FINAL REPORT
2010 UPPER GREEN RIVER OZONE STUDY

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2010 UPPER GREEN RIVER WINTER OZONE STUDY
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1.0 INTRODUCTION

Elevated ozone episodes have been observed at air monitoring stations during winter and early spring in Wyoming's Upper Green River Basin (UGRB) since 2005. Concentrations of ambient ozone exceeding the National Ambient Air Quality Standard, currently 75 ppb daily maximum eight-hour average, were recorded in 2005, 2006, and 2008.

During the winters of 2007 through 2009, the Wyoming Department of Environmental Quality – Air Quality Division (AQD) contracted with Environ International (subcontractors T & B Systems, Sonoma Technology, Inc. and Meteorological Solutions Inc.) to perform a study of ozone formation in the UGRB called the Upper Green River Winter Ozone Study (UGWOS). Quality assurance project plans, data and reports from the 2007-2009 field campaigns can be found on AQD's Monitoring Information Page.[1] Data were collected from a network of permanent air quality monitoring stations, a mesonet of temporary monitoring stations installed for the duration of the wintertime field effort, upper air data from soundings and SODAR's and various ozone precursor measurement efforts during the field program.

Results from the 2008 UGWOS study[2] confirmed several important features of the UGRB winter ozone episodes:

- A stable vertical atmospheric structure resulting from high pressure and relatively warm air aloft with colder air trapped near the surface;
- Clear skies and light surface winds;
- A diurnal wind reversal at the surface from northwest winds during the night and morning hours to southeast during the afternoon which recirculates pollutants within the basin;
- Extensive snow cover which significantly limits daytime solar heating and resulting vertical convection and nearly doubles the total (actinic) flux of UV radiation which drives photochemical reactions;

[1] http://deq.state.wy.us/aqd/Monitoring%20Data.asp

[2] Final Report: 2009 Upper Green River Winter Ozone Study, ENVIRON, March, 2010

- Ozone and ozone precursor pollutants trapped in a shallow surface layer throughout all or most of the day.

As a follow-up to the 2007-2009 studies, AQD sponsored UGWOS 2010 to continue operation of a network of meteorological and ozone monitoring equipment in the UGRB during the winter months. The purpose of the study was to obtain ambient air quality and meteorological data during winter to monitor possible periods of elevated ozone in the UGRB. AQD contracted with Meteorological Solutions Inc. (MSI) (subcontractors T & B Systems, Environ International, and the University of Houston) to focus primarily on monitoring spatial and temporal patterns of ozone and meteorology rather than researching ozone formation mechanisms as was done in previous years. Planning for UGWOS 2010 began in early December 2009 on the heels of the AQD sponsored ”Ozone Technical Forum” and continued through early January 2010. Routine field operations commenced on January 15, 2010 and continued through March 31, 2010. Daily weather forecasts were issued by MSI’s forecast meteorologist for the purpose of identifying imminent elevated ozone events and to provide an alert to field technicians so that calibration activities would not be scheduled during elevated ozone periods. Routine operations during UGWOS 2010 included an expanded network of temporary, “mesonet” monitoring sites similar to sites used in previous UGWOS efforts. In addition, as in 2009, a second air quality monitoring shelter (Boulder II) was positioned temporarily next to the WDEQ Boulder monitoring site to provide specialized ozone precursor measurements. During UGWOS 2010, continuous nitrous acid (HONO) measurements were collected at this monitoring station. HONO may play a role in the rapid buildup of ozone observed during some episode day mornings in the UGRB. The objective of the HONO measurements was to shed light on a potentially important source of hydroxyl (OH) radicals central to ozone formation. The WDEQ BAM trailer was located at the former WDEQ-Jonah monitoring site and continuously measured ozone, oxides of nitrogen, $PM_{2.5}$ and affiliated meteorology.

This report presents a summary of UGWOS 2010 field operations, quality assurance activities, and results of the field measurement program. Section 2 presents an overview of the mesonet and ozone precursor measurements as well as the daily forecasts and project website features. Section 3 describes data quality assurance, data validation, and archiving procedures. Routine monitoring results are described in Section 4 and a concise results summary, conclusions and recommendations are presented in Section 5. UGWOS 2010 measurement data are available in an ACCESS database on the WDEQ-AQD website.

2.0 SUMMARY OF FIELD OPERATIONS

UGWOS 2010 field operations were scheduled for January 15, 2010 through March 31, 2010. Planning for the field effort started in early December, 2009 and was enhanced by the two-day Ozone Technical Forum sponsored by the WDEQ and held Cheyenne, Wyoming on December 8 and 9, 2009. A field trip to the UGRB to explore potential locations of additional monitoring sites was conducted on December 15 and 16, 2009. Field program planning continued through early January, 2010 when monitoring site installation commenced. All UGWOS monitoring sites were installed, calibrated, and operational by January 14, 2010. Forecasting for elevated ozone conditions started on January 15, 2010 and continued through March 31, 2010 when the field monitoring program ended. A map showing the monitoring sites is presented in Figure 2.1.

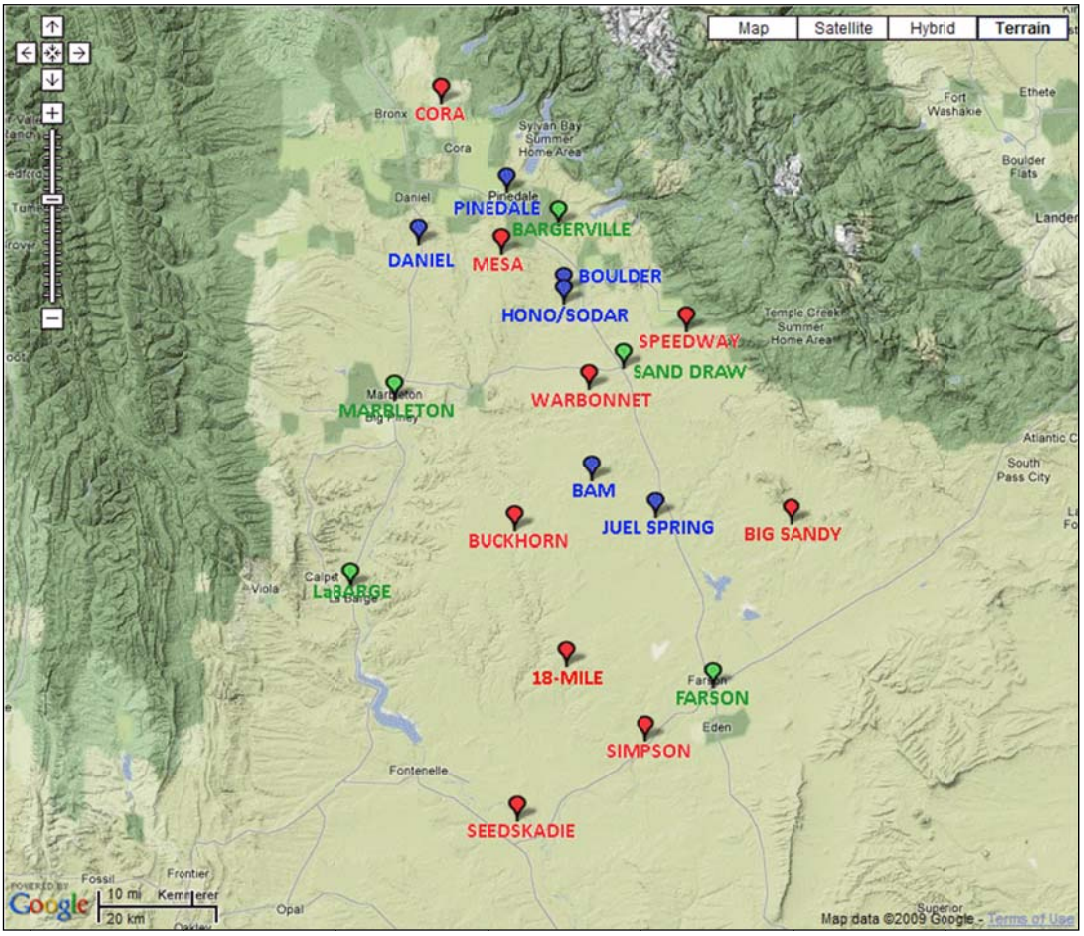

Figure 2.1 UGWOS 2010 Monitoring Site Locations

This map shows the nine UGWOS Mesonet monitoring stations (shown in red) and the locations of the five WDEQ permanent air quality monitoring stations and the HONO/Sodar installation collocated with the WDEQ-Boulder site (shown in blue). It also includes five monitoring sites (shown in green) that were not officially part of the UGWOS study but were operated as part of the Sublette County Human Health Risk Study. This same map showing the monitoring site locations along with the drill rig sites (black dots) and compressor station sites (purple dots) that were active during the UGWOS 2010 program is shown in Figure 2.2. Drilling rig and compressor station locations were provided by the WDEQ-AQD. A summary of the measurement methods and instruments used is provided in Table 2-1.

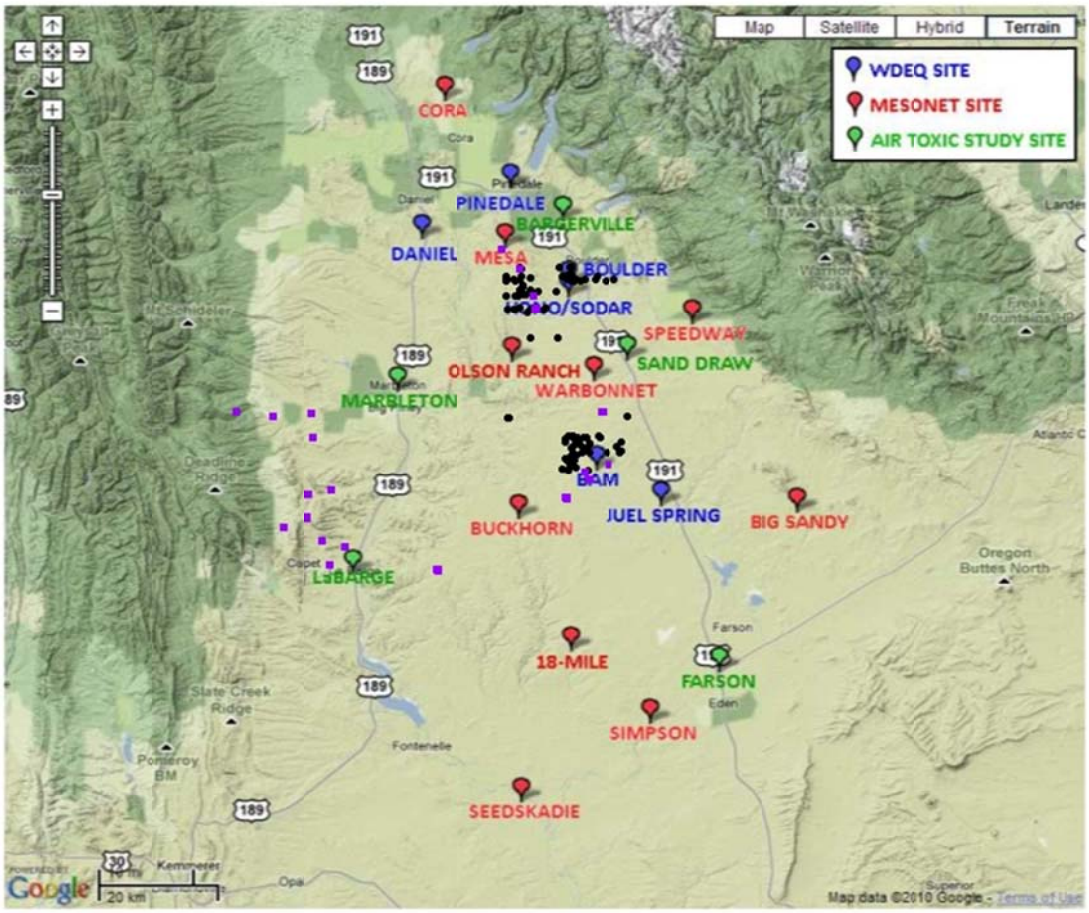

Figure 2.2 Locations of Drilling Rig and Compressor Stations

Table 2-1
Summary of Measurement Methods used During UGWOS 2010

Platform	Measurement	Instrumentation	
		Method	Model
Mesonet Sites	Wind Speed	Propeller Anemometer	RM Young 05305
	Wind Direction	Vane	RM Young 05305
	Temperature	Thermistor Probe	CSI 109
	Ozone	UV Photometric	2B Technologies, 202
SODAR	Upper Level Winds	Doppler Sodar	ASC 4000 miniSODAR
	Mixing Height	Doppler Sodar	ASC 4000 miniSODAR
	Surface wind speed, wind direction, temp, RH, pressure and precip. detection	Integrated sonic anemometer, thermistor probe, RH and pressure sensors with separate precip. detection sensor	Vaisala WXT-510
Boulder II	Nitrous Acid (HONO)	Long Path Absorption Photometry (LOPAP)	QUMA LOPAP-O3 HONO
WDEQ Permanent Monitoring Sites	Ozone	UV Photometric	T-API 400E/400A
	NO_x	Chemiluminescence	T-API 200E/200A
	PM_{10}	Tapered Element Oscillating Microbalance	TEOM 1400a (Daniel and Boulder)
	Methane/TNMHC	FID	Baseline-Mocon 9000 (Boulder)
	$PM_{2.5}$	Beta Attenuation	BAM 1020 (Pinedale)
	WS, WD, T, RH,BP,Solar Rad.,Precip	Various	Various
Boulder	Net Radiation	Selenium Barrier-layer Cell	Eppley TUVR
Jonah/BAM Trailer	WS, WD, T	Various	Various
	$NO/NO_x/NO_2$	Chemiluminescence	T-API 200E
	Ozone	UV Photometric	T-API 400E
	$PM_{2.5}$	Beta Attenuation	BAM 1020

2.1 Continuous Measurements

All measurement systems operated continuously for the duration of the field study during UGWOS 2010. These measurements included surface and boundary layer meteorological data and surface air quality data. During previous UGWOS field efforts, some measurements were only implemented during periods when elevated ozone concentrations were forecast (Intensive Operational Periods or IOP's).

2.1.1 Mesonet

Continuous ozone and meteorological measurements were conducted using a network of nine tripod-mounted stations (mesonet sites) distributed around the UGRB to represent basin-wide coverage. Two new locations were added for UGWOS 2010 at Big Sandy and 18-Mile. Mesonet sites included a wind sensor mounted at approximately three meters above ground level (agl) and ambient temperature and ambient ozone sample inlet positioned at approximately two meters agl. Ozone measurements were made with a battery-powered 2B Model 202 analyzer mounted inside of an insulated cooler. For UGWOS 2010, all 2B ozone analyzers were outfitted with lamp heaters for more stable performance. All measurements were recorded on CSI Model CR206 dataloggers which stored five-minute averages of all parameters. AirLink Raven modems allowed cellular telecommunications with dataloggers providing data updates on the UGWOS project website approximately every 15-30 minutes. The monitoring system was powered with deep-cycle batteries also mounted in the cooler and connected to a solar panel for recharging. Figure 2.3 shows an example of a mesonet site during UGWOS 2010 at Big Sandy.

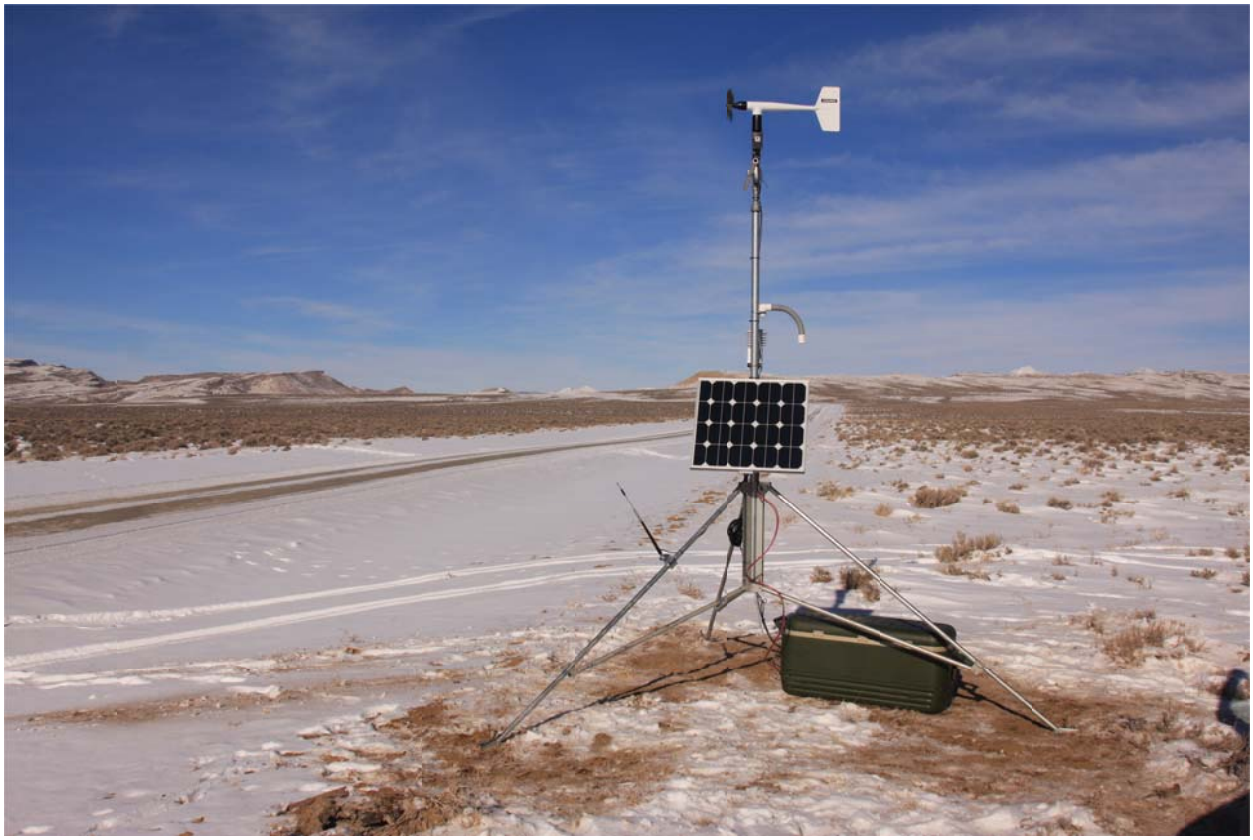

Figure 2.3 Example of a Mesonet Site at Big Sandy

2.1.2 WDEQ Permanent Monitoring Sites

Routine aerometric monitoring was conducted at the permanent WDEQ monitoring sites which are: Boulder, Pinedale, Daniel, and Juel Springs. Meteorological measurements at these sites included wind speed, wind direction, temperature, solar radiation, relative humidity, precipitation and barometric pressure. Aerometric measurements included ozone, NO_x, and continuous PM_{10}. Continuous $PM_{2.5}$ measurements were recorded at the Pinedale site and continuous methane/total non-methane hydrocarbon measurements were conducted at the Boulder site. In addition, a pair of upward and downward facing radiometers continued to provide net radiation measurements at the Boulder site location. Figure 2.4 presents a picture of the Pinedale Station.

Figure 2.4 WDEQ Pinedale Monitoring Station

2.1.3 Boulder II: HONO

In 2010, additional specialized measurements were conducted from an air monitoring shelter temporarily positioned adjacent to the permanent WDEQ Boulder monitoring site as was done for other specialized measurements during UGWOS 2009. This location allowed easy access to power and provided already existing collocated supporting measurements from the Boulder site. Nitrous acid (HONO) measurements were performed at this location in an attempt to shed more light on a potentially important source of hydroxyl (-OH) radicals central to ozone formation. Figure 2.5 shows the Boulder II HONO monitoring shelter at the Boulder monitoring site. Figure 2.6 shows the HONO measurement system inside the Boulder II monitoring shelter.

Figure 2.5 Boulder Station including (left to right) Boulder Shelter, Boulder II HONO Shelter, Tower, and SODAR

Figure 2.6 HONO Measurement System Inside the Boulder II Monitoring Shelter

2.1.4 MiniSODAR

During UGWOS 2010, the WDEQ Wind Explorer miniSODAR was relocated from its former position approximately 10 miles to the west, to a site adjacent to the Boulder monitoring site. The miniSODAR's speaker monitor board hardware was upgraded before the start of the 2010 UGWOS field study to provide improved diagnostics and maintenance. Figure 2.7 shows the miniSODAR at the Boulder monitoring site location.

Figure 2.7 WDEQ Wind Explorer miniSODAR

2.1.5 Jonah/BAM Trailer

Continuous ozone, oxides of nitrogen and $PM_{2.5}$ air quality measurements were performed at the location of the former WDEQ-Jonah monitoring station which had been re-located to the Juel Springs site. Affiliated meteorological measurements including wind speed and direction and ambient temperature were also conducted at this site during UGWOS 2010. Figure 2.8 presents a photograph of the BAM trailer at the Jonah monitoring site.

Figure 2.8 WDEQ BAM Trailer at the Jonah Monitoring Site

2.1.6 Other (Non-UGWOS)

In addition to the UGWOS 2010 measurements in the summary above, several other UGRB meteorological and air quality measurements were collected by other organizations during the same time period. These included:

- An extensive air toxics measurement program sponsored by Sublette County and carried out under the direction of the Sublette County Commission, the Wyoming Department of Health and the WDEQ - Air Quality Division which began in February 2009. The study included a network of five ozone, air toxics, and meteorological monitoring sites as well as nine air toxics sites with meteorology located in Sublette and Sweetwater counties.
- A moveable air quality monitoring shelter operated by the University of Wyoming which measured ozone, oxides of nitrogen and meteorology. This station was located at Olson Ranch along Highway 351 for the duration of the UGWOS 2010 field study.

2.2 Forecasts for Elevated Ozone Events

The content of the forecasts for the 2010 UGWOS was altered slightly this year as their purpose changed from providing information for Intensive Operational Periods (IOP's), which had been the main focus in the three previous year's studies, to one of general information to project participants. Additionally, forecasts provided information on elevated ozone development to the project personnel to more effectively schedule maintenance to avoid impacting data collection during elevated ozone events. Forecasts were issued seven days a week by 10:00 AM MST and were posted to the UGWOS website. The forecast consisted of three sections. The first section contained a synopsis of the current weather features and their expected development over the next week. The second section was a short term forecast out to three days which discussed the expected weather details important to the study such as winds, snowfall, inversion development, and others. The third section was a longer range outlook for days four through seven. Both the short and longer term sections contained a brief discussion on whether ozone development could be expected during those periods. An example forecast is presented in Figure 2.9.

Upper Green Winter Ozone Study

Weather Outlook

PLEASE NOTE: This product is not a public weather forecast and is solely intended to be used as a guide by UGWOS study participants to determine if and when conditions potentially favorable for field operations might occur. This product is independent of the Wyoming Department of Environmental Quality's (WDEQ) Ozone Advisory forecasting process and is not intended for assessing the potential for unhealthy air quality. The WDEQ Ozone Advisory can be accessed at: http://deq.state.wy.us

Issued: **Monday, March 1, 2010 at 1000 MST/0900 PST**

SYNOPSIS

High pressure is shifting eastward into the Rockies today, with the ridge line passing over the study area tonight, and by Wednesday this high will be replaced by a low pressure trough which will drag across the central Rockies through Friday, and be followed closely by another storm which will move into the Rockies late in the weekend.

SHORT TERM FORECAST (THRU DAY 3)

Yesterday saw ozone readings briefly touch 70 ppb at a few locations. Today and Tuesday will be mostly clear as high pressure moves across the study area. There will be increasing high level clouds Tuesday night with the approach of the next storm system. This storm will move through the study area Wednesday with a stronger system quickly following it Thursday and Friday. Yet another storm is expected for Saturday and Sunday.

OZONE: Elevated ozone may develop today and on Tuesday higher readings are possible when the high pressure ridge will be just east of western Wyoming. Wednesday should see lower readings.

LONG RANGE OUTLOOK (DAY 4 TO 7) AND BEYOND

Thursday and Friday will be mostly cloudy with a chance of light snow over the study area. Saturday will see increasing clouds and Sunday will have cloudy skies with a chance for light snow.

OZONE: Elevated ozone is not expected through the long range period.

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Figure 2.9 Example Forecast during UGWOS 2010

2.3 UGWOS Website

The UGWOS website was improved for the 2010 field study and allowed remote access to station data for all UGWOS participants. The UGWOS web-site home page is presented in Figure 2.10 below. This included mesonet sites installed for the field effort as well as permanent WDEQ monitoring sites and Sublette County Air Toxics study sites. These sites were color-coded by agency – blue for permanent monitoring locations, red for the project mesonet sites, and green for the monitoring sites from the on-going air toxics study. Real-time data were plotted on a project base map and updated every 15-minutes. Recent air quality and meteorological data were presented as a single station display (See Figure 2.11) or as a grouping of strip charts which allowed intercomparison of a selected parameter between all sites (Figure 2.12). A site equipment matrix provided information which was updated continually regarding equipment status and repair (Figure 2.13). New features in 2010 included links to other critical project aspects such as current weather and ozone forecast, access to raw data files from mesonet and stationary sites with period selectable graphical presentation, live camera imagery from several of the monitoring sites, and photos of mesonet sites with views in the cardinal directions (Figure 2.14). A new addition in 2010 was an animation feature which allowed users to view the prior day's ozone concentrations, wind data, or temperature data portrayed as dynamically changing isopleths hour by hour superimposed on the UGWOS study area base map (Figure 2.15).

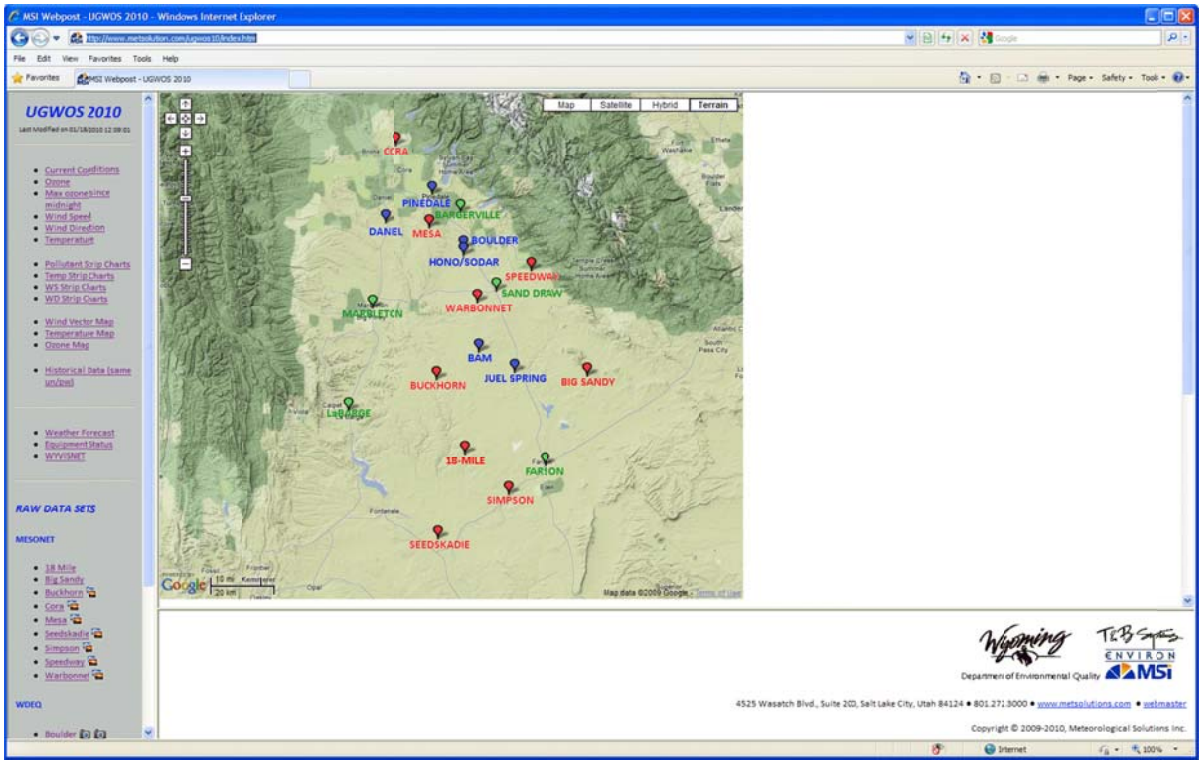


Figure 2.10 UGWOS Website Home Page

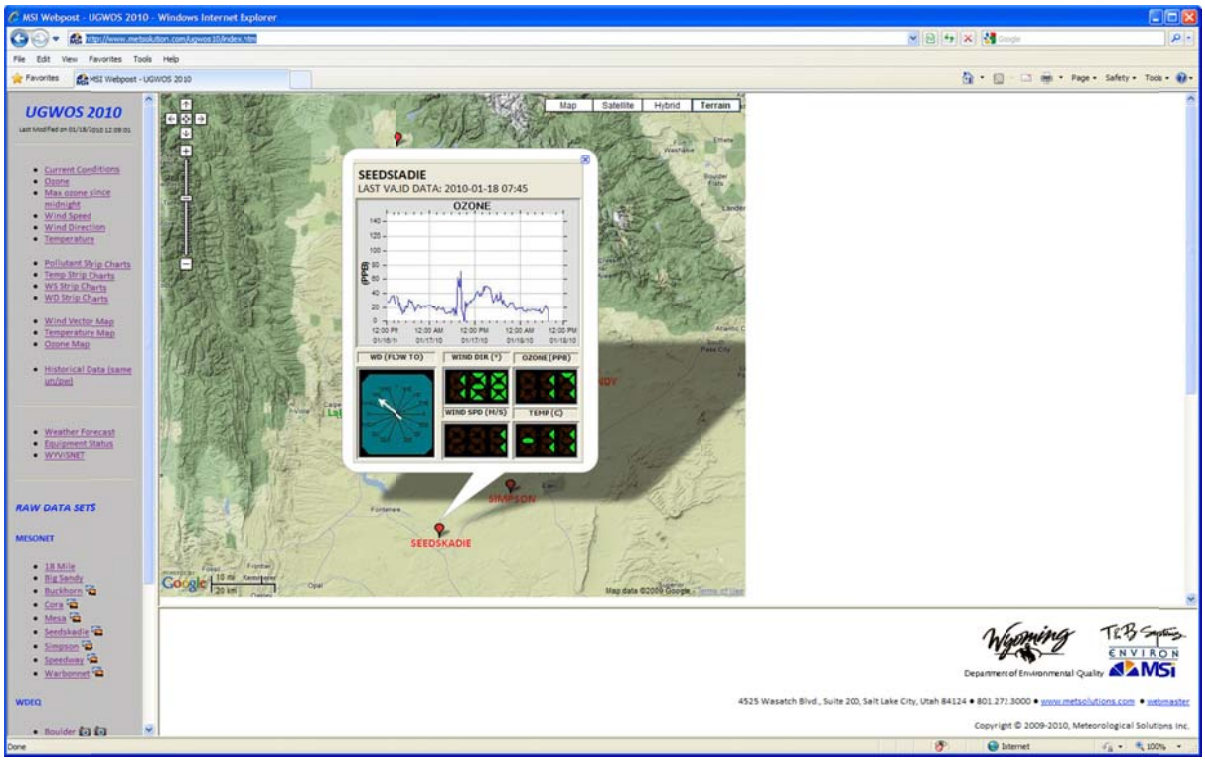


Figure 2.11 Single Station Data Display

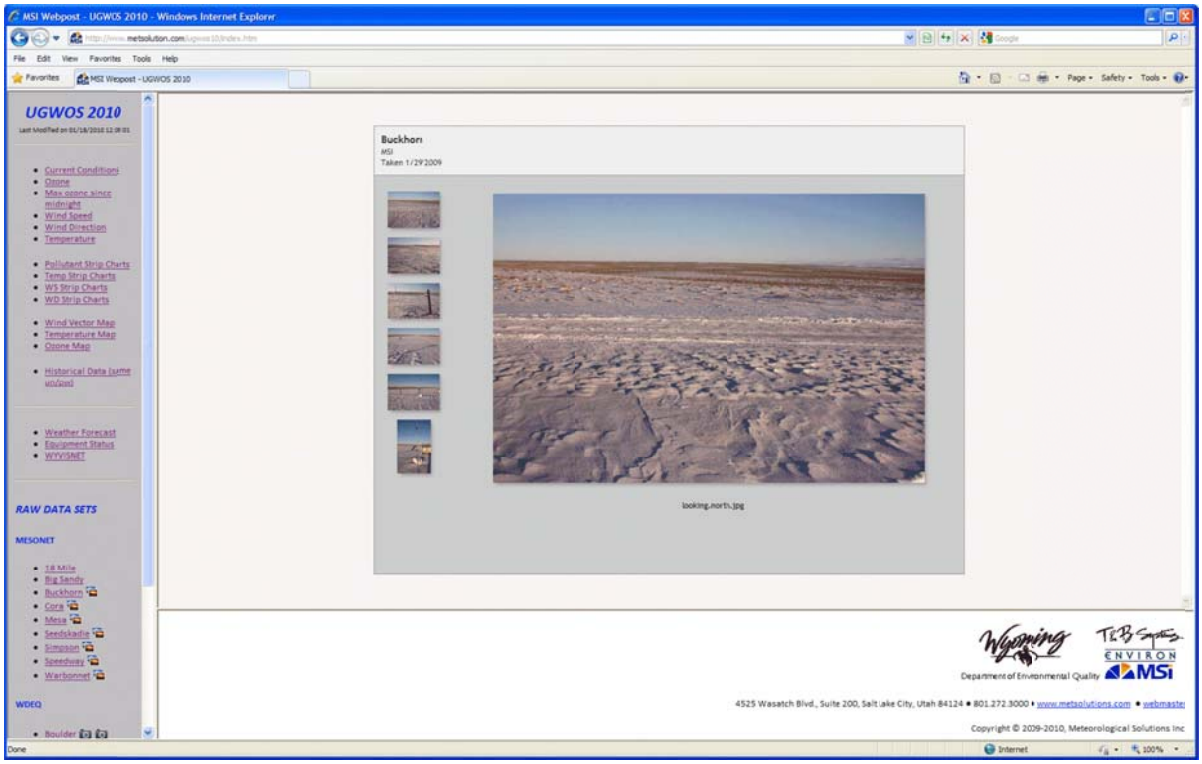


Figure 2.14 Individual Site Photographs

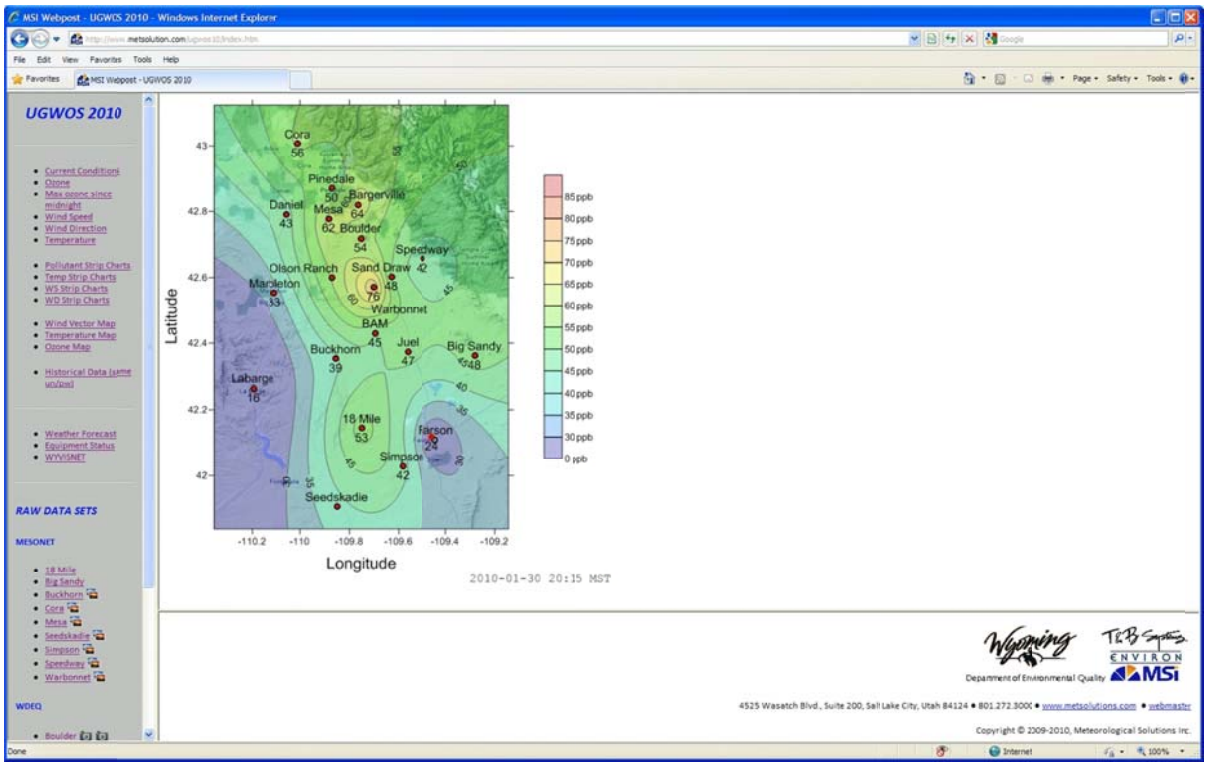


Figure 2.15 Hourly Isopleth Images

MSI hosted a second server (Figure 2.16) which provided separate air quality and meteorological parameter plots for each site with graphical displays of user selectable periods of the most current or historical data. A pollutant rose function linked air quality parameters to wind data (Figure 2.17). A note feature allowed field technicians and equipment managers to keep a continuously updated electronic logbook of significant site events including equipment failures, calibration and audit visits, and equipment failures and repairs (Figure 2.18).

A second version of the web-site was developed and made available to the public. This version contained a large subset of information from the main project website and included eight-hour rolling average ozone data from study area monitoring stations.

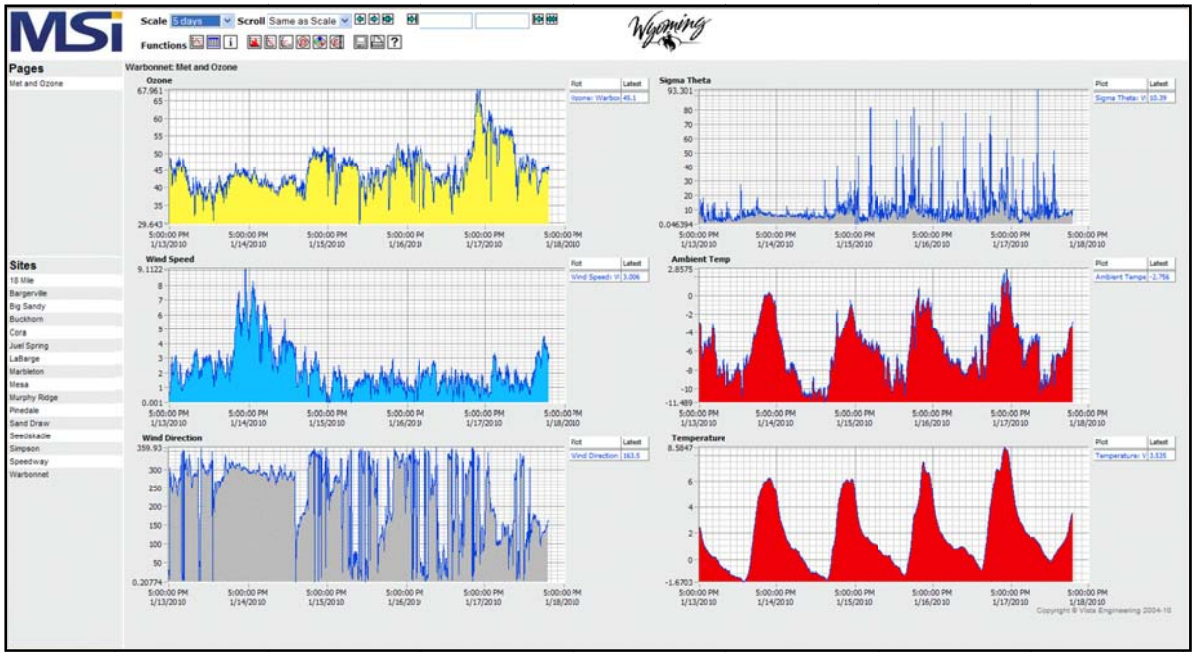


Figure 2.16 UGWOS Data Server Display

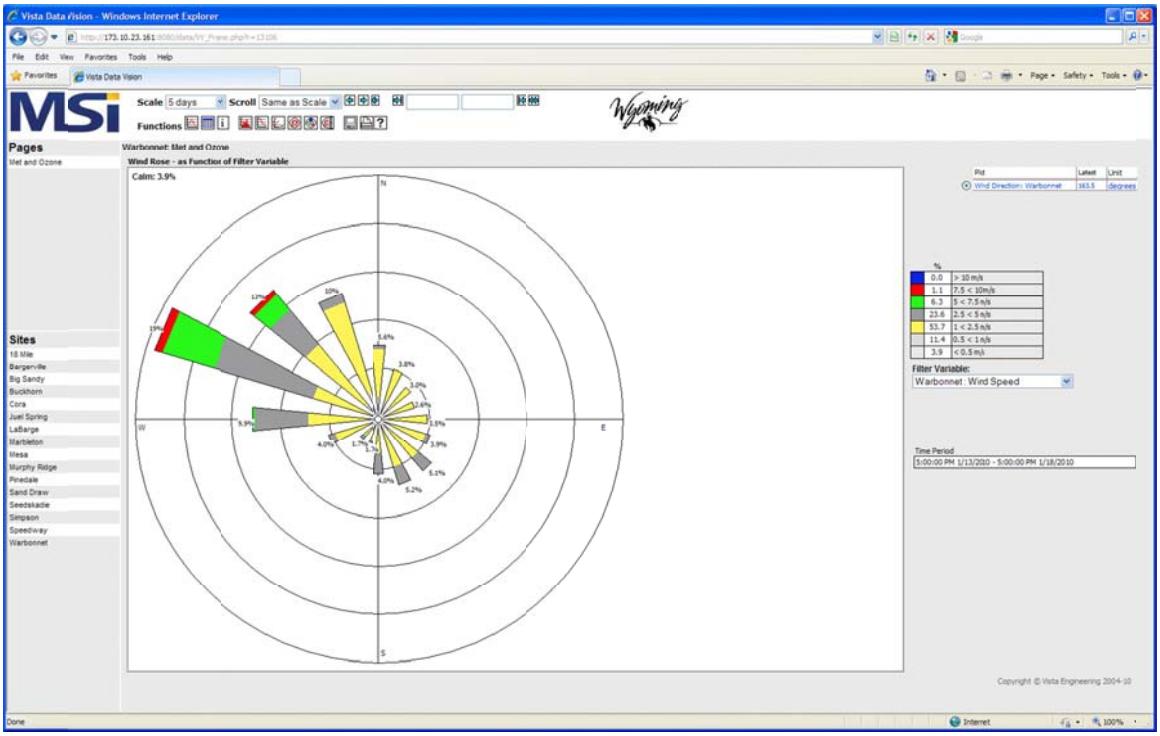


Figure 2.17 Pollution Roses

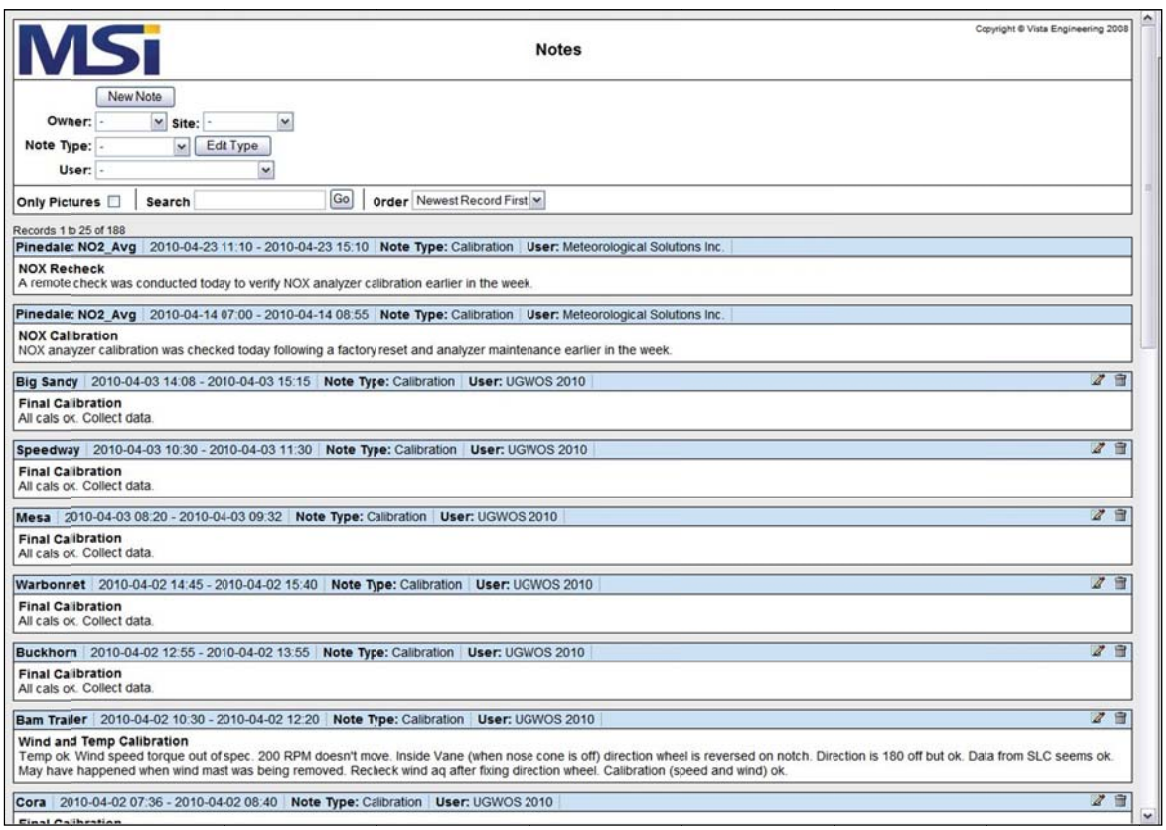


Figure 2.18 Website Note Feature

3.0 DATA QUALITY ASSURANCE, VALIDATION AND ARCHIVING

A primary study objective was to produce a validated data set from the field measurements that is well defined and documented. The data management system used was designed to be straightforward and easy to maintain. For entry into the project database, all data were quality-assured and submitted to the Data Manager in a prescribed format. A brief summary of procedures used is provided in this section. A complete description of data collection, quality assurance, validation, and data reporting procedures is available in Appendix A.

3.1 Data Management and Reporting

The overall goal of the data management effort was to create a well-documented system such that data could be readily inputted and easily accessed. A Monitoring and Quality Assurance document was prepared and approved by all the project participants (see Appendix A). Each of the participants that provided data was responsible for reviewing and validating their respective data. This included flagging values for instrument downtime and performance tests, applying any adjustments for calibration deviation, investigating extreme values, and applying appropriate flags.

Flags used for the UGWOS data set are presented in Table 3-1. Each data provider was also responsible for documenting their validation process so that it could be provided to the Data Manager and other analysts if needed.

Table 3-1

Data Flags Used in UGWOS Database

Flag	Description
V	Valid
S	Suspect. Data appears to be a data spike or outside normal data range
I	Data invalid.
M	Missing. Measurement not taken.
U	Invalidated Data - User is responsible for validation
N	Instrument noise detected in sub hourly data used to create hourly average.

In addition, each data provider was responsible for furnishing information to the Data Manager regarding the monitoring equipment used in the field study and any additional information requested to enhance the overall documentation of the study. In particular, participants provided the Monitoring Quality Objectives (MQOs) defining the quality of all data submitted as "valid." These MQOs contained the accuracy, precision, lower quantifiable limit, resolution and completeness of each measurable. This information is available in metafiles that accompany the database.

Standards for time reference, averaging period, parameter names and units were all defined beforehand and are consistent throughout the database. Data fields have a second column for each measured value for the accompanying QC code as needed. Data flagged as invalid or missing were given a value of -999. Suspect data were flagged as such with the data still included in the database.

3.2 Quality Assurance

As part of the quality assurance program, quality control procedures were implemented to assess and maintain control of the quality of the data collected. A Monitoring and Quality Assurance Plan was submitted to the WDEQ and approved prior to the start of monitoring (See Appendix A). This document provides a detailed discussion of the quality assurance program implemented in this study. A summary of key elements of the QC program for each measurement is presented in the remainder of this section.

All equipment underwent a complete checkout and acceptance prior to the start of monitoring. Standard Operating Procedures (SOPs) for measurements were completed prior to the start of monitoring.

All ozone analyzers and samplers were routinely checked using a traceable transfer standard following operating procedures consistent with EPA guidelines. Mesonet 2B analyzers were verified using a portable 2B calibrator which was periodically checked against a T-API Model 400E ozone transfer standard. This unit was used by MSI to check the ozone analyzer at the BAM trailer. The 400E transfer standard is certified each quarter using MSI's Dasibi 1008 PC local primary standard. MSI's primary standard is certified annually by US EPA Region VIII. Calibrations were conducted on the mesonet ozone analyzers approximately twice a month. Linear regressions were calculated for each calibration. The averages of the linear regression slopes and intercepts from all of the calibrations performed on each analyzer during the course of the study were used to adjust the raw data. More discussion on the adjustment of the ozone data is presented in Section 3.2.2.

The status of the miniSodar was checked daily via remote access of the data. When problems were noted, WDEQ field staff or MSI's UGWOS field technician were called upon to assist in correcting them. In addition, the miniSodar data were available in real time so that team members were able to use the data to assist in special monitoring and forecasting. Additional information on quality assurance procedures for these data is provided in Appendix A.

3.2.1 Calibrations

The purpose of a calibration is to establish a relationship between the ambient conditions and an instrument's response by challenging the instrument with known values and adjusting the instrument to respond properly to those values. The calibration method for each of the air quality and meteorological variables is detailed in the Monitoring and Quality Assurance Plan (Appendix D).

Calibrations of the ozone instruments were performed upon initial installation and at the end of the study period, as well as approximately twice per month during the study period. Additional calibrations were performed on an as-needed basis in the event of equipment repair or replacement. All calibrations were performed in accordance with the manufacturer's recommendations and were consistent with USEPA guidelines. Calibration checks of all ozone monitoring equipment were conducted using a transfer standard traceable to a primary ozone standard maintained by MSI at their office in Salt Lake City, Utah following EPA's guidelines.

This primary standard in turn has also been verified against the US EPA Region 8 primary standard maintained at Boulder, CO. Calibration checks on BAM trailer monitors were conducted at the beginning and end of the measurement period.

All meteorological sensors were calibrated at the beginning and end of the study. Wind speed sensors were calibrated using an RM Young constant rpm motor simulating wind speeds at several points across the sensor's operating range. Wind direction sensors were calibrated by checking responses at standard increments. Temperature sensors were calibrated using a water bath.

The HONO measurement system was cleaned by flushing with de-ionized water and NaOH alternately and then calibrated using a freshly mixed calibration standard approximately once per week. Zero air measurements were performed before and after each calibration and automatically every eight hours during routine operation. From these zero measurements, a "zero base line" was calibrated using graphical fitting software.

3.2.2 Quality Assurance Audits

As part of the UGWOS quality assurance program, an independent audit program was implemented by T&B Systems, WDEQ's quality assurance contractor, to verify the site operations and data accuracy. The auditor and the equipment used for the audit were independent of the measurement program. Audits were performed in accordance with the principles set forth by the US EPA.

Ozone analyzers were audited using a Dasibi Model 1008 PC transfer standard that is certified against T&B Systems' primary standard maintained following EPA's guidelines at their office in Valencia, CA. In addition, the transfer standard was certified against the EPA Region 9 primary standard maintained at Richmond, CA. The Model 1008 PC is an ozone photometer equipped with self-contained zero air and ozone generation. For audits at the mesonet sites, the transfer standard was operated within the audit vehicle using a true sine wave inverter, and was allowed to warm up prior to the audit to a point where the temperature within the standard's photometer cell was relatively stable. Ozone concentrations were fed to the mesonet site's sample inlet with an 8-foot ¼" Teflon line, with a venting tee placed at the inlet.

The airflow to the tee was approximately 2.5 lpm, minimizing residence time within the line. For ozone analyzers sited within buildings, introduction of the audit concentrations through the sample inlet was not possible, though the setup was configured to go through as much as the sample train as possible.

At the mesonet sites, wind speed sensors were audited using an RM Young constant rpm motor simulating wind speeds at several points across the sensor's operating range. Wind direction sensors were audited by checking the sensor orientation and responses in 30° or 45° increments using the marks on the wind direction sensor. The wind speed starting threshold was checked using an RM Young torque disc.

Wind sensors were left in place during the audit to minimize the audit effort and prevent any accidental damage to the monitoring system. This setup likely resulted in a decrease in the precision of the wind direction checks, particularly under windy or extremely cold conditions. In addition, wind direction starting thresholds could not be directly checked, though the bearings were inspected by feel.

Temperature sensors were audited using a water bath and a certified audit sensor. Two points were checked using an ice bath and an upscale water bath between 10° and 20°C. For sites where the ambient temperatures were well below zero during the audit, an additional check at a sub-zero level was conducted using a collocated temperature sensor.

The following summarizes the audit results, including any noted recommendations.

3.2.2.1 Mesonet

A. No problems were noted with any of the wind or temperature sensors audited.

B. The Big Sandy ozone analyzer showed a significant zero offset. Unusually high readings at this site were being actively investigated by MSI during the time of the audit. The analyzer audited at this site had previously been installed at the Simpson Gulch site, during which no problems were noted. Similarly, the analyzer previously used at the Big Sandy site, which also produced questionable data, was audited after the exchange at the Simpson Gulch site, again with no operational problems noted, though the analyzer response was low. All data obtained during the audits lead to a likely conclusion that a ground loop problem existed with the data logger. The problem was confirmed and fixed by MSI on January 28, 2010. Ozone data obtained prior to this date at Big Sandy were ultimately invalidated.

Ozone audit results are summarized in Table 3-2. Three sets of values are shown: 1) audit results, and 2) original field calibration results from the corresponding recent field performance check by MSI, and 3) field calibration results after adjustment of the ozone source concentration values based on further review of the data.

Table 3-2

Mesonet Ozone Audit Results

Station		Audit	Original		Adjusted	
			Site	Difference	Site	Difference
Speedway	Slope	0.9253	1.0281	10.3%	0.9638	3.8%
	Intercept (ppb)	4.7	4.0	-0.7	-3.4	-8.1
	Correlation	1.0000	1.0000			
Warbonnet	Slope	0.9131	1.0193	10.6%	0.9580	4.5%
	Intercept (ppb)	5.2	5.6	0.4	-4.3	-9.5
	Correlation	0.9999	1.0000			
Mesa	Slope	0.9284	1.0063	7.8%	0.9858	5.7%
	Intercept (ppb)	0.9	2.5	1.6	-1.1	-2.0
	Correlation	1.0000	0.9999			
18-Mile	Slope	0.8943	1.0265	13.2%	0.9715	7.7%
	Intercept (ppb)	1.0	-0.2	-1.2	2.5	1.5
	Correlation	0.9999	1.0000			
Buckhorn	Slope	0.9321	1.0267	9.5%	0.9650	3.3%
	Intercept (ppb)	2.1	3.6	1.5	-2.2	-4.3
	Correlation	0.9993	1.0000			
Big Sandy (analyzer audited at Simpson)	Slope	0.8245	0.9260	10.1%	0.8704	4.6%
	Intercept (ppb)	1.0	1.4	0.4	-0.1	-1.1
	Correlation	0.9998	0.9998			
Simpson Gulch	Slope	0.9362	1.0334	9.7%	0.9714	3.5%
	Intercept (ppb)	-0.1	-1.6	-1.5	3.2	3.3
	Correlation	1.0000	0.9998			
Seedskedie	Slope	0.9583	1.0510	9.3%	0.9920	3.4%
	Intercept (ppb)	-3.0	2.5	5.5	-1.0	2.0
	Correlation	0.9997	0.9999			
Cora	Slope	0.9429	1.0190	7.6%	0.9575	1.5%
	Intercept (ppb)	-3.7	-2.0	1.7	3.7	7.4
	Correlation	0.9996	0.9999			

Looking first at comparisons versus the original calibrations, recorded analyzer responses were generally consistent between the auditor and the field checks and fell within the ±15% audit criteria. However, results showed an apparent bias, with calibration slopes on average about 10% higher than the audit slopes.

This 10% bias was larger than expected and considerable effort was made to resolve the discrepancy. This included comparisons of primary and field ozone transfer standards for both T&B Systems and MSI, a reassessment of operating procedures for both the audit and field calibrations, recertification of the audit transfer standard, and field comparisons employing a second audit transfer standard. Based on these investigations, there appeared to be the following potential sources of "error" associated with the 10% bias between the audit and calibration results:

1. T&B Systems' primary transfer standard appeared to read about 3 to 4% higher than MSI's primary transfer standard standard. This is not uncommon given that the two are traceable to different EPA primary standards, and this difference is well within expectations and EPA requirements.
2. The ozone concentrations generated using the 2B Technology transfer standard during the field calibrations varied depending on the power source in use. During certification against a second standard, the 2B transfer standard was powered using a stand-alone 12 volt battery, with an actual voltage likely around 12.5 volts. However, during field use, the 2B transfer standard was powered using the 12 volt cigarette lighter receptacle, which with the truck engine on was likely putting out around 13.5 volts. Comparisons showed that ozone concentrations with the truck engine running were 3-4% higher than during certification. This was determined by MSI during checks performed on the 2B calibrator versus MSI's ozone transfer standard approximately every 10 days during the field program. From February 11, 2010 until the end of the program, 2B calibrator checks were performed with the truck engine running and then also with a stand-alone deep cycle battery. The average difference from each check point was applied retroactively to each 2B calibrator output point prior to discovery of this problem.
3. In addition to the above issue, output concentrations from the 2B transfer standard seemed to experience some variability with time. During the comparison check following the audit, the output was adjusted downward by about 4%. MSI eventually established output concentration values based on an average of the certification checks over the course of the study.

4. Tests showed that the audit transfer standard had the potential to read about 10% high if cell temperatures dropped below 25°C. The cell temperatures of the audit transfer standard during the audits were greater than or equal to 25°C, with the notable exception of Cora, where the cell temperature was 21°C. However, the results for Cora were consistent with those for the other sites. Given the overall consistency of the results, it seems unlikely that this potential temperature effect is a factor, especially given that the bias can be explained by other issues.

Based on audit results and additional field data, MSI modified procedures and adjusted calibration source values to account for issues 2 and 3, above. Table 1 shows comparison results after these adjustments, demonstrating overall agreement between the calibrations and the audits to within about 4%, consistent with the likely inherent 4% difference between T&B Systems and MSI noted in issue 1.

1. The audit results for the ozone Big Sandy analyzer, which was audited after it was moved to Simpson Gulch, showed a slope of 0.8245, falling outside of the ±15% audit criteria. However, the MSI calibration for this analyzer showed a similarly low response, likely due to trying to adjust the analyzer in the presence of the offset issue described above. MSI ultimately invalidated data for this analyzer during the audit period.

3.2.2.2 BAM Trailer

The audit results for the BAM trailer are summarized in Table 3-3. No problems were noted.

Table 3-3

BAM Trailer Audit Results – UGWOS Measurements

Analyzer		Slope	Intercept (ppb)
NO_x	NO	0.951	0
	NO_x	0.942	1
	NO_2	0.947	-2
O_3		1.0	2
$PM_{2.5}$	Flowrate % diff.	-3.6	

3.2.2.3 Sodar

A system audit was conducted of the sodar located at the Boulder site. This included a check of the antenna alignment and level, and a review of the data being collected. No problems were noted.

3.2.2.4 Boulder HONO

No obvious issues were noted during the system audit. The system audit included observation of maintenance procedures, a walk through of the calibration procedures, and inspection of the chemicals used for calibrating and maintaining the system. Tyler Ward, who was conducting routine maintenance and calibrations of the system, indicated that data collected early in the study were affected by an interferent that appeared to be outgassing from the insulation used to wrap the sample inlet. This had been corrected by the time of the audit.

3.3 Data Validation

Each study participant was responsible for reviewing and validating their collected data. The data were validated to *Level 1* as described by Watson, et al. (2001) before being submitted to the database. This included flagging values for instrument downtime and performance tests, applying any adjustments for calibration deviation, investigating extreme values and applying appropriate flags.

Mesonet data from all sites were plotted together and reviewed for inconsistencies. In addition, the five-minute average data for each site were reviewed for any unusual spikes that may have affected the one-hour averages. Data from each mesonet ozone analyzer were adjusted for calibration results by applying the average slopes and intercepts for the period to the final data. Table 3-4 summarizes the average slopes and intercepts applied to Mesonet analyzer data.

Table 3-4

Average Slopes and Intercepts from Calibration Results

Site	Slope (m)	Intercept (b)
Cora	1.04	2.2
Warbonnet	1.04	-4.1
Big Sandy	1.05	-1.3
Simpson	1.03	-1.3
Mesa	1.04	-2.6
Speedway	1.04	-4.6
Seedskadee	1.04 1.02*	2.5 1.8*
Buckhorn	1.03	-1.6
18-Mile	1.02	0.8

* Seedskadee analyzer sent to factory for repair from 2/3/10 - 2/8/10.
Calibration results different after 2/8/10 requiring different average m+b.

3.4 Data Archiving

All validated data were merged into an integrated relational Microsoft ACCESS database. The database contents and format are described in Appendix B. Data were formatted into the final database with the following unit configurations and naming conventions:

- Parts per million for O_3, NO, NO_2, NO_x
- Micrograms per cubic meter for PM_{10} and $PM_{2.5}$
- Meters per second for wind speed
- Degrees Celsius for ambient temperature
- Percent for relative humidity
- Parts per Billion Carbon for non-methane hydrocarbon species
- Watts/m^2 for radiation
- SITE = Alpha-numeric site code identifier
- DATE = (MM/DD/YY)
- HOUR= Nearest whole begin hour (HH) (MST)
- TIME, START_TIME or END_TIME = Time stamp of data (HH:MM:SS) (MST)
- HEIGHT = Elevation in meters above MSL
- QC_CODE, WS_QC, WD_QC, O3_QC, etc =
  "V" (valid), "M" (missing), "I" (invalid), "S" (secondary MQOs)
- NOTES = any additional information

The ACCESS database was spot-checked for accuracy against validated input files containing meteorological and air quality parameters.

4.0 RESULTS

This section describes weather conditions and the results of meteorological and air quality measurements conducted during UGWOS 2010 and how they compared to previous UGWOS studies.

4.1 Summary of 2010 Meteorological and Air Quality Conditions and Comparison with Prior Years

Based on an analysis of prior high ozone events in the study area, meteorological conditions conducive to the formation of elevated ozone levels during the winter and early spring in the UGRB were determined to be characterized by clear skies, light winds, and a stable atmosphere. Objective criteria for the values of several meteorological parameters were determined that would provide guidance in forecasting elevated ozone events in the UGRB. These criteria were determined to be:

- Mean Sea Level Pressure 1020 mb or higher
- Surface wind speeds less than 8 knots
- 700 mb pressure higher than 3060 meters
- 700 mb pressure temperatures 0 to -8ºC
- 700 mb pressure level wind speeds less than 20 knots
- 500 mb pressure level higher than 5700 meters
- 500 mb pressure level winds less than 30 knots
- Surface snow cover

Snow cover was determined to be an important factor since it minimizes daytime surface heating which further stabilizes the lower boundary layer and also reflects incoming UV radiation increasing the UV flux and photolysis rates.[1]

[1] 2007 Upper Green River Winter Ozone Study, ENVIRON, 2007

This section discusses the levels of these parameters in 2010 and how they compared to levels recorded in prior studies.

4.1.1 Comparison of Meteorological Patterns: 2010 vs. 2007-2009

The UGWOS project has occurred yearly since 2007. A summary of the conditions that occurred in 2010 as compared with each of these years is discussed in this section. In past years' reporting (2007 – 2009), averaged charts showing surface pressure and pressure heights, temperature and wind speed data for the surface and upper air levels have been developed for the months of February and March. These charts were developed from National Centers for Environmental Protection (NCEP) reanalysis datasets and were produced on Earth System Research Laboratories (ESRL) website (http://www.esrl.noaa.gov/psd/cgi-bin/data/composites/printpage.p1). Charts for 2010 were constructed and can be found in Appendix C. Summaries of the parameter comparisons provided by these charts are shown in tables in this section.

4.1.1.1 Pressure and Pressure Heights

Of the three variables discussed in this section averaged pressure varies the most from year to year, and yet still does not vary by much. The amount of variance can be seen in Table 4-1. In 2010 pressure at all levels fell within the spread that has developed in the prior years of the study.

The surface pressure pattern in 2010, which may be more important than the averaged pressure value, looked very similar to both 2009 and 2007 with a high center over southwest Montana and northeast Idaho. In 2008 this high center was shifted well to the west over south central Oregon. At 700 mb the 2010 averaged pattern had a ridge axis to the west of Wyoming stretching from southwest Montana to southern California. In 2009 this ridge was similarly placed while in 2007 and 2008 it was shifted well to the west. The average 700 mb height has varied by as much as 24 meters over the last four years.

In 2010 the 500 mb average pressure pattern showed a ridge line from eastern Idaho south into western Nevada and central California. In prior years, the ridge has been either non-existent or located much farther west. The average 500 mb height has varied by as much as 52 mb during the four years of the study.

Table 4-1

Surface Pressure, 700 and 500 mb Pressure Heights for the February and March Period

February/March Period	Surface Pressure (mb)	700 mb Height (m)	500 mb Height (m)
2007	1019.7	3042	5604
2008	1020.8	3018	5552
2009	1019.0	3024	5565
2010	1019.4	3023	5559

4.1.1.2 Temperatures

As with the pressure levels, temperature averages for 2010 fell within the range that has been recorded in the 2007 to 2009 periods for the February and March period. The average surface pattern in 2010 looks very similar to the other years with a cold core center stretching from western Montana through western Wyoming and into central Colorado. The 2010 study period was the second coldest at both the surface and 700 mb levels. This seems a bit of an anomaly as the coldest year, 2008, had the best ozone development of all four years while 2010 had essentially no significant elevated ozone periods. The 700 mb level temperature pattern in 2010, unlike the other three years, showed the coldest part of the air mass was well east of the study area while the other years showed the coldest area just west of western Wyoming. Table 4-2 presents the average surface and 700 millibar temperatures for February and March 2010.

Table 4-2

Average Surface and 700 mb Temperatures for the February and March Period

February/March Period	Surface Temperature (°C)	700 mb Temperature (°C)
2007	-2.6	-5.1
2008	-5.2	-8.2
2009	-4.0	-6.5
2010	-4.2	-7.0

4.1.1.3 Wind Speeds

Wind speeds in 2010 were the one parameter that fell outside of the range developed by the previous three years, as at both the surface and 700 mb levels they were considerably lighter than has been seen in the past. This difference may be explained by the unusual winter that occurred in 2010 with El Nino conditions causing the storm track to split on a regular basis allowing only very weak storms to cross over western Wyoming. There were no significant storms during February and March. Surface and 700 millibar scalar wind speeds for February and March 2010 are presented in Table 4-3.

