FINAL REPORT
2011 UPPER GREEN RIVER OZONE STUDY

Prepared for:

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October 2011

FINAL REPORT
2011 UPPER GREEN RIVER WINTER OZONE STUDY
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C Weather Charts
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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.

The Wyoming Department of Environmental Quality - Air Quality Division (AQD) has been the sponsor of the Upper Green Winter Ozone Study (UGWOS) since 2007. During the past two winters, 2010 and 2011, AQD has contracted with Meteorological Solutions Inc. (MSI) (sub-contractors T & B Systems, the University of Houston, and ENVIRON International) to perform the UGWOS study of winter ozone formation in the UGRB.

Quality assurance project plans, data and reports from previous UGWOS field efforts can be found on AQD's Monitoring Information Page.[1] Data were collected from a network of permanent air quality monitoring stations, temporary monitoring stations installed for the duration of the wintertime field effort, upper air data from soundings and mini-SODAR's and various ozone precursor measurement efforts during the field program.

The purpose of UGWOS 2011 was to continue to study the formation of wintertime ozone in the UGRB by focusing on the vertical distribution of ozone and ozone precursors. This emphasis came as a recommendation of the AQD-sponsored Ozone Technical Advisory Group and the UGWOS 2010 team. Field operations for UGWOS 2011 started on January 15, 2011 and continued through March 31, 2011. Daily weather forecasts were issued by MSI's forecast meteorologist in order to identify two periods when ambient ozone concentrations in the UGRB were likely to be elevated and to provide an alert to field personnel so additional measurements could be implemented during these intensive operational periods (IOP's).

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

UGWOS 2011 field operations included continuous multi-level ozone, hydrocarbon, and meteorological measurements on a tall tower and during IOP's a tethered balloon monitoring system each instrumented at four levels to measure meteorology and ozone and ozone precursor concentrations. The Boulder monitoring site was again expanded to include more specialized ozone precursor measurements as well as upper air measurements.

This report presents a summary of UGWOS 2011 field operations, quality assurance activities, and results of the field measurement program. Section 2.0 presents an overview of the ozone and ozone precursor measurements as well as the daily forecasts and project website features. In addition, this section provides synoptic weather summaries for the two intensive operational periods. Section 3.0 describes database management, quality assurance, data validation, and data archiving. Monitoring results are described in Section 4.0. Section 5.0 presents a summary of the findings, conclusions based on the findings, and recommendations. UGWOS 2011 measurement data are available in an ACCESS database on the AQD website.

2.0 SUMMARY OF FIELD OPERATIONS

This section provides a description of measurement platforms active during UGWOS 2011, project website features, and synoptic weather summaries during 2011 IOP's.

2.1 Overview

UGWOS 2011 field operations were scheduled for January 15, 2011 through March 31, 2011. All UGWOS 2011 monitoring sites were installed, calibrated, and ready for operations by January 14, 2011. Forecasting for elevated ozone conditions started on January 15, 2011 and continued through March 31, 2011 when the field monitoring program ended.

2.1.1 Planning Process

The AQD-sponsored Technical Advisory Group provided input to AQD and the UGWOS team and recommended that field efforts focus on vertical distribution of ozone and ozone precursors during UGWOS 2011.

In order to provide measurements of ozone and ozone precursors in the vertical, the UGWOS team leased a 73-meter tall tower from Questar Infocomm which was instrumented at multiple levels for the duration of the UGWOS field measurement period. In addition, Shell Exploration and Production provided a space near their field operations facility in the New Fork River plain where an AQD mobile air quality and meteorological monitoring trailer was located during UGWOS 2011. Instrumentation collected data continuously during the UGWOS field program and the air quality analyzers in the mobile station were switched to sample inlets connected to a tethered balloon at multiple levels during IOP's.

As in prior studies, specialized measurements were added to the Boulder site to enhance understanding of ozone precursor mechanisms. These included Nitrous Acid (HONO) measurements provided by the University of Houston, an investigation of nitrogen species including NO_y by Air Quality Design, Inc. and $PM_{2.5}$ and VOC canister speciation by Air Resource Specialists.

All of the currently operating permanent AQD monitoring stations provided meteorological and air quality data for the UGWOS database. A map showing the measurement stations active during the UGWOS 2011 program is shown in Figure 2.1. Areas marked on the map with colored shading indicate proposed and active industrial (oil and gas) development projects which are potential sources of ozone precursor emissions. A summary of the instrumentation and parameters measured by sampling platform is presented in Table 2-1.

Figure 2.1 Active Monitoring Stations and Proposed Industrial Development Areas (Colored Shading) in the UGWOS 2011 Study Domain.

