FINAL REPORT

Upper Green River Basin Winter Ozone
Summary of Public Information about the Wyoming Phenomenon

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UPPER GREEN RIVER BASIN WINTER OZONE:
A SUMMARY OF PUBLIC INFORMATION ABOUT THE WYOMING PHENOMENON

1. EXECUTIVE SUMMARY

1.1. Non-Attainment Process

Poor air quality conditions, including high ozone levels, have been observed during some winters in Wyoming’s Upper Green River Basin (UGRB) since 2005 (Environ International Corporation, 2008). In 2009, the state of Wyoming recommended that the UGRB be designated as “non-attainment” with respect to the national ozone standard. The suggested non-attainment area included all of Sublette County, and adjacent sections of Sweetwater and Lincoln counties.

A technical support document submitted with the recommendation provided an analysis of air quality, emissions, meteorology, and geographical data, as well as other factors relating to the non-attainment area and winter ozone formation in Wyoming. The analysis concluded, “Sources within the Basin emit significant levels of precursors [...] and emissions from outside the [Basin] do not significantly influence the formation of ozone during and immediately preceding episodes of elevated ozone” (WDEQ, 2009). Population densities, traffic, and commuting patterns were not found to be important factors. Terrain and meteorology factors, however, caused temperature inversions that allowed ozone precursors to become more concentrated within the inversion layer. The Environmental Protection Agency (EPA) supported Wyoming’s recommendation.

1.2. Contingency Plan

In response to the EPA’s non-attainment designation, the State of Wyoming will produce a State Implementation Plan for reducing ozone levels (WDEQ, 2008). In the meantime, Wyoming plans to continue with its contingency plan for reducing ozone levels that stipulates field studies, increased federal reference monitors, models that replicate high winter ozone conditions, partnerships with emissions sources to reduce air pollution, additional requirements for new permits, voluntary emissions reductions, and short-term emissions reduction plans and public notifications when high ozone is forecast. A citizen task force has also been charged with advising the Wyoming Department of Environmental Quality (WDEQ) on potential solutions to air quality problems.

1.3. Reports

1.3.1. Models

Modeling efforts began with a photochemical box model that assumed that all chemical and physical processes occurred within a well-mixed column of air. One day was chosen to represent a “base case” of winter ozone formation, and the simulation for this day produced a peak ozone concentration consistent with observed values. Additional box model simulations showed that small-to-moderate NOx reductions were actually likely to increase ozone.

The state also developed a conceptual model of winter ozone events in the UGRB in order to “select ozone episodes for photochemical modeling, evaluate model performance, and prepare evidence to develop and support regulatory decisions” (Stoeckenius and Ma, 2010).
conceptual model report included detailed analyses of factors and known information relevant to winter ozone formation. The report concluded, “Photochemical modeling of UGRB winter ozone episodes should include the period from the beginning of February 2008 through at least 12 March” (Stoeckenius and Ma, 2010).

In preparation for the photochemical model, a CALMET wind field was developed and executed for February 1 – March 31, 2008. “Output compared favorably to observational data” (TRC, 2009).

The state hired a contractor to run the CALGRID photochemical grid model to replicate high winter ozone levels in the UGRB. Results were provided for five runs, focused on ozone formation at the Jonah site, which is very close to emission sources. One run over-predicted ozone concentrations, while all other runs under-predicted ozone concentrations. Photochemical grid modeling is still underway in 2012.

1.3.2. Annual Studies

Since 2007, WDEQ has sponsored annual winter ozone studies. The 2007 study was curtailed mid-way through the study period because elevated ozone concentrations were not observed.

Conditions in 2008 were more favorable to ozone formation due to more extensive snow cover and longer periods of low-level inversions. High ozone concentrations were observed on 14 days during the study period. The 2008 study provided information to develop a conceptual understanding of high ozone events and provided data needed for model development.

Conditions were less favorable to ozone formation in 2009, yet the 2009 study confirmed the findings of the 2008 study and provided an expanded database of monitoring data to contribute to the conceptual understanding and modeling of ozone events in the UGRB.

While there were no elevated ozone events in 2010, this year’s study provided valuable monitoring data for comparison to the other studies.

The 2011 study focused on “vertical distribution of ozone and ozone precursors” (Meteorological Solutions Inc. et al., 2011). A shallow inversion and low mixing height were found to be critical to initial ozone development, but there is evidence of ozone development within a plume of precursors at any given level. Elevated ozone concentrations were observed unexpectedly at Wyoming Range, a high elevation site at the western edge of the UGRB, indicating that no area of the UGRB was isolated from potential ozone transport.

Snow cover was found to be one of the most important factors for ozone formation. Other ozone forecasting criteria, developed using data from annual studies, include low wind speeds and relatively strong, low-level inversion conditions.

The table below lists the number of days on which the 8-hour ozone concentration exceeded the national standard of 75 ppb at at least one of the sites included in the study. If the average of the fourth highest 8-hour average ozone concentration over the last three years exceeds 75 ppb, the ozone standard is not met.
1.3.3. University of Wyoming

The University of Wyoming was also studying the UGRB ozone phenomenon. This effort included short-term ozone and precursor monitoring at five sites throughout the study area, continuous monitoring at a mobile laboratory, and spatial ozone surveys. Results were consistent with the WDEQ studies.

1.3.4. Nature Geoscience

Scientists from the National Oceanic and Atmospheric Administration (NOAA), WDEQ, and Air Resource Specialists, Inc. published a paper on the winter ozone phenomenon in Wyoming in *Nature Geoscience* in 2009. The paper presented many of the findings of the 2008 state-sponsored study and noted that winter ozone production could also be occurring in other areas, “where fossil fuel extraction occurs in similar terrain and under similar meteorological conditions” (Schnell et al., 2009).

1.3.5. Health Risks Assessment

An air toxics study was conducted from February 2009 to March 2010 to provide data for the health risks assessment and observed no elevated ozone events during the study period. The health risks assessment concluded risks from ozone and toxic organic compounds were low at the study sites.

1.4. Emissions Inventories

Beginning in 2009, specific emissions inventories were conducted during the first three months of the year in the UGRB for use as model input. In Wyoming, emissions inventories were created via source-based estimations, often using EPA’s AP-42 emission factors.

A 2011 emissions inventory study found, “A significant number of engines were not operating within their permitted level” (Dietrich, 2011). In particular, Caterpillar 3600 engines, which are used for gas compression in the UGRB, were often found uncontrolled, due to operator error, and with emissions similar to that of an uncontrolled rich burn.
1.5. Databases

Several databases and websites were available with information about winter ozone formation in Wyoming, complete datasets from each year of the State-sponsored study, and/or live air quality and meteorological data from the State, from the University of Wyoming’s mobile lab, and from the EPA.

2. INTRODUCTION

This report reviews technical documents and other literature regarding winter ozone events in the UGRB of southwestern Wyoming, and draws on documents and reports found primarily at the WDEQ website [http://deq.state.wy.us]. It is a solicited, independently prepared supplement to the 2012 Uintah Basin Winter Ozone and Air Quality Study, an effort aimed at studying similar ozone events in the Uintah Basin of northeastern Utah. Both basins experience elevated atmospheric ozone during some winters, and because of similar meteorology, climate, topography, and industrial activity, it was widely believed that the cause of winter ozone was essentially the same in both basins. However, the discovery of winter ozone in the UGRB predated that of the Uintah Basin by several years, so Wyoming had had several years’ more experience in measuring and studying the phenomenon. This review is designed to assist researchers who wish to draw on Wyoming’s experience. Figure 8-1 shows a map of both basins.

![Figure 8-1. Uintah and Upper Green River Basins.](image)

The UGRB is located mostly within Sublette County, of which Pinedale (population of 2,030 in 2010) was the largest community (EPA). The county had a total population of 10,247 in 2010, which reflects a 72% increase since 2000 (EPA). Much of the county’s growth was due to increased oil and gas exploration in the area. Other communities in the UGRB (Daniel, Marbleton, LaBarge, Farson, Big Piney) had much smaller populations than Pinedale.