Table 4-3

Surface and 700mb Scalar Wind Speeds for the February and March Period

February/March Period	Surface Wind Speed (m/s)	700 mb Wind Speed (m/s)
2007	4.2	10.4
2008	3.8	10.1
2009	3.9	9.6
2010	2.9	6.8

4.1.2 Snow Cover: 2010 vs. 2007-2009

The web site for the National Operational Hydrologic Remote Sensing Center (NOHRSC)[2] under the National Oceanic and Atmospheric Administration (NOAA) provides maps of estimated snow depth for most of the United States. These images were used to provide a snapshot view of conditions over the entire UGWOS area for 2010 as well as for the 2007, 2008 and 2009 study periods. Additionally, images archived by the WDEQ cameras located within the Upper Green River Basin were reviewed. Maps showing snow depth over the UGWOS area during the four study years at the middle of and ending of each month are shown in Figures 4.1 through 4.6d.

[2] http://www.nohrsc.nws.gov/interactive/html/map.html

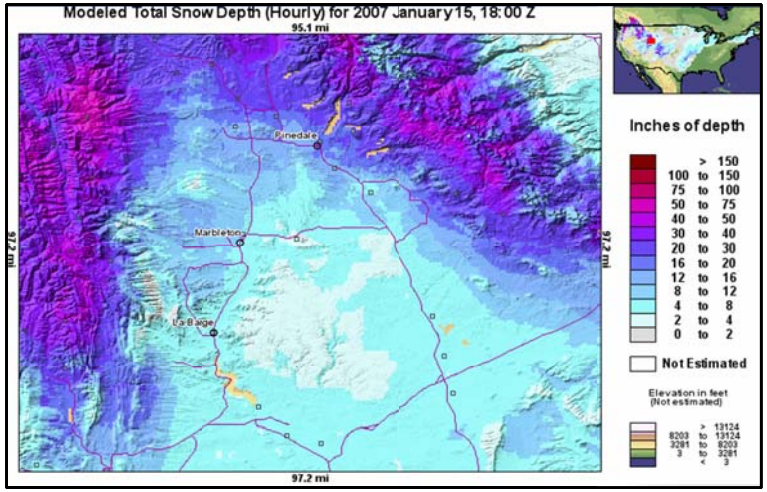


Figure 4.1A - January 15, 2007

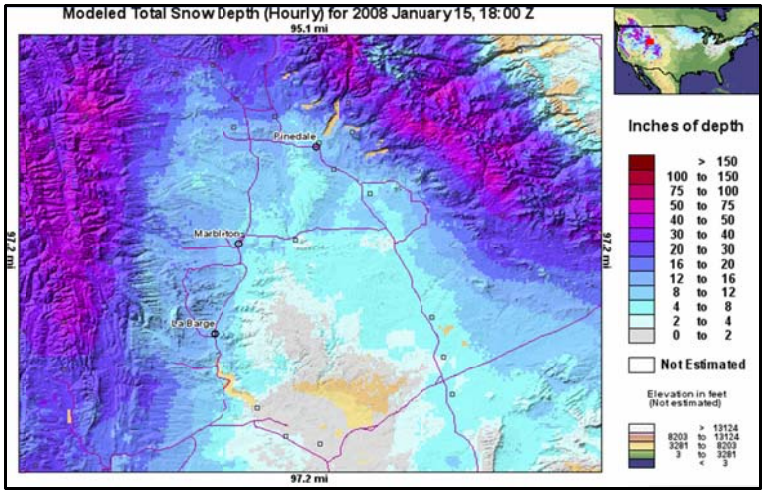
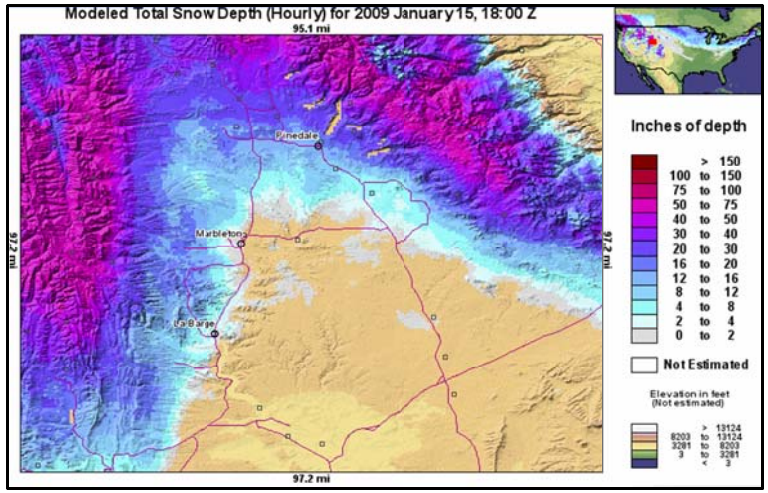


Figure 4.1B - January 15, 2008



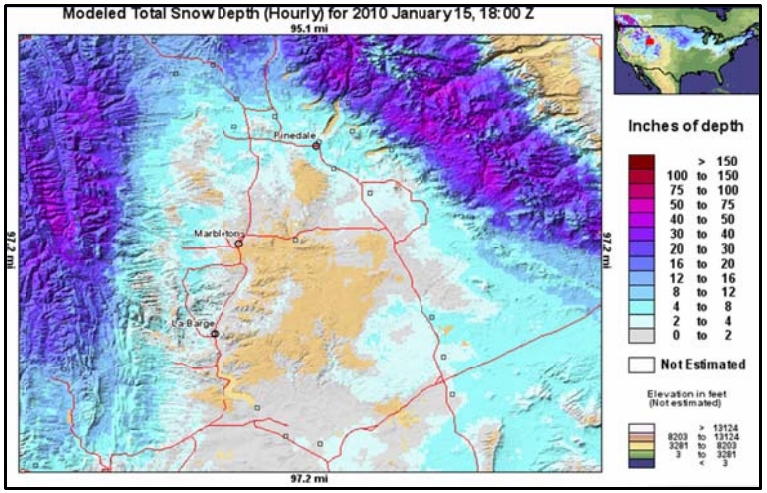
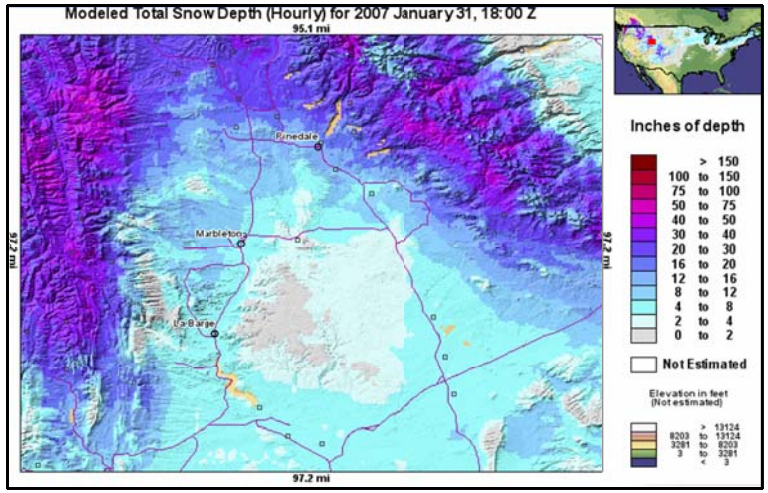
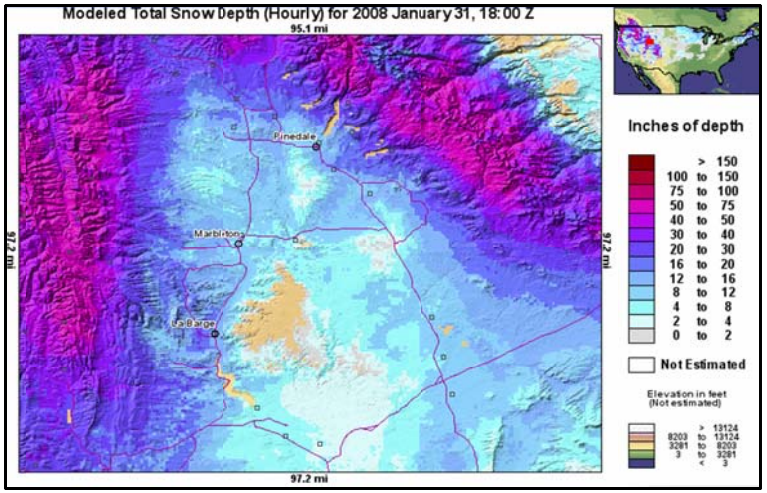


Figure 4.1D - January 15, 2010


Modeled Total Snow Depth (Hourly) for 2007 January 31, 18:00 Z
95.1 mi
97.2 mi
97.2 mi
97.2 mi
Pinedale
Marbleton
La Barge
Inches of depth
> 150
100 to 150
75 to 100
50 to 75
40 to 50
30 to 40
20 to 30
16 to 20
12 to 16
8 to 12
4 to 8
2 to 4
0 to 2
Not Estimated
Elevation in feet
(Not estimated)
> 13124
8203 to 13124
3281 to 8203
3 to 3281
< 3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Pinedale
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Inches of depth
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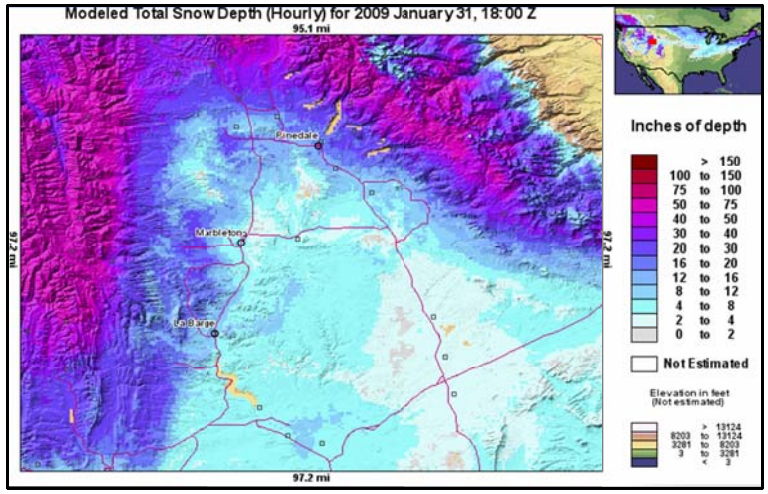
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Inches of depth
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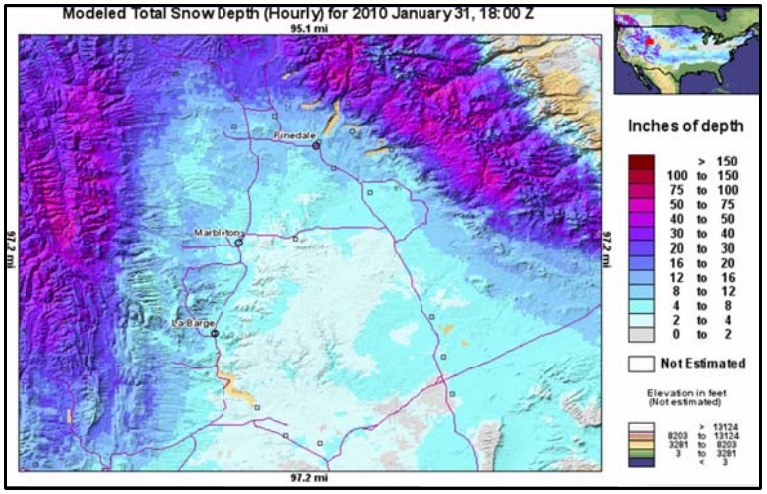
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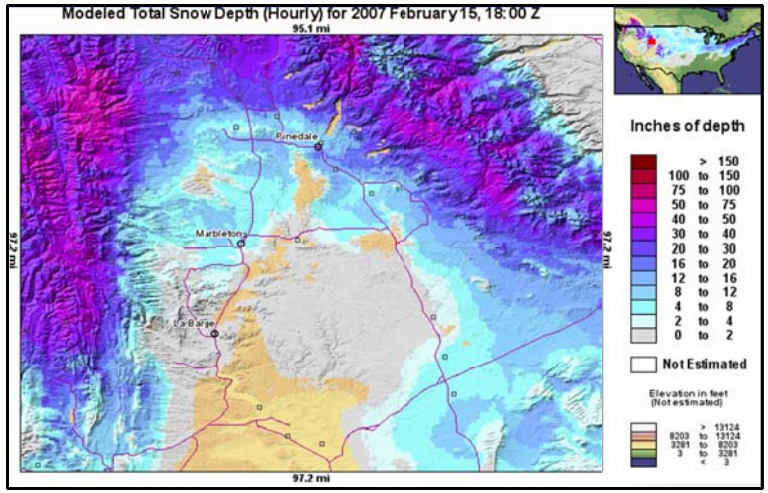
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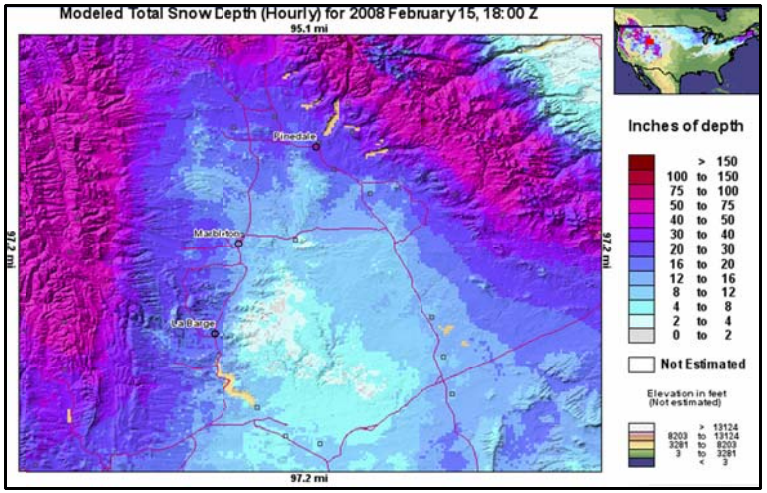
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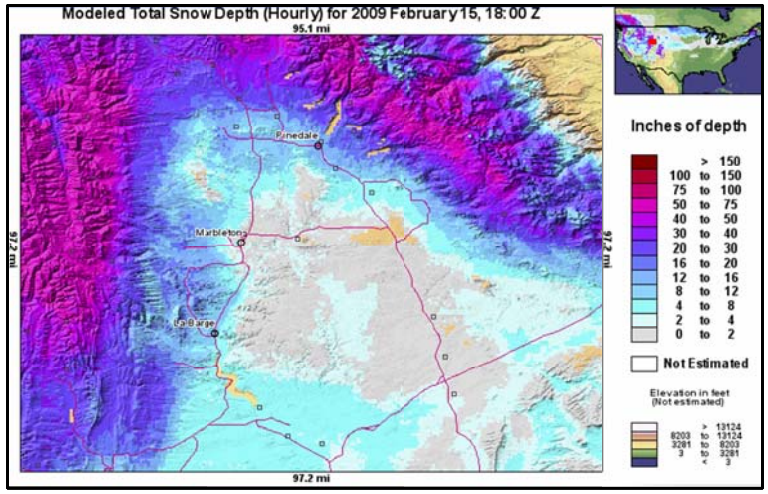
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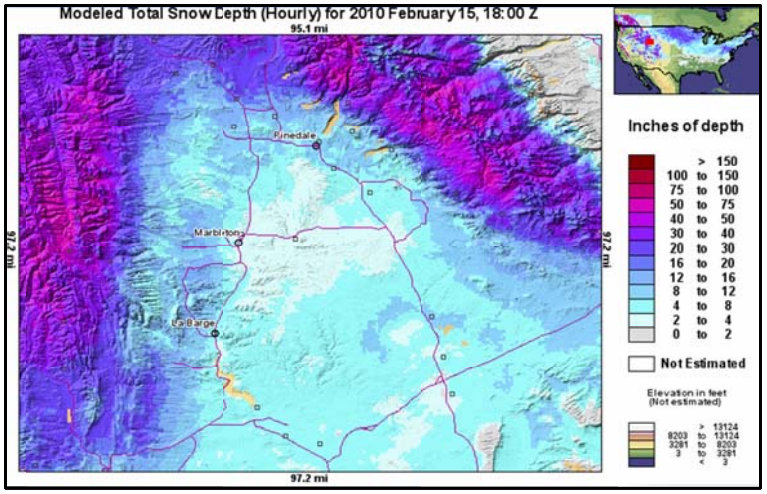
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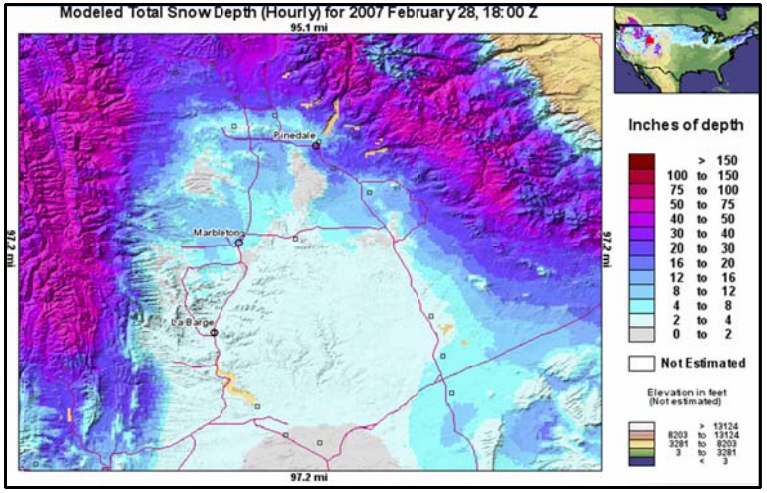
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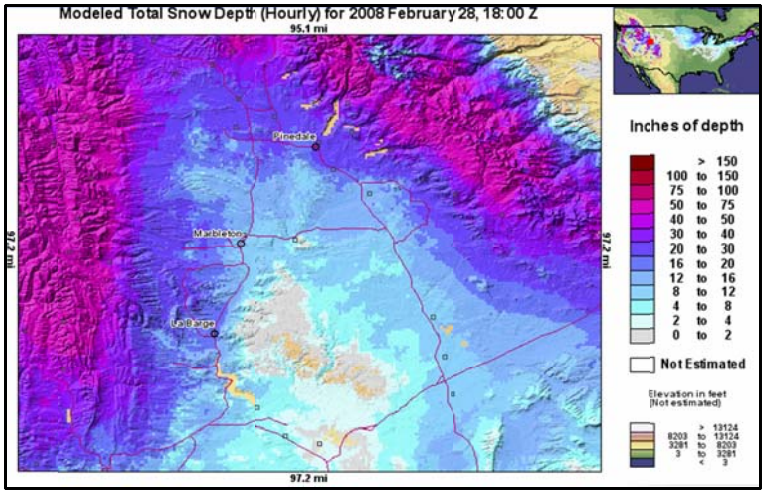
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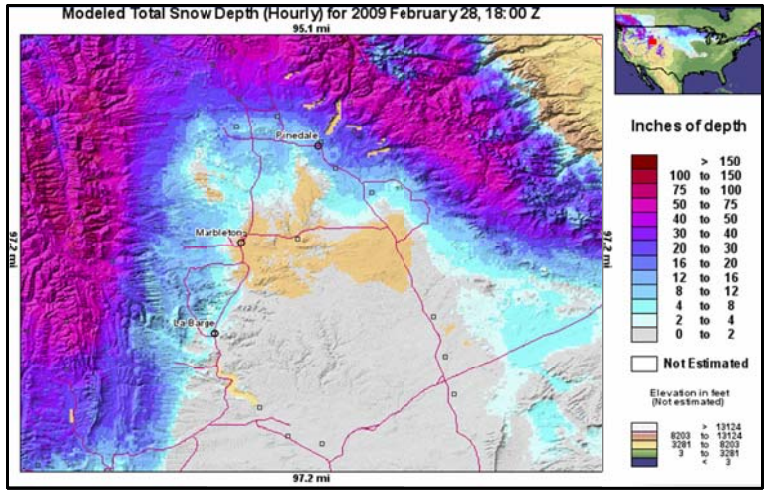
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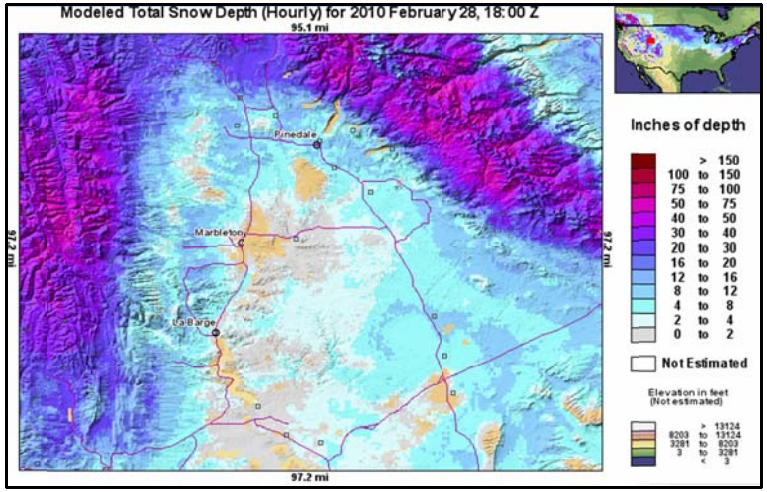
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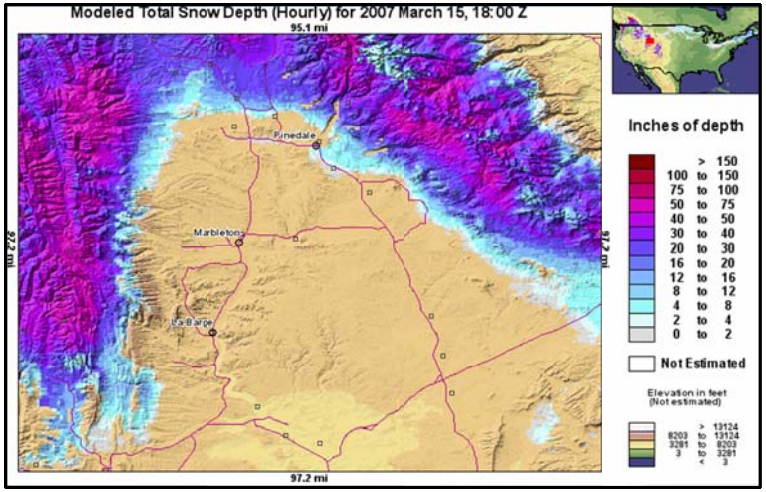
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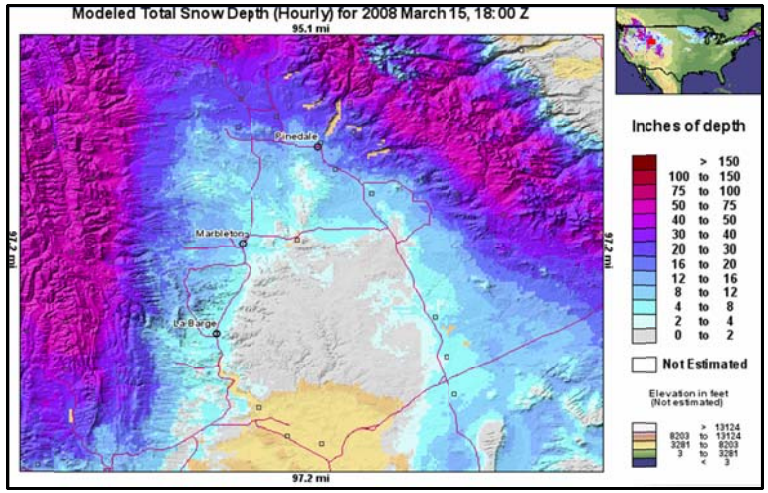
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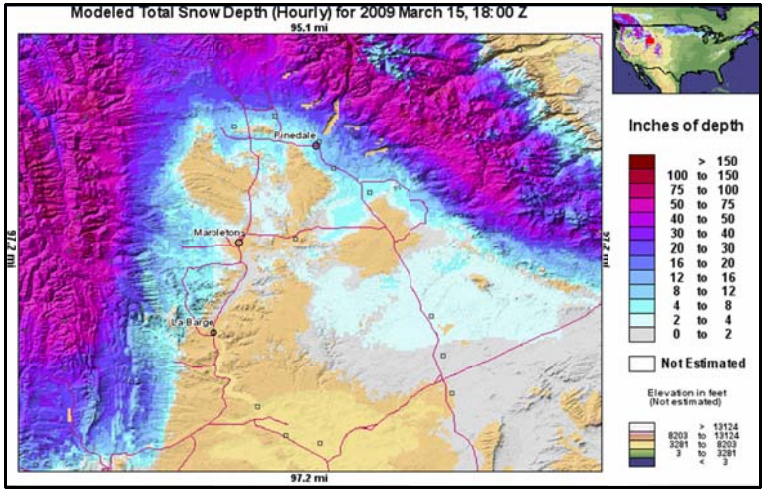
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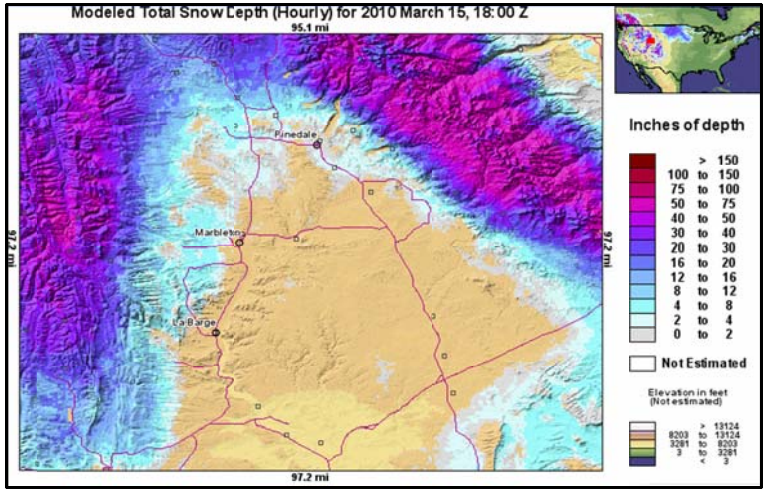
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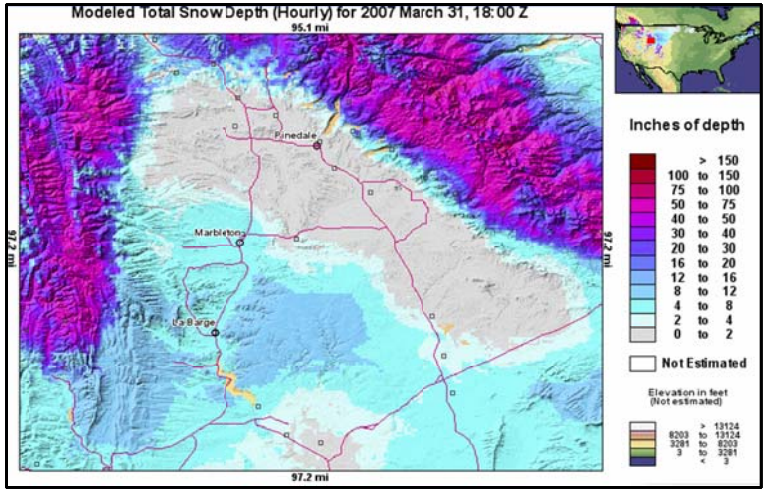
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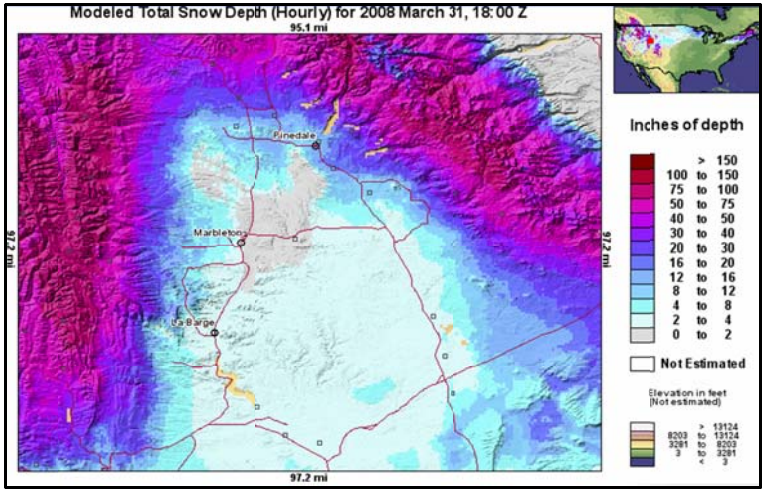
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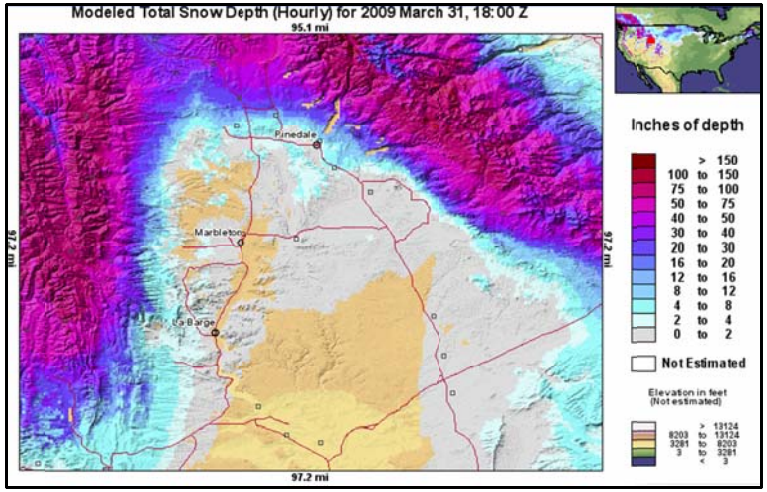
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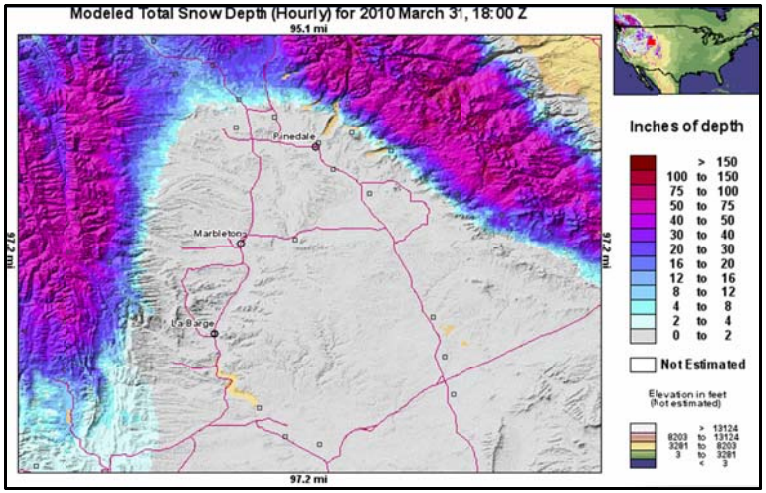
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Snow cover throughout the 2010 UGWOS period was generally light. The figures above show a thin to non-existent snow cover in 2010 over much of the basin at the beginning of the study period on January 15. As would be expected, the higher terrain on the east and west sides as well as the north end of the basin showed more depth with as much as 4 to 8 inches. By the end of January, after several weak storms passed through the basin, the snow cover had improved with 2 to 8 inches covering most of the area, and 8 to 12 inches having accumulated in the higher terrain. Figures 4.7 and 4.8 show snow cover conditions located at the WDEQ Pinedale and Juel Springs monitoring sites at the end of January.

Figure 4.7 Snow Cover at WDEQ's Pinedale Station on January 31, 2010

Figure 4.8 Snow Cover at WDEQ's Juel Springs Station on January 31, 2010

The middle of February had a slightly improved snow cover, but by the end of the month it was on the decrease and continued to be minimal through the end of March. The exception was on March 19 when a relatively wet storm brought snow to parts of the basin. This snow only lasted until early on March 21. Otherwise, conditions ranged between bare ground and a couple of inches. One of the stronger storms of the season occurred on the final two days of the study and continued into early April. This storm started out warm and precipitation that initially fell was in the form of rain or melting snow. Figures 4.9 and 4.10 show snow cover conditions at Juel Springs on March 4, 2010 when there was no snow cover, and March 19 after one of the heavier snows of the year.

Figure 4.9 Snow Cover at WDEQ's Juel Springs Station on March 4, 2010

Figure 4.10 Snow Cover at WDEQ Juel Springs Station on March 20, 2010 after a Storm

A comparison between 2010 with the same two and one-half month study period in 2007 showed a deeper snow cover in general during 2007. One exception was in mid-February where much of the central and southern portion of the area was bare, though the northern part of the basin had similar or more snow than 2010, particularly around Pinedale. The second exception was at the very end of March when the central and southern parts of the basin were bare in 2007, though there was still 2 to 8 inches in the Pinedale area. A storm that was occurring during this period in 2010 brought some snow to the area, which for the previous three weeks had been essentially bare.

In 2008, the snow cover was similar to 2010 over the central and southern part of the basin, while the northern portion from about Pinedale north had more snow cover in 2008 than in 2010. The largest differences occurred in mid to late February 2008 over the northern basin where snow cover was reported to be in the 12 to 30 inch range while in 2010 it was in the 4 to 12 inch range.

For 2009, conditions were very similar to 2010 in all parts of the basin for the entire period. Overall the bi-monthly snapshots shown in Figures 1a-d through 6a-d for 2009 indicate a little less snow cover than in 2010.

In summary, 2010 was a poor year for snow cover in the study area. Although there were numerous storms, particularly in January and March, they tended to be quite weak over the basin bringing very little in the way of new snow. On average, 2007 and 2008 had more snow than 2010 while 2009 had less snow. The lack of significant snow cover was likely one reason that there was no significant ozone development in 2010.

4.1.3 Comparison of Ozone in 2010 with 2005-2009

Ozone data have been recorded at permanent monitoring sites in the UGRB since 2005. The Jonah, Boulder, Daniel, and Juel Springs sites are operated as WDEQ monitoring sites and utilize Federal Equivalent Method (FEM) air quality monitors. Eight-hour ozone averages and maximums by month from these sites are presented in Table 4-4.

Table 4-4

Eight-Hour Monthly Average and Maximum Ozone by Year for Jonah/BAM, Boulder, Daniel, and Juel Springs

January	**Average 8-Hour Ozone (ppb)**				**Maximum 8-Hour Ozone (ppb)**			
Year	Jonah/BAM	Boulder	Daniel	Juel	Jonah/BAM	Boulder	Daniel	Juel
2005	35	NA	NA	NA	78	NA	NA	NA
2006	33	41	43	NA	49	67	53	NA
2007	27	43	40	NA	57	71	53	NA
2008	29	39	42	NA	47	58	56	NA
2009	24	34	37	38*	52	55	48	64*
2010	34	38	39	40	57	69	49	55
February	**8-Hour Ozone (ppb)**				**8-Hour Ozone (ppb)**			
Year	Jonah/BAM	Boulder	Daniel	Juel	Jonah/BAM	Boulder	Daniel	Juel
2005	42	51	NA	NA	98	89	NA	NA
2006	39	48	49	NA	93	71	82	NA
2007	29	42	40	NA	46	59	57	NA
2008	40	54	50	NA	102	122	76	NA
2009	33	42	43	40*	69	67	64	62*
2010	44	51	46	46	54	62	52	53
March	**8-Hour Ozone (ppb)**				**8-Hour Ozone (ppb)**			
Year	Jonah/BAM	Boulder	Daniel	Juel	Jonah/BAM	Boulder	Daniel	Juel
2005	40	48	NA	NA	58	71	NA	NA
2006	44	48	50	NA	68	67	71	NA
2007	32	44	40	NA	44	65	55	NA
2008	39	53	50	NA	98	102	75	NA
2009	39	46	43	42*	63	70	67	67*
2010	48	53	48	49	55	66	54	53

*Temporary Mesonet site with 2B ozone analyzer prior to permanent site.

Maximum eight-hour ozone levels during February and March 2010 were lower than those observed during the same period in 2005-2009 with the exception of 2007. During 2007, meteorological conditions during February and March were not favorable for ozone formation as described in ENVIRON (2008a)[3]. Maximum eight-hour ozone concentrations for January 2010 were similar to January 2007 and, except for 2005, were greater than January, 2006-2009. Average eight-hour ozone concentrations during the January through March period were slightly higher in 2010 than in 2009.

[3] 2007 Upper Green River Winter Ozone Study, ENVIRON, 2008a.

Average eight-hour ozone levels during February and March were higher at the Jonah site in 2010 than in other years with measurements. This may be due to fewer local sources of NO_x scavenging of ozone since the Encana Oil & Gas USA base for Jonah field operations, which was located near the Jonah site, moved east about 8-9 miles prior to the 2010 field program.

4.1.4 Comparison of NO_x and PM during UGWOS 2010 with 2006-2009

Average monthly NO and NO_2 concentrations at WDEQ monitoring sites in the UGRB are presented in Table 4-5.

Table 4-5

Monthly Average One-Hour NO and NO_2 Concentrations by Year for Boulder, Daniel, and Jonah/BAM

January	**1-Hour NO (ppb)**			**1-hour NO_2 (ppb)**		
Year	Boulder	Daniel	Jonah/BAM	Boulder	Daniel	Jonah/BAM
2006	1.7	0.04	11.2	7.2	0.5	16.9
2007	0.9	0.05	24.6	4.5	0.7	22.6
2008	NA	0.01	27.2	NA	0.2	26.2
2009	2.5	0.01	20.6	5.6	0.2	24.4
2010	2.1	NA	4.9*	8.0	0.7	11.2*
February	**1-Hour NO (ppb)**			**1-hour NO_2 (ppb)**		
Year	Boulder	Daniel	Jonah/BAM	Boulder	Daniel	Jonah/BAM
2006	0.9	0.04	16.3	4.8	0.7	18.1
2007	0.4	0.01	19.6	1.7	0.1	16.8
2008	NA	0.00	24.0	NA	0.1	19.0
2009	1.9	0.00	10.6	5.7	0.4	16.2
2010	1.3	NA	8.1	4.6	0.3	10.4
March	**1-Hour NO (ppb)**			**1-hour NO_2 (ppb)**		
Year	Boulder	Daniel	Jonah/BAM	Boulder	Daniel	Jonah/BAM
2006	0.3	0.01	4.4	1.8	0.4	9.0
2007	0.2	0.00	20.3	0.7	0.05	16.1
2008	0.03	0.00	13.1	0.9	0.02	14.6
2009	0.3	0.00	2.6	2.0	0.2	6.9
2010	0.2	NA	7.0	1.7	0.4	6.6

*January 15-31, 2010
NA - Data not available

Average monthly PM_{10} and $PM_{2.5}$ concentrations at WDEQ monitoring sites in the UGRB are presented in Table 4-6.

Table 4-6

Monthly Average PM_{10} and $PM_{2.5}$ Concentrations by Year for Boulder, Daniel, and Pinedale

January	**Average PM_{10} ($\mu g/m^3$)**		**Average $PM_{2.5}$ ($\mu g/m^3$)**
Year	Boulder	Daniel	Pinedale
2006	7.1	5.0	NA
2007	NA	5.2	NA
2008	6.9	6.4	NA
2009	6.7	4.9	4.1
2010	6.7	4.3	4.1*
February	**Average PM_{10} ($\mu g/m^3$)**		**Average $PM_{2.5}$ ($\mu g/m^3$)**
2006	7.4	6.1	NA
2007	5.0	4.8	NA
2008	7.4	5.7	NA
2009	6.9	6.6	3.6
2010	6.3	4.4	2.4
March	**Average PM_{10} ($\mu g/m^3$)**		**Average $PM_{2.5}$ ($\mu g/m^3$)**
2006	7.7	6.8	NA
2007	8.5	6.7	NA
2008	7.5	6.7	NA
2009	10.9	11.2	4.3
2010	8.2	6.6	3.0

* January 15-31, 2010.
NA - Data not available

Table 4-6 shows that average PM_{10} concentrations in March of 2009 were substantially higher at Boulder and Daniel than during March of other years in this summary. This was likely due to a more widespread particulate event which occurred on March 3 and 4, 2009.

4.2 Weather Conditions during the 2010 Study

In general, the 2010 UGWOS occurred during a period when the weather pattern was very active with frequent storms moving through the area. These storms were for the most part mild, fast moving and did not provide much precipitation to the study area, all features that are not favorable for ozone development. However, there were two periods during the 2010 UGWOS project when the ozone levels appeared modestly elevated above the regional background. During these periods hourly ozone levels climbed above 65 ppb. They occurred on January 28 - 30 and again on February 28 through March 1. In the following section, the two days prior to and after these dates will be included in the discussion in order to bracket the period of higher ozone.

4.2.1 Synoptic Weather Summaries of Elevated Ozone Events

In the elevated ozone event that occurred from January 28 through 30, a weak low pressure system moved through Wyoming on January 26 prior to the beginning of this episode. After this system passed to the east, higher pressure aloft moved in from the west while surface high pressure moved south from Canada into the Rockies and northern Plains states. By January 29, the surface high was centered over western Wyoming and the high pressure ridge axis aloft was centered just to the west of the study area. Both these positions are favorable for ozone development. Figures 4.11 and 4.12 show the pressure patterns at the surface and aloft, respectively, on January 29, 2010.

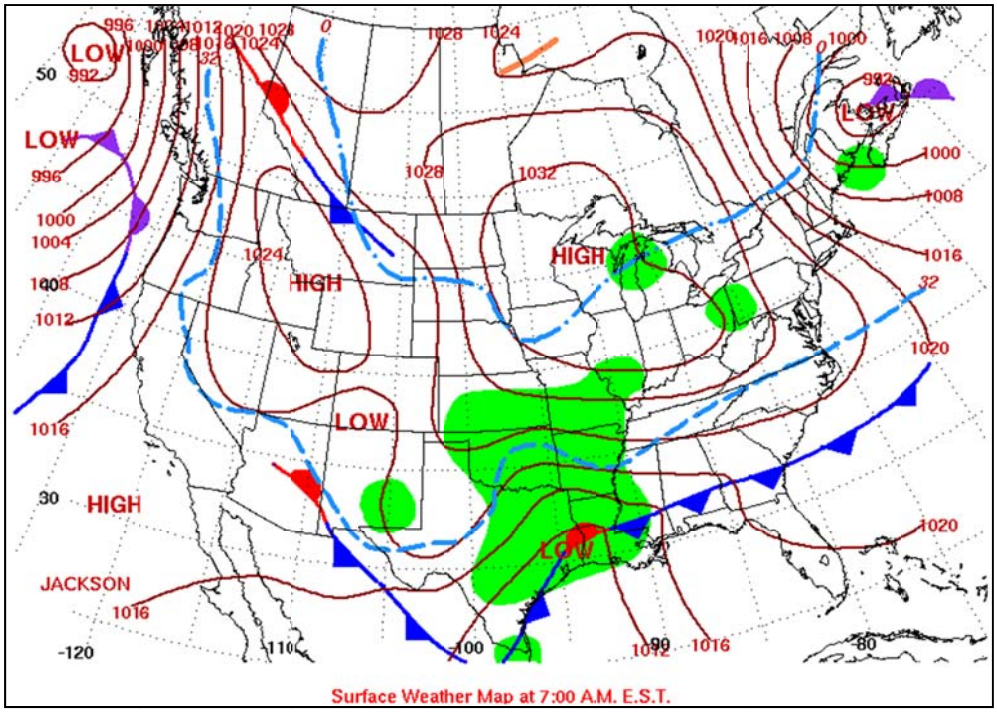


Figure 4.11 Surface Chart - January 29, 2010

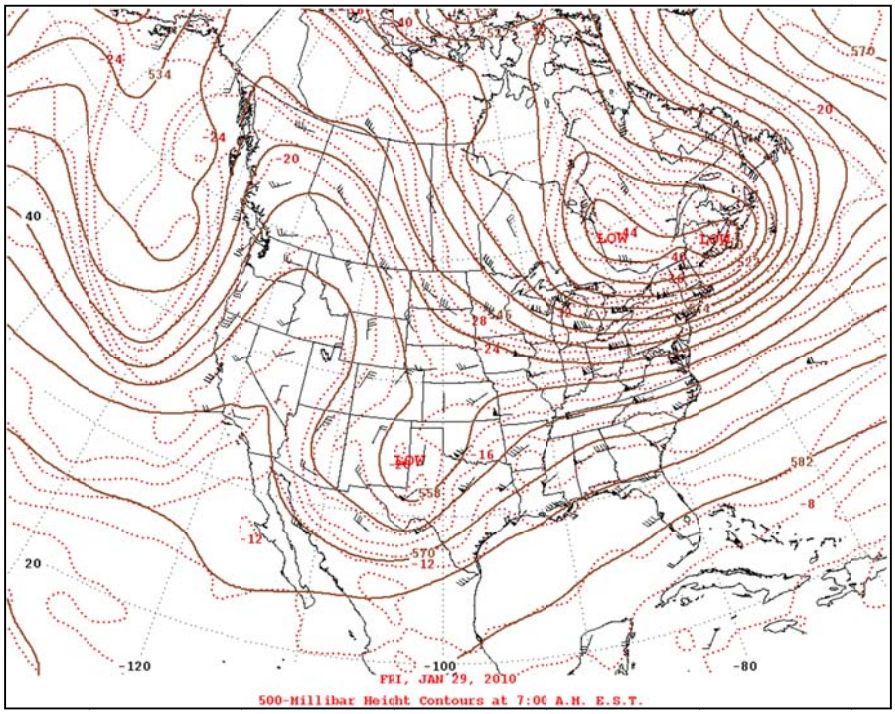


Figure 4.12 Upper Air Chart - January 29, 2010

Source: "NOAA Daily Weather Maps", http://www.hpc.noaa.gov/dailywxmap

By January 30, the strength of the high pressure over the area peaked early in the day and began to weaken rapidly as a storm approached the area from the west. On January 31, this storm moved across the state and exited into the Plains states on February 1.

In the elevated ozone event that occurred between February 28 and March 1, 2010 a high pressure ridge was weakening over the study area on February 26 as it moved eastward on this day. By February 27, the surface low from a storm moving onto the west coast was over northern California moving into Nevada and the upper ridge axis had moved into eastern Wyoming that morning. On the morning of February 28, low pressure both aloft and at the surface had moved to a position south of Wyoming over the four corners states. Higher pressure building from the west aloft and from the north at the surface occurred through the day and overnight that night. On March 1, higher pressure continued to build over western Wyoming. By March 2, the high pressure ridge axis aloft was over western Wyoming early in the day but was moving to the east. At the surface, low pressure was already pushing into the state by morning and continued to move into the state during the day. On March 3, Wyoming was in southwest flow aloft with the high pressure over the plains states and low pressure along the west coast. Conditions during this period were never strongly favorable for ozone development, but a brief period from late on February 28 through early in the day on March 1 was somewhat favorable. The obstacle to ozone formation during this episode was the brevity of the time high pressure was over the area (less than 24 hours) and the lack of snow cover. Figures 4.13 and 4.14 show the surface and upper air charts for March 1.

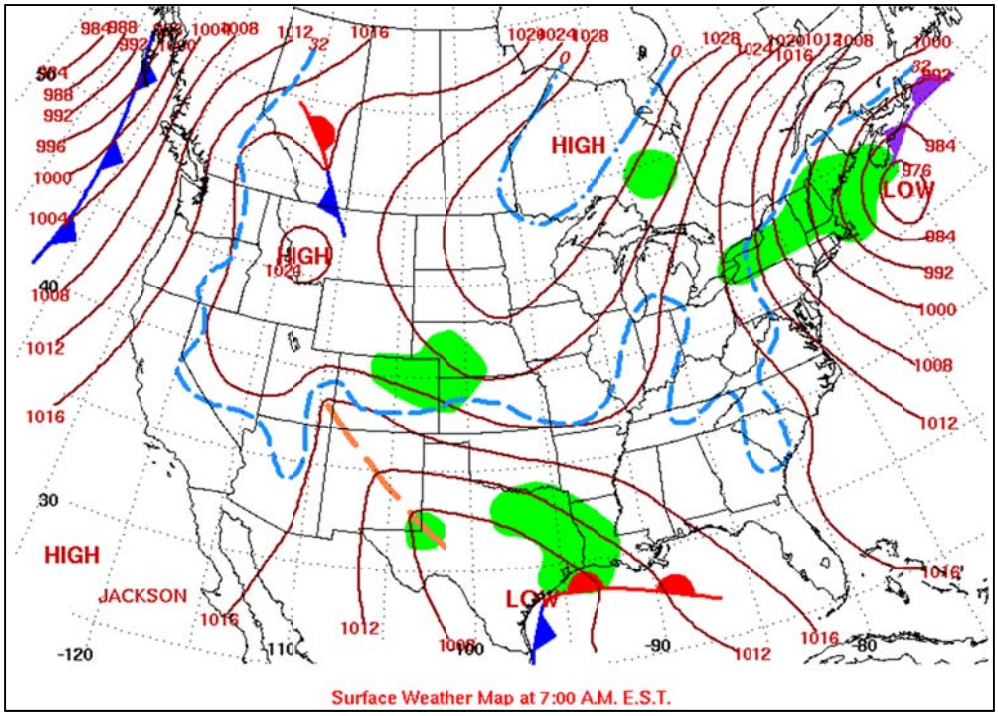


Figure 4.13 Surface Chart - March 1, 2010

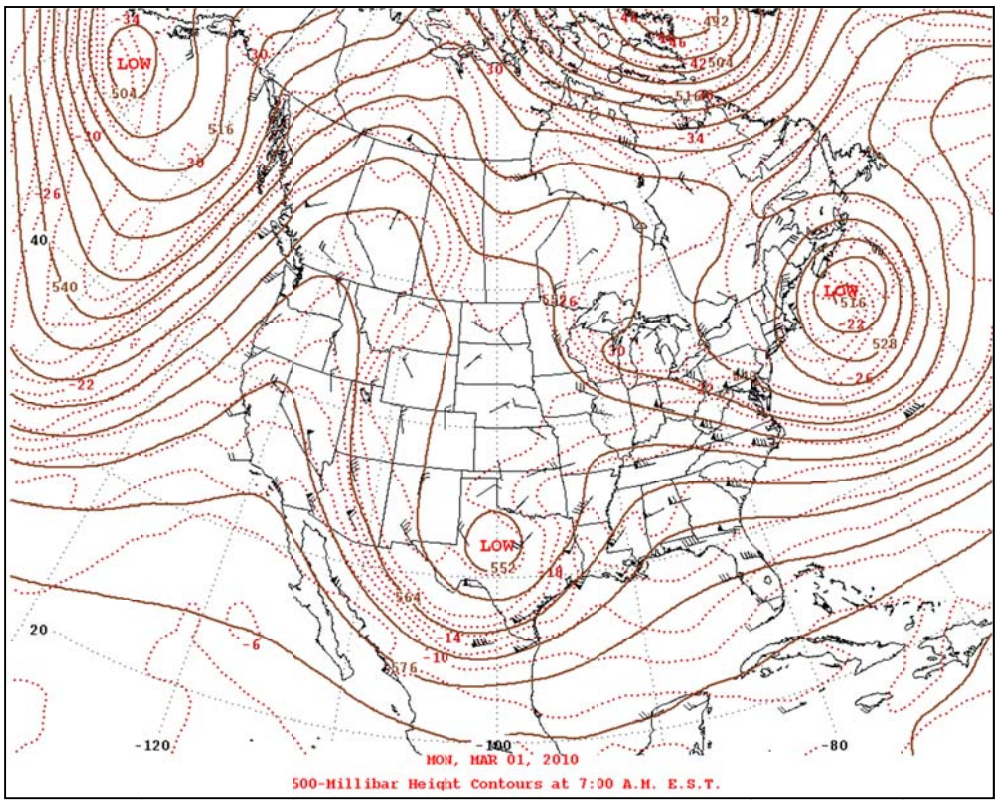


Figure 4.14 Upper Air Chart - March 1, 2010

Source: "NOAA Daily Weather Maps", http://www.hpc.noaa.gov/dailywxmap

4.3 Ozone Concentrations During UGWOS 2010

There were no exceedances of the US EPA ozone eight-hour standard (75 ppb) observed at any air quality monitoring stations in the UGRB during the first quarter of 2010. It should be noted that the EPA plans to release a revised eight-hour ozone standard by August 31, 2010 which is expected to fall within the 60 - 70 ppb range. There was only one day during UGWOS 2010 when eight-hour ozone concentrations exceeded 65 ppb and that occurred on January 30, 2010. Maximum eight-hour ozone concentrations at UGRB and other Wyoming sites during the UGWOS 2010 field measurement period are shown in Figure 4.15. The three sites which recorded eight-hour ozone values exceeding 65 ppb during this period are Warbonnet, Bargerville, and Boulder. Warbonnet was part of the UGWOS 2010 Mesonet. Bargerville is part of the Sublette County Health Risk Network and Boulder is a permanent WDEQ monitoring station. Table 4-7 shows maximum running eight-hour average ozone concentrations during the two elevated ozone periods which occurred during UGWOS 2010. The UGRB network daily maximum is indicated across the bottom of the table. As mentioned in previous UGWOS reports, caution is required in comparing results from different types of monitoring sites shown in Figure 4.15 and Tables 4-7 and 4-8. Data from the UGWOS Mesonet monitoring sites including Cora, Warbonnet, Big Sandy, Simpson, Mesa, Speedway, Seedskadee, Buckhorn and 18-Mile were collected using solar/battery powered 2B ozone analyzers that do not meet Federal Equivalent Method (FEM) monitoring requirements for ozone since they were operated in unheated enclosures. Only FEM analyzer data can be compared directly with EPA's ambient air quality standard to determine if an exceedance has occurred. Non-FEM instrumentation such as the 2B ozone analyzers provides approximate ozone concentrations that do not meet EPA's legal requirements for quantifying ozone in ambient air.[4]

Running eight-hour ozone data for the UGWOS 2010 period January 15 to March 31 are shown in Figure 4.16 and 4.17 at mesonet and non-mesonet sites, respectively. Overall, mesonet and non-mesonet ozone monitors in the UGRB recorded similar highs and maximums. There were only a few instances of eight-hour ozone concentrations exceeding 60 ppb and sites recording the highest values were usually grouped together in the same part of the study area.

[4] Final Report: 2009 Upper Green River Winter Ozone Study, ENVIRON, March 2010

Table 4-7

Maximum Eight-hour Average Ozone Concentrations During Elevated Ozone Periods in 2010

Station	Jan 26	Jan 27	Jan 28	Jan 29	Jan 30	Jan 31	Feb 01	Feb 26	Feb 27	Feb 28	Mar 1	Mar 2	Mar 3
Cora	42	41	41	55	51	46	37	44	54	53	49	47	55
Warbonnet	43	48	46	51	71	43	40	46	51	58	53	51	51
Big Sandy	NA	NA	NA	53	50	45	42	43	48	53	53	50	50
Simpson	NA	NA	NA	NA	45	39	NA	41	45	48	48	46	49
Mesa	NA	NA	44	48	58	46	41	47	55	52	51	51	52
Speedway	40	44	53	49	54	42	40	48	50	57	60	47	53
Seedskadee	35	NA	NA	NA	NA	NA	NA	42	46	52	50	44	50
Buckhorn	45	49	43	47	58	41	39	43	48	49	50	49	NA
18 Mile	41	42	44	46	49	41	37	40	44	47	47	46	48
BAM	41	47	41	50	57	41	37	43	50	53	51	51	50
Bargerville	45	51	49	59	68	48	41	52	55	62	62	53	55
Farson	34	42	39	41	40	41	36	41	45	45	47	45	47
LaBarge	35	34	36	39	43	37	34	37	42	44	44	43	45
Marbleton	37	39	41	45	45	51	37	44	50	50	50	47	50
SandDraw	39	42	42	48	62	43	37	46	49	58	53	49	51
Daniel	44	42	44	45	47	49	40	45	52	46	50	47	51
Boulder	42	54	54	53	69	45	44	42	52	53	49	47	48
Pinedale	41	44	43	52	61	45	40	46	53	63	60	52	NA
Juel Springs	43	46	45	52	52	42	40	47	48	57	53	51	53
Murphy	38	38	40	39	37	39	39	46	48	51	47	47	51
Olson Ranch	43	45	41	46	57	47	41	42	52	53	49	47	48
Network Max.	**45**	**54**	**54**	**59**	**71**	**51**	**44**	**52**	**55**	**63**	**62**	**53**	**55**

NA - Data not available
Daily Maximum in Red

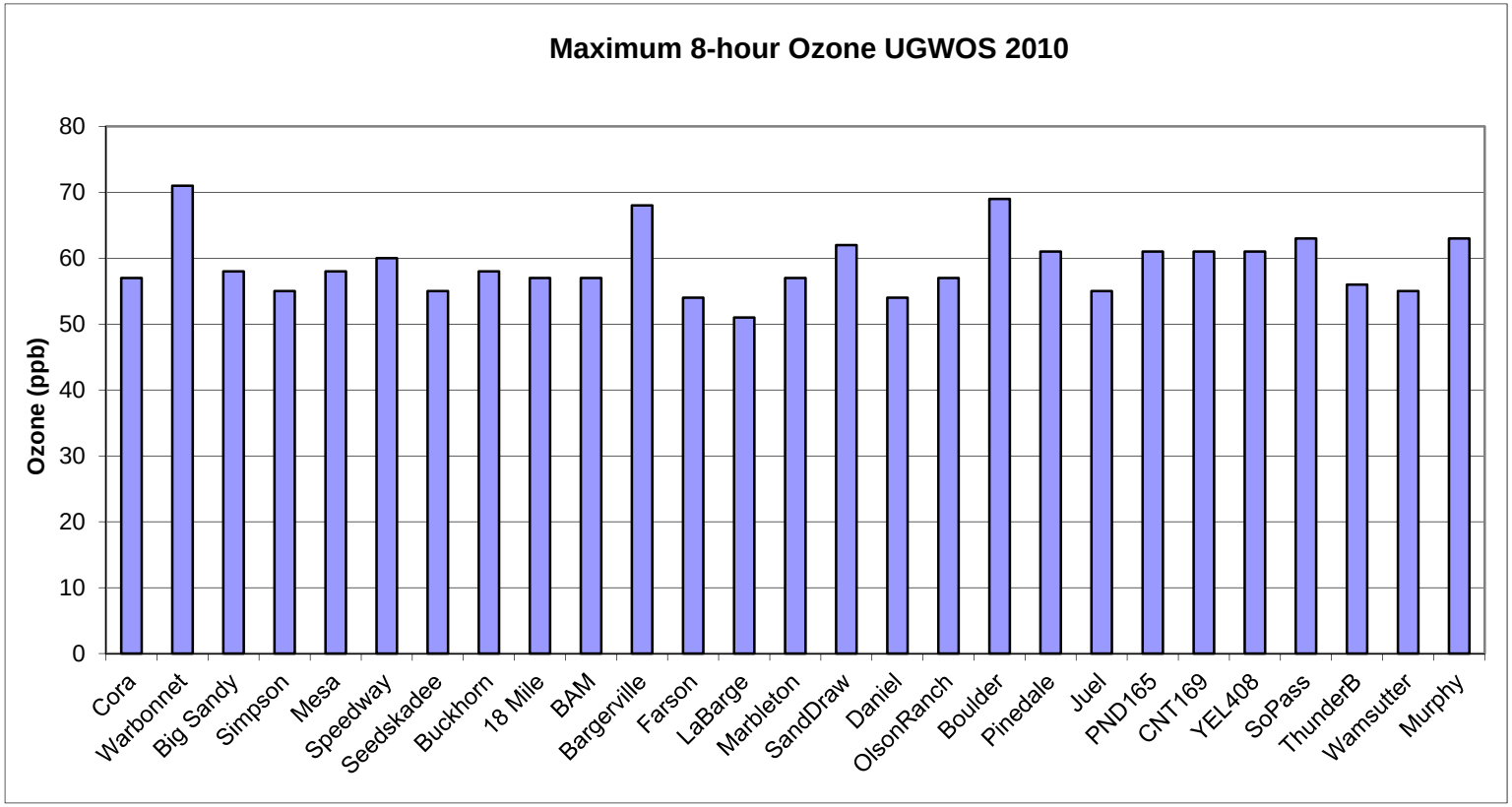


Figure 4.15 Maximum Eight-Hour Average Ozone Concentrations in the UGRB and other Wyoming Sites during the UGWOS 2010 Period

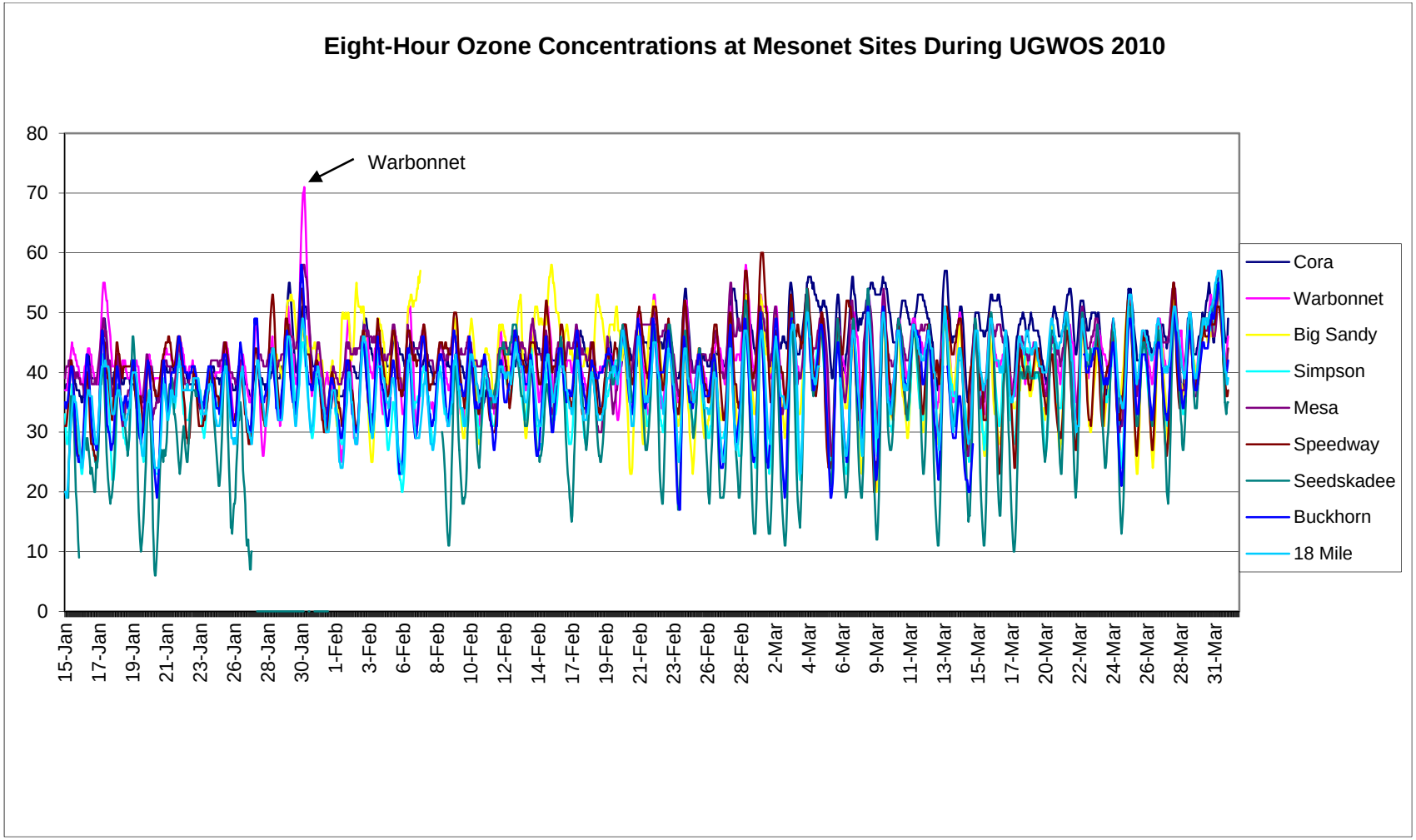


Figure 4.16 Running Eight-Hour Ozone Concentrations at Mesonet Sites

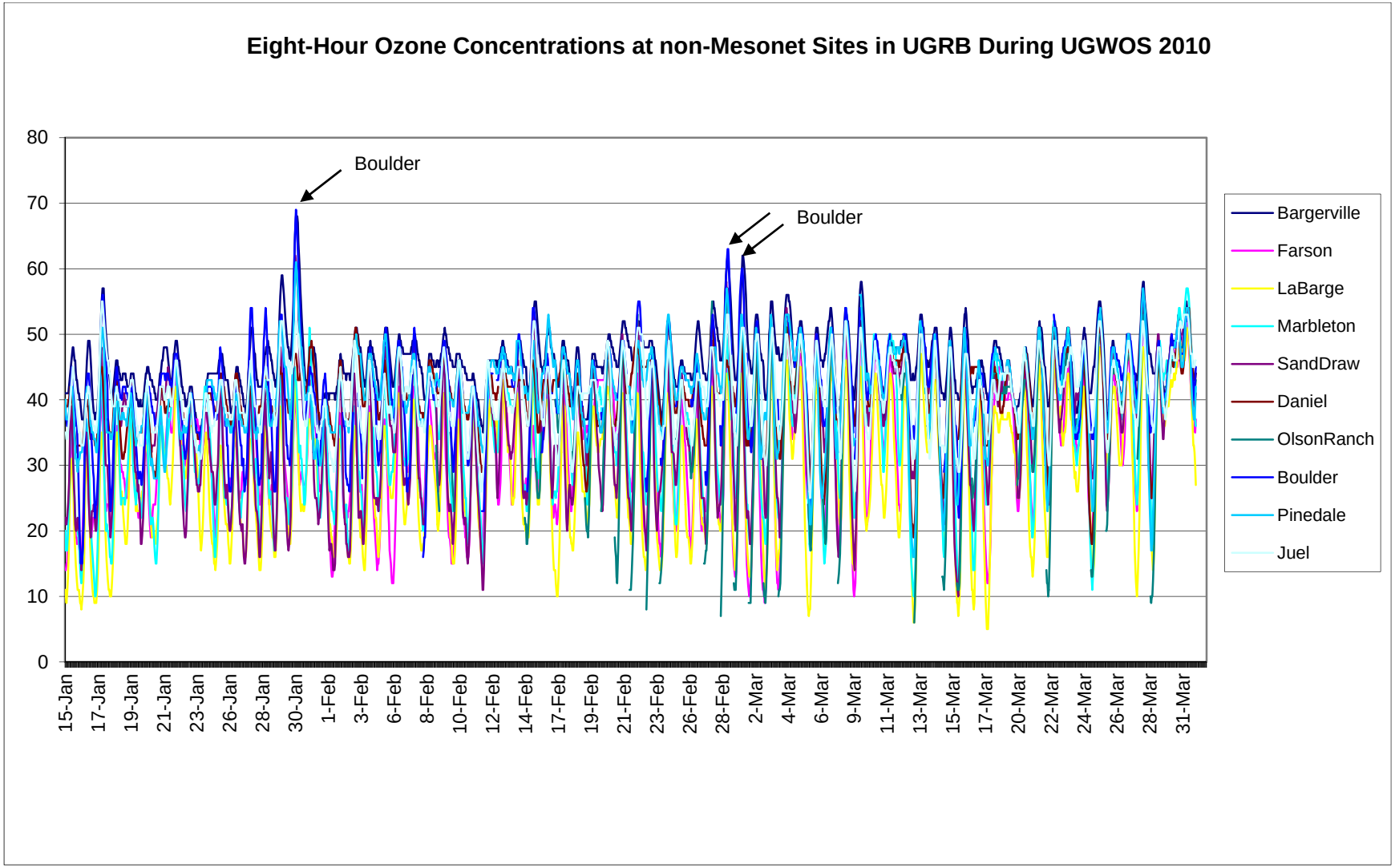


Figure 4.17 Running Eight-Hour Ozone Concentrations at Non-mesonet Sites

A comparison of the maximum daily eight-hour ozone concentrations in the UGWOS study area with data from other Wyoming sites outside of the study area is shown in Figure 4.18. This figure also includes data from the EPA CASTNET Pinedale monitor (PND 165) which is located 220 meters above and to the east of the town of Pinedale. Although not as dramatic as in previous years, the UGWOS ozone concentration is higher than concentrations in other areas of Wyoming particularly in the period prior to March 5, 2010 when snow cover was still present. This is consistent with findings from previous UGWOS years which provided evidence that UGRB ozone is formed from local precursor sources.