Table 2-1

Summary of Measurement Methods Used During UGWOS 2011

Platform	Measurement	Instrumentation	
		Method	**Model**
Tall Tower	Ozone	UV Photometric	T-API 400E
	NO_x	Chemiluminescence	T-API 200E
	Methane/TNMHC	FID	Baseline-Mocon 9000 (Boulder)
	$PM_{2.5}$	Beta Attenuation	BAM 1020 (Pinedale)
	WS, WD, T	Various	RM Young 05305, 41342
	RH	Capacitive Chip	Vaisala HMP 45C
Tethered Balloon/Mobile Trailer	Ozone	UV Photometric	T-API 400E
	NO_x	Chemiluminescence	T-API 200E
	Methane/TNMHC	FID	Baseline-Mocon 9000 (Boulder)
	$PM_{2.5}$	Beta Attenuation	BAM 1020
	WS, WD, T, RH, BP, Solar Rad., Precip	Various	Various
Boulder Complex	HONO	Long Path Absorption Photometry	QUMA LOPAP O_3 - HONO
	Trace NO, NO_2, NO_y	Chemiluminescence	High Performance 2-Channel Analyzer
	Speciated $PM_{2.5}$	Speciation Trends Network/IMPROVE	Met One SASS, URG 3000 N
	Speciated VOC	TO-15 Canister	GC/MS w/Tentatively Identified Compounds
AQD 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
	WS, WD, T, RH, BP, Solar Rad., Precip.	Various	Various
mini-SODAR	Upper Level Winds	Doppler Sodar	ASC 4000 mini-SODAR
	Mixing Height	Doppler Sodar	ASC 4000 mini-SODAR
	Surface wind speed, wind direction, temp, RH , pressure and precip. detection	Integrated sonic anemometer, thermistor, RH and pressure sensors with separate precip. detection sensor	Vaisala WXT-510

2.1.2 UGWOS Website

The UGWOS website was streamlined for the 2011 field study and allowed remote access to real-time station data for all UGWOS participants. The UGWOS web-site home page is presented in Figure 2.2 below. The web page displayed near real-time ozone information for the following stations:

- Wyoming Range
- Pinedale
- Daniel
- Boulder
- Mobile Trailer/Tethered Balloon
- Tall Tower
- Juel
- South Pass
- Moxa

In addition to real-time ozone information, wind speed, wind direction, and temperature data were displayed on similar pages. 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 by clicking on the station information. (See Figure 2.3). The data collected on the tall tower were displayed on an individual page (Figure 2.4). The data collected from the tethered balloon platform were displayed on an individual page (Figure 2.5). The project forecast page was updated on a daily basis (Figure 2.6). A site equipment matrix provided information which was updated continually regarding equipment status (Figure 2.7).