The UGRB is bounded by the Wind River Range to the west, where elevation reaches 13,800 ft. above mean sea level (amsl) and the Wyoming Range to the north and east, where elevation reaches 11,300 ft.
Mountain elevations decrease moving southward along both ranges. Elevation in the lowest parts of the UGRB ranges from 7,000 to 7,400 ft. amsl (WDEQ, 2009).

The terrain greatly influenced local meteorology. In times of calm weather, conditions had been known to create strong, surface-based temperature inversions persisting for days, especially in the presence of snow cover. Poor air quality conditions, including high ozone levels, had been measured during some of these inversions since 2005 (Environ International Corporation, 2008). Since high ozone concentrations are usually observed in urban areas in the summer when an abundance of solar radiation and pollutants are available for ozone formation, elevated ozone levels had not been expected in rural Wyoming, particularly during the winter.

Pollution from oil and gas exploration in the UGRB was thought to contribute to elevated ozone levels. Though emissions from oil and gas exploration are less reactive than emissions from urban sources, volatile organic compounds (VOC) and NO\textsubscript{x} from oil and gas industry sources become highly concentrated when trapped close to the surface during winter inversions (Environ International Corporation, 2008).

Low winter sun angles limit the available solar radiation needed to produce ozone, but snow, which reflects solar radiation and allows inversions to persist, can almost double available radiation and is important for winter ozone production (Environ International Corporation).

In 2009, the State of Wyoming submitted a technical support document to the EPA recommending non-attainment status for all of Sublette County and adjacent portions of Sweetwater and Lincoln Counties. Section 2 below reviews this document as well as the EPA’s response. The final decision regarding non-attainment is expected in 2012. In the interim, the state has already instituted an “Ozone Contingency Plan.” This plan, summarized in Section 4, includes,

- Additional requirements for new oil and gas permits,
- Voluntary reductions on “Ozone Action Days” (days of forecasted high ozone),
- Public notifications when high ozone is expected,
- Additional and ongoing studies and models of winter ozone events in the UGRB (detailed in Section 4), and
- Report summaries of annual State-sponsored winter ozone studies, ongoing University of Wyoming’s studies, pertinent published articles related to Wyoming winter ozone, and the 2010 health risks assessment.

Section 5 summarizes a guidance document provided by the State of Wyoming to help oil and gas operators meet permitting requirements and conduct emissions inventories. Section 5 also summarizes the 2011 emissions inventory study (revealing of major discrepancies between reported and actual emissions). Section 6 lists several public databases where information on winter ozone can be found.

### 3. NON-ATTAINMENT PROCESS

On March 12, 2009, the governor of Wyoming sent a letter to the EPA recommending that the entire state of Wyoming “be designated as attainment/unclassifiable with respect to the eight-hour ozone standard except for Sublette County and partial sections of adjacent Sweetwater and Lincoln counties” (Freudenthal, 2009). One of three monitors in Sublette County had exceeded the 75 ppb
standard for the fourth highest eight-hour ozone level averaged over three years (Freudenthal, 2009). The technical support document, sent under separate cover, included a nine-factor analysis and is summarized below. Figure 8-2 outlines in red the non-attainment area.

Figure 8-2. Proposed non-attainment area (outlined in red) for the UGRB (WDEQ, 2009).

3.1. Technical Support Document Summary

3.1.1. Air Quality Data
Ozone levels exceeding the EPA standard were measured at one of the three Federal Equivalent Method (FEM) monitors in the UGRB. Winter ozone studies had found that elevated ozone in the UGRB generally occurred in January, February, and March under specific meteorological conditions. “VOC detected in ambient air in the UGRB have a strong oil and gas signature [...] Measured ozone levels have not exceeded the standard in the counties adjacent to the UGRB” (WDEQ, 2009).

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3.1.2. Emissions Data (location of sources and contribution to ozone concentrations)

“Oil and gas production and development is the only significant industry emission source within the UGRB” (WDEQ, 2009). The proposed boundary encompassed areas of oil and gas development that were the most likely sources of ozone precursors in the UGRB. Although other areas in Sweetwater County had sources with larger emissions, other factors suggested that those emissions were not contributing to violations in Sublette County.

3.1.3. Population Density & Urbanization (including commercial development)

All urban areas were geographically distant from the UGRB. “Meteorological conditions associated with elevated ozone episodes greatly limit the possibility of emissions transport” from urban areas (WDEQ, 2009).

3.1.4. Traffic & Commuting Patterns

“Traffic volumes are low in Sublette County” (WDEQ, 2009) and “the volume of commuters is low” (WDEQ, 2009). It is unlikely that the interstate, 80 miles south of Boulder, contributed to elevated ozone events.

3.1.5. Growth Rates & Patterns

Population growth in Sublette County was expected to remain at five per cent annually for the foreseeable future. Industrial growth in Sublette County, driven by oil and gas, had increased steadily since 2000, surpassing the surrounding counties.

3.1.6. Meteorology (weather/transport patterns)

The 2008 State-sponsored winter ozone study found that meteorological conditions conducive to ozone formation in the UGRB include “a stable atmosphere, characterized by light, low-level winds, clear or mostly sunny skies, low mixing heights or capping inversions, extensive snow cover, [and] low temperatures” (WDEQ, 2009).

In order to determine the non-attainment boundary, several models were used to create trajectories for air parcels entering and leaving the UGRB. Two-dimensional AQplot back trajectories from ozone monitors showed that air parcels remained in close proximity to the corresponding monitors during the 12 hours leading up to elevated ozone levels. A high-resolution CALMET model wind field “was developed to evaluate ozone-specific meteorology associated with the February 18-23, 2008 ozone episode” (WDEQ, 2009). “Trajectory analyses using this wind field led to the conclusion that regional transport is insignificant, and local-scale precursor emissions transport is the dominant means of transport during the high ozone periods” (WDEQ, 2009).

CalDESK visualization software was also used with the wind field to run forward trajectory analyses from major emissions sources south of the UGRB during the 18-23 February 2008 ozone episode. “These trajectories indicate that the southern boundary of the recommended non-attainment area defines an appropriate demarcation” (WDEQ, 2009), as most trajectories from sources to the south never enter the UGRB. “Most, if not all, of the impact on the Boulder monitor just prior to and during these elevated ozone episodes is from emission sources located in the non-attainment area” (WDEQ, 2009).
3.1.7. Geography/Topography (mountain ranges or other air basin boundaries)
Mountain ranges to the north, east, and west prevented ozone and precursors from moving into and out of the UGRB. The southern boundary of the proposed non-attainment area lied along two significant drainage divides that influenced airflow.

3.1.8. Jurisdictional Boundaries (counties, air districts, etc.)
“The recommended non-attainment area boundary does not fall under a single authority, other than the State of Wyoming” (WDEQ, 2009). Several Indian Tribal Nations and other counties were included in the analysis.

3.1.9. Level of Control of Air Emissions
Wyoming’s statewide New Source Review permitting program required new and modified emission sources to demonstrate that proposed facilities would not prevent the attainment or maintenance of any ambient air quality standard. “The Best Available Control Technology [BACT] process is applied statewide to new [major and minor] sources” (WDEQ, 2009).

Since 2008, permit applicants had been required to demonstrate compliance for ozone. Most applicants chose to offset their emissions, and permit conditions had been established to make their commitments federally enforceable. Most emission sources had also volunteered (at the State’s request) particularly to reduce their emissions in the UGRB when high ozone levels were forecast.