Figure 4.19 shows the number of cases of running eight-hour average of ozone greater than 55 ppb. In the UGRB, Bargerville is the location with the highest ozone impacts during UGWOS 2010. Figure 4.20 shows the number of cases of running eight-hour averages of ozone less than 25 ppb. Sites with frequent low ozone values include Seedskadee, Farson, La Barge, and Olson Ranch. Frequent very low values suggest the influence of fresh NO_x emissions.

During the two somewhat elevated ozone episodes which occurred during UGWOS 2010, there were five days when one-hour average ozone concentrations exceeded 65 ppb. Table 4-8 shows maximum one-hour average ozone observed on these days and the days prior to and after these episodes peaked at monitoring sites in the UGRB and in other Wyoming locations. Figure 4.21 provides a graphical presentation of Table 4-8. Elevated ozone concentrations were highest and most widespread on January 30 with 80 ppb recorded at Warbonnet. Other sites on this day with one-hour average concentrations above 65 ppb were: 79 ppb at Sand Draw, 78 ppb at Boulder, 74 ppb at Bargerville, 68 ppb at Pinedale and Buckhorn, and 67 ppb at Mesa.

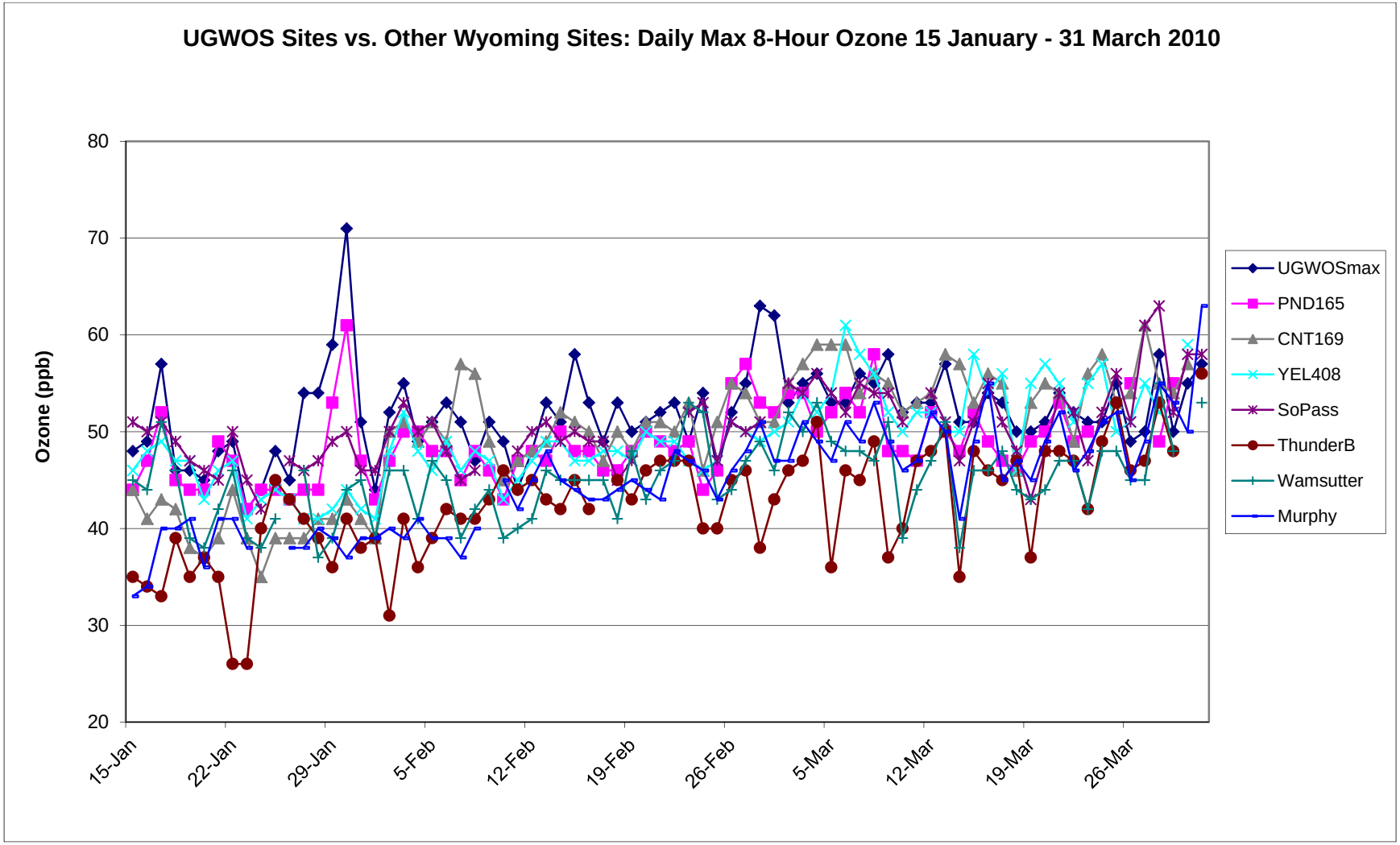


Figure 4.18 Daily Maximum Eight-hour Ozone, UGWOS and Other Wyoming Sites

Figure 4.19

Running Eight-Hour Average Ozone Cases Greater than 55 ppb

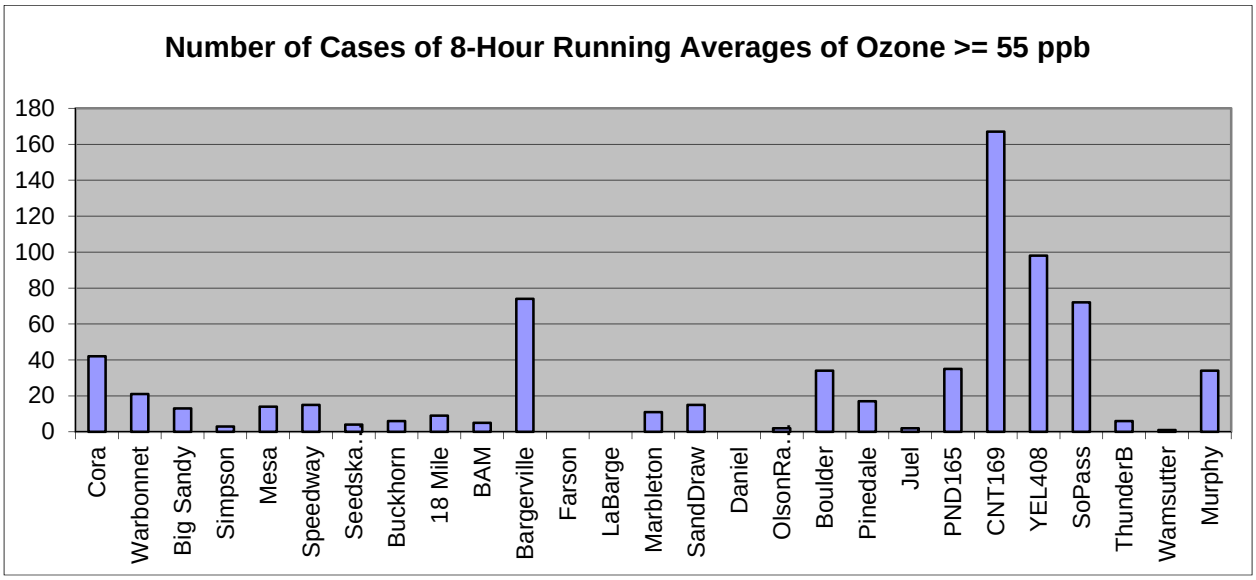


Figure 4.20

Running Eight-Hour Average Ozone Cases Less than 25 ppb

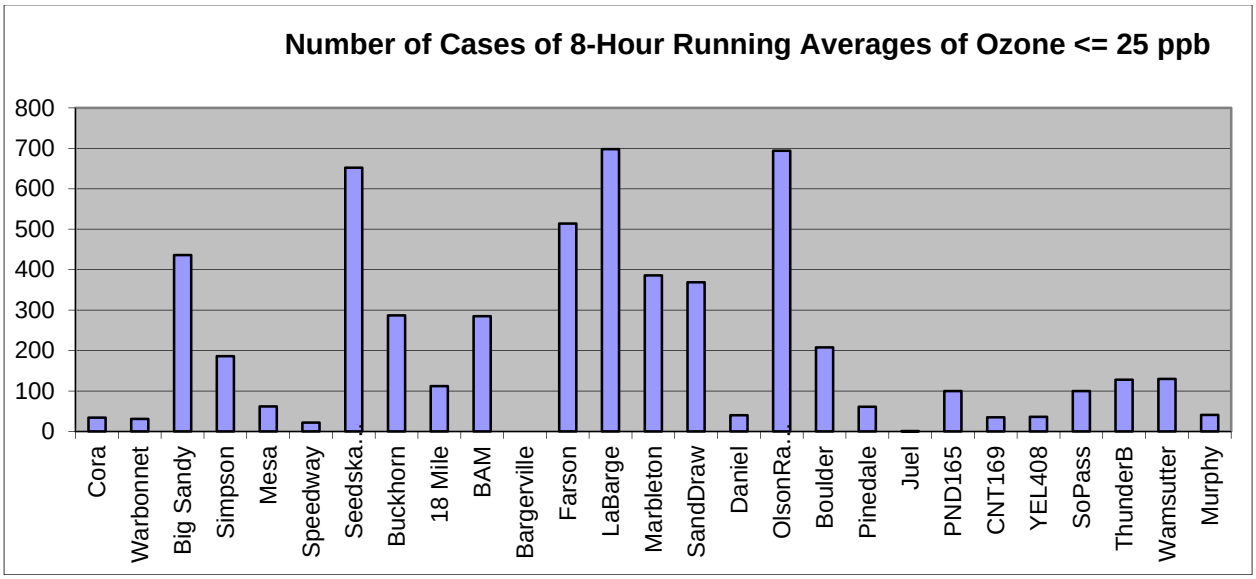


Table 4-8

Maximum One-hour Average Ozone Concentrations During Elevated Ozone Periods in 2010

Station	Jan 26	Jan 27	Jan 28	Jan 29	Jan 30	Jan 31	Feb 01	Feb 26	Feb 27	Feb 28	Mar 1	Mar 2	Mar 3
Cora	44	43	42	61	55	52	38	46	57	56	54	51	60
Warbonnet	46	54	49	58	80	51	45	47	57	59	57	56	54
Big Sandy	NA	NA	NA	55	53	48	45	49	53	57	57	57	55
Simpson	NA	NA	NA	NA	49	42	38	45	49	52	52	49	51
Mesa	NA	NA	46	57	67	53	42	49	60	60	55	59	55
Speedway	43	50	63	57	59	47	44	52	54	67	68	53	57
Seedskadee	46	NA	NA	NA	NA	NA	NA	44	51	57	55	50	53
Buckhorn	49	61	46	51	68	44	42	44	54	52	52	52	51
18 Mile	43	46	47	48	53	42	38	42	48	50	49	49	50
BAM	47	56	45	55	62	45	41	45	54	59	54	55	52
Bargerville	46	55	52	64	74	52	46	56	57	66	72	64	60
Farson	41	44	48	49	50	43	40	46	50	53	51	51	51
LaBarge	42	41	43	43	51	45	38	41	48	49	49	48	49
Marbleton	48	46	50	49	54	60	41	47	57	53	54	54	54
SandDraw	45	48	54	62	79	48	46	49	55	76	58	55	57
Daniel	49	45	46	49	53	54	42	47	59	48	54	50	55
Boulder	45	62	70	56	78	47	64	48	58	69	76	60	NA
Pinedale	45	49	46	62	68	51	42	50	61	62	57	66	59
Juel Springs	47	49	49	56	57	46	43	45	53	58	54	56	53
Murphy	40	41	42	42	41	41	40	49	54	54	50	52	53
Olson Ranch	51	56	48	57	74	54	43	44	63	62	52	52	52
Network Max.	**49**	**62**	**70**	**64**	**80**	**60**	**64**	**56**	**61**	**76**	**76**	**66**	**60**

NA - Data not available

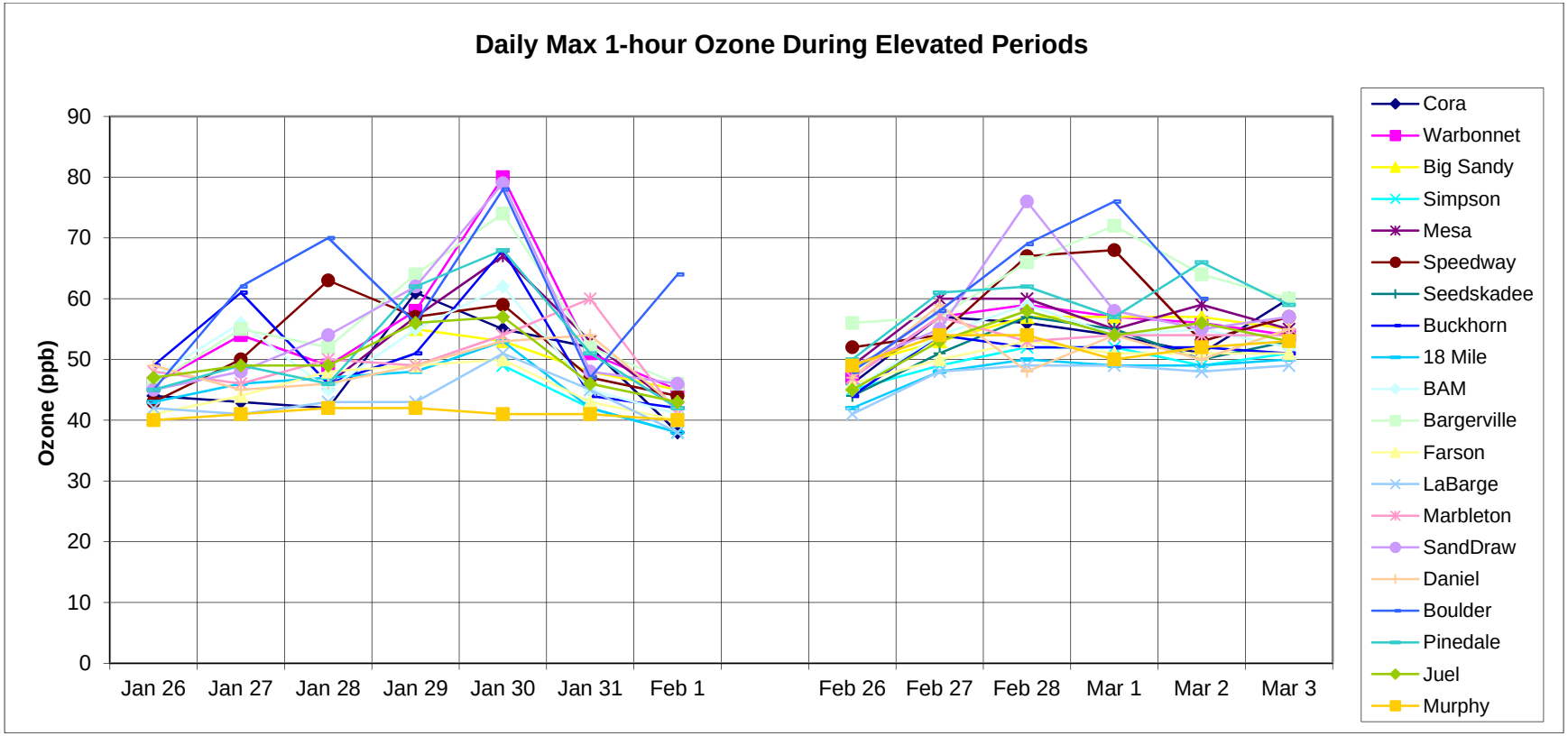


Figure 4.21 Daily Maximum One-hour Ozone During Elevated Periods

4.4 Ozone Spatial and Temporal Distribution

In order to better characterize the ozone distribution in the UGRB, the monitoring network operated in 2009 and previous years was expanded in 2010 to include the Big Sandy and 18-mile monitoring sites as part of the temporary Mesonet. Big Sandy is located in the southeast part of the study domain, southeast of Speedway and east of Juel Springs. 18-Mile lies midway between Buckhorn and Seedskadee and east of the line joining the two sites. The addition of these two sites provided monitoring data for areas that previously were gaps in the southern portion of the study domain. (See map in Figure 2.1).

This section provides an overview of ozone development at UGRB sites during the two elevated ozone periods which occurred during UGWOS 2010. Figures 4.22 and 4.23 provide an easy mechanism for quickly identifying which monitoring sites in the UGRB recorded the highest concentrations during the first elevated ozone period, January 26 through February 1, 2010. The highest concentrations ranged spatially from Buckhorn in the middle of the basin then northeast to Warbonnet, Sand Draw, Speedway, Boulder, Bargerville, Pinedale and north to Cora.

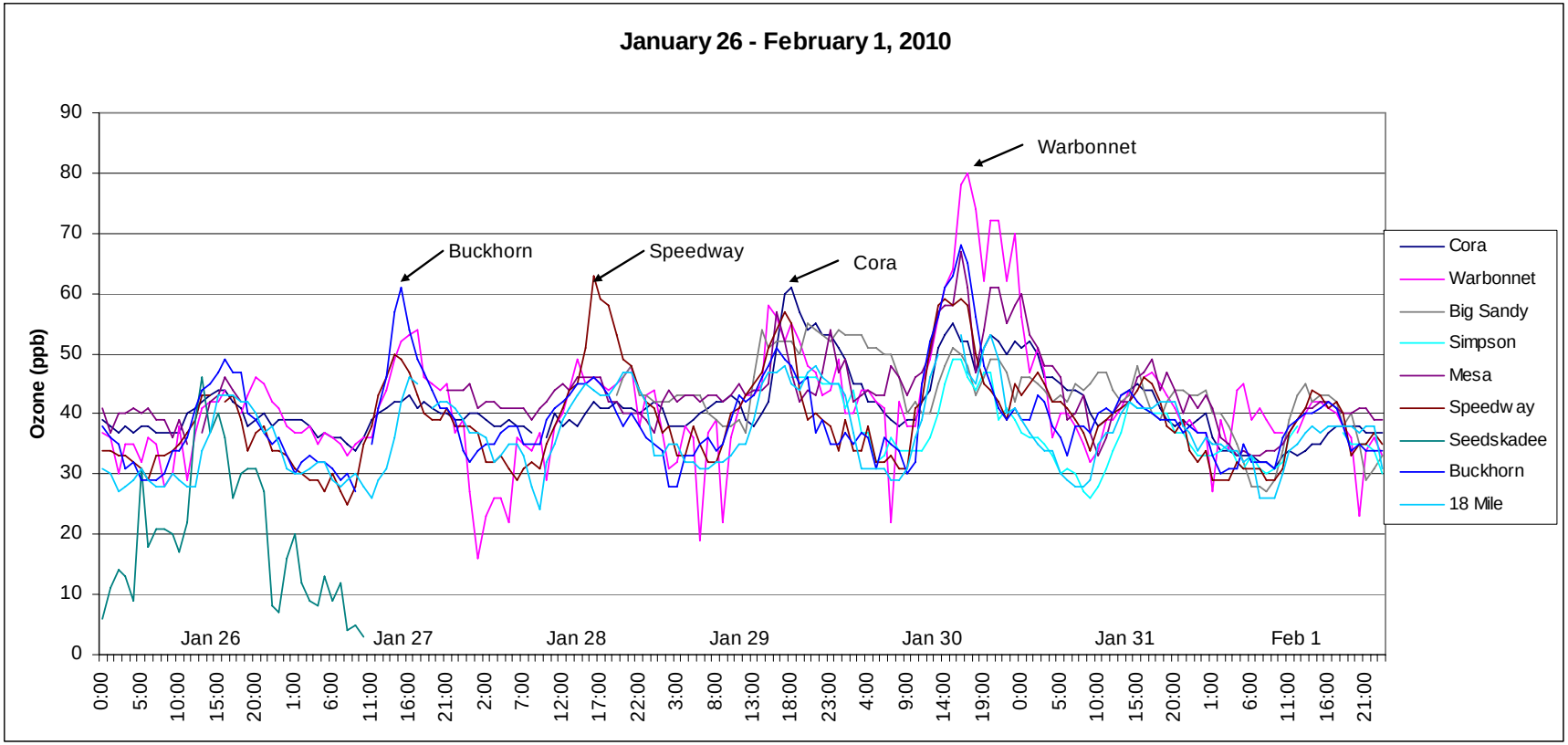


Figure 4.22 One-Hour Ozone at UGWOS 2010 Mesonet Sites

January 26 - February 1, 2010

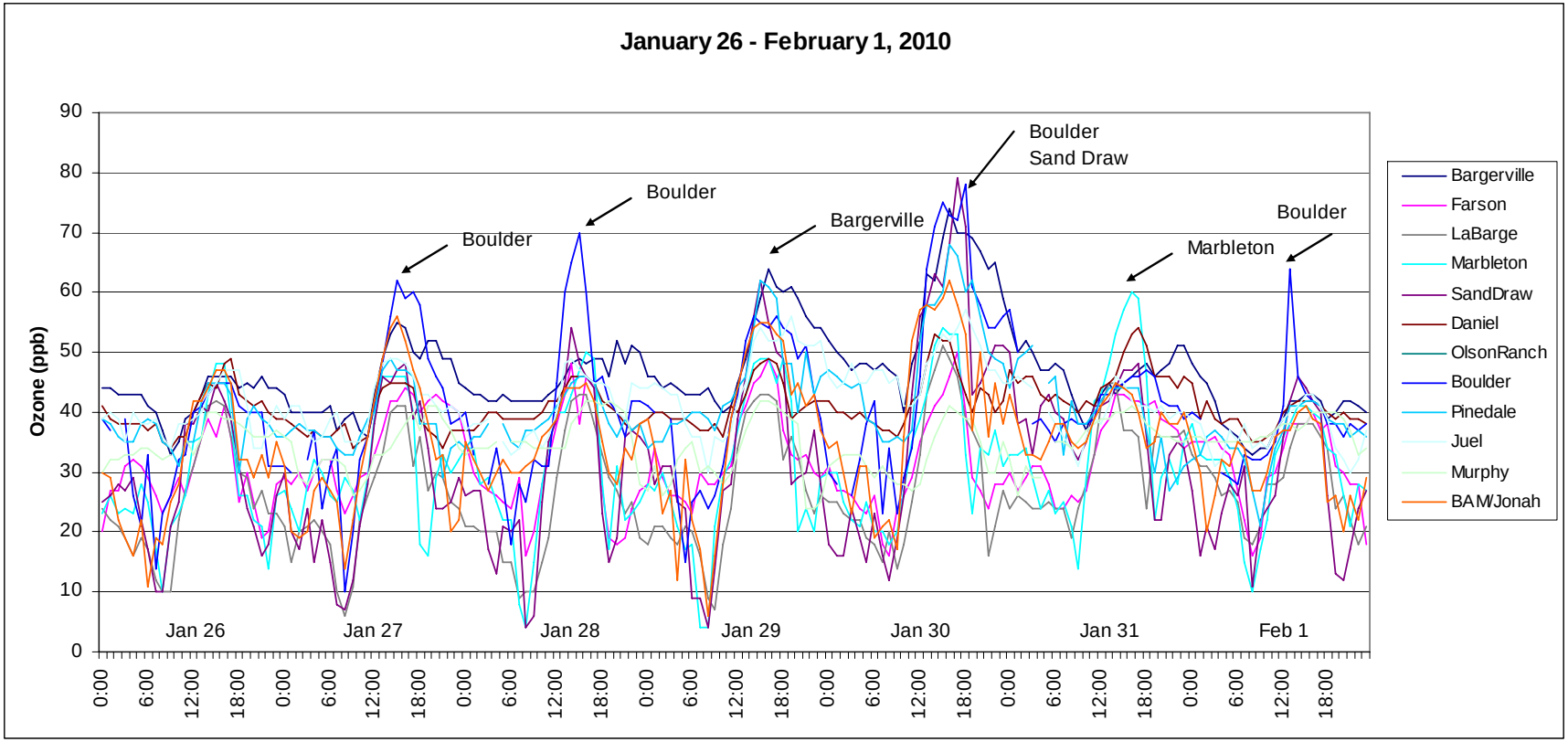


Figure 4.23 One-Hour Ozone at Other UGRB Sites January 26 - February 1, 2010

During the second UGWOS 2010 elevated period, February 26 through March 3, 2010, Figures 4.24 and 4.25 show the highest ozone concentrations ranging spatially from Warbonnet to Sand Draw, Speedway, Boulder, Bargerville, and Pinedale.

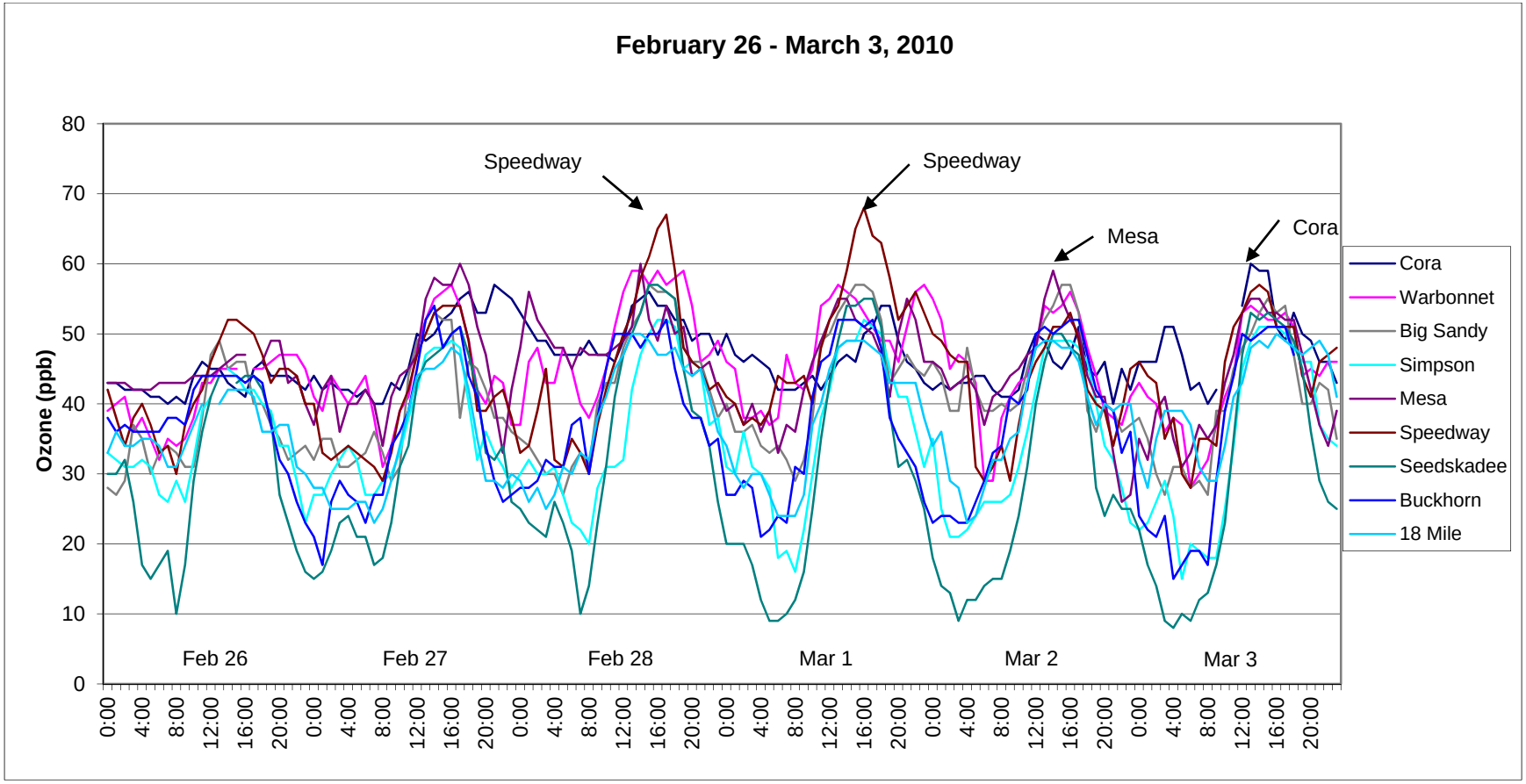


Figure 4.24 One-Hour Ozone at UGWOS 2010 Mesonet Sites February 26 - March 3, 2010

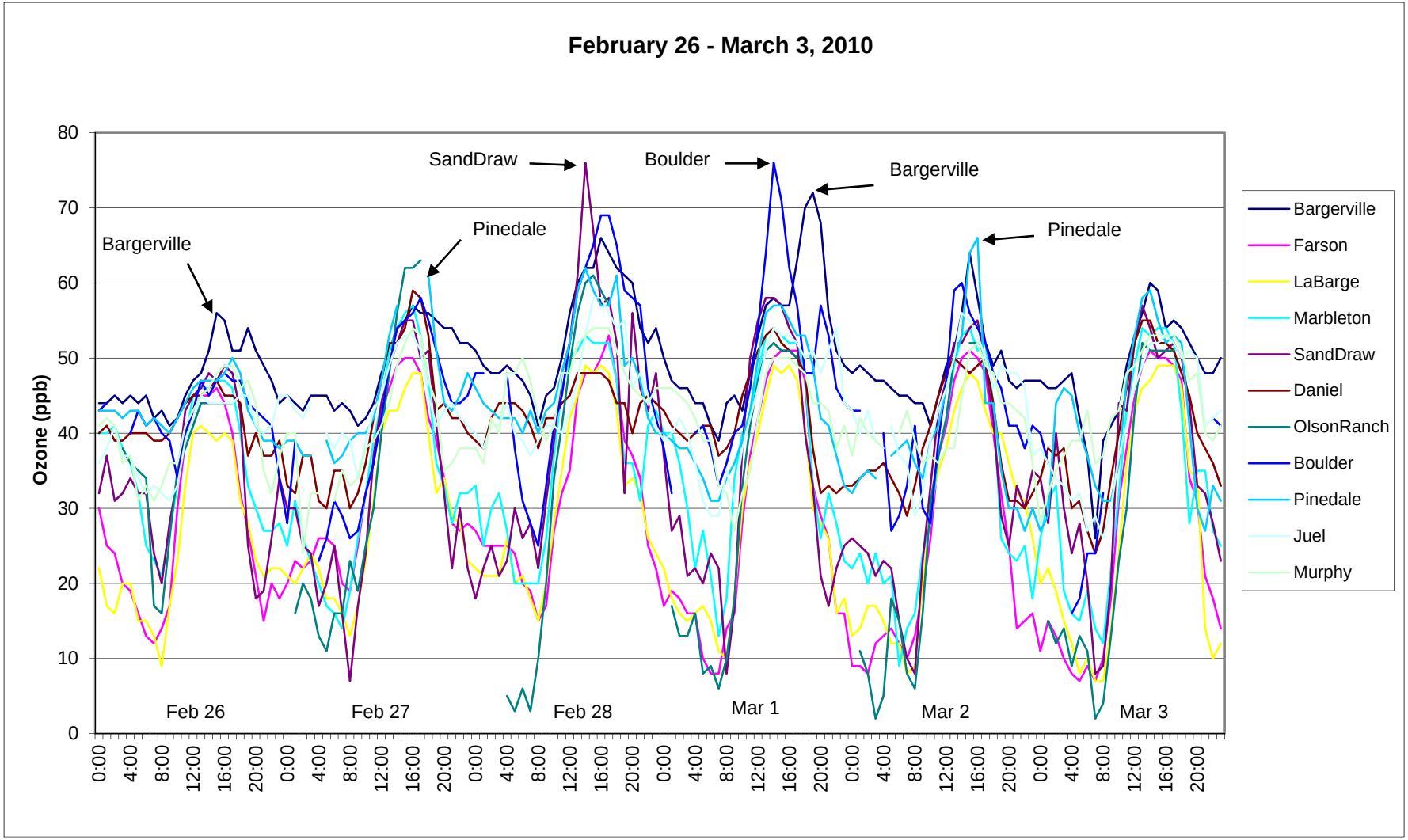


Figure 4.25 One-Hour Ozone at Other UGRB Sites February 26-March 3, 2010

The spatial distribution of the highest ozone concentrations recorded in the UGRB during the 2010 field study is further confirmed by inspection of Figure 4.26 which shows a contour plot of one-hour maximum ozone values at each site during the study period. Elevated ozone during UGWOS 2010 occurred mainly in the portion of the study domain which could be defined by lines interconnecting Buckhorn, Speedway, and Pinedale.

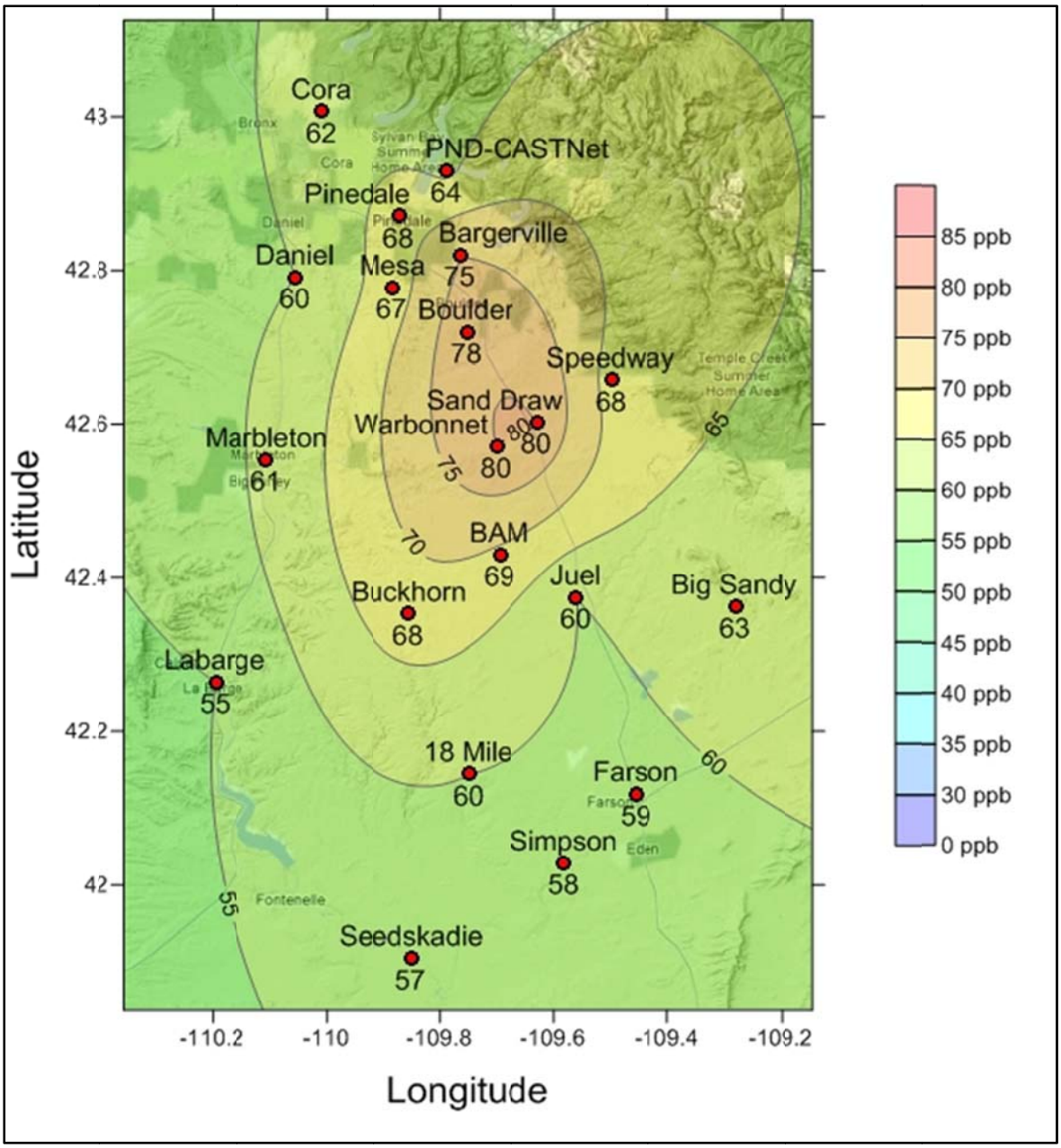


Figure 4.26 One-Hour Maximum O_3 Concentrations during the Period January 15 - March 31, 2010

Figure 4.27 shows the same contour plot as Figure 4.26 with the addition of drill rig sites (black dots) and compressor station sites (blue dots) that were active during the UGWOS 2010 study period. Drill rig and compressor station locations were provided by the WDEQ-AQD.

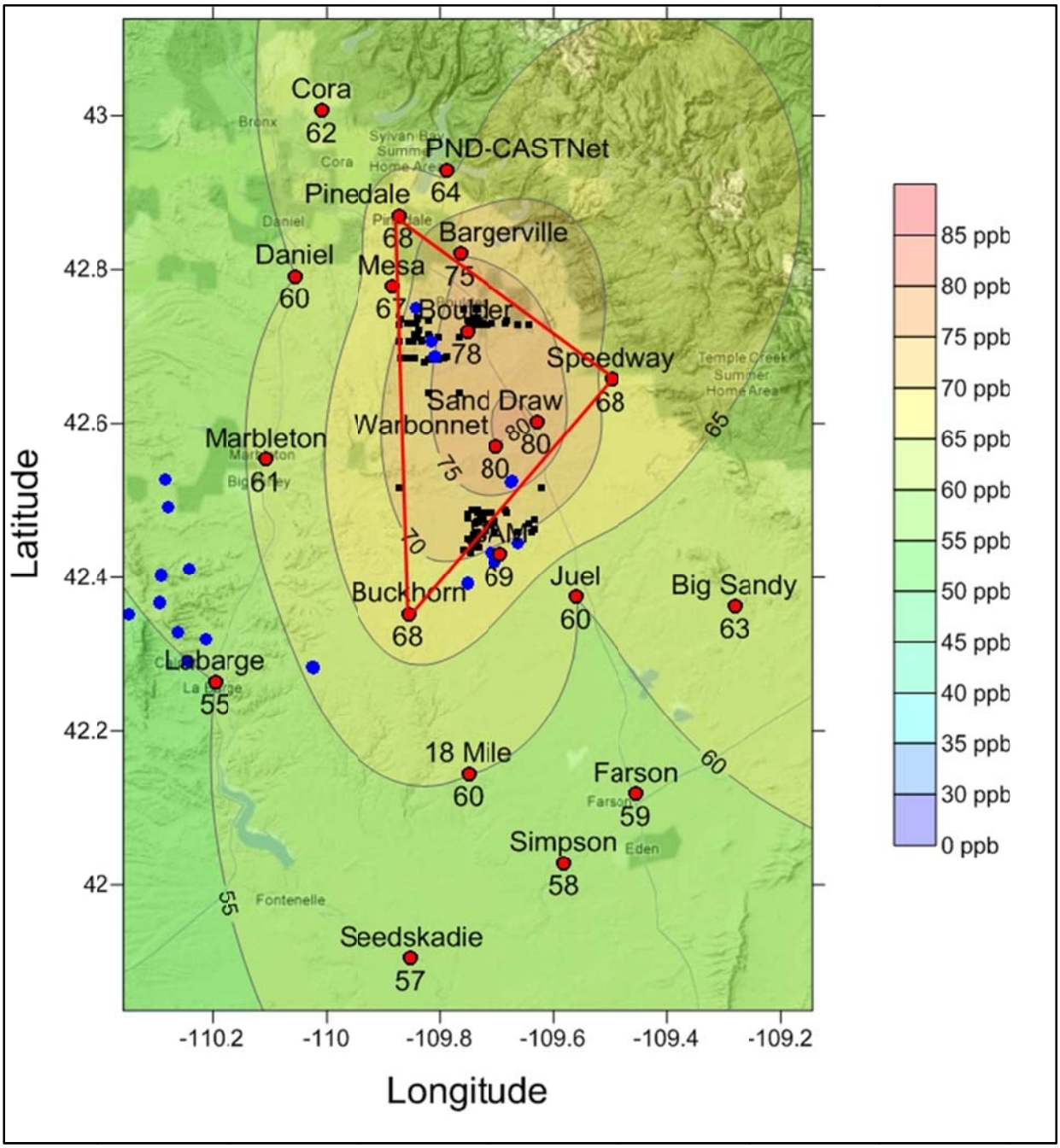


Figure 4.27 Locations of Drilling Rigs and Compressors and One-Hour Maximum O_3 Concentrations during the Period January 15 - March 31, 2010

4.4.1 One-Hour Average Diurnal Ozone Patterns

Diurnal ozone patterns show early morning minimums in the 10-45 ppb range. Morning ozone production generally starts between 0800 and 1100 and peaks in the mid-afternoon or early evening between 1400 and 1900. Ozone maximums ranged from 40-80 ppb during the first elevated period in late January and from high 40's to 70-75 ppb during the second elevated period a month later. Figures 4.28 through 4.31 show examples of diurnal patterns at mesonet and other UGRB sites during a representative day for each elevated period - January 30 and March 1, 2010. Both of these days experienced light and variable winds and ozone concentrations appeared to fluctuate as air masses meandered locally. Figure 4.28 provides an example of this occurrence at Warbonnet in the latter part of the day from about 1600 to midnight. Early morning ozone minimums at Warbonnet evident in this same figure suggest NO_x scavenging of ozone between 0600 and 0800 due to increased road traffic during this period. This appears to occur at other sites subject to increased early morning vehicle activity as evident in Figures 4.30 and 4.31 at Farson, Sand Draw, Olsen Ranch, Marbleton, and LaBarge.

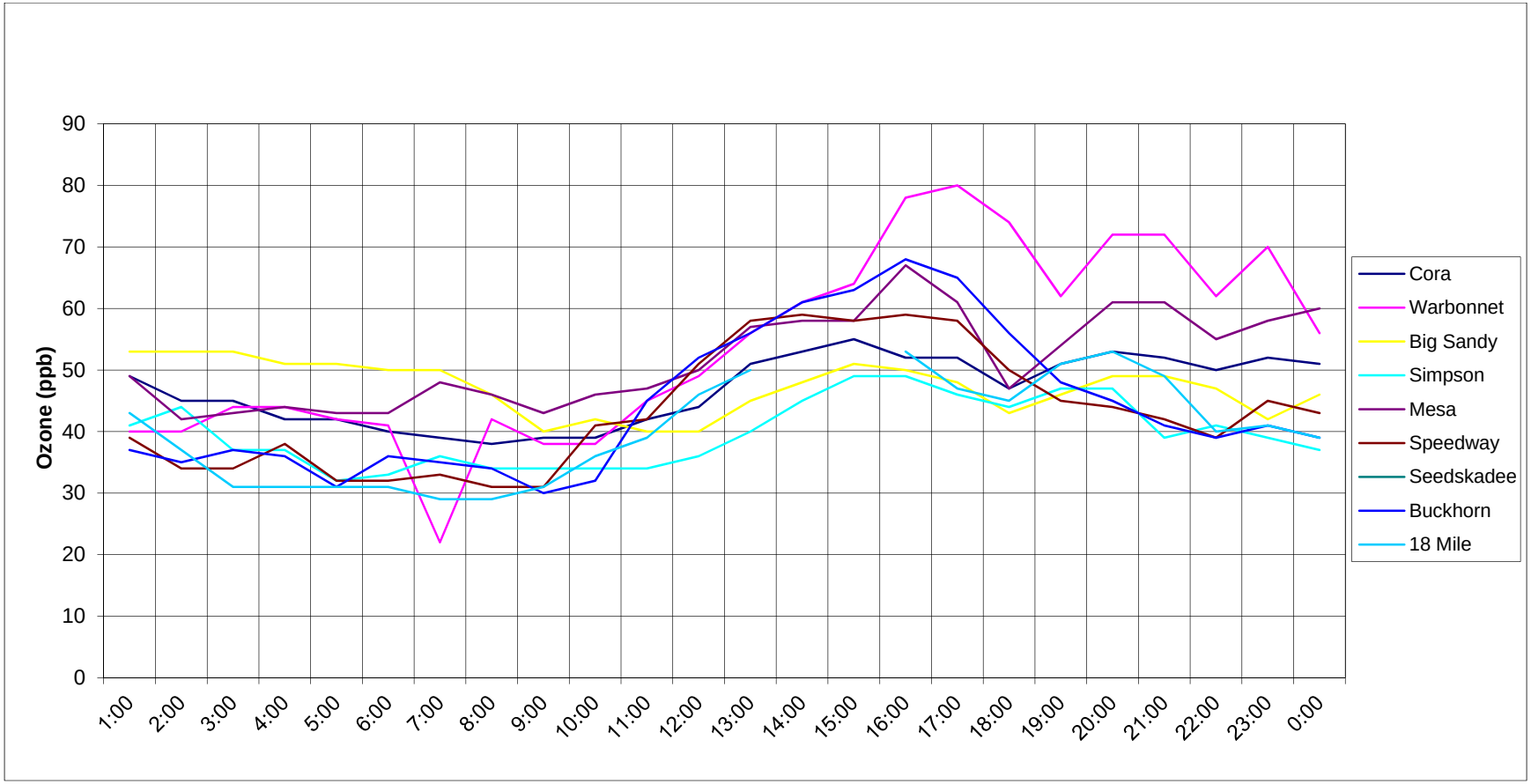


Figure 4.28 One-Hour Ozone at UGWOS 2010 Mesonet Sites on January 30, 2010

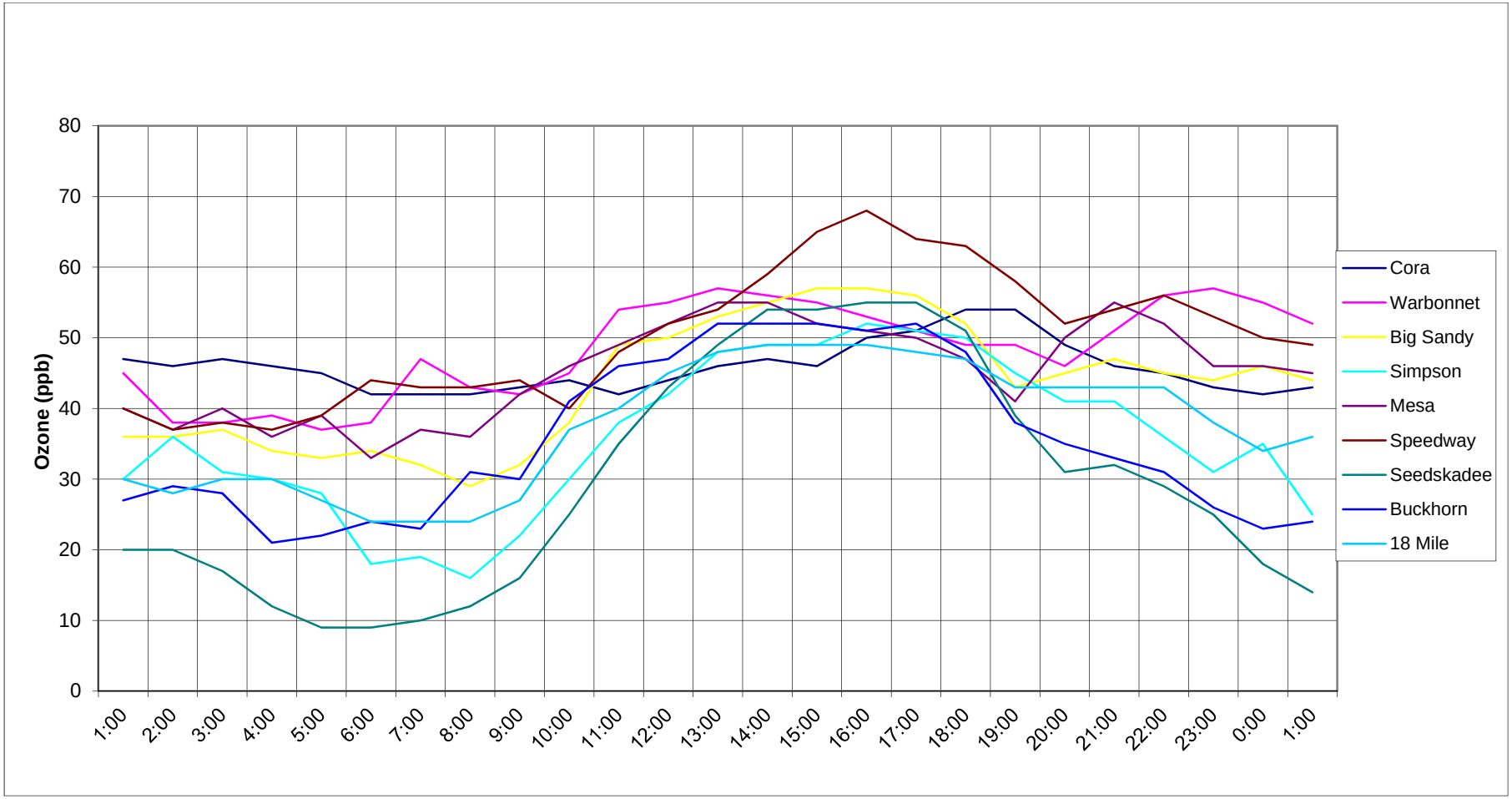


Figure 4.29 One-Hour Ozone at UGWOS 2010 Mesonet Sites on March 1, 2010

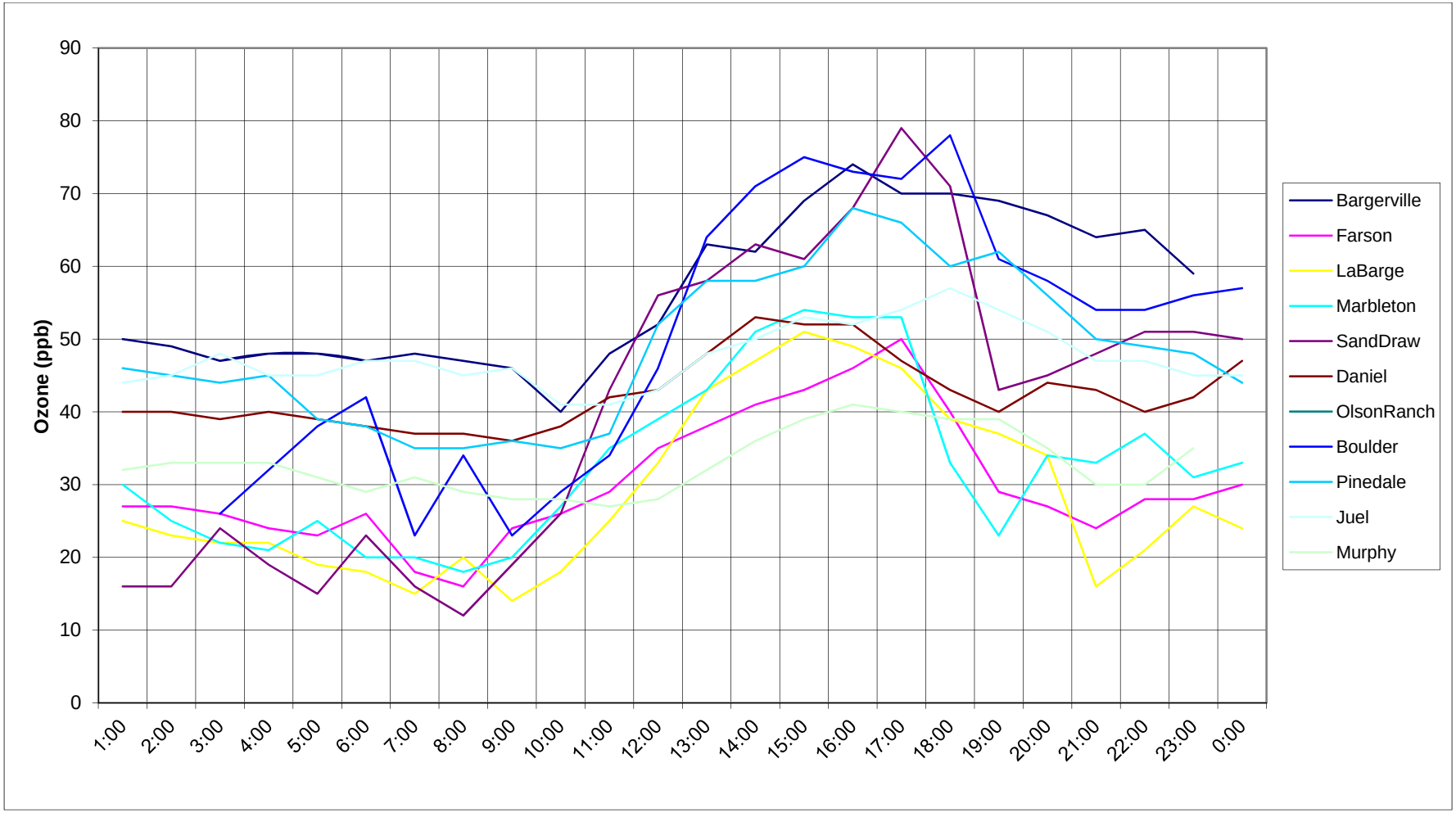


Figure 4.30 One-Hour Ozone at Other UGRB Sites on January 30, 2010

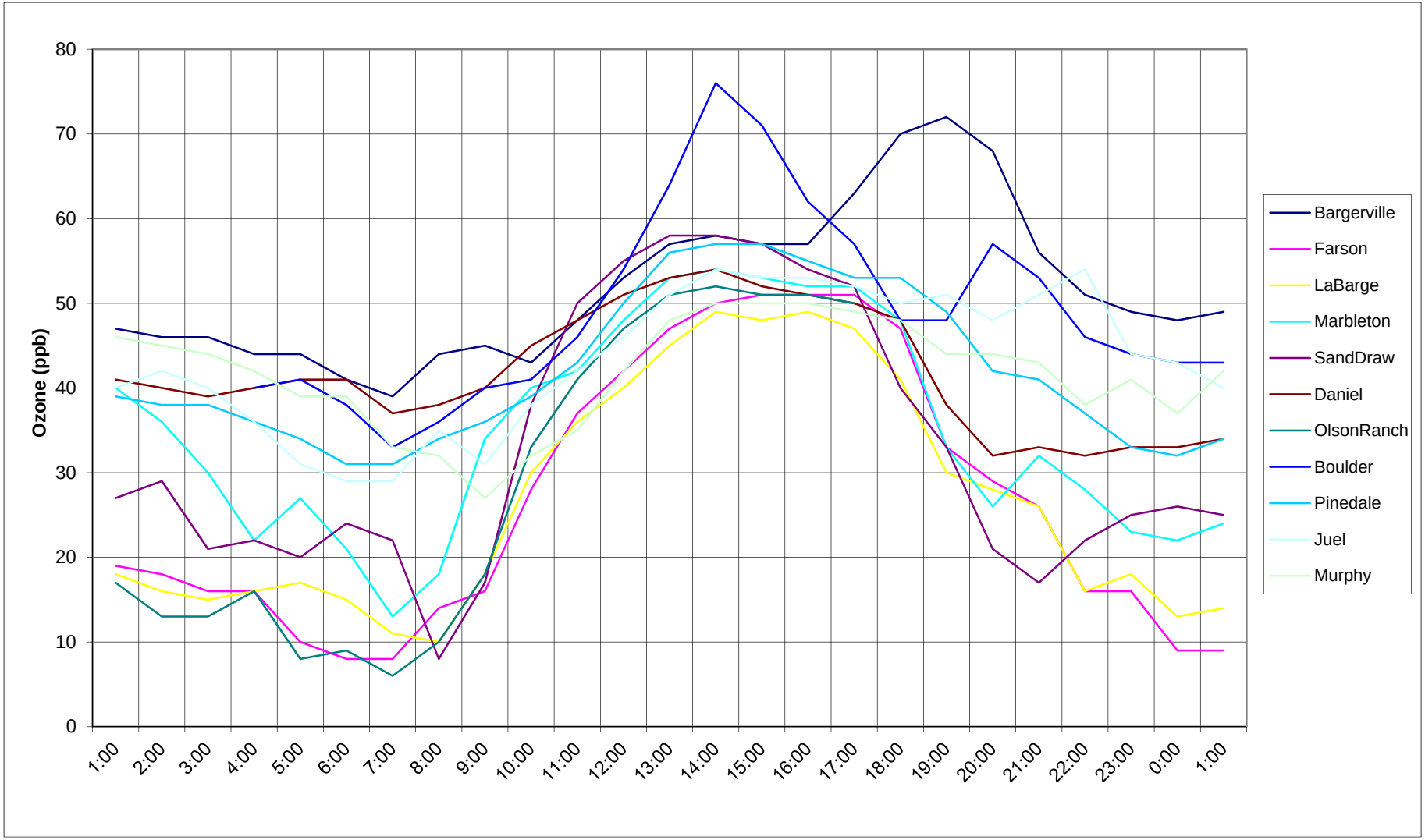


Figure 4.31 One-Hour Ozone at Other UGRB Sites on March 1, 2010

4.4.2 Surface Wind and Ozone Patterns During Elevated Ozone Periods

In an effort to facilitate the analysis and understanding of ozone formation and transport during UGWOS 2010, a series of maps were created which depict observed ozone concentrations, ambient temperature, and wind over the entire study area. Additionally, the observed variables were interpolated to a model grid using the Kriging method. Thus, maps of observed and interpolated ozone, temperature, and wind were created for every 15-minute period during the study. While the focus of this section is on surface wind and ozone patterns, examination of the temperature field can sometimes give significant insight into atmospheric conditions that affect ozone transport such as the presence or absence of cold air pools. This was particularly true on January 28, which is the only day whose accompanying illustration includes a temperature analysis. While the remainder of the figures in this discussion includes analyses of ozone and/or wind only, it should be known that the temperature field was always examined in the evaluation of each day when elevated ozone levels were observed.

It should be noted that unlike the official UGWOS database, analysis times on these maps are period-ending. Thus, the values shown on a map with a timestamp of 14:15 MST should be understood to be the average of that parameter measured between 14:01 MST and 14:15 MST inclusive. For those stations which measure data every five minutes, 15-minute averages were derived for the purpose of these maps. For those stations which measure data every 60 minutes, the hourly value is used to populate the 15-minute value during the collection hour. For example, the hourly value obtained by averaging a parameter from 14:01 MST to 15:00 MST inclusive will be used on the maps valid at 14:15 MST, 14:30 MST, 14:45 MST, and 15:00 MST. It is expected that the error introduced by mixing 15-minute and hourly averages is small.

It should also be noted that care should be exercised in the interpretation of these maps, especially in areas on the periphery of the study area. The user should keep in mind that parameter values are known only at the observing sites, and that parameter values across the domain are likely to be highly influenced by local terrain and other factors, none of which are known by the gridding algorithm.

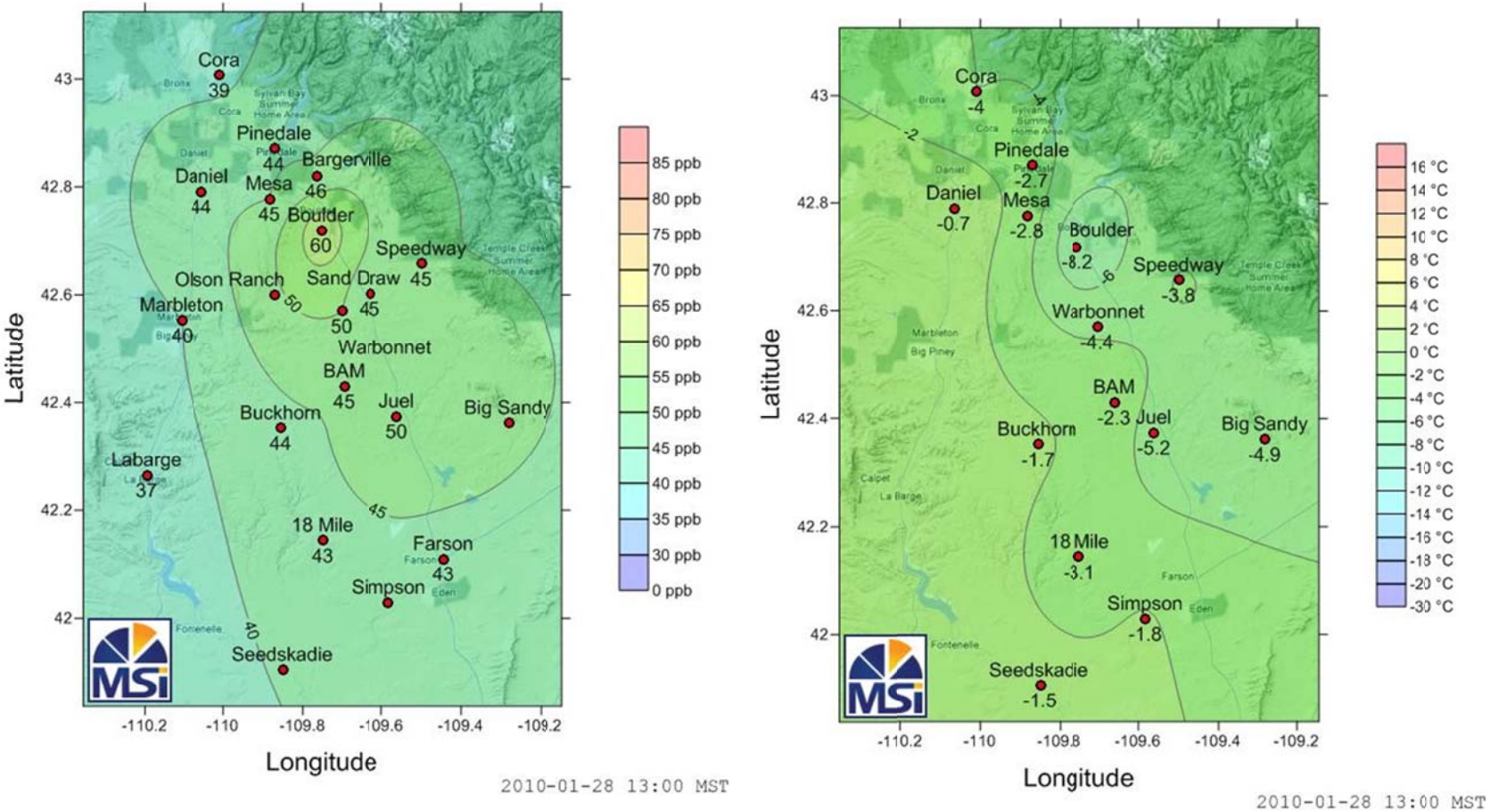
Thus, ozone, temperature, and wind fields over the Wind River Range should be discounted. Even within the interior of the study area, the terrain is quite complex. Thus, it should be expected that actual ozone, temperature, and wind fields are much more complex than the analyses would indicate due to the relative low number of data points and the siting of observing stations. For example, some of the sharpest ozone and temperature gradients are seen between Warbonnet and Sand Draw, which are separated by less than five miles. This can largely be explained by local activities and station siting: Sand Draw sits in a relative low point near a stream bed while Warbonnet is located on an exposed ridge. Similar sharp gradients in ozone and temperature likely exist throughout the map domain, but only rarely are captured by the analysis. The grids are not initialized by any other model, and have no memory from one time step to the next; each analysis stands alone. Since the analysis exactly fits the existing observations, artifacts such as bull's-eyes and strongly diffluent or confluent flow may be depicted. Such artifacts should be interpreted with caution.

4.4.2.1 Elevated Ozone Period (EOP) 1 January 28 – January 30

As stated in Section 4.2.1, the study area during the EOP1 was under the influence of an upper-level ridge. Such conditions are characterized by light winds aloft and at the surface, as well as by a stable temperature profile which inhibits vertical mixing of air and contributes to increased pollution due to stagnation. The ridge began building into the area on January 26 and was in place on the peak ozone day of January 30. On January 31, the ridge was replaced by a trough of low pressure, which quickly evacuated the polluted air at the surface and thus brought an end to EOP 1.

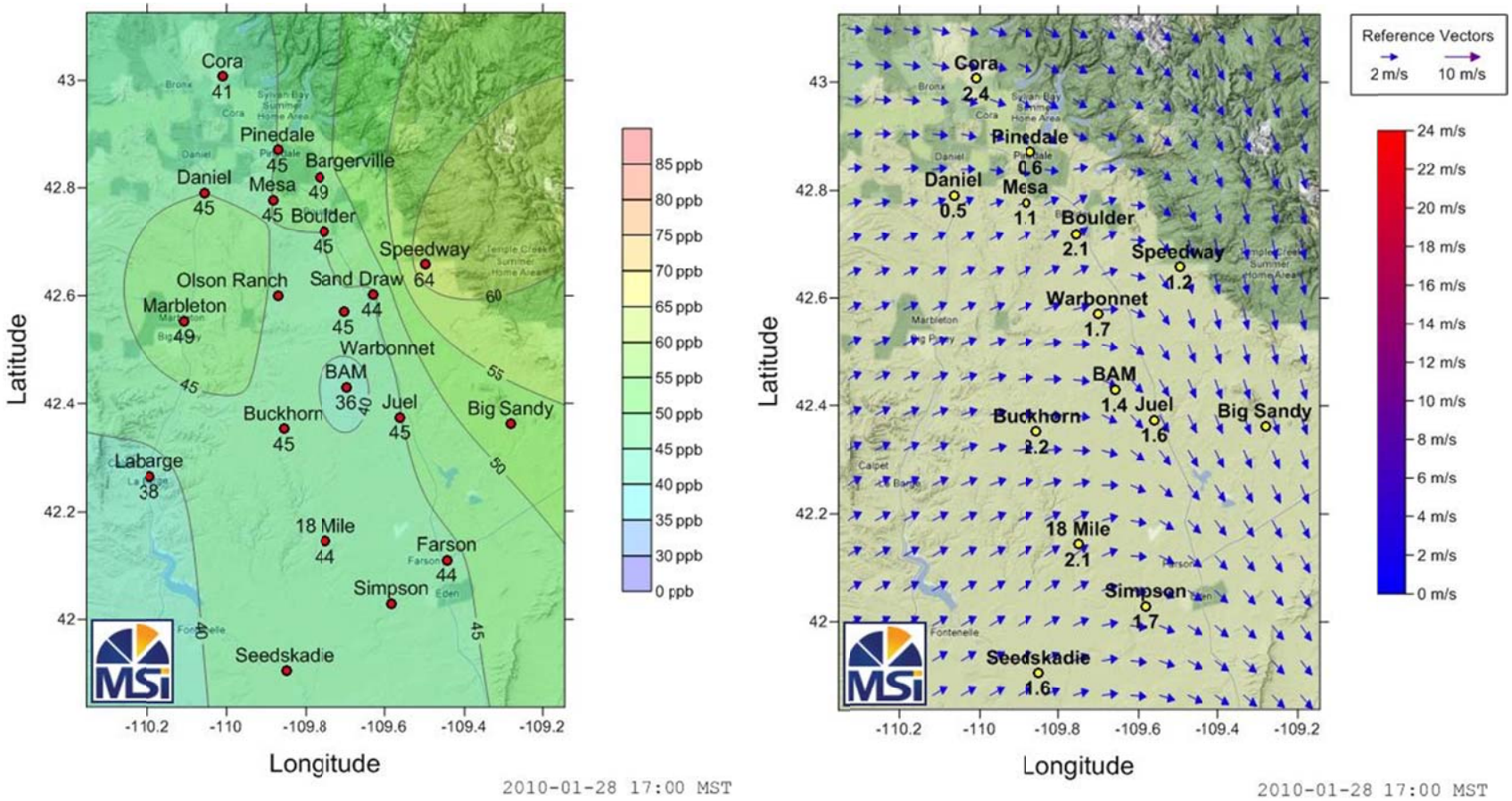
Elevated ozone concentrations were generally confined to the northern half of the study area north of the Jonah/BAM trailer, and east of Marbleton and Daniel.