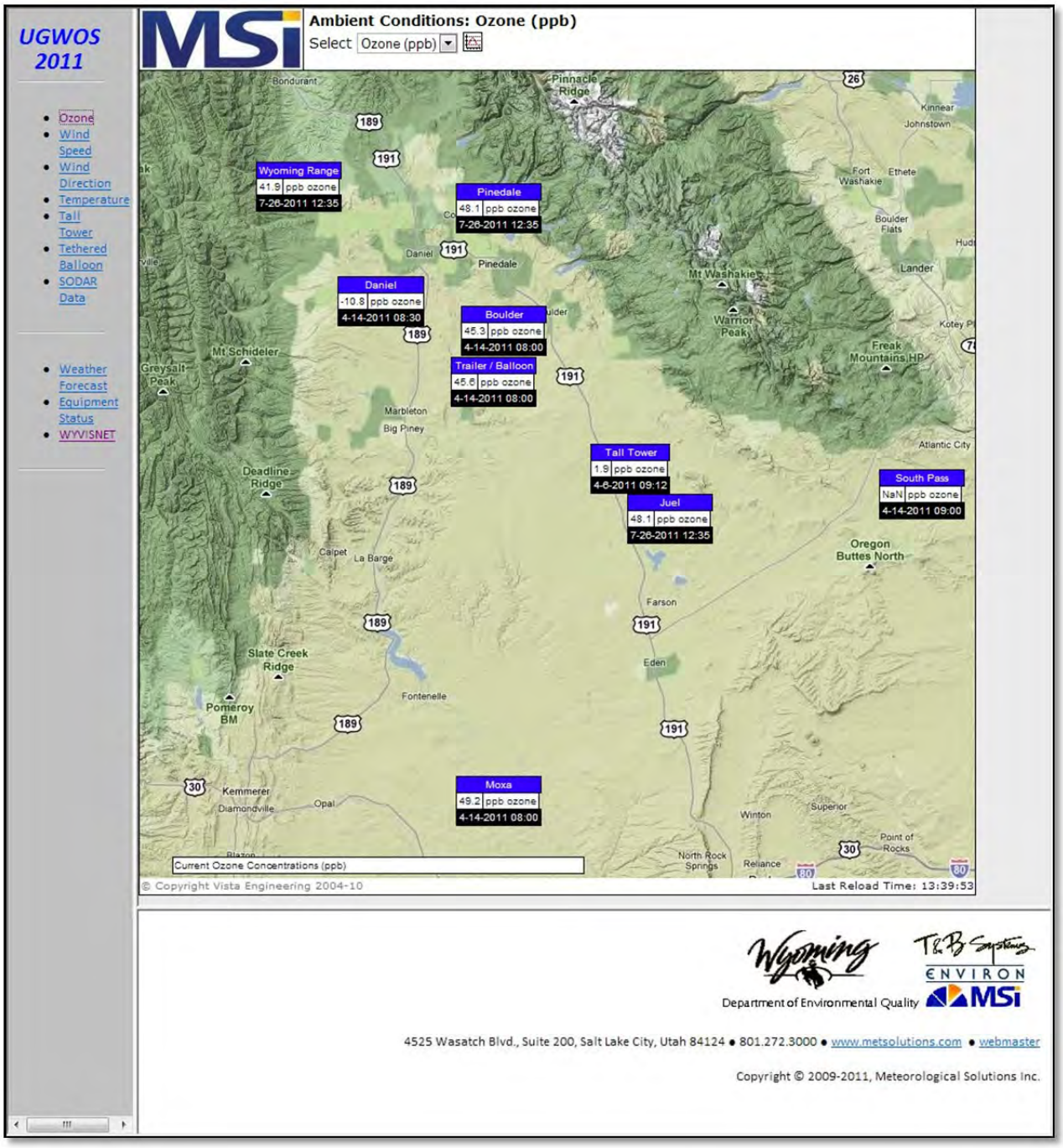


Figure 2.2 Real-time Ozone Concentrations

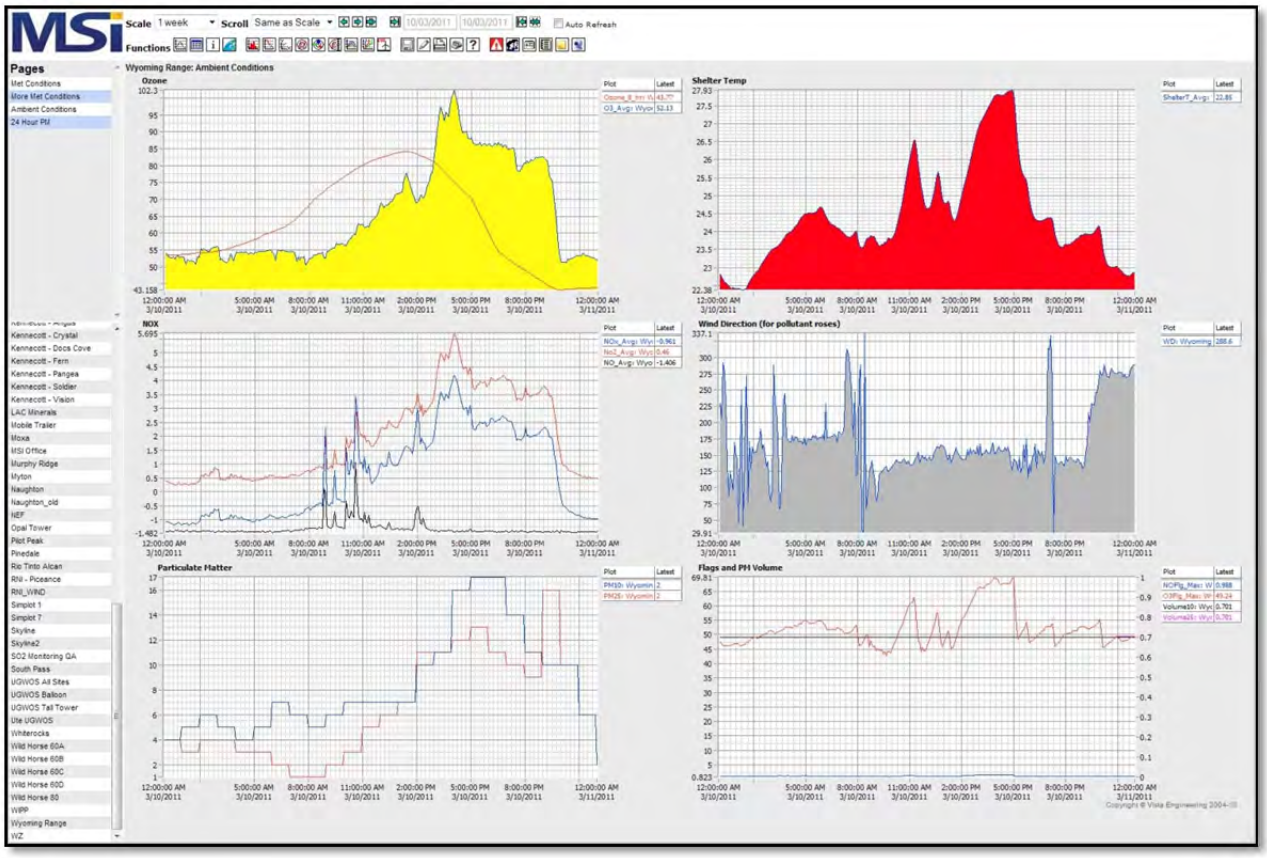


