone levels. Activity fluctuations on shorter time scales (monthly or seasonal) may also be significant. It must be noted, however, that ozone formation is a result of nonlinear chemical reactions between precursors and that, at high ratios of NO_x/VOC, NOx reductions can sometime cause increases in ozone. Therefore reductions (or increases) in NO_x precursor emissions do not necessarily lead to reductions (or increases) in ozone concentrations.

Finding A.2.1: While changes in precursor emissions between 2009 and 2013 in the Uinta Basin have not been quantified, the drop off in ozone concentrations in 2012 was not associated with a significant decrease in oil and gas production activities.

Ozone precursor emission inventories representative of the 2010 - 2013 mid-winter seasons are not currently available. However, drilling and production data from the Utah Department of Natural Resources suggest that activity in in the Uinta Basin has held relatively steady and may actually have increased somewhat between 2010 and 2013 (Figure 2-4). Furthermore, no significant new emission control measures were introduced during this period. Given the overall level of oil and gas exploration and production activity in the basin, it is unlikely that the emission inventory would have changed so significantly as to account for the drop in ozone levels observed in 2012. On the other hand, the ozone differences between 2011 or 2013 and 2012 match closely with the occurrence of meteorological conditions (snow cover, strong temperature inversions, and light surface winds) found to be conducive to ozone formation as discussed under Question A.1 above.

Conclusions

Meteorological conditions are the primary driving factor behind the recent inter-annual variations in Uinta Basin ozone concentrations.

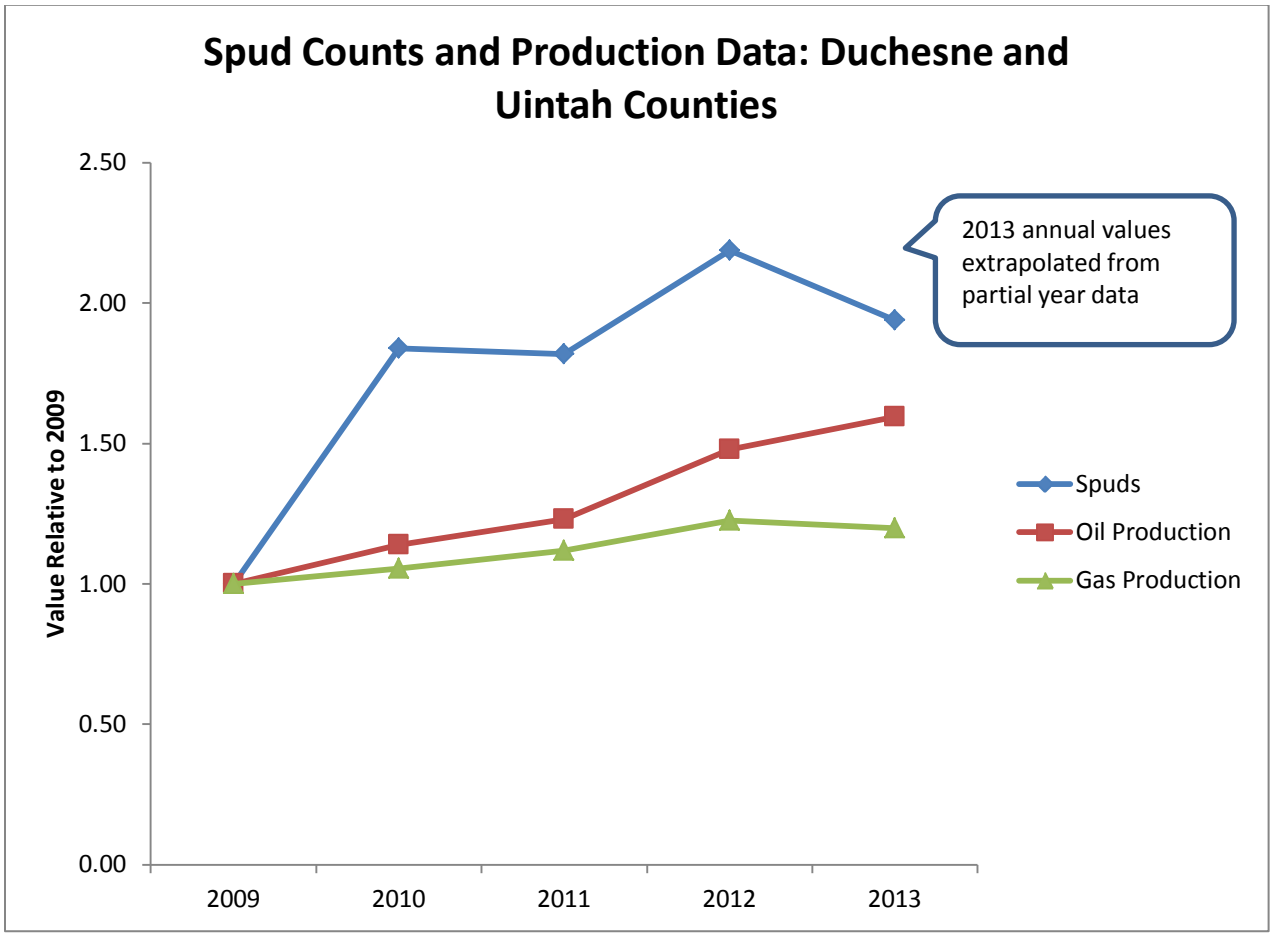


Figure 2-4. Recent annual drilling and production activity trend in the Uinta Basin relative to 2009 (note 2013 spud counts [indicating number of wells where drilling was started] are extrapolated based on January – October data; 2013 production statistics are extrapolated based on January – June data; all data from the Utah Dept. of Natural Resources http://oilgas.ogm.utah.gov).

A.3: What is the climatological frequency of meteorological conditions that are conducive to ozone formation in the Uinta Basin?

Background

Ozone concentrations in excess of the NAAQS were observed in the Uinta Basin during the first three months of 2010, 2011, and 2013 but concentrations were much lower in 2012. These inter-annual fluctuations have been demonstrated to be caused almost entirely by variations in the frequency and severity of meteorological conditions favorable to ozone formation (see responses to questions A.1 and A.2 above). A similar situation exists in the Upper Green River

Basin of southwestern Wyoming as illustrated in Figure 2-5: ozone NAAQS exceedances are observed in some years but concentrations remain well below the NAAQS in other years.

Attainment of the ozone NAAQS is based on a three year average of the annual fourth highest daily maximum 8-hour average concentration. Thus, the frequency of occurrence of meteorological conditions conducive to ozone formation plays a crucial role in determining the attainment status of the Basin. Estimates of the frequency of occurrence of ozone conducive conditions are also useful in planning future field studies.

Finding A.3.1: Analyses of data from 1950 – 2012 indicates that ozone conducive conditions occur on at least some days during about half of all winter seasons, and ozone levels characteristic of a severe season such as the 2010-2011 season can be expected to occur approximately 20% of the time (an average of one in five seasons) given the level of precursor emissions characteristic of the past three seasons.

Mansfield and Hall (2012SR, Ch. VII) performed an analysis of meteorological conditions in the Uinta Basin over the 63-year period 1950 – 2012 and estimated the historical frequency of meteorological conditions conducive to formation of elevated ozone levels. Mansfield and Hall developed a quadratic regression model that predicts the daily maximum 1-hour average ozone concentration at Ouray based on key meteorological parameters including but not limited to snow depth, low level temperature lapse rate and surface temperature at 1,400 m asl (representing the lowest point in the basin). The model was fitted to data from three consecutive mid-December to mid-March winter seasons starting with the 2009-2010 season (the first season for which ozone data were available). Model predictions of daily maximum ozone concentrations were then examined for the full 63-year meteorological data set to determine the predicted frequency of conditions associated with high ozone concentrations. Results of this analysis showed that, *assuming emission levels equivalent to the average levels occurring during the 2010, 2011, and 2012 winter seasons*, five out of the last 23 winter seasons (22%) are estimated to have had conditions at least as favorable to the formation of high ozone events as occurred during the high ozone winter of 2010-2011, whereas 7 out of the last 23 winter seasons (30%) are estimated to have had conditions at least as unfavorable to ozone formation as occurred during 2011-2012. In addition, the regression model results show that approximately half of all seasons had meteorological conditions capable of producing at least 10 days with 1-hour ozone exceeding 75 ppb. It must be noted, however, that these results are based on observations of the correlations between ozone and meteorological conditions over just three winter seasons (2010, 2011, and 2012); inclusion of 2013 data may alter the estimated frequencies of conditions conducive or not conducive to ozone episodes.

Conclusions

Based on the limited data currently available, meteorological conditions conducive to ozone exceedances of 75 ppb occur in approximately half of all winter seasons, although the high (low) ozone conditions in 2011 (2012) were the result of more extreme events corresponding to approximately the 20^{th} (70^{th}) percentile years. These estimates may change when 2013 data

are included in the analysis. It is worth noting that ozone exceedances were recorded in the Basin in three of the last four winter seasons.

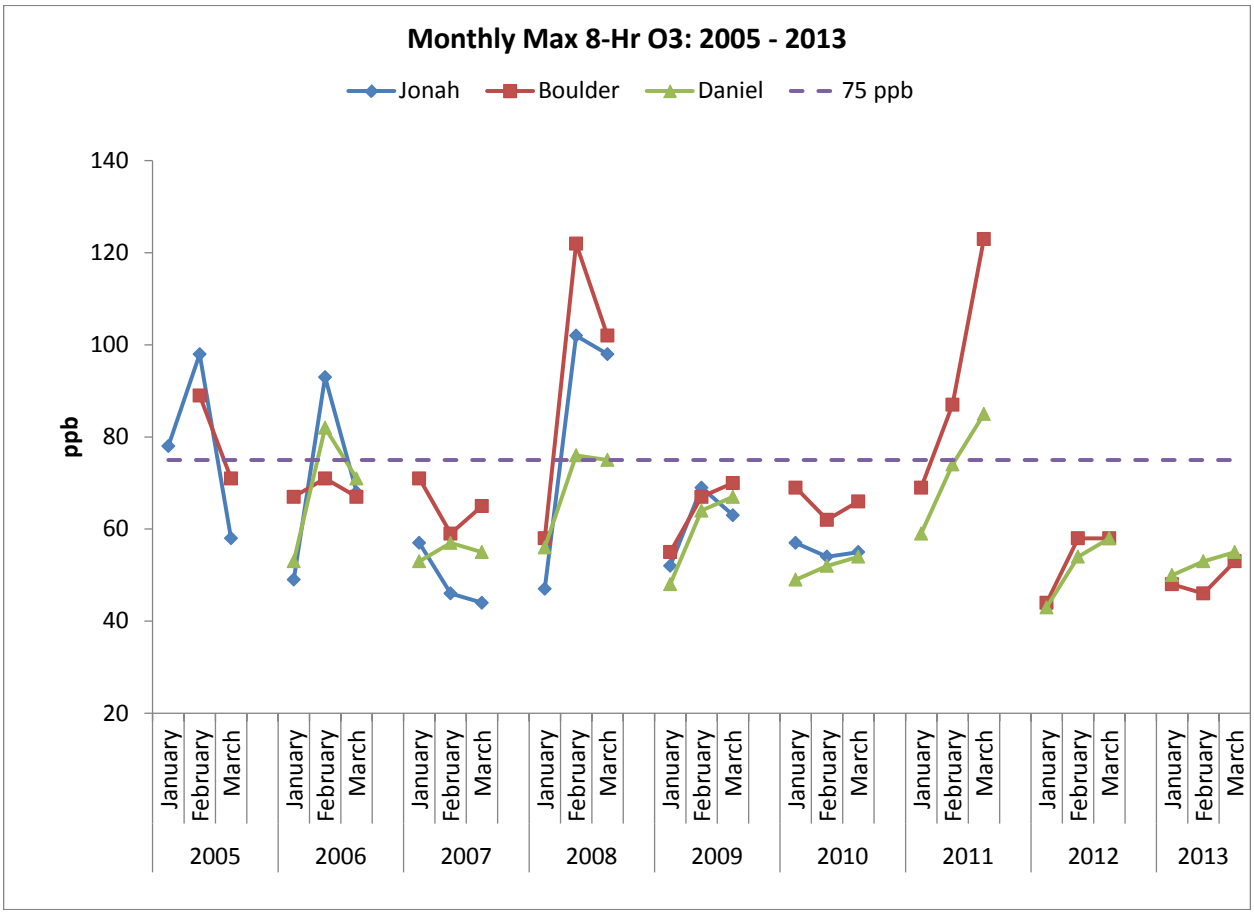


Figure 2-5. Monthly maximum 8-hour average ozone concentrations during the winter ozone season at monitoring sites in the Upper Green River Basin of southwestern Wyoming.

A.4: What role does transport of ozone or ozone precursors into the Basin play in generating elevated ozone concentrations?

Background

Determining the relative contributions of sources located outside of the Basin to ozone episodes in the Basin is a fundamentally important step in designing an appropriate control strategy. While studies conducted to date have not specifically focused on the question of transport of ozone and precursors into the Uinta Basin, they do provide a considerable amount of information about the likely influence of transport on Basin air quality.

Regional background ozone measured at remote locations in the intermountain West have been reported by Vingarzan (2004) to range from 37 to 47 ppb (range of annual medians for Yellowstone and Rocky Mountain National Parks) and by Brodin et al. (2010) to range from 27 to 50 ppb (10th to 90th percentile range for wintertime near Boulder, Colorado). Ozonesonde

data collected well above the surface inversion during January through March 2008 in the UGRB showed concentrations ranging between 55 and 65 ppb (ENVIRON, 2008). In the absence of local production, ozone within the Uinta Basin is expected to be transported from global and regional sources, and concentrations are expected to fall within the range of these background values.

In evaluating the significance of the role of background ozone in local ozone episodes, it is important to keep in mind that local ozone production does not simply add to the pre-existing background ozone. Instead, local precursor emissions and resulting reaction products interact with background ozone and ozone precursors in complex ways. As a result, the contribution of background pollutants transported into the Basin to in-Basin ozone levels depends on the chemical conditions existing in the Basin and can be best evaluated using a photochemical model that accurately simulates ozone formation under winter conditions. Modeling tools such as Ozone Source Apportionment Technology (OSAT; ENVIRON, 2013) and sensitivity analyses such as the higher-order direct decoupled method (Hakami et al., 2003; Cohan et al., 2005) can then be used to evaluate the contributions of transported species to ozone production in the Basin.

Finding A.4.1: The occurrence of high surface ozone concentrations within the Basin during UBOS 2013 cannot be attributed to transport of ozone or precursors from outside of the Basin. Strong evidence exists that the large majority of NO_x and VOC in the Basin are emitted by local sources.

Daytime ozone concentrations at regional locations outside of the Uinta Basin at the time of high surface ozone events inside the basin ranged from 30 to 60 ppb (see Figure 2-6). Ozone concentrations measured inside the Basin above the temperature inversion by balloon borne sensors, the TOPAZ lidar, and aircraft during these periods were also in the 40 to 60 ppb range as described in Sections 4, 5, 6 and 8. These values are consistent with the typical western US winter background ozone levels described above and confirm the isolation of the air mass within the Basin below the inversion from air outside of the Basin and over the Basin above the inversion.

The lack of any nearby precursor sources and the isolation of the surface air mass within the Basin from the surrounding region under the strong, shallow inversions characteristic of episode events strongly suggest that precursor transport into the basin is not an important factor (Martin et al., 2011). Measurements of alkanes (the least reactive and therefore longest lived VOC species) made at the upwind Fruitland monitoring site averaged far lower than at sites within the Basin proper (see Section 3). Aircraft measurements of methane above the temperature inversion during high ozone periods were close to hemispheric background levels as compared to the much higher values observed below the inversion (Section 4) and VOC concentrations in the Basin were observed to be highly correlated with methane (Section 5).

Meteorological data collected during UBOS 2013 showed the presence of light boundary layer winds and recirculation patterns within the Basin (Section 3), further confirming that ozone

formation within the shallow Basin boundary layer is not influenced to any significant extent by transport of material from outside the Basin.

Conclusions

Taken together, observations of the horizontal and vertical distributions of ozone, ozone precursors, and winds from the 2013 ozone episodes clearly show that ozone buildup within the Basin boundary layer to levels far above typical intermountain western US background levels is a local phenomenon which is not linked to any outside source.