January 28. Elevated ozone levels appeared first at Boulder at 1300 MST (See Figure 4.32a). At the same time, surface temperature analysis (Figure 4.32b) illustrates that cold air was still entrenched in the lower New Fork River Valley while other sites were several degrees warmer. During the course of the afternoon, the cold pool eroded and the temperature at Boulder rose to values similar to surrounding sites. Wind flow during the afternoon was up-valley at both Boulder and Speedway (southwesterly and northwesterly, respectively), as illustrated in Figure 4.33b. This allowed the wind to transport the ozone, and by 1700 MST, the elevated ozone levels had shifted up-valley from Boulder to Speedway (Figure 4.33a).



(a) **(b)**

Figure 4.32 EOP 1. January 28, 1300 MST. Surface Ozone Analysis (a) and Surface Temperature Analysis (b).

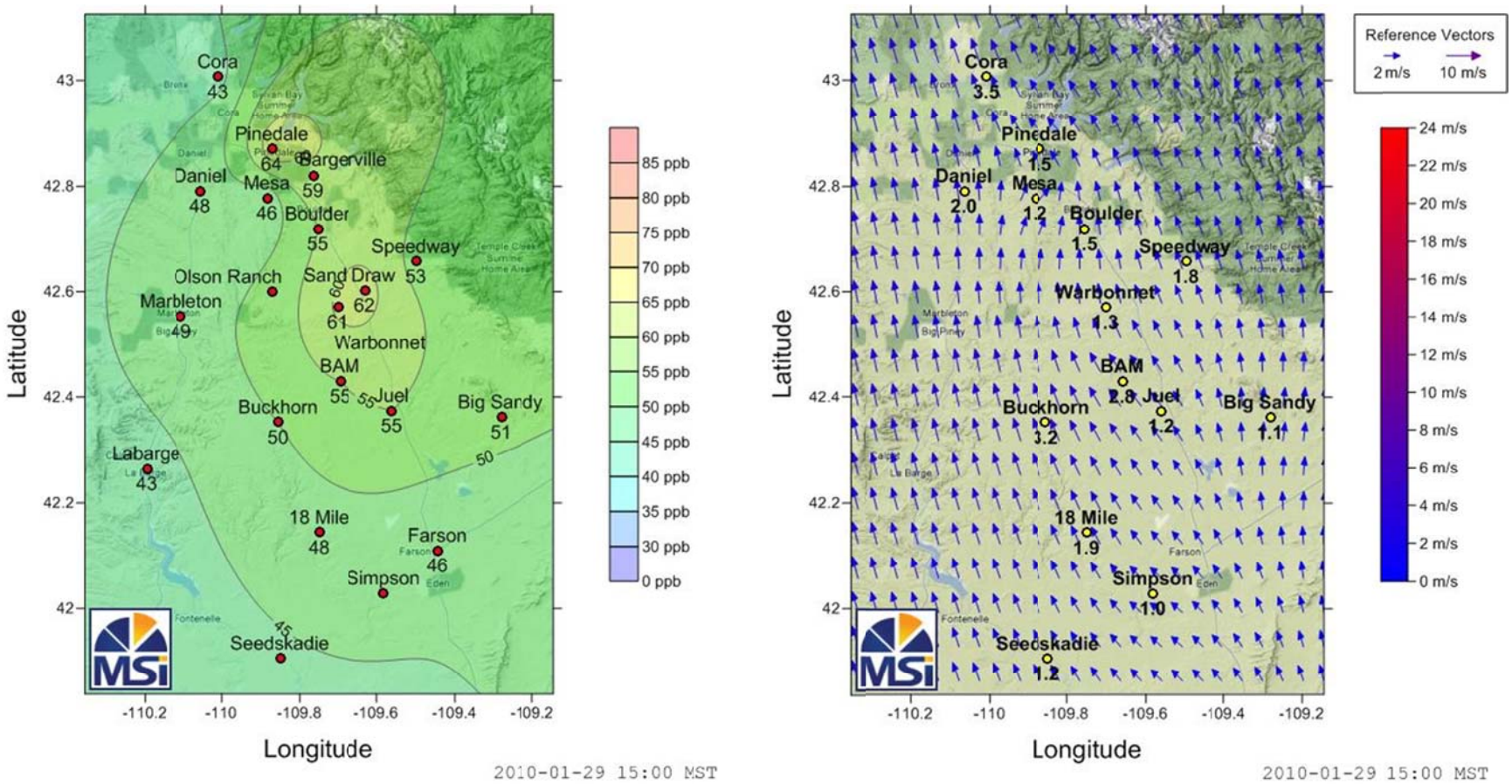


(a) **(b)**

Figure 4.33 EOP 1. January 28, 1700 MST. Surface Ozone Analysis (a) and Surface Wind Analysis (b).

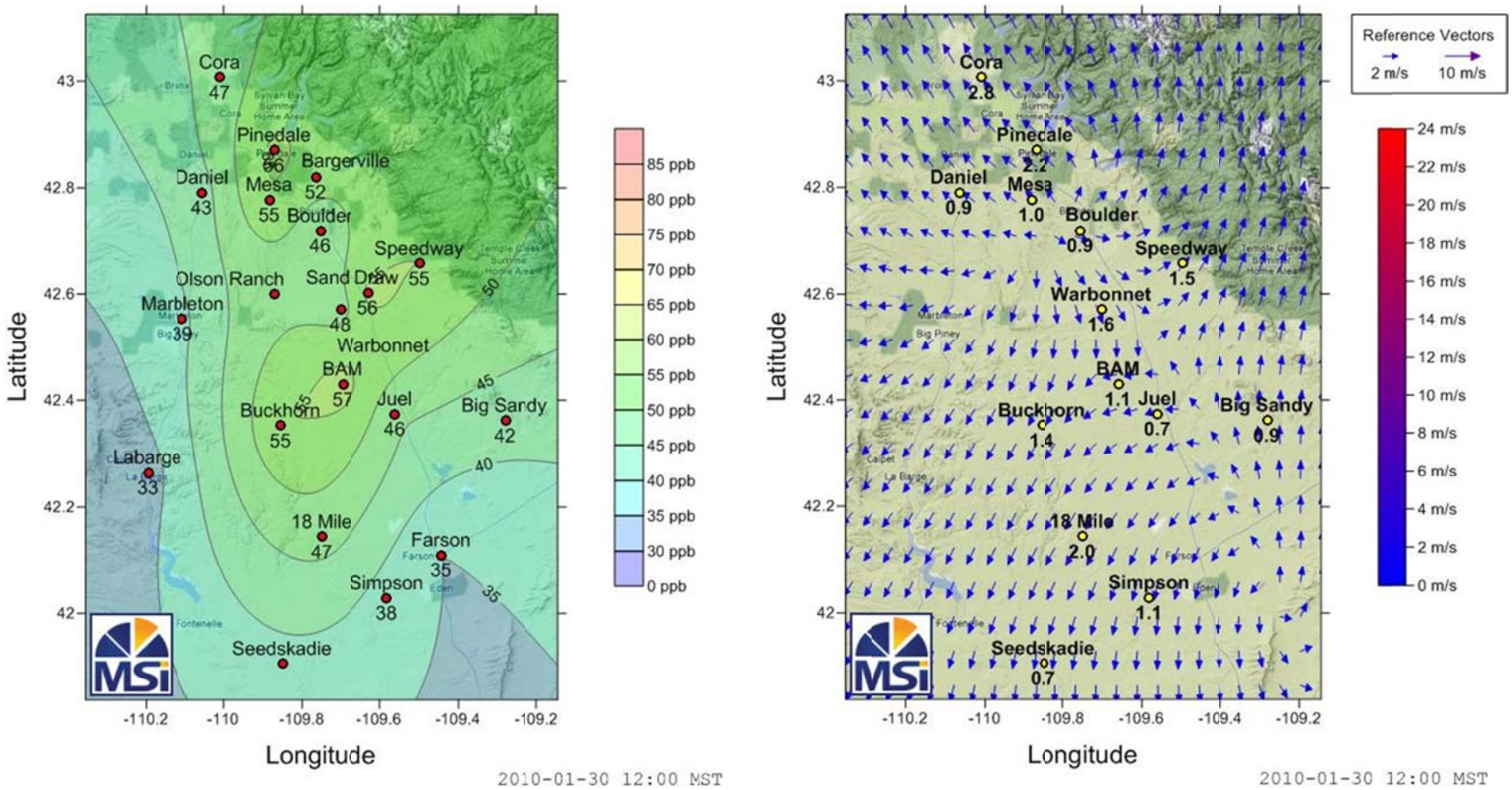
January 29. Slightly elevated ozone levels were detected on this day with peak concentrations between 60 and 65 ppb. Wind was generally from the south-southeast throughout the day which helped transport ozone that formed near Warbonnet and Sand Draw north to Bargerville, Pinedale, and Cora. (See Figure 4.34).

January 30. The highest ozone levels measured during the study were seen on this day with peak concentrations above 80 ppb. Boulder, Warbonnet, and Sand Draw were the sites with the highest measured ozone on this day, and are all within the same area of the New Fork drainage. The day was characterized by light and variable winds (generally less than 2 m/s) and some terrain-driven flows. Between 10:00 MST and 12:00 MST (Figure 4.35) ozone levels were rising across the study domain with the highest concentrations near the Jonah/BAM trailer and Sand Draw. Between 12:00 MST and 13:00 MST (Figure 4.36), concentrations at Boulder and Bargerville rose sharply with a wind shift at Boulder from northwesterly to southwesterly. At this time, winds at Warbonnet were upslope from the northwest and remained there most of the day while ozone concentrations rose steadily. By 15:00 MST (Figure 4.37), the highest ozone concentrations were at Boulder and Warbonnet while a broad area of elevated ozone continued to reside along a north-south line across the middle of the study domain. The peak of ozone activity for this day was near 16:45 MST (Figure 4.38). At this time, Warbonnet measured 82 ppb, Sand Draw was close behind at 79 ppb, while Boulder and Bargerville were both at or above 70 ppb. The rest of the evening of January 30 saw the area of highest ozone concentrations meander among the stations in the middle of the study domain. At Warbonnet and the Jonah/BAM trailer, large fluctuations in ozone concentration occurred repeatedly during the evening hours. Warbonnet achieved a secondary maximum of 85 ppb and 81 ppb at 18:30 MST and 19:45 MST, respectively. (Figure 4.39a and c).



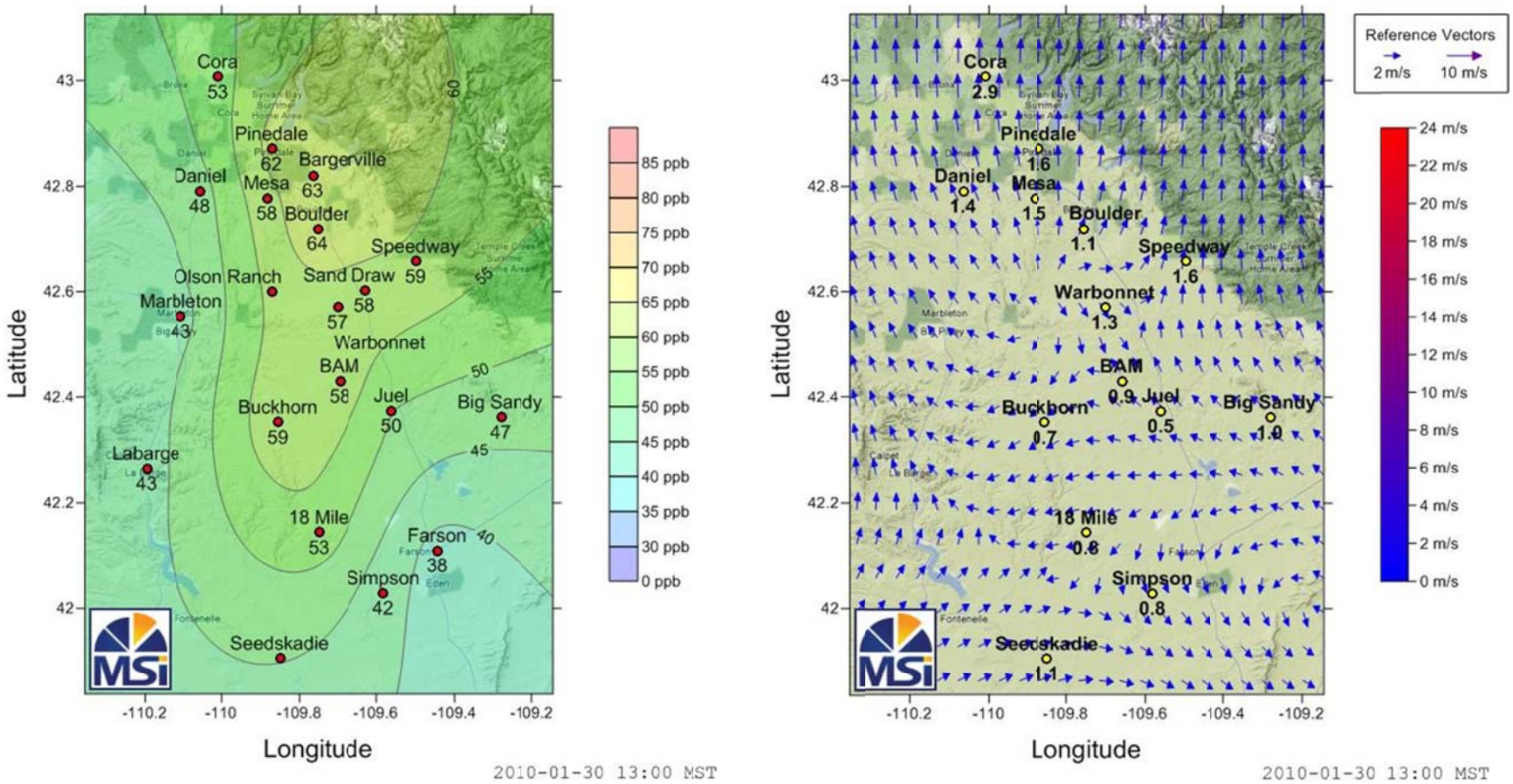
(a) **(b)**

Figure 4.34 EOP 1. January 29, 1500 MST. Surface Ozone Analysis (a) and Surface Wind Analysis (b).



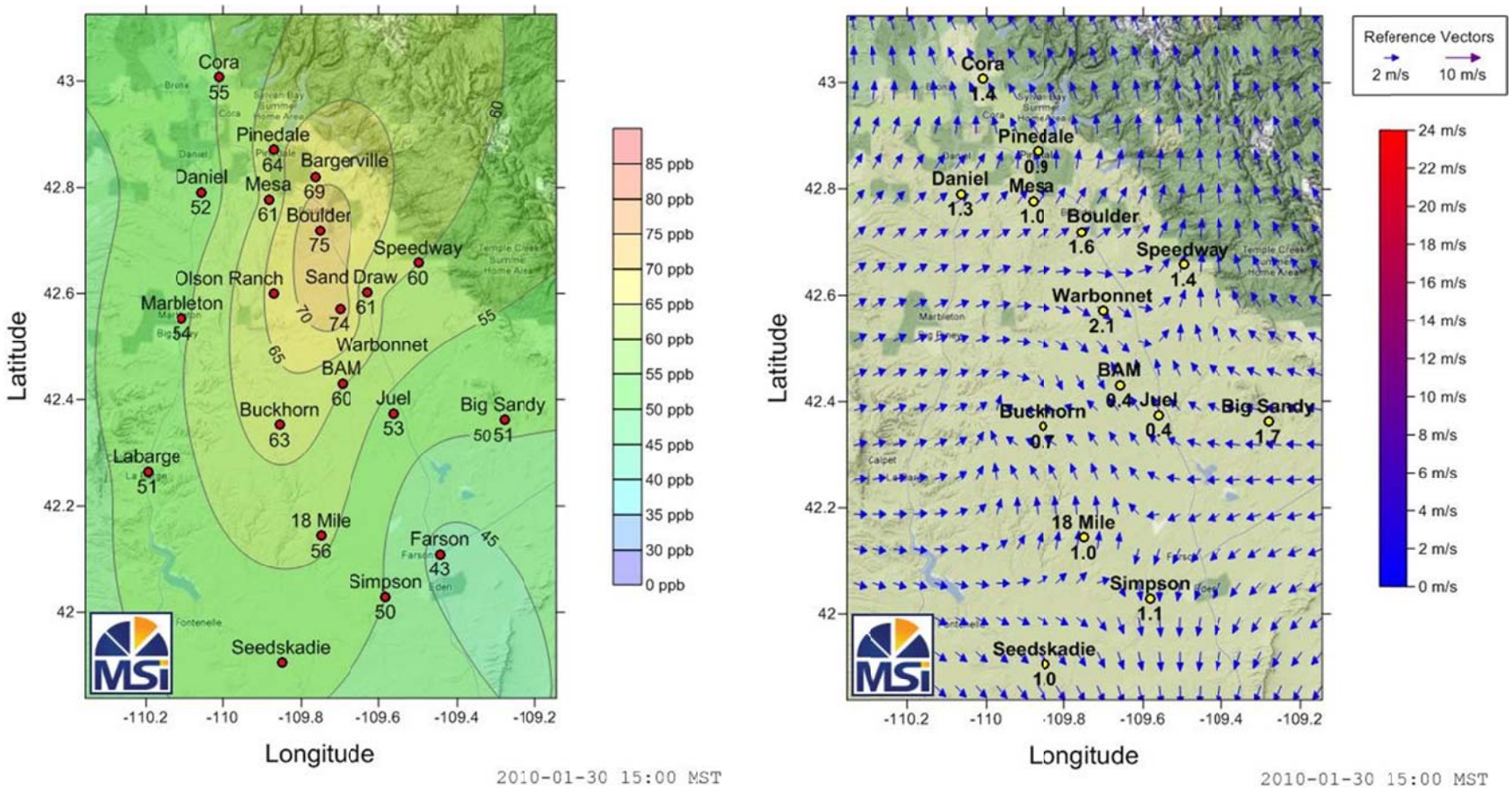
(a) **(b)**

Figure 4.35 EOP 1. January 30, 1200 MST. Surface Ozone Analysis (a) and Surface Wind Analysis (b).



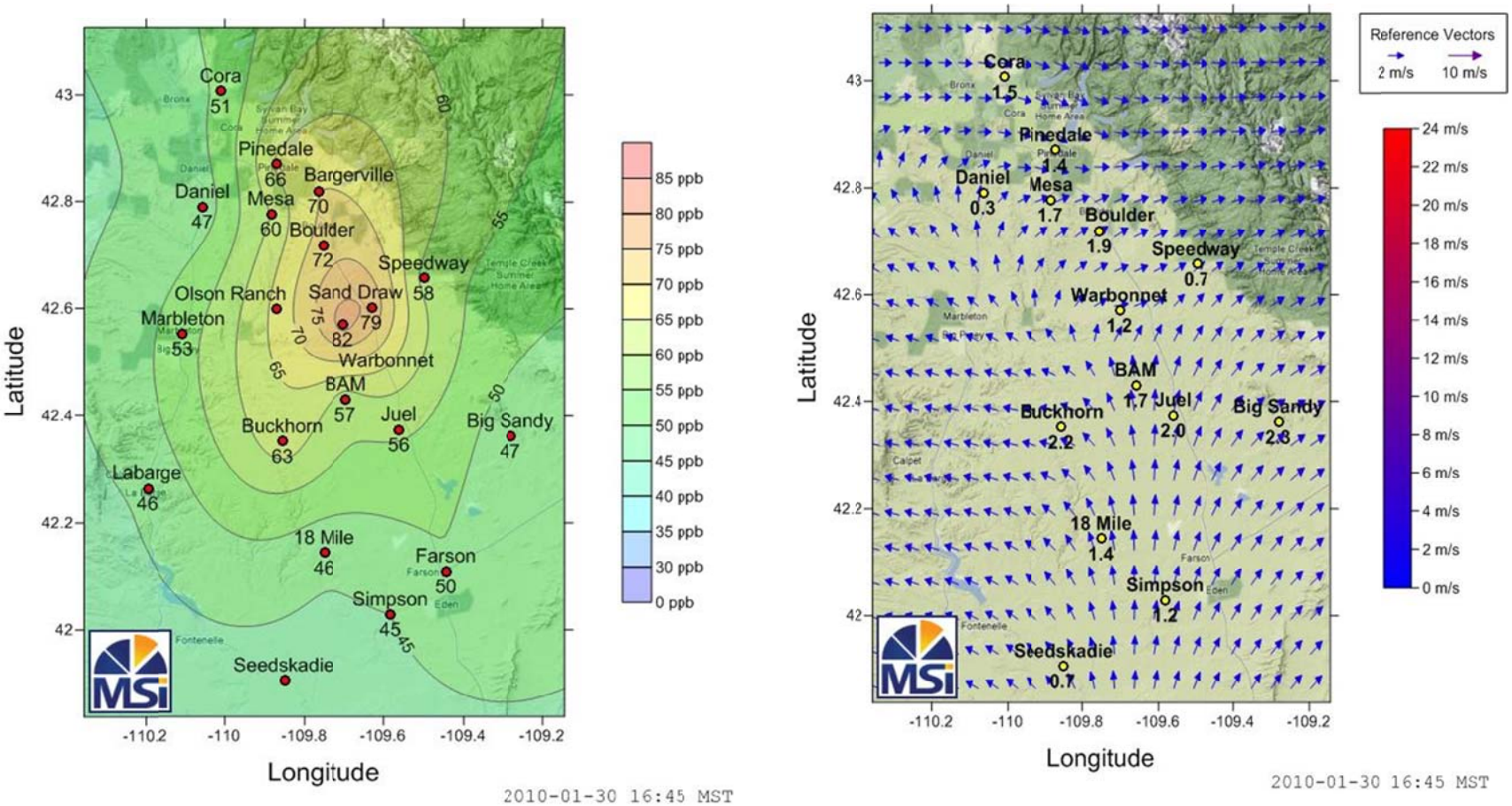
(a) **(b)**

Figure 4.36 EOP 1. January 30, 1300 MST. Surface Ozone Analysis (a) and Surface Wind Analysis (b).



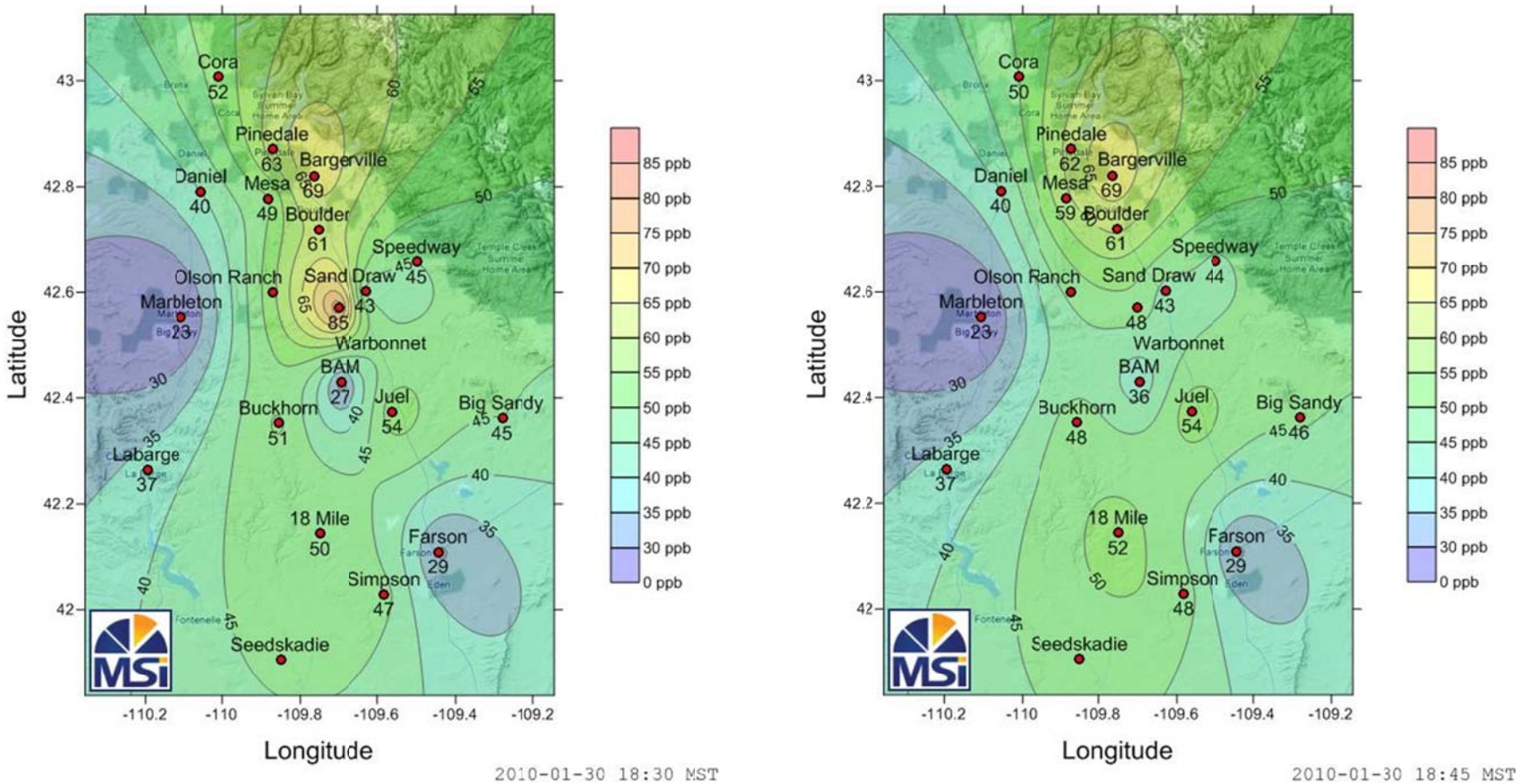
(a) **(b)**

Figure 4.37 EOP 1. January 30, 1500 MST. Surface Ozone Analysis (a) and Surface Wind Analysis (b).



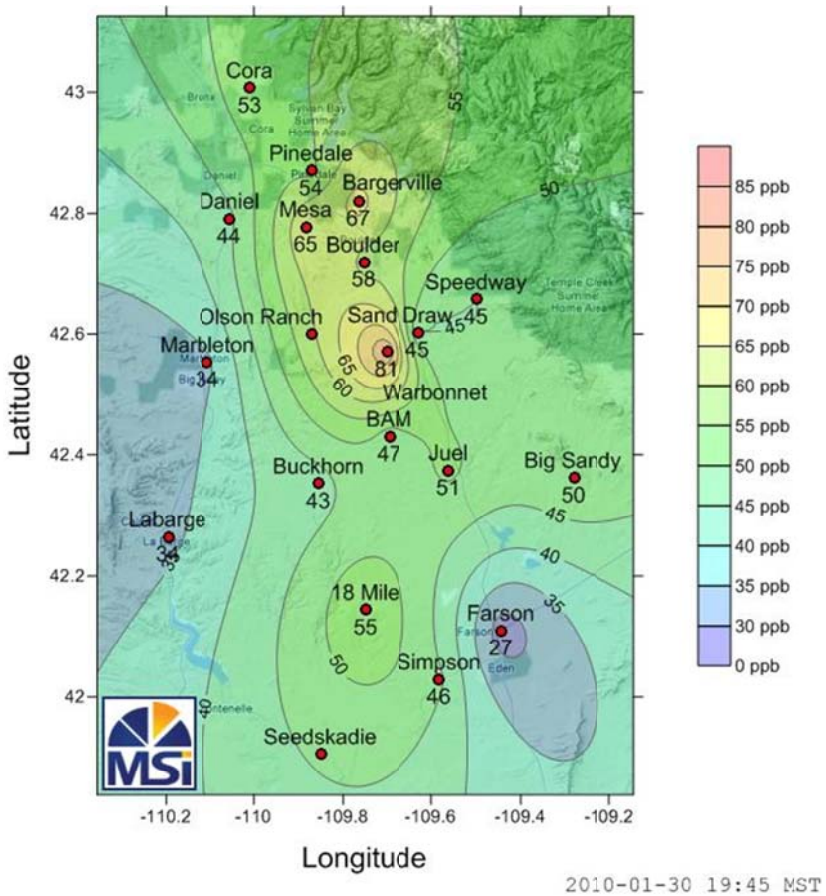
(a) **(b)**

Figure 4.38 EOP 1. January 30, 1645 MST. Surface Ozone Analysis (a) and Surface Wind Analysis (b).

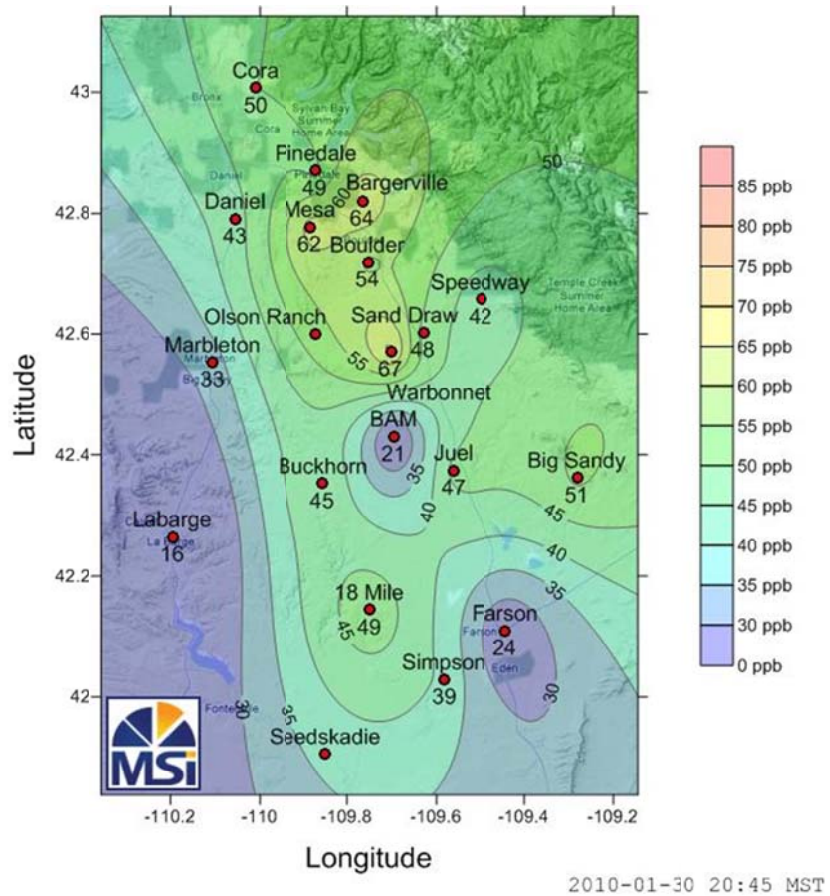


(a) **(b)**

Figure 4.39 EOP 1. January 30. Surface Ozone Analysis at (a) 18:30 MST and (b) 18:45 MST



(c)



(d)

Figure 4.39 Continued EOP 1. January 30. Surface Ozone Analysis at (c) 19:45 MST, and (d) 20:45 MST.

4.4.2.2 Elevated Ozone Period (EOP) 2 February 28 – March 1

While EOP 1 was characterized by pronounced ridging at upper levels, the pressure and upper-level wind fields during EOP 2 were weak per NCEP analysis of 700 hPa height, temperature, and wind. In the days surrounding and including the EOP, a mean upper ridge was in place over western North America. Within the mean ridge, an upper low broke away from the parent Aleutian low and translated south along the west coast of North America. The upper low closed off and the center of the low passed through central California on the afternoon of February 27, Arizona the morning of February 28, New Mexico the afternoon of February 28, and Texas by the morning of March 1. The 700 hPa flow over the study area was weak during this period as the study area was between the upper low to the south and the mean ridge to the north. Thus, large-scale forcing was weak at best during EOP 2, and consequently, surface winds were weak as well.

February 28. This day saw modest elevated ozone levels of 65 to 70 ppb at stations in the north-central area of the study domain including Speedway, Sand Draw, Boulder, and Bargerville. Ozone concentrations at Sand Draw did spike up to 76 ppb for one hour. Wind patterns were light and variable during the course of the day, but were generally southeasterly at the stations affected by elevated ozone, especially Bargerville and Boulder. (See Figures 4.40 through 4.42).

March 1. The second day of EOP 2 saw levels of ozone greater than 65 ppb at Boulder, Speedway, and Bargerville. Figure 4.43 shows that Boulder was the first site to see elevated ozone levels this day in local southeasterly flow. By 16:00 MST (Figure 4.44), Speedway's ozone level increased while under upslope flow from the west. Boulder's wind continued from the southeast at this time and ozone levels begin to gradually decline over the next few hours.

Also at this time, Bargerville's wind was out of the east-southeast, and remained from that direction as ozone levels began to rise there. By 18:00 MST (Figure 4.45), Bargerville had the highest ozone concentration at 70 ppb with a south-easterly wind. As evening progressed at 19:00 MST (Figure 4.46), nocturnal drainage winds developed. The wind turned northeasterly at Bargerville and north to northwesterly at Daniel, Cora, Pinedale, and Mesa. At 20:00 MST (Figure 4.47), ozone levels at Mesa and Boulder actually increased, suggesting transport of ozone from Bargerville to these sites.

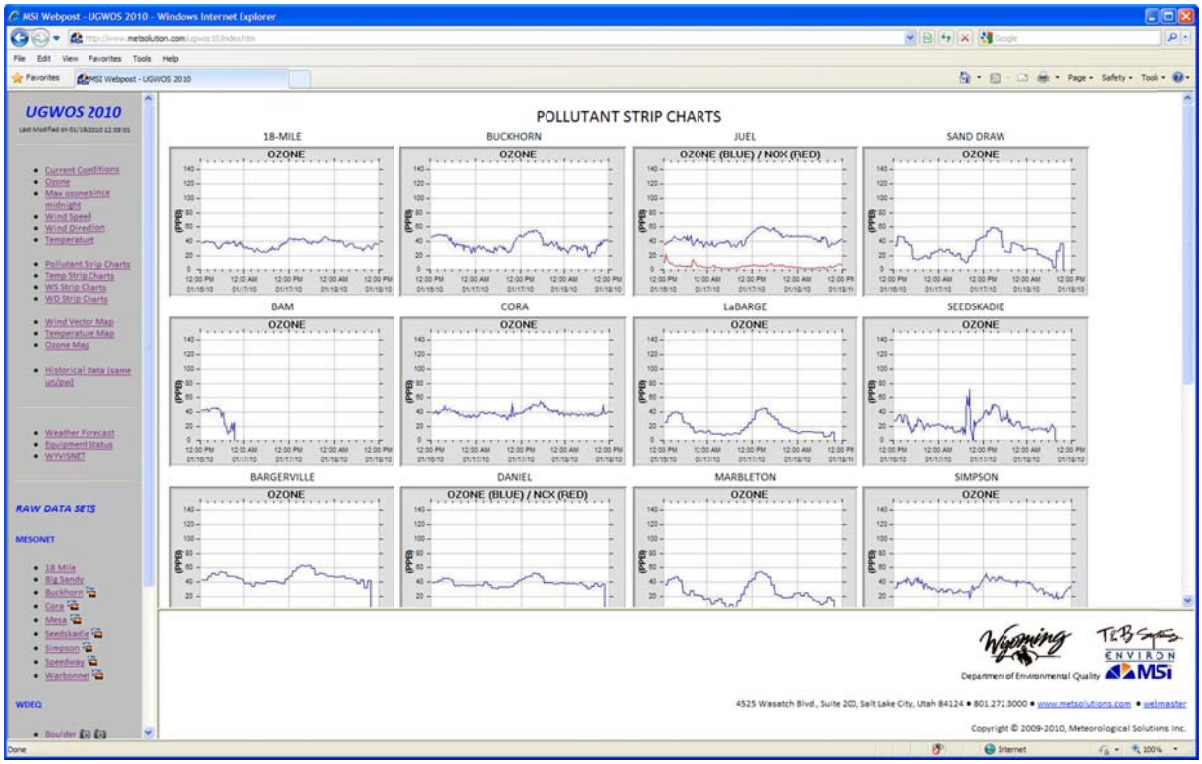


Figure 2.12 Pollutant Strip Charts

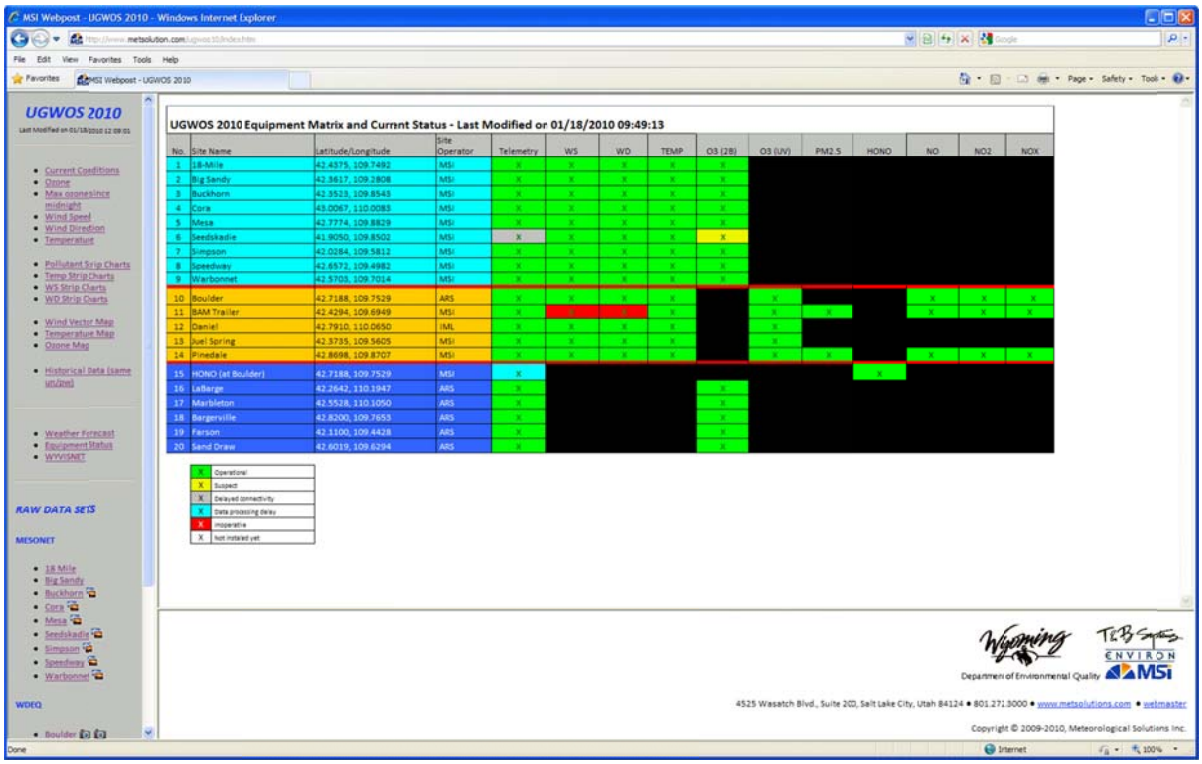
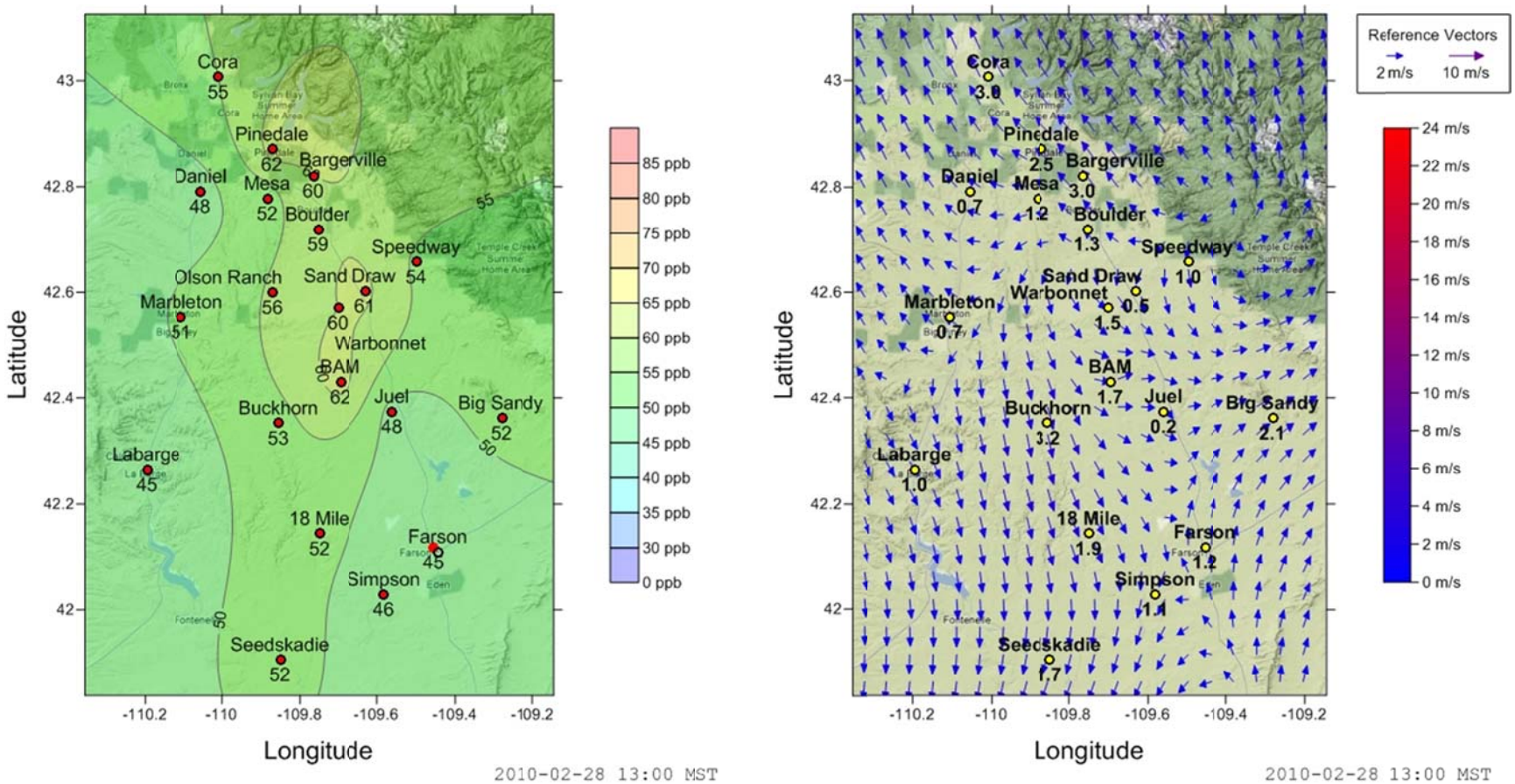
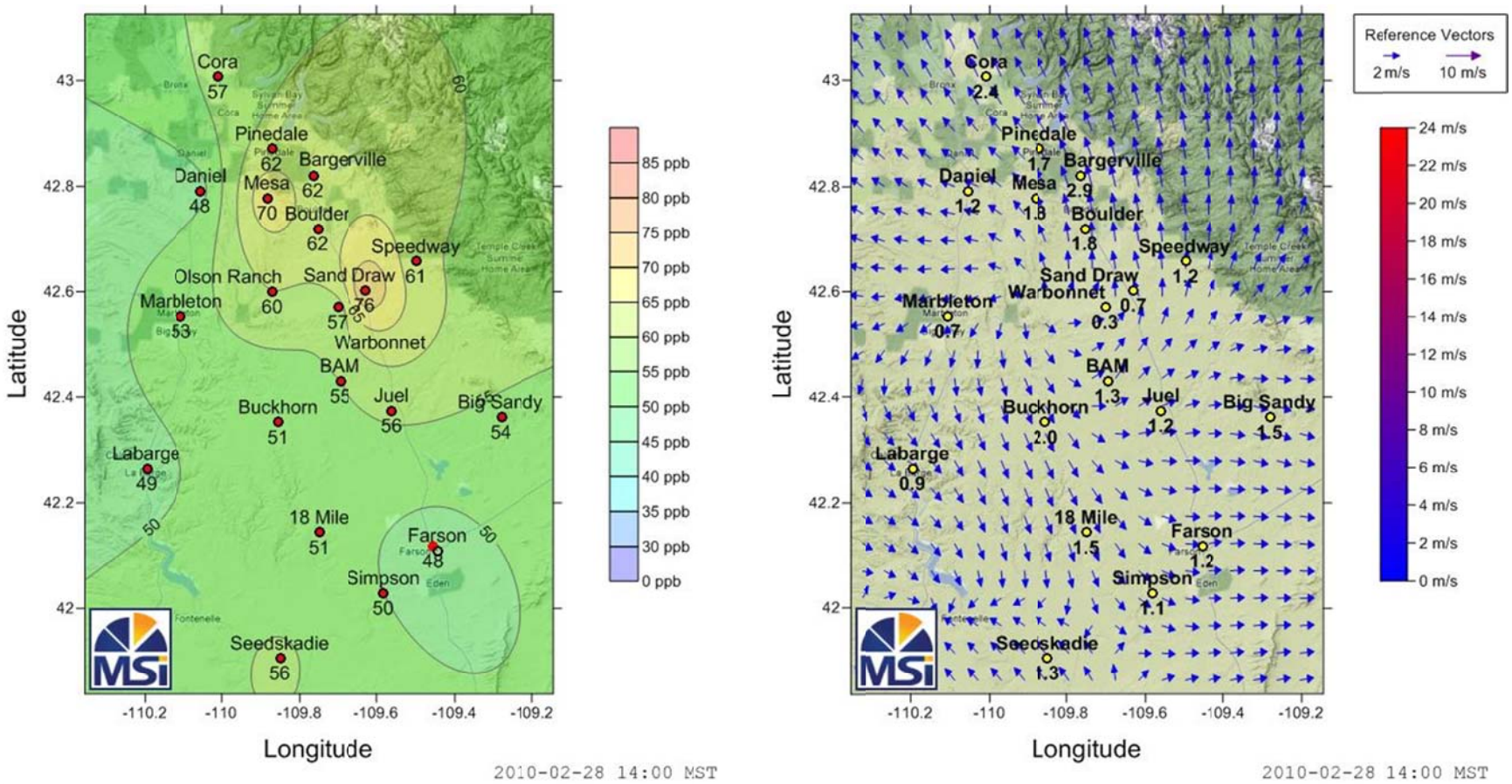


Figure 2.13 Equipment Status Matrix



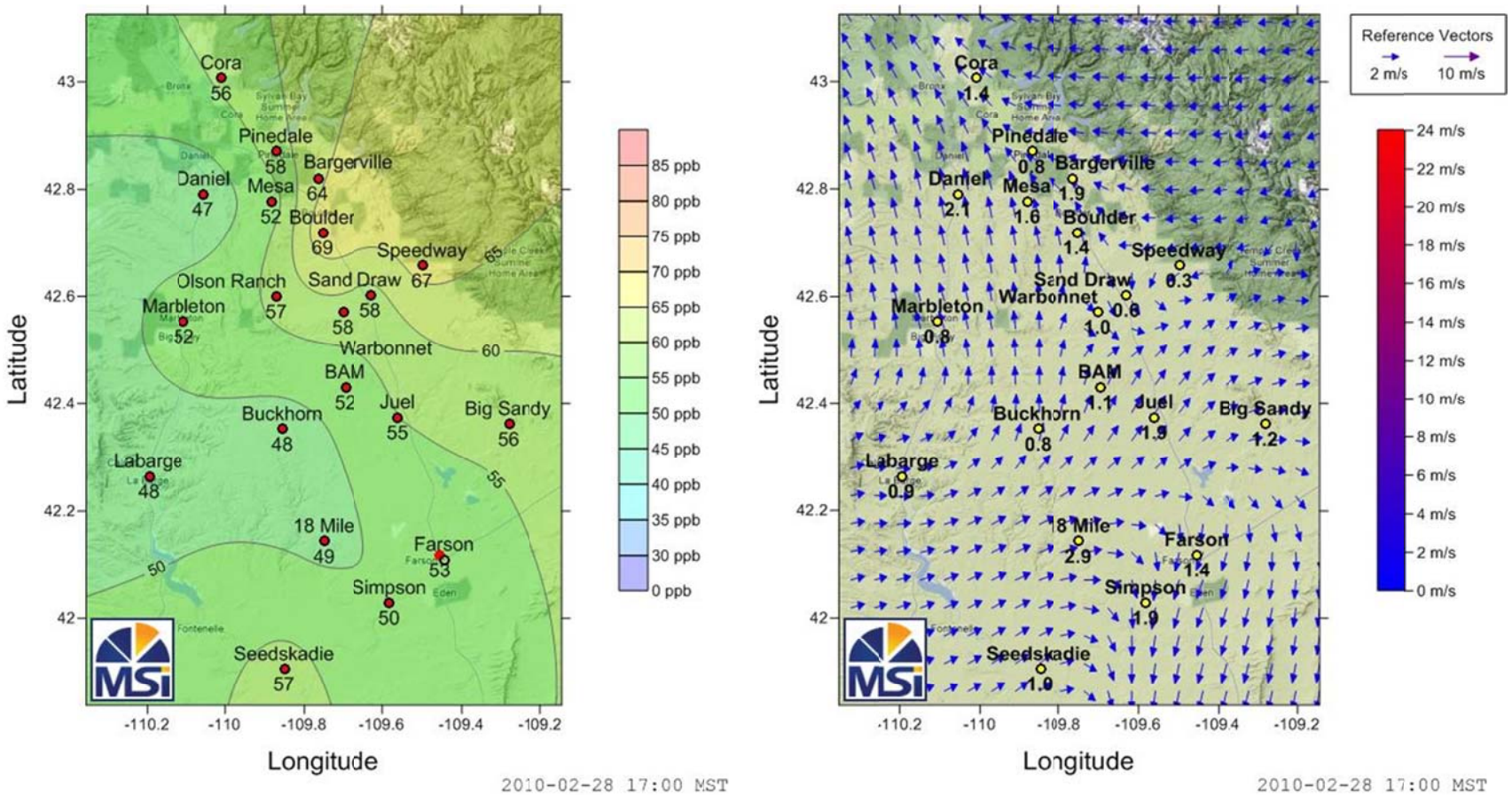
(a) **(b)**

Figure 4.40 EOP 2. February 28, 13:00 MST. Surface Ozone Analysis (a) and Surface Wind Analysis (b)



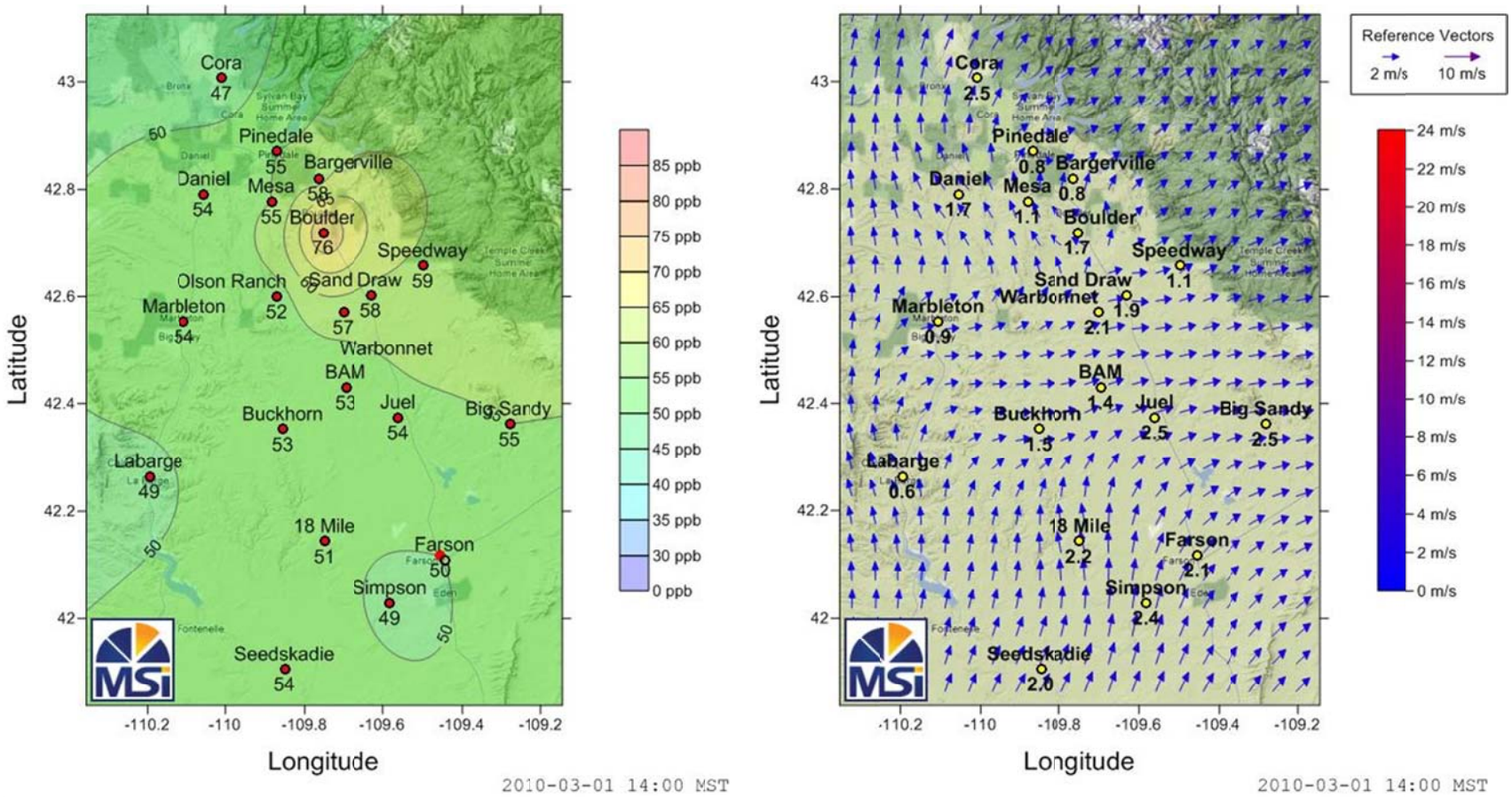
(a) **(b)**

Figure 4.41 EOP 2. February 28, 14:00 MST. Surface Ozone Analysis (a) and Surface Wind Analysis (b)



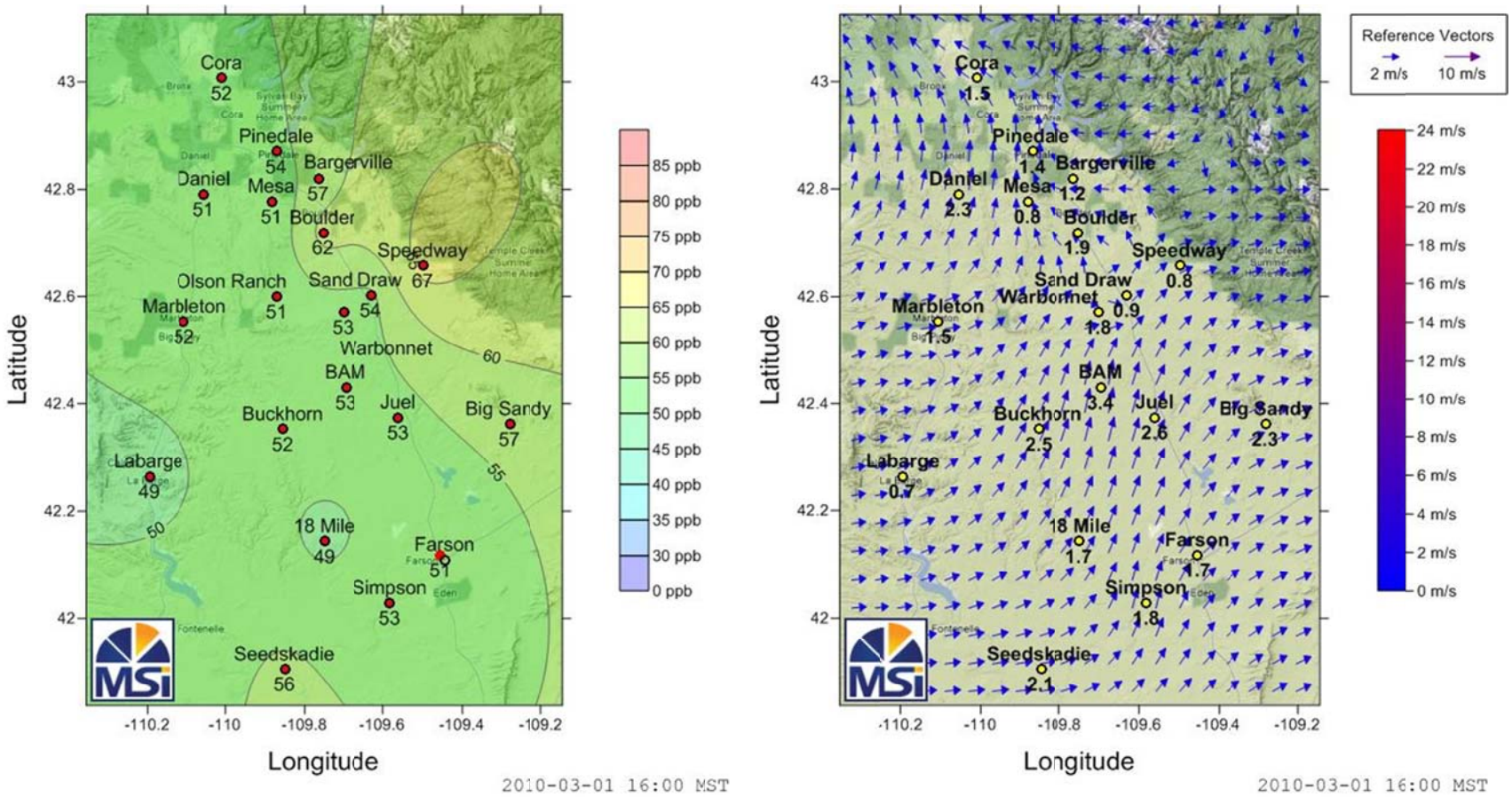
(a) **(b)**

Figure 4.42 EOP 2. February 28, 17:00 MST. Surface Ozone Analysis (a) and Surface Wind Analysis (b)



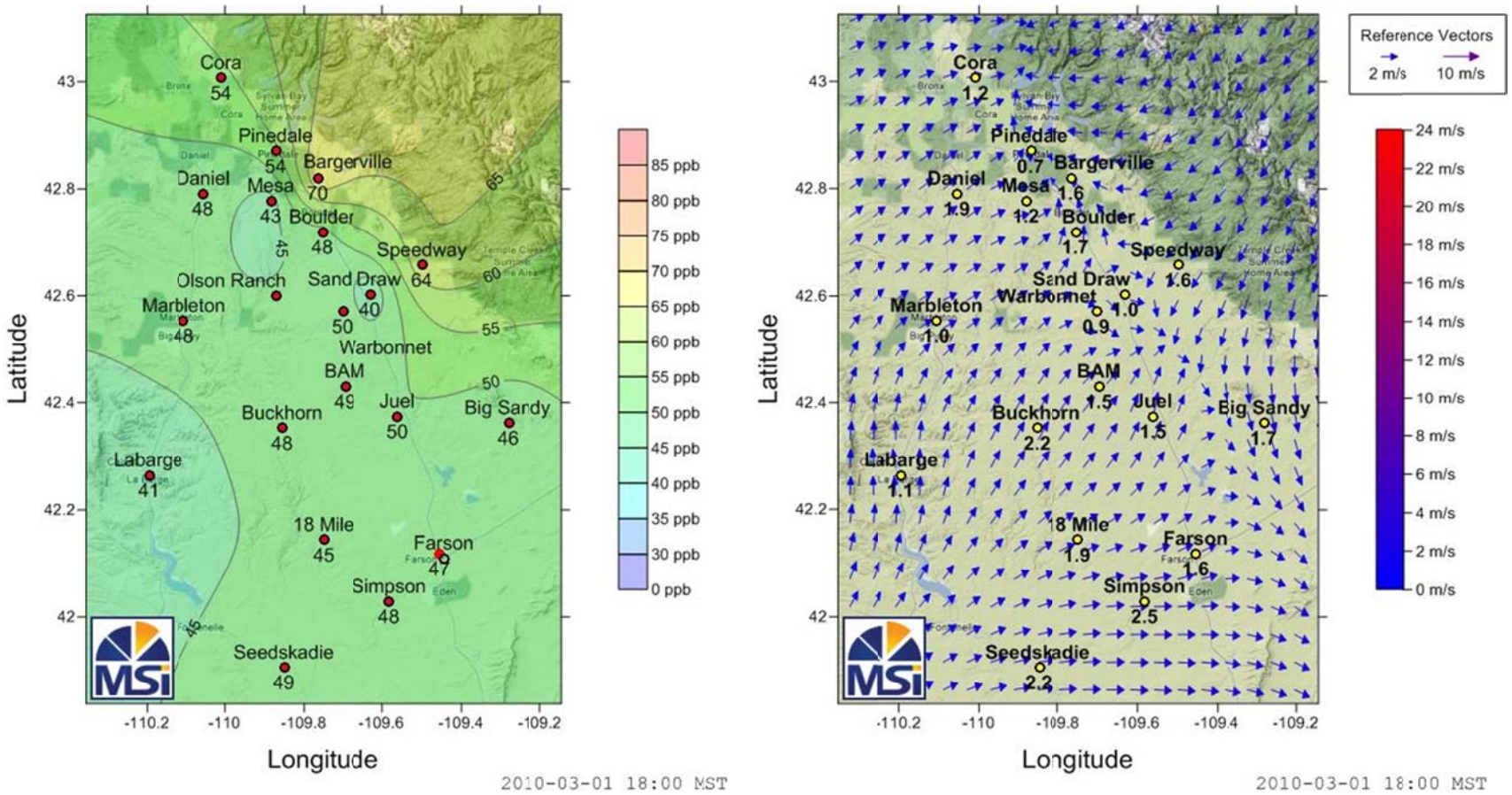
(a) **(b)**

Figure 4.43 EOP 2. March 1, 14:00 MST. Surface Ozone Analysis (a) and Surface Wind Analysis (b)



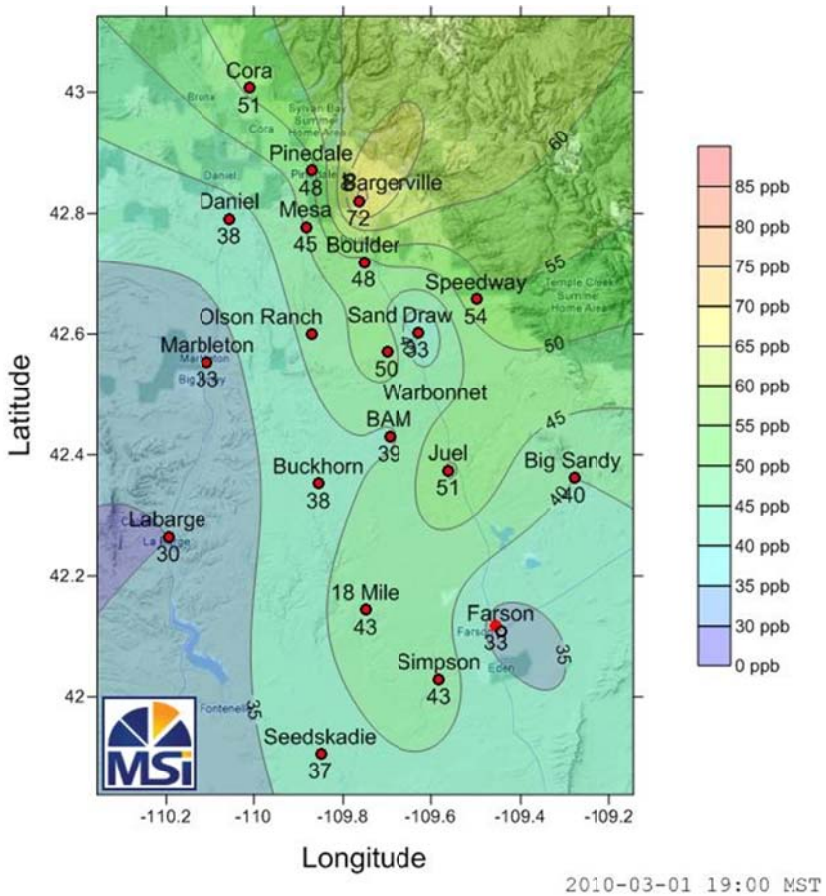
(a) **(b)**

Figure 4.44 EOP 2. March 1, 16:00 MST. Surface Ozone Analysis (a) and Surface Wind Analysis (b)

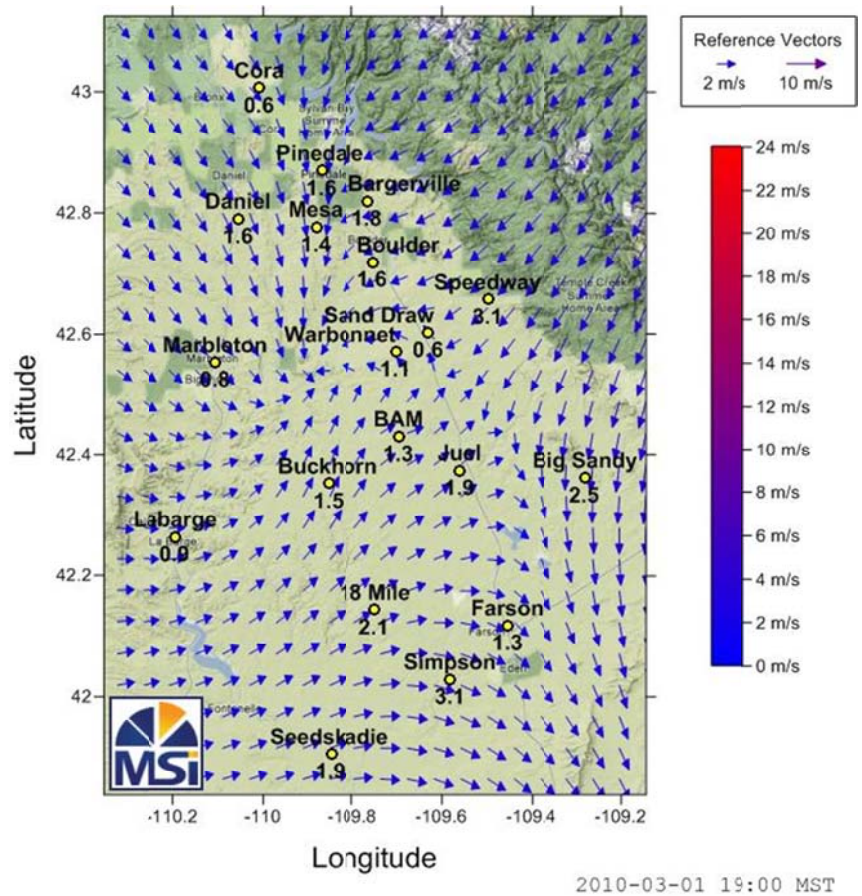


(a) **(b)**

Figure 4.45 EOP 2. March 1, 18:00 MST. Surface Ozone Analysis (a) and Surface Wind Analysis (b)

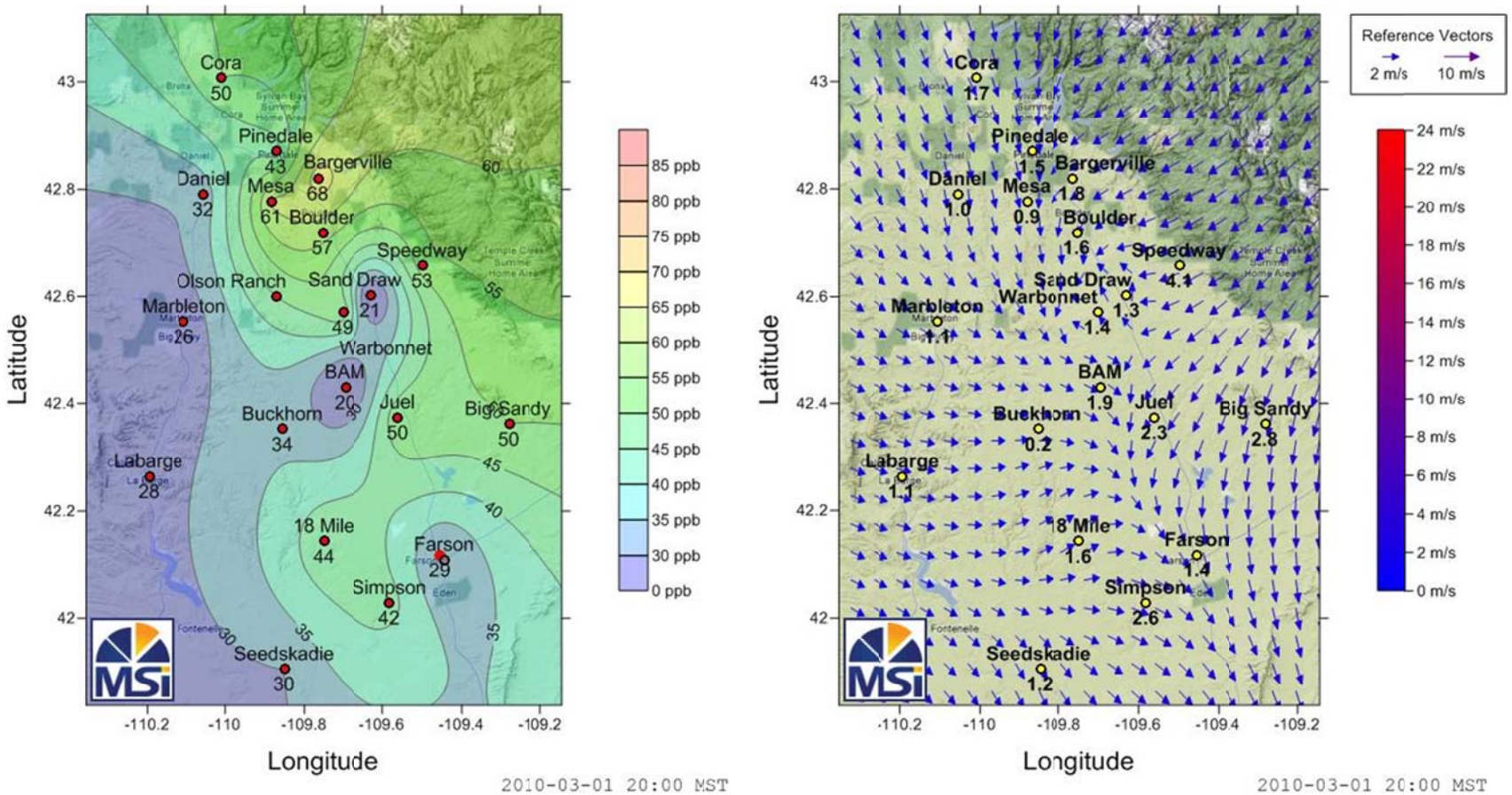


(a)



(b)

Figure 4.46 EOP 2. March 1, 19:00 MST. Surface Ozone Analysis (a) and Surface Wind Analysis (b)



(a) **(b)**

Figure 4.47 EOP 2. March 1, 20:00 MST. Surface Ozone Analysis (a) and Surface Wind Analysis (b)

4.5 Conditions Aloft

The WDEQ Wind Explorer miniSODAR™ (Sodar) provided the only field measurements performed during UGWOS 2010 to characterize more localized conditions aloft. For the 2010 field study, the Sodar was moved from its previous location near the intersection of Highway 351 and Paradise Road to the WDEQ Boulder monitoring site. The Sodar provided wind and mixing height information up to 200 meters above ground level at the Boulder site. Routine, rawinsonde balloon soundings conducted by the National Weather Service (NWS) at Riverton, Wyoming provided more broad scale upper-level conditions aloft used for daily UGRB forecasts.