Figure 2.3 Station Strip Charts Example

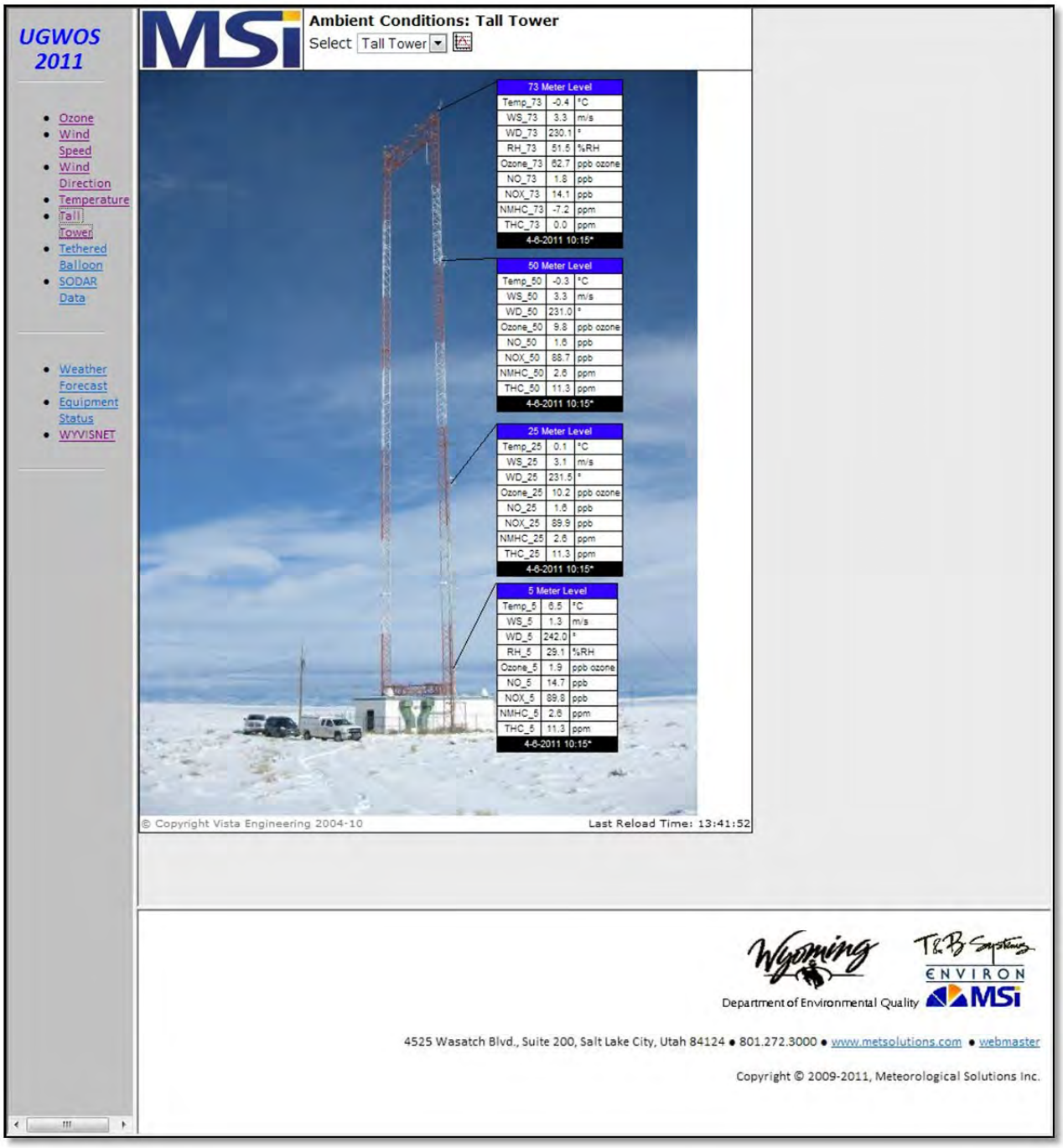