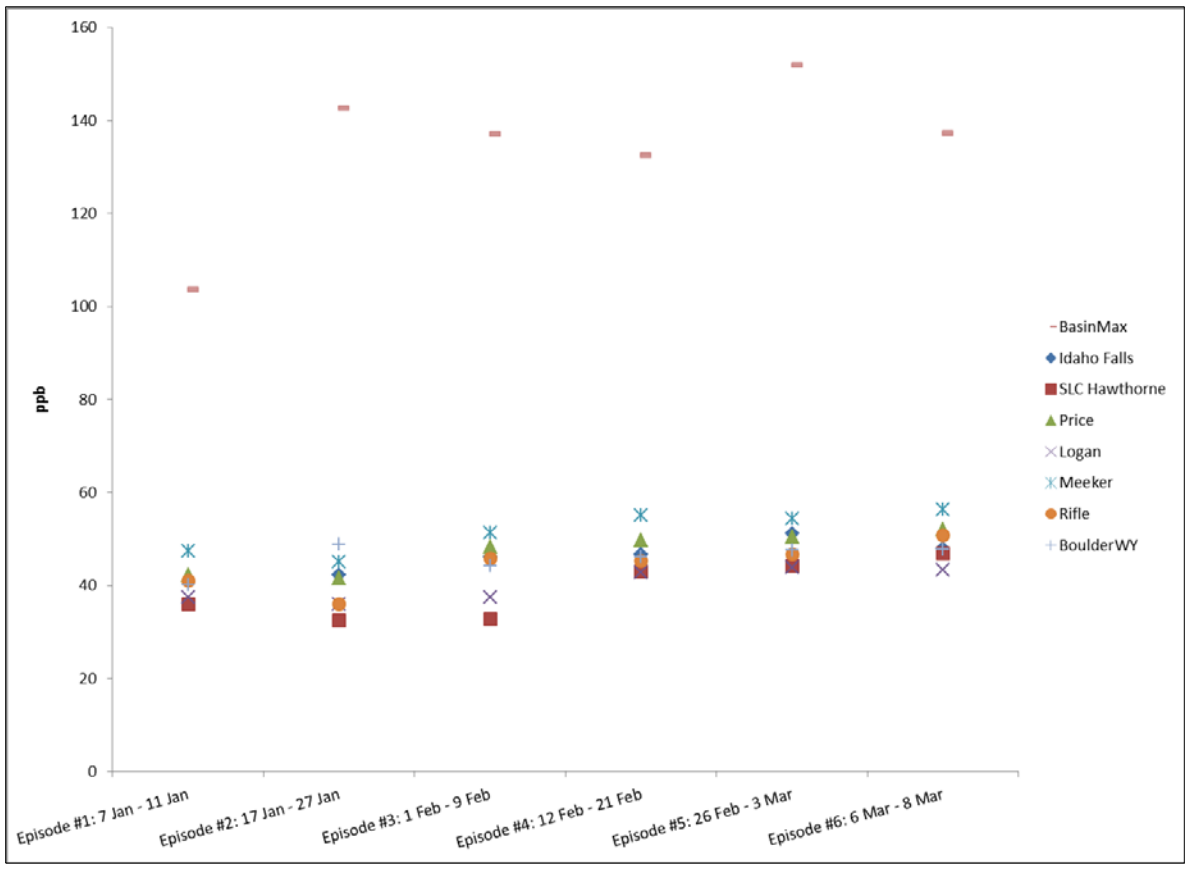


Figure 2-6. Daily maximum 8-hour average ozone concentrations at locations outside of the Uinta Basin and the maximum concentration over sites within the Basin during each January – March 2013 ozone episode.

A.5: What similarities and differences are there between the Uinta Basin and the Upper Green River Basin in Wyoming?

Background

Winter ozone episodes have been observed in both the Upper Green and Uinta Basins and these basins share many similar features. Comparisons of conditions in the Upper Green River Basin (UGRB) with conditions in the Uinta Basin are therefore relevant to understanding the

factors associated with Uinta Basin ozone episodes. A significant amount of data collection and analysis has been conducted in the UGRB, and results from the UGRB studies can help inform the analysis of data collected in the Uinta Basin and guide future work in both basins.

Finding A.5.1: Winter ozone episodes in the Uinta Basin and UGRB have many key characteristics in common and data collected in either location are likely to be informative of factors associated with episodes in both basins.

Both the Uinta Basin and the UGRB are arid basins surrounded by higher terrain and located in sparsely populated portions of the Green River drainage (Figure 2-7). The two basins are separated by a distance of roughly 250 km and share a similar climate, although the UGRB is about 600 m higher in elevation and 2.5° more northerly in latitude than the Uinta Basin. The Uinta Basin is larger, covering approximately 27,700 km^2 compared to 18,700 km^2 for the UGRB. Both basins experience elevated ozone concentrations during winter cold pool events that can last up to several days at a time. Both basins contain intensive oil and gas exploration and production activity. However, oil production is greater in the Uinta Basin while gas production dominates in the UGRB (see Figure 2-8). The Uinta Basin contains about 8,000 active wells (Utah Department of Natural Resources; http://oilgas.ogm.utah.gov/Statistics/Statistics.cfm), the UGRB about 5,500 (WOGCC, 2012).

Annual emissions estimates from oil and gas activity in Duchesne and Uintah counties for 2011 are 17,838 tons of NO_x and 111,289 tons of VOC (Section 9). By comparison, estimated annual oil and gas emissions in the UGRB ozone nonattainment area for 2011 are 4,558 tons of NO_x and 15,688 tons of VOC (http://deq.state.wy.us/aqd/Actual%20Emissions.asp). It should be noted however that oil and gas emission estimates in general, and VOC emission estimates in particular, are subject to large uncertainties, making emission comparisons between the two basins less meaningful than they would otherwise be.

Populations in both basins are concentrated in small towns. Uintah and Duchesne counties have a combined population of 51,195 (1.8 people per km^2), while the population of Sublette County, Wyoming is 10,247 (0.5 people per km^2; from 2010 Census).

A review of field measurements, data analyses, and modeling results for the UGRB was prepared by Hall et al. (2012). These analyses clearly confirm the association of winter ozone episodes with snow cover, strong inversions, and light winds. Elevated ozone concentrations have not been observed in the UGRB in the absence of snow cover. Data collected during the 2011 and 2013 winter ozone episodes in the Uinta Basin (Martin et al., 2011 and this report) show that meteorological conditions during those events were very similar to those observed during UGRB ozone events with respect to the presence of snow cover, strong inversions, and light surface winds. Similar to the UGRB, data collected during UBOS 2011-12 showed little local ozone production in the absence of snow cover. During the 2012-13 winter, however, ozone levels were quite high in the Uinta Basin, with 8-hour average concentrations exceeding 75 ppb on many days as described in Section 3. In contrast, snow cover was much sparser and generally windy conditions prevailed in the UGRB, resulting in generally low ozone levels with no exceedances of the 75 ppb 8-hour standard (MSI, 2013).

Despite the similarities noted above, some important differences in the characteristics of ozone episodes exist between the two basins. Of particular importance is the fact that early season (December to mid-February) ozone episodes in the Uinta Basin have a characteristically longer time scale than in the UGRB, often exhibiting a gradual buildup of pollutant levels over a period of several days (Section 3, Figure 3-1). Although multi-day episodes do occur in the UGRB, episode lengths tend to be shorter (Hall et al., 2012). These differences are consistent with the larger size of the Uinta Basin which is hypothesized to result in a more persistent cold air pool. There also appears to be a slight shift in the winter ozone season between the two basins, with episodes more common in January and less common in late March in the Uinta Basin. This seasonal shift is likely associated with the 2.5° more southerly latitude and 600 m lower elevation of the Uinta Basin.

Despite the differences between the two basins noted above, the overall similarities of climate, emission sources, and winter ozone episode characteristics of the two air basins suggest that collection and analysis of field study data in either basin can provide valuable information applicable to both.

Finding A.5.2: The Uinta Basin has some unique characteristics that will require development of an ozone control strategy designed specifically for the Basin.

Some details of ozone production in the Uinta Basin are likely to be different from the UGRB. Given the greater amount of oil production in the Uinta Basin, VOC speciation and reactivity and VOC/NO_x ratios are likely to differ between the two basins. As discussed in Section 3, the mix of VOC in oil-producing areas of the Uinta Basin is different than in the gas-producing areas; a higher alkane/aromatic ratio was observed at Wells Draw where oil production dominates as compared to Seven Sisters where gas production dominates. It should be noted that the presence of the 500-MW coal-fired Bonanza power plant within the Uinta Basin does not appear to be a factor in the basin's ozone production because the plume is lofted above the cold pool, which is isolated within the shallow boundary layer (as shown in Section 8). The UGRB does not contain a comparable large point source of NO_x emissions, but this is not likely to be a differentiating factor. NO_x emission sources and distribution are also different for the two basins. Data presented in Section 3 show less NO_x in oil-producing than in gas-producing areas. The Uinta Basin has a higher population (and associated urban and traffic emissions) and significantly more agricultural production than the UGRB (Hall et al., 2012).

ENVIRON (2008) showed that ozone episodes in the UGRB are associated with recirculation of pollutants driven by a diurnal nighttime drainage and daytime upslope flow pattern. Measurements and analysis of surface flow patterns during 2013 Uinta Basin ozone events described in Section 3 also showed a similar diurnal pattern in the river drainages, but overall surface flow patterns were more complex due to the greater complexity in topography of the Uinta Basin and the larger size of the Basin, especially in the east-west dimension, which increases the influence of westerly winds aloft on surface flow patterns as described in Section 10.

Conclusions

Sufficient similarities between the Uinta Basin and the UGRB exist to support the application of data analysis results from one basin to gain a better understanding of ozone production dynamics in the other. Surface air flow and the mix of precursor emissions in the Uinta Basin, however, are different from the UGRB, and the design of emission control strategies for the Uinta Basin cannot rely solely on studies from the UGRB (or vice versa).

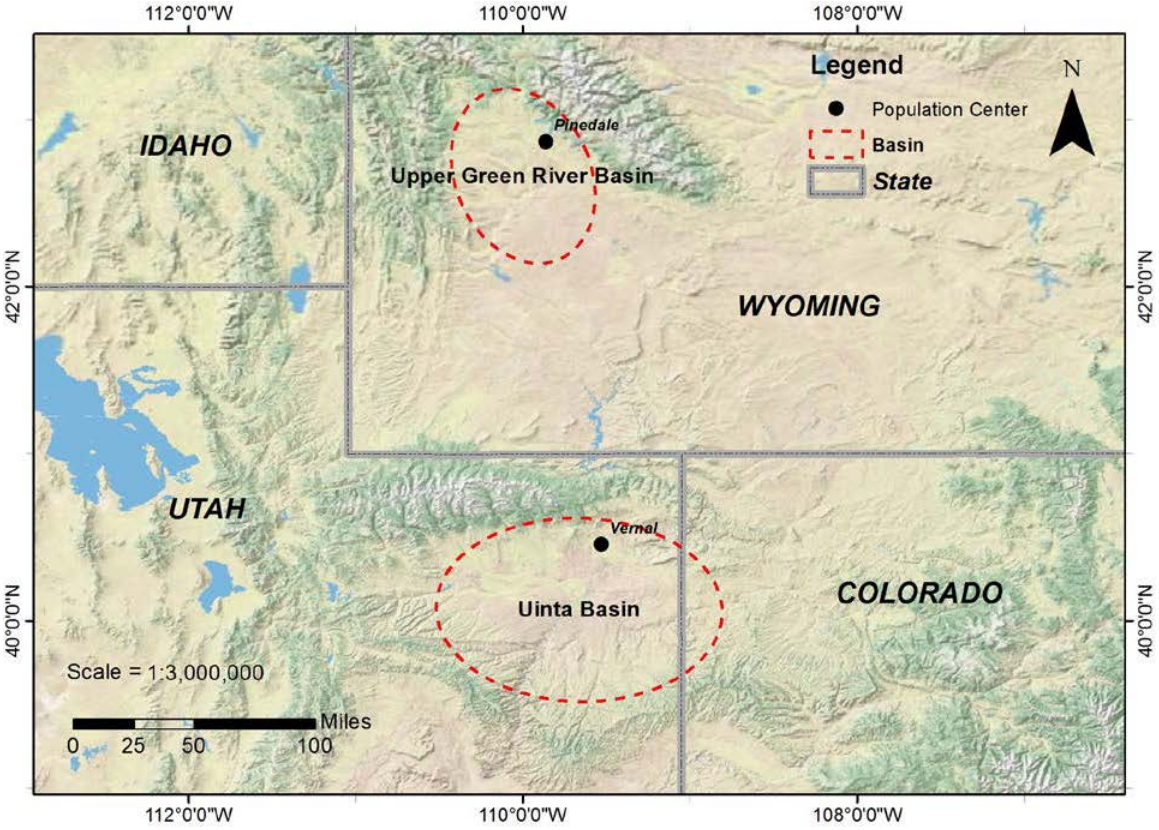
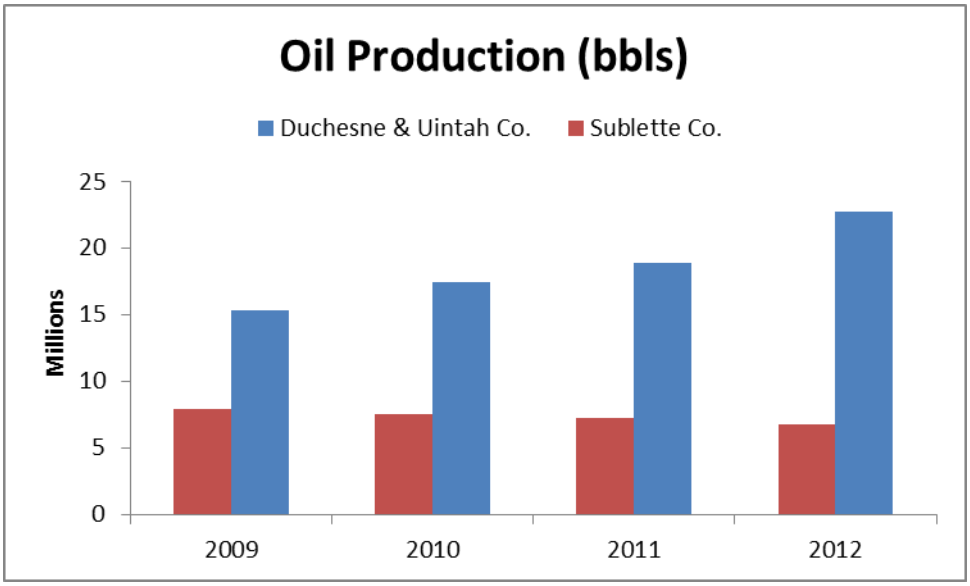


Figure 2-7. Uinta and Upper Green River basins.



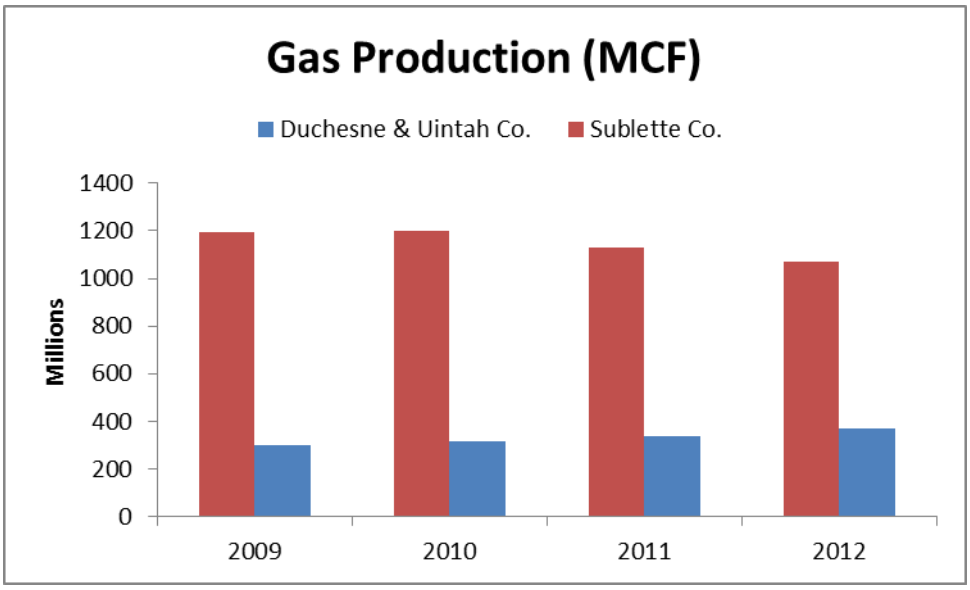


Figure 2-8. Annual oil and gas production in the Uinta Basin (Duchesne and Uintah counties; Utah DOGM, 2013) and the Upper Green River Basin (Sublette County; WOGCC, 2013).

A.6: Is there significant vertical stratification of precursors and, if so, what role does this play in ozone formation?

Background

VOC emissions in oil and gas production operations are expected to be released closer to the surface and to be less thermally buoyant than NO_x emissions. While NO_x emissions occur almost entirely from fuel combustion sources and are released as heated exhaust gasses at heights ranging from near surface (e.g., heaters and boilers, on- and off-road vehicles) to small-

or medium-sized stacks at stationary sources (e.g., compressor stations) to tall stacks (e.g., power plants), a large portion of VOC emissions are released from well sites or other equipment at approximately the same temperature as the surrounding air (Section 9). Some researchers have hypothesized the presence of a vertical stratification of VOC and NO_x under the very stable atmospheric conditions characteristic of ozone episodes. Any resulting vertical gradients in VOC/NO_x ratios would produce vertical variations in ozone production and destruction rates and could impact ozone responses to emission control strategies. For example, ozone formation during the morning hours may proceed more rapidly at locations and elevations with optimal VOC/NO_x ratios, and these rapidly formed ozone plumes could later impact downwind monitoring stations after being mixed to the surface during the late morning and afternoon. Knowledge of any such vertical stratification is needed to fully explain and accurately model the pattern of ozone and precursors observed over surface monitoring networks and the impacts of alternative emission control strategies.