4.5.1 miniSODAR™ Data

Prior to discussing the 2010 Sodar data, it is important to note that the location of the Sodar was changed in 2010 from that in 2008 and 2009. The Sodar was moved to the Boulder air quality monitoring site, approximately 10 miles northeast of its prior location near the intersection of Paradise Road and Highway 351 (Figure 4.48). Most notably, the elevation of the new location is 2157 meters, compared to the previous location's elevation of 2106 meters. Thus, the new location is located 50 meters above the previous location which has the potential of being significant due to the low mixing height associated with ozone episodes.

Figure 4.48 Current and Previous Sodar Locations

Figure 4.49 presents monthly wind roses from both locations for the months of February and March. Looking first at the two 30-meter data sets, the following observations become apparent:

- Both locations show a high frequency of winds from the northwest – the prevailing wind direction for the study area. However, in 2010, approximately 45% of the reported winds came from the NW or NNW. In contrast, in 2009, only about 15% of the winds came from these directions. This could be due to two reasons. First, with the new location already 50 meters higher than the old location, it may be that the first measurement height at 30-meter level is more frequently above the mixing layer and more frequently subjected to the prevailing wind direction. Second, and more likely, it appears that the meteorology for 2010 is inherently different from that for 2009. The prevailing wind appears to simply have been even more dominant during 2010 than 2009, with fewer stagnant wind periods. This is supported to a large degree by the lower frequency of higher ozone concentrations during 2010.

- Low wind speeds were significantly less frequent in 2010 than in 2009, for the same reasons presented above.
- The 2009 wind roses have notable wind rose“nodes” of winds coming from the northeast and the west. Light winds dominate the NNE/NE node, indicative of drainage winds down the New Fork River during light wind conditions (see Figure 4.47). Some upslope directing of winds is evidenced by the west node. In contrast, aside from the prevailing wind direction, winds reported at the new location in 2010 show a fairly even distribution from all directions.

Again, it may be that the 30-meter data from both locations should not be compared directly, due to the 50-meter increase in altitude for the new location. 2009 data for the 60-meter level is therefore also presented at the bottom of Figure 4.49, which may be more comparable with the 30-meter data from the new location. However, there is little significant difference between the 2009 30-meter and 60-meter data, other than a less obvious directing of drainage winds down the river from the NNW/NW, which is to be expected given the higher measurement altitude.

Also worth reviewing are potential differences in the measured mixing heights at the two locations. Figure 4.50 plots the mixing height frequency distributions for 2009 versus 2010, expressed in number of hourly occurrences of a given mixing height over the study period. The left and center plots present data for the old location (2009) and new location (2010), respectively. For each plot, the large bar on the right side represents hourly occurrences when no mixing height top was detected. Notable is that the number of hours with an identifiable mixing height top is essentially the same for both 2009 and 2010.

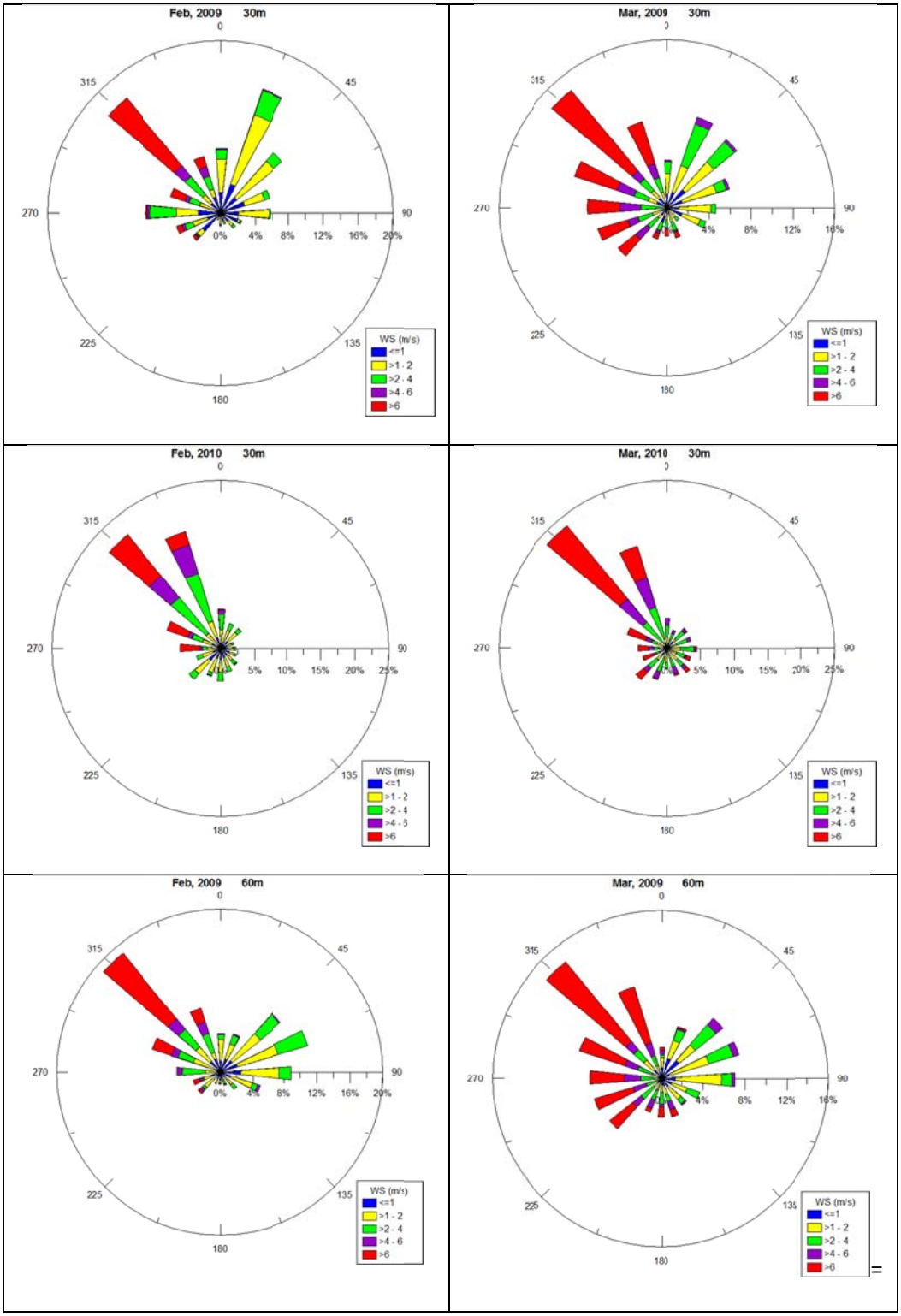


Figure 4.49 Comparisons of 2009 and 2010 Upper Level Winds

The mixing heights in 2009 on average are higher than those in 2010, with the highest heights in 2009 approximately 50 meters higher than those in 2010. However, this is consistent with the fact that the Sodar location in 2009 was 50 meters lower in elevation than in 2010. Thus, in terms of elevation above sea level, the mixing height data are very similar for the two years. This is demonstrated by the right-most plot in Figure 4.50, which presents the 2009 data adjusted for the 50-meter change in site altitude. This is done somewhat simplistically by combining the bins for the first 50 meters with the first bin above 50 meters, and adjusting the height scale accordingly. Accounting for the likeliness that the terrain will influence the mixing heights at the lowest levels by raising them somewhat (moving occurrences in the first bin to the second bin), the similarities between 2009 and 2010 are more apparent.

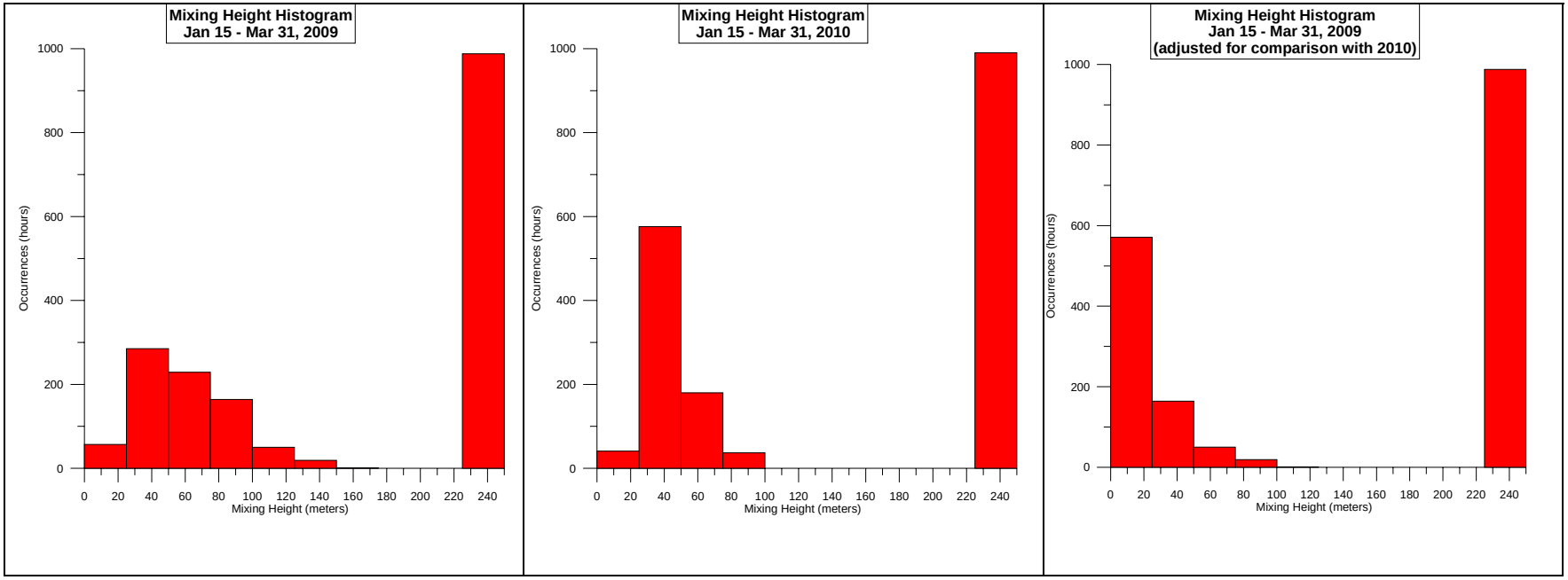


Figure 4.50 Mixing height frequency distributions for 2009 versus 2010. For each plot, the large bar on the right side represents hourly occurrences when no mixing height top was detected. The right-most plot presents the 2009 data adjusting for the 50-meter change in site altitude.

4.5.2 2010 miniSODAR™ Data

The miniSODAR™ (Sodar) produces a number of metrics that are potentially useful for identifying conditions leading to high surface ozone concentrations. As with the 2008 and 2009 studies, the most interesting data obtained from the Sodar were the mixing heights estimated from the Sodar's facsimile data. As an example, Figure 4.51 is the facsimile chart for March 1, 2009, a day that eight-hour ozone concentrations greater than 75 ppb were recorded at the Sodar site. Figure 4.51 demonstrates graphically the depiction of mixing heights from the Sodar data, including multiple layers. Mixing layer tops, as well as elevated layers, are identified by a relatively rapid decrease with height in the return signal strength with a relatively smooth border, as demonstrated by the boundary lines drawn in Figure 4.51. In contrast, as depicted in the example plot for the early afternoon hours, a spiked appearance with a more uniform decrease with height indicates increased mixing, often with no distinctive mixing layer top.

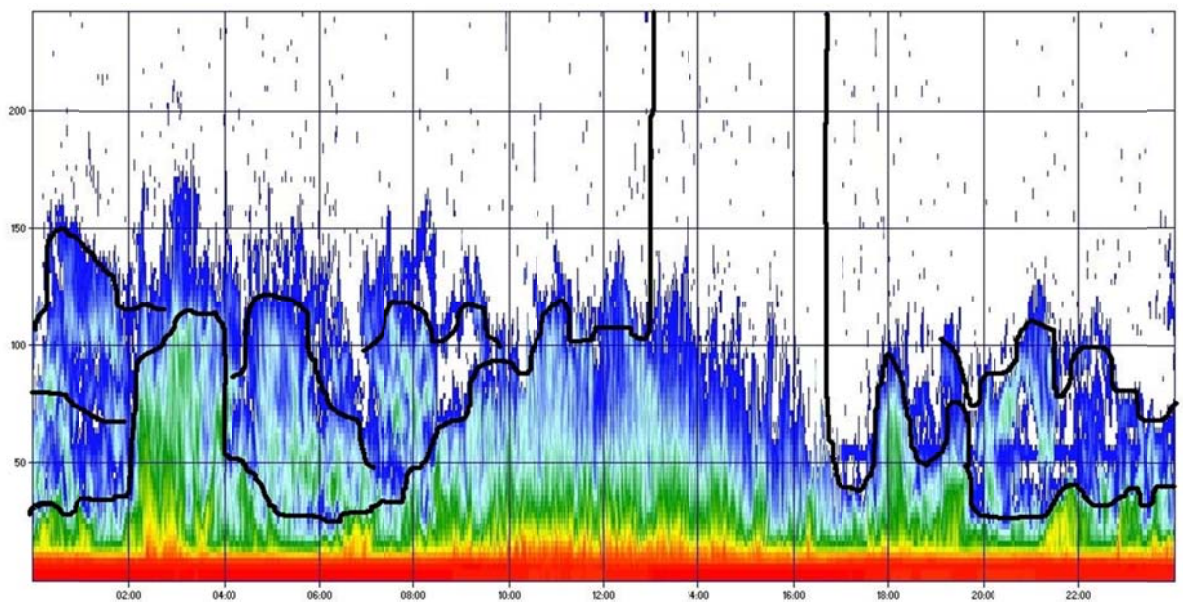


Figure 4.51 March 1, 2009 Example of Sodar Facsimile Display

Table 4-9 summarizes key metrics obtained from the Sodar data during UGWOS 2010 relevant to conditions leading to high ozone. These metrics include the following:

- Median mixing height – The median mixing height is reported for four periods: "AM" referring to midnight to noon, "Morning" referring to hour 0600 to 1100, "PM" referring to noon to midnight, and "Afternoon", referring to hours 1200 to 1700. Each of these periods can potentially play a role in determining the occurrence and duration of an ozone event. Because reported mixing heights of 250m actually mean greater than 250m, it is more appropriate to look at the median rather than the mean when summarizing the mixing heights.

- 30-meter winds – Winds measured by the Sodar at 30 meters are presented as being representative conditions within the mixed layer, while still being largely unaffected by the surface terrain. Winds are presented for two periods: 0600 – 1200 (morning) during which ozone precursors are likely accumulating, and 1200 – 1800 (afternoon), the period when higher concentrations were typically observed.

- UV radiation – UV radiation reported from the Boulder site is presented due to its role in creating ozone and its relationship with the reported mixing height. Total Watt-hours per meter squared are presented for both incoming and outgoing (reflected) radiation.

- Peak one-hour and eight-hour ozone from the study area – For previous reports, data collocated with the Sodar were used. For this report, all data for the study area were considered, given the limited number of high ozone concentrations recorded during 2010.

Table 4-9

Sodar Metrics Relevant to Conditions Leading to Elevated Ozone

	Median Mixing Height (m)				30-m Vector Winds (m/s)				UV (W-hr/m^2)		Peak Ozone (ppb)	
Date	AM	Mornng	PM	Afternoon	Morning WS	Morning WD	After. WS	After. WD	Incoming	Outgoing	1-hr avg	8-hr avg
1/15/2010	163	250	53	250	0.59	18	1.03	65	156	107	51	48
1/16/2010	55	55	68	160	0.49	327	1.29	0	134	85	55	49
1/17/2010	58	50	50	250	0.47	319	0.43	197	162	105	64	57
1/18/2010	60	58	250	250	0.59	106	1.14	120	92	77	53	46
1/19/2010	250	250	53	250	3.28	158	1.96	186	140	116	52	46
1/20/2010	35	40	45	45	1.9	314	0.87	41	136	122	59	45
1/21/2010	250	45	43	30	1.47	102	3.75	148	119	119	51	48
1/22/2010	250	250	148	250	6.69	155	4.96	201	180	142	51	49
1/23/2010	48	38	250	250	0.85	191	6.96	295	173	131	46	42
1/24/2010	250	250	250	250	8.66	312	8.68	307	203	157	46	44
1/25/2010	38	75	40	50	0.15	8	0.64	126	185	144	56	48
1/26/2010	60	60	40	40	0.52	210	0.37	333	115	114	51	45
1/27/2010	50	50	50	250	0.36	213	0.49	204	166	128	62	54
1/28/2010	38	43	50	148	0.85	250	1.1	229	192	130	70	54
1/29/2010	28	43	35	250	0.78	207	1.35	146	193	155	64	59
1/30/2010	38	35	53	165	0.48	273	1.13	224	203	156	80	71
1/31/2010	48	50	48	250	1.97	135	2.01	126	157	116	60	51
2/1/2010	38	40	250	250	0.71	181	6.23	297	204	172	64	44
2/2/2010	60	50	58	250	0.83	350	0.77	211			58	52
2/3/2010	45	45	45	145	1.08	302	0.7	289	177	135	58	55
2/4/2010	45	40	250	250	0.67	263	4.71	305	209	157	55	49
2/5/2010	48	48	38	250	0.56	95	0.48	103	181	97	54	51
2/6/2010	250	60	250	250	1	307	4.15	305	205	123	59	53
2/7/2010	250	80	50	250	1.43	308	1.95	259	230	174	65	51
2/8/2010	70	55	250	250	1.21	242	0.29	200	164	146	51	47
2/9/2010	250	250	250	250	2.73	340	0.71	157	241	176	56	51
2/10/2010	58	58	155	155	1.12	268	3.72	316	236	174	53	49
2/11/2010	43	40	250	250	0.69	175	7.71	304	241	173	49	44
2/12/2010	40	40	250	250	1.54	330	5.88	309	219	152	57	48
2/13/2010	250	250	250	250	6.57	317	10.89	309	248	153	56	53
2/14/2010	250	250	58	250	2.3	144	1	189	251	149	56	51
2/15/2010	163	53	43	250	0.4	98	1.31	166	201	111	69	58
2/16/2010	50	48	250	250	0.82	7	2.04	185	217	70	61	53
2/17/2010	250	250	250	250	2.21	37	6.95	311	245	135	51	49
2/18/2010	250	250	250	250	1.06	28	1.5	180	234	110	56	53
2/19/2010	250	163	250	250	0.63	251	2.25	152	152	169	55	50
2/20/2010	40	48	63	250	3.22	321	1.83	245	173	199	57	51
2/21/2010	150	165	40	250	0.95	292	1.26	272	256	235	58	52
2/22/2010	55	40	45	250	0.23	127	1.1	99	285	232	71	55
2/23/2010	250	160	250	250	1.13	320	7.64	299	293	223	54	49
2/24/2010	50	48	250	250	0.37	29	0.43	32	209	80	59	54
2/25/2010	250	250	250	250	10.28	311	10.63	306	302	156	47	46
2/26/2010	250	250	73	250	2.14	321	1.24	218	295	143	56	52
2/27/2010	40	55	60	250	0.08	161	0.77	131	264	79	63	55
2/28/2010	65	75	155	250	0.32	116	1.14	140	289	136	76	63
3/1/2010	60	60	78	250	1.25	323	1.19	142	295	110	76	62
3/2/2010	85	85	60	250	1.65	330	1.82	209	265	75	66	53
3/3/2010	50	55	75	250	1.37	57	0.78	194			60	55
3/4/2010	83	73	250	250	0.79	106	7.13	125	270	27	60	56
3/5/2010	250	250	250	250	5.6	326	8.5	309	253	37	56	53
3/6/2010	80	68	250	250	0.43	121	4.4	149	246	16	56	53
3/7/2010	158	65	48	250	2.45	335	1.15	220	175	9	59	56
3/8/2010	175	48	250	250	2.94	310	8.89	311	274	16	57	55
3/9/2010	155	50	250	250	0.37	153	1.23	166	247	12	61	58
3/10/2010	250	250	250	250	9.42	317	6.82	309	303	19	53	52
3/11/2010	250	250	250	250	11.68	314	11.6	304			55	53
3/12/2010	250	250	65	250	3.9	328	3.22	320			54	53
3/13/2010	63	50	250	250	1.32	95	2.39	89	218	13	62	57
3/14/2010	250	250	170	250	4.53	32	3.81	64	235	14	54	51
3/15/2010	150	45	250	250	1.04	323	3.01	312	312	17	56	51
3/16/2010	250	250	250	250	0.74	201	1.72	327	314	19	60	54
3/17/2010	250	250	250	250	1.12	297	6.58	333	293	19	55	53
3/18/2010	250	250	250	250	8.73	327	7.19	312	170	11	53	50
3/19/2010	250	35	250	250	4.06	320	6.15	227	186	13	53	50
3/20/2010	55	40	250	250	1.1	240	5.75	302	352	99	56	51
3/21/2010	250	150	250	250	1.27	313	3.79	233	318	20	58	54
3/22/2010	250	78	250	250	2	10	7.05	299	208	14	55	52
3/23/2010	250	250	250	250	5.55	326	1.86	166	240	15	53	51
3/24/2010	145	40	250	250	0.44	291	3.05	203	311	20	55	51
3/25/2010	250	250	250	250	1.67	127	7.69	236	250	17	58	55
3/26/2010	250	35	250	250	6.83	310	12.26	315	312	10	50	49
3/27/2010	250	250	250	250	7.34	328	4.9	299	357	15	52	50

Yellow Highlighting = Peak 1-Hour Ozone Average > 60 ppb.
Orange Highlighting = Peak 8-Hour Ozone Average > 60 ppb.

Within the table, days of higher ozone concentration have been highlighted, with hourly averages greater than 60 ppb highlighted in yellow and eight-hour averages greater than 60 ppb highlighted in orange. A total of 16 days are identified in this manner, which for simplicity will be referred to as "high days" for the remainder of this discussion. Similarly, days when concentrations less than or equal to 60 ppb are recorded will be referred to as "low days."

The report for UGWOS 2009 presented key conditions common with periods of higher ozone concentrations, which included the following:

- Median morning (AM) mixing heights are less than or equal to 60 meters, indicating stable conditions that trap surface emissions during the morning.
- Surface wind directions are from the northeast, the direction of local sources associated with drilling and production on the Mesa.
- Surface wind speeds are less than 2 m/s, typically both in the morning and the afternoon – a further indication of the stable, stagnant conditions necessary for keeping precursor emissions within the area.
- Median afternoon mixing heights are typically greater than 100 meters.
- Reflected UV radiation is at least 50% of the incoming UV radiation - a direct result of the amount of snow on the surface. Note that since the UV sensor is looking at only a small patch of the ground, outgoing UV radiation may not be entirely representative of regional snow cover. However, the lack of any significant outgoing UV radiation after approximately March 3 (Figure 4.9) is consistent with the discussion of snow cover in Section 4.1.2.

As seen from Table 4-9, in 2010 these conditions continue to define the period of increased ozone. The one exception is the condition that winds are from the northeast, which again is likely due to the change in the Sodar location. Looking at the data, low wind speeds again appear as a critical condition necessary for the development of high days. Table 4-10 is a subset of Table 4-9, showing only those days when the morning and afternoon wind speeds averaged less than 2 m/s. Simply applying this filter to the data set identifies 13 of the original 16 high days, with three high days removed due to higher afternoon winds that occurred after the mid-day increase in ozone. 15 low ozone days also remain.

Table 4-10

Sodar Metrics Relevant to Conditions Leading to Elevated Ozone – Wind Speeds < 2 m/s

	Median Mixing Height (m)				30-m Vector Winds (m/s)				UV (W-hr/m^2)		Peak Ozone (ppb)		NOx (ppb)
Date	AM	Mornng	PM	Afternoon	Morning WS	Morning WD	After. WS	After. WD	Incoming	Outgoing	1-hr avg	8-hr avg	1-hr avg
1/15/2010	163	250	53	250	0.59	18	1.03	65	156	107	51	48	3
1/16/2010	55	55	68	160	0.49	327	1.29	0	134	85	55	49	20
1/17/2010	58	50	50	250	0.47	319	0.43	197	162	105	64	57	13
1/18/2010	60	58	250	250	0.59	106	1.14	120	92	77	53	46	13
1/20/2010	35	40	45	45	1.9	314	0.87	41	136	122	59	45	14
1/25/2010	38	75	40	50	0.15	8	0.64	126	185	144	56	48	4
1/26/2010	60	60	40	40	0.52	210	0.37	333	115	114	51	45	10
1/27/2010	50	50	50	250	0.36	213	0.49	204	166	128	62	54	13
1/28/2010	38	43	50	148	0.85	250	1.1	229	192	130	70	54	16
1/29/2010	28	43	35	250	0.78	207	1.35	146	193	155	64	59	15
1/30/2010	38	35	53	165	0.48	273	1.13	224	203	156	80	71	18
2/2/2010	60	50	58	250	0.83	350	0.77	211			58	52	18
2/3/2010	45	45	45	145	1.08	302	0.7	289	177	135	58	55	18
2/5/2010	48	48	38	250	0.56	95	0.48	103	181	97	54	51	8
2/7/2010	250	80	50	250	1.43	308	1.95	259	230	174	65	51	22
2/8/2010	70	55	250	250	1.21	242	0.29	200	164	146	51	47	28
2/15/2010	163	53	43	250	0.4	98	1.31	166	201	111	69	58	9
2/18/2010	250	250	250	250	1.06	28	1.5	180	234	110	56	53	2
2/21/2010	150	165	40	250	0.95	292	1.26	272	256	235	58	52	4
2/22/2010	55	40	45	250	0.23	127	1.1	99	285	232	71	55	6
2/24/2010	50	48	250	250	0.37	29	0.43	32	209	80	59	54	7
2/27/2010	40	55	60	250	0.08	161	0.77	131	264	79	63	55	11
2/28/2010	65	75	155	250	0.32	116	1.14	140	289	136	76	63	10
3/1/2010	60	60	78	250	1.25	323	1.19	142	295	110	76	62	4
3/2/2010	85	85	60	250	1.65	330	1.82	209	265	75	66	53	12
3/3/2010	50	55	75	250	1.37	57	0.78	194			60	55	11
3/9/2010	155	50	250	250	0.37	153	1.23	166	247	12	61	58	2
3/16/2010	250	250	250	250	0.74	201	1.72	327	314	19	60	54	10

Yellow Highlighting = Peak 1-Hour Ozone Average > 60 ppb.
Orange Highlighting = Peak 8-Hour Ozone Average > 60 ppb.

Further filtering for only days when the median morning and PM mixing heights are less than 250 meters (indicating the stable conditions and capping necessary for accumulating higher concentrations) reduces the number of low days to 9 losing only one additional high day (the last reported high day on March 13, when the 1-hr average reached 61 ppb). By further removing all days when the total (incoming plus outgoing) daily UV radiation is less than 267 W-hrs/m^2 leaves 12 high days and only 4 low days.

The correct classification of 12 of the 16 high days using familiar conditional criteria (low wind speed, stable conditions, high UV radiation) provides additional support to the existing conceptual model for ozone formation in the study area. However, it is also appropriate to ask why 4 days with similar conditions (January 25, February 3, February 5, and February 21) did not produce any notable increase in ozone concentrations. To investigate these occurrences, the average AM NO_x from the Boulder air monitoring site is included in Table 4-9 to provide some rudimentary indication of available ozone precursors. Of the four low days, three (January 25, February 5 and February 21) have AM averages of less than 10 ppb, notably lower than most high days. Furthermore, February 5 and 21 both have low outgoing UV radiation, indicating a lack of snow cover. Therefore, of these four days, February 3 would seem to have the most favorable conditions for increased ozone.

Figures 4.52 through 4.55 present the Sodar data for four days – the three days with the highest one-hour and eight-hour ozone concentrations (January 30, February 28, and March 1, 2010) as well as the contrasting day of February 3, 2010. Each figure presents the data for one day (24 hours), and consists of the following three panels:

- Hourly ozone averages from the Boulder air monitoring station. The scale is from 0 to 90 ppb, with 10 ppb tick marks.
- The Sodar facsimile chart. The scale is from 0 to 250 meters, with 50-meter tick marks. Note that the bar at 100 meters is an artifact of recent efforts to increase the sensitivity of the system, resulting in the detection of some electronic noise. The bar should be ignored.
- The Sodar time/height cross-section plot. The scale is from 0 to approximately 250 meters, with 50-meter tick marks beginning at 40 meters. Winds are displayed in knots using the standard weather map convention.

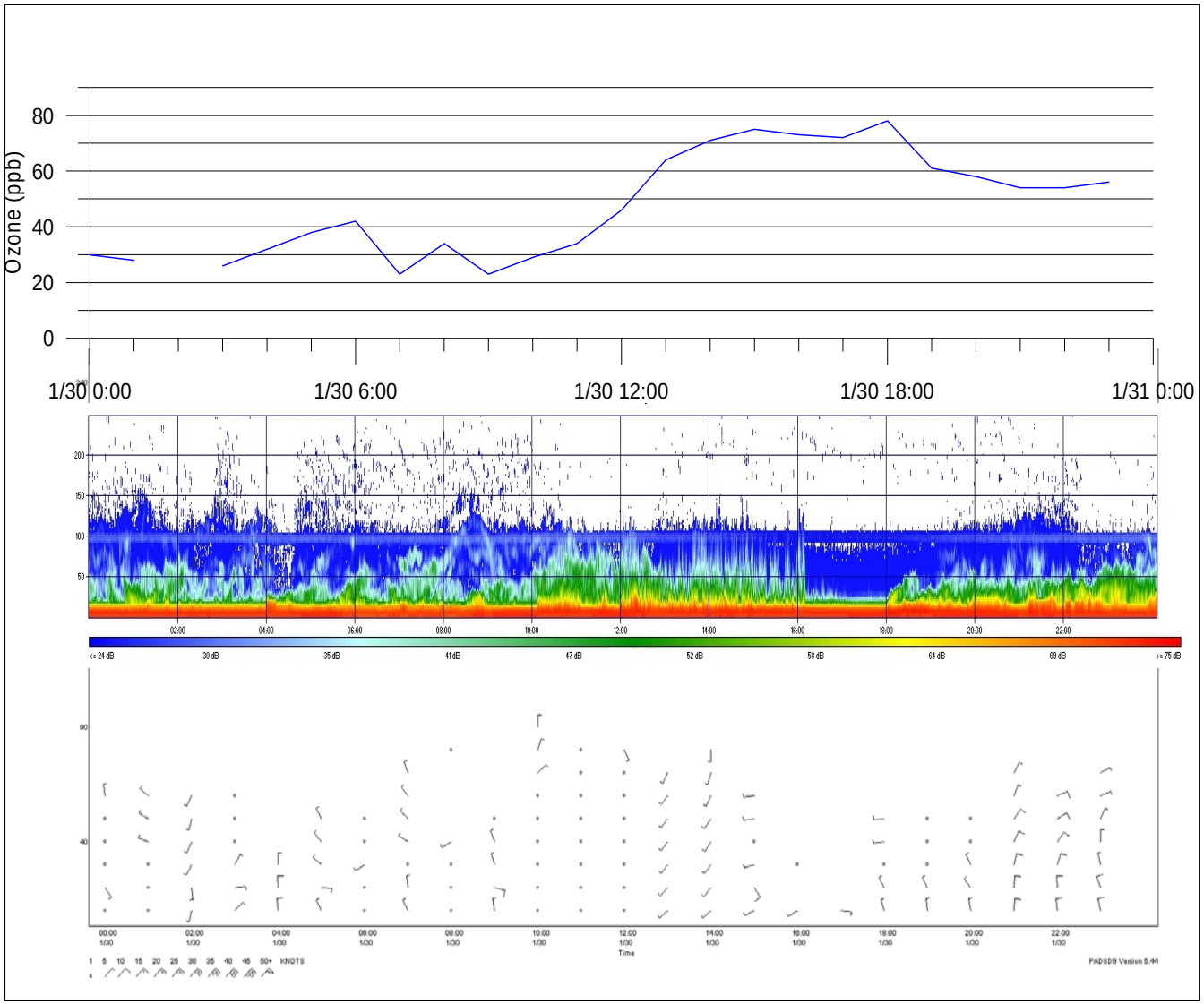


Figure 4.52– January 30, 2010

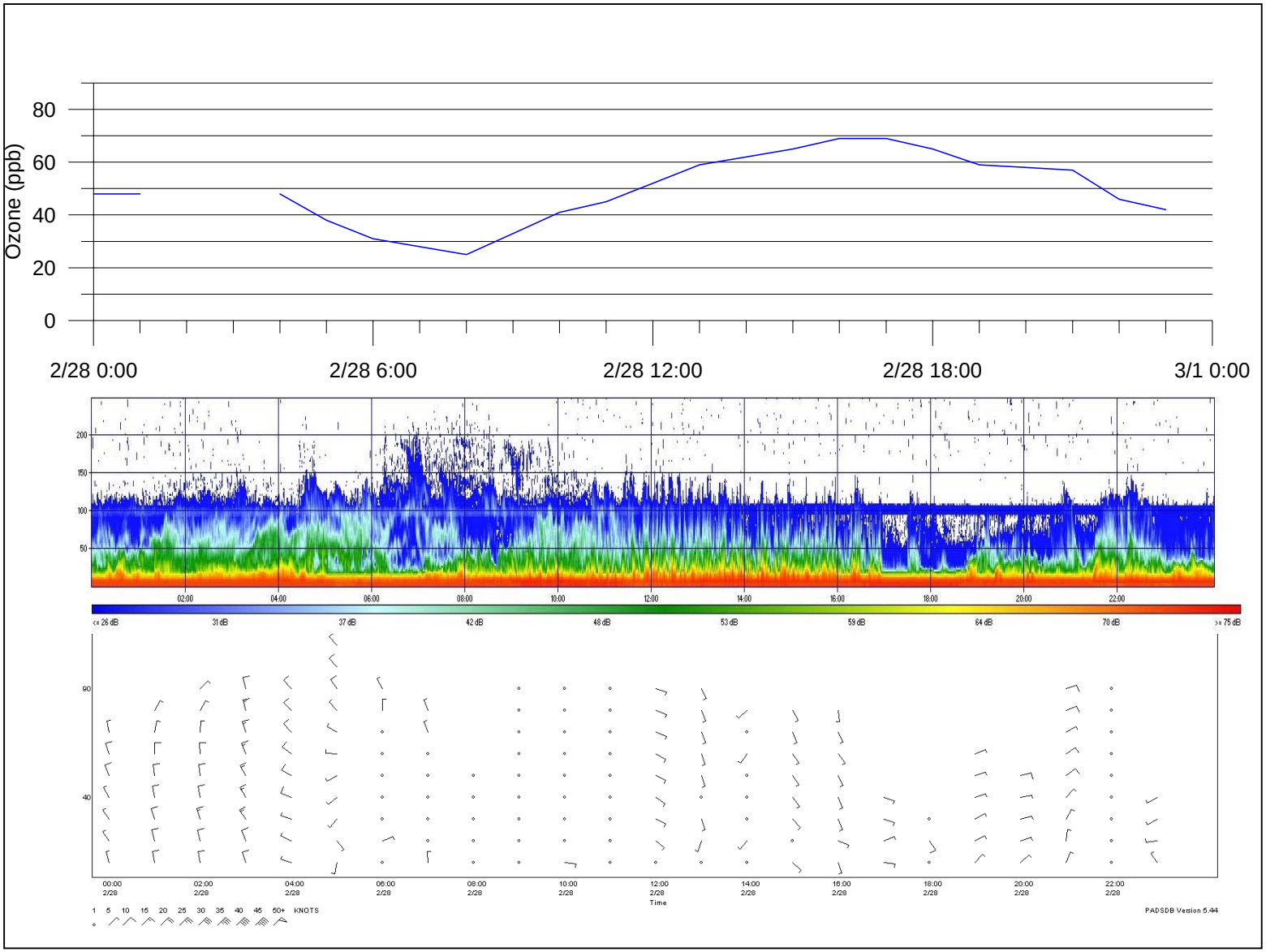


Figure 4.53 – February 28, 2010

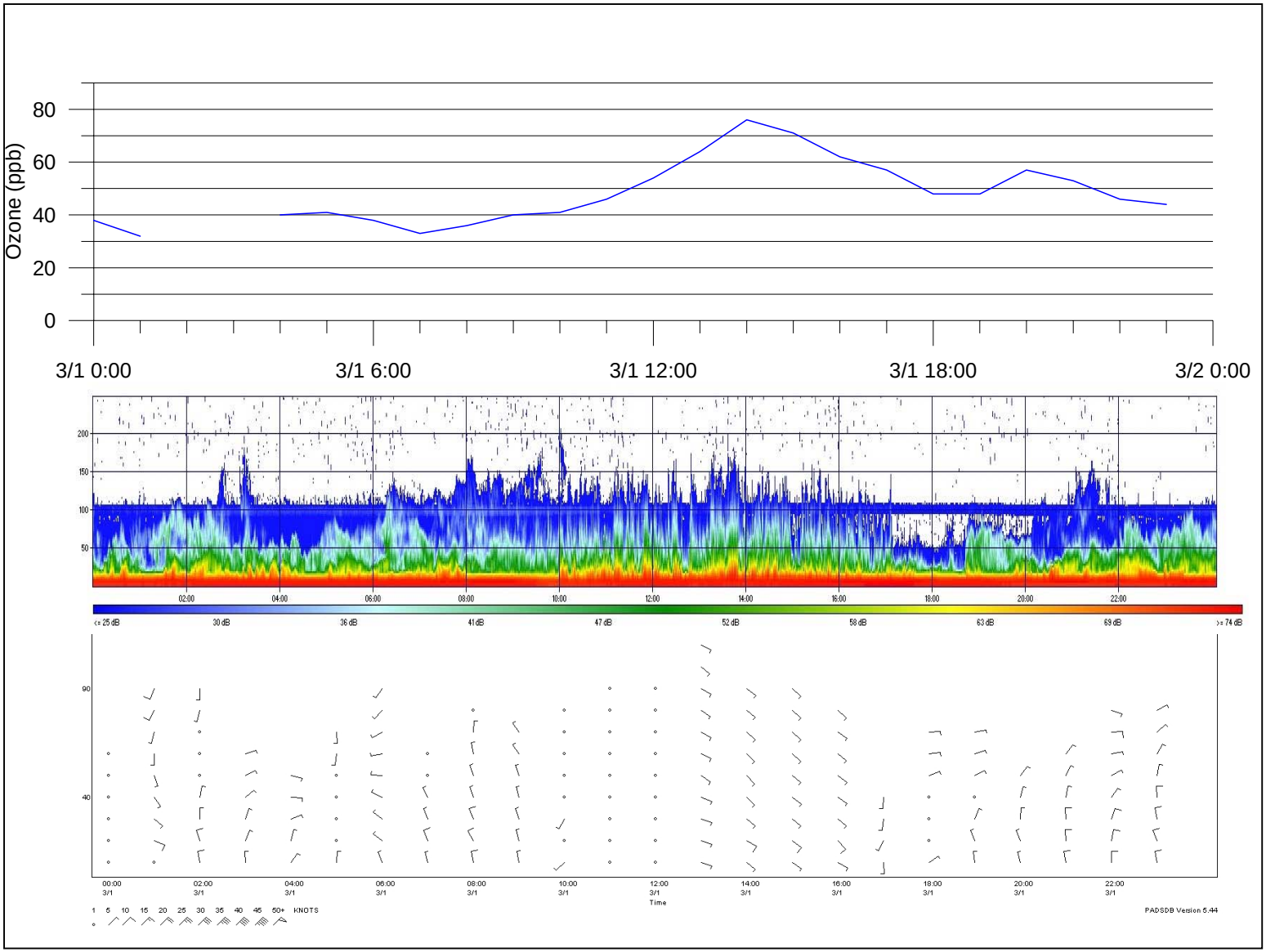


Figure 4.54 – March 1, 2010

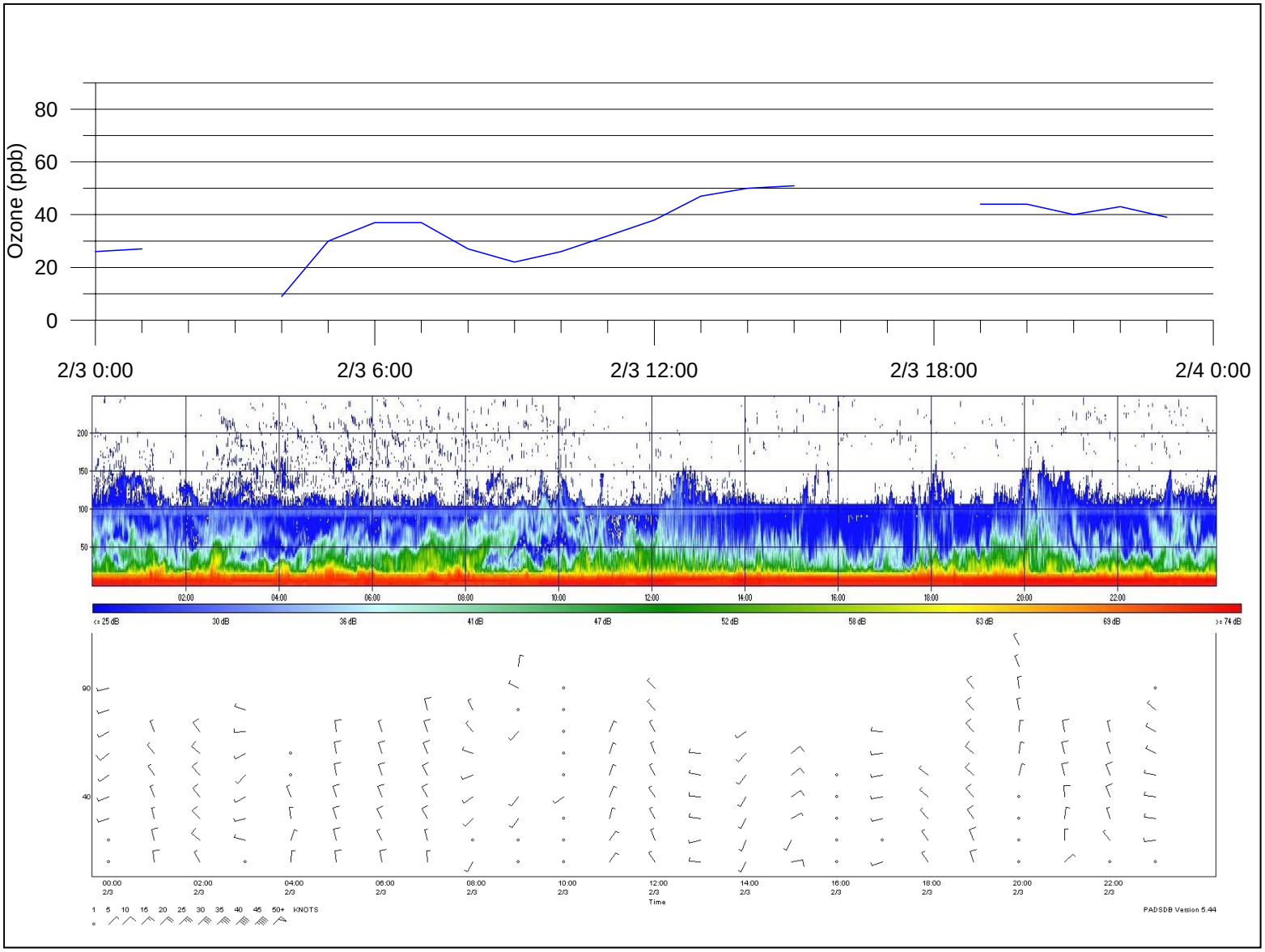


Figure 4.55 – February 3, 2010

January 30, 2010

This day (Figure 4.52) produced the highest eight-hour average of 2010, and was defined by the following:

- Mixing heights remained low (around 50 meters) throughout the morning, until about 10:00. Variability in the wind profile during these hours demonstrates the wind shear associated with the boundary of the mixed layer.
- Starting at 10:00, winds are essentially calm at all levels for a three-hour period, allowing precursors/ozone to collect. The vertical profile becomes more uniform, indicating increased mixing heights, confirmed by the more spiky appearance of the facsimile chart. Ozone concentrations rise rapidly during this period, possibly due to mixing of precursor/ozone concentrations located above the morning mixed layer, or possibly due to winds shifting to a southerly component, entraining ozone from sources south of Boulder.
- Winds remain light throughout the afternoon, allowing ozone concentrations to remain high.
- Late in the afternoon at about 16:00, a very stable layer develops with a very low mixing height (25 meters), further concentrating ozone concentrations and causing a notable bump in the ozone trace.

February 28, 2010

While showing the same general characteristics as January 30 (defined mixing heights during the morning, increased mixing starting around 10:00, a three- to four-hour period of calm winds in the late morning, sustained light winds through the afternoon), there are notable differences in conditions during this day (Figure 4.53):

- The mixed layer during the early morning hours is somewhat higher (75 meters) than during January 30, with notably less shear.

- The wind speed at 3:00 is around 15 knots (about 7 m/s) and is relatively high for much of the early morning, almost certainly preventing the accumulation of precursors during this period. However, the relatively high ozone concentrations by the afternoon demonstrate how rapidly conditions favorable to ozone formation can develop, with just four to six hours of calm winds necessary for initiating the process. Nevertheless, the fact that ozone concentrations did not reach particularly high values this day may be due to the late occurrence of favorable conditions.

March 1, 2010

This day (Figure 4.54) is very similar to January 30, with the following exceptions:

- Early morning mixing heights are somewhat higher (about 70 meters on average).
- Winds in the early afternoon are more persistent – steady from the southeast for a four-hour period. These winds appear to have prevented truly high ozone concentrations from occurring, and actually appear to have contributed to a lowering of concentrations over the course of the afternoon.
- There is a brief increase in ozone concentrations once more stable conditions set up around 19:00
- Similar to January 30, the relatively rapid rise in ozone coincides with increased mixing around the noontime hours. Again, this could imply the mixing downward of ozone/precursor concentrations aloft that are kept from impacting the surface during stable conditions during the morning.

February 3, 2010

As discussed above, while this day had conditions that would seem to be favorable for ozone development, no high ozone concentrations were recorded. The time/height cross-section panel in Figure 4.55 reveals a likely reason. In contrast to the three high ozone days discussed above, February 3 does not have a 3- to 4-hour period of calm winds at all levels in the late morning. It therefore seems likely that precursors did not have sufficient opportunity to accumulate. (Note that some ozone data were missing from the Boulder site in the mid-afternoon, though data from nearby sites indicated that regional ozone concentrations remained low during the affected period.) Further review of the Sodar data showed that this late morning calm period occurred, in addition to the three days above, on February 5, 7, 15, 22, 24, and 27. As is the case for the days above, the mixing height during these calm periods is not particularly low – typically about 90 meters. Looking again at Table 4-9, February 5 and 24 both had low morning NO_x concentrations and, based on the ratio of incoming and outgoing UV radiation, low snow cover, during which no notable increases in ozone concentrations were noted. The remaining days all had notable ozone increases.

In addition to reviewing specific days, an overall comparison of 2009 data and 2010 data, including data presented in Table 4-9, was conducted, which revealed the following:

- As discussed above, the percentage of hours during which a mixing height (less than 250 meters) was identified was roughly the same for 2009 and 2010 (44% and 46%, respectively). This supports a conclusion that moving the site has not inherently affected the detection of a mixing layer, when a mixed layer indeed exists. In addition, the upper extent of the measured mixing heights, measured in elevation above sea level, were essentially the same for both 2009 and 2010, despite moving the site to a higher location with different terrain influence. This implies that the mixing height may be both regionally consistent and have an upper limit.

- In contrast, the percentage of hours from noon to early afternoon period (hours 11 – 15) during which a mixing height was identified is notably different for 2009 and 2010 (27% versus 9%, respectively). Relatively stable conditions during this period may be critical for the formation of higher ozone concentrations. This provides a supporting reason for the generally lower ozone concentrations recorded in 2010 relative to 2009.

4.5.3 Summary and Recommendation

The new Sodar location would appear to be appropriate for determining regional mixing layer conditions during the winter. To summarize:

- The overall detection of mixing layer tops did not appear to change due to the increased site elevation.
- The new location does not show the effects of channeling by local topography as the old location did, and therefore might offer better representativeness regionally.
- Results from the new location continue to correlate well with observed ozone concentrations, with measured mixing heights and low wind speeds resulting in higher ozone concentrations.
- The new location has one disadvantage in that it likely misses some very low mixing heights, particularly when multiple layers exist.
- Based on the above, combined with the availability of collocated air quality measurements, it is recommended that the Sodar be maintained at this site during future wintertime investigations.

The 2010 Sodar data were consistent with the following observations:

- The prevailing northwest wind was more prevalent in 2010 than in 2009, limiting sustained stable periods.
- Conditions when higher ozone concentrations were noted were consistent with those identified in 2008 and 2009, namely light winds, stable conditions, low mixing heights, and snow cover.

- The development of higher ozone concentrations in 2010 appeared to be dependent to some degree on the existence of a late-morning calm period lasting three to four hours. This calm period consists of a well-defined mixing layer with a mixing height typically around 90 meters (as measured at the Boulder site). Winds throughout this layer are consistently calm.
- As mentioned in the 2009 report, there is some evidence that mid-day mixing may be important in order for possible ozone/precursors aloft to impact the surface. It seem plausible that precursor emissions from combustion sources may have sufficient buoyancy to rise above the relatively low morning mixing layer, becoming decoupled from the surface. However, given that 2010 had both higher mixing heights and lower ozone concentrations than 2009, there is opposing evidence that stable afternoon conditions are needed for high ozone episodes. This remains one of the unanswered questions for UGWOS. It is recommended that future studies specifically address this question. However, in the interim, it is further recommended that the 2008 aircraft data be revisited to see if some answers are available. The $PM_{2.5}$ data obtained during the flights is a possible surrogate for combustion-produced ozone precursors, and the $PM_{2.5}$ data was not analyzed as thoroughly as the ozone data during the 2008 study.

4.6 Precursors

As a subcontractor to MSI, the University of Houston performed continuous measurements of nitrous acid (HONO) at the Boulder II site during the 2010 UGWOS field program. The LOPAP instrument started collecting HONO data on January 15, 2010 and ran continuously until April 02, 2010. During the first two weeks technical problems in the sample inlet set up were identified and overcome remotely with the assistance of MSI's UGWOS field technician. Valid one-minute data are available from January 30, 11:23 MST until April 02, 2010 14:31 MST.

Based on one-minute values, one-hour average values were calculated and Figure 4.56 presents a time-series plot of one-hour HONO data for the period January 30-March 31, 2010. The gaps which appear in this data plot are due to routine calibrations and zero checks.

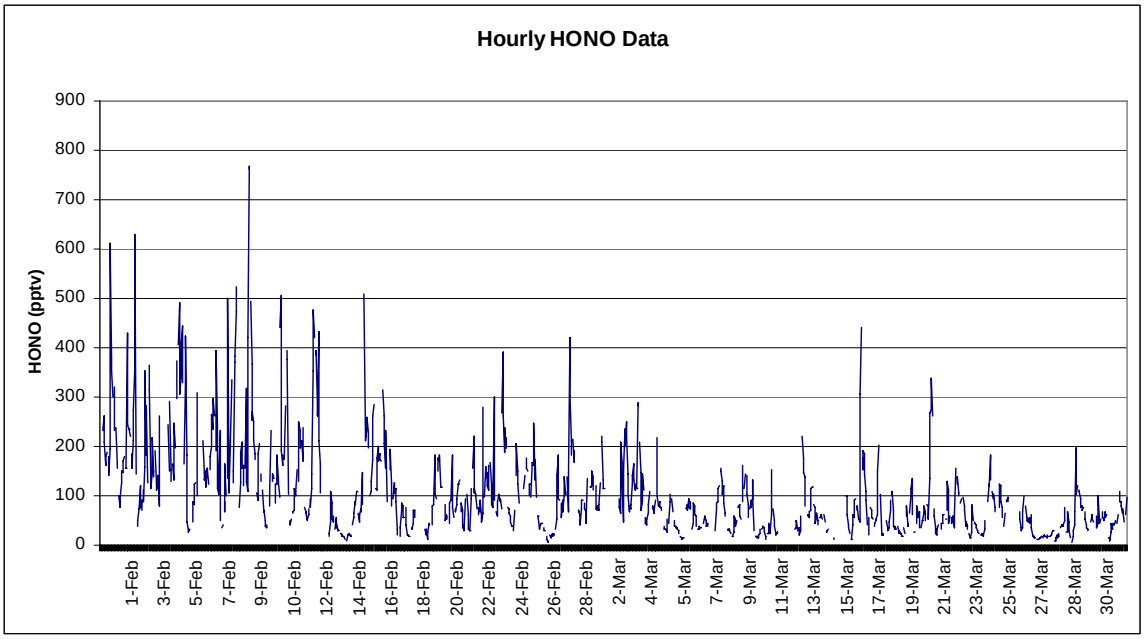


Figure 4.56 One-Hour HONO Data for the Period January 30 - March 31, 2010

Based on the data set obtained from January 30 - March 31, 2010, the main findings include the following:

- HONO levels are correlated with NO_2 and NO_x (however, NO_2 makes up the largest portion of NO_x at the Boulder site). To a lesser extent it is also correlated with non-methane hydrocarbons (NMHC) and also methane (CH_4). No correlation was found with particulate matter (PM_{10}).
- During nighttime periods HONO levels are generally enhanced under WNW-S flow conditions. During daytime periods, HONO concentrations are usually lower and show relatively enhanced values under WSW-S flow conditions. Interestingly, HONO shows enhanced values under ESE conditions which even surpass corresponding nighttime values. HONO levels decrease with increasing wind speed.
- Snow cover appears to enhance total UV radiation. It has been found that UV radiation correlates with HONO levels[5]. This finding suggests photo-induced formation of HONO. HONO levels were higher at the Boulder site during the period when snow cover was present.

[5] Kleffmann (2007)

- The results indicate that high levels of relative humidity are conducive to high levels of HONO.
- HONO/NO_x ratios tend to have minimum values when nitrogen oxides are at a diurnal maximum. This ratio increases when nitrogen oxide levels decrease. These observations suggest that HONO is produced secondarily through nitrogen oxides which may have deposited previously on the snow surface and have undergone heterogeneous conversion.

The University of Houston's report on HONO monitoring during the UGWOS 2010 field study is presented in Appendix D. Detailed analysis findings include statistical summaries and correlations with snow cover as well as meteorological and air quality parameters measured at the Boulder monitoring site. These include wind speed and direction, solar radiation, relative humidity, O_3, oxides of nitrogen, CH_4, TNMHC and PM_{10}.

5.0 SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

For the last three years (2007-2009) WDEQ-AQD has sponsored the Upper Green River Winter Ozone Study (UGWOS) to characterize wintertime ozone formation in Wyoming's Upper Green River Basin. During the winter of 2010, AQD funded a continuation of UGWOS to obtain ambient air quality and meteorological data to monitor possible periods of elevated ozone in the UGRB. The 2010 study focused on monitoring spatial and temporal patterns of ozone and meteorology rather than researching ozone formation mechanisms as was done in previous years. Meteorological and air quality measurements performed continuously in the UGRB during UGWOS 2010 included the following: A nine station network including two new locations of temporary, tripod-mounted monitoring stations recording wind, temperature and ozone concentrations; continuous monitoring of nitrous acid(HONO) at the Boulder II air quality monitoring shelter adjacent to WDEQ's permanent Boulder monitoring site; boundary layer wind profiles using WDEQ's Wind Explorer mini-SODAR also located adjacent to the Boulder monitoring site. Forecasts were issued on a daily basis to identify conditions favorable for elevated ozone formation.

In contrast to the UGWOS 2008 and 2009 field seasons, during UGWOS 2010 there were no eight-hour average ozone concentrations above 75 ppb observed at monitoring stations in the UGRB. There were only a few occurrences of eight-hour ozone concentrations exceeding 60 ppb during two somewhat elevated ozone events. During 2010, higher concentrations were generally seen in the northeast quadrant of the UGRB study domain.

The 2010 study period was characterized by frequent but weak storms. Strong, persistent upper-level high pressure ridges which affected the UGRB in 2008 did not occur in 2010. The weak storms did not generate much precipitation and snow cover, which has been identified in previous studies to be crucial to elevated ozone episodes in the UGRB, was relatively light and mostly gone by early March. In 2010, there were fewer instances of defined mixing layers than in 2008 and 2009 resulting in fewer opportunities for ozone development.

A voluntary emissions reduction program was in place for the winter of 2010, whereby operators in the Jonah and Pinedale Anticline gas development areas of Sublette County would take steps to reduce emissions on days when the WDEQ issued a Health Advisory. Health Advisories were based on ozone forecasts predicting ozone concentrations likely to exceed the standard. The emissions reduction program was never implemented since weather conditions never set up to be favorable for elevated ozone to exceed the EPA standard.

5.1 Recommendations

UGWOS study results obtained since 2007 have allowed us to identify the major features of elevated ozone events in the UGRB. The weak episodes in 2010 and 2009 were more limited spatially than the stronger episodes which occurred in 2008. We recommend continued future monitoring using a network of permanent and temporary measurement sites similar to the network available in 2010. One possible modification to the network would be to move/add stations to locations prone to drainage flows, such as river drainages. This may provide a better understanding of nighttime movement of ozone within the UGRB. Supplementing one or more of these sites with NO_x measurements would provide the same information on nighttime movement of this important precursor.

The HONO measurements performed during UGWOS 2010 yielded some interesting results and correlations with other parameters such as oxides of nitrogen, NMHC, and UV radiation even though elevated ozone episodes were weak. Future HONO monitoring during stronger elevated ozone episodes would provide a better understanding of hydroxyl radical formation and the mechanisms leading to elevated ozone on episode day mornings. The deployment of a formaldehyde analyzer is recommended in addition to HONO measurements. It is likely that enhanced total UV radiation due to snow cover may also lead to enhanced photolysis of formaldehyde, another important ozone precursor.

Based on favorable comparisons with the 2009 data, combined with the availability of collocated air quality measurements, it is recommended that the Sodar be maintained at the Boulder air quality site during future wintertime investigations. Based on review of the data, the Boulder site appears to be representative of general regional conditions. However, more localized conditions may be important for explaining ozone concentrations in specific areas within the study domain. For example, the Boulder site likely misses some very low mixing heights previously detected at its prior location near the New Fork River (an area prone to higher ozone concentrations in 2009), particularly when multiple layers exist. Thus, it is recommended that an additional Sodar, or Sodars, be considered for concurrent monitoring in areas of interest during future wintertime studies to characterize the regional, above surface, wind flow and mixing patterns. The use of relatively inexpensive ceilometers is also a possibility that can be explored to obtain a more complete aerial characterization of mixing heights within the study area.

The question as to whether or not ozone is developed in layers above the surface, requiring some afternoon mixing to impact the surface, remains unanswered. It is recommended that future studies specifically address this question. This could be investigated using aircraft measurements similar to those conducted in 2008, with the addition of portable NOx monitors that are appearing on the market. Another possibility is long-line sampling of ozone and precursors on a tall (up to 100 meters) tower. While more costly initially, the installation could be permanent, supplying continuous data on a routine basis. Both of these efforts have been proposed previously. In the interim, it is recommended that the 2008 aircraft data be revisited to see if some answers are available. The $PM_{2.5}$ data obtained during the flights is a possible surrogate for combustion-produced ozone precursors, and the $PM_{2.5}$ data was not analyzed as thoroughly as the ozone data during the 2008 study.

While the Sodar data provides a continuous interpreted measure of the atmospheric mixing, the ability to measure the atmospheric stability by a temperature-based method could greatly enhance the development of a more quantitative understanding of the stability of the atmosphere in the layers in which the ozone and precursors will accumulate. This understanding should improve the ability of models to simulate and predict the concentrations within these lowest layers. To this end, we would encourage the use of a profiling radiometer to obtain a continuous record of temperature profiles during future research years, and to integrate the data obtained into the regional model development.

6.0 ACKNOWLEDGEMENTS

Many individuals and groups in addition to the staff of Meteorological Solutions, Inc. (MSI), T&B Systems, ENVIRON, and the University of Houston Department of Earth and Atmospheric Sciences contributed to the successful completion of the 2010 Upper Green River Winter Ozone Study and its presentation in this report. Cara Keslar, serving as Project Manager for the Wyoming Department of Environmental Quality (WDEQ) arranged funding, interfaced with Federal and State agencies and other WDEQ contractors, managed contracting details, and provided helpful direction, guidance and comments throughout the study. Jennifer Frazier, WDEQ's Jonah Interagency Office representative, continued to provide field support facilitating project logistics and field measurements. Bill Lanning of the Bureau of Land Management's Pinedale Field Office assisted with providing the necessary land use permits for the temporary mesonet sites located on public lands. Deb Noble of the Chemistry Department at Pinedale High School graciously allowed the periodic use of the chemistry laboratory's fume hood so MSI's field technician could mix chemicals used for the HONO measurement system. Air Resource Specialists (ARS), Inter-Mountain Laboratories and the University of Wyoming's School of Energy and Natural Resources provided meteorological and air quality data they were collecting at the Boulder, Daniel and the Olson Ranch sites, respectively. The Sublette County Commissioners allowed the use of ozone and meteorological data which was being collected at the Air Toxics Study sites by ARS.

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Appendix A
Quality Assurance Plan

MONITORING AND QUALITY ASSURANCE PLAN

for the

UPPER GREEN RIVER WINTER OZONE STUDY - 2010

Prepared for

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Department of Environmental Quality, Air Quality Division
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February 26, 2010

Prepared by

Meteorological Solutions Inc.

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ENVIRON

UGWOS 2010 QAPP APPROVAL

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SECTION 1

INTRODUCTION AND PROJECT OVERVIEW

This monitoring and quality assurance plan provides the basis for the collection of air quality and meteorological data for the Upper Green River Winter Ozone Study (UGWOS) for the winter of 2010, sponsored by the Wyoming Department of Environmental Quality (WY DEQ). While research in nature, the monitoring methods and objectives described in this plan are consistent whenever possible with EPA quality assurance guidance for the collection of air quality and meteorological data (US EPA 2008a and 2008b) and the most recent guidance for the collection of meteorological data for regulatory modeling applications (US EPA, 2000).

Recent high ozone events observed in this area have raised concerns regarding potential adverse health and ecological effects associated with monitored concentrations greater than the U.S. Environmental Protection Agency's ozone standard (currently set at an 8-hour average concentration of 0.075 ppm[1]). Ozone formation in the Upper Green River Basin is unusual in that the highest concentrations have been recorded during the late winter and early spring (February to April) when sun angles are relatively low and temperatures are generally below freezing. This is in stark contrast to ozone exceedances in other areas, which occur during the warm summer months when abundant solar radiation and high temperatures act to increase precursor emissions and enhance the atmospheric reactions that result in ozone formation near the earth's surface (i.e., within the planetary boundary layer). Due to the pressing need to manage ozone air quality in the Upper Green River Basin and the limited amount of information currently available about the nature and causes of these unusual events, the WY DEQ funded a comprehensive field study (the Upper Green Winter Ozone Study or UGWOS) which was conducted during the late winter – early spring seasons of 2007, 2008, and 2009. While meteorological conditions unfavorable to ozone formation were encountered during the 2007 study period resulted in only limited monitoring, more favorable meteorological conditions during 2008 and to a lesser degree during 2009 resulted in several days of high ozone concentrations, including a large number of days when the 0.075 ppm Federal ozone standard was exceeded. Additional measurements have been planned for the winter of 2010. This QA plan addresses the 2010 monitoring effort.

[1] EPA is currently considering revisions to the ozone standard which would lower the level to somewhere between 0.060 and 0.070 ppm.