Figure 2.4 Tall Tower Data Display

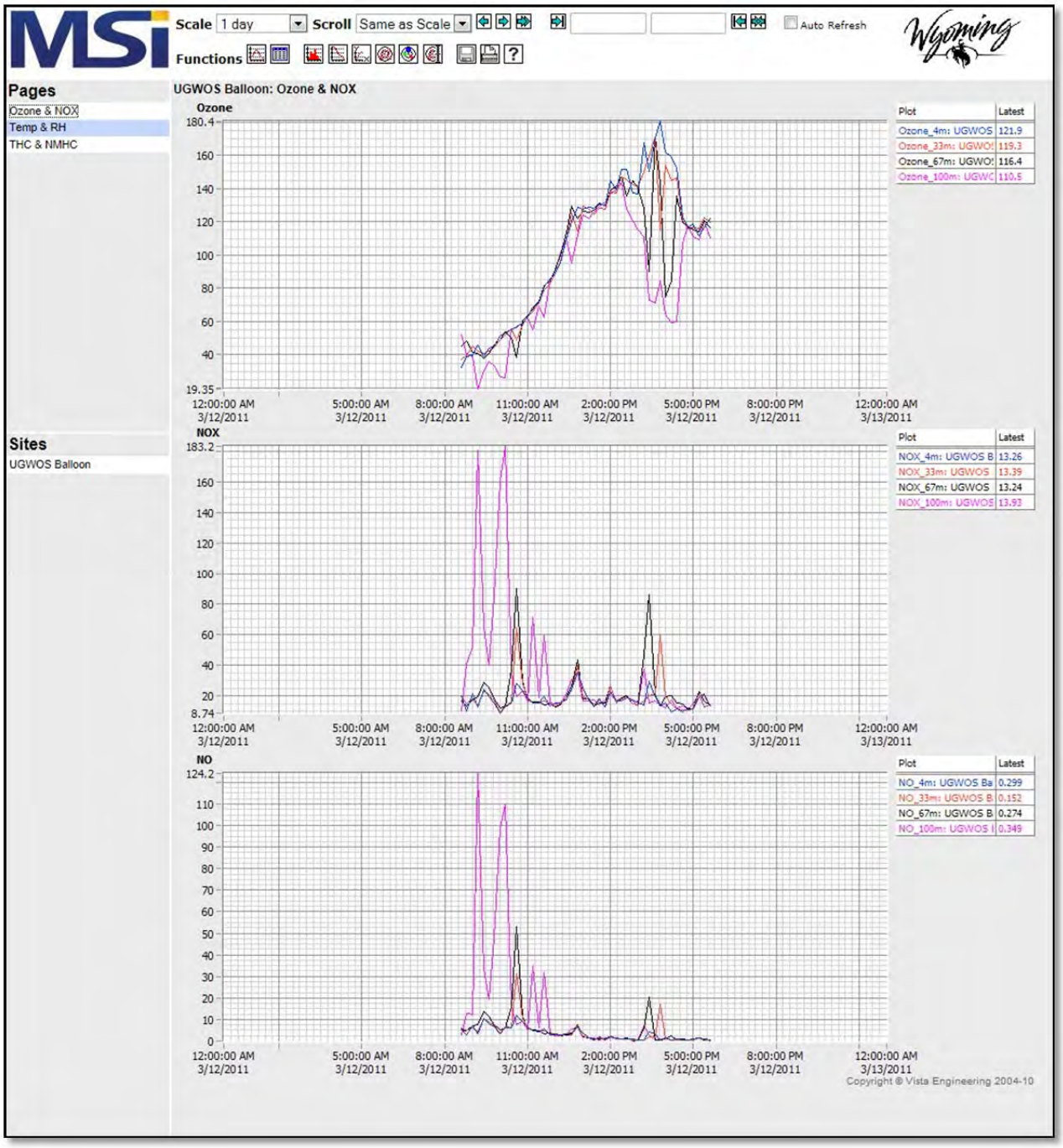
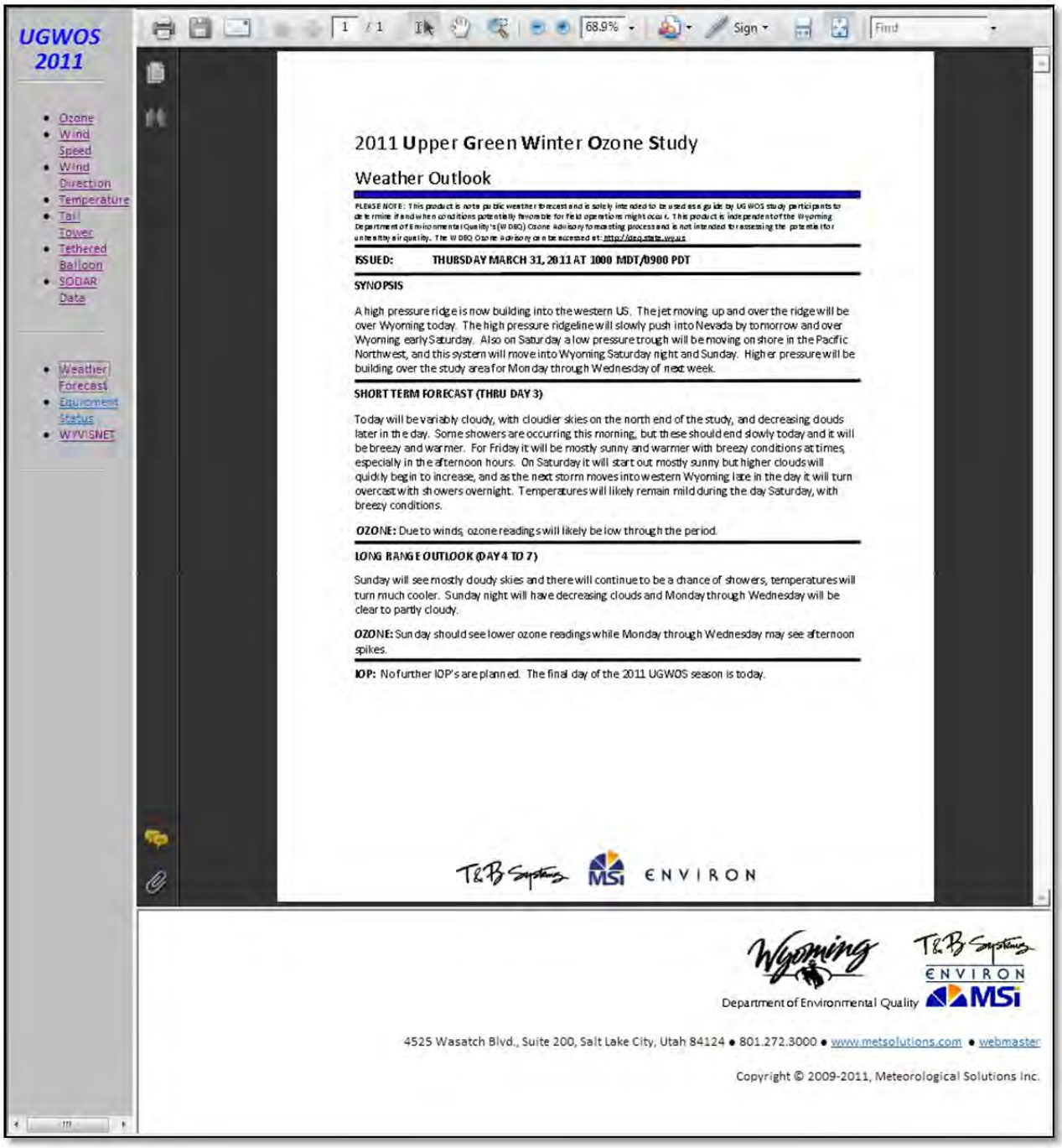