Finding A.6.1: Vertical gradients in ozone precursors were observed at Horsepool.

Measurements of NO_x and speciated VOC at four levels between 2 m and 150 m at Horsepool are consistent with near surface sources of VOCs and NO_x, although NO_x appears to be somewhat more evenly mixed within the first 50 m as shown in Figures 6-8 and 6-11 in Section 6. NO_x may be more evenly mixed because sources of NO_x emissions are of varying heights and some plume rise from these sources can be expected. However, the NO_x measurement used to obtain these vertical profiles is also known to suffer from a positive bias due to interference from NO_z species formed in the atmosphere from NO_x emissions, and NO_z can be expected to be more well mixed than the primary NO_x. High-resolution time series of both VOC and NO_x measurements, as well as for methane, show numerous short-period spikes consistent with impacts at Horsepool from multiple point sources of both pollutants (Section 5). Vertical profiles of VOC/NO_x ratios were not analyzed. However, vertical ozone profiles from the tethersonde measurements made during UBOS 2013 show ozone formation taking place simultaneously at all vertical levels within an approximately 80 m deep layer as shown in Figure 2-9 (see also Section 8, Figures 8-34 – 8-40), indicating that any vertical variations in precursors do not appear to have resulted in any significant vertical stratification of ozone. These findings are consistent with either a rapid mixing (at least on the timescale of ozone formation) within an approximately 80 m deep daytime turbulent boundary layer at Horsepool (based on the observed 1650 m asl mixed layer top and 1569 m asl Horsepool site elevation), even during the cold pool events as shown in Section 8, a constant rate of ozone formation throughout the mixed layer, or both.

Finding A.6.2: Available data combined with one dimensional modeling employing reasonable assumptions suggests that high daytime HONO concentrations, if real, are most likely confined to a very shallow layer, at most a few tens of meters deep.

Measurements of HONO during 2013 ozone episode conditions between 1 and 7.25 m agl showed high concentrations correlated with solar radiation intensity as described in Section 5, consistent with a photochemically driven source, although the validity of these measurements is still uncertain. Concentrations at 7.25 m were consistently lower than at 1 m during the day,

whereas the opposite was true at night (see Section 5, Figure 5-35), indicating the presence of a daytime photochemical source of HONO from the snow surface and HONO loss at the surface overnight. Application of a simple 1-dimensional model of turbulent vertical diffusion and HONO loss via photodissociation suggests that, even if they are correct, the high daytime HONO concentrations drop off rapidly with height, approaching very small values within a few tens of meters above the surface. A more detailed examination of vertical ozone profiles is needed to determine if these measurements are valid and if there is a discernible effect of this shallow HONO layer on ozone formation.

Conclusions

There is no strong evidence to suggest that the vertical profiles of VOCs and NO_x within the polluted boundary layer differ significantly enough to impact ozone formation. This conclusion is supported by the observation of near uniform morning ozone production throughout the boundary layer seen in the tethersonde data. There is evidence of stratification of NO_x from the Bonanza plume above the inversion layer and associated ozone titration as shown in Sections 4, 5, and 8, but this does not affect the high ozone concentrations observed within the polluted boundary layer.

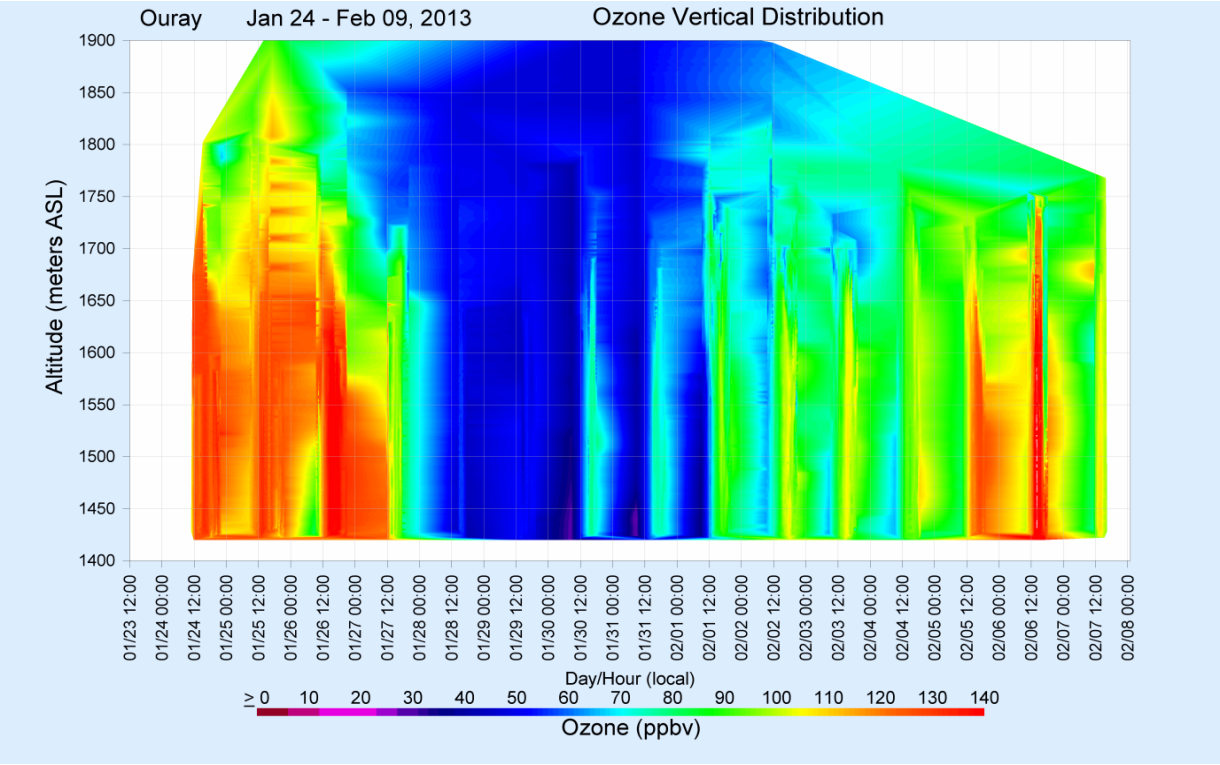


Figure 2-9. Contour plot of ozone concentrations above the Ouray Wildlife Refuge January 24 - February 7 based on thethersonde data (see Section 8).

2.3 Part B: Atmospheric Chemistry of Ozone Formation

B.1: Do VOC speciation and reactivity in the Basin have unique characteristics that contribute to wintertime ozone production?

Background

VOC emissions from oil and gas exploration and production activities result from releases of natural gas (e.g., venting, blowdowns, pneumatic device bleeding), evaporative emissions from gas processing (dehydration and sweetening), and produced liquids handling and storage, as well as oil handling and storage and a variety of combustion sources. These sources have very different VOC speciation profiles from VOC sources typically found in large urban areas. Due to the widely differing reactivities of individual VOC species, variations in VOC composition can have significant impacts on ozone formation and the relative efficacy of VOC and NO_x control strategies. A thorough understanding of VOC speciation in the Uinta Basin and of the reactivities of VOC species under winter ozone episode conditions is therefore an important prerequisite to the design of effective ozone control strategies.

Finding B.1.1: Observed hydrocarbon species abundances at most locations sampled in the Uinta Basin differ significantly from those found in large urban areas, but are similar to those found in other western U.S. oil and gas production regions.

Methane concentrations in the Uinta Basin were often eight times above background values in 2013 as compared to as much as five times above background in 2012 (Section 6). Elevated methane has also been observed in the UGRB (ENVIRON, 2008) and the Denver – Julesburg Basin (Petron et al., 2012). Urban area methane levels are significantly lower than in the oil and gas basins. Natural gas NMHC speciation is heavily weighted towards ethane and other light alkanes, resulting in an ambient NMHC mixture in the gas fields that is markedly different from mixtures typically encountered in large urban areas. Data collected during UBOS 2012 and 2013, as well as in the UGRB, show that NMHC emissions throughout the basin are strongly influenced by fugitive releases of natural gas as evidenced by high methane levels and strong correlations of alkanes with methane (see Section 5). Resulting NMHC compositions in the Uinta Basin are thus very different from those in typical urban areas such as Pasadena, CA as shown in Figure 2-10. Concentrations of iso-pentane and n-pentane were much higher at Horsepool than in the Pasadena samples and are more similar to samples collected by NOAA researchers in Weld County, Colorado, in the Wattenberg Gas Field (Figure 2-12). In addition, ratios of iso- to n-pentane at Horsepool were significantly lower than in the Pasadena samples. As pointed out in 2012SR, the Horsepool and Weld County ratios are similar to iso- to n-pentane ratios found in Wattenberg gas composition analyses, whereas the Pasadena ratio is similar to that of light duty vehicle exhaust. Detailed raw gas composition analyses for the Uinta Basin are needed to validate these findings, and comparisons with NMHC speciation in the UGRB are needed.

High methanol concentrations were observed at Horsepool and spikes in methanol levels were correlated with spikes in formaldehyde (see SR2012). Further data collection and analysis is needed in the UGRB to determine if similar conditions exist there.

While the Uinta basin data in Figure 2-10 are from 2012, the 2013 NMHC composition for directly emitted species was very similar to that in 2012, but most species concentrations in 2013 were enhanced by a factor of 1.5 to 3.5 due to the much shallower boundary layer in 2013 as compared to 2012. This was also true for methanol and formaldehyde as shown in Figure 2-11, but other secondary VOC oxidation products such as acetone, acetaldehyde, and methyl ethyl ketone (MEK) levels were 8 to 12 times higher in 2013, consistent with a greater production rate of these oxygenated VOCs as a result of enhanced photochemical activity in 2013.

Analysis of NMHC samples collected during UBOS 2013 at different locations in the Basin (Section 3) showed that aromatics were enriched relative to alkanes at locations in the gas field (Seven Sisters) as compared to the oil field (Wells Draw). Methanol concentrations were also highest in the gas field as measured at Horsepool and Seven Sisters. Based on higher total NMHC concentrations, greater aromatic fraction and methanol, the overall reactivity of NMHCs in the gas field is higher than in the oil field (Section 3, Table 3-4).

Conclusions

Data collected over the past two winters in the Uinta Basin show that the characteristics of the VOC mixture in the Basin are very different from those found in urban areas. VOCs in the Basin are dominated by relatively unreactive alkanes associated with natural gas exploration and production sources as is the case in other oil and gas producing basins. NMHC concentrations reach high levels in areas of the Basin with many active wells; concentrations of alkanes at Horsepool during the 2013 study were roughly a factor of two higher in 2013 than in 2012 (see Sec. 5, Figure 5-16). Results from the 2012 study (2012SR) showed that concentrations of alkane, cycloalkane, and aromatic VOCs in the Basin were an average of 6.5 times higher than those in Weld County, Colorado, an area with intensive oil and gas production and that $C_2 – C_8$ alkanes and $C_6 – C_8$ aromatics during the 2012 study averaged 18 times higher than the average mixing ratios for 25 U.S. cities reported by Baker et al. (2008). Thus, concentrations of alkanes and aromatics averaged on the order of 10 times higher during 2013 in the Basin as compared to Weld County and roughly 40 times higher than in other U.S. urban areas. Alkanes at Horsepool during the 2013 study were hundreds of times above global background levels (see Section 6, Table 6-1). In contrast, highly reactive alkenes are nearly absent in the Basin, which is in sharp contrast to typical urban VOC mixtures where gasoline powered motor vehicles and other combustion and evaporative sources of alkenes are more common. Thus, ozone production in the Basin appears to be dominated by the relatively slow reactions involving alkanes (see summary of MIR-weighted concentrations in Section 3, Table 3-4 and OH-reactivity weighted abundances in Section 5, Figure 5-13). High methanol concentrations are also observed in the Uinta Basin and methanol concentration spikes are correlated with formaldehyde spikes indicating a common source. Formaldehyde was found to be a key contributor to radical production as discussed in Finding B.2.1 below, so identifying and quantifying formaldehyde sources is important for development of ozone control strategies.

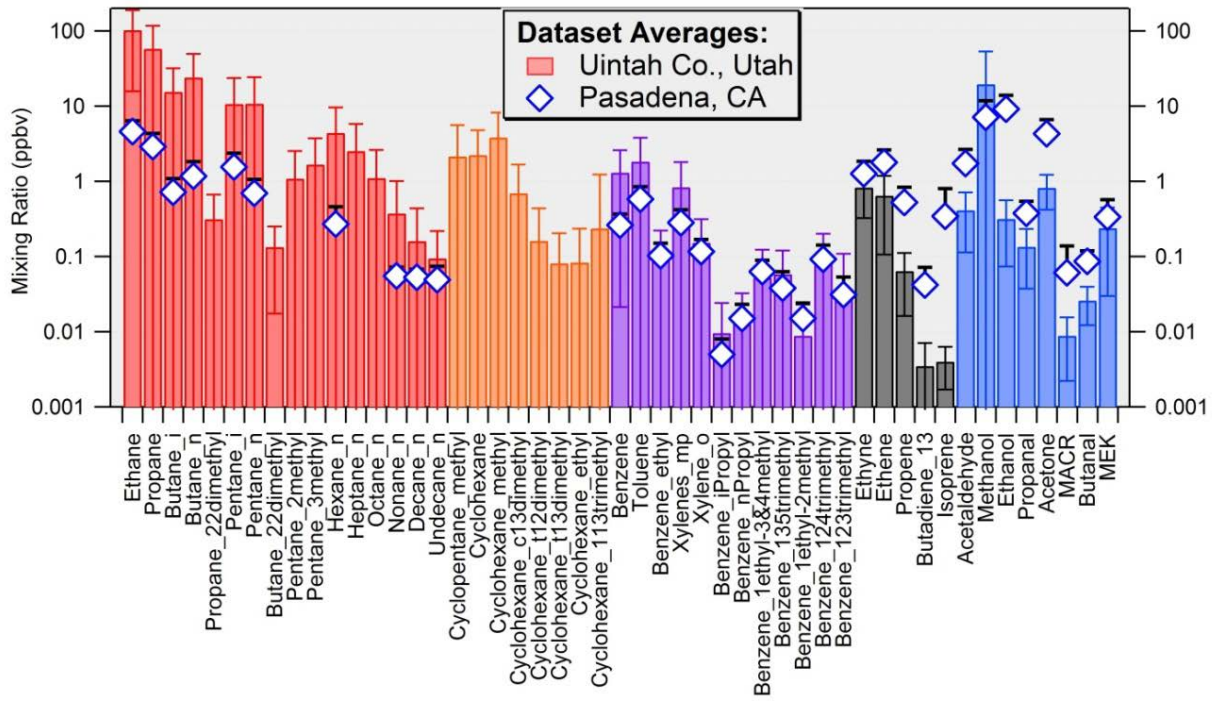


Figure 2-10. Mean mixing ratios collected during 15 January – 29 February, 2012 at Horsepool and during May – June 2010 at Pasadena, CA (Source: 2012SR).