The analysis concluded (1) “Sources within the UGRB [emitted] significant levels of precursors [...] and] emissions from outside the UGRB [did] not significantly influence the formation of ozone during and immediately preceding episodes of elevated ozone” (WDEQ, 2009); (2) the pace of oil and gas industry growth corresponded to a more rapid increase in emissions in the UGRB, (3) population densities, traffic, and commuting patterns were not important factors; and (4) terrain and meteorology factors caused temperature inversions that allowed ozone precursors to become more concentrated within the inversion layer.

3.2. EPA Response
In December 2011, after conducting a similar analysis, the EPA decided to support Wyoming’s recommendations for the UGRB (EPA, 2011; Martin, 2011), and on April 30, 2012, officially issued the non-attainment designation with respect to the 2008 national ground level ozone standard (Jackson, 2012). The designation was classified as “marginal,” the closest of six classifications to meeting the ozone standard (Jackson, 2012; EPA, 2012).

4. OZONE CONTINGENCY PLAN
In response to the EPA’s non-attainment designation, the State of Wyoming planned to produce a State Implementation Plan for reducing ozone levels to concentrations under the national standard of 75 ppb (WDEQ, 2008). In the meantime, Wyoming had been employing a contingency plan to reduce ozone levels. Elements of that plan included the following:
4.1. **Field Studies (Freudenthal, 2009)**

The Upper Green River Winter Ozone Study had monitored air quality and meteorological conditions since 2007. The study aimed to better understand ozone episodes and provide data for modeling studies. A health risks assessment had been produced using data from an air toxics study conducted in 2009. The Wyoming Department of Health was conducting an epidemiologic study in 2012 (WDEQ, 2012). The University of Wyoming was also conducting a separate spatial monitoring study in the UGRB.

4.2. **Federal Reference Monitors (Freudenthal, 2009)**

The number of federal reference monitors in the UGRB had increased from three to six since 2008 (Wyoming Air Quality Monitoring Network, 2012).

4.3. **Winter Ozone Models (Freudenthal, 2009)**

Several contractors had developed box, conceptual, wind field models. Three-dimensional photochemical grid modeling was still underway (WDEQ, 2012).

4.4. **Emissions Reductions via Permitting Process (Freudenthal, 2009)**

Wyoming Air Quality Standards and Regulations (WAQSR) required permit applicants to demonstrate that a proposed new or modified facility would not prevent the attainment or maintenance of any ambient air quality standard (Finley, 2008). The requirements also included the use of Best Available Control Technology (BACT) to reduce emissions wherever possible.

Air quality modeling was often used to demonstrate compliance for air quality standards other than for ozone (Finley, 2008). Until 2008, since there was no evidence to suggest that the ozone standard was threatened, modeling for ozone was not required (Finley, 2008). Now, “permit applications for sources in Sublette County must include demonstration of compliance with the [...] requirement for ozone” (Finley, 2008).

Because there are no good models available for ozone in the UGRB, most permit applicants had chosen to offset their new emissions by reducing current emissions at one of their facilities. After Aug 1, 2008, applications required an offset of 1.5:1 for VOC emissions increases and 1.1:1 for NOx emissions increases (Finley, 2008). Inter-company trading was considered on a case-by-case basis (Finley, 2009).

4.5. **Voluntary Emissions Reductions (Dietrich, 2011)**

Existing levels for precursors of ozone must be reduced in order to reach the ozone standard. The Air Quality Division (AQD) had requested that operators in Sublette County propose and implement voluntary emission reduction activities above those required through the permitting program (Finley, 2008). Efforts to reduce emissions could be banked against future emissions reduction requirements that would be part of the State Implementation Plan (Dietrich, 2011).

4.6. **Short-Term Emissions Reductions (Cederle, 2011)**

Operators in Sublette County submitted short-term emissions reduction plans that could be implemented within 24 hours (Cederle, 2011). An Ozone Action Day was declared when high ozone levels were forecast. Operators committed to reducing ozone in as many of the following ways as possible (WDEQ, 2011):

- Providing awareness training and alerting their employees to Ozone Action Day status;
- Avoiding the overfilling of gas tanks, and tightening vehicle fuel caps;
• Minimizing the idling of vehicles and engines;
• Deferring truck and equipment refueling to evening hours;
• Keeping vehicles tuned up and tires properly inflated;
• Using environmentally safe paints, cleaning products, and chemicals;
• Reducing driving speed by five mph for the entire Ozone Action Day;
• Minimizing the use of ancillary equipment on Ozone Action Days;
• Minimizing vehicle traffic and miles traveled on Ozone Action Days;
• Utilizing various leak detection techniques to prevent the venting of gas;
• Deferring liquid hauling into and out of the field on Ozone Action Days;
• Rescheduling the use of diesel and/or gasoline powered equipment on Ozone Action Days;
• Postponing construction and maintenance activities on Ozone Action Days;
• Limiting drilling operations on Ozone Action Days;
• Postponing fracking and blowdown operations on Ozone Action Days;
• Postponing the initiation of completion and re-completion actions on Ozone Action Days;
• Controlling uncontrolled pneumatic heat trace pumps on Ozone Action Days;
• Delaying line pigging and the charging of desiccant dehydration units on Ozone Action Days;
• Shutting down uncontrolled equipment on Ozone Action Days;
• Adding emission reduction control technology to uncontrolled equipment;
• Suspending all energy recovery and production operations on Ozone Action Days; and
• Enacting any other emission control activity suggested by the operators.

After each Ozone Action Day, operators reported emissions-reducing activities to the AQD (Davis, 2011).

4.7. Public Notifications
On the AQD website, users could sign up to receive daily ozone forecast e-mails, and WDEQ issued daily ozone forecasts through the local radio stations and in the local newspaper (WDEQ, 2008). Government agencies, local businesses, and residents of Sublette County were also asked to reduce emissions in any way possible on Ozone Action Days (Cederle, 2011).

4.8. Citizen Advisories
“The purpose of the Upper Green River Basin Air Quality Citizens Advisory Task Force [was] to consider and advise [WDEQ] on potential solutions to reduce ozone” (WDEQ, 2012). The task force included Sublette County citizens; representatives from local conservation groups; government officials from the State, County and city levels; representatives from oil companies that operate in the area; and representatives from the WDEQ, Bureau of Land Management, and the US Forest Service (WDEQ, 2012). These stakeholders met in Pinedale five times between February and June 2012 and were expected to meet again in the summer of 2012 (WDEQ, 2012). The University of Wyoming’s Ruckelshaus Institute guided the task force in collaborative decision making. The meeting in June focused on evaluating the options the group had generated for solving air quality problems in the UGRB. Most options focused on reducing industry emissions in the area (Ruckelshaus Institute, 2012).
5. REPORTS

5.1. Modeling
Ozone data from Roosevelt, Horse Pool, and all other study sites are discussed in Study Component 2.

5.1.1. Photochemical Box Model
“A box model is a simple representation of the atmosphere which assumes that all thermodynamic and other chemical and physical processes occur within a well-mixed column of air extending from the ground to the top of the mixed layer” (Nopmongcol et al., 2010). This assumption fit well for ozone episodes in the UGRB, as air is trapped within the mixed layer in the UGRB during ozone episodes. A contractor (Environ) used the OZIPR photochemical box model with the CB05 chemical mechanism for the simulation. The NO$_2^*$ reaction was added to the chemical mechanism in an attempt to increase accuracy. Model inputs were obtained from UGWOS 2008.

20 February 2008 was determined to be the best day to represent a “base case” of winter ozone formation in the UGRB for the box model. The base case simulation produced a 122 ppb peak ozone concentration, which was consistent with observed values.

One hundred additional box model simulations with varying initial NMOC (Non-Methane Organic Compounds) and NO$_x$ were used to construct EKMA (Empirical Kinetic Modeling Approach) diagrams. These diagrams showed “a NO$_x$ dis-benefit across a broad range of NO$_x$ concentrations,” meaning that small-to-moderate NO$_x$ reductions are likely to increase ozone, an example of which is included in Figure 8-3 (Nopmongcol et al., 2010).