Figure 2.5 Tethered Balloon Data Display



UGWOS 2011

- Ozone
- Wind Speed
- Wind Direction
- Temperature
- Tall Tower
- Tethered Balloon
- SODAR Data
- Weather Forecast
- Equipment Status
- WYVISNET

2011 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 to assessing the potential for unhealthy air quality. The WDEQ Ozone Advisory can be accessed at: http://deq.state.wy.us

ISSUED: THURSDAY MARCH 31, 2011 AT 1000 MDT/0900 PDT

SYNOPSIS

A high pressure ridge is now building into the western US. The jet moving up and over the ridge will be over Wyoming today. The high pressure ridgeline will slowly push into Nevada by tomorrow and over Wyoming early Saturday. Also on Saturday a low pressure trough will be moving on shore in the Pacific Northwest, and this system will move into Wyoming Saturday night and Sunday. Higher pressure will be building over the study area for Monday through Wednesday of next week.

SHORT TERM FORECAST (THRU DAY 3)

Today will be variably cloudy, with cloudier skies on the north end of the study, and decreasing clouds later in the day. Some showers are occurring this morning, but these should end slowly today and it will be breezy and warmer. For Friday it will be mostly sunny and warmer with breezy conditions at times, especially in the afternoon hours. On Saturday it will start out mostly sunny but higher clouds will quickly begin to increase, and as the next storm moves into western Wyoming late in the day it will turn overcast with showers overnight. Temperatures will likely remain mild during the day Saturday, with breezy conditions.

OZONE: Due to winds, ozone readings will likely be low through the period.

LONG RANGE OUTLOOK (DAY 4 TO 7)

Sunday will see mostly cloudy skies and there will continue to be a chance of showers, temperatures will turn much cooler. Sunday night will have decreasing clouds and Monday through Wednesday will be clear to partly cloudy.

OZONE: Sunday should see lower ozone readings while Monday through Wednesday may see afternoon spikes.

IOP: No further IOP's are planned. The final day of the 2011 UGWOS season is today.