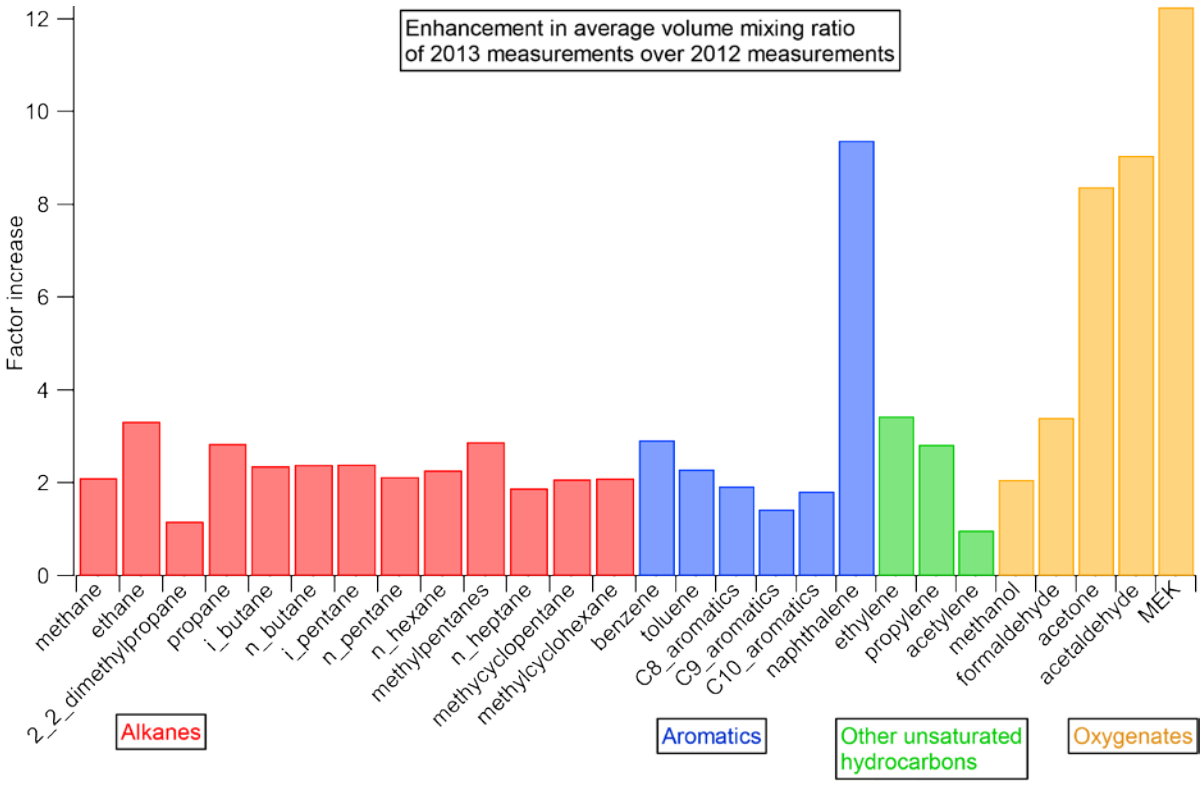


Figure 2-11. Fractional increase in all measured VOCs at Horsepool from 2012 to 2013 (see Section 5).

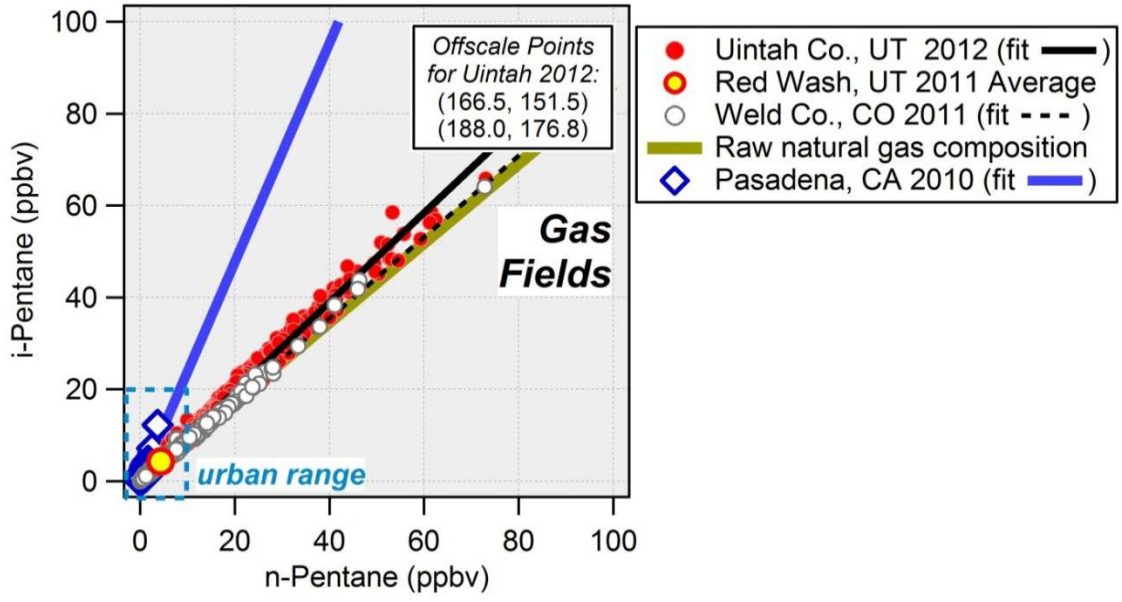


Figure 2-12. Iso-pentane to n-pentane ratios from data collected during 15 January – 29 February 2012 at Horsepool, during 21 – 25 February 2011 at Red Wash, during 2011 in Weld County, CO, and during May-June 2010 in Pasadena, CA (source: 2012SR).

B.2: Do pathways for ozone production exist that are unique to wintertime ozone events?

Background

Our current understanding of ozone formation processes in polluted environments is based mostly on summertime ozone episodes occurring in large urban areas. Comparatively little is known about winter ozone formation in rural areas where the emissions budget is heavily influenced by oil and gas exploration and production activities. Studies of winter ozone episodes in the UGRB have shown that these winter episodes are associated with snow cover and very stable "cold pool" atmospheric conditions, and that ozone formation under these conditions is largely driven by the strong actinic UV flux resulting from the high albedo of the snow surface and the elevated concentrations of precursor pollutants trapped under the low level temperature inversion (ENVIRON, 2008; Schnell et al., 2009; Stoeckenius and Ma, 2010). Analyses of field study data and photochemical box modeling studies performed to date (Nopmongcol et al., 2010; Martin et al., 2011; Carter and Seinfeld, 2012) suggest that these two factors are key to the production of elevated winter ozone concentrations. In this respect, winter episodes are no different from summer episodes; both require a high UV flux, stable atmospheric conditions, and adequate concentrations of precursors. Recent studies suggest, however, that there may be some significant unique features of winter episode chemistry in the Upper Green River and Uinta basins which set these winter episodes apart from those occurring during the summer months in urban areas.

Winter conditions in the Uinta Basin and UGRB differ from urban summer conditions primarily with respect to temperature, VOC composition, and the presence of snow on the ground. As a result of these key differences, modeling techniques traditionally used to evaluate potential control strategies for reduction of summer urban ozone levels may not work well for analysis of winter ozone.

In general, low winter temperatures decrease chemical reaction rates, alter the branching of some key reactions, and reduce volatility, though the effect of temperature on some reaction rates is not fully understood (2012SR, Section 7; Martin et al., 2011; Carter and Seinfeld, 2012). Low temperatures also limit water vapor mixing ratios; for example, the water vapor mixing ratio at 0°C, 50% humidity, and atmospheric pressure of 850 mbar is 2 g/kg, compared to more than 15 g/kg at 30°C and 50% humidity. A major pathway for the production of OH radicals in summer urban ozone episodes is photolysis of ozone followed by reaction of the freed oxygen atom with water vapor. Less water vapor in the atmosphere will limit OH production from that pathway.

VOC composition in the winter ozone basins is heavily skewed towards alkanes associated with raw natural gas as compared to more common fuel combustion and evaporative profiles found under warmer conditions in urban areas as described under Question B.1 above. Significant amounts of methanol (which may additionally be contaminated with formaldehyde) have also been found in the winter ozone basins, reflecting its use as an antifreeze agent in oil & gas operations. In addition, methane concentrations are well above levels found in urban areas.

Finally, the snow surface has many chemical properties which differ from surfaces typical of urban areas in the summer. Analyses of data from pristine remote environments (Greenland and Antarctica) have identified sources of alkenes and NO_x within snow that appear to evolve via heterogeneous photochemistry (Swanson et al., 2002; Helmig et al., 2007). Heterogeneous reactions on snow surfaces could contribute to winter ozone formation. For example, elevated mid-day HONO concentrations over snow have been reported in the UGRB (ENVIRON, 2010; Rappenglueck, 2010). This finding is consistent with a hypothesized mechanism of formation of HONO from nitrites found in the snow in the presence of sunlight (Grannas et al., 2010). Daytime heterogeneous HONO production has the potential to significantly increase peak ozone concentrations under VOC limited conditions.

Finding B.2.1: The dominant sources of radicals that drive ozone production during winter episodes in the Uinta Basin are formaldehyde and HONO rather than ozone photolysis, as is typical of summer urban area episodes. The magnitude of the HONO source during the winter episodes is still uncertain.

Analyses of measurements conducted at the Horsepool site in 2013 and comparisons with similar measurements taken during the 2012 study reveal several key features that are unique to winter ozone chemistry. Foremost among these is the report of high daytime concentrations of a species that is apparently HONO at levels between 1 and 7.25 m above the ground during the 2013 episodes. The average concentration in 2013 was ten times the 2012 average when snow was absent. The average concentration in 2013 was well in excess of the steady state concentration of HONO expected from reaction of NO with OH radical, indicating the presence of a strong source. Diurnal profiles showed peaking during the middle of the day in 2013 in sharp contrast to the night and early morning peaks found in 2012 (see Figure 2-13). Analysis of the 1 – 7.25 m gradient in the apparent HONO in 2013 showed that the species generally decreases with height during the day and increases with height at night. These results are consistent with a photochemical source of HONO in the snow; estimates of the maximum surface HONO flux (3.6 ppbv/hr) developed as described in Section 5 are on the same order of magnitude as an estimate of 2.25 ppbv/hr developed by Rappenglück, based on measurements during winter ozone episodes in the UGRB (Rappenglück et al., 2013).

Calculations of radical production rates from photolysis of ozone, HONO, HCHO, and $ClNO_2$ described in Section 5 show that HONO and HCHO were the dominant radical sources during the 2013 study. This is in sharp contrast to urban summer conditions observed in Pasadena, CA during the CALNEXT 2010 study where radical production was more balanced between photolysis of ozone, HONO, and HCHO (see Figure 2-14). This makes the winter ozone episodes "unconventional" in the sense that radical production (which is the key driving factor in ozone production) is largely due to HONO and HCHO photolysis rather than ozone photolysis, and this unconventional feature of the winter episodes must be accurately represented in models used to evaluate control strategies.

As noted in Section 5, the large contribution of HONO photolysis to OH radical production calculated for the 2013 Uinta Basin episodes is based on HONO concentrations measured at 7.25 m agl. However, calculations based on a 1-dimensional model under reasonable

assumptions described in Section 5 indicate that the high HONO concentrations are most likely confined to a shallow layer above the surface no more than on the order of 10 m deep. Thus, it appears very likely that average HONO within the ~150 m deep mixed layer are much lower due to a rapid decrease of HONO with height and the HONO radical production rate would therefore be lower than shown in Figure 2-14. Nevertheless, the combination of HONO and HCHO photolysis is clearly the main radical source during winter episodes, and this has significant implications for control strategies. Production from $ClNO_2$ was lower in the Uinta Basin in 2013 as compared to 2012, most likely because the snow cover helped suppress the availability of Cl from soil dust.

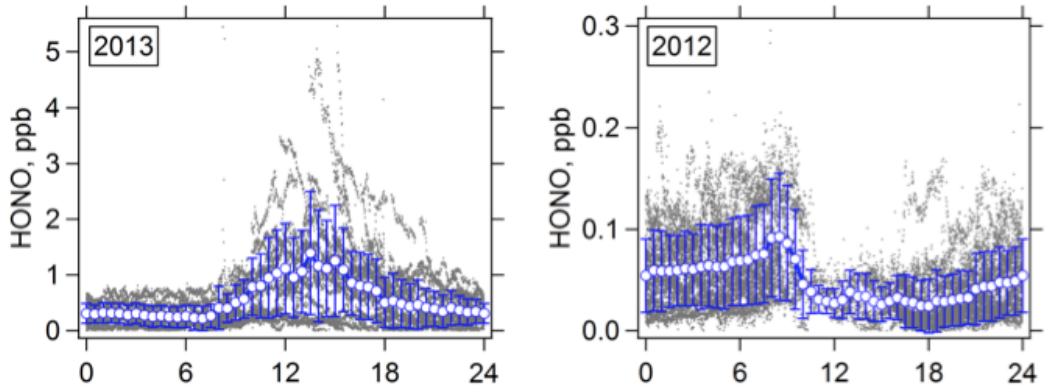


Figure 2-13. Diurnal variations of a species that is apparently HONO in 2012 and 2013 at Horsepool (Source: Sec. 5).

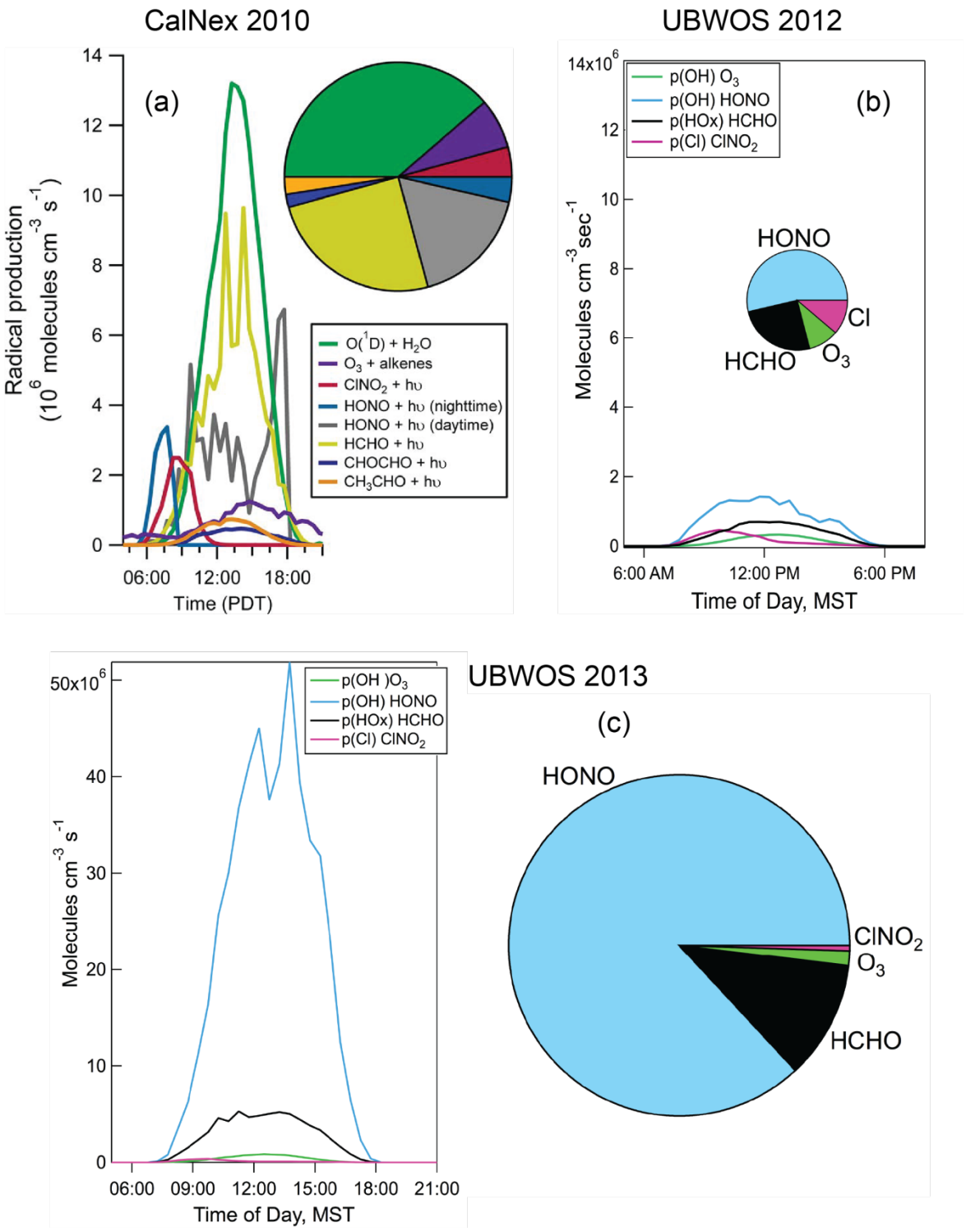


Figure 2-14. Summaries of the radical sources found during (a) CalNex2010, (b) UBOS 2012, and (c) UBOS 2013. Note that the CalNex and UBOS 2012 results are on the same scale, HONO (HCHO) is shown in light blue (black) in (b) and (c) but in medium blue and gray (yellow) in (a) and the areas of the pie charts are scaled to the total of the radical sources (Source: Sec. 5).

Finding B.2.2: Nighttime conversion of NO_x to HNO_3 is a major factor in the total reactive nitrogen budget and nitrate deposited on the snow and particle surfaces may possibly be an important source of daytime HONO production.

An understanding of the reactive nitrogen budget is an important prerequisite for designing an effective ozone control strategy. NO_x emissions from combustion sources take part in the photochemical reactions that form ozone and are processed over the course of the day into other odd nitrogen species including HONO, HNO_3, PAN and $RONO_2$. In addition, N_2O_5 and $ClNO_2$ are formed at night. These NO_x production species are collectively referred to as NO_z.

While NO_x concentrations at Horsepool during 2013 were similar to those observed during 2012, NO_y concentrations were significantly higher, indicating a much higher degree of photochemical processing of NO_x during 2013. The major NO_z (operationally defined as NO_y minus NO_x) species observed in 2013 were HNO_3 and PANs with some contribution from HONO during the daylight hours. Concentrations of HNO_3 were observed to be eight times higher in 2013 as compared to 2012 at Horsepool (see Section 5, Figure 5-33), and nitrate and nitrite concentrations in the top 1 cm of snow increased with time after fresh snow was deposited (see Section 5, Figure 5-39). Daytime HONO production in the snow surface, if real, is possibly linked to HNO_3 deposition as described under Finding B.2.1 above. The resulting recycling of NO_y species into NO_x makes NO_x controls less effective for ozone reduction than would otherwise be the case.