![Figure 8-3. EKMA diagram of effects of changes in NO$_x$ and VOC concentrations on predicted ozone in box model for UGRB.](image-url)
“A comprehensive photochemical grid modeling analysis would be needed to evaluate the effectiveness of VOC vs. NOx controls in southwest Wyoming” (Nopmongcol et al., 2010). The box model did not account for the introduction of additional emissions.

“Ozone production was found to be very sensitive to UV albedo (i.e., snow cover) and aloft ozone concentration, while being relatively insensitive to CO and CH4 concentrations. Daily maximum ozone was higher when atmospheric mixing height was low confined to a shallow layer past mid-day” (Nopmongcol et al., 2010). Xylenes and formaldehyde were found to be most likely to form ozone, followed by alkenes and acetaldehyde, then toluene and, finally, alkanes.

5.1.2. Conceptual Model
The State developed a conceptual model of winter ozone events in the UGRB in order to “select ozone episodes for photochemical modeling, evaluate model performance, and prepare evidence to develop and support regulatory decisions” (Stoeckenius and Ma, 2010).

Review of scientific literature
A review of relevant literature was presented on issues that included “questions about the level of ‘background’ ozone in the western U.S. and the role of snow packs in photochemical processes occurring within the atmospheric boundary layer [...] and] potential ozone measurement biases” (Stoeckenius and Ma, 2010).

“Reported background levels at [other rural western US] sites [were] consistent with the roughly 55-65 ppb ozone levels observed in the Jonah-Pinedale area, both at the surface and aloft during a deep, well mixed northwest flow event above the strong low-level inversion” (Stoeckenius and Ma, 2010).

In Antarctica, vertical ozone profiles above snow, under stable atmospheric conditions, [showed] a decrease in ozone with height, consistent with photochemical ozone formation at the snow’s surface. Studies have shown that sunlight activates chemical processes in the top-most layer of snow-packs, releasing NOx into the boundary layer and resulting in the production of ozone.

Due to the high level of VOC measured in the UGRB and a possibility of ozone measurement interference from the VOC, the UGWOS compared the UV method to chemiluminescence and a potassium iodide electrochemical methods and found no evidence of interference.

Analysis of historical trends in area ozone concentrations
Researchers analyzed the past ten years of available ozone data from Wyoming and surrounding states. No significant trends were noted (except at one site in Colorado, determined to be a local phenomenon). The Pinedale site, where ozone concentrations are consistently lower than at the Boulder site, was the only site in the UGRB that had data available for all ten years.

Analyses of meteorological and air quality conditions
Meteorological conditions associated with elevated ozone events in 2008 included,

- A mean pressure ridge (an area of high pressure) west of Wyoming,
- Elevated 700 mbar pressure-level height,
- Warmer temperatures aloft,
• Low wind speeds aloft and at the surface,
• Lack of directional wind shear,
• Light or no cloud cover,
• Mixing depths less than 125 m above ground level,
• Extensive snow cover, and
• A mid-day wind reversal from northeasterly to southwesterly.

There was a strong correlation between monitoring sites within the UGRB for elevated ozone events, but UGRB ozone episodes were not correlated with episodes outside the basin. Aircraft data suggested that high ozone concentrations were bounded by the mountains that create the UGRB. Ozone levels above the inversion layer were consistent with non-episode days.

Examination of magnitudes and locations of emission sources
Wellheads and compressor stations were the dominant precursor emission sources in the UGRB. Sources were lined along a northwest-to-southeast axis. When winds blew northwesterly and southeasterly during ozone episodes, as they often did, emission build-up was magnified.

Analysis of meteorology and air quality during high ozone events
“Ozone episodes in the UGRB [had] been observed as early as late January and as late as mid-March. Low solar elevation angles prior to late January limited available UV radiation flux, while shorter nights and strong solar insolation after about mid-March lessened overnight surface cooling, inhibited snow cover, and resulted in greater daytime mixed layer growth” (Stoeckenius and Ma, 2010).

Trajectories produced by the AQplot model indicated “high concentrations of precursor emissions [were] associated with tightly spaced well pads and multiple, closely-spaced drill rigs operating in clusters at key locations” (Stoeckenius and Ma, 2010).

Comparisons of ozone precursors (field study vs. emission inventory)
Emissions inventory VOC/NOx ratios were significantly lower than the observed ratios from the 2008 UGWOS study, suggesting that VOC emissions were under-estimated and NOx emissions were overestimated. However, “lack of mixing within the stable morning boundary layer could skew the comparison” because NOx emissions were “subject to buoyant plume rise, whereas most VOC [were] from more neutrally buoyant [...] sources” (Stoeckenius and Ma, 2010).

Review of carry-over evidence during multi-day episodes
There was no compelling evidence of ozone carry-over during multi-day episodes. If carry-over did occur, it did not play an overwhelming role in determining ozone concentrations on the following day. Significant ozone development could occur in a single day.

5.1.3. CALMET Diagnostic Model
CALMET Phase I included an initial evaluation of the CALMET wind field developed using routine hourly observational data and intensive periodic data from the UGWOS study, 18-24 February 2008. Phase II was designed to develop a two-month database using the same domain definition and type of data.
The Phase II CALMET database used meteorological data from UGWOS (continuous spatial, SODAR, and high resolution data gathered periodically), ten industrial sites, 35 National Weather Service sites, three regional upper air sites, and 89 hourly precipitation sites.

A 1 km$^2$ grid resolution was used for a refined definition of land-cover types and to account for the complex wind patterns of mountain ranges. Geophysical properties of snow-covered cells were modified based on snow depth and age rather than static values.

The EPA-approved version of CALMET was executed for 01 February through 31 March 2008, and “model output compared favorably to observational data” (TRC, 2009).

5.1.4. CALGRID Photochemical Model
TRC was contracted to run the CALGRID photochemical grid model to replicate high winter ozone levels. Results were provided for five runs, focused on ozone formation at the Jonah site, very close to emission sources. Photochemical grid modeling was still underway in 2012.

Model input
“The emission inventory [was] one of the most important and complex model inputs for photochemical modeling” (TRC, 2010). TRC and WDEQ processed the emissions inventories to conform to the CB-IV chemical mechanism, which lumps compounds according to structure into four categories: inorganic species, organic species that are important to represent explicitly, carbon bond surrogates, and molecular surrogates.

The Emission Modeling Clearinghouse Speciation methodology/data, which was the primary technique, assigned a code for each source. The VOC amount was then scaled to include methane and ethane, after which the code was matched against a profile code, providing the lookup index to a table of mass fractions. Formaldehyde values were replaced with actual values from the inventory. The total mass was preserved by rescaling the non-formaldehyde species.

“Another technique converted each reported organic pollutant in the emissions inventory into CB-IV species” (Newman et al., 2010). Unknown compounds were assumed to be zero.

“The model also [required] stack parameters to calculate the plume rise (if any) of emissions. Many stationary sources [...] had defined stack parameters” (TRC, 2010). Representative parameters for well production sources were developed and assessed. Runs 1 through 4 used well production stack parameters that minimized the plume rise and Run 5 used more refined stack parameters.

“Each of the five runs [...] represented] an additional emission inventory assumption, with each assumption generally considered to be an improvement or a refinement over the prior analyses” (TRC, 2010). For Run 5, operator-reported speciation was used, when possible; compressor stations were changed to reflect actual emissions; drill rigs were run at their reported values; and mobile sources were added to the inventory.

The meteorological database was developed using the CALMET model as described in the section above.

The CALGRID model was run at 30 steps per hour in order to maintain smooth concentration fields. The UV factor was increased to 2 to account for snow cover.
Model performance
Runs 1 and 2 used an overall average profile, which may have over-estimated some VOC emission rates for model input. Run 1 had similar values to Runs 3 through 5 and produced more ozone due to its more reactive mix of VOC. Run 2 over-predicted ozone concentrations, while all other runs under-predicted ozone concentrations.