Data from the 2010 study will be used to refine a conceptual model of ozone formation developed on the basis of prior year'ss studies of ozone formation. The conceptual model will be used along with the field data to develop accurate meteorological and air quality numerical simulations of the ozone events. Both the conceptual and numerical models will in turn be used to develop effective air quality management strategies needed to adequately protect public health and the environment in accordance with applicable State and Federal laws.

SECTION 2

SAMPLING PROGRAM DESCRIPTION

The sampling period for UGWOS 2010 will run from January 15, 2010 through March 31, 2010. Sampling that will be conducted for UGWOS during this period is described below.

2.1 Forecasting Protocol

The UGWOS effort for 2010, in contrast to prior years, does not have an intensive operating period (IOP) component. However, the UGWOS team will continue to provide ozone forecasts throughout the study period to assist the WY DEQ in identifying potential high ozone periods. The current conceptual model of the meteorological conditions conducive to the formation of high ozone levels in the Pinedale-Jonah fields during the winter and early spring is characterized by mostly clear skies, light winds, extensive snow cover and a stable atmosphere. These conditions occur during periods when the synoptic weather is dominated by high pressure over the western Rockies, Intermountain area and the northern Great Basin. The primary broad scale characteristics dominating the Green River basin during the high probability events are weak pressure gradients within the context of a subsidence-dominated air mass.

In an effort to formulate the conceptual model, the synoptic scale weather patterns prior to occurrences of escalated ozone values in the study area during the winters of 2005 and 2006 were examined. Practical experience from the 2007, 2008 and 2009 studies has provided further understanding of conditions leading to higher ozone concentrations. Although many different nuances of the general pattern were encountered, the basic characteristics of the conceptual model did emerge. Figures 2-1 through 2-4 present composite views of the 700 mb and 500 mb configurations for all of the days with surface 8-hour averaged ozone concentrations greater than 60 ppb in 2004 through 2006. Figure 2-1 shows the ridging pattern of the 500 mb height contours; Figure 2-2 presents the wind speed isotachs at 500 mb; Figure 2-3 shows the ridging pattern of the 700 mb height contours; and Figure 2-4 demonstrates that there was warmer air aloft just above the surface, indicating air mass subsidence.

National Weather Service numerical synoptic-scale models such as the North American Mesoscale model (NAM) and the Global Forecast System model (GFS), coupled with regional NWS Forecast Discussion guidance, will provide the experienced MSI and T&B Systems weather forecasters with the basis for daily long and medium range operational forecasts. An additional factor that appears to prove critical in operational forecasting is the presence of sufficient

snow cover to provide the strong UV radiation flux and enhanced low level stability needed for development of high ozone concentrations. Local observations will provide this information on a day-to-day basis.

We will also be evaluating the usefulness of the Rapid Update Cycle model (RUC), the Weather Research and Forecasting model (WRF) and the RAMS model from CSU in our short-term operational forecasting mode and possibly incorporate them into our daily forecasts.

A forecast will be issued by 10 MST each day that will include both a short-term (days 1 to 3) and long-term (days 4 to 7) forecast. Quality control testing of equipment will be minimized on days of anticipated higher ozone concentrations in order to optimize data recovery.

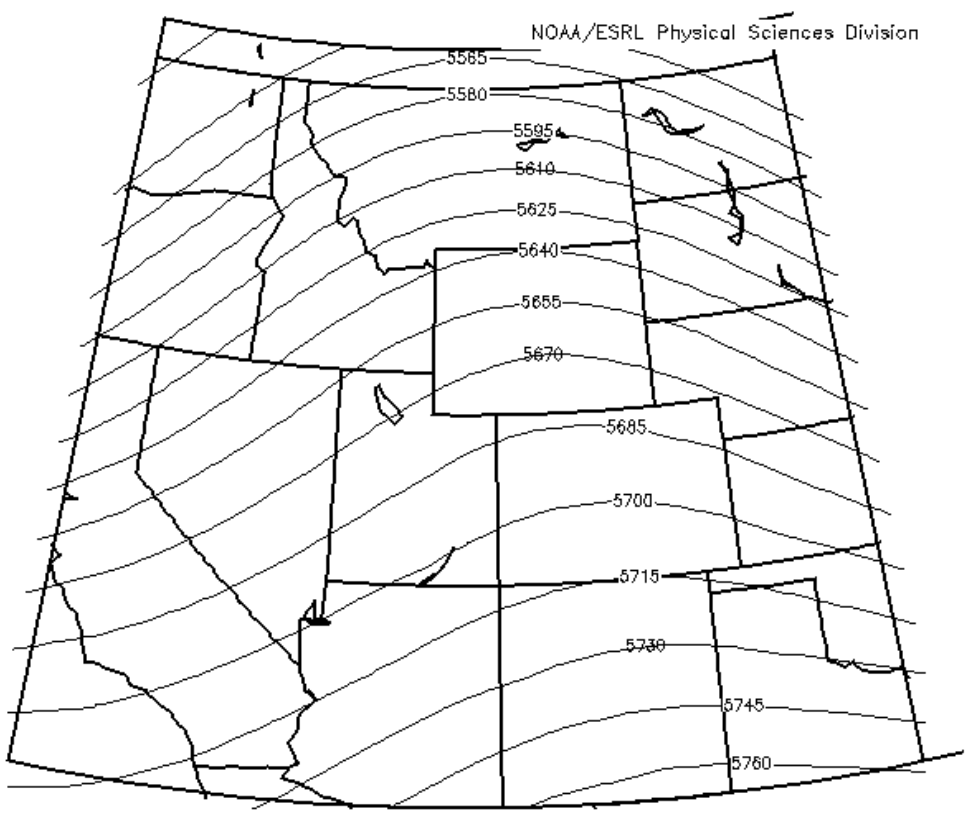

Figure 2-1 Composite 500 mb Heights During High Ozone Periods

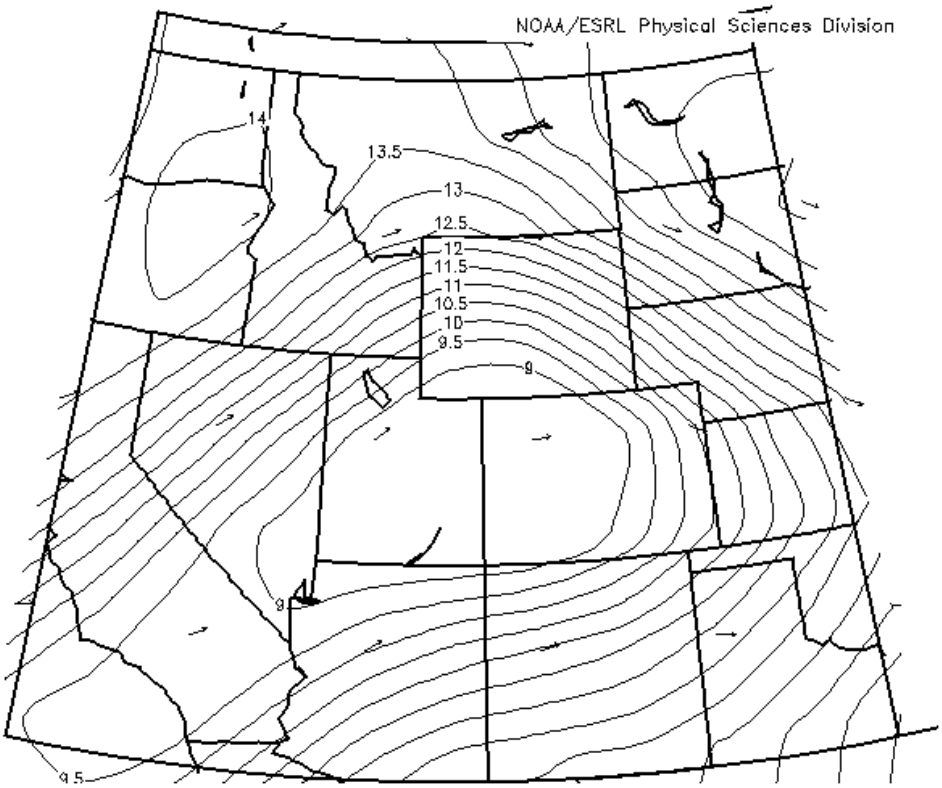

Figure 2-2 Composite 500 mb Winds During High Ozone Periods

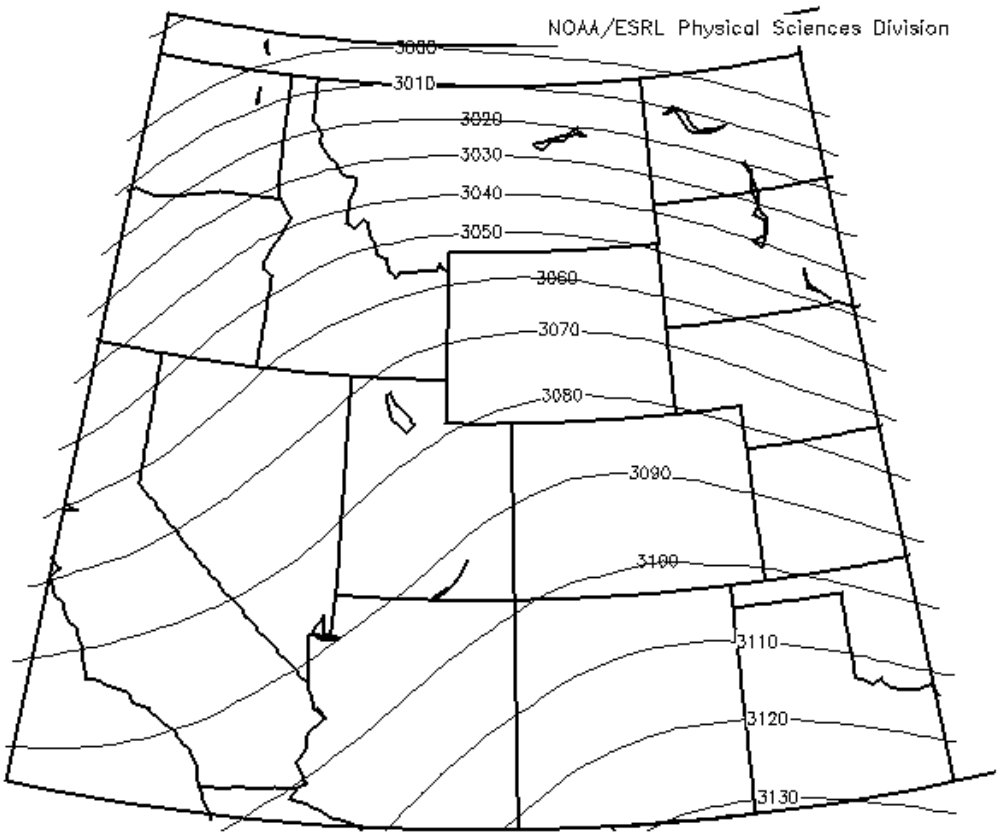

Figure 2-3 Composite 700 mb Heights During High Ozone Periods

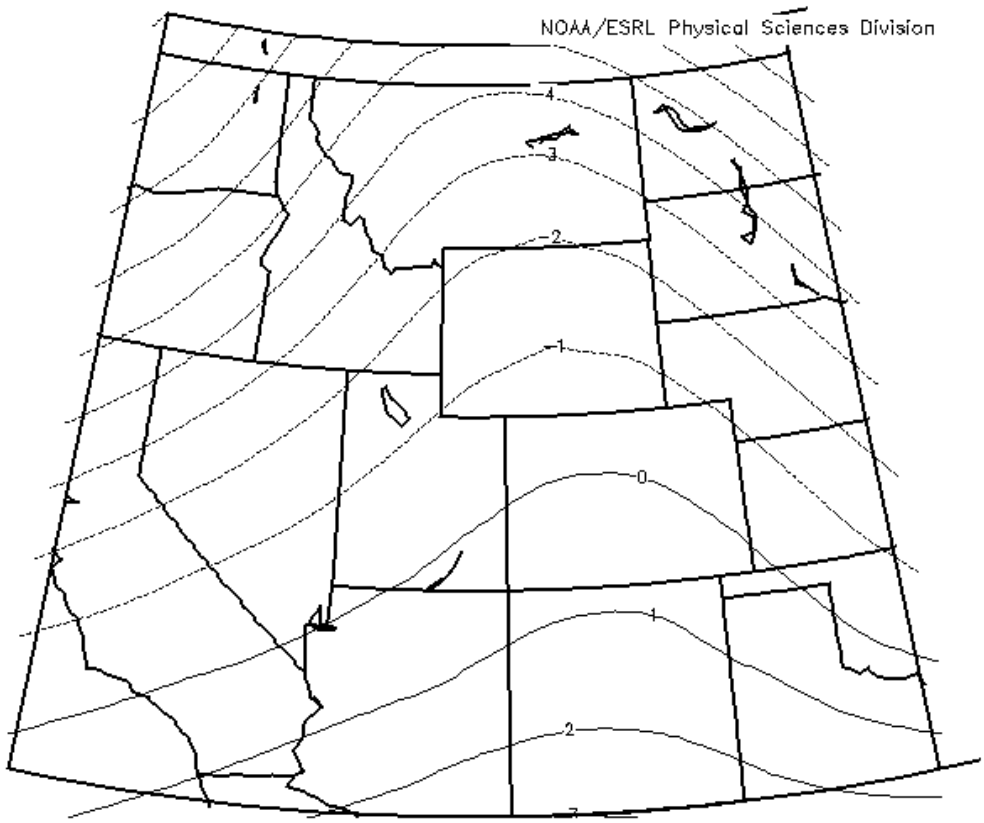

Figure 2-4 Composite 700 mb Temperature During High Ozone Periods

2.2 Continuous Measurements

Project-specific measurements to be continuously obtained over the complete field program period include surface and winds aloft, supplemental surface ozone and meteorology, and nitrogen species.

2.2.1 Mesonet Measurements

Surface ozone, wind, and temperature measurements will be taken from an 9-site mesonetwork (mesonet). All sites will be equipped with cellular telemetry, allowing remote polling and real-time review of data.

The mesonet ozone analyzers will operate continuously over the course of the study and routine performance checks of the analyzers will be conducted approximately once per week. Their operation on-site will be checked using the 2-B ozone generator and zero-scrubber, and any zero and span deviations

noted. An MSI air quality technician will be assigned to the project area for the duration of the 2010 measurement period to conduct the routine checks.

2.2.2 SODAR Upper Level Winds

For the 2010 monitoring effort, the WY DEQ MiniSodar (sodar) will be moved to the existing WY DEQ monitoring site at Boulder. Both surface and aloft winds will be measured continuously. The sodar is equipped with a battery bank, solar panels and a backup generator, providing continuous measurements without the need of AC power. However, the chosen site for operations does include available AC power. Remote communications is made possible with a cellular modem. All data will be posted near real-time on a web page as well as archived data posted automatically on a FTP server. These sodar data can be reviewed remotely, as necessary.

The WY DEQ will service the sodar as necessary. T&B Systems will review the data on a daily basis.

2.2.3 Nitrogen Species

The existing WY DEQ Boulder site will be expanded to included measurements of HONO. Dr. Bernhard Rappenglueck of the University of Houston will provide equipment and setup for the measurements. Routine checks of the equipment will for the most part be conducted remotely by University of Houston personnel, though MSI will be conducting regular visits to the Boulder site.

NO/NO_x measurements will be added to the existing mobile BAM $PM_{2.5}$ site operated by the WY DEQ, which will be located at the former WY DEQ Jonah monitoring site for the duration of the 2010 study. T&B Systems will provide the NOx analyzer. MSI will install and calibrate the analyzer and provide regular site checks.

2.3 Supplemental Monitoring and Data Collection

<u>UV Radiation</u>

Direct and reflected UV radiation sensors (radiometers) initially installed during the 2007 effort at the WY DEQ Boulder site will be an important part of the UGWOS data set. The sensors will be physically checked regularly throughout the study period by MSI, in addition to any checks conducted by the Boulder site operator (ARS).

Archiving of NOAA Products

Archiving of selected NOAA data products will occur on a daily basis. The items that will be archived for the period from January 15 through March 31, 2010 are listed below:

- MSI routinely archives 00Z and 12Z surface and upper air maps for 700 mb, 500 mb and 850 mb. (Also readily available from on-line archives)
- MSI routinely archives data from all rawinsonde sites in the United States for both 00Z and 12Z time periods. (Also readily available from on-line archives)
- MSI routinely archives Visual and IR, US east and west satellite images every 15 minutes. (Also readily available from on-line archives)

In addition to the above, the following data are currently archived on the web and available for analysis:

- Snowpack - available at NOAA's National Operational Hydrologic Remote Sensing Center
- Total Column Ozone - A web site from NASA provides historical ozone global charts, and Dobson Unit measurements for any lat/long on any particular day.
- Local Camera Images - The current local camera images from Daniel, Juel, Boulder and Pinedale can be viewed on line at the WY DEQ or UGWOS web sites, and there is also a 2 week image archive on the WY DEQ site which consists of an image at 9:00 12:00 and 15:00 MST each day. Archived images can also be requested from Air Resource Specialists, Inc. or InterMountain Labs.

SECTION 3

MONITORING SITE DESCRIPTIONS

Figure 3-1 presents a map of the UGWOS site locations. Tables 3-1 and 3-2 present coordinates and site selection rationale (monitoring objectives), respectively, for each of the sites. Photographs of the sites can be found in Appendix A.

Also included in Figure 3-1 and Table 3-1 are the locations of additional ozone monitoring sites in the study region. Specifically, five of the WY DEQ Air Toxics Network sites and four WY DEQ routine air monitoring sites monitor ozone. While not part of UGWOS study, data from these sites are anticipated to play a substantial role during the analyses of the UGWOS data.

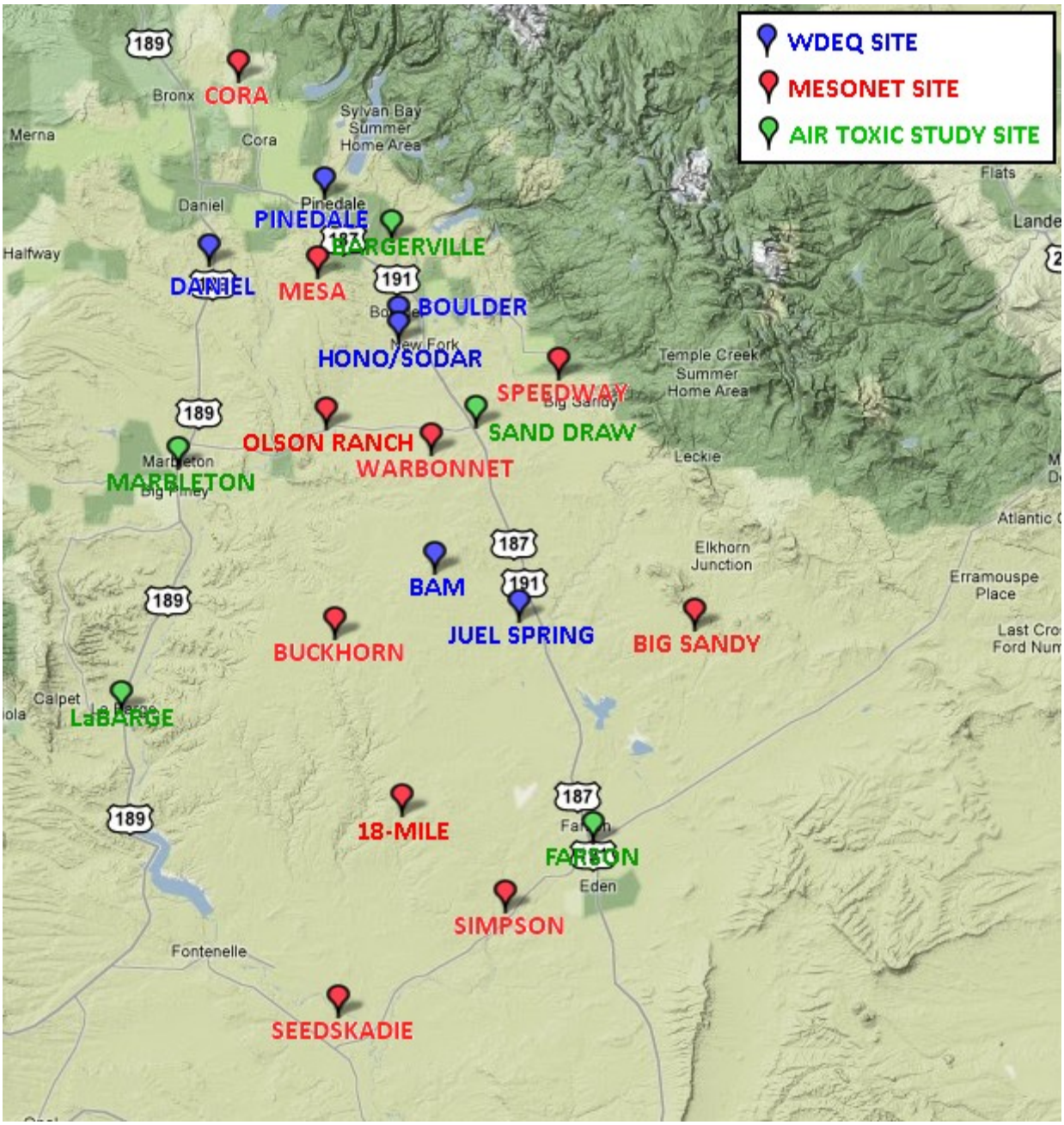

Figure 3-1. Map of UGWOS and Additional Ozone Monitoring Site Locations
Mesonet (red), WY DEQ / UGWOS (blue), Air Toxics Network (green)

Table 3-1. Network Locations and Identifiers

		Latitude	Longitude	Elev.
	MESONET SITES			
Site 1	18-mile Road	42.1438	-109.7491	6905’
Site 2	Big Sandy	42.3617	-109.2808	7112’
Site 3	Buckhorn	42.3523	-109.8543	7087’
Site 4	Cora	43.0065	-110.0088	7539’
Site 5	Mesa	42.7774	-109.8829	7522’
Site 6	Seedskadie NWR	41.9050	-109.8502	6315’
Site 7	Simpson Gulch	42.0280	-109.5819	6662’
Site 8	Speedway Pit (Big Sandy)	42.6573	-109.4983	7200’
Site 9	Warbonnet	42.5703	-109.70214	7397’
	SODAR / HONO SITE			
	Boulder	42.7188	-109.7529	7078’
	BAM / NOX SITE			
	Jonah BAM Trailer	42.4296	-109.6951	7108’
	ADDITIONAL MONITORING SITES OF INTEREST			
	Pinedale (WY DEQ)	42.8698	-109.8707	7186’
	Boulder (WY DEQ)	42.7188	-109.7529	7078’
	Juel Springs (WY DEQ)	42.4653	-109.5771	6848’
	Daniel (WY DEQ)	42.7910	-110.0650	7084’
	Bargerville (Air Toxics)	42.8200	-109.7653	7345’
	Sand Draw (Air Toxics)	42.6019	-109.6294	7235’
	Marbleton (Air Toxics)	42.5528	-110.1050	6915’
	La Barge (Air Toxics)	42.2642	-110.1947	6600’
	Farson (Air Toxics)	42.1100	-109.4428	6595’
	Castnet	42.9284	-109.7880	7853’

Table 3-2. Major Objectives of UGWOS 2010 Sites

Site 1	18-mile	Additional coverage between Buckhorn and Seedskadie
Site 2	Big Sandy	Southeastern boundary site
Site 3	Buckhorn	Representative of area SW of Jonah emissions
Site 4	Cora	Northern boundary site upwind from prevailing winds
Site 5	Mesa	Representative of northern Pinedale Anticline
Site 6	Seedskadie	Southern boundary site
Site 7	Simpson Gulch	Southeastern boundary site
Site 8	Speedway Pit	Impact on Wind River Range foothills
Site 9	Warbonnet	Representative of middle and southern Pinedale Anticline
	Sodar / HONO	WY DEQ Boulder site - Historic area of high ozone concentrations, collocated surface wind and NOx data
	BAM site	Old WY DEQ Jonah site - Ozone precursor emissions from the Jonah Field

SECTION 4

MONITORING EQUIPMENT DESCRIPTION

The following section describes the monitoring equipment that will be used for UGWOS. Monitoring quality objectives (MQOs) are presented for each of the monitoring methods.

4.1 MESONET OZONE MONITORING

All equipment used at the mesonet ozone monitoring sites will be housed in 70 to 100-quart insulated containers. Two 110 amp-hour deep cycle 12-Volt battery will power all equipment. Each site will be equipped with solar panels, allowing continuous monitoring and an Airlink Raven digital cellular modem for remote telecommunications.

The following equipment will be at each of the mesonet sites:

<u>2B Model 202 Ozone Analyzer</u>

The 2B Ozone Monitor will be used for the mesonet Monitoring. This monitor has a low power consumption (12v DC, 0.33 amp, 4.0 Watt) relative to conventional instruments allowing operation with deep cycle batteries. Additionally, it does not require a temperature-controlled environment. The 2B Technologies Model 202 Ozone Monitor™ is designed to enable accurate and precise measurements of ozone ranging from low ppb (precision of ~1 ppbv) up to 100,000 ppb (0-100 ppm) based on the well established technique of absorption of light at 254 nm. "Absorption spectroscopy" is a chemical analysis technique made possible by the phenomenon that a given molecule absorbs light at selected wavelengths. The wavelengths absorbed are characteristic of each molecule's atomic features. The amount of light radiation absorbed by a substance depends on two factors: the number of molecules in the path of the light, and the characteristics of the molecule (e.g., absorption cross-section). Measurement of changes in the light intensity as it passes through the molecules, and the use of calibration and reference data, enable the determination of the number of molecules encountered.

Accuracy (performance checks)	±5%
Precision (performance checks)	±5%
Resolution	0.001 ppm
Lower Quantifiable Limit	0.002 ppm

RM Young Model 05305 Wind Monitor AQ

For surface monitoring of wind speed and wind direction at the mesonet sites, we will employ RM Young 05305 Wind Monitor AQ wind speed and direction sensors. These sensors employ a propeller anemometer. The sensors will be mounted on 3-meter tripods (Figure 4-1), resulting in a measurement height of 3 meters. All sensors will be oriented to true north using either the GPS walk-off method or solar alignment method for orienting wind speed sensors.

Figure 4-1. Tripod mounting of wind sensors.

Monitoring quality objectives for the supplemental surface wind measurements are presented below.

Accuracy (instrument specifications)	
Horizontal Wind Speed	±(0.2 m/s + 5% of observed)
Horizontal Wind Direction	±5 degrees
Precision (performance checks)	
Horizontal Wind Speed	±0.1 m/s
Horizontal Wind Direction	±2 degrees
Output Resolution	
Horizontal Wind Speed	0.1 m/s
Horizontal Wind Direction	1 deg.
Starting Threshold	0.5 m/s

Campbell Scientific 109-L Temperature Probe

Ambient temperature will be monitored using a Campbell Scientific 109 temperature probe. The 109-L Temperature Probe is a thermistor designed for use specifically with the CR200-series data loggers and has a measurement temperature range of -50° to +70°C.

Accuracy (performance checks)	±0.5°C
Precision (performance checks)	±0.2°C
Resolution	0.1°C

Campbell Scientific CR206 Data Logger

All data will be stored using a Campbell Scientific CR206 data logger. Both 5-minute and 60-minute averages will be stored, though the 5-minute data will be used primarily for QC purposes. Based on the number of measurements and statistics being recorded, the CR206 can operate for a period of up to approximately two weeks before it is necessary to download data. The CR206 data logger is equipped with a 915 MHz radio, allowing remote accessing and downloading of data. Additionally, CDMA cellular modems will be used to retrieve the data via a real-time data connection with attempts every 15 minutes.

4.2 NITROGEN SPECIES MEASUREMENTS

NO/NO_x

The basic principle for measuring NO and NO_x is chemiluminescent detection (CLD) of NO. Sample air is reacted with ozone in a low-pressure reaction chamber. NO in the sample combines with ozone to form NO_2 and produces light (chemiluminescence) that is detected by a photo multiplier tube.

Ambient sample is first drawn through a very short Teflon sample line and split into two parallel flow channels using a ½ inch PFA Teflon tee. Channel 1 passes through a Teflon filter and then directly to the detector, while Channel 2 first passes through a catalytic converter before going through a Teflon filter to the detector. The catalytic converters reduce NO_2 to NO. Flow from each channel is alternately fed to the detection chamber to detect the NO. For NO_x, the converter is located within the analyzer.

Accuracy (performance checks)	±10%
Precision (performance checks)	±10%
Noise	0.0005 ppm
Lower Quantifiable Limit	0.001 ppm
Converter efficiency	>96%

HONO

The LOPAP (Long Path Absorption Photometry) instrument is described thoroughly in Heland et al. [2001] and Kleffmann et al. [2002]. It is a wet-chemical in situ instrument that consists of an external sampling unit where ambient gaseous HONO is directly sampled in a stripping coil using a mixture of sulfanilamide in hydrochloric acid. No sampling lines are used thus minimizing sampling artifacts on surfaces. The stripping reagent is transferred to the instrument where it is converted to an azodye by the reaction with N-naphthylethylenediamine-dihydrochloride. The absorption of the light from a white light-emitting diode is measured in long path absorption tubes made of Teflon AF2400 using a minispectrometer. In the external sampling unit, two stripping coils are used in series. In the first channel, HONO as well as possible interferences are determined, while in the second channel only the interferences are quantified. The difference of these two channels yields the HONO signal. The sampling time is between 1-5 min depending on the desired measurement range. The detection limit is about 1-2 pptv. The LOPAP instrument has been tested against DOAS measurements both in smog chamber studies as well as in field campaigns [Kleffmann et al., 2006].

Accuracy (performance checks)	±10%
Precision (performance checks)	±5%
Range	0.005 – 10 ppb
Detection Limit	1 – 2 ppt
Sample efficiency	>98%

4.3 REMOTE SENSING UPPER AIR METEOROLOGY

An ASC Model 4000 miniSodar will be used to collect the upper air meteorology data, providing vertically and temporally resolved boundary layer winds and boundary layer depth (i.e., mixing height) data. The system also includes a surface-based meteorological system. The Sodar provides continuous (hourly and 10-minute) wind data with a vertical resolution of 10 m at heights from about 20 m up to about 250 m agl. The exact height coverage at any given time depends on atmospheric conditions. Continuous (hourly or sub-hourly) boundary layer depth can be derived from the Sodar reflectivity data. An example of this is shown in Figure 4-4. The sodar will be operated under a configuration that produces the highest quality data for the typical atmospheric conditions found in the Upper Green River Basin.

Accuracy (instrument specifications)	
Horizontal Wind Speed	0.5 m/s
Horizontal Wind Direction	±5°
Maximum Altitude	250 meters
Sampling Height Increment	5 meters and greater
Minimum Sampling Height	15 meters
Transmit Frequency	4500 Hz.
Averaging and Reporting Interval	1 to 60 minutes

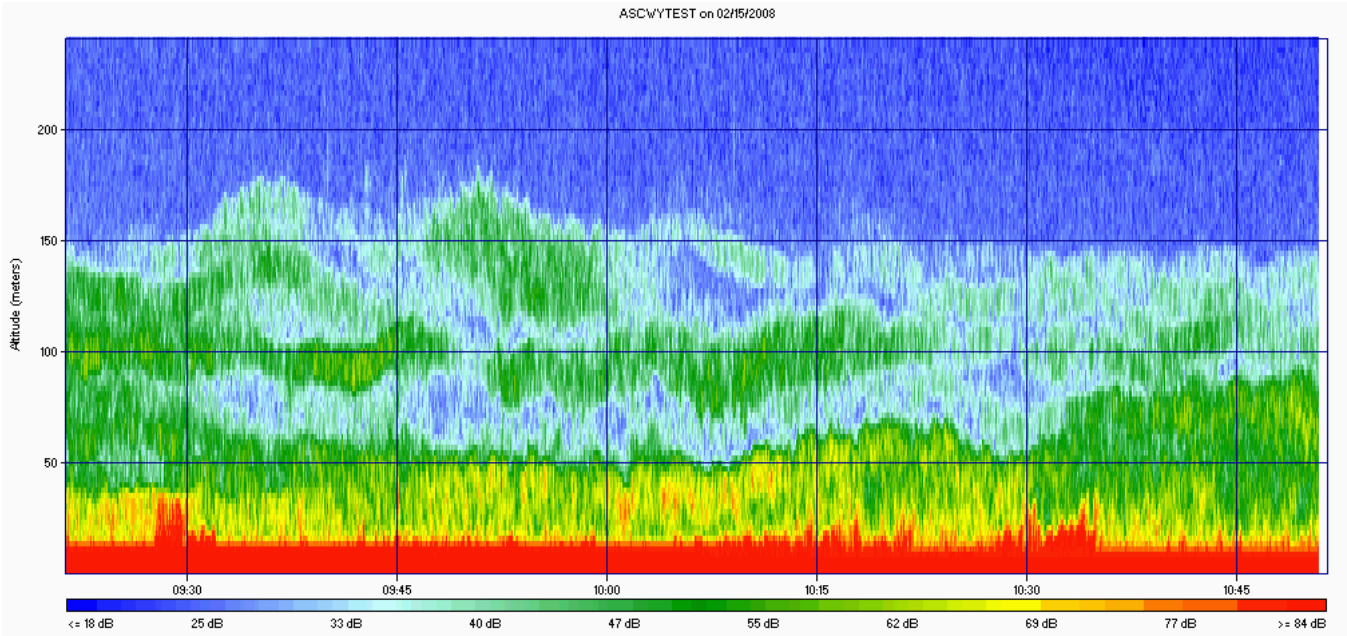

Figure 4-4. Example of sodar backscatter data capturing the daytime mixing height layers under cold wintertime conditions.

4.4 ADDITIONAL MEASUREMENTS

Total UV Radiation

UV radiation will be measured using two Eppley Total UV Radiation (TUVR) sensors – one facing upward to the sky and one facing downward to the ground. The Eppley Ultraviolet Radiometer consists essentially of a selenium barrier-layer photoelectric cell with a sealed-in quartz window, a bandpass filter to restrict the wavelength response of the photocell to the designed range, generally 295-385 nm (i.e. adhering closely to the generally accepted limits for solar ultraviolet radiation reaching the earth's surface, even at altitudes as high as 15,000 feet) and virgin Teflon diffusing disk. The purpose of this disk is twofold, - to reduce the light intensity at the filtered photocell (and thus to increase its stability with exposure time) and also to improve the adherence of the instrument to the Lambert cosine law (and is shaped with this object in view).

These sensors were installed at the Boulder site during the initial 2007 study and are currently being operated by Air Resource Specialists Inc.

SECTION 5

DATA REPORTING

5.1 DATA MANAGEMENT PLAN

A primary study objective is to produce an adequately validated data set from the field measurements that is well defined and documented, and available to researchers in a timely manner. The overall goal of the data management effort is to create a system that is straightforward and easy for users to obtain data and provide updates.

MSI will collect all measurements remotely on at least an hourly basis. Preliminary data will be posted on a near real-time basis on the UGWOS web site at http://www.metsolution.com/ugwos10/index.htm. Both 5-minute and hourly averages will be collected, though only the hourly averages will be reported. 5-minute data will be used to validate the hourly averages. The data loggers are all equipped with internal memory that can store data for the duration of the study. Thus, if telemetry fails at a given site, data can be collected manually. All polled data are backed up at least daily, minimizing the chance of data loss.

Each data provider will be responsible for reviewing and validating their collected data. The raw data will be validated to Level 1 as described in "The Measurement Process: Precision, Accuracy, and Validity" (Watson, 2001) before being submitted to the database. This includes flagging values for instrument downtime and performance tests, applying any adjustments for calibration deviation, investigating extreme values and applying appropriate flags. Flags used for UGWOS are presented in Table 5-1. Each data provider will be responsible for documenting the validation process so that it could be provided to the data manager and other analysts if needed.

In addition, each data provider will be responsible for furnishing information regarding the monitoring equipment used in the field study and any additional site information to the data manager as requested to enhance the overall documentation of the study. In particular, participants will provide the Monitoring Quality Objective (MQOs) defining the quality of all data submitted as "valid." These MQOs contain the following:

- Accuracy
- Precision
- Lower quantifiable limit
- Resolution
- Completeness

If cases exist where data do not meet the primary MQOs but is still deemed useable and can be defined with a secondary set of MQOs, these additional MQOs and the dates to which they apply will also be submitted.

Flag	Description
V	Valid. Data meets primary MQOs.
S	Valid, but does not meet primary MQOs. Secondary MQOs in effect.
I	Data invalid.
M	Missing. Measurement not taken.

Table 5-1. Data Flags.

Once the data have been validated to Level 1, the data will be prepared for submittal to the database in a form that clearly define the time reference, averaging period, parameter names and units. The time reference for the database is **local standard time (Mountain Standard Time)** and the averaging period reference will be standardized to **hour beginning (0 – 23)**. The data will be submitted as ASCII comma delimited text files or excel spreadsheet files, with data columns well defined to clarify site identification, parameters, instrumentation, units, and time reference.

Data will be submitted in a format similar to that of the final database structure, as outlined below. This basically has a second column for each measured value for an accompanying QC code. Data flagged as invalid or missing will be given a value of -9999. In the event that data for a given measurable is either all valid (meeting primary MQOs) or all missing, participants need not supply the flag column, though this must be specifically stated.

Database Management Design

MSI will be responsible for assimilating the submitted data into an integrated relational Microsoft ACCESS database and is managing the data for subsequent distribution and analysis. The database will consist of both information and data files. The goal is to make the database very usable by data analysts and all participants.

The following describes the design for the database, which was similarly implemented during the 2007, 2008 and 2009 field studies. The database includes an inventory spreadsheet file to help users track and ensure that all of

the data were submitted and processed in a timely and consistent manner. All data files submitted will be examined to verify unique names for all sites, instruments, and parameters so that no orphan or duplicate records exist in any of the tables. A system is in place for identifying the version and or modification date of all data files. All files are backed up daily.

The data have the following flat format:

Surface Hourly Meteorological Data

SITE, DATE, HOUR, WS, WS_QC, WD, WD_QC, TP, TP_QC, and any additional met parameters and QC codes, if collected.

Ozone 8-hour averaged:

SITE, DATE, HOUR, O3_8HR, O38HR_QC

Hourly Surface Air Quality:

SITE, DATE, HOUR, OZONE, O3_QC, NO, NO_QC, NOx, NOx_QC, NOy, NOy_QC, PAN, PAN_QC and any additional air quality parameters if collected and QC codes.

Upper level meteorological and air quality data

SODAR data will be stored in both a flat file format and a CDF (common data format) or similar tabular format. CDF files are used for plotting the data. Participants should include both flat files and CDF files with their data submissions. The final flat format will be as follows:

SITE, DATE, HOUR, TIME, HEIGHT, WS, WS_QC, WD, WD_QC

The data will be formatted into the final database with the following unit configurations and naming conventions:

- Parts per billion (ppb) for O3, NO, NO_2, and NOx
- Parts per trillion for HONO
- Meters per second for wind speed (as a general rule, metric units will be used)
- Degrees Celsius for ambient temperature
- Watts/m^2 for radiation

- SITE = Alpha-numeric site code identifier
- DATE = (MM/DD/YY)
- HOUR= Nearest whole begin hour (HH) (MST)
- TIME, START_TIME or END_TIME = Time stamp of data (HH:MM:SS) (MST)
- HEIGHT = Elevation in meters above MSL
- QC_CODE, WS_QC, WD_QC, O3_QC, etc =

"V" (valid), "M" (missing), "I" (invalid), "S" (secondary MQOs)

- NOTES = any additional information

The Level 1 data files along with the documentation files will be available for download on an FTP server.

5.2 DATA REPORTING

Files of all data collected during the study will be transmitted to WY DEQ by June 15, 2010.

The team will review the validated data collected during the field study and prepare descriptive summaries in a report format for delivery to WY DEQ. The Team will prepare summaries of air quality and meteorological conditions during the study period. In addition, the Team will prepare more detailed descriptive analyses of the air quality and meteorology measured during any high ozone events during the study period. As part of the Level 1 data validation procedures, the Team will carefully examine all of the measurements. This process typically provides insight into the critical processes that determine the extent of pollution loading such as atmospheric stability, wind shear (low-level jets, etc), layers aloft, and boundary layer development (growth rate, peak mixing heights), including the nocturnal boundary, convective boundary, and residual layer. The meteorology leading up to and during periods with high ozone levels and the diurnal behavior of ozone aloft during these periods will be characterized.

Supporting the analyses discussion, products that will be produced in this phase of the study include but are not limited to:

1. Time-series plots of continuous measurements such as ozone, ambient temperature, radiation;
2. Vertical profiles of winds;
3. Horizontal mapping of ozone, precursors, ambient temperature, and winds—both at the surface and aloft;
4. Time-height cross sections of ozone, winds, and mixing heights;
5. Time-height cross sections of transport statistics including scalar transport distance, vector transport distance, and recirculation factors;
6. Wind roses at the surface;
7. Pollution roses at the surface; and
8. Summary tables of 1-hour and 8-hour averaged ozone as well as statistical summaries showing hourly averages and maximums.

A final report will be prepared presenting:

- The above-mentioned information and associated analyses in an easy to comprehend format.

- A summary of field operations. A measure of the associated data capture rates will be included. Problems encountered during the field operations will be discussed.
- Details of the database design including descriptions of the metafiles; field descriptors; and the accuracy, precision, lower limits, resolution, and completeness of each measurement.

A draft version of the report will be presented to WY DEQ by August 31, 2010. Voluminous tables and figures will be incorporated into electronic appendices as appropriate. All report materials will be made available via a project web site with access restricted in accordance with WY DEQ policies and procedures.

SECTION 6

QUALITY ASSURANCE PROGRAM

6.1 PROJECT MANAGEMENT

Mr. George Wilkerson will serve as overall project manager. Mr. Bill Hauze will serve as the Field Operations Manager for the study. He will be responsible for coordinating and verifying corrective action for any measurement-related problems.

Study personnel responsibilities and contact information is presented in Table 6-1.

A UGWOS study web site has been developed to assist in communications between study participants and to display real-time data. This web site can be found at http://www.metsolution.com/ugwos10/index.htm. Operational status of all UGWOS equipment can also be viewed at this site.

While it is not anticipated that the scope of the monitoring effort will change over the relatively short duration of the effort, any changes will result in a revised version of this QAPP. Mr. David Bush is responsible for the writing and distribution of the QAPP. Revisions will be distributed based on the distribution list at the beginning of this document.

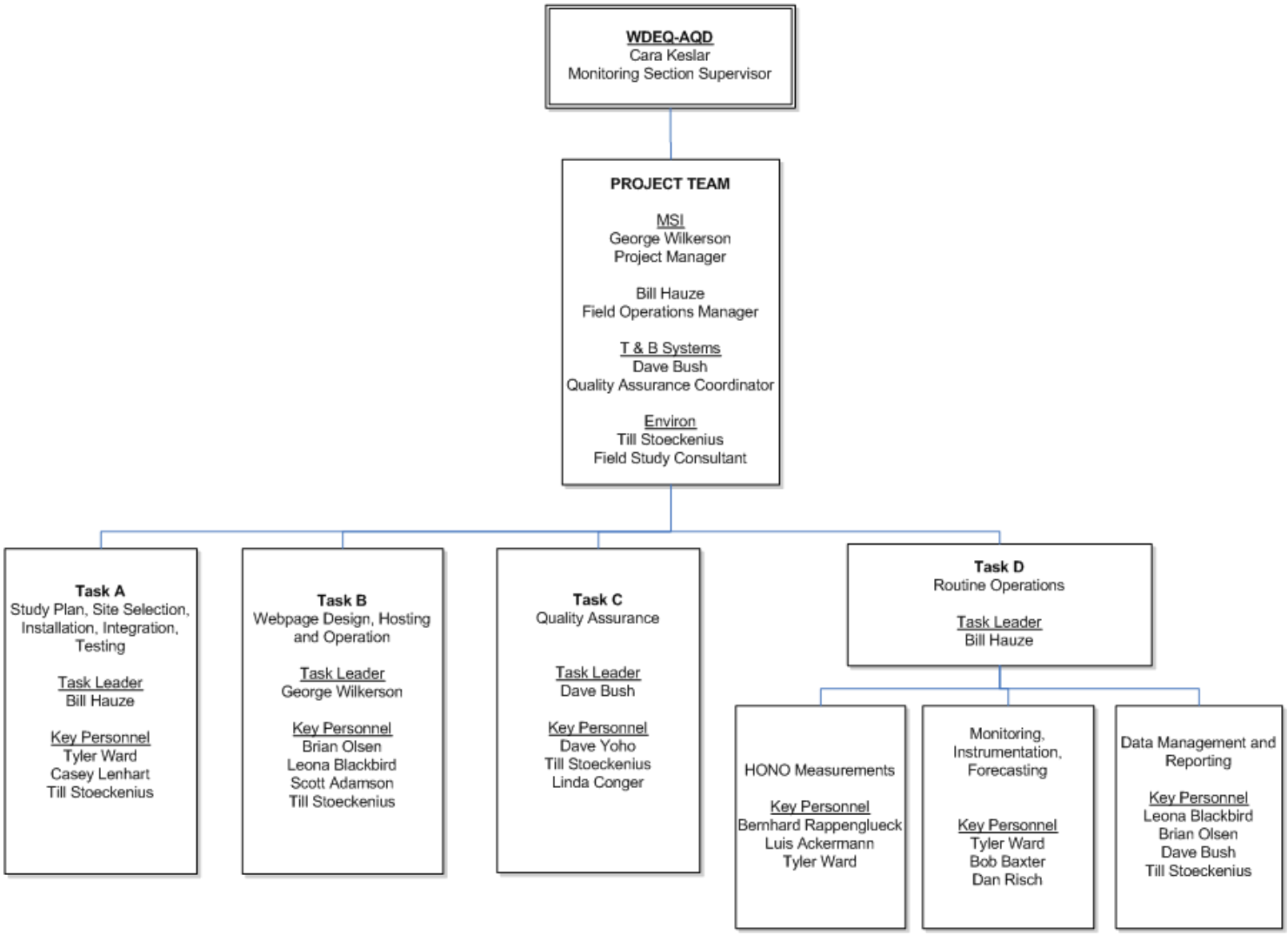

Figure 6-1. Project organization.

Table 6-2. Project Responsibilities and Contacts

Name	Organization	Key Responsibilities	Phone Numbers
Cara Keslar	Wyoming DEQ	Contract Manager	(307) 777-8684 (307) 421-9953 (cell)
Jennifer Frazier	Wyoming DEQ	Pinedale support Daniel site operations	(307) 231-2387 (cell)
George Wilkerson	MSI	Project Manager	(801) 272-3000
Bill Hauze	MSI	Field Manager	(801) 272-3000 (801) 450-3776 (cell)
Dan Risch	MSI	Forecasting	(801) 272-3000
Leona Blackbird	MSI	Data polling Data processing and validation	(801) 272-3000
Tyler Ward	MSI	Full-time onsite field support Mesonet Site Checks	(928) 814-3926 (cell)
David Bush	T&B Systems	Quality Assurance QAPP	(530) 647-1169 (530) 903-6831 (cell)
Bob Baxter	T&B Systems	Measurements support Sodar operations	(661) 294-1103 (661) 645-0526 (cell)
Bill Knuth	T&B Systems	Forecasting	(707) 279-1661 (707) 975-4413 (cell)
Till Stoeckenius	Environ	Data analysis and reporting	(415) 899-0709 (415) 717-0039 (cell)
Bernhard Rappenglueck	University of Huston	HONO measurements	(713) 743-1834
Luis Ackermann	University of Huston	HONO measurements support	(832) 396-8501
Lincoln Sherman	ARS	Boulder Site Operations Air Toxic network	(970) 222-5362

6.2 DATA QUALITY OBJECTIVES

Specific monitoring quality objects have been presented for each measurement in Section 4 of this document. The overall objectives for the collection of valid data will be as follows:

Air quality data: 80% of the possible data

Meteorological data: 90% of the possible data

For the above calculation, data lost during calibrations, maintenance or audits are considered invalid.

6.3 ASSESSMENT AND OVERSIGHT

QUALITY CONTROL PROCEDURES

As part of the quality assurance program, detailed quality control procedures have been implemented to assess and maintain control of the quality of the data collected. All equipment will undergo complete checkout and acceptance prior to the start of monitoring on January 15, 2010. This checkout will occur during the week prior to the start of monitoring, as well as during setup and installation of the equipment. Standard operating procedures (SOPs) for measurements will be completed prior to the start of monitoring. SOPs can be found in Appendix B.

A summary of key elements of the QC program for each measurement is presented below:

<u>Ozone Analyzers</u>

All ozone analyzers and samplers will be routinely checked using a certified transfer standard, following operating procedures consistent with EPA guidelines. This will consist of zero and span checks conducted approximately weekly. For FEM ozone analyzer, these checks will be conducted using a transfer standard certified against a primary standard maintained following EPA's guidelines at MSI's office in Salt Lake City, UT. For the mesonet equipment, a 2B model 306 (S/N 2) portable ozone calibrator will be used. This portable ozone calibrator will also be compared regularly against MSI's primary standard. A pass/fail criterion of +/-10% will be used when evaluating the span and calibration data, after which corrective measures will be implemented.

<u>MiniSodar</u>

The status of the instruments will be checked daily via remote access of the data. If any problems are encountered that could affect data recovery, repairs will be made promptly. The data will be transferred hourly to T&B's server, using a cellular modem. Data can also be accessed in real time via a web site so that team members can use the data to assist in special monitoring and forecasting. The link to the web site is: http://tbsys.serveftp.net/ugwossodar/.

NO/NOx

Zero/span checks of the analyzer will be conducted periodically using a certified standard. A pass/fail criterion of +/-10% will be used when evaluating the span and calibration data.

HONO

The instrument is calibrated by exchanging the sample stripping reagent with a nitrite standard (Merck, Titrisol) diluted in the stripping solution, while running under zero air. Concentrations are calculated using the concentration of the liquid standard and the measured liquid and gas flows. Zero air measurements are automatically performed in regular intervals by a second flow controller and a magnetic valve. The zero air is injected by a small PFA line directly into the inlet of the stripping coil. Zeroes are conducted every 8 hrs for 20 minutes. Calibrations are done once every 8 days or after replacing tubings or reagents, whatever occurs earlier.

CALIBRATIONS

The purpose of a calibration is to establish a relationship between the ambient conditions and an instrument's response by challenging the instrument with known values and adjusting the instrument to respond properly to those values. The calibration method for each of the air quality and meteorological variables is summarized in Table 6-3.

Calibrations of the ozone instruments and the NO/NOx analyzer will be performed upon initial installation and at the end of the study period. Additional calibrations will be performed on an as-needed basis in the event of equipment repair or replacement. All calibrations will be performed in accordance with manufacturers recommendations and consistent with USEPA guidance (USEPA, 1994, 1995, 2000).

Calibrations and zero/span checks of all ozone monitoring equipment will be conducted using a transfer standard (2B Model 306, S/N 002) certified against a local ozone standard. This local standard in turn has been certified against MSI's primary standard maintained following EPA's guidelines at their office in Salt Lake City, UT, as well as against the US EPA Region 8 primary standard maintained at Boulder, CO.

Ozone data will be adjusted if the calibration slope is off by more than ±5% or if the zero is off by more than ±5 ppb.

The NO/NOx analyzer will be calibrated using a certified dilution calibrator and a certified gas standard. Standard gas phase titration (GPT) methodologies will be used for calibration of NO_2 channels.

All meteorological sensors will be calibrated at the beginning and end of the study. Wind speed sensors will be calibrated using an RM Young constant rpm motor simulating wind speeds at several points across the sensor's operating range. Wind direction sensors will be calibrated by checking responses in a least

90° increments. Temperature sensors will be calibrated using a water bath and a certified thermometer. Calibration of the UV radiometers is provided by the manufacturer.

Table 6-3. Calibration methods for the monitored variables.

Measurement Variable	Calibration Method
Ozone (O_3)	Multipoint comparison of ozone concentrations with ozone transfer standard
NO/NOx	Multipoint comparison of concentrations against a dilution of a certified gas standard
Wind Speed	Rotational rate using a selectable speed anemometer drive
Wind Direction	Alignment using true north and linearity with a directional protractor
Temperature	Water bath comparisons to a certified transfer standard

INDEPENDENT AUDITS

As part of the quality assurance program, an independent audit program will be implemented that will use an independent entity to verify the site operations and data accuracy. These audits will be performed using personnel independent of the measurement program. This will establish confidence in the data collected and allow the measurement processes to be supported through independent verification. Audits will be performed in accordance with the principles of the US EPA.

System audits will be conducted of all data collection operations. System audits will address the following:

- Siting
- Adherence to SOPs
- QA/QC procedures
- Documentation
- Data collection and chain of custody

In addition to the system audits, performance audits will be conducted at the mesonet sites and of the UGWOS-specific nitrogen oxide measurements. Performance audits will be conducted using equipment and standards independent of those used in the field.

At the mesonet sites, wind speed sensors will be audited using an RM Young constant rpm motor simulating wind speeds at several points across the sensor's operating range. Wind direction sensors will be audited by checking responses in 30° or 45° increments. Temperature sensors will be audited using a water bath and a certified audit sensor. The ozone monitors will be audited using an ozone transfer standard that is certified against T&B's primary standard

maintained following EPA's guidelines at their office in Valencia, CA. T&B's ozone standards were certified on January 7, 2010 against the EPA Region 9 primary photometer located at their laboratory in Richmond, CA.

The UGWOS-specific nitrogen oxide measurements will be audited using a certified dilution system and a certified cylinder of NO.

Mr. David Bush will conduct the audits of all measurement platforms, with the exception of the nitrogen oxide analyzer, which will be audited by David Yoho. These audits will be conducted near the beginning of the study, after the continuous measurements have become operational. Comments and recommendations resulting from the audits will be discussed with measurement personnel at the time of the audit, with a written memo report provided to study management within 48 hours of the audit. Mr. Bush will work with Mr. Hauze to verify that any deficiencies noted during the audit are addressed.

6.4 DATA VALIDATION

All data collected for UGWOS will be validated to Level 1 validation (see Section 5). As part of the validation effort, participant's data will be evaluated to verify that they meet the stated MQOs. If data clearly do not meet MQOs, they will be removed from the database as invalid data. If, however, data miss meeting the primary MQOs in a definable way to the point where the data are still considered useful, secondary MQOs will be assigned to the data in question. This use of secondary MQOs will be specifically documented in metafiles associated with the data.

SECTION 7

REFERENCES

Heland J., J. Kleffmann, R. Kurtenbach, P. Wiesen, (2001), A new instrument to measure gaseous nitrous acid (HONO) in the atmosphere, Environ. Sci. Technol., 35, 3207-3212.

Kleffmann, J., J. C. Lörzer, P. Wiesen, C. Kern, S. Trick, R. Volkamer, M. Rodenas, and K. Wirtz (2006), Intercomparison of the DOAS and LOPAP techniques for the detection of nitrous acid (HONO), Atmos. Environ., 40(20), 3640-3652.

Kleffmann, J., J. Heland, R. Kurtenbacj, J. C. Lörzer, and P. Wiesen (2002), A new instrument (LOPAP) for the detection of nitrous acid (HONO), Environ. Sci. Pollut. Res., 9, 48-54.

United States Environmental Protection Agency (2008): Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II: Part I, Ambient Air Quality Monitoring Program Quality System Development. Document EPA-454/B-08-003. Office of Air Quality Planning and Standards.

United States Environmental Protection Agency (2008): Quality Assurance Handbook for Air Pollution Measurement Systems, Volume IV, Meteorological Measurements. Document EPA – 454/B-08-002. Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, North Carolina.

United States Environmental Protection Agency (1999): EPA Requirements for Quality Assurance Project Plans. Document EPA QA/R-5. U.S. EPA Quality Staff Interim Final Report, Research Triangle Park, North Carolina. November.

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Watson, J.G., B.J. Turpin, and J.C. Chow (2001). The measurement process: Precision, accuracy, and validity. In *Air Sampling Instruments for Evaluation of Atmospheric Contaminants,* 9th ed., B. Cohen, Ed. American Conference of Governmental Industrial Hygienists, Cincinnati, OH, in press.

Zafonte, L.; Rieger, P.L.; and Holmes, J.R. (1977) Nitrogen dioxide photolysis in the Los Angeles Atmosphere. *Environ. Sci. Technol.* **11**:483-487.

APPENDIX A

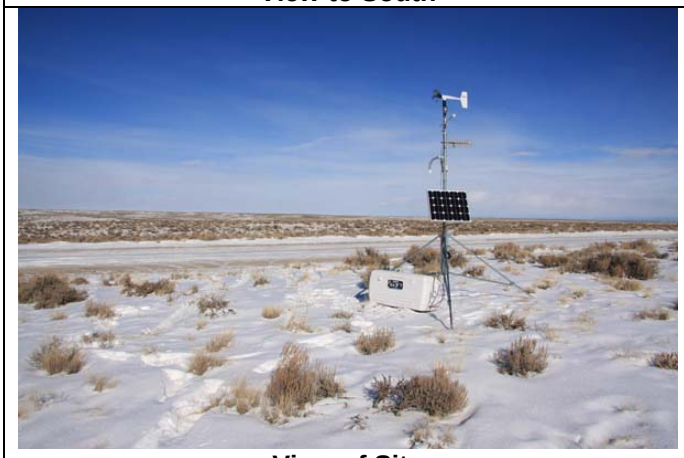
SITE PHOTOS

View to North

View to East

View to South

View to West



View of Site

18-mile Road

View to North

View to East

View to South

View to West

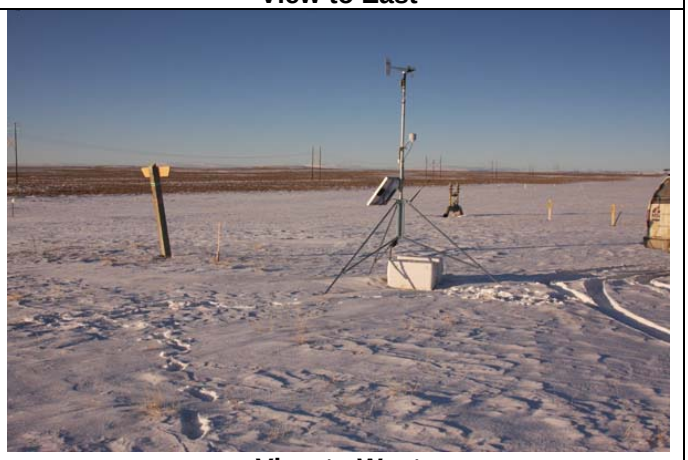
View of Site

Big Sandy

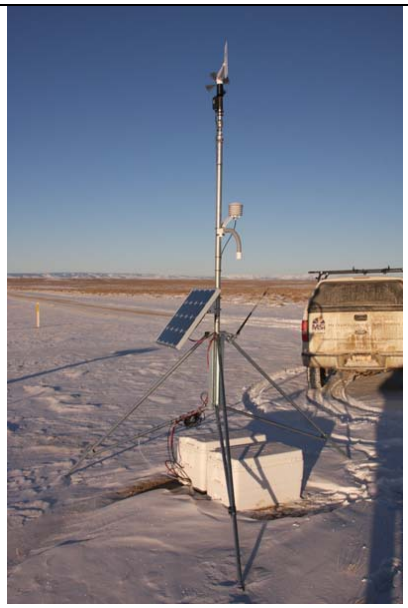
View to North

View to East

View to South

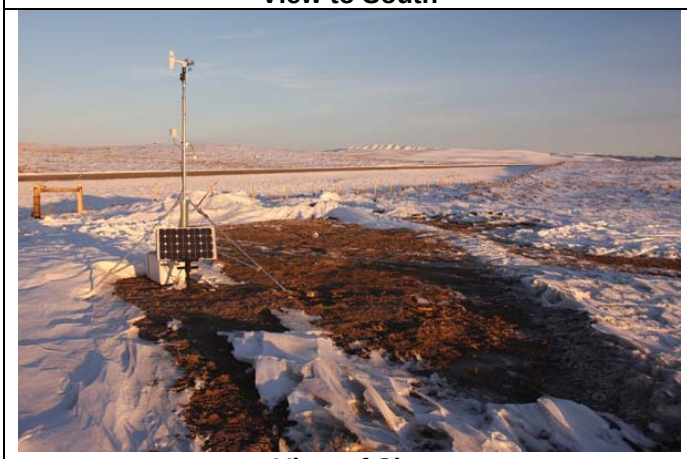


View to West



View of Site

Buckhorn

View to North	View to East
View to South	View to West
 View of Site	

Cora

View to North

View to East

View to South

View to West

View of Site

Mesa

View to North

View to East

View to South

View to West

View of Site

Seedskadie

View to North

View to East

View to South

View to West

View of Site

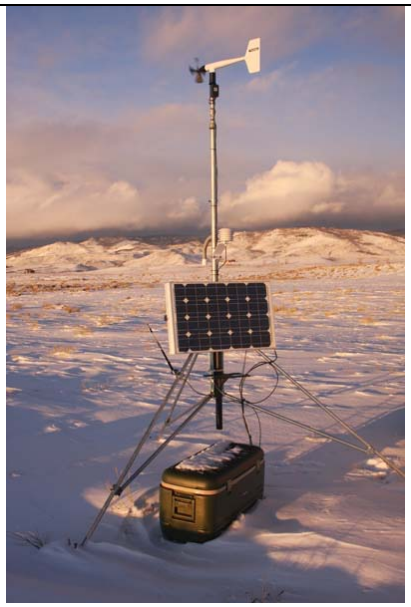
Simpson

View to North

View to East

View to South

View to West

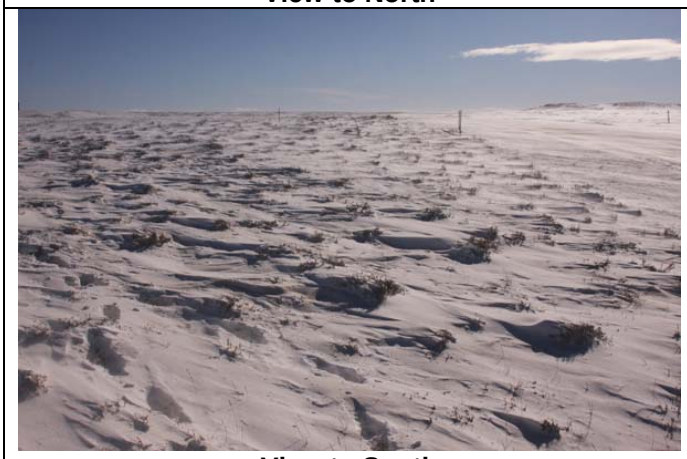


View of Site

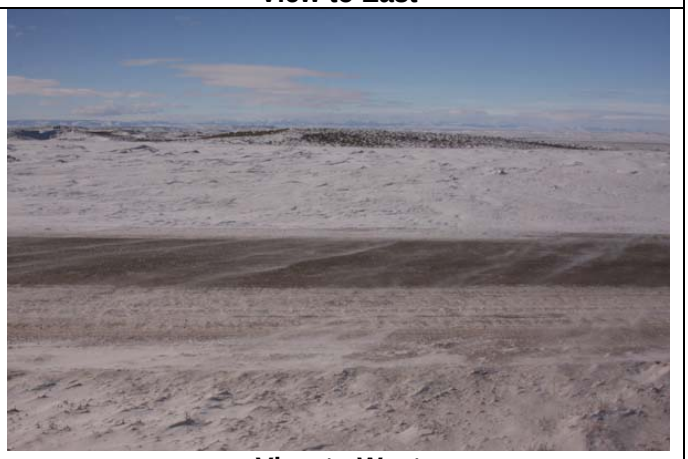
Speedway

View to North

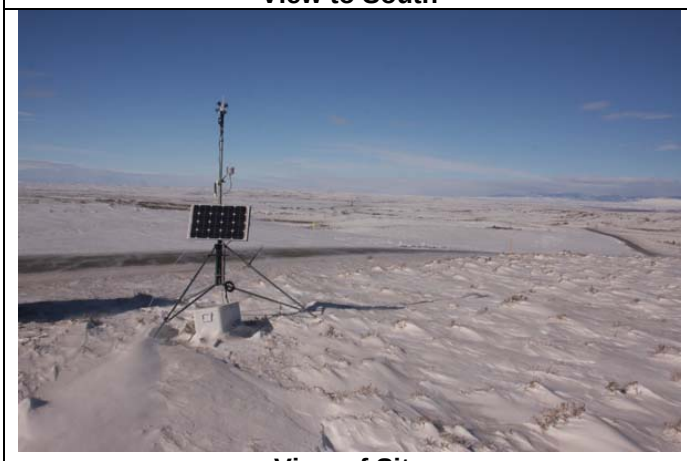
View to East



View to South

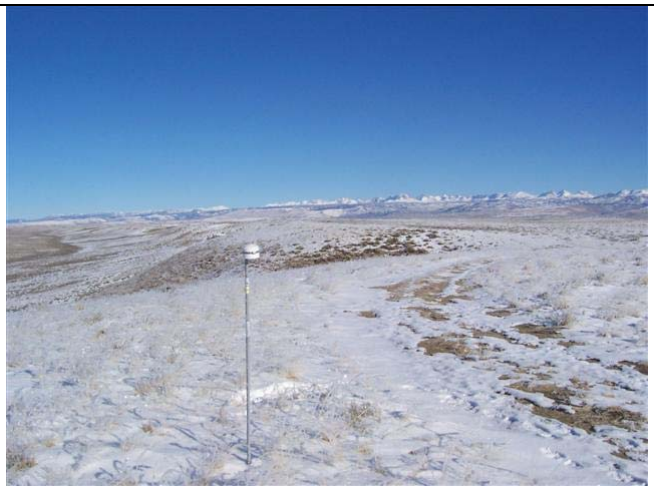


View to West



View of Site

Warbonnet



View to North

View to East

View to South

View to West

View of Sodar V path (SW)

View of Sodar U path (NW)

MiniSodar and HONO (Boulder) Site

View of MiniSodar	**HONO inlet with Mini Sodar in Background**

MiniSodar and HONO (Boulder) Site

View to North	View to East
View to South	View to West
View of Site	

BAM PM2.5 and NOx (Old Jonah Site)

APPENDIX B

STANDARD OPERATING PROCEDURES

Appendix B
ACCESS Database Description

The Upper Green Winter Ozone Study (UGWOS) 2010 Database

1.0 Introduction

This document describes the Upper Green Winter Ozone Study (UGWOS) database for 2010. Included are a review of the study measurements and descriptions of the key data reporting elements such as naming conventions, time reference and units. This document describes the overall structure of the database with a description of the data tables and file formats.

2.0 Overview of Measurements and Field Study Participants

The 2010 UGWOS field study included hourly measurements of surface air quality and meteorological data during the period of January through March 2010 in the upper Green River Basin region of southwestern Wyoming. Winds aloft were measured by a mini-SODAR and are reported on an hourly basis. Measurements of HONO were conducted at an additional Boulder site.

The following lists the UGWOS participants and the data they submitted:

<u>Wyoming Department of Environmental Quality</u>

WDEQ Monitoring network data consisting of some or all of the parameters below (at Daniel, Juel Springs, Boulder, Pinedale, Murphy Ridge, Wamsutter, Thunder Basin, and South Pass)

- 1-hr ozone
- 8-hr ozone
- 1-hr PM_{10}
- 1-hr $PM_{2.5}$
- 1-hr NO/NO_2NO_X
- Wind speed

- Wind direction
- Ambient Temperature
- Additional met parameters (relative humidity, barometric pressure, solar radiation, sigma theta, and precipitation)
- UV Radiation at Boulder

T&B Systems

- SODAR measurements (Boulder site)
  - Wind speed
  - Wind direction
  - Mixing heights

Meteorological Solutions, Inc.