Conclusions

Results from UBOS 2013 reveal several aspects of ozone formation chemistry unique to winter events. Formaldehyde, and to an unknown extent HONO, were found to be the biggest contributors to the pool of chemical radicals responsible for ozone formation, rather than the traditional radical source, photolysis of O_3 itself. However, the quantitative contribution of HONO to the radical pool is uncertain at this time because of uncertainties in the HONO measurement and because the high HONO concentrations observed up to 7.25 m agl, which were used as the basis for the radical production estimates, may not be valid, and, even if they are valid, most likely do not extend throughout the mixed layer. Better estimates of the daytime HONO concentrations, vertical profile, and source term as well as a more complete understanding of the sensitivity of this source to NO_x emissions are a critical requirement for development of useful models of winter ozone formation.

2.4 Part C: Sources of Ozone Precursor Emissions

C.1: What are the primary sources of ozone precursor emissions in the Basin? What is the spatial distribution of precursor sources?

Background

Ozone precursor emissions in the Uinta Basin are associated with a variety of sources. Oil and gas extraction activities dominate. Associated sources include gas plants, compressors, well site sources (drill rigs, frac pumps, pump jacks, tanks, dehydrators, fugitives, etc.), pipelines, on-road and non-road mobile sources, produced water evaporation ponds, reserve pits, and other

miscellaneous sources (Figure 2-15). Other anthropogenic emissions consist of typical urban (residential, commercial, and light industrial) source emissions associated with the approximately 50,000 Basin residents, agricultural activities, a 500 Megawatt coal-fired electric generation unit (the Bonanza plant), and phosphate and gilsonite mining. Non-anthropogenic emissions in the Basin include biogenic emissions of isoprene and other VOC and natural hydrocarbon seeps.

A complete and accurate emissions inventory is a fundamental component of air quality management, and is vital to the development of an accurate photochemical model simulation for use in ozone control strategy design. Uncertainties in emission totals and the spatial and temporal patterns of emissions are a significant source of potential errors in model predictions. Emission inventories should therefore be evaluated for consistency with available independent data sources. For example, ratios of key species in the inventory should match ratios obtained from ambient measurements and any discrepancies should be investigated before the inventory is used as the basis for making major regulatory decisions.

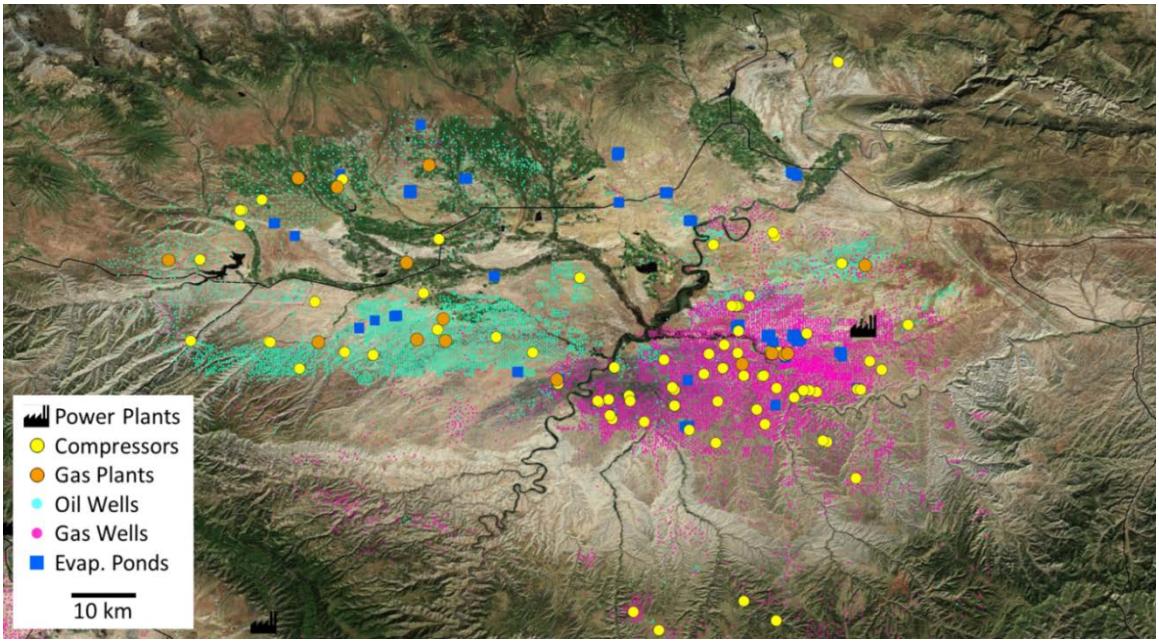


Figure 2-15. Locations of oil and gas related emissions sources in the Uinta Basin (the location of the Bonanza power plant is also shown).

Finding C.1.1: Oil and gas-related sources are responsible for the majority of NO_x and VOC emissions in the Uinta Basin.

A discussion of emissions data for the Uinta Basin is presented in Section 9. Emissions data for Duchesne and Uintah counties from the 2011 UDAQ submittal to the National Emissions Inventory together with the Western Regional Air Partnership (WRAP) Phase III oil and gas inventory are listed in Table 2-2 and illustrated in Figure 2-16. The oil and gas sector is by far the dominant source of VOC and low level NO_x emissions. Although biogenic VOC emissions are

significant (31% of total VOC on an annual basis), they are reduced to near zero levels during the winter months. NO_x emissions from the Bonanza power plant contribute 22% to total NO_x from all sources but, as pointed out below, emissions from the Bonanza plant are lofted above the low-level inversion during ozone episode conditions and therefore do not contribute significantly to ozone formation.

Observations made during the 2013 study confirm that the Bonanza power plant plume does not appear to contribute any significant amount of NO_x or other contaminants to the polluted boundary layer during ozone episodes. As shown in Figure 2-17, the thermally buoyant Bonanza plume rises upwards from the 183 m (600 ft) stack and penetrates through the temperature inversion layer. As a result, emissions from the Bonanza plant are effectively isolated from the boundary layer in which the high ozone concentrations occur. While it is possible that some of the plume material may eventually be re-entrained into the mixed layer at the Basin margins, the amount of recirculation is likely to be minimal, especially during the strong inversion periods associated with high ozone levels. Other observations of the Bonanza plume include four aircraft vertical profiles in which a plume of enhanced CO, CO_2, and NO_2 and depressed ozone can be seen between 1800 and 1900 m asl, well above the ~1650 m asl mixed layer top (Sections 4 and 8).

Another indication of the dominance of oil and gas sources in the Basin is the strong correlation (r^2 = 0.88) of average VOC concentration measured at surface sites with the number of producing wells within 15 km of the monitoring site as presented in Section 3, although the relationship of NO_x to oil and gas sources is more difficult to discern in these data.

Conclusions

Results from the 2012 and 2013 field studies, as well as the available emission inventory data, all support the conclusion that emissions of VOCs and NO_x from oil and gas exploration and production activities are the primary drivers of ozone formation in the Basin. Although the Bonanza power plant is a major source of NO_x in the Basin, this material does not contribute significantly to ozone formation in the Basin during winter episodes.

Table 2-2. UDAQ 2011 Emissions Inventory (tons/year) based on the Utah NEI submittal and updated WRAP Phase III inventory (Source: Sec. 9, Table 9-2).

County	Source	NO_x	$PM_{2.5}$	SO_x	VOC
Duchesne	Oil & Gas	7,805		125	34,787
	All Other Activity	3,220	382	18	1,864
	Biogenic - Summer Only - Trees, Crops, Plants	0		0	22,390
Uintah	Oil & Gas	10,033		209	76,502
	All Other Activity	1,728	978	20	1,921
	Biogenic - Summer Only - Trees, Crops, Plants	0	0	0	29,153
	Bonanza Power Plant	6,590	433	1,178	46
TOTAL	Oil & Gas	17,838	0	334	111,289
	All Other Activity	4,948	1,360	38	3,785
	Biogenic - Summer Only - Trees, Crops, Plants	0	0	0	51,543
	Bonanza Power Plant	6,590	433	1,178	46

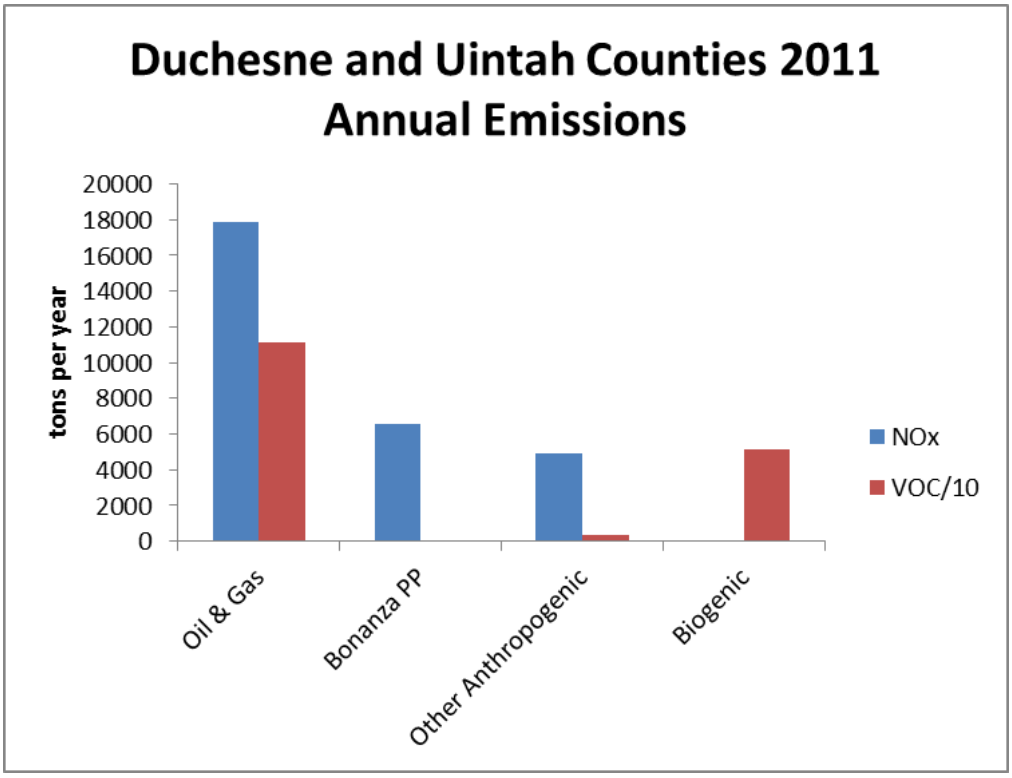


Figure 2-16. Summary of emissions by source category. (Source: Sec. 9, Table 9-2).

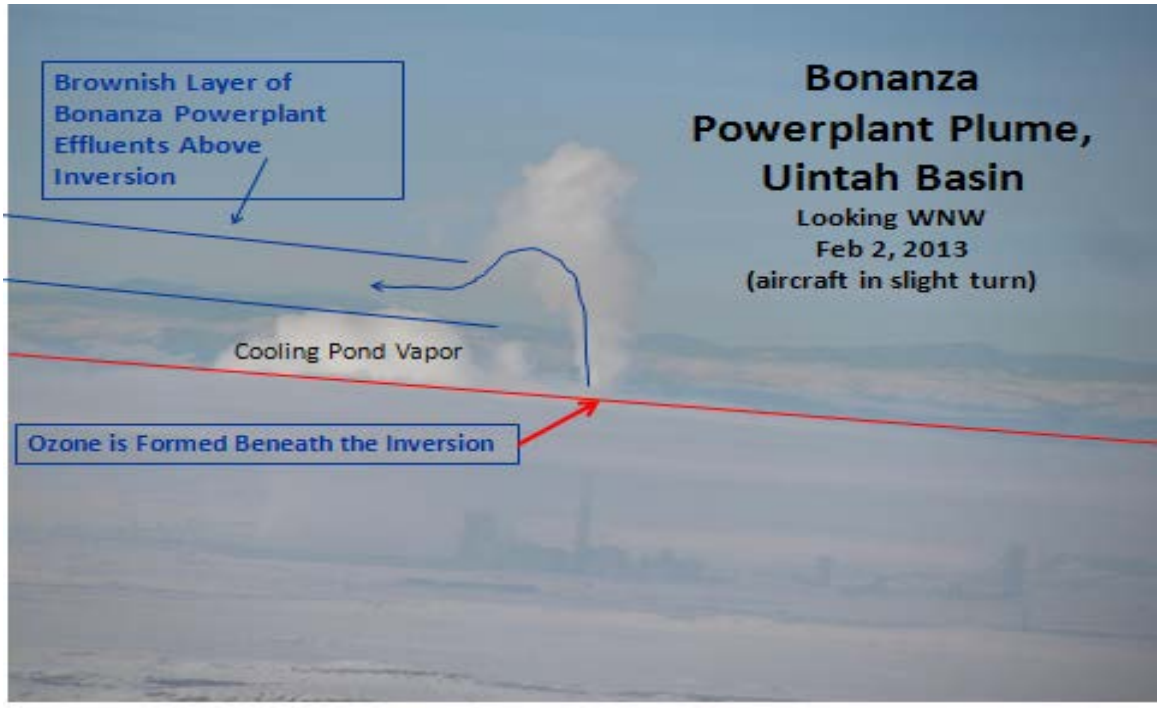


Figure 2-17. Bonanza power plant with buoyant exhaust plume and water vapor from the cooling ponds during a winter temperature inversion on 2 February 2013. The top of the stack is 1715.8 m and the plume generally rose an additional 2 to 3 stack heights before leveling out in the 1900 to 2200 m range; the inversion base was generally between 1600 and 1750 m (photographed by Colm Sweeney, CIRES/NOAA).

C2: Do ambient measurements and emission inventories agree for ozone precursor emissions in the Basin?

Background

Development of reliable estimates of the expected response of ozone to reductions in precursor emissions requires an accurate emission inventory for input to photochemical models. However, activity data and emission factors used to develop inventories are subject to uncertainties which may be significant for some types of sources, such as fugitive emissions of natural gas. Quality assurance of emissions inventories via reconciliation with ambient air quality data is therefore an important component of air quality management.

Various techniques can be used to validate emissions estimates using ambient data. One approach is to measure pollutant fluxes downwind of a source or group of sources and apply inverse modeling to back calculate the corresponding source emission rate. This method has been used to estimate methane emissions from the Denver-Julesburg Basin in Weld Co., CO. (Petron, et al., 2012). Pollutant flux measurements have also been successfully conducted downwind of evaporation ponds using remote sensing techniques (Thoma, 2009). Researchers from the Utah State University recently completed a preliminary assessment of fluxes from

evaporation ponds in the Uinta Basin under winter conditions (see Section 9). Flux measurement methods require collection of a sufficient amount of concentration data to adequately characterize the pollutant flux within the source plume, and such extensive data sets are not always available. This is particularly challenging for complexes of sources which may not have coherent plumes. In addition, these methods are unable to provide information on emissions from individual sources which may be contributing to the overall source complex plume.

Another approach to inventory evaluation involves reconciliation of emissions ratios of key ozone precursor species (e.g., VOC/NO_x) with corresponding ratios in the ambient data. This approach can provide useful information on potential inaccuracies in the inventory, so long as emissions of one species (typically NOx) can be assumed to be reasonably well characterized. Care must also be taken to include only data that are not significantly impacted by *in situ* chemical transformations and that data are properly filtered to insure that the comparisons are performed on a consistent "apples to apples" basis (e.g., Stoeckenius et al., 2004).

Direct comparisons of predicted species ratios from photochemical models with observations can also provide a useful check on the inventory so long as the simulation of chemical transformations can be assumed to be reasonably accurate.

Finding C.2.1: Near source measurements performed by the NOAA mobile laboratory in 2012 are generally consistent with emissions profiles for various source types used in the 2008 WRAP inventory.

Measurements of VOCs were performed by the NOAA GMD mobile laboratory during UBOS 2012 at locations immediately downwind of different gas wells and oil wells in Uintah and Duchesne counties, gas wells near Rangely, CO, a flow-back pond from a well undergoing fracking, a newly producing gas well, and various other point sources (compressor stations, etc.). As described in Section 5, VOC composition varied significantly by source type. VOC emissions from oil wells were found to be skewed more towards heavier compounds as compared to emissions from gas wells with particular enhancement in aromatics. Results from the mobile lab drive-by of a gas well showed that methane was found to be highest downwind of the separator, toluene, and other aromatics downwind of the condensate tank, and methanol downwind of the methanol and condensate tanks. Overall, results from the mobile lab are in qualitative agreement with VOC composition variations by source type included in the 2008 WRAP emission inventory. However, mobile lab results do not provide a quantitative assessment of emission rates.