Run 5 model results and observed canister data were compared to identify any systematic model bias. Species such as formaldehyde, xylene, and toluene had values of the same magnitude, indicating proper emission inputs but flawed transport and dispersion. Some species, like olefins and higher aldehydes, were consistently under predicted.

The CB-IV mechanism was tested by simplifying model inputs until they represented a box model. This box model produced ozone concentrations similar to the box model that used the CB05 chemical mechanism. The chemical mechanism was not the sole reason for under prediction of ozone.

Sensitivity analyses
There was high sensitivity to the magnitude and reactivity profiles of the emissions. Sensitivity analyses also indicated the need for the additional UV radiation from snow cover to generate photochemistry.

No significant difference was observed when vertical velocities were suppressed. No significant difference was observed when Run 5 emissions were used as input for the new version of CALMET. Initial results from the new version of CALGRID are similar to those obtained from the old version.

5.2. Annual Upper Green River Winter Ozone Study (UGWOS) Reports
Concentrations of NO\textsubscript{x} were variable on short time scales at both Roosevelt and Horse Pool, reflecting

5.2.1. UGWOS 2007
Although elevated ozone concentrations were recorded in 2005 and 2006, there were only a few days in 2007 on which slightly elevated ozone concentrations were recorded. The most likely reason for low ozone levels in 2007 was a lack of snow cover. Measurements from days when snow cover was present indicated that up to 80% of incoming UV radiation was reflected, considerably increasing the amount of UV radiation available for ozone chemistry, while as little as 10% of incoming radiation was reflected when snow cover was not present (Environ International Corporation, 2008). Snow also allows temperature inversions to persist late into the day by limiting surface heating.

UGWOS operations were curtailed mid-way through the study period and remaining resources were allocated for the 2008 study. Conditions were much more favorable for ozone formation in 2008 because snow cover was present for almost the entire study period (Environ International Corporation, 2008).

5.2.2. UGWOS 2008
Field Operations
Surface meteorological and air quality measurements were recorded continuously from mid-January through the end of March. Monitors were located at three permanent WDEQ sites, the Pinedale CASTNet site, the miniSODAR site (which also collected upper air data), and on an
extended network of five other temporary “mesonet” sites, which used portable 2B ozone analyzers. Incoming and reflected radiation were measured at the WDEQ Boulder site, but radiation data were compromised and invalidated.

There were three Intensive Operating Periods (IOP) when conditions favorable to ozone formation were forecast. During IOP, VOC sampling was conducted three times daily at WDEQ sites; airline sampling flights were conducted twice daily; and rawinsondes were released three times daily. Rawinsondes collected ozone data during two of the daily flights.

**Results**
Continuous and intensive measurements indicated that elevated ozone events in 2008 were characterized by high pressure and a temperature inversion which created a stable vertical atmosphere, clear skies and light surface winds, an afternoon wind reversal at the surface from northwest to southeast that recirculated pollutants within the UGRB, and extensive snow cover. High ozone generally occurred mid-day on the day after favorable conditions developed. Elevated ozone peaked in the afternoon and could last until midnight. Ozone or precursors seemed to carry over from previous days, but the 2011 study found no evidence of carryover (UGWOS 2011 Report Summary). Elevated ozone persisted until brisk winds arrived and scoured the area.

The 8-hour average ozone concentration exceeded 75 ppb on 14 days during the study. Concentrations at Boulder were usually highest. “Elevated ozone was confined to a relatively shallow, mixed layer, extending at most a few hundred meters above ground level on IOP days” (Environ International Corporation, 2008). Peak ozone concentrations were often above the surface but within the stable layer.

The aircraft measured regional background ozone concentrations of 50-60 ppb above the inversion layer during elevated ozone events. “Both surface and aircraft data showed that ozone and PM [particulate matter] concentrations within the mixed layer were frequently positively correlated” (Environ International Corporation, 2008).

“Most [VOC] samples contained only a limited range of fairly common hydrocarbon species” associated with oil and gas exploration (Environ International Corporation, 2008). The total reactivity of VOC found in the study region is low compared to typical urban air samples because of the high percentage of alkanes in the study region. VOC and NOx concentrations were very high at Jonah when temperature inversions were present. Concentrations at Daniel and Boulder were elevated but lower than at Jonah. It was recommended that the 2009 study investigate the unidentified organic compounds collected at the Boulder site.

The 2008 study provided information to develop a conceptual understanding of high ozone events and provided data needed to develop models designed to numerically re-create high ozone events in the UGRB.

**5.2.3. UGWOS 2009**

**Field Operations**
As in 2008, surface meteorological and air quality data were collected continuously at permanent sites and temporary mesonet sites. Upper air data were collected at the SODAR site. Data from monitoring sites, which were part of the Sublette County Health Risks Study, were
also included. A temporary shelter next to the Boulder site continuously collected SO$_2$, CO, and nitrogen species data, and a pair of UV radiometers measured incoming and outgoing radiation.

During IOP, VOC and carbonyl measurements were performed at Boulder and Jonah. These measurements were also performed at the SODAR site during the third IOP. Rawinsondes were released four times daily and usually measured ozone during the two afternoon launches. On IOP days, and several other days with snow cover, an actinometer measured the NO$_2$ photolysis rate at Boulder.

**Quality Assurance**

A quality assurance audit revealed a bias in the 2B ozone analyzer data. Most likely, the apparent 2B analyzer bias is due to the placement of the mesonet sites. At Boulder, a 2B ozone analyzer and a FEM analyzer were co-located for comparison. Data initially showed considerable disagreement. After a faulty pump was changed on the 2B analyzer, however, data showed better agreement.

Ozonesonde readings were lower than ground truth readings for the first IOP, but were closer by the third IOP. Sondes had been stored in a cold environment despite the manufacturer’s recommendation that they be stored in a warmer environment.

VOC canister duplicates generally agreed well. Carbonyl duplicates did not show good agreement one day, but showed better agreement at a later date. Ethanol results for the 2009 study are suspicious.

**Results**

Snow cover was not as extensive or long-lived in 2009 as it was in 2008. Mixing heights were generally higher in 2009, which also lowered surface ozone concentrations. The frequency and severity of ozone episodes during 2009 were not as extensive as in 2008. Ozone over 75 ppb was observed on just three days during the study but never at any of the permanent monitoring sites. However, high ozone levels were unexpectedly measured one day at South Pass, between midnight and dawn. South Pass is a high elevation site in the Wind River mountain range.

The expanded network of sites allowed for the creation of ozone isopleths. “There was significant spatial variability in ozone with isolated peak concentrations occurring at locations determined by the predominant wind directions on each day” (Environ International Corporation, 2010). Below is an example of an isopleth created for 2 March 2009 at 12:00 (on the left) and 14:00 (on the right) (Environ International Corporation, 2010). Green arrows indicate wind direction and speed.
Rawinsondes and ozonesondes generally confirmed known characteristics of ozone episodes. However, during two of the IOP, elevated layers of higher ozone concentrations were measured at 100-300 meters above ground level. Ozone may have been generated aloft or transported from upwind areas. Elevated plumes of ozone that were observed in 2008 upper-air data sometimes impacted the surface, but plumes in 2009 were decoupled from the surface boundary layer.

At the SODAR site, key conditions common for periods of higher ozone concentrations included:

- Morning mixing heights \( \leq 60 \) meters, which create stable conditions that trap morning surface emissions,
- Surface wind direction from the northeast where local sources associated with drilling and production are located,
- Surface wind speeds \(< 2\) m/s morning and afternoon,
- Median afternoon mixing heights > 100 meters,
- Reflected UV \( \geq 50\% \) of the incoming UV radiation (enough snow cover). The UV sensor may not be representative of regional snow cover. (Environ International Corporation, 2010)

Non-methane hydrocarbon (NMHC) sampling in 2009 confirmed the importance of toluene, m-p-xylene, and benzene. Carbonyl species concentrations were similar to 2008.