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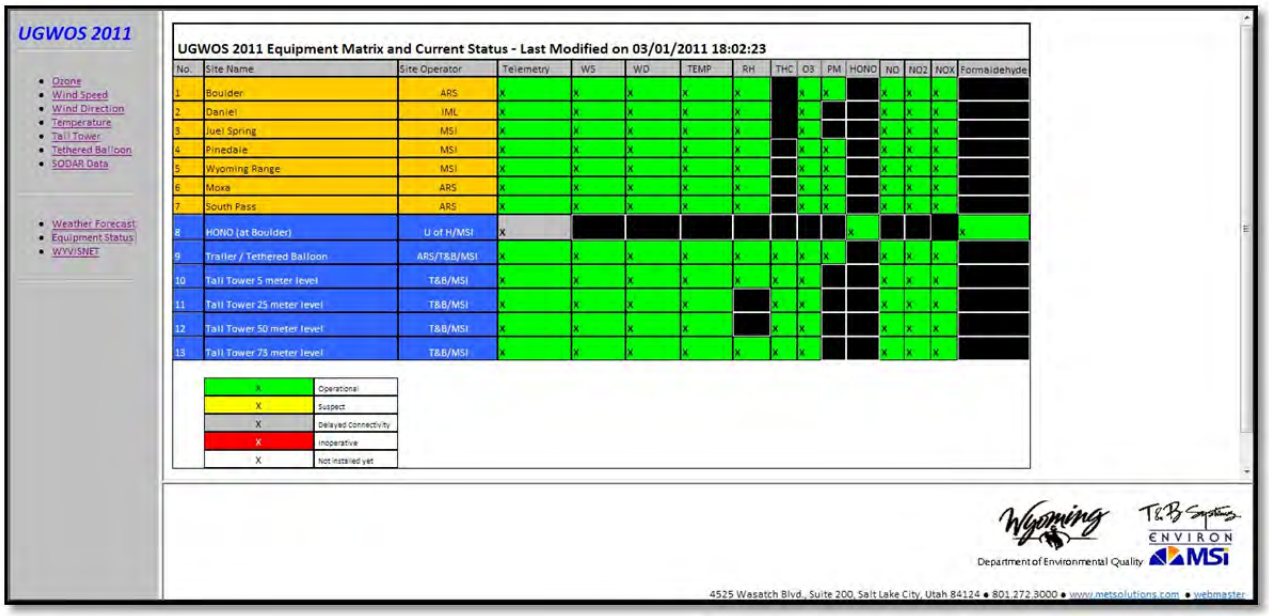
Figure 2.6 Project Forecast Example



UGWOS 2011

- Ozone
- Wind Speed
- Wind Direction
- Temperature
- Tall Tower
- Tethered Balloon
- SODAR Data

- Weather Forecast
- Equipment Status
- WYVISNET

UGWOS 2011 Equipment Matrix and Current Status - Last Modified on 03/01/2011 18:02:23

No.	Site Name	Site Operator	Telemetry	WS	WD	TEMP	RH	THC	O3	PM	HONO	NO	NO2	NOX	Formaldehyde
1	Boulder	ARS	X	X	X	X	X		X	X		X	X	X	
2	Daniel	IML	X	X	X	X	X		X			X	X	X	
3	Juel Spring	MSI	X	X	X	X	X		X			X	X	X	
4	Pinedale	MSI	X	X	X	X	X		X	X		X	X	X	
5	Wyoming Range	MSI	X	X	X	X	X		X	X		X	X	X	
6	Moxa	ARS	X	X	X	X	X		X	X		X	X	X	
7	South Pass	ARS	X	X	X	X	X		X	X		X	X	X	
8	HONO (at Boulder)	U of H/MSI	X								X				X
9	Trailer / Tethered Balloon	ARS/T&B/MSI	X	X	X	X	X	X	X	X		X	X	X	
10	Tall Tower 5 meter level	T&B/MSI	X	X	X	X	X	X	X			X	X	X	
11	Tall Tower 25 meter level	T&B/MSI	X	X	X	X		X	X			X	X	X	
12	Tall Tower 50 meter level	T&B/MSI	X	X	X	X		X	X			X	X	X	
13	Tall Tower 75 meter level	T&B/MSI	X	X	X	X	X	X	X			X	X	X	

X	Operational
X	Suspect
X	Delayed connectivity
X	Inoperative
X	Not installed yet

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Figure 2.7 Equipment Status

2.2 Continuous Measurements

Active measurement stations which provided data for the UGWOS 2011 database included the permanent AQD monitoring stations already operating in the Upper Green River Basin study area and the mini-SODAR located adjacent to the Boulder monitoring station. In addition, specialized measurements conducted during the UGWOS field measurement period included meteorological and air quality measurements on a tall tower instrumented at multiple levels, as well as nitrogen species and speciated VOC and particulate matter (PM) measurements at the Boulder monitoring complex.

2.2.1 AQD Permanent Monitoring Sites

AQD monitoring stations in the UGRB which were actively collecting data during UGWOS 2011 included Wyoming Range, Daniel South, Boulder, Pinedale, Juel Springs, South Pass, and Moxa. These sites were typically measuring wind speed and direction at 10 meters, temperature, relative humidity, barometric pressure, solar radiation and precipitation. Air quality parameters measured at these sites included ozone, oxides of nitrogen and particulate matter. Figure 2.8 presents a photograph of the permanent monitoring station at Wyoming Range.