Finding C.2.2: While a wealth of data was collected during UBOS 2012 and 2013, additional analyses of these data are needed to provide results that can be used to infer quantitative information concerning emissions. These analyses will be reported as they are completed.

Although reconciliation of emission inventories with ambient measurements is difficult and subject to numerous sources of uncertainty, it is likely to provide some useful information

regarding the accuracy of inventory estimates and an indication of where additional scrutiny of the inventory is most needed.

Conclusions

Oil and gas exploration and production activities are the dominant sources of ozone precursors in the Uinta Basin, though other significant sources exist. Further work to refine emissions estimates and to verify inventories using ambient measurements is needed along with comparisons of modeled to measured concentrations.

2.5 Part D: Mitigation Strategies

D.1: What possible mitigation strategies should be considered for adoption in the Uinta Basin?

Background

Determination of an optimal ozone control strategy for the Uinta Basin will require the development of a high quality photochemical modeling database. Data available from the UBOS are insufficient by themselves to determine the level of control that could eventually be required to achieve ozone-reduction objectives. Furthermore, it is not known at this time whether winter ozone problems in the Basin will be more effectively mitigated by NO_x or VOC controls, nor is it known whether control requirements will need to vary across the Basin. NO_x emissions reductions under VOC limited conditions (low VOC/NO_x ratios) can result in increases in ozone (Nopmongcol et al. 2010; Carter and Seinfeld, 2012). VOC emission reductions, on the other hand, do not typically lead to an increase in ozone formation, but marginal reductions in VOCs may be largely ineffective under strongly NO_x limited conditions (very high VOC/NO_x ratios). In general, ozone production can be expected to transition between VOC and NO_x limited conditions at different times and locations. Thus, application of state-of-the-art photochemical grid models is necessary to identify the best combination of VOC and NO_x controls needed to achieve ozone reduction goals. Photochemical simulations using a simple box model (Gery and Crouse, 1990) with data collected at different times and locations in the UGRB showed ozone formation to be VOC limited in some cases and NO_x limited in another (Carter and Seinfeld, 2012). Box model simulations of conditions in the Uinta Basin during the UBOS 2012 study, when snow cover was not present, showed that the limited amount of ozone production which did occur was most likely radical limited and thus sensitive to reductions in VOC rather than NO_x (Edwards et al., 2013). These findings do not necessarily apply under the snow covered, cold air pool conditions associated with ozone episodes, however. Several groups, including the Utah Department of Environmental Quality (UDEQ), U.S. EPA, and Utah State University, have begun meteorological and photochemical modeling studies of the Basin. A preliminary meteorological modeling study of the 26-30 January 2013 inversion episode is described in Section 10.

Finding D.1.1: Episodic or seasonal emission controls may be a useful ozone reduction strategy for the Uinta Basin.

Ozone levels in excess of EPA's current ambient standard only occur during winter inversion periods which require very specific conditions (generally fair weather with weak pressure gradients, low sun angles, and snow-covered ground). Ozone on the majority of days during the year is below the EPA standard and exceedances of the standard do not occur every year. Thus, control measures designed to reduce ozone under the specific winter inversion conditions or during the time when such conditions are likely to occur have the potential to be a cost-effective strategy. For example, certain types of activities such as blowdowns for which operators have some scheduling flexibility could be avoided during winter inversion events. Similarly, spuds could be scheduled as much as possible for months outside of the peak winter ozone season (roughly mid-January to mid-March). As noted above, UDEQ has instituted a set of recommended voluntary seasonal emission controls and an air quality forecast system (http://www.airquality.utah.gov/aqp/forecast.php?id=vl) for Uintah and Duchesne counties.

Finding D.1.2: Reductions in emissions of VOCs, especially highly reactive VOCs, are likely to be beneficial.

Under most conditions, VOC reductions will result in ozone reductions, although the sensitivity of ozone to VOC reductions will vary. Highly reactive VOCs such as formaldehyde and aromatics are of particular importance (formaldehyde was found to be a major source of the radicals that drive ozone production at Horsepool, as described in Section 5) and these VOCs are preferentially emitted from specific sources. Sources such as dehydration units and produced liquids evaporative losses are rich in aromatics. Primary formaldehyde sources include diesel engine exhaust and potentially the use of formaldehyde contaminated methanol (as evidenced by the high correlation of formaldehyde and methanol concentration spikes observed at Horsepool in 2012 and 2013, see Section 5). Formaldehyde is also formed in the atmosphere from VOC precursors, so reducing emissions of these precursors will result in lower formaldehyde concentrations and less production of radicals. The relative contributions of primary and secondary sources to total formaldehyde are currently uncertain. A simple regression model derived in Section 5 from data collected in 2013 based on the assumption that secondary production scales with the O_x (sum of O_3 and NO_2) mixing ratio suggests that 63% was from secondary production, 30% from primary sources, and 7% background. Additional data are needed to identify the most effective formaldehyde reduction strategies. Analysis of VOC samples collected during UBOS 2013 indicates low concentrations of alkenes and therefore little if any contribution of these highly reactive species to the overall VOC reactivity in the Basin (Sections 3 and 5).

Finding D.1.3: Emission reductions at the Bonanza power plant are unlikely to have any effect on winter ozone episodes.

As summarized in Section 2.4, results from the UBOS 2013 study clearly show that the Bonanza power plant plume is injected above the inversion layer during winter ozone episodes and therefore does not contribute significantly to the high ozone levels observed below the

inversion layer. Therefore, reductions in emissions from Bonanza would not result in a significant ozone reduction benefit under episode conditions.

Finding D.1.4: Additional data collection and analysis is needed to more fully evaluate the likely sensitivity of peak ozone concentrations to reductions in NO_X emissions.

The effectiveness of NO_x reductions will depend on the degree to which unreactive NO_z is converted to reactive NO_x by heterogeneous chemistry on snow or suspended particle surfaces, e.g., the conversion of HNO_3 to HONO in snow. As discussed in Section 2.3 above, measurements from Horsepool indicate that photochemical production of HONO in the snow is occurring, although the validity and strength of this source remains uncertain. The most likely mechanism behind this HONO source involves photolysis of nitrates that have been deposited on the snow, forming nitrites which then undergo a reversible acid-base reaction to form HONO as described in Section 5. Evidence for this includes daytime near surface HONO concentrations that correlate with solar radiation and generally decrease with height (thus indicating an upward flux of HONO) along with high nitrite concentrations in the snow which increased day-to-day during the ozone episode and which correlated with snow nitrate concentrations. While HONO production from snow therefore likely scales with nitrate deposition which would in turn be sensitive to NO_x, the form of this relationship may very well not be a simple linear one in which a given percent reduction in NO_x produces an equivalent percent reduction in nitrate deposition and HONO production. Additional study is needed to further evaluate the relationship of HONO to NO_x emissions under winter episode conditions.

Conclusions

Additional work is needed to understand the potential sensitivity of ozone to NO_x and VOC emission reductions during winter episodes. Of particular importance is quantification of the strength of the HONO source(s) and further investigation of the heterogeneous chemical reactions involved so as to gain a better understanding of the potential impact of NO_x emission reductions on HONO production. Additional work is also needed to evaluate effective controls targeting formaldehyde. Absent this additional information, VOC reductions – particularly controls focused on large reductions in fugitives and targeted reductions of sources of aromatics and primary formaldehyde – can be expected to result in lower ozone levels.

Recent rulemakings by the U.S. EPA and the UDEQ are expected to result in reductions of VOC emissions in the Basin. Applicable EPA rule revisions issued in April, 2012 include New Source Performance Standards (NSPS) for the oil & gas industry (http://www.epa.gov/airquality/oilandgas/) which targets VOC emissions from well completions (requiring so-called “green completions”), liquids storage tanks, and some new or modified well-site equipment and compressor stations and National Emission Standards for Hazardous Air Pollutants (NESHAPS) which limit VOC emissions from new and existing glycol dehydrators. EPA also instituted a permitting program for sources in Indian Country in 2011 (http://www.gpo.gov/fdsys/pkg/FR-2011-07-01/pdf/2011-14981.pdf). UDEQ recently implemented a General Approval Order mechanism which is applicable to upstream oil and gas sources and is expected to result in emissions reductions (particularly VOC emission reductions)

from new sources via implementation of Best Available Control Technology requirements. UDEQ has also compiled a set of recommended Voluntary Seasonal Ozone Controls (http://www.deq.utah.gov/locations/uintahbasin/seasonalcontrols.htm) which are mostly targeted at detection and reduction of fugitive VOC emissions and avoiding carrying out of maintenance procedures, such as blow downs, that result in bursts of VOC emissions during winter inversion conditions.

2.6 Part E: Additional Information Needs and Modeling Issues

E.1: What special challenges does the basin pose for meteorological modeling?

Background

The Uinta basin is a broad, 27,700 km^2 mountain basin containing numerous, relatively low (order of tens to hundreds of meters) topographic features. During the high ozone periods in the 2011 and 2013 Uinta Basin campaigns, the region had relatively light (1 - 4 m/s) low-level (surface to 500 m agl) winds. Light wind conditions in mountainous terrain typically feature thermally driven slope and mountain-valley wind systems associated with differential diurnal surface heating and cooling cycles. These wind systems, often referred to as katabatic wind systems, blow up-valley or upslope during the day and downslope or down-valley at night (nocturnal drainage flows). At a given time of day, in other words, the local winds blow from a preferred direction for several hours each day, so that the winds and their effects (e.g., transport) show up in multiday averages or composites of the data.

Thermal forcing of katabatic wind systems may be weak during the winter months due to low solar angles and short day lengths, making the systems difficult to detect. So important questions are: Is there a discernible diurnal signature to the low-level winds in the Uinta Basin under winter ozone episode conditions and what impact do these local thermally driven slope flows have on the transport of pollutants? Of particular interest is the potential for recirculation of pollutants as a result of the diurnal upslope/downslope wind reversal. This type of recirculation pattern has been documented in the Upper Green River Basin (ENVIRON, 2008).

When larger scale synoptic pressure patterns produce winds blowing across the upstream rim of the Uinta Basin, the resulting dynamic forcing on the top of the pool of cold, stable air contained within the Basin may introduce dynamic forces resulting in perturbations on the weakly forced katabatic surface wind regimes within the Basin. The resulting complex wind patterns are known to be difficult to reproduce with current mesoscale meteorological models.

Winds blowing across the upstream rim of the Basin often appear as wave-like features impinging into the basin (most commonly from the west) and can bring clean air into the basin. Radiosonde vertical profiles of wind and temperature (Section 8) and initial modeling work (Section 10) suggest that winds from the east just above the surface develop in response to this upstream dynamical forcing. Future modeling studies will provide more insight into these terrain-flow interactions as possible transport mechanisms for ozone and its chemical precursors in addition to the thermally-driven flows.

During the 2011 and 2013 measurement campaigns, the concentrations of ozone were found to vary considerably across the Basin, consistent with both spatial variations in precursor sources and terrain elevations. Transport over the complex terrain within the Basin also plays a role in determining the spatial ozone pattern. High concentrations were measured at the lowest-elevation sites in the Green River valley, which could be explained by drainage flows, but high concentrations were also seen at higher-elevation sites to the east of the river-valley sites.

Weak winds require a precise measurement system to detect them. Data from NOAA/ESRL's High-Resolution Doppler Lidar (HRDL) has been shown to satisfy this requirement. Although a scanning system, HRDL is able to produce accurate profiles of the mean wind at vertical resolutions of less than 5 m through the lowest several hundred meters of the atmosphere, extending up to 2 km. The HRDL was located at the Horsepool site during UBOS 2012 and 2013, so it sampled the wind conditions in the eastern portion of the basin. While the instrument was able to capture fine detail at this site, results from meteorological data collected at multiple sites within the Basin presented in Section 3 indicate that wind conditions at Horsepool are likely not representative of other regions within the basin.

The traditional meteorological models that would likely be used to support air quality modeling in the basin were developed with a primary goal of weather forecasting. As such, much of the research focus and evaluation of the models has focused on the ability of the models to replicate the weather phenomena important to weather forecasting (i.e., frontal passage movement, hurricane track, cyclogenesis). Fewer development resources have been spent on the applicability of the models for simulating the important features for weakly forced flows under cold pool conditions such as would be important in the Uinta Basin. In addition, current numerical model boundary-layer schemes struggle to accurately simulate aspects of highly stable atmospheric conditions. It is important that particular attention be given to the model application and evaluation methodology, and that physics parameterizations most appropriate for use in the extremely stable environment be used when applying the models in the basin.

Finding E.1.1: Very different wind patterns and dynamic processes were identified under strong as compared to weak wind regimes during UBOS 2012 and 2013.

During UBOS 2012, strong-wind periods were generally dominated by synoptic-scale meteorological systems (winter storms) typical of mid-latitude locations in winter. Under these conditions, the near-surface winds reflect the stronger winds aloft, as illustrated in Figure 2-18.

During weak-wind periods when the synoptic-scale pressure gradients are minimal, the effects of local forcing become evident so long as the forcing is strong enough. Figure 2-19 shows the evolution of wind profiles on a day when such forcing is clear. On this day, the near-surface winds were light, but the nighttime winds had a distinct easterly component, and daytime winds were from the west up to a height of several hundred meters. Although many light-wind days during UBOS 2012 exhibited perturbations superimposed on the local winds by traveling disturbances, the diurnal pattern was observable in HRDL profiles on most light-wind days, and in composites of all days when the winds aloft were light (< 4 m/s). Thus HRDL was able to detect a diurnal pattern in the near-surface winds in the vicinity of Horsepool, with light

easterly flow draining toward the Green River valley at night and light westerly upslope flow during daytime hours. The easterly flow is consistent with the appearance of high concentrations in the lowest areas of the basin, and the daytime westerlies can explain the secondary appearances of high concentrations on higher ground to the east of the river bottom.

Finding E.1.2: Meteorological data collected at stations around the Basin showed significant variations in winds across the basin and with time of day. Meteorological models must capture the spatiotemporal variability of boundary layer flows above the surface layer that are not observed by the surface meteorological network.

Figure 2-20 shows average day and night wind vectors at 14 meteorological stations around the Uinta Basin during February 2012. The black arrows indicate monthly mean wind direction from 13:00 to 15:00 local time, and red arrows indicated monthly mean wind direction from 03:00 to 05:00 local time. The size of the arrow is proportional to the mean wind speeds for each time period. These results show that day and night mean wind directions are not consistent across the Basin, even among some sites that are in relatively close proximity. Most of the sites exhibit upslope/downslope flow that leads to near-180 degree shifts in wind direction between night and day. The directions of the day-night flows are not consistent at different sites, and appear to be influenced by the local terrain. Thus, the complex topography of the Basin likely leads to complex surface flows that transport ozone and its precursors around the Basin. This spatial heterogeneity can be magnified during inversion conditions conducive to ozone formation, since temperature inversions are typically accompanied by low speed surface winds and variable wind directions. Afternoon winds during 2013 ozone episodes show significant spatial heterogeneity (see Figures 2-21 and 2-22). Because of the complex topography of the Basin and its influence on surface flow and, by extension, pollutant transport, it will be critical that models of ozone formation include high resolution simulations of topography and meteorology. Data from the extensive network of meteorological stations used in UBOS work will be able to inform and validate such an effort. In addition, data from vertical profiles of wind from radiosondes, tethersondes, and the HRDL lidar (Sections 5 and 8) indicate significant variations in wind speed and direction with height. Thus, modeling efforts to provide spatiotemporal details on above-surface winds will be critical.

Finding E.1.3: Transport in the basin is influenced both by locally induced flows and interactions with synoptic scale flows. Meteorological models must adequately capture both phenomena to accurately simulate flows within the basin.

During high ozone periods in the 2013 measurement campaign the basin was observed to have Persistent Cold Air Pools (PCAPs) characterized by relatively light winds and a strong temperature inversion (Section 3.1). However, the basin was periodically cleaned out by larger scale synoptic flows in between the high ozone periods. Figure 2-21 shows wind conditions and the low ozone concentrations on 28 January, just two days after one of the season's highest ozone days in the basin. A storm front arrived on 27 and 28 January and was associated with relatively high winds in many parts of the Basin on 28 January. Winds at high elevation sites during this period were from the south. Wind speeds within the Basin were lower on

subsequent days, allowing another inversion to form and ozone concentrations to rebuild. By the afternoon of 6 February (Figure 2-22), ozone concentrations exceeded 100 ppb at many sites. Wind at high elevations continued to be from the south throughout this period, and wind at lower elevation sites in the Basin was light and variable. On 8 February, however, wind at high elevation sites changed directions and blew from the north (Figure 2-23). Following this synoptic scale change, wind at low elevation sites within the Basin continued to be light and variable, but a partial mix-out of ozone from the Basin nevertheless occurred, and ozone concentrations dropped to less than 100 ppb at all sites.