The 2009 study confirmed the findings of the 2008 study and provided an expanded database of monitoring data to contribute to the conceptual understanding and modeling of ozone events in the UGRB.
5.2.4. UGWOS 2010

Field Operations
In 2010, UGWOS focused on monitoring spatial and temporal patterns of ozone and meteorology. All measurements were continuous. Meteorological and air quality measurements included wind, temperature, and ozone measurements performed at sites throughout the UGRB; boundary layer wind profiles from the miniSODAR, which was moved to the Boulder site; and HONO measurements at the Boulder site.

Results
Frequent, weak storms did not generate much precipitation during the 2010 ozone season. Lack of snow cover most likely contributed to weak ozone development. There were fewer instances of defined mixing layers in 2010 than in previous years.

Only a few eight-hour ozone concentrations exceeding 60 ppb were recorded during two events in 2010. Higher concentrations were generally in the northeast quadrant of the study area. High maximum one-hour ozone concentrations were recorded in the vicinity of drill rigs (black dots) and compressor stations (blue dots) (Meteorological Solutions Inc. et al., 2011).

![Figure 8-5. Ozone concentrations for 15 Jan. through 31 Mar. 2010.](image-url)
Ozone events in 2010 were generally characterized by the same elements as in previous years. Days on which ozone levels were high also had a three-to-four hour period of calm winds in the late morning. This morning calm period might have been important to precursor accumulation.

A slightly better mixed atmosphere in the afternoon may also have been important for ozone formation. Some mixing might have allowed ozone or precursors that were trapped above the mixed layer in the morning to affect the surface. However, some elevated ozone events occurred without afternoon mixing and data on the subject is inconsistent.

Main findings of the HONO study:

- HONO levels were correlated with \( \text{NO}_2 \) and \( \text{NO}_x \) and (to a lesser extent) hydrocarbons.
- HONO levels were not correlated with \( \text{PM}_{10} \).
- HONO levels were most enhanced under ESE flow conditions. HONO levels decrease with increasing wind speed.
- UV radiation correlated with HONO levels, suggesting that HONO formation is photo-induced.
- High levels of relative humidity were conducive to high levels of HONO.
- HONO might have been produced secondarily through nitrogen oxides. (Meteorological Solutions Inc., et al., 2011)

Although conditions were not conducive to ozone formation, the 2010 study provided valuable monitoring data for comparison.

5.2.5. UGWOS 2011

UGWOS 2011 focused on “vertical distribution of ozone and ozone precursors” (Meteorological Solutions Inc. et al., 2011). An unexpected finding of the 2011 study was that a number of high ozone days occurred at elevated sites on the Wyoming Range at the western edge of the UGRB, see below. (All data below comes from Meteorological Solutions Inc. et al., 2011.)

Field operations

Seven permanent monitoring stations provided continuous surface air quality and meteorological data. The Boulder site also had the mini-SODAR and instruments which measured HONO, trace NO, \( \text{NO}_2 \), and \( \text{NO}_x \) and speciated VOC and PM. A 73-meter tower and a tethered balloon system took continuous meteorological and air quality measurements at different vertical levels. Daily forecasts alerted crews when elevated ozone was expected so that they could prepare for IOP. During the two IOP, the tethered balloon and three-to-four ozonesondes or rawinsondes were released each day.

Results

Tethered balloon data collected during IOP were used to create vertical profiles, and tall tower data were averaged together to produce generalized profiles. These general characteristics in vertical profiles were noted:

- Presence of NO resulted in scavenging in the morning and evening.
- Inversions were strongest in the morning and weakened throughout the day.
- NMHC levels were highest at the surface, and \( \text{NO}_x \) levels were highest at 25 m.
Days with elevated ozone concentrations were further characterized by,

- Stronger morning inversions,
- Stronger NMHC gradient,
- High precursor concentrations,
- A higher NO$_2$/NO ratio at the time of maximum ozone.

Measurements were nearly always below the top of the mixing layer, but these observations from tethered balloon and tall tower data were noted:

- A shallow inversion and low mixing height was critical for initial ozone development.
- Commonly, precursors were trapped at the base of elevated inversions.
- There was no evidence of ozone carryover aloft.
- There was no significant evidence of ozone consistently developing in layers aloft and subsequently being mixed down to the surface in the afternoon. There was, however, evidence of ozone development within a plume of precursors at any given level. A correlation between ozone and NMHC was noted at all levels especially in the afternoon/evening when NMHC < 6 ppm.
- VOC concentrations were highest at the surface and NO$_x$ concentrations were highest above the surface.
- The NMHC/NO$_x$ ratio was higher near the surface in the morning. Balloon data suggested this was due to higher NO$_x$ in the stable layer aloft, while tall tower data suggest it was associated with low level NMHC sources.
- NO$_x$ plumes aloft were frequent at the balloon site but non-existent at the tall tower site (the tower was farther away from local emission sources). VOC plumes were noted at both sites. Fresher plumes were closer to the ground.

“The typical inversion base was much higher than the 100 meter measurement limit” (Meteorological Solutions Inc. et al., 2011). Observations were limited to available collected data from below the inversion base.

**Wyoming Range**
The Wyoming Range site is on the far western edge of the UGRB at high elevation. High ozone concentrations at the site were unexpected, but 11 days had eight-hour concentrations above 65 ppb, and two days had concentrations above 80 ppb. An analysis of a high ozone event at Wyoming Range revealed these conclusions:

- Persistent (not necessarily light) southeast winds were within lower levels of the inversion transport ozone.
- High ozone at Wyoming Range developed 6-24 hours after sites at lower elevations.
- As the inversion strengthened and deepened, ozone/precursor-laden air was transported northwestward.
- Strengthening inversions could be deep enough to build over Wyoming Range, allowing for the ozone-laden air to be transported with minimal dispersion.
- Snow cover enhanced these episodes.
Clear skies and abundant radiation enhanced the atmospheric chemistry that creates these events.

Daily variability showed that ozone can quickly be formed and transported to outlying areas.

There were likely no areas of the UGRB isolated from potential ozone transport.

**Precursors**

“In reviewing the Boulder 2011 hydrocarbon data, a strong linear correlation between NMHC [Non Methane Hydrocarbons] and THC [Total Hydrocarbons] was noted on high ozone days” (Meteorological Solutions Inc. et al., 2011). NMHC concentrations were higher in 2011, possibly due to more snow cover in 2011, which created stronger inversions and lower mixing heights. “Ozone concentrations appear highly correlated to NMHC, though NMHC is likely a good surrogate for all ozone precursors” (Meteorological Solutions Inc. et al., 2011).

HONO concentrations correlated with HNO₃ and UV radiation. Nighttime HONO correlated with NO₂/NO₃, while daytime HONO correlated with NOₓ. HONO was less correlated with NMHCs and CH₄ and not correlated with PM.

The HONO/NOₓ ratio peaked in the afternoon with ozone. HONO formation might have occurred through NOₓ conversion in highly polluted air masses. HONO levels were enhanced under SW-WSW wind conditions. A shallow daytime mixing layer and/or high relative humidity enhanced HONO.

**General Conclusions**

Snow cover was important for ozone development. “The tower data showed that, with snow on the ground, temperature inversions formed at or near the surface nightly. When wind speeds remained low (less than 10 m s⁻¹), these inversions persisted into the afternoon hours, capping ozone precursor concentrations as well as the generated ozone. The height of the inversion cap played a part both in the concentration and regional extent of ozone episodes” (Meteorological Solutions Inc. et al., 2011).
Table 2. Maximum concentrations (ppb) and number of days exceeding EPA ozone standard, 2008-2011.