- Mesonet monitoring network data (at 9 locations)
  - 1-hr ozone
  - Wind speed
  - Wind direction
  - Ambient Temperature
  - O_3 (chemiluminescent)

- Air Quality Trailer (BAM Trailer)
  - 1-hr ozone
  - Wind Speed
  - Wind Direction
  - Ambient Temperature
  - 1-hr $NO/NO_2/NO_X$

University of Houston

- Second shelter at Boulder
    - HONO

Supplemental data included hourly surface ozone and meteorological data from three CASTNET (Clean Air Status and Trends Network) sites, five Sublette County Hazardous Air Pollutant (HAP) sites, and the University of Wyoming's Olson Ranch Trailer all located in the Upper Green River Basin.

Each contracted organization reviewed and validated their collected data to level 1 before the data set was submitted to the database. The data were examined by the responsible organization and any adjustments for calibration deviations were applied. Appropriate flags were assigned for extreme values, instrument downtime and performance tests. A description of the flags used are given in Table B-1 and also listed in the table QC_FLAGS in the UGWOS 2010 database.

Table B-1 Data Flags

Flag	Description
V	Valid
S	Suspect. Data appears to be a data spike or outside normal data range.
I	Data invalid.
M	Missing. Measurement not taken.

3.0 UGWOS Database Design

Meteorological Solutions Inc. assimilated the submitted data into an ACCESS 2003 database called UGWOS_2010_Database_Version?.?_MMDDYYY.mdb (where ?.? indicates version number and MMDDYYYY is the month, day and year of the version). The database consists of both information and data files. It has a simple straightforward design. The Sites table contains all of the site information (site name, site identification code used in all of the data tables, site location including latitude, longitude, elevation, and a tabular list of what parameters were measured at each site and the organization responsible). The Parameters table lists parameter codes used in the data tables. The table named Updates lists all information pertaining to modifications and versions of the data. The name of the database includes a version number and date to help users identify the most up to date version of the database.

All data files submitted were examined carefully to verify unique site codes for all sites, instruments, and parameters so that no orphan or duplicate records exist in any of the tables. The valid data were examined for completeness and reasonableness of data ranges. All invalid or missing data were verified to have the value –999. All of the date and times are in begin hour (0-23) Mountain Standard Time. The data were organized and grouped together by platform, averaging period and data type. Table 1.2 lists the names of the data tables and a description of the data included in each of the tables.

The **Hourly Air Quality** table includes hourly average data of criteria pollutants (ozone, oxides of nitrogen, particulate matter) measured at each of the sites. Other pollutants such as methane, non-methane hydrocarbons and total hydrocarbons are also included in the Hourly Air Quality Table. Data included in the **Hourly Meteorology** table represent hourly averages of meteorological data parameters such as wind speed, wind direction, standard deviation of the wind direction, and temperature. Select sites have additional meteorological parameters such as relative humidity, solar radiation, barometric pressure, dew point temperature, precipitation, and UV radiation.

The **8 Hour Ozone** table includes the leading 8 hour average of ozone for each of the sites. Data included in the HONO table represent hourly HONO data collected at the Boulder site.

The data from the upper level wind monitoring SODAR is included in the **Upper Level Wind** table. The **Mixing Heights** table contains data derived from the SODAR data.

The data tables all have a flat format with the identifying information in the starting columns. The most common parameters are listed first. An empty data column and quality control flag indicates no measurements obtained at the site for that parameter. Additional documentation that includes a complete description of the data column, units, etc. is provided by ACCESS 2003 at the bottom of the computer screen when the user is accessing the column. All data tables include a Record Number column at the end of the table, this column is intended to keep data sorted by site to match the Sites table. With this option, a user can sort the table any way he or she chooses and have the capability of sorting the table into its original format. Table B-2 shows the variables available in each of the tables embedded within the database.

Table B-2

UGWOS 2010 Table Variables

SITES	HOURLY AQ	HOURLY MET	8 HOUR O3	HOURLY HONO	1 MIN. HONO	UPPER LVL WINDS	MIXING HEIGHTS
ID	ID	ID	ID	ID	SITE CODE	SITE CODE	Site_Code
Site Code	Site_Code	SITE CODE	SITE_CODE	SITE CODE	DATE	DATE	Date
Site Name	Date	DATE	DATE	DATE	TIME	TIME	Hour
Site Type	Hour	HOUR	HOUR	HOUR	HONO	HOUR	Mix_Height
Site Number	O3	WS	O3_8HR	HONO	HONO_QC	HEIGHT	Mix_Height_QC
Latitude	O3_QC	WS_QC	O3_8HR_QC	HONO_QC	ERROR	VWS	Flag
Longitude	NO	WD	RECORD_ID	ERROR	ERROR_QC	VWS_QC	Description
UTM_E	NO_QC	WD_QC		ERROR_QC		WD	
UTM_N	NO2	WS_VECT				WD_QC	
Elevation	NO2_QC	WS_VECT_QC				WWS	
O3_1HR	NOx	WD_UNIT				WWS_QC	
O3_8HR	NOx_QC	WD_UNIT_QC				SD_WWS	
NO/NO2/NOX	PM10	SIGTH				SD_WWS_QC	
PM10	PM10_QC	SIGTH_QC					
PM2_5	PM25	GUST					
Winds	PM25_QC	GUST_QC					
Temp	CH4	T					
Delta Temp	CH4_QC	T_QC					
RH	NMHC	T_10M					
Pressure	NMHC_QC	T_10M_QC					
Solar Rad	THC	RH					
Sigma Theta	THC_QC	RH_QC					
Precip	RECORD_ID	DT					
UV Rad		DT_QC					
SODAR		SR					
Mixing Depth		SR_QC					
Stability Code		BP					

Table B-2 Continued

UGWOS 2010 Table Variables

SITES	HOURLY AQ	HOURLY MET	8 HOUR O3	HOURLY HONO	1 MIN. HONO	UPPER LVL WINDS	MIXING HEIGHTS
CH4		BP_QC					
NMHC		PRECIP					
THC		PRECIP_QC					
HONO		UV_IN					
		UV_IN_QC					
		UV_OUT					
		UV_OUT_QC					
		UV_NET					
		UV_NET_QC					
		SRDT					
		SRDT_QC					
		RECORD_ID					

The data have the following general unit configurations:

- Parts per billion for O3, NO, NO2, NOx,
- Meters per second for wind speed
- Degrees Celsius for ambient temperature and dew point temperature
- Watts per meter squared for solar radiation and ultra violet radiation
- Micrograms per cubic meter for PM_{10} and $PM_{2.5}$
- Parts per Trillion for HONO
- Percent for relative humidity

The 2010 UGWOS database contains data queries for quick data sorting based on a users needs. There are four queries for users to gain access to data (Days and Hours of Data, Individual Site Data, Sort 1-hour Ozone Data, and Sort 8-hour Ozone Data). Once a user opens the query he or she will be asked some pertinent questions for the query. After the questions have been answered, the query will sort the data as designed. A more complete description of each query is below:

Days and Hours of Data- this query simply asks for the date and hours of data the user is looking for. The user is first asked to give a "Starting Date" and an "Ending Date" these should fall within the UGWOS period of January 15, 2010 and March 31, 2010. Next the user will be asked for an hour beginning and an hour ending, the data are in hour beginning format (0-23). Data not between the specified beginning and ending hours will be removed for all days between the starting and ending dates.

Individual Site Data- The database has several tables with data sorted by air quality, meteorological, site information parameters, etc. This query takes all of the air quality and meteorological data from one station and places it into an individual table. The user will be asked for the five character alpha numeric "Station Code" found in the Sites table. Once a matching station code is entered the meteorological and air quality data will be output into one table.

Sort 1-hour Ozone Data- the purpose of this query and the **Sort 8-hour Ozone Data** query are to sort any data above a user specified threshold. The user will be asked to provide a level of which no data records with an ozone level below that threshold will be displayed. Common parameters are displayed in each data record.

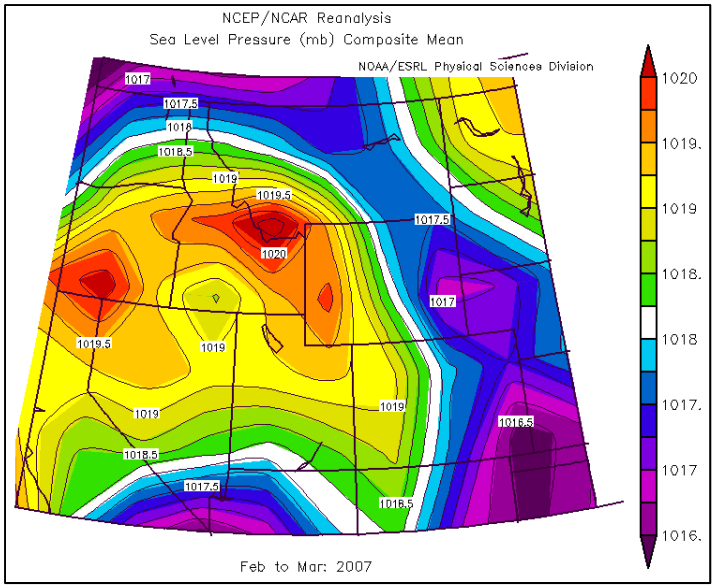
All additional field names are described in the Parameters table. Users wishing to be notified of updates to the database can send their e-mail address to the UGWOS Database Manager, Scott Adamson, at scott.adamson@metsolution.com.

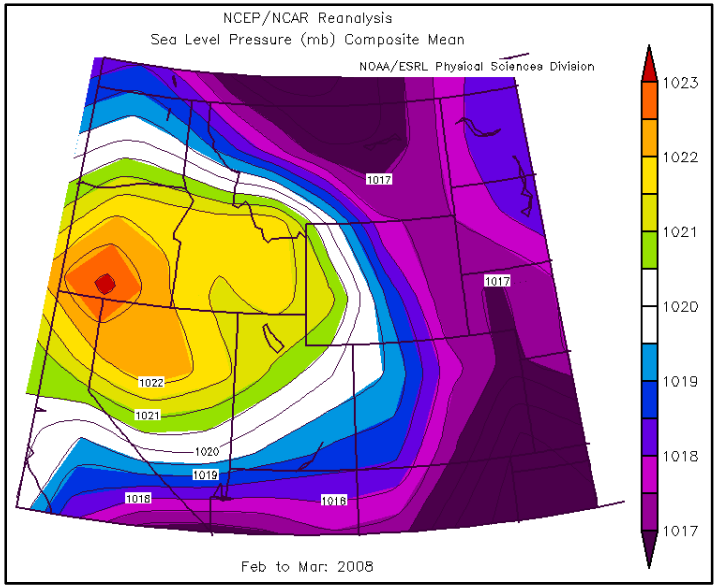
4.0 Summary

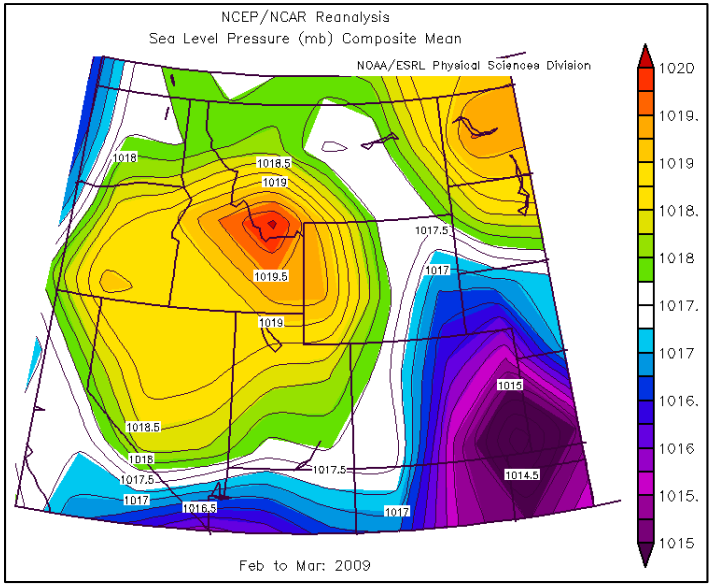
This document describes the 2010 UGWOS database. Feedback from study participants concerning this document and the database is requested and any suggestions for improvement are highly encouraged and appreciated.

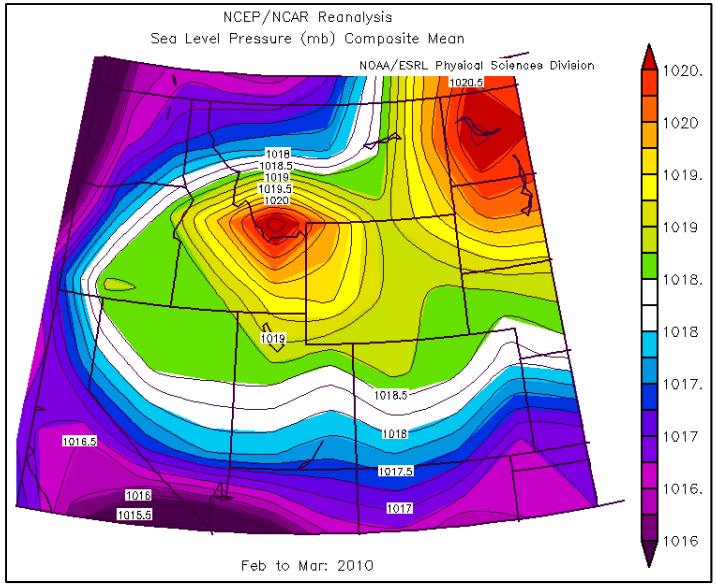
Appendix C
Weather Charts

Weather Charts - Surface Pressure

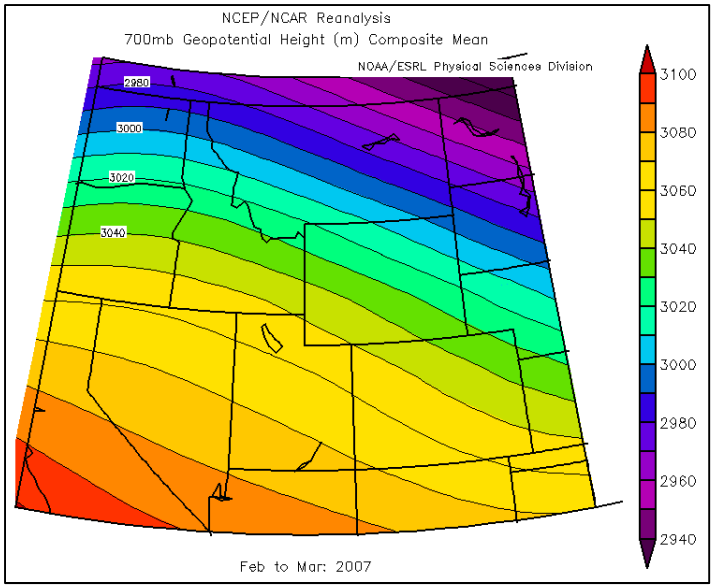


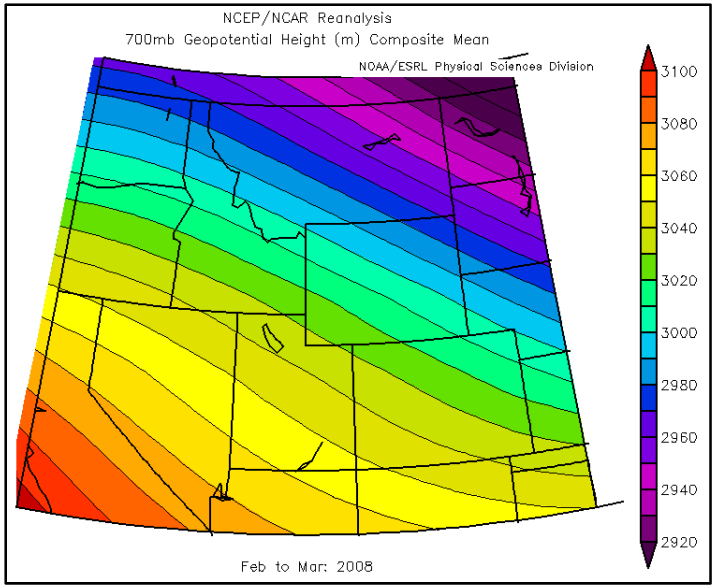


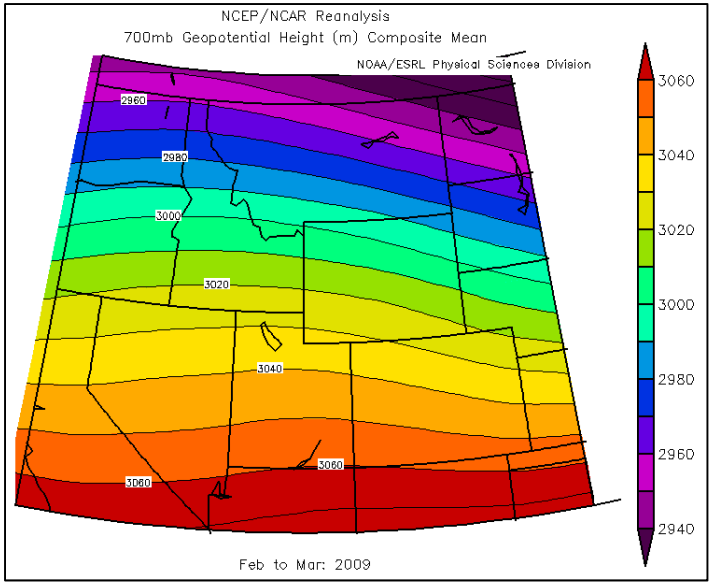


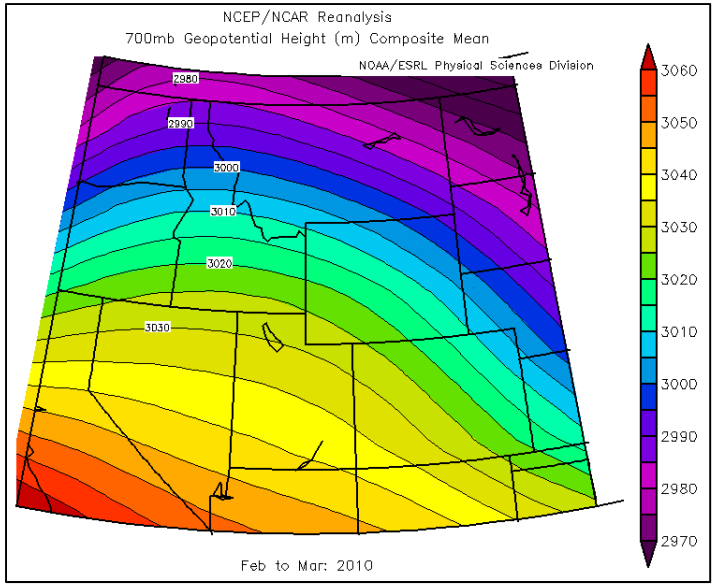


Weather Charts - 700 mb Pressure

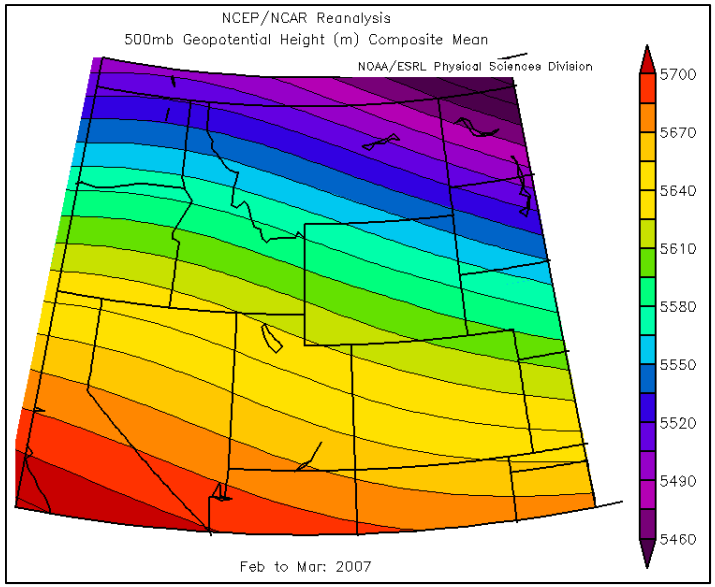


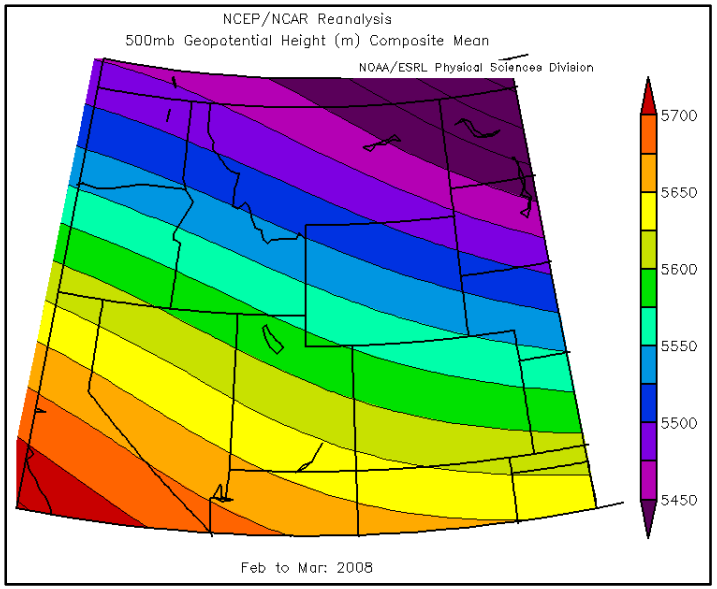


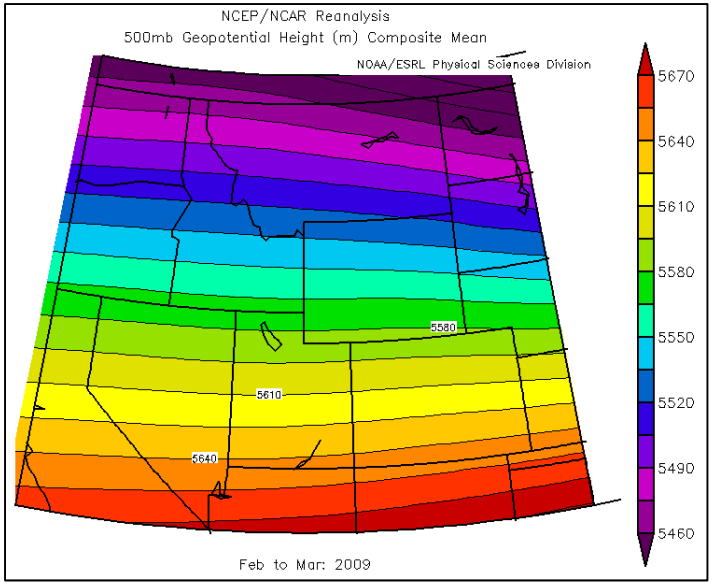


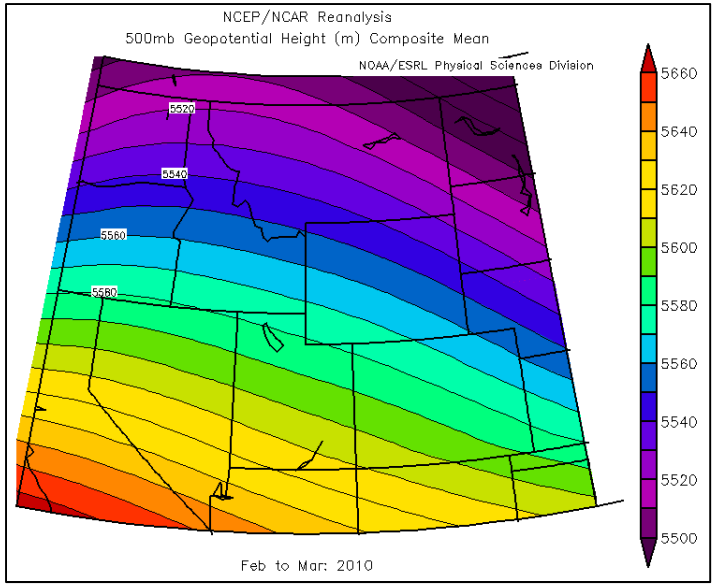


Weather Charts - 500 mb Pressure

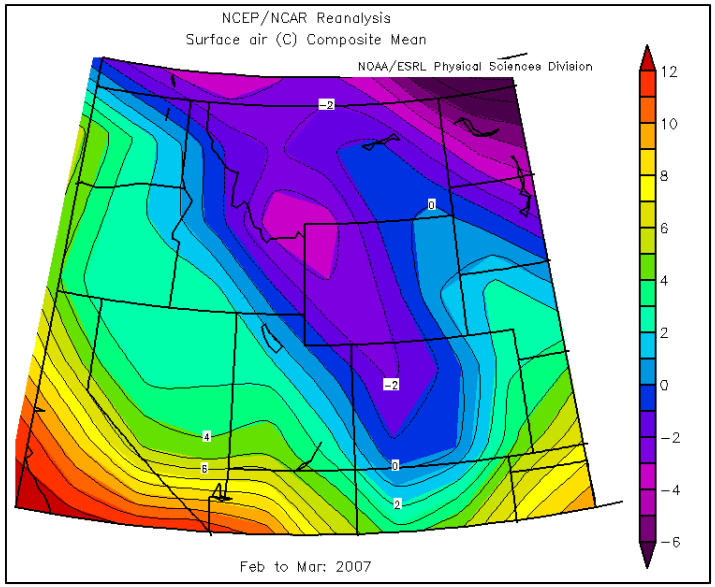


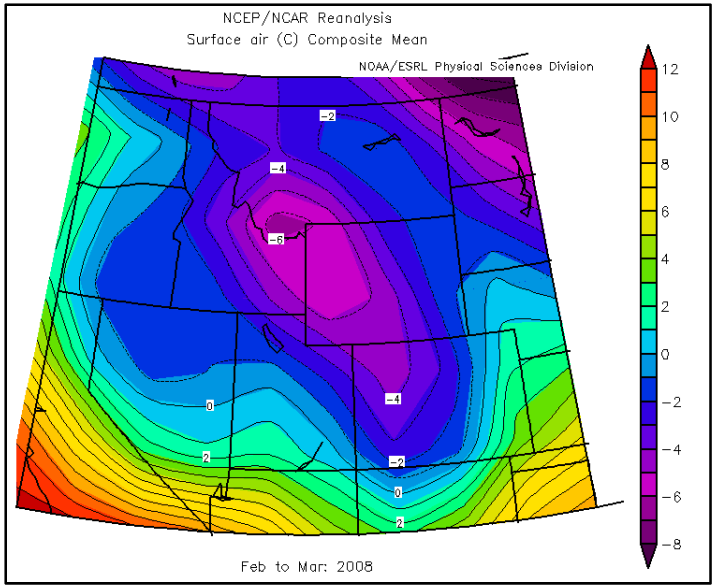


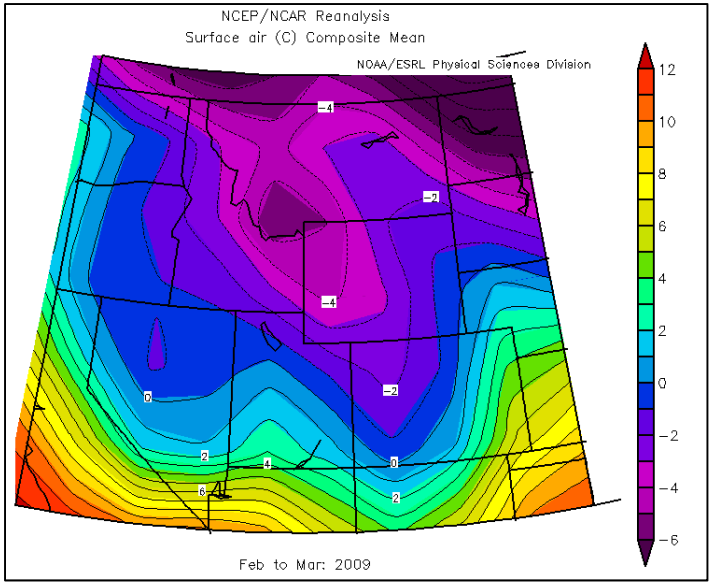


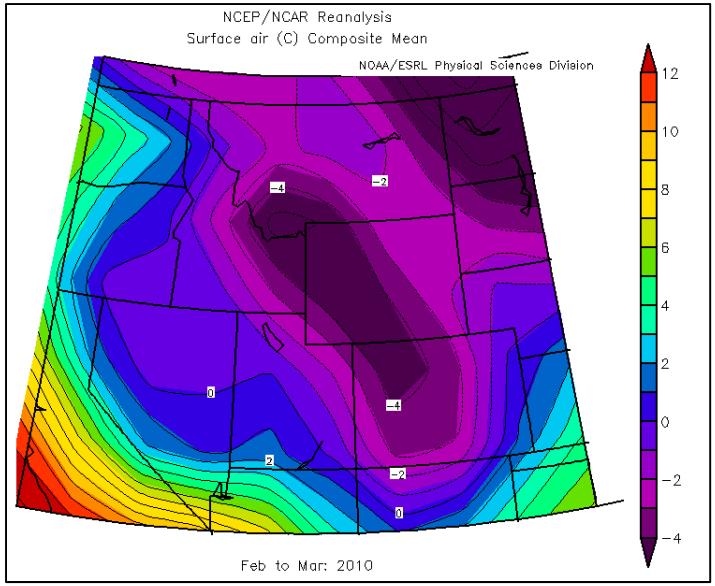


Weather Charts - Surface Temperature

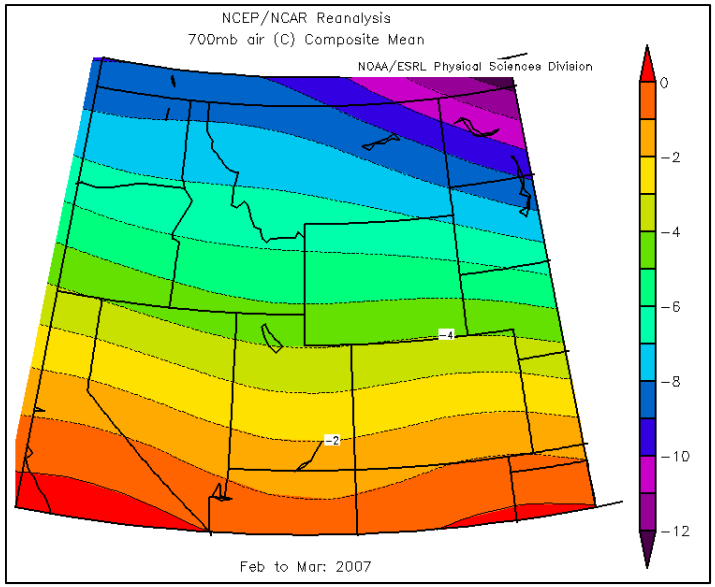


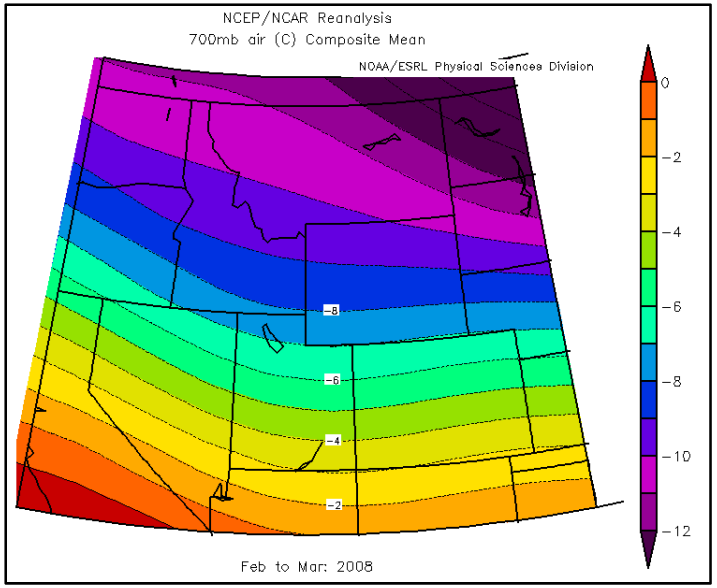


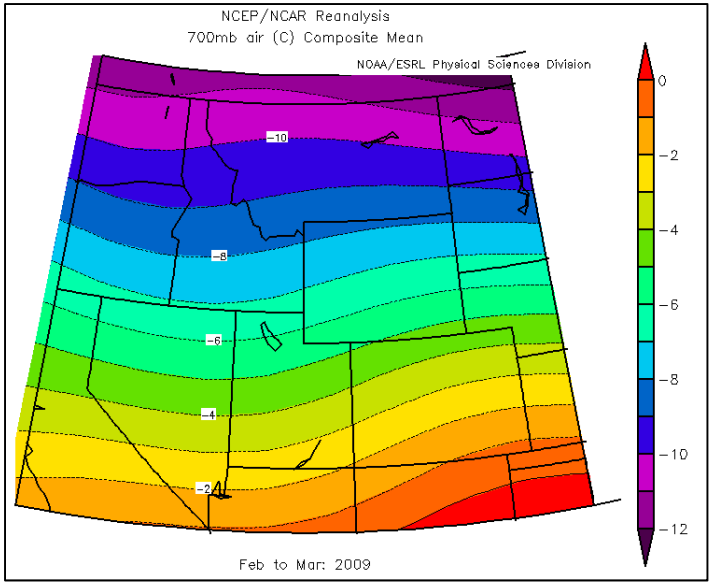


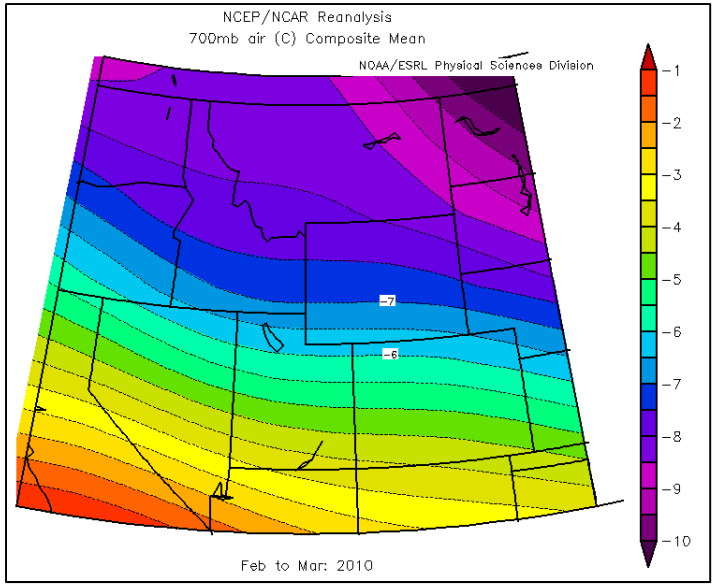


Weather Charts - 700 mbTemperature

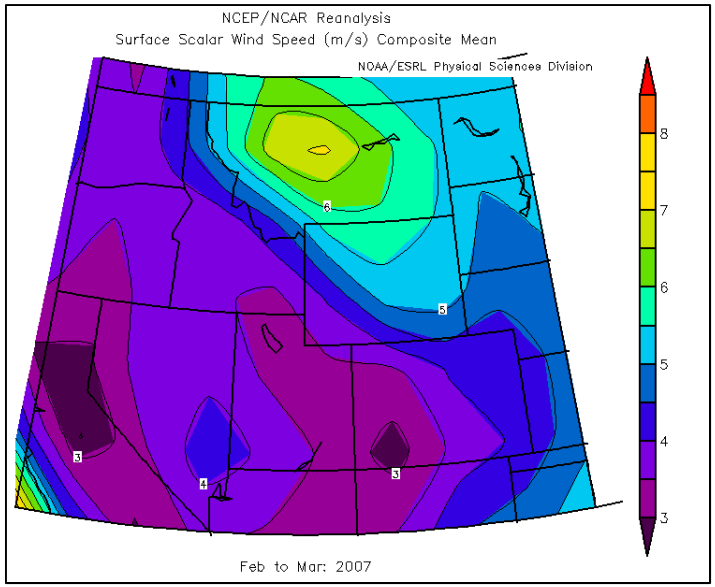


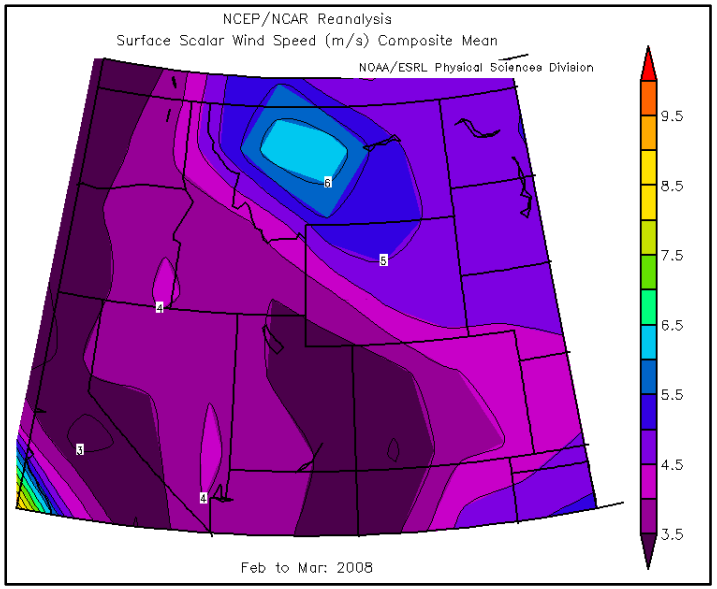


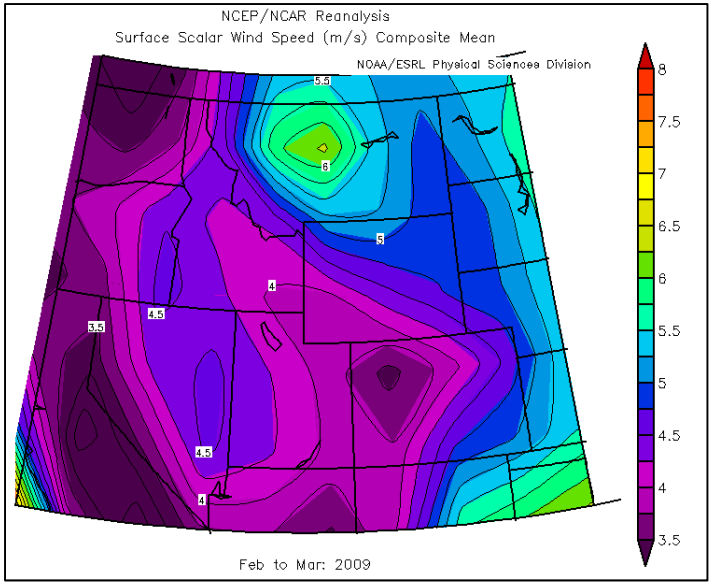


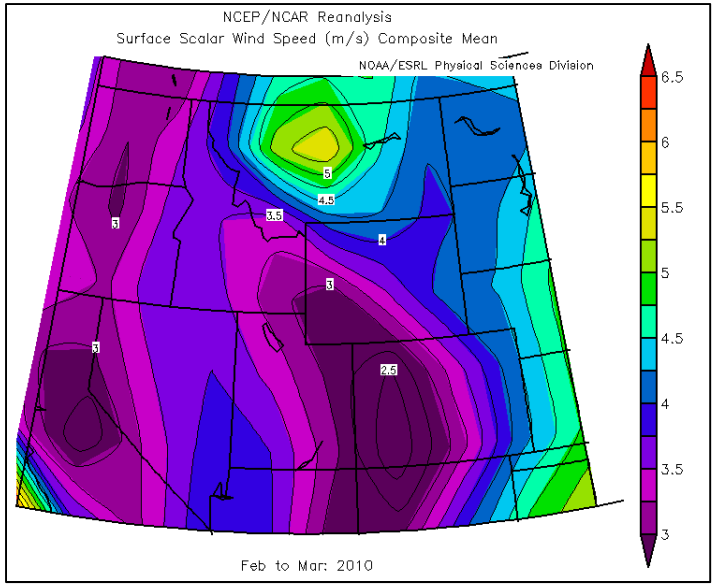


Weather Charts - Surface Wind Speed

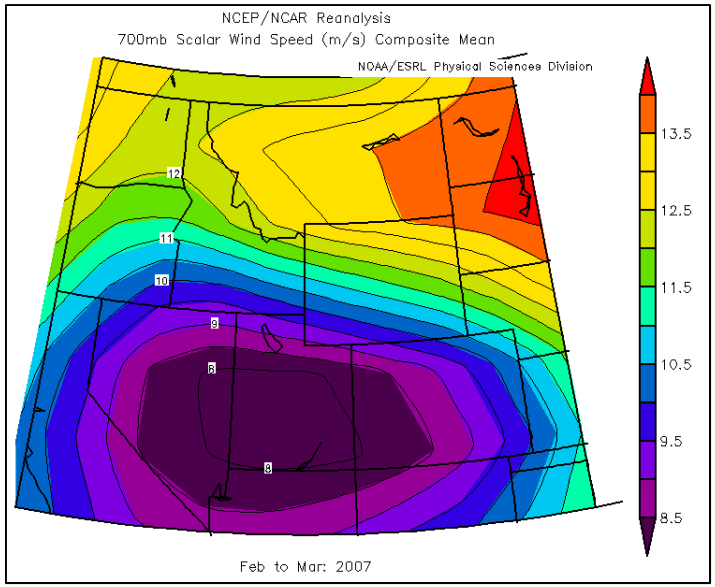


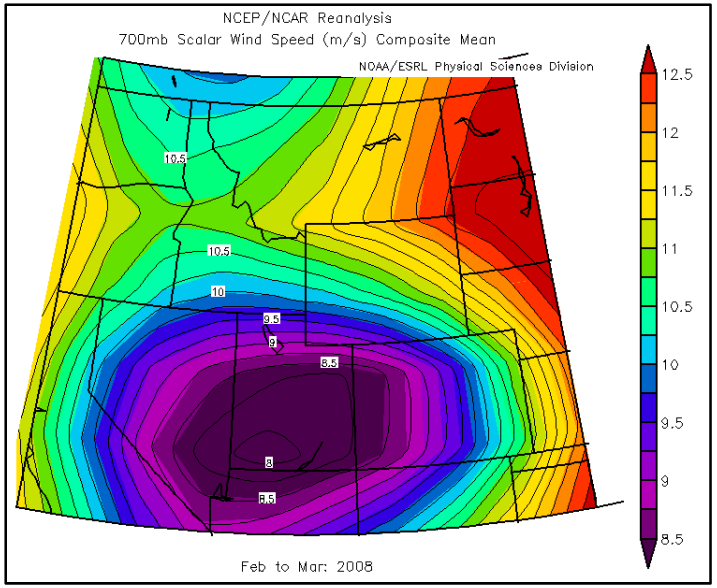


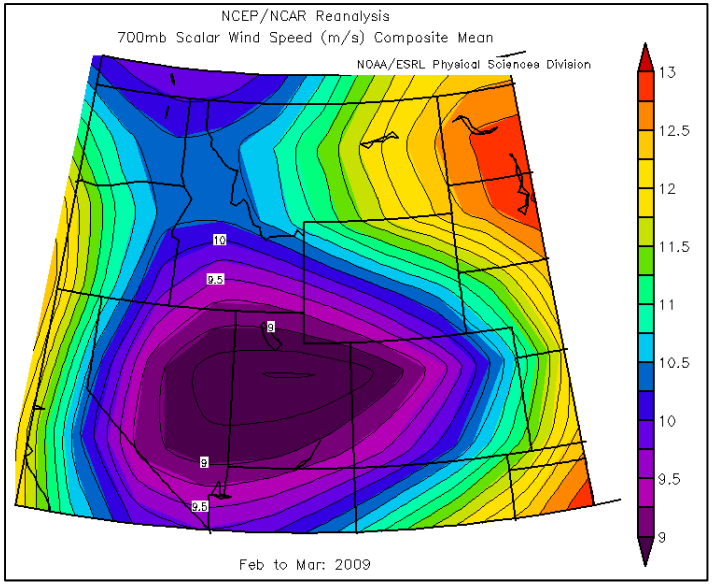


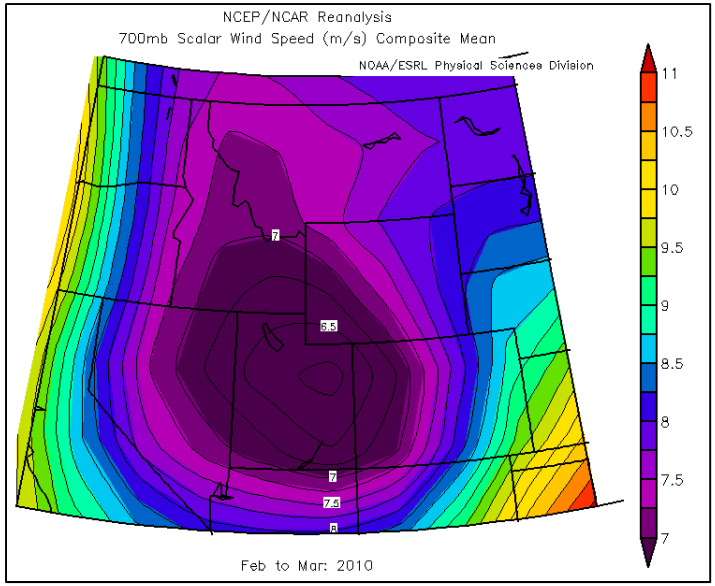


Weather Charts - 700 mb Wind Speed









Appendix D
HONO Report

U N I V E R S I T Y *of* H O U S T O N

WDEQ UGWOS 2010 HONO Measurements

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3.2 Conditions associated with elevated HONO readings; relationships with other parameters 9

4. Findings and Recommendations 24

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1. Summary of HONO data

The University of Houston (UH) performed continuous measurements of nitrous acid (HONO) during the Wyoming Department of Environmental Quality (WDEQ) Upper Green Winter Ozone Study (UGWOS) at the Boulder site in Wyoming. Based on the data set obtained from January 30 - March 31, 2010, the main findings are as follows:

- Considering nighttime conditions (defined as time periods with solar radiation less than 1 W/m^2), HONO levels are well correlated with NO_2. Since NO_2 forms most part of NO_x at the Boulder site, HONO levels are correlated with NO_x in similar way. To a lesser extent it is also correlated with non-methane hydrocarbons (NMHC) and also methane (CH_4). No correlation was found with particulate matter (PM-10).
- During nighttime periods, HONO levels are generally enhanced under WNW-S flow conditions. During daytime periods, HONO mixing ratios are generally lower than nighttime values except for E-SE wind directions. Similar to nighttime conditions, daytime HONO levels continue to show enhanced values under WSW-S conditions. HONO levels decrease with increasing windspeed.
- Snow cover leads to enhanced total UV radiation. It has been found that UV radiation correlates with HONO levels. This finding suggests photo-induced formation of HONO.
- Case studies showed high HONO levels around noontime coinciding with peak ozone levels. The high ozone levels were associated with wind directions turning from S to NW bringing in significant amounts of NO_x. While NO_x levels tended to decrease with increasing radiation and mixing layer height, HONO levels increased and actually coincided nicely with the peak ozone levels.
- The results indicate that high values of relative humidity favor the presence of high levels of HONO.
- HONO/NO_x ratios tend to have minimum values when nitrogen oxides are at a diurnal maximum in the morning. This ratio increases while nitrogen oxide levels decrease. These observations suggest that HONO is produced secondarily through nitrogen oxides which may have deposited previously at the snow surface and have undergone heterogeneous conversion.

2. Background

Photochemical processes leading to the formation of secondary species like ozone (O_3) frequently occur in areas where enhanced values of volatile organic compounds (VOC) and nitrogen oxides (NO_x) are found. In addition to the chemical environment, meteorological conditions (e.g. intense solar radiation, boundary layer variations, local and regional flows), influence the formation and distribution of ozone (O_3).

Fig. 1 describes in principle the fast reaction cycles involved in the formation of secondary species as well as the removal mechanisms from those cycles for nitrogen and carbon containing species. The hydroxyl radical (OH) is the most important oxidant in the atmosphere and controls the atmospheric lifetimes of most trace gases. OH is produced in photolysis processes of ozone (O_3), formaldehyde (HCHO) and nitrous acid (HONO). OH may also be produced in reactions involving alkenes and ozone via a formation pathway that does not require sunlight. OH initiates oxidation reactions with NO_x, CO, and anthropogenic and biogenic VOCs. These reactions form peroxy radicals (RO_2) which in turn will cause the conversion of NO to NO_2 and subsequently the formation of O_3. Within the degradation of VOC also carbonyls will be formed which either may be photolyzed (e.g. HCHO) or oxidized by OH and finally contribute to the formation of peroxycarboxylic nitric

anhydrides (PANs). Loss mechanisms for OH involve reactions between peroxy radicals leading to hydrogen peroxide (H_2O_2) and organic peroxides, e.g. methylhydroperoxide (MHP) and hydroxyl-methylhydroperoxide (HMHP), and reactions with NO_2 leading to nitric acid (HNO_3) and PAN.

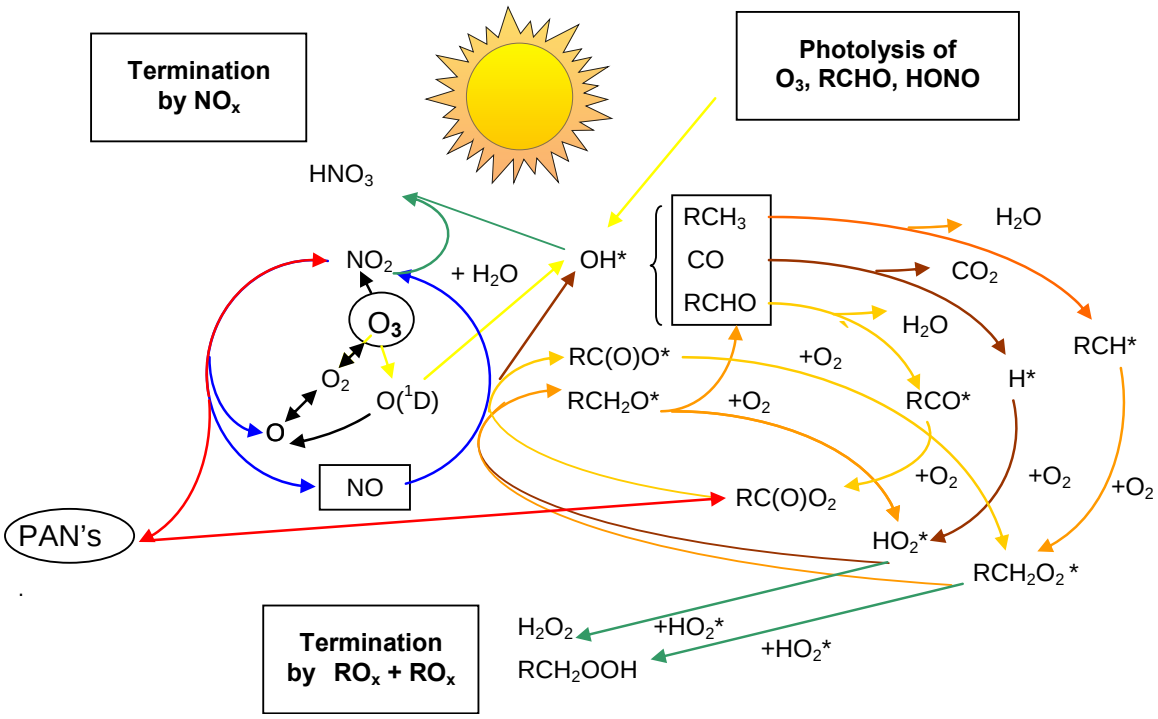

Figure 1: Daytime photochemical Processes.

According to an analysis by Elshorbany et al. [2009] HONO photolysis can contribute to about 52% of radicals on a 24-h average, followed by alkene ozonolysis (about 20%), HCHO photolysis (about 15%) and ozone photolysis (about 4%). A recent study by Mao et al. [2010] reports that contributions to the radical pool from HONO photolysis may be highest in high NO_x environments. Regardless of the emission environment, a specific diurnal sequence of the various radical sources occurs: shortly after sunrise HONO photolysis is the most dominant OH source due to the very short lifetime of HONO. In the late morning HCHO photolysis tends to become a major source, while ozone photolysis is more important in the afternoon. Alkene-ozonolysis is the only OH formation mechanism which does not require sunlight. Thus it is most dominant during nighttimes.

Though formaldehyde mainly occurs as a secondarily formed intermediate from oxidation of both anthropogenic and biogenic hydrocarbons such as ethylene and isoprene, formaldehyde is also emitted directly from incomplete combustion processes such as occur in mobile and a variety of industrial sources [Zweidinger et al., 1988; Altshuller, 1993; Chen et al., 2004; Dasgupta et al., 2005; Rappenglück et al., 2010]. Similarly, HONO can also be emitted from various combustion processes [Kirchstetter et al., 1996; Kurtenbach et al., 2001] and emissions from mobile sources can significantly contribute to observed HONO levels. However, it has increasingly become evident that ambient HONO concentrations are higher than can be accounted for by direct emissions and that heterogeneous processes on surfaces may lead to enhanced ambient HONO levels. In particular, these processes tend to occur on surfaces with adsorbed water in the dark [Finlayson- Pitts et al., 2003; Jenkin et al., 1988; Kleffmann et al., 1998] based on the following reaction [Goodman et al., 1999; Kleffmann et al., 1998]:

$$NO_2 + NO_2 + H_2O \rightarrow HONO + HNO_3$$

Over the last decade a variety of photo-enhanced HONO formation mechanisms have been discussed to explain observations of elevated daytime HONO levels [Kleffmann, 2007], among them:

- photolysis of surface adsorbed nitrate or nitric acid [Zhou et al., 2001; Zhou et al., 2002; Ramazan et al., 2006].
- photolysis of ortho-nitrophenols [Bejan et al., 2006].
- light-induced NO_2 reduction on surface adsorbed humic acid films [Stemmler et al., 2007].
- gas-phase reaction of electronically excited NO_2, due to photolysis, with water [Li et al., 2008].
- conversion of HNO_3 to HONO on primary organic aerosol [Ziemba et al., 2010].

First air quality model studies confirm the necessity to include heterogeneous reactions [Sarwar et al., 2008] and the inclusions of detailed surface emissions may even improve the vertical resolution of HONO in lower boundary layer [Czader and Rappenglück, 2009].

3. Analysis of Boulder HONO data

The University of Houston (UH) deployed a LOPAP (Long Path Absorption Photometry) instrument at the Boulder/WY site during the 2010 UGWOS study period. This instrument is described thoroughly in Heland et al. [2001] and Kleffmann et al. [2002]. It is a wet-chemical in situ instrument which consists of an external sampling unit where ambient gaseous HONO is directly sampled into a stripping coil using a mixture of sulfanilamide in hydrochloric acid. No sampling lines are used thus minimizing sampling artifacts on surfaces. The stripping reagent is transferred to the instrument where it is converted to an azodye by the reaction with N-naphtylethylendiamine-dihydrochloride. The absorption of the light from a white light-emitting diode is measured in long path absorption tubes made of Teflon AF2400 using a minispectrometer. In the external sampling unit two stripping coils are used in series. In the first channel HONO as well as possible interferences are determined, while in the second channel only the interferences are quantified. The difference of these two channels yields the HONO signal. The sampling time is between 1-5 min depending on the desired measurement range. The detection limit is about 1-2 pptv. The LOPAP instrument has been tested against DOAS measurements both in smog chamber studies as well as in field campaigns [Kleffmann et al., 2006]. Excellent agreement was obtained between these techniques during daytime as well as nighttime.

3.1 Summary Statistics

The LOPAP instrument started collecting data on January 15, 2001 and ran continuously until April 02, 2010. Analysis of preliminary data collected during the first two weeks of the study revealed a problem with the setup of thermal insulation on the unit. This was subsequently corrected and valid 1-min data is available from January 30, 11:23 MST until April 02, 2010 14:31 MST. Based on 1-min values 1-hour average values were calculated and merged with other data sets available at the Boulder site. The subsequent discussion will focus on this merged data set which comprises the time frame from January 30, 11:00 MST until March 31, 23:00 MST. Table 1 provides an overview of data statistics for this time period. In addition, this table shows specific results of the two portions of the entire field campaign: Part I (January 31 - March 5) and Part II (March 5 - March 31). In Part I, snow cover was observed at Boulder on every day. Starting around March 5, the snow cover began to disappear and by March 10 the snow cover was completely gone. According to table 1 it seems there is a significant change in the HONO levels with regard to these two different parts of the campaign.

Table 1: Statistical overview UH-HONO measurements at the Boulder site (hourly values)

Parameter	Entire campaign (January 30 - April 2, 2010)	Part I (January 30 - March 5, 2010)	Part II (March 06 - April 2, 2010)
Number of measurements above DL (DL=2 pptv)	1130	829	662
Mean [ppt]	104	137	61
Median [ppt]	75	110	50
Maximum [ppt]	769	769	442

Figure 2a shows HONO levels and their dependence on wind direction during the entire field campaign split into day- and nighttime periods. This split was done to discriminate between times when HONO photolysis is important (daytime) and times when it is negligible. During nighttime periods HONO levels are generally enhanced under WNW-S flow conditions. During daytime periods HONO mixing ratios are generally lower than nighttime values except for E-SE wind directions. Similar to nighttime conditions, daytime HONO levels continue to show enhanced values under WSW-S conditions. Similar plots for ozone (Figure 2b) show that elevated HONO under night time WNW-S winds is associated with lower ozone, indicative of ozone titration by fresh NO emissions. This is consistent with locations of large NO_x sources (compressors and drill rigs) operating during January – March 2010 relative to the Boulder monitoring site as shown in Figure 3. Daytime median ozone for the study period is dominated by background conditions and shows little variation with wind direction. The daytime ozone/HONO/NO_x relationship is explored in more detail in the discussion of several elevated ozone case studies below.

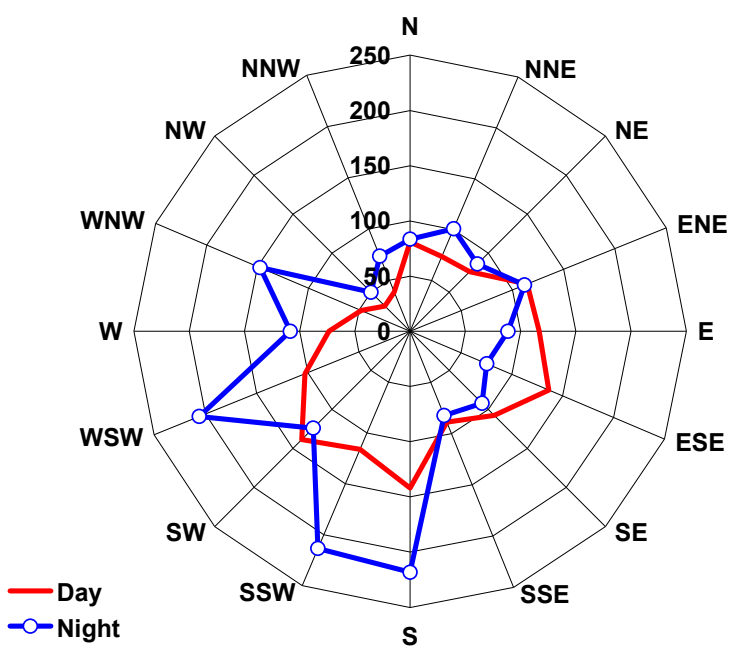

Figure 2a: Median of hourly HONO levels and their dependence on wind direction during the time period January 30 - March 31, 2010. Daytime was assumed when solar radiation values were above 1 W m^{-2}.

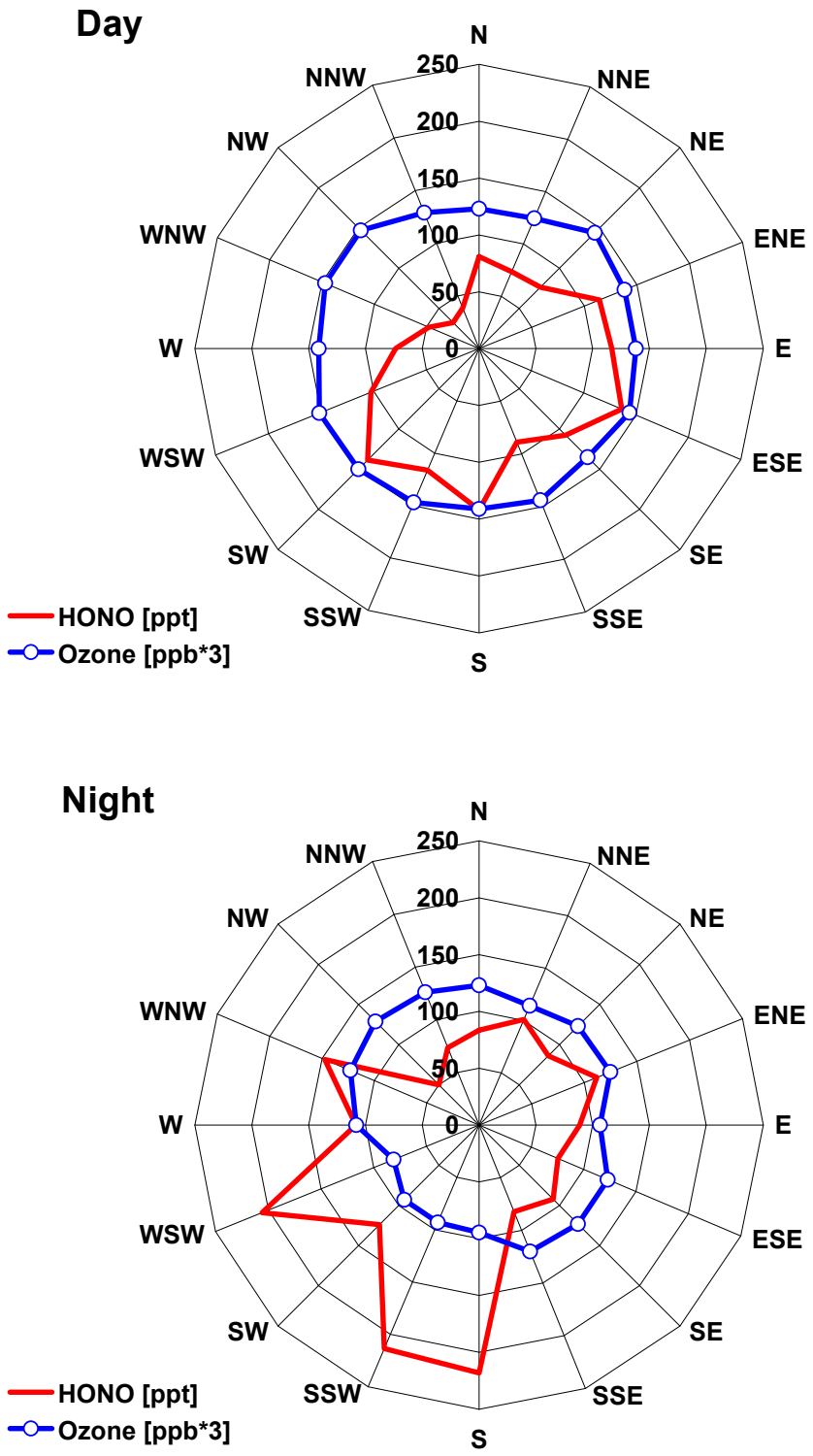

Figure 2b: As in Figure 2a but for HONO and ozone during daytime hours (top) and night time hours (bottom).

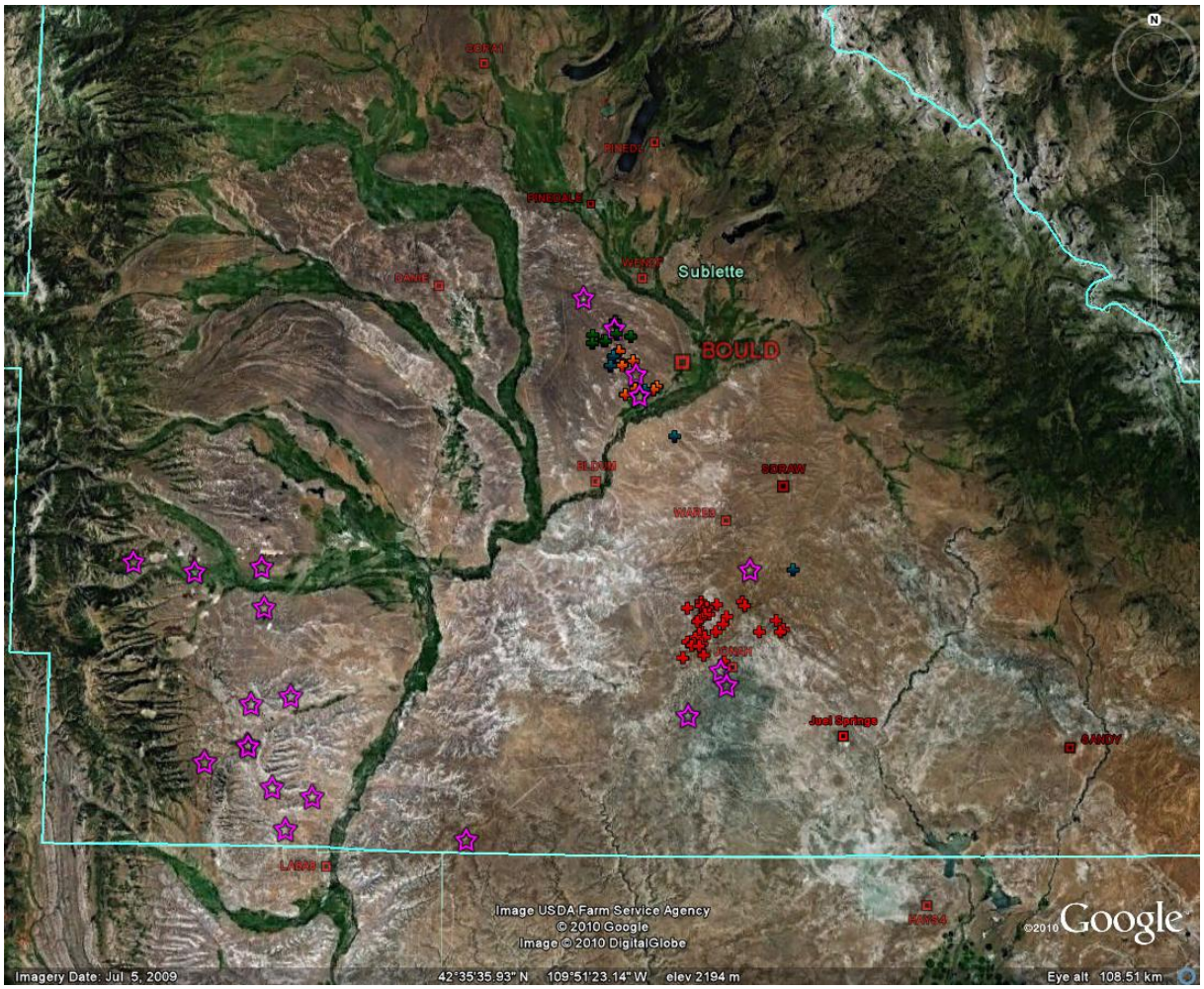

Figure 3: Locations of compressors (pink stars) and drill rigs (red crosses) operating during January – March 2010 relative to the Boulder monitoring site.