To properly simulate the evolution of the high ozone events will require that the meteorological model be able to simulate both the synoptic scale forced conditions during low ozone events and mix-out conditions, as well as the more locally generated PCAP events during the high ozone periods. In addition, the ability of the models to simulate partial mix-outs arising from terrain-flow interactions immediately downwind of the surrounding mountain ranges will be critical during long-lived PCAPs.

Finding E.1.4: Many shallow layers are observed during persistent cold air pools and models must include adequate vertical resolution to capture observed phenomena.

The boundary-layer depth and structure during UBOS persistent cold air pools were estimated using backscatter and backscatter gradients from the two University of Utah ceilometers deployed in the basin (Section 3.2). On most days, distinct layering of the vertical structure of the boundary-layer backscatter was observed (Figure 2-24). Another feature that is apparent from Figure 2-24 is the diurnal variations in the depth of the surface-based polluted layer. These diurnal variations are associated with similar variations in the temperature structure of the boundary-layer. On the 24th January, the depth of the surface-based polluted layer was observed to be near 300 m during the overnight hours, but increased to nearly 500 m during the afternoon.

The University of Colorado Balloon based ozone monitor (Section 6) also showed significant vertical structure in ozone concentration. The vertical distribution of ozone throughout the duration of the campaign is illustrated in Figure 2-25 as a color contour plot showing the full record of the ECC sonde ozone data for Horsepool. The three high ozone build-up events are evident in the warmer colors on the color scale, which here goes to 175 ppbv. The vertical structure reveals that ozone builds up in both mixing ratio (concentration) and in height during the inversion events. The highest ozone is consistently confined within the lowest 100 – 150 m above ground level and at many times appears to be well-mixed within the shallow boundary layer. With the exception of one day in mid-February, relatively low ozone (i.e., < 75 ppbv) was present above 1900 m asl throughout the measurement period. The clean-out periods (i.e., January 28 – 31 and February 10 – 11) brought this relatively clean background air down to the surface, resulting in ground-level ozone values on the order of 30 – 60 ppbv.

The meteorological models must be configured to properly capture the vertical stratification observed during UBOS 2013. This may require higher vertical resolution than is typically employed for meteorological modeling for air quality applications. It will also require testing

various PBL schemes and other physics parameterizations as well as model initialization to determine which settings are most appropriate for these high-stratification events. It will also be critical to evaluate the photochemical model against the aloft special study data to assure that the model is able to adequately reproduce the observed phenomenon. Some initial modeling analyses are presented in Section 10.

Conclusions

During high ozone periods the low-level transport is dominated by fairly shallow (50-400 m deep), weak (1-4 ms^{-1}), and highly variable locally driven flow patterns. During mix-out and partial mix-out events the flows are more influenced by stronger (> 10 ms^{-1}) winds associated with large-scale weather disturbances. Additionally, during high ozone events vertical profiles of pollutants and winds within the basin were observed to have quite distinct layering structure that could impact pollutant transport. It is critical that the meteorological model be configured to capture these local scale flow features, and future research focused on developing model physics parameterizations appropriate for the extremely stable environment is needed. In addition, accurate specification of land use and snow cover will be a critical component for any meteorological modeling efforts.

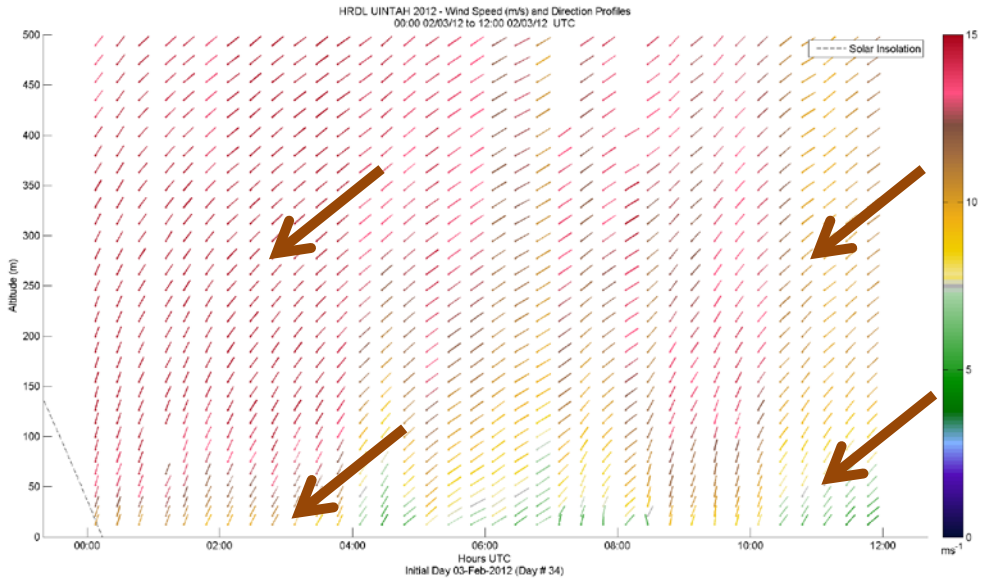


Figure 2-18. Profiles of 20-min wind speed and direction at Horsepool for 0000-1200 UTC on 3 February 2012, showing strong northeasterly flow at 500 m above ground, extending down to the surface (arrows). Wind barbs indicate direction from which winds were blowing, and color coding of barbs indicates wind speed as shown on color bar. Horizontal axis is time (UTC, which is 7 hr ahead of MST), and vertical axis is height above ground (m).

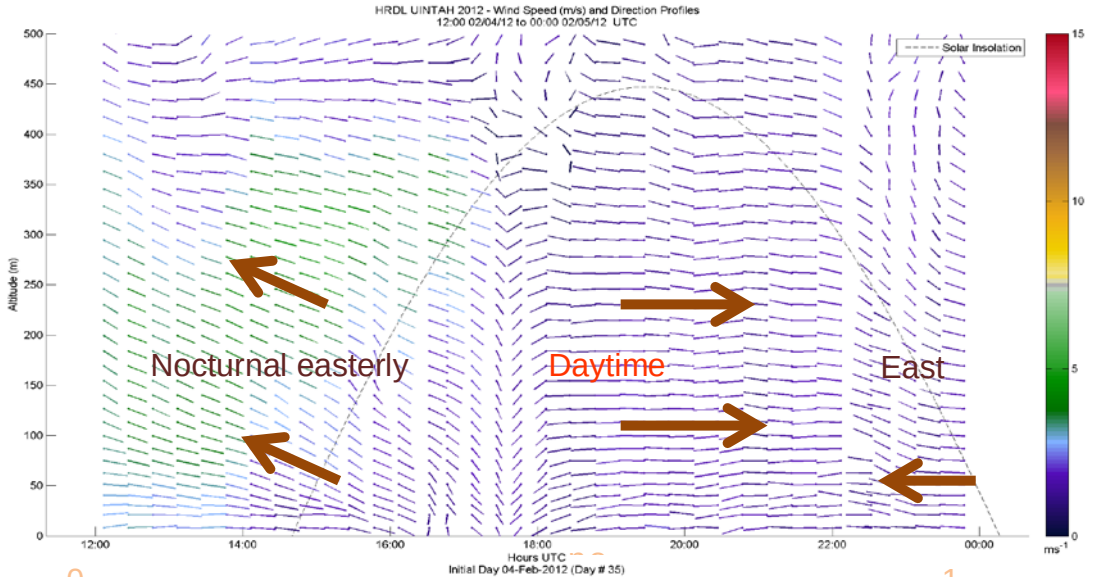


Figure 2-19. Profiles of 20-min wind speed and direction at Horsepool for 1200 UTC, 4 Feb to 0000 UTC, 5 Feb 2012, showing diurnal cycle of winds below 500 m. Dotted black curve is clear-sky solar flux, indicating time of day. Wind barbs and axes as in Figure 2-18.

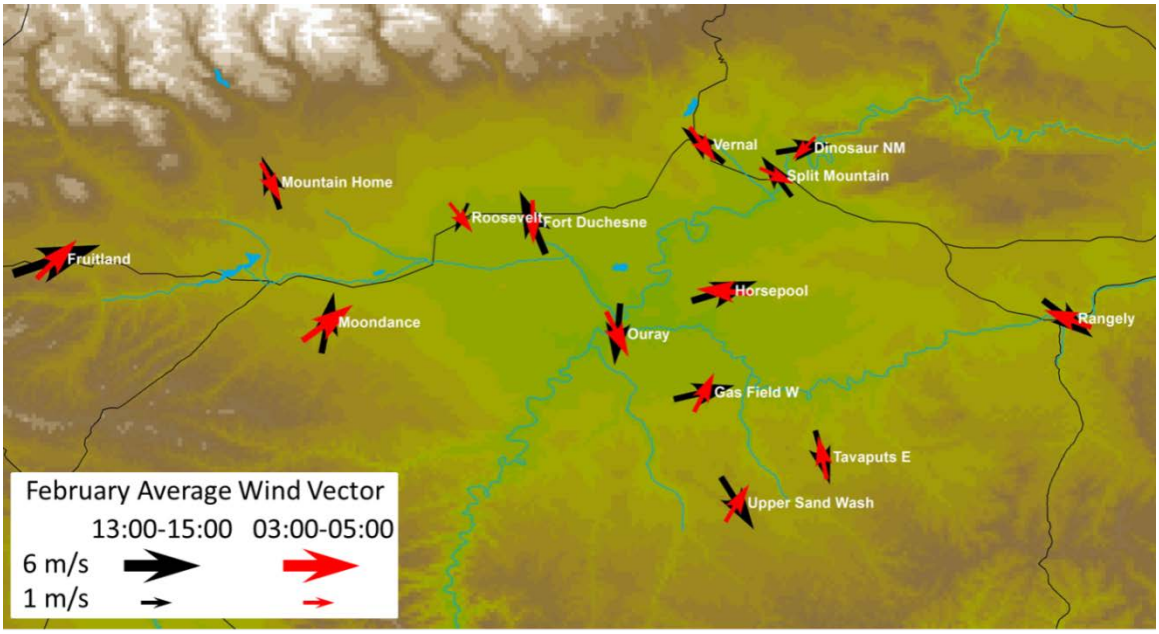


Figure 2-20. Mean day and night wind vectors at 14 meteorological stations around the Uinta Basin in February 2012. (Source: SR2012).

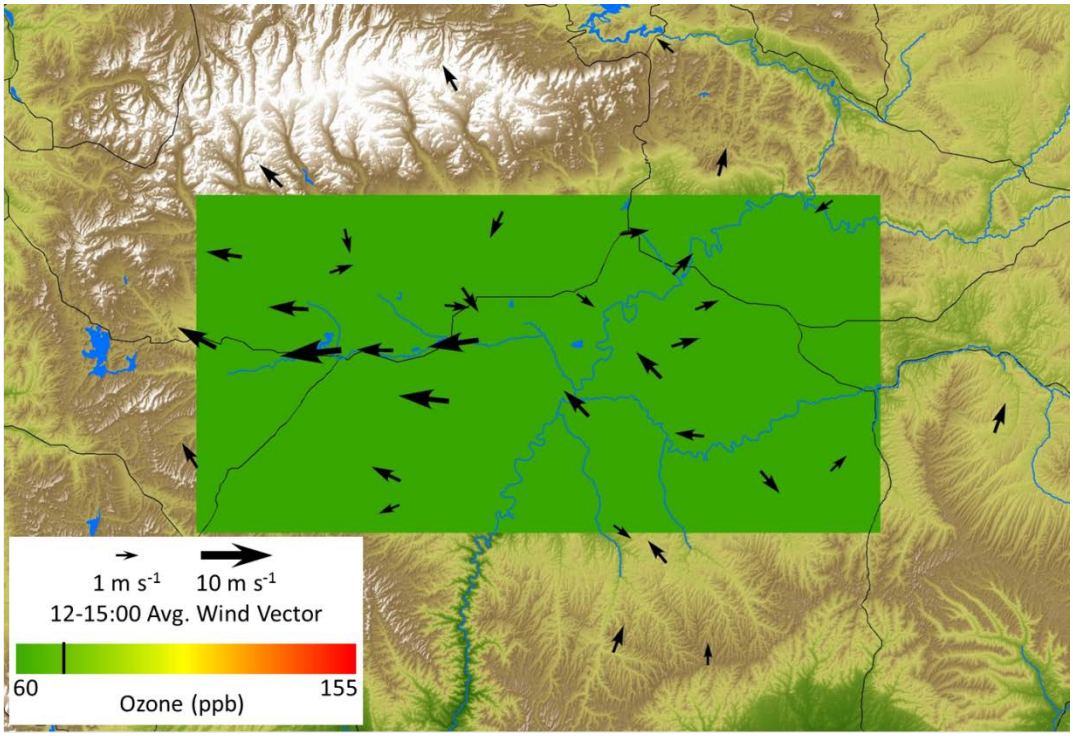


Figure 2-21. Daily maximum ozone concentrations and afternoon composite wind vectors from surface sites on 28 January 2013 during a stormy period between inversion episodes. Arrows indicate wind direction. The black line on the ozone color scale indicates 75 ppb.

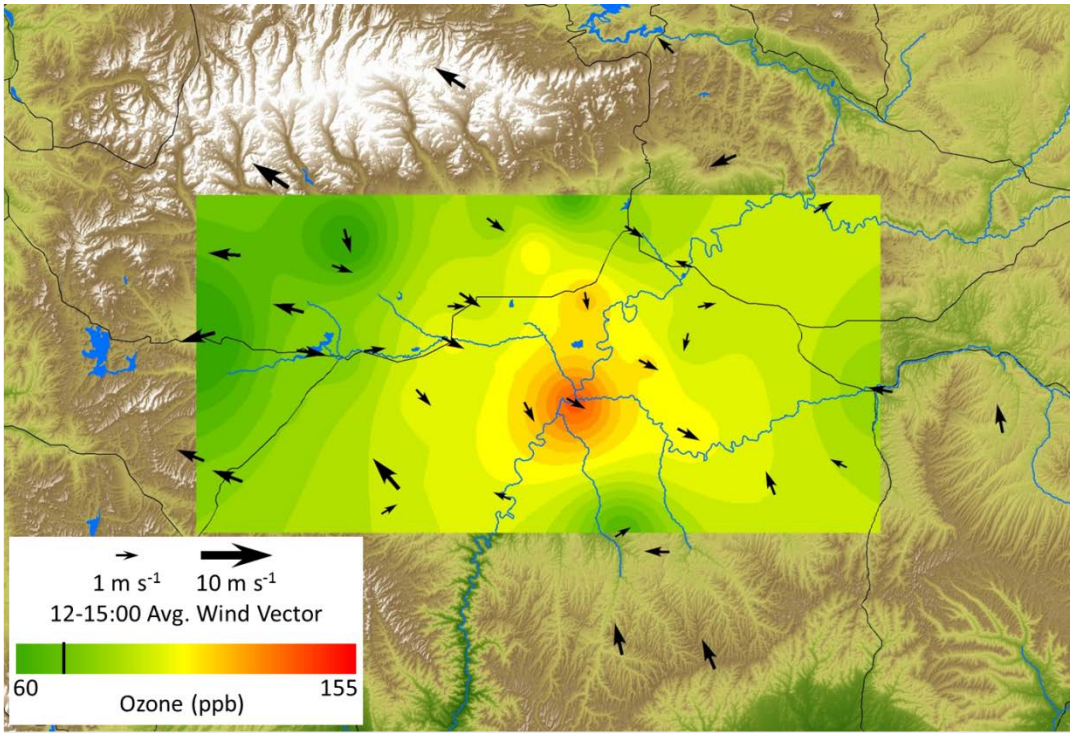


Figure 2-22. Daily maximum ozone concentrations and afternoon composite wind vectors from surface sites on 6 February 2013 during an inversion episode.

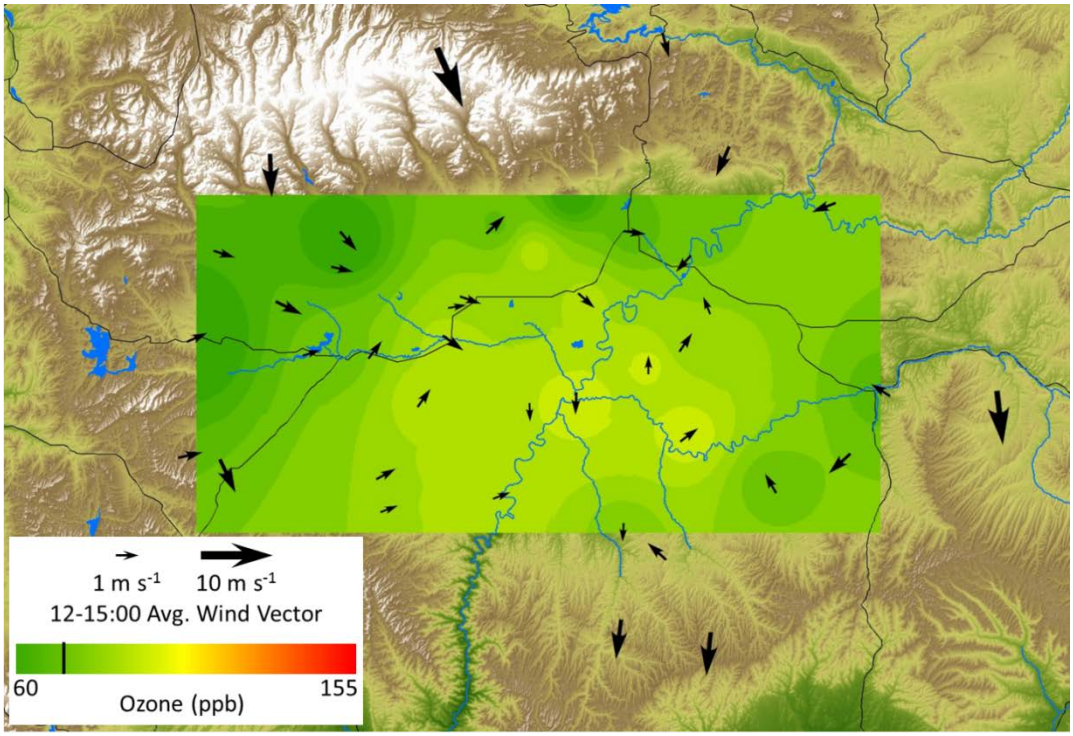


Figure 2-23. Daily maximum ozone concentrations and afternoon composite wind vectors from surface sites on 8 February 2013.