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<td>Wyoming Range</td>
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</tr>
</tbody>
</table>

5.2.6. UGWOS 2012

UGWOS 2012 will continue ozone, NOₓ, meteorological, and camera operations at 2011 sites and at Jonah (WDEQ, 2012). Snow sticks will be added to four sites. MiniSODAR and true NO₂ operations will continue at Boulder with the addition of NOₓ sampling. Speciated VOC samples will be collected at four sites and a comparison analysis will be conducted by a contractor.
5.2.7. UGWOS Forecasting Criteria

Based on a comparison of weather patterns associated with ozone formation in the UGRB over the years, these criteria have been developed for forecasting ozone episodes (Meteorological Solutions Inc., 2011):

- Surface wind speeds < 8 knots,
- 700 mbar pressure-level wind speed < 20 knots,
- Snow cover,
- Surface and 700 mbar delta temperature about 10°C,
- Surface and 700 mbar lapse rate about 0.010°C/m.

Refining forecast data for delta temperature and lapse rate may require more sounding data.

5.3. University of Wyoming Reports

In 2009, the University of Wyoming conducted an ozone study in the UGRB. Outcomes included,

- “Short term ozone and ozone precursor monitoring took place at five sites throughout the study area.” The mobile laboratory monitored ozone, oxides of nitrogen, methane, and other hydrocarbons.
- “To conduct ozone spatial surveys during periods when high ozone levels were forecast,” fifty ozone samplers were placed throughout the study area by volunteers. Ozone isopleth maps and movies were created (University of Wyoming Department of Atmospheric Sciences, 2012).

In 2010, the Pinedale Anticline Spatial Air Quality Assessment (PASQUA) began. “Monitoring was conducted from November of 2010 through April of 2011, and will continue during the 2011-12 ozone season [...] The project consists of continuous monitoring at the UW MAQML [University of Wyoming Mobile Air Quality Monitoring Lab], a spatial BTEX [Benzene, Toluene, Ethylbenzene, and Xylenes] survey, a spatial NO–NO₂–NOₓ survey and six [VOC] canister sampling surveys” (University of Wyoming Department of Atmospheric Sciences, 2012). The spatial assessment included 60 sites in UGRB. The mobile laboratory was positioned downwind of major oil and gas fields. Study data can be used to assess emissions inventories and will provide better inputs for modeling (University of Wyoming, 2009).

5.3.1. Spatial Surveys of BTEX and NOₓ

The BTEX/NOₓ spatial survey was conducted 22 February to 1 March 2011. The gel on the NO₂ filter froze, and so only NOₓ values were reported.

“BTEX compound values were highest along Mesa Road within the PAPA (Pinedale Anticline Project Area) [...] NOₓ levels had a different distribution to that of BTEX. Highest concentrations [of NO₃] were reported in three regions: Gobblers Knob near the junction of Mesa and Paradise Roads, along Middle Crest Road, and in the Buckhorn Draw area” (Field and Soltis, 2011).

5.3.2. Spatial Surveys of VOC

Surveys one and two were designed to assess pollutant distribution for the entire area. Surveys three and five focused on the PAPA. Survey five was collocated with the BTEX and NOₓ samplers for a week and measured values along a northwest-southeast line transecting PAPA. Surveys four and six transect through the most concentrated oil and gas development.
“Alkanes [were] by far the dominant hydrocarbon class (85%), followed by aromatics (10%). The highest levels of aromatics were measured at the Mesa sites” (Field and Soltis, 2011).

5.3.3. UW Mobile Air Quality Laboratory Measurements

The Boulder South Road site was east of the Pinedale Anticline Project Area and north of Jonah Field and represented an area not covered by permanent monitoring sites. The mobile lab measured air quality and meteorological parameters continuously from November 2010 through April 2011.

“NOₓ and NO measurements [were] often elevated at the same times as elevated CH₄, NMHC, and VOC levels” (Field and Soltis, 2011).

Wind-rose diagrams indicated that northwesterly and southerly wind patterns were most important. Wind flows from the south had the highest concentrations for most of the air quality measurements. Elevated ozone levels were more evenly dispersed.

The national standard for ozone was exceeded on 11 days. “Elevated ozone levels occurred during the time period between mid-February and March” (Field and Soltis, 2011). The coldest season was associated with higher pollution levels.

5.4. Nature Geoscience Report

Scientists from NOAA, the WDEQ, and Air Resource Specialists, Inc. published a paper on the winter ozone phenomenon in Wyoming in *Nature Geoscience* in 2009. A summary of their article is included here.

The article points argues that production of OH, the primary source of radicals in most areas with summertime ozone production, is likely curtailed in winter. OH is produced from the reaction of O atom with water vapor, and water vapor concentrations are limited in cold air. Thus, alternative radical sources likely exist in areas with significant winter ozone production.

High pressure over western Wyoming brings cold temperatures and lower wind speeds. These conditions, coupled with snow cover, produce strong temperature inversions that curtail vertical mixing, trapping ozone precursors at the surface.

Exceptionally high photochemical ozone production observed in the UGRB in winter is the result of NOₓ and VOC released in the production of natural gas. These precursors become contained within a shallow, stagnant air-layer near the surface and are then rapidly converted into ozone, which is also trapped in the stable layer.

Vertical profiles of ozone show uniformly lower ozone levels in the morning and higher ozone levels in the afternoon beneath the boundary layer. At some sites, ozone was lower in the morning possibly because wind flow had not yet brought ozone and precursors to the site from the gas field. Ozone concentrations track solar radiation with a one- to two-hour time lag. NOₓ concentrations show anti-correlation with ozone, as expected.

The tropospheric ultraviolet and visible radiation model was used to calculate hourly actinic flux and spectral photolysis for ozone formation during a high-ozone winter day and a summer day in Wyoming. Due mostly to snow cover, the photolysis rate for NO₂ was calculated to be 50% greater in the winter than in the summer.
The study showed “no evidence of stratospheric air contributing to the high surface ozone levels” (Schnell et al., 2009). Vertical profiles confirm that ozone was confined to the stable surface layer and diurnal profiles confirm that ozone is correlated with solar insolation.

Winter ozone production could also be occurring in other areas “where fossil fuel extraction occurs in similar terrain and under similar meteorological conditions” (Schnell et al., 2009).

5.5. Health Risk Assessment

Winter ozone formation is highly dependent on reflectance of sunlight by snow (Schnell et al., 2009).

5.5.1. Air Toxics (Air Resource Specialists, Inc., 2010)

Fourteen air toxics monitoring sites (including two co-located sites) collected data between February 2009 and March 2010 for a health risks assessment. Canister and cartridge data included 24-hour integrated filter samples collected every sixth day (Air Resource Specialists Inc., 2010). Hourly meteorological data were collected at all sites. Five sites were also equipped with EPA-equivalent method ozone analyzers. Most sites collected at least 94% valid data.

Ozone levels were highest January through March 2009 and sometimes elevated in April and June of 2009. Formaldehyde, acetaldehyde and Hazardous Air Pollutant (HAP) concentrations were highest over the summer.

5.5.2. Health Risks Assessments (Walther, 2011)

Fifty-one Toxic Air Contaminants (TAC) were chosen for analysis based on professional consultation, UGWOS VOC data, and a citizen request. Compounds beyond the TAC list were tentatively identified in the canister analysis to avoid overlooking important data. Ozone data were also collected and analyzed separately.

Chronic and acute screening concentrations were developed for each TAC in the study to determine which TAC warranted a more detailed risk assessment. TAC with maximum measured concentrations below screening concentrations were deemed to be of no concern to public health. Screening concentrations for short-term health impacts were based on a table from the EPA. Short-term (acute) health effects “relate to exposures to a pollutant for a period of 24 hours or less.”

“Screening concentrations for chronic [long term] health impacts were the lower (more protective) of the concentration that results in a lifetime cancer risk of one in a million, and one tenth of the non-cancer chronic reference concentration” (Walther, 2011).

“Long term health effects include both the risk of developing cancer due to exposure to pollutants [...] and non-cancer health effects associated with exposures to pollutants for more than 24 hours” (Walther, 2011).