3.2 Conditions associated with elevated HONO readings; relationships with other parameters

<u>Relationship with Non-Methane Hydrocarbons (NMHC), nitrogen oxides (NO, NO_2, NO_x) and particulate matter PM-10:</u>

Figures 4 and 5 show times series based on hourly values for the entire field campaign for NMHC, NO, NO_2, NO_x, and PM-10. Apart from PM-10, all other compounds are well correlated with HONO. They also follow the similar trend with decreasing values from January to March. Figure 6 shows correlations between HONO, NMHC, NO_2, and NO_x for nighttime conditions. For NO most values were at 0 ppb and only a few excursions occurred which makes correlation analysis less meaningful. Nethertheless Figure 6 clearly shows the close relationship between HONO and NO_2/NO_x. The good relationship with NMHC is most likely due to the fact that emission sources which emit NO_x are primarily located close to NMHC sources. As indicated previously there is no obvious relationship between NO and PM-10 at this site.

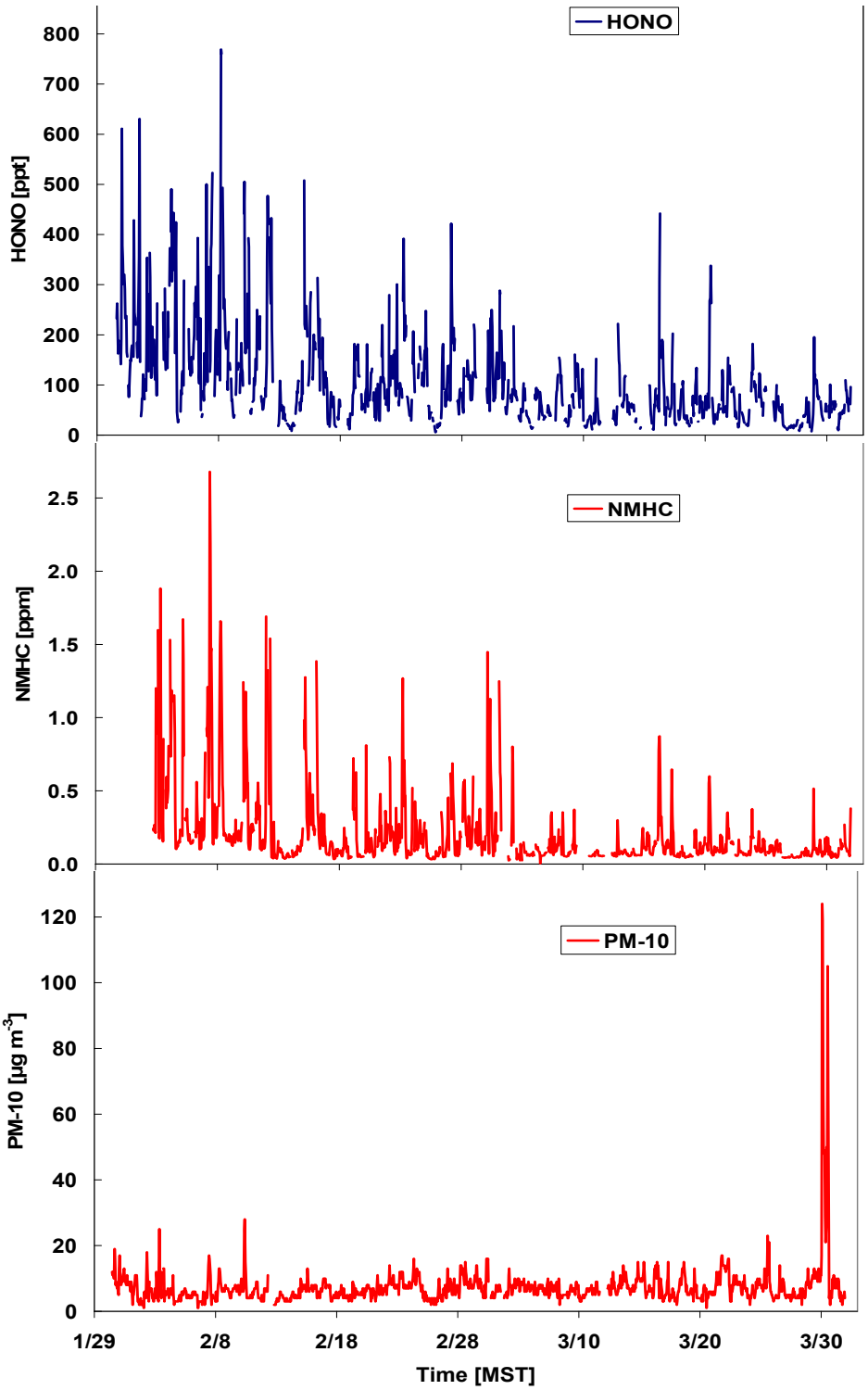

Figure 4: Time series of HONO, NMHC and PM-10 from January 30 - March 31, 2010. Hourly values are shown.

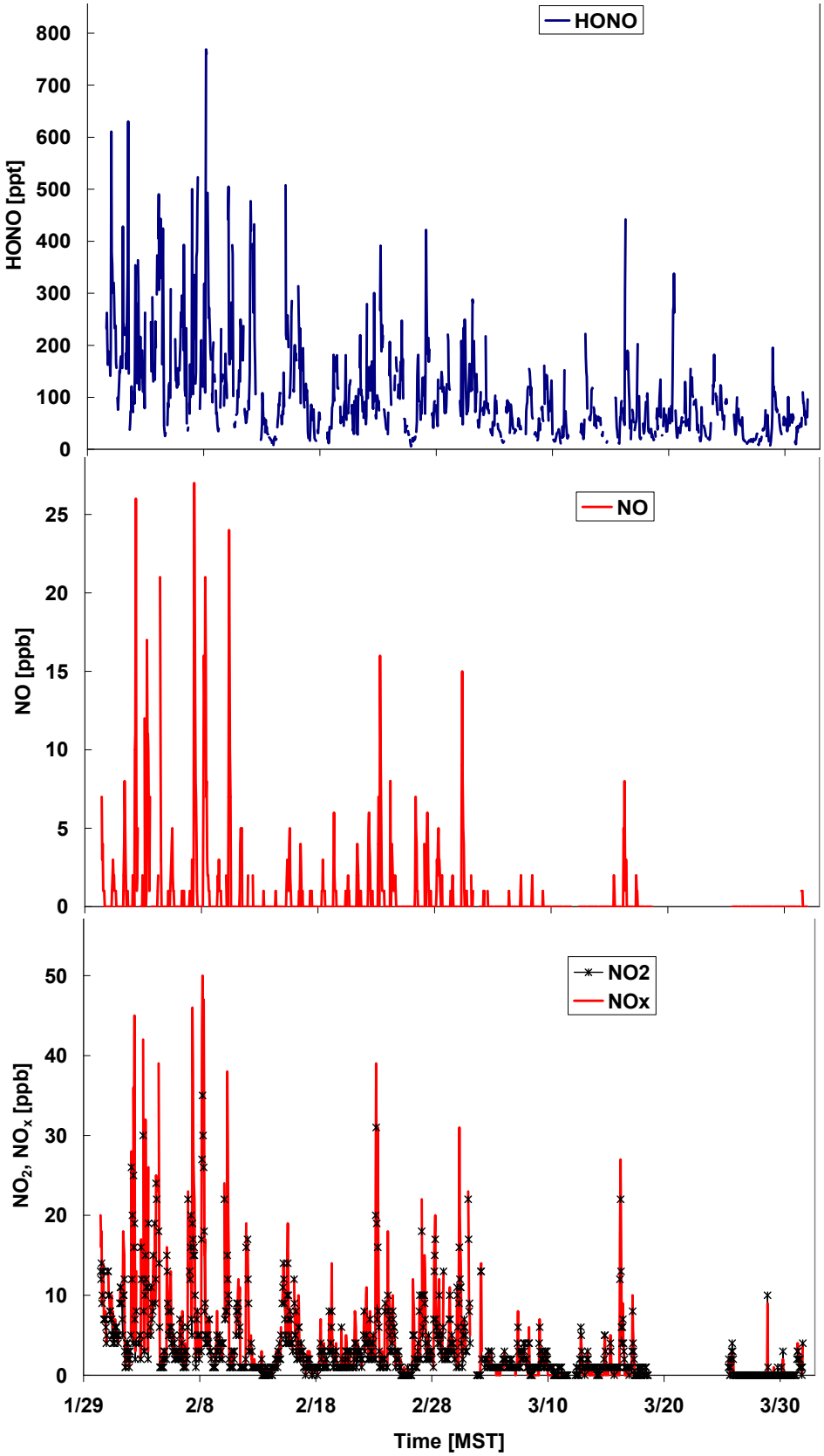

Figure 5: Time series of HONO, NO, NO_2 and NO_x from January 30 - March 31, 2010. Hourly values are shown.

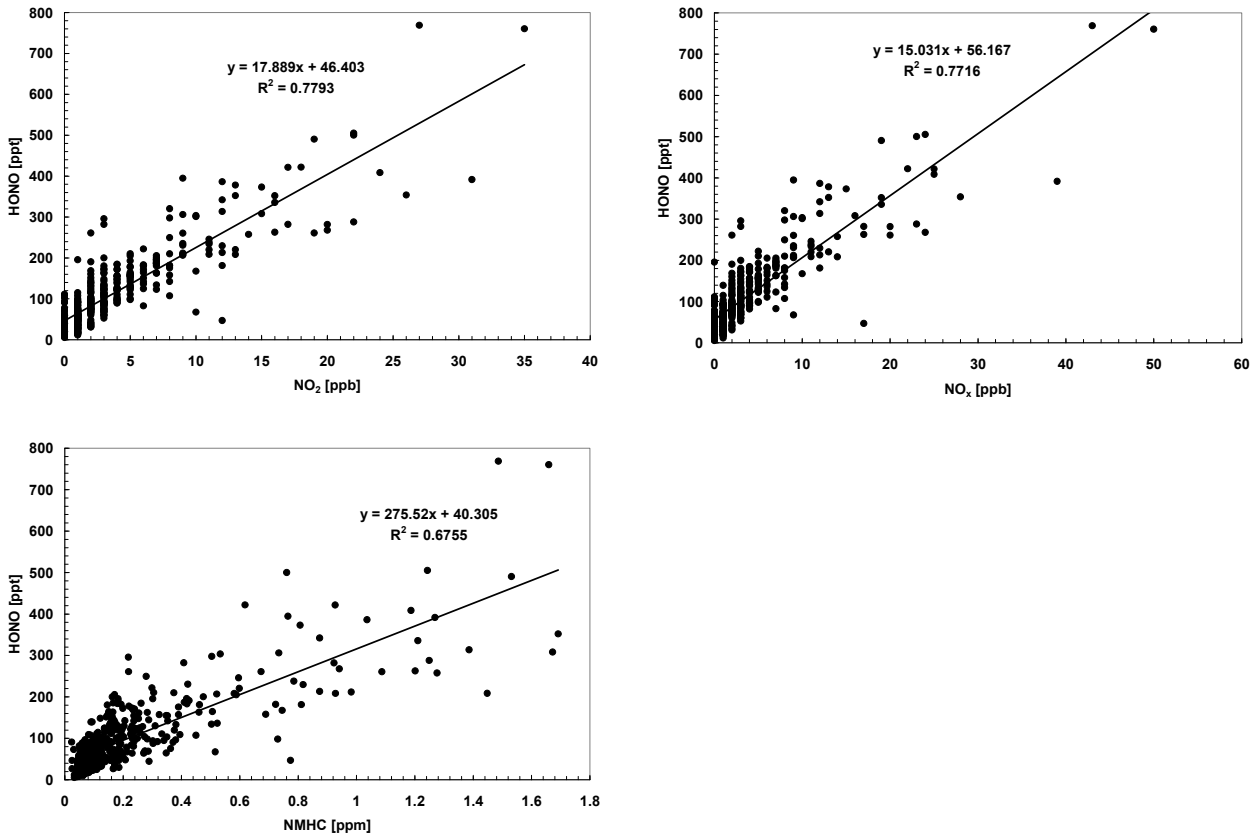

Figure 6: Correlations of hourly HONO vs. NO_2 (top left), NO_x (top right) and NMHC (bottom) during night-time hours.

Relationship with wind data:

As far as the dependence on wind direction is concerned NMHC, NO, NO_2, NO_x, and to some extent CH_4 follow the pattern of HONO. Again, PM-10 does not show any obvious correlation with all these compounds. For brevity, figure 7 only shows nighttime conditions which also eliminate daytime photochemical processes. Interestingly, it seems that CH_4 is also enhanced under WNW-S conditions indicating sources which emit nitrogen oxides, NMHC and CH_4 or different sources located in the same area which may overlap. This is consistent with locations of compressors and drill rigs operating during January – March 2010 (which emit primarily NO_x) relative to well head equipment (which emits primarily CH_4 and NMHC) as shown in Figure 8. While NO_2 and NO_x are strongly enhanced under these flow conditions, the HONO/NO_x ratio is relatively low compared to the other wind directions. This may be an indication that HONO is dominated by secondary production (potentially on surfaces through conversion of deposited nitrogen oxides) rather than primary emissions.

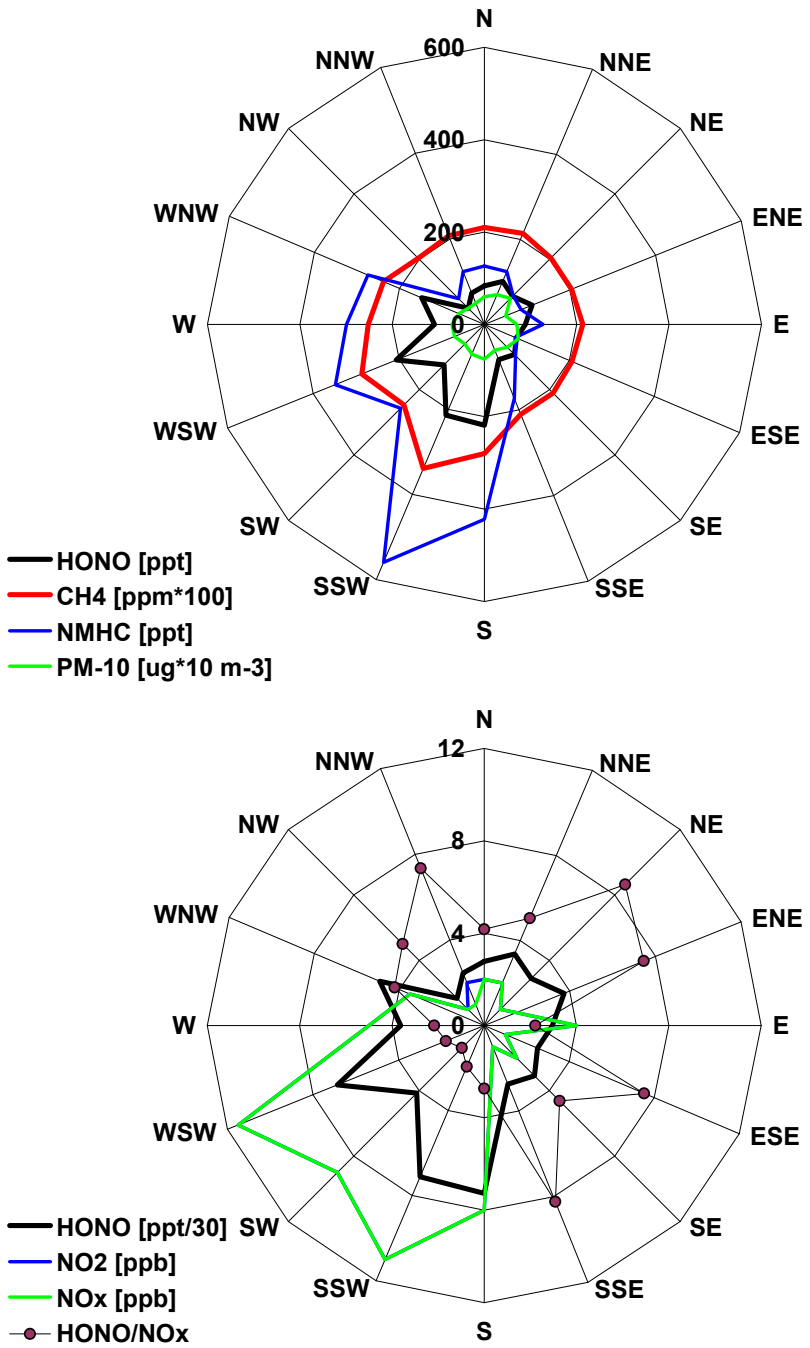

Figure 7: Wind directional dependence of HONO, CH_4, NMHC, PM-10, NO_2, NO_x, and the HONO/NO_x ratio for the time period January 30 - March 31, 2010 for night-time conditions (defined as time periods with solar radiation less than 1 W/m^2). NO did not show appreciable values. Note: most NO_x consists of NO_2, thus the green line for NO_x is almost identical with the blue line for NO_2. Median hourly values are shown in this figure.

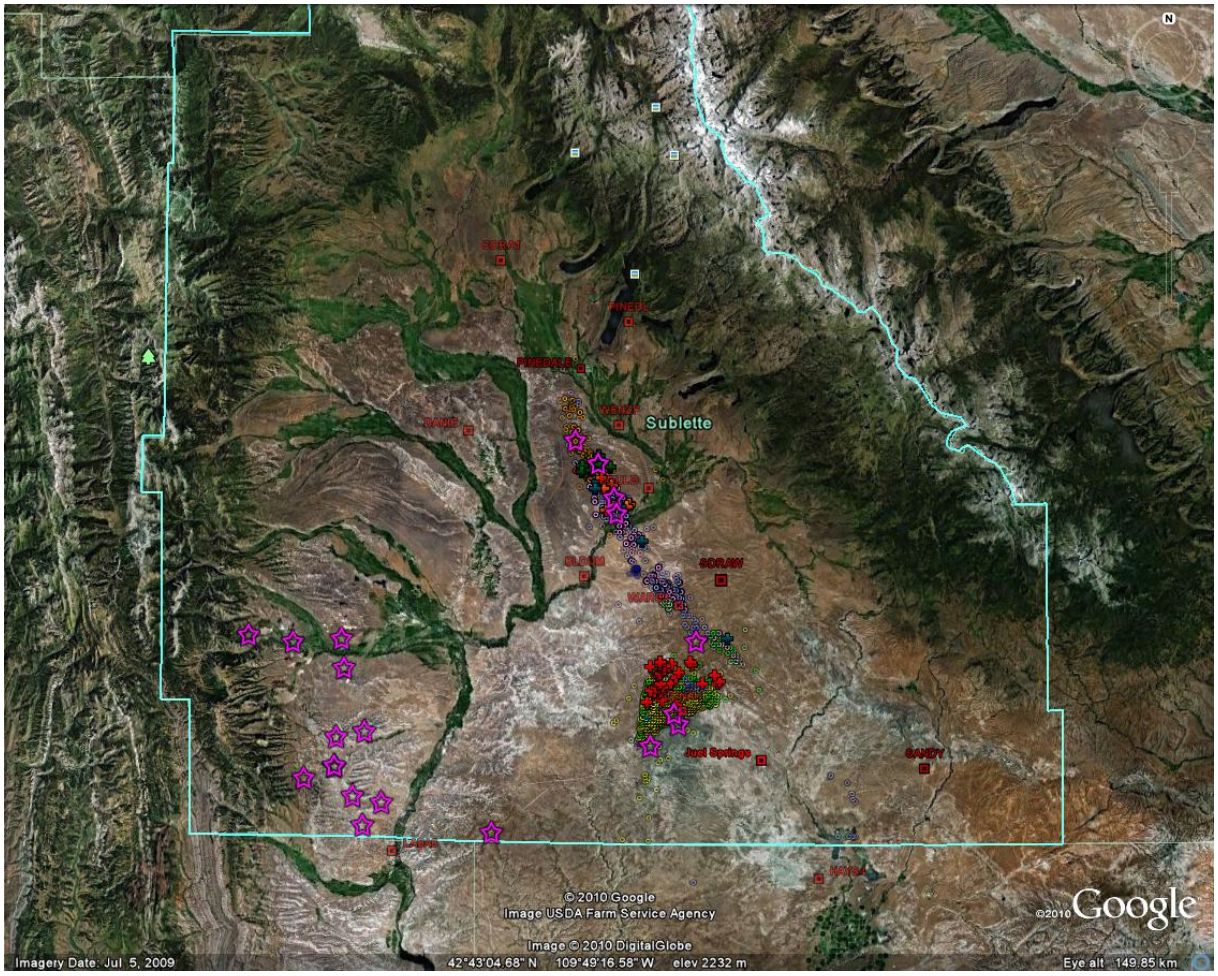

Figure 8: Locations of wells (small bulls eyes) compressors (pink stars), and drill rigs (plus signs) operating during January – March 2010 relative to the Boulder monitoring site.

Relationships with radiation and relative humidity:

Some photo-enhanced heterogeneous reactions are currently being discussed as likely daytime HONO sources [Kleffmann, 2007]. As in previous years, total solar radiation, as well as incoming and outgoing UV radiation were measured at Boulder. Figure 9 displays the average annual increase in daily solar radiation during the first three months of the year. Apparently, this increase is not reflected in the HONO time series.

The picture is different when UV radiation is considered, in particular if both incoming and outgoing UV radiation are taken into account. Figure 10 clearly shows the impact of snow cover on radiation. The high albedo of snow leads to a significant amount of outgoing UV radiation until about March 5 (i.e. Part I of the campaign). The missing snow cover after March 5 reduces the outgoing UV radiation significantly during Part II of the campaign. Important for atmospheric photolysis processes is the overall available amount of UV radiation, i.e. incoming plus outgoing UV radiation. This total UV radiation is plotted in figure 11 together with the HONO time series. There appears to be a good correlation between HONO the total UV radiation, thus indicating the potential presence of photo-induced HONO formation. This is illustrated further in Figure 12 which shows the relationship between HONO and UV radiation during parts I and II of the campaign stratified by high and low

NO_2 and wind speed conditions. Only midday (10:00 – 14:00 MST) data are shown to capture the maximum ozone formation period and avoid periods dominated by carryover of HONO formed overnight which may mask the daytime photochemical HONO formation. Although the number of days in each Part/NO_2/Wind Speed bin is very limited, some key features of these results are noteworthy:

- HONO levels are higher during Part I (when snow cover was present)
- During Part I, higher HONO occurred with higher total UV when NO_2 was relatively high (i.e., greater than 7 ppb) but not when NO_2 was low. This is true for both high and low wind speed days.
- During Part II, NO_2 was always low but there is some indication of a positive correlation of HONO with total UV under low wind speed conditions.

Although not definitive due to the small data set, the above observations are consistent with a hypothesized source of HONO via heterogeneous reactions on the snow surface in the presence of NO_2 during Part I and possibly HONO production from NO_2 in contact with humic acids on bare soil during Part II.

As pointed out by Stutz et al. (2004) relative humidity may be favorable for HONO formation, at least in urban environments. Figure 13 suggests that with increasing diurnal range in relative humidity, in particular, when the snow cover has gone, also HONO levels may tend to decrease. Further support for the impact of relative humidity is shown in figure 14: nighttime data of HONO vs relative humidity indicates that strongly elevated HONO levels only occur at relative humidities above 80%.

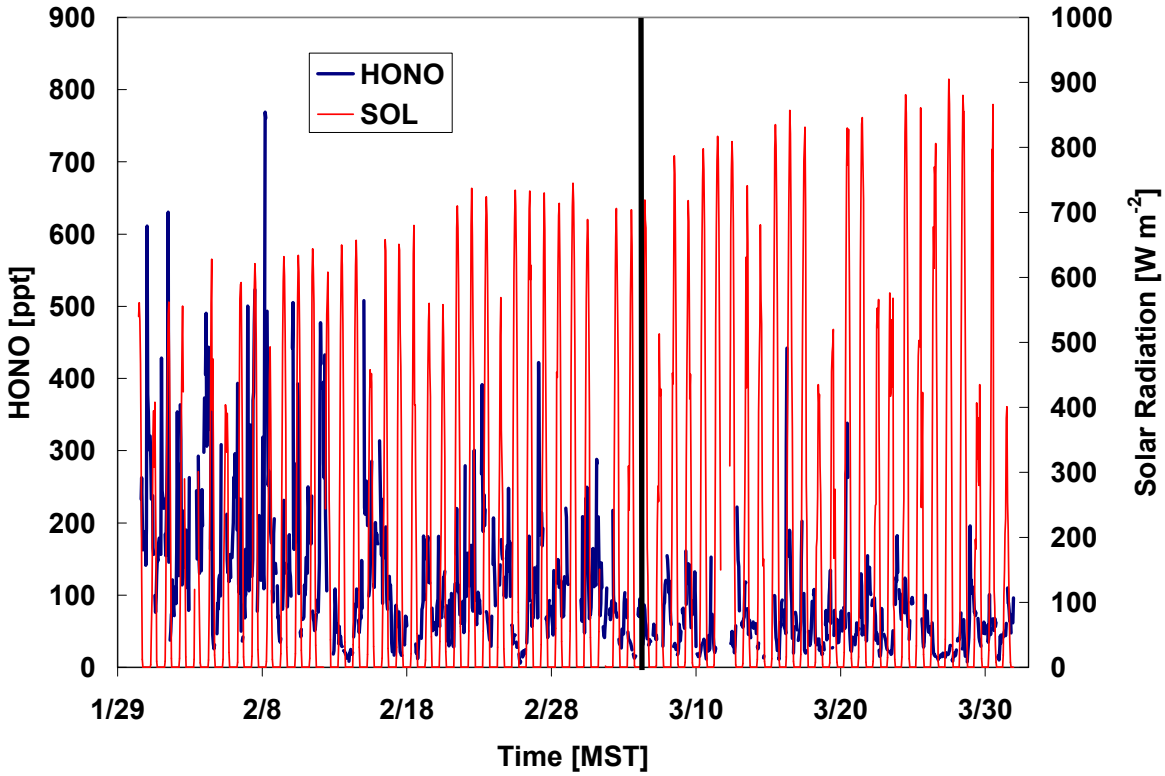

Figure 9: HONO and solar radiation time series for the time period January 30 - March 31, 2010. The vertical bar on March 5, 2010, separates Part I (snow cover present) from Part II (no snow cover). Hourly values are shown.

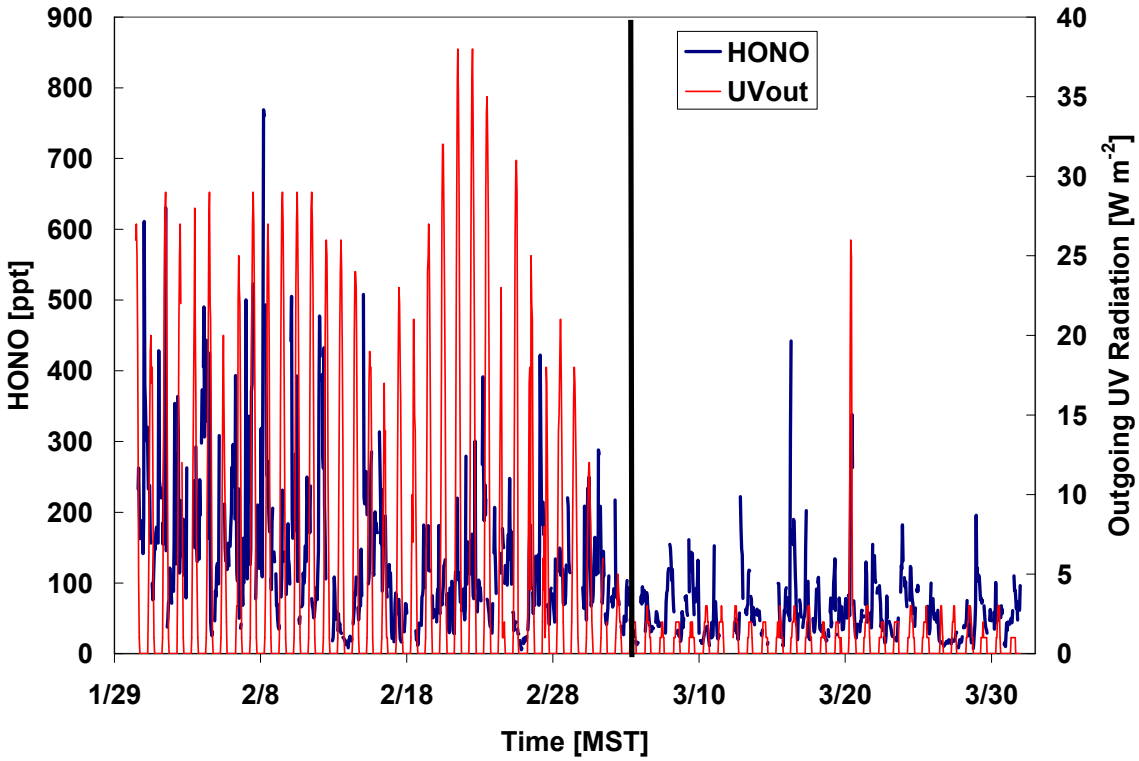

Figure 10: HONO and outgoing UV radiation time series for the time period January 30 - March 31, 2010. The vertical bar on March 5, 2010, separates Part I (snow cover present) from Part II (no snow cover). Hourly values are shown.

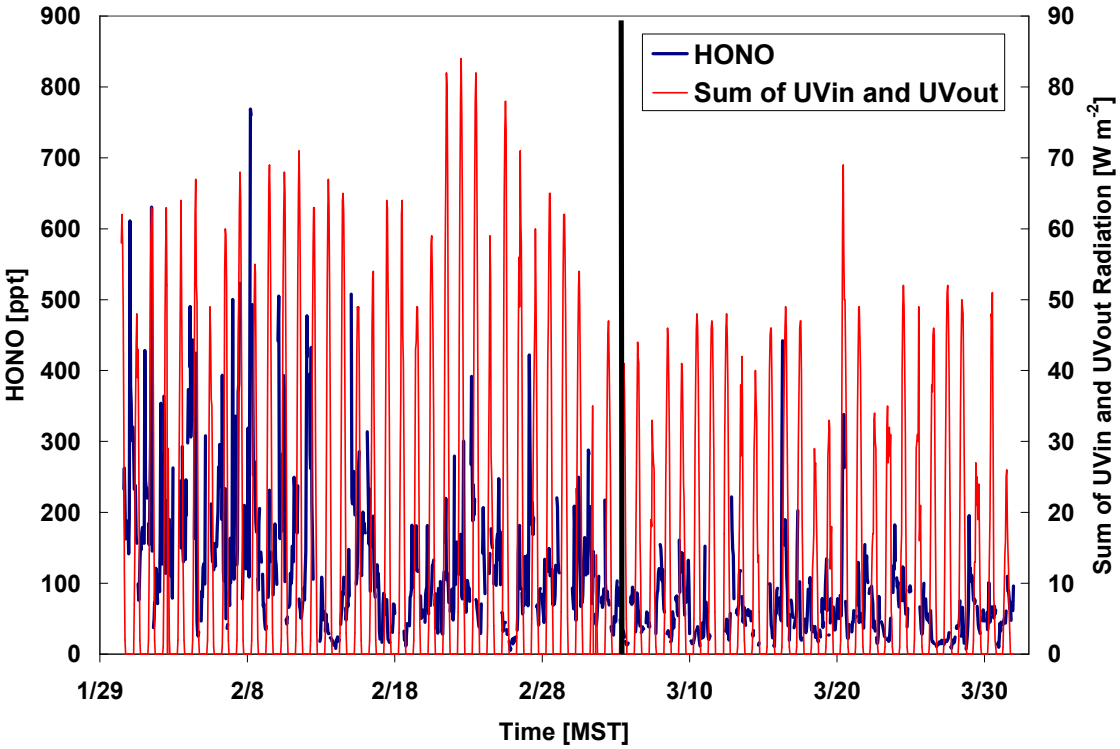

Figure 11: HONO and total UV radiation time series for the time period January 30 - March 31, 2010. The vertical bar on March 5, 2010, separates Part I (snow cover present) from Part II (no snow cover). Hourly values are shown.

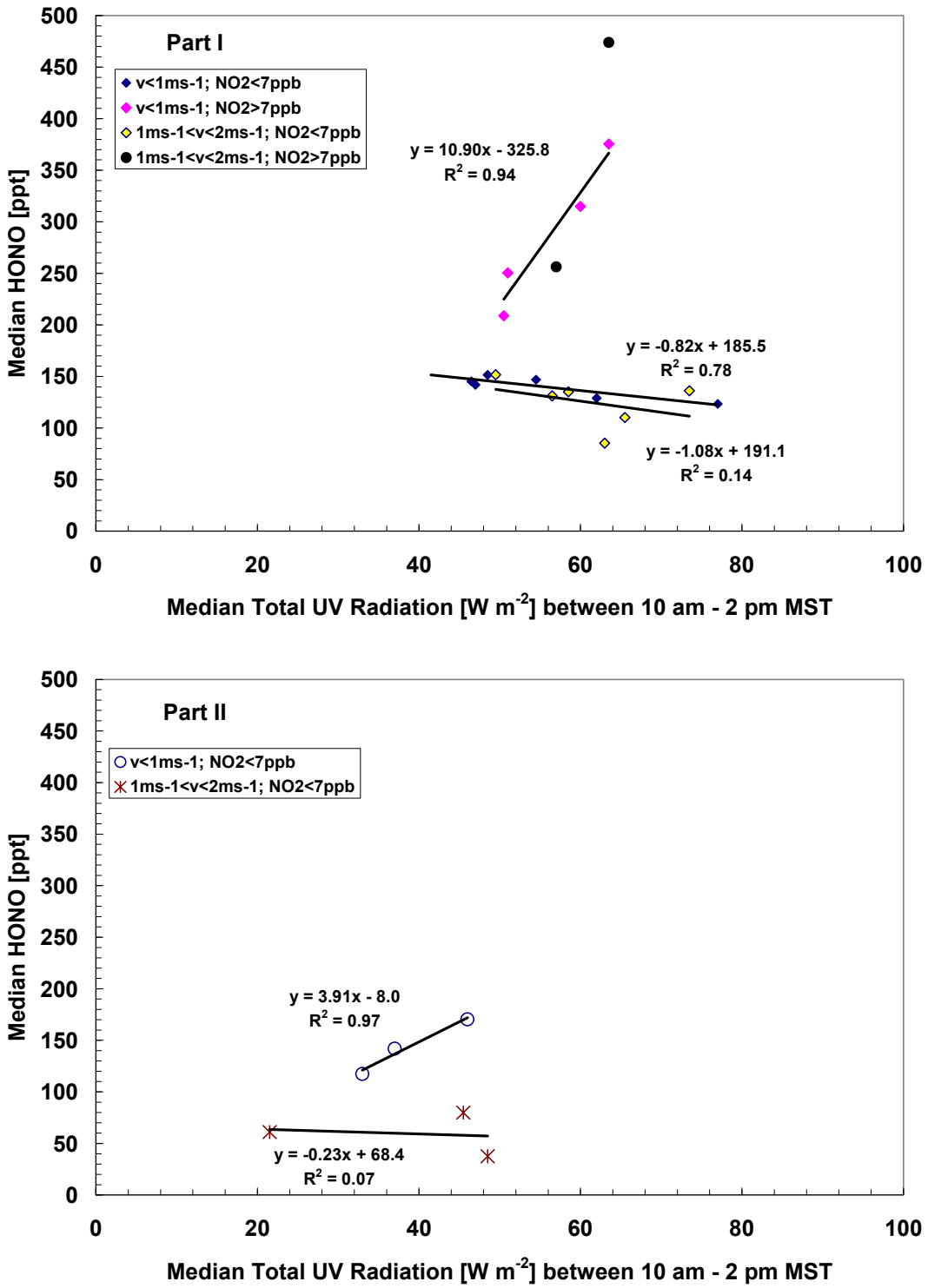

Figure 12: Relationship of 10:00 – 14:00 MST median HONO with median total UV radiation for Part I of the study period (top) and Part II (bottom) as a function of NO2 concentration and wind speed.

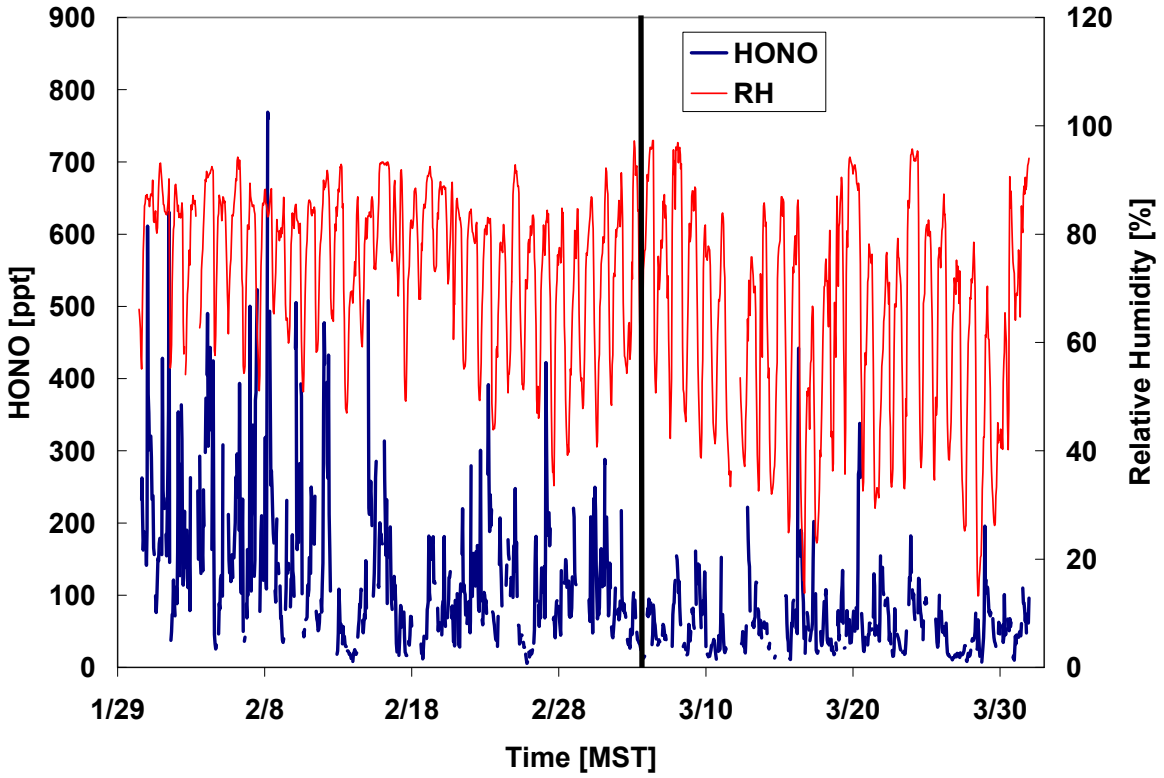

Figure 13: Time series of HONO and relative humidity for the time period January 30 - March 31, 2010. The vertical bar on March 5, 2010, separates Part I (snow cover present) from Part II (no snow cover). Hourly values are shown.

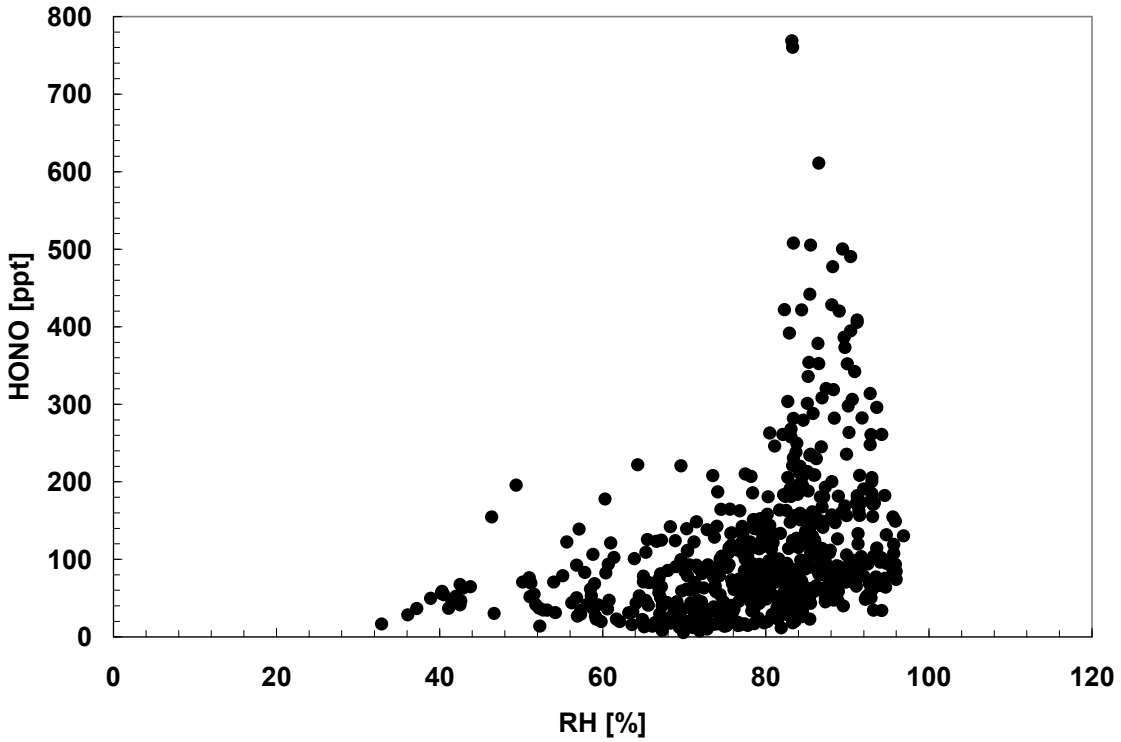

Figure 14: Dependence of HONO on relative humidity during nighttime conditions for the time period January 30 - March 31, 2010. Hourly values are shown.

Diurnal variation:

Figures 15 and 16 display composite diurnal variations of pollutant species and total UV separated between Part I (snow cover at Boulder) and Part II (no snow cover at Boulder) of the field campaign. The total UV radiation is significantly enhanced during Part I. Also, all primary trace gases are found at enhanced levels during Part I of the campaign. Contrary to most primary trace gases which exhibit a diurnal peak at around 9:00 MST during Part I and a bit earlier during Part II, HONO continues to increase after 9:00 am MST and peaks around noon coinciding with the diurnal maximum of radiation. It should also be noted that this HONO peak occurs while atmospheric stability is at a diurnal minimum. It appears likely that HONO is being produced through photo-enhanced formation processes which are most efficient when snow cover is present. HONO/NO_x ratios tend to have minimum values when nitrogen oxides are at a diurnal maximum. This ratio increases while nitrogen oxide levels decrease.

Figure 17 summarizes the mean diurnal observations during Part I (snow cover present at Boulder). HONO shows a significant daytime peak around noon, which compared to other locations is quite unusual (see e.g. Stutz et al. [2010]). The mean HONO levels at noon are around 200 pptv, which is 1/4 of HONO levels observed at highly frequented Houston highway junction [Rappenglück et al., 2010]. The HONO/NO_x ratio is between 2-5%, which is similar to other locations. From 9:00 am until 1:00 pm the HONO/NO_x increases as does HONO, which indicates that more HONO is being formed through NO_x conversion. During the same time period also O_3 increases. When HONO decreases after 1:00 pm, ozone does not increase any longer.

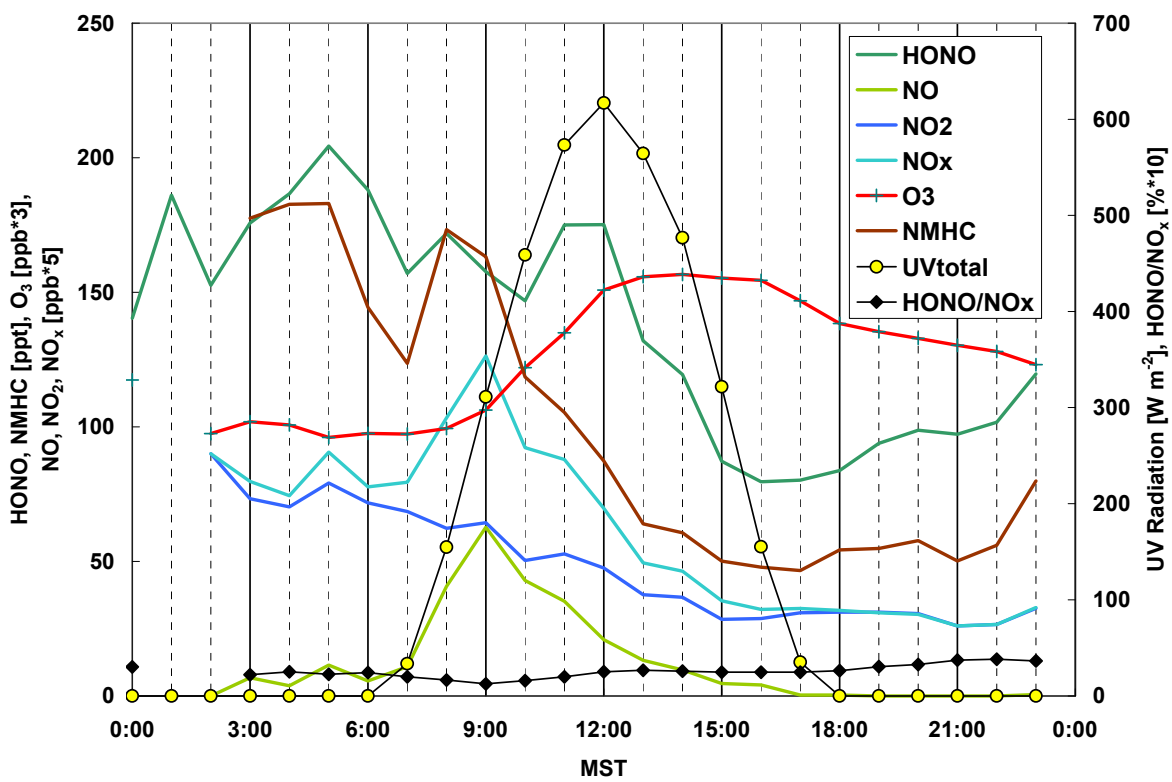

Figure 15: Composite diurnal variation of HONO, NO, NO_2, NO_x, O_3, NMHC, total UV radiation, and HONO/NO_x ratio during Part I of the campaign (January 30 - March 5, 2010). Hourly values are shown.

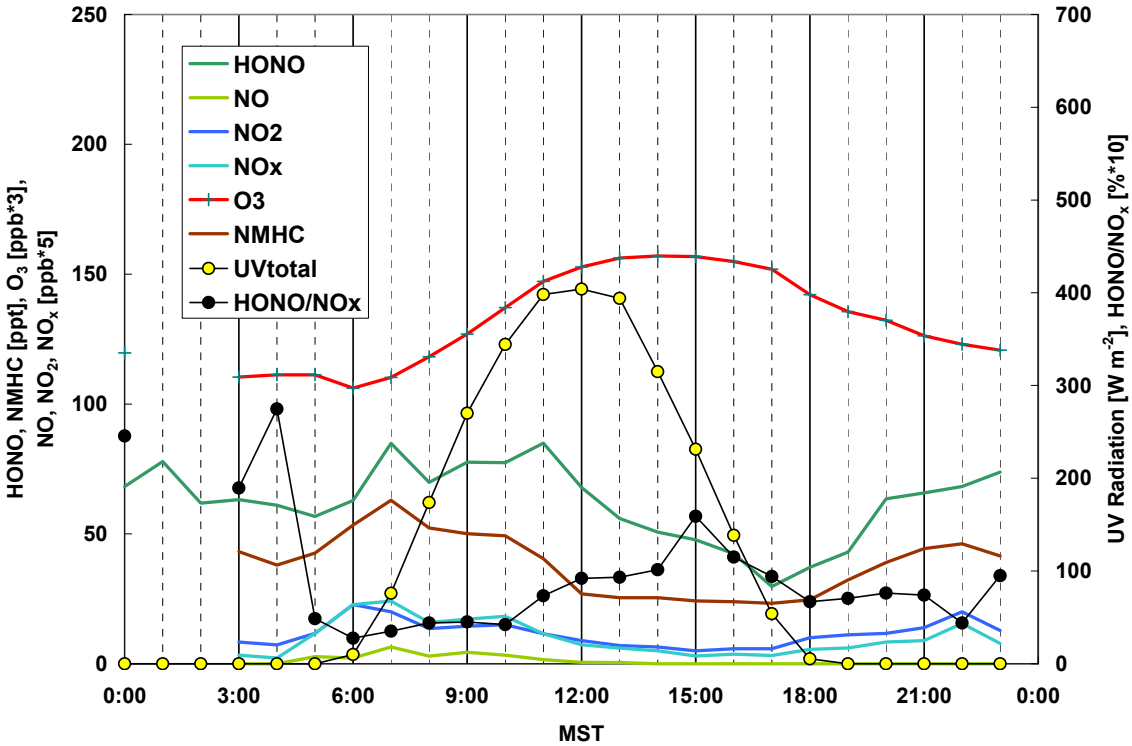

Figure 16: Composite diurnal variation of HONO, NO, NO_2, NO_x, O_3, NMHC, total UV radiation, and HONO/NO_x ratio during Part II of the campaign (March 5-31, 2010). Hourly values are shown.

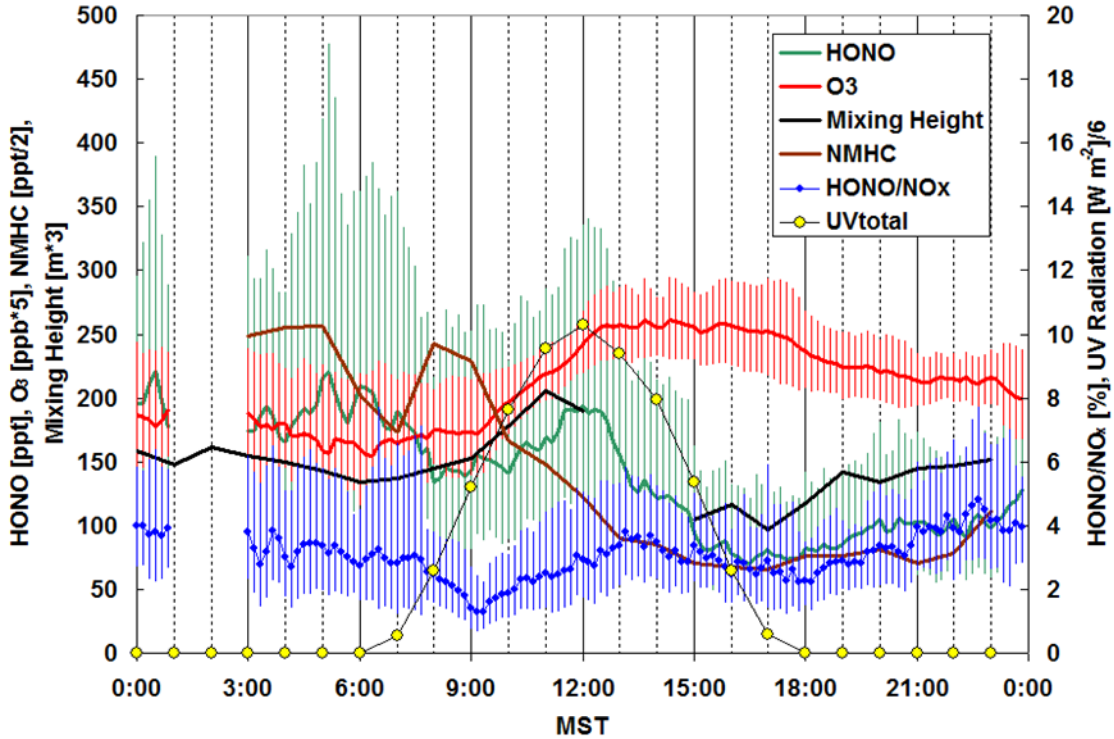

Figure 17: Composite diurnal variation of HONO, NO, NO_2, NO_x, O_3, NMHC, total UV radiation, HONO/NO_x ratio and the mixing layer height during Part I of the campaign (January 30 - March 5, 2010). Bars indicate standard deviation of the measurements. Hourly values are shown apart from ozone, HONO, and HONO/NO_x, which are 10-min values.

Data in Figure 17 also show that HONO increases while total UV radiation increases and as the boundary layer height increases and the low level inversion breaks up. Conventional thinking would suggest that HONO levels would rather decrease due to photolysis and increased mixing in the boundary layer. NMHCs on the other hand follow the classic assumption that the ambient mixing ratios would rapidly decrease with increasing boundary layer height. Also, photochemical oxidation will lead to lower NMHC concentrations. These observations suggest that photo-enhanced HONO formation occurs during this period with snow cover present and subsequent photolysis of HONO may yield OH radicals which in turn will oxidize NMHCs eventually leading to an increase in ozone.

Case Studies:

Figures 18-21 display some case studies during Part I of the campaign when sunny weather conditions prevailed. The first case studies (1 Feb, 4 Feb, 7 Feb) have some common features: high ozone peaks are observed around noontime; the boundary layer height already reached altitudes above the maximum SODAR detection limit. The high ozone levels were associated with wind directions turning from S to NW bringing in significant amounts of NO_x. While NO_x levels tended to decrease with increasing radiation and mixing layer height, HONO levels increased and actually coincided nicely with the peak ozone levels. HONO maximum levels reached 500-700 pptv around noontime.

Figure 21 (13 Feb) shows a case when wind directions were consistently from the NW during the daytime. No increase of NO_x levels were observed. Consequently, also HONO levels were low and there was no significant ozone production. Presumably there were insufficient NO_x precursors available for photo-enhanced formation of HONO.

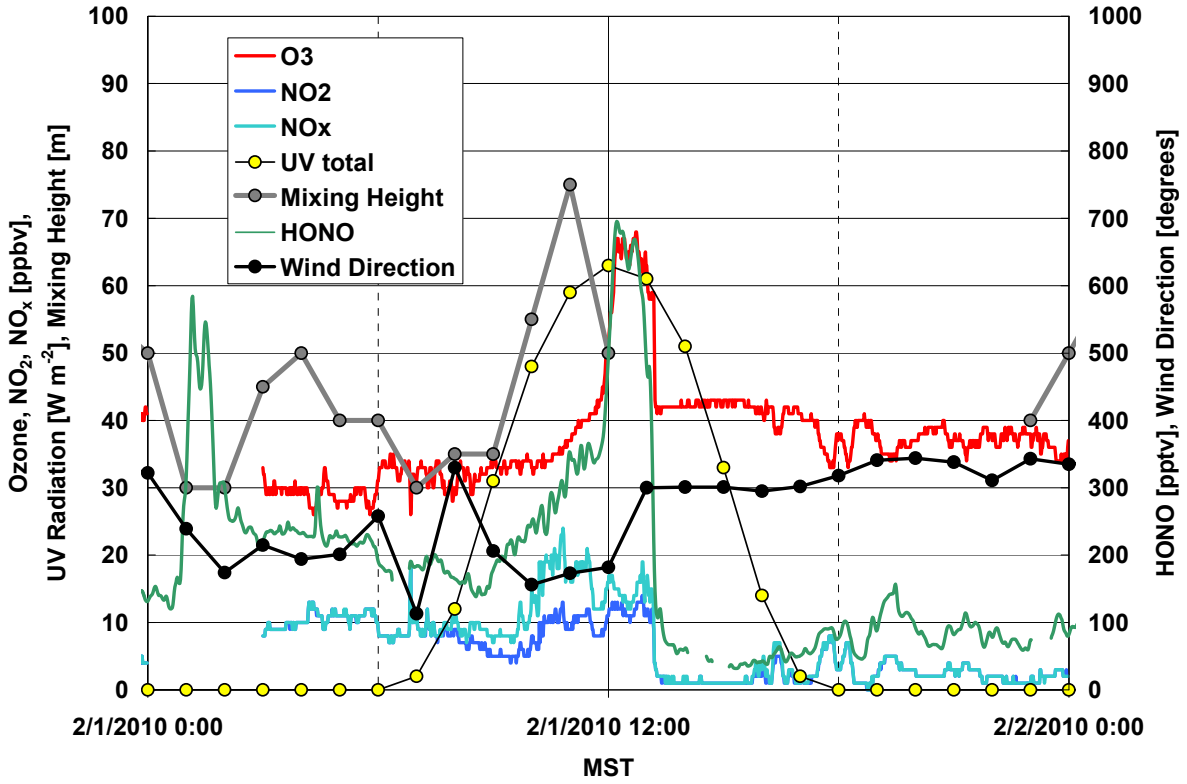

Figure 18: Case study 2/1/2010. O_3, NO_2, NO_x, and HONO shown as 1-min values. UV radiation, mixing height and wind direction shown as hourly values.

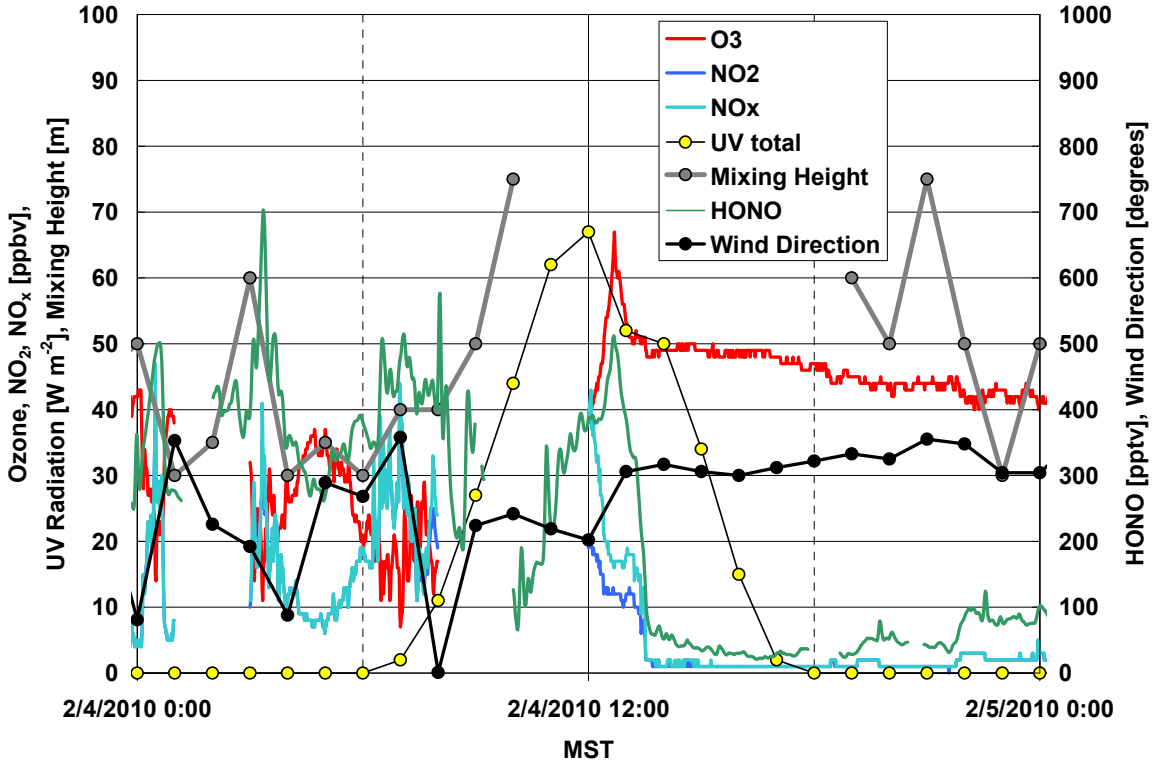

Figure 19: Case study 2/4/2010. O_3, NO_2, NO_x, and HONO shown as 1-min values. UV radiation, mixing height and wind direction shown as hourly values.

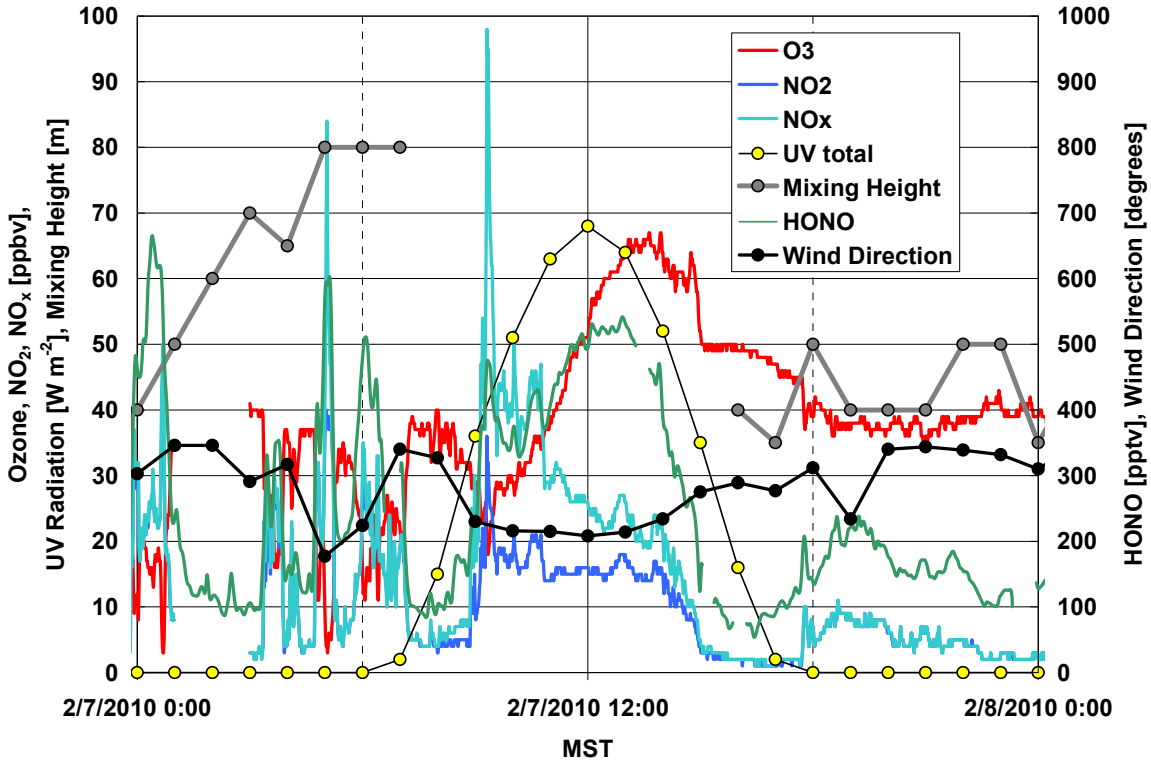

Figure 20: Case study 2/7/2010. O_3, NO_2, NO_x, and HONO shown as 1-min values. UV radiation, mixing height and wind direction shown as hourly values.

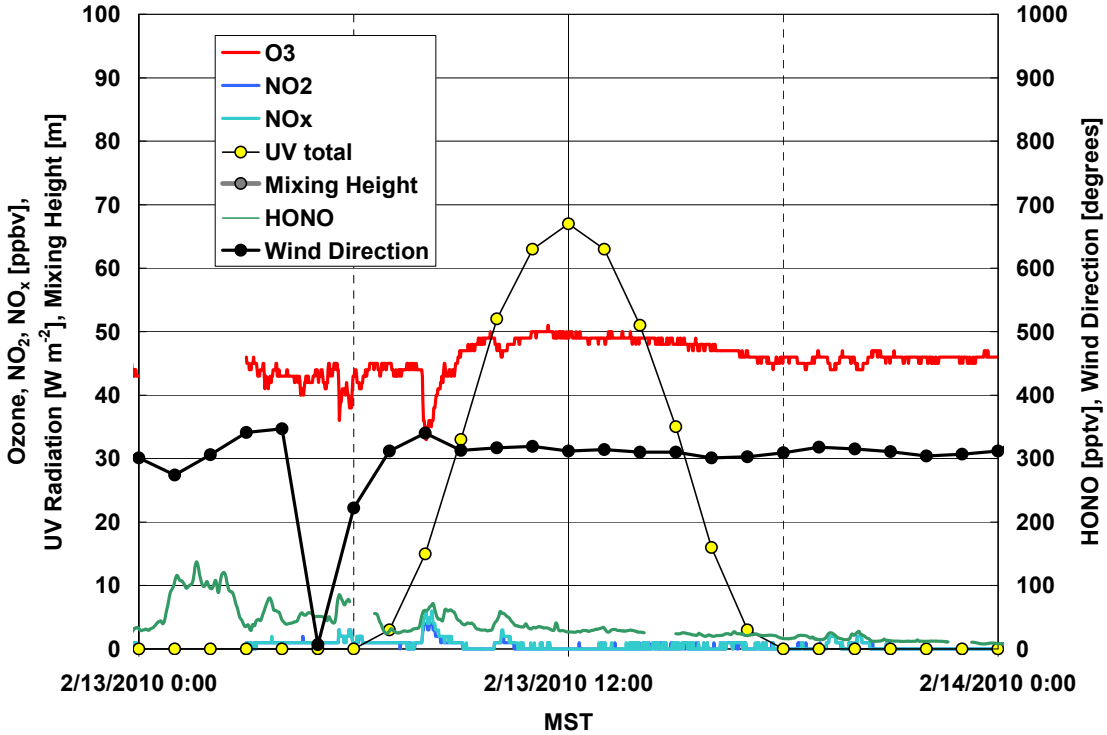

Figure 21: Case study 2/13/2010. O_3, NO_2, NO_x, and HONO shown as 1-min values. UV radiation, mixing height and wind direction shown as hourly values.

4. Findings and Recommendations

HONO measurements performed by UH during UGWOS 2010 yielded some interesting results:

- Nighttime HONO levels are well correlated with NO_2 (and NO_x). To a lesser extent HONO is also correlated with non-methane hydrocarbons (NMHC) and methane (CH_4). No correlation was found with particulate matter (PM-10).
- During nighttime periods, HONO levels are generally enhanced under WNW-S wind conditions. During daytime periods, HONO mixing ratios are generally lower than nighttime values except for E-SE wind directions. Similar to nighttime conditions, daytime HONO levels continue to show enhanced values under WSW-S winds. HONO levels decrease with increasing windspeed.
- Snow cover leads to enhanced total UV radiation and UV radiation correlates with HONO levels. This finding suggests photo-induced formation of HONO.
- Case studies of three moderately elevated ozone events showed high HONO levels around noontime coinciding with peak ozone levels. On two of the three days, high ozone levels were associated with wind directions turning from S to NW bringing in significant amounts of NO_x. On the third day, elevated ozone was associated with a change in wind direction from NW to SW, corresponding more closely to the mid-day wind reversal regime observed during high ozone events in previous winters.
- While NO_x levels tended to decrease with increasing radiation and mixing layer height during the morning hours, HONO levels increased and exhibited a midday peak which coincided closely with peak ozone levels.
- Data collected in this study indicate that high values of relative humidity favor the presence of high levels of HONO.
- HONO/NO_x ratios tend to have minimum values when nitrogen oxides are at a diurnal maximum in the morning. This ratio increases while nitrogen oxide levels decrease. These observations suggest that HONO is produced secondarily through nitrogen oxides which may have deposited previously at the snow surface and have undergone heterogeneous conversion.

Based on the above results, our recommendation for obtaining more conclusive information about processes which determine air quality in the Upper Green River Basin include:

- Obtain higher time resolution (i.e. 10 min or less) for ancillary data sets so as to better elucidate small scale process which involve nitrogen oxides and radiation. Higher time resolution would also allow multiple correlation analysis with a larger number of data points and thus make this analysis more robust.
- Obtain better resolution of nitrogen oxide measurements to allow for a more precise correlation analysis.
- Deployment of a formaldehyde analyzer is recommended in addition to HONO measurements. It appears that also NMHC emissions play a role in this area. It is likely that enhanced total UV radiation due to snow cover may also lead to enhanced photolysis of formaldehyde, another important ozone precursor. Formaldehyde measurements would be critical to perform a complete radical budget calculation based on HONO photolysis, ozone photolysis, HCHO photolysis and alkene ozonolysis (see discussion in section 2 above) and to determine the individual contributions. Alkene ozonolysis might be estimated based on speciated VOC analysis using canister sampling. .

5. References

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