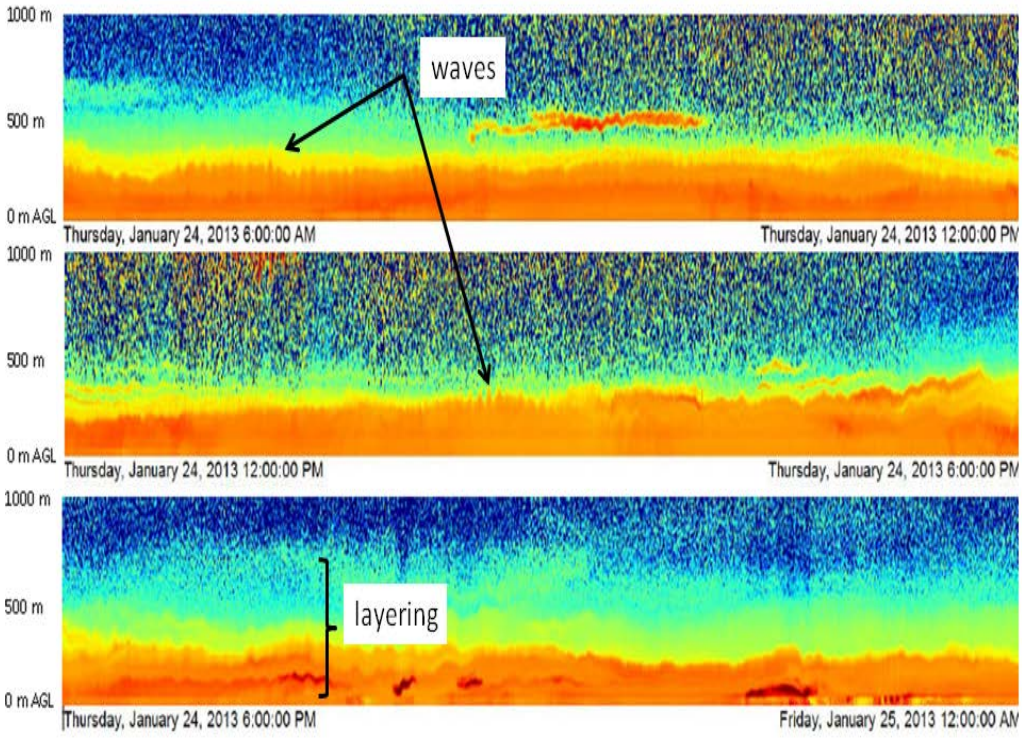


Figure 2-24. Ceilometer aerosol backscatter on 24 January 2013 at Roosevelt, UT. Higher (lower) backscatter implying higher (lower) aerosol concentration denoted by warm (cool) colors.

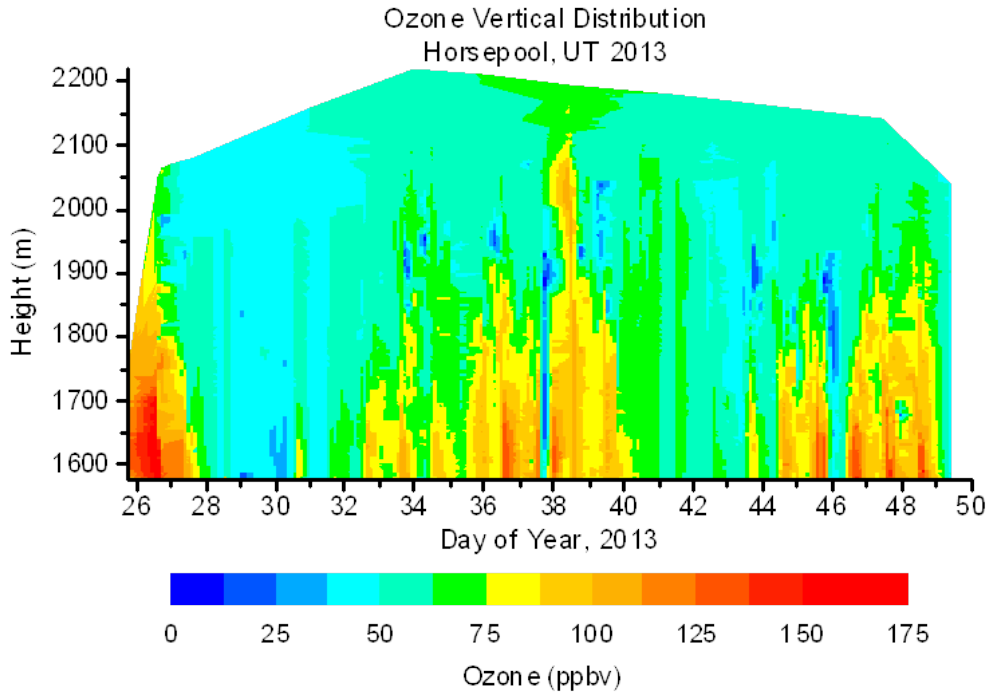


Figure 2-25. Contour plot showing the complete record of ozone measurements acquired from the ECC tethersondes launched by the CU-INSTAAR group at Horsepool between 26 January and 18 February, 2013.

E.2: Can the formulation of existing 1-D box and more complex transport and chemical models represent the observed phenomena in the Basin? If not, what are the most urgent measurement needs for improving the model representation?

Background

Three dimensional photochemical modeling is the most comprehensive tool available for 1) understanding details of the ozone formation process, 2) evaluating ozone sensitivities to changes in precursor emissions, and 3) predicting the effects of emissions control strategies. One-dimensional photochemical box models are useful tools for evaluating chemical mechanisms and performing sensitivity analyses. For model simulations to be useful, however, they must faithfully reproduce key mechanisms of ozone formation and transport operating in the Uinta Basin. Merely demonstrating that a model is able to accurately reproduce the observed temporal and spatial distribution of ozone is not sufficient, as this does not ensure that ozone sensitivities to changes in precursor emissions will also be accurately predicted. Modelers typically refer to this problem as "getting the right answer for the wrong reason." Models must be carefully evaluated against ambient measurements of ozone, precursors, and meteorological parameters.

In contrast to urban summertime ozone episodes for which all existing photochemical models used in regulatory applications were originally developed and evaluated, relatively little is

known about winter ozone episodes in air basins in which emissions are dominated by oil and gas sources. Research is needed, therefore, to fully evaluate the applicability of existing models to winter ozone events and to identify any necessary modifications to model formulation.

Finding E.2.1: Data from the UBOS and UGRB studies indicate that current model chemical mechanisms may need to be modified to account for 1) potential daytime HONO formation and 2) temperature effects on chemical reaction rates.

As pointed out in Section 2.3, the radical budget during winter ozone episodes at Horsepool is primarily driven by a combination of production from formaldehyde and potentially HONO rather than ozone photodissociation as is the case in most summer urban episodes, and apparent high concentrations of near-surface HONO appear to be associated with a daytime production via heterogeneous reactions on the snow surface. Current air quality models do not represent the accumulation and transformation of nitrogen species in snow that may be associated with this HONO source. Using additional measurements of HONO that will be carried out in the 2014 UBOS, however, it may be possible to develop simple parameterizations to represent the source of HONO in snow.

Box modeling of ozone formation in the UGRB by Carter and Seinfeld (2012) and Nopmongcol et al. (2010) showed that existing chemical mechanisms (SAPRC-07 and CB05, respectively) generate peak ozone levels on par with observed values. However, sensitivity analyses performed by Carter and Seinfeld identified significant differences in VOC reactivities between the winter conditions in the UGRB and standard summer urban conditions. They also showed that the potential daytime production of HONO from NO_2 via heterogeneous reactions on the snow surface could contribute significantly to ozone production under some conditions.

Box modeling based on conditions observed in the Uinta Basin during the UBOS 2012 study (Edwards et al., 2013) showed that ozone production during this period was radical limited and thus highly sensitive to VOC levels, despite the observed high VOC/NO_x ratios. Attempts by Edwards et al. to reproduce higher levels of ozone by approximating conditions expected to have occurred if snow cover had been present and a cold air pool had formed (higher UV albedo and lower mixing height with higher precursor concentrations) increased predicted maximum ozone but did not reproduce the high levels of ozone observed in previous years, suggesting that additional factors are at play during winter episodes. This finding raises uncertainties regarding the sensitivity of ozone to precursor reductions under snow covered, cold air pool conditions.

As indicated by Martin et al. (2011), existing chemical mechanisms that were developed and evaluated against data representative of summer urban conditions may not fully account for the effects of cold winter temperatures on reaction rates and the relative distributions of reaction products. Carter and Seinfeld (2012) also noted that the temperature sensitivities of some reaction mechanisms have not been fully evaluated. While results from these studies suggest that overall reactivity is lower under colder temperatures, quantitative research in this area is needed.

Finding E.2.2: Results from initial attempts to simulating meteorological conditions in the Uinta Basin using a prognostic mesoscale model show that significant additional evaluation of various combinations of the available model physics options and possibly additional model development will be needed to properly simulate meteorological fields characteristic of winter ozone episode events.

WRF simulations of the Jan 26-30, 2013 high ozone period have been prepared by researchers at Utah State University (Section 10). Preliminary analysis of simulation results showed that in general the WRF captured the timing and basic structure of the inversion at sites within the basin and captured the inversion breakup on Jan 28 caused by a storm passage. However, the model appeared to have a systematic warm bias during the high ozone period and underestimated the observed near surface temperature gradient between Ouray and Horsepool (Figure 2-26). Near-surface warm bias is a common problem encountered in simulation of cold pool events (Holstag et al., 2013). During the period studied using various combinations of model physics options, WRF was ultimately found to overestimate wind speeds in the near-surface layer with a relatively large bias of up to 4 m/s. Increasing horizontal grid resolution from 1300 m to 800 m did not improve model performance in simulating wind speed and other meteorological quantities in the near-surface layer. While the WRF simulation described in Section 10 shows promise, it is going to be necessary to more fully examine the WRF model performance against the rich observation network and to more fully explore the impact of alternative combinations of available model options on model performance. It is likely that additional model development will be necessary to properly capture the subtle but important meteorological features in the Basin. Meteorological modeling of the Basin is being conducted by other research groups, including the University of Utah, as described in Section 3 (Section 3.2).

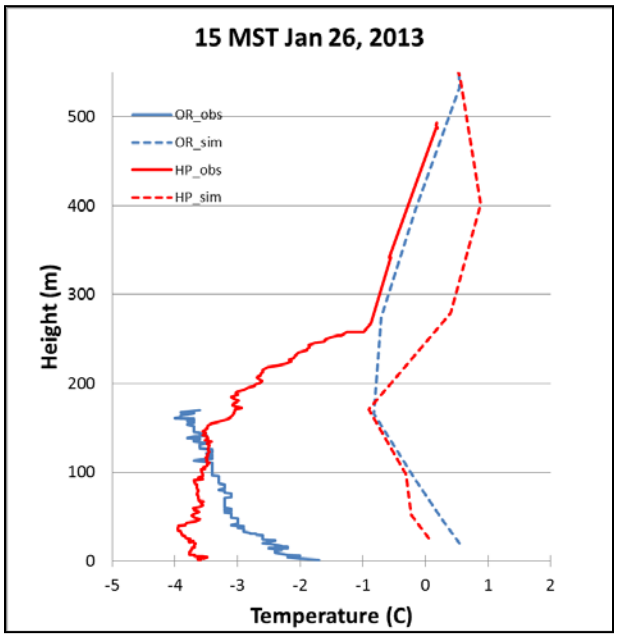


Figure 2-26. Observed (solid) and simulated (dash) temperature vertical profiles at Ouray (blue) and Horsepool (red) at 15 MST on Jan 26, 2013.

Conclusions

Additional development of both meteorological and photochemical models is needed to adequately simulate wither ozone episodes. While current model chemical mechanisms are able to roughly reproduce observed peak ozone concentrations when used in simple box models with observed initial conditions, there are concerns whether these mechanisms, when used in photochemical grid models, might not be able to accurately simulate the impact of emission reductions on ozone levels. Results from UBOS 2013 and the Upper Green Winter Ozone Study indicate that winter ozone models must incorporate additional chemical reactions involved in mid-day HONO production and properly account for the impact of cold temperatures on reaction rates and branching ratios. Additional work on meteorological models is also needed as current modeling approaches have significant difficulty simulating the cold pool conditions associated with winter ozone episodes.

E.3: What are the main issues regarding winter ozone formation that should be the focus of future studies?

Background

Results from the UBOS 2012 and 2013 studies, together with results from the Upper Green Winter Ozone Study, have significantly improved our understanding of the key characteristics of winter ozone episodes in western oil and gas basins. Of particular value are the comparisons of measurements made during UBOS 2012 when ozone episodes did not occur with those made during UBOS 2013 when several high ozone episodes were observed. As with any scientific endeavor, however, these studies have also identified several issues which require further investigation.

Finding E.3.1: Additional measurements are needed to investigate the validity of the reported HONO measurements to determine if the hypothesized large HONO source is in fact important. If it is, additional measurements are needed to validate and accurately characterize the vertical distribution and temporal variations of HONO and reduce uncertainties in vertical flux calculations for HONO and related species (HCHO, HNO_3 and N_2O_5). Model chemical mechanisms must be updated to incorporate heterogeneous HONO production.

Results from UBOS 2013 identified a potentially significant daytime, surface HONO source when snow is present as discussed in Section 2.3 and Section 5, but much uncertainty remains about the strength of this source and the resulting vertical extent of elevated daytime HONO concentrations. It must be noted that the HONO concentration measurements were made using a single method (acid CIMS – see Section 5.2.9) and require verification by comparison with other measurement methods such as LP-DOAS (Stutz et al., 2000) and LOPAP (Kleffmann et al., 2002). HONO measurements by instruments utilizing a variety of detections schemes are needed at higher elevations above the surface to better quantify the source strength.

Finding E.3.2: Additional data are needed to quantify the contributions of different sources of primary formaldehyde.

Results from UBOS 2013 showed that formaldehyde is a key source of radicals that drive ozone production under winter episode conditions, but the relative contributions of different potential sources of directly emitted formaldehyde such as use of methanol contaminated with trace amounts of formaldehyde or diesel engines, are not well characterized. This makes it difficult to design control strategies that target formaldehyde. Chemical analysis of methanol used during winter oil and gas operations for possible formaldehyde contamination and better inventories of other formaldehyde sources are needed.

Finding E.3.3: Additional work is needed to build a meteorological model simulation able to accurately capture the key features of cold pool conditions associated with winter ozone episodes.

Current meteorological models have well known deficiencies when it comes to simulating cold pool conditions (see, for example, Holstag et al., 2013). Initial attempts at simulating Uinta Basin winter cold pool events by several groups including Utah State University, University of Utah, and NOAA are consistent with this experience, exhibiting overestimation of surface temperature, PBL height, and surface wind speeds. Additional evaluation of alternative model options and model development will be needed to achieve more accurate simulations of these challenging conditions.

Finding E.3.4: Additional emission inventory development work and inventory evaluation studies are needed.

Simulations of ozone episodes in the Uinta Basin are crucially dependent on accurate spatially and temporally resolved emissions data. Current emission inventory development work as described in Section 9.1 requires further refinement although inventory data have been used in model simulations which have been found to produce elevated ozone concentrations. Additional inventory development work is needed, focusing in particular on refining VOC speciation profiles and evaluating poorly characterized sources such as methanol use (and hypothesized associated formaldehyde) and produced water storage and treatment for which current data are limited (see Section 9.2).

Conclusions

While much has been learned about winter ozone episodes from the UBOS and UGWOS studies, additional, targeted data collection and analysis as described in Findings E.1.1 – E.1.6 above is needed to complete our understanding of these unusual events.

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