Short-Term Health Effects

“The screening analysis of the data indicate[d] that there [was] no potential for significant acute health impacts from the TAC measured by the monitoring network” (WDEQ, 2009-2011).

Long-Term Health Effects

“The potential excess cancer risk from the total set of TAC monitored [...] ranged from 14 to 50 in one million” (Walther, 2011). Actual cancer risk is likely to be much lower. These levels were
much lower than risks in most urban and rural areas. Excess cancer risk below 100 in one million was considered acceptable by the EPA.

“The potential average non-cancer chronic health hazard index from the TAC monitored in this study ranges from 0.28 to 0.53” (Walther, 2011). Actual risk was likely to be much lower. An index below one was not considered significant.

Health Effects from Ozone
Because the study coincided with two seasons with little snowfall (winters 2009 and 2010), large ozone concentrations were not recorded. The fourth highest eight-hour averages for ozone during the study were between 57 and 65 ppb. Higher ozone levels were measured in the years previous to the air toxics study and the year after.

Conclusions
“The estimated health impacts ... are not high enough to suggest a need for a more refined health risk assessment” (Walther, 2011).

The study represented a snapshot in time of ambient concentrations of TAC and ozone for characterizing community-wide exposure. The study was not designed as a workplace exposure assessment or to determine which sources contributed to measured concentrations. The study did not account for changes in emissions patterns over time.

6. EMISSIONS INVENTORIES
In Wyoming, emissions inventories are created by estimating emissions based on their source as described below. Starting in 2009, specific emissions inventories were conducted for the first three months of the year in the UGRB for use as model input. Totals from those inventories are included below (WDEQ, 2009-2011):

<table>
<thead>
<tr>
<th>Year</th>
<th>Total PM</th>
<th>Total NOx</th>
<th>Total VOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>2009</td>
<td>28.24</td>
<td>735.26</td>
<td>3,616.85</td>
</tr>
<tr>
<td>2010</td>
<td>28.04</td>
<td>669.45</td>
<td>2,709.05</td>
</tr>
<tr>
<td>2011</td>
<td>23.71</td>
<td>640.72</td>
<td>2,767</td>
</tr>
</tbody>
</table>

6.1. Emissions Estimates
The general equation for emissions estimation is (US Environmental Protection Agency):

\[ Emissions = Activity \ Rate \times Emissions \ Factor \times (1-\text{Emission \ Reduction \ efficiency \ percentage}) \]

An emissions factor is a representative value that attempts to relate the quantity of a pollutant released with an associated activity. Usually, factors are averages of all available data of acceptable quality. The EPA publishes various emissions factors on their website. Most emissions estimations in Wyoming are made using AP-42 emission factors. Instructions for estimating emissions are provided on the WDEQ website. Selections from an oil and gas guidance document are summarized below.
6.1.1. Storage Tanks
"Flashing and standing/working/breathing losses [...] occur when hydrocarbon liquids are exposed to temperature and pressure changes causing hydrocarbon vapors to be released from the liquids [...] Vapors may contain VOC, HAPs, and H₂S" (WDEQ, 2010).

AQD accepted models were those using Peng-Robinson or S-R-K methods including software like PROMAX, HYSIM, HYSYS, K-FLASH, PROISM, and API E&P TANKS v2.0. Input included chemical properties of the fluids handled and physical operating parameters of the systems and production equipment. Output included volumes, rates and chemical components.

Emissions from storage tanks may also have been physically measured if tank vapors were only allowed to exit through a metered outlet.

6.1.2. Pressurized Vessels
"The same flash emission models mentioned above, for tank flash emissions, are often used to estimate emissions from pressurized vessels” (WDEQ, 2010).

6.1.3. Dehydration Units
The GRI-GLYCalc model was used to estimate emissions released from re-boiler still vents and glycol flash separators. “Input [...] includes an extended hydrocarbon analysis of wet gas [...] actual operating parameters of all associated equipment, and physical properties of the dry and wet gas streams. The model provided an estimate of individual emission components and the rates of vapor and liquid streams exiting each process vent of a dehydration unit” (WDEQ, 2010).

6.1.4. Natural Gas Heaters
“NOₓ, CO, and VOC emissions from process unit heaters should be calculated using emission factors [...] from EPA AP-42” (WDEQ, 2010).

6.1.5. Flares
The NOₓ and CO emissions for flares are based on “0.14 lb. NOₓ/MMBtu and 0.0035 lb. CO/MMBtu” emissions factors (WDEQ, 2010). These factors are considered more accurate for flares in Wyoming than AP-42 factors.

6.1.6. Pneumatic Pumps
“If a pneumatic pump uses natural gas as the motive gas, the pump will release VOC and HAP emissions each time it strokes since all motive gas is vented by the pump” (WDEQ, 2010). Gas usage information from the manufacturer and the hydrocarbon composition of the motive gas can be used to determine emissions from the pump.

6.1.7. Truck Loadings
“VOC emissions from loading oil or condensate into tank trucks should be estimated using the following formula with data from AP-42 tables.

\[ L_L = 12.46 \times S \times P \times M/T \]

Where: \( L_L \) = loading loss, lb/1000 gallons of liquid loaded
S = a saturation factor
P = true vapour pressure of liquid loaded (psia)
M = molecular weight of tank vapours (lb/lb-mol)
T = temperature of bulk liquid loaded (ºR)(ºR = ºF + 460)” (WDEQ, 2010).

6.1.8. Fugitives
“The easiest way to calculate total hydrocarbon fugitive emissions is to multiply the number of components at a site by the EPA average emissions factors [...] Speciated hydrocarbon emission rates can be estimated by multiplying the total hydrocarbon emission rates [...] by actual measured weight fractions” (WDEQ, 2010). Fugitive emissions do not include emissions from components that are improperly designed or maintained.

6.1.9. Combustion Engines
“The method for calculating engine emissions is to use emission factors provided by the engine manufacturer, the maximum site-rate horsepower and the annual operating hours” (WDEQ, 2010).

6.2. 2011 Emissions Inventory
The Air Quality Division conducted an independent, statewide engine emissions study in 2011. Five weeklong studies tested NOx and CO emissions for 130 engines around the state.

Observations found:

- “A significant number of engines were not operating within their permitted level” (Dietrich, 2011). Thirty-four per cent of tested engines failed. Fifty-two percent of engines tested in Sublette County failed.
- “Rich burn engines can result in significant excess emissions. Neglect [...] can result in a twenty-fold increase in [...] emissions” (Dietrich, 2011).
- In Sublette County, Caterpillar 3600 engines are used for gas compression. The air/fuel ratio control option on these engines turns off if the load falls below 60%. “If the AFRC is not functioning due to low load, engine emissions can be similar to that of an uncontrolled rich burn (Dietrich, 2011).

“Excess emissions [...] are attributed to lack of maintenance or operational problems [...] There appears to be great differences in engine emissions monitoring practices between operators and in different areas” (Dietrich, 2011).
7. DATABASES

7.1. UGWOS
The complete dataset from each of the UGWOS campaigns is available at the WDEQ website.


7.2. Wyvisnet.com
Live air quality and meteorological data for the entire State of Wyoming also is available at the WDEQ site. Validated data are available from each site dating from its inception.

http://www.wyvisnet.com/

7.3. UWYO Live Data
The University of Wyoming posts live data from its mobile lab on its website.

http://www-das.uwyo.edu/ozone/Projects/PASQUA/Live_Data/live_data.html

7.4. AIRNOW.gov
The EPA offers nation-wide, live meteorological and air quality data including ozone.

http://www.airnow.gov/

8. REFERENCES

Air Resource Specialists Inc.: Sublette County Air Toxics Inhalation Project, 2010.


Meteorological Solutions Inc.: Comparison of Weather Conditions during the 2011 Upper Green River Basin Winter Ozone Study to Past Study Seasons, 2011.