Figure 2.8 Permanent Monitoring Sites Example: Wyoming Range

2.2.2 Tall Tower Measurements

Continuous measurements of ozone, oxides of nitrogen, and methane and non-methane hydrocarbons were performed on an existing 73-meter tower using long line sampling methods. The tower is owned by Questar Infocomm and is located just off Highway 191 North approximately 20 kilometers south of the junction with Highway 351. Figure 2.9 shows a photo of the tall tower with the equipment shelter at its base. Long sample inlet lines were installed on the tower to four levels: 73, 50, 25, and 5 meters. Ambient air was continuously drawn down to the surface monitoring shelter using 3/8" O.D./5/16" I.D. Teflon tubing at a rate of 4 lpm resulting in only a slight vacuum in the sample lines while maintaining a residence time of less than 20 seconds. Sample air from each level was directed to ozone, NO_x and hydrocarbon analyzers in the shelter simultaneously using a switching mechanism that sequentially sampled each level for 3 minutes during a 12-minute cycle. Each three-minute sample included 2.5 minutes of equilibration and 1.0 minute of actual sampling. Hourly data for each level consisted of five 1.0-minute averages.

Meteorological monitoring was also conducted at each level of the tall tower. Wind speed and direction and motor-aspirated temperature sensors were mounted on a boom installed at each measurement level. Relative humidity sensors were mounted at the 73-meter and 5-meter levels. A datalogger stored 15-minute averages of meteorological parameter data. Figure 2.10 shows a photo of the tall tower with the equipment booms installed at four levels. Figure 2.11 shows the long inlet line sample level switching system located in the monitoring shelter at the tower base along with the air quality analyzers shown in Figure 2.12.

Figure 2.9 Tall Tower

Figure 2.10 Tall Tower Meteorological Sensor Booms

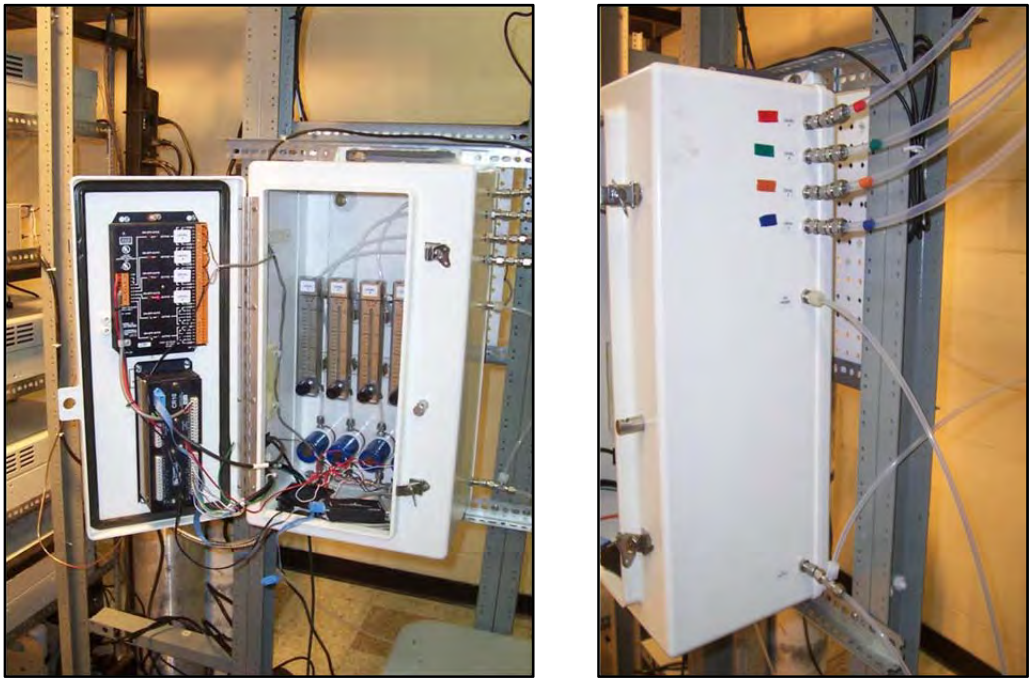


Figure 2.11 Tall Tower Long Line Sample Level Switching System

Figure 2.12 Tall Tower Air Quality Analyzers

2.2.3 Tethered Balloon/Mobile Trailer Measurements

One of AQD's mobile monitoring trailers operated by ARS was located at a Shell Exploration facility approximately 6 kilometers southwest of the Boulder monitoring site along the New Fork River drainage. The mobile trailer site is approximately 34 meters lower in elevation than the Boulder site where the mini-SODAR and the ozonesonde launches were located and 26 meters lower than the tall tower base. This trailer was outfitted with a 10-meter tower and the same ozone, oxides of nitrogen and hydrocarbon analyzers as were used at the tall tower. Figure 2.13 shows a view of the tethered balloon in operation with the mobile trailer as the base monitoring shelter. The mobile trailer, shown in Figure 2.14, was operated in its normal monitoring mode for the duration of the UGWOS study except on intensive study period days when the air quality analyzers were used with a tethered balloon multi-level sampling system. A tethered balloon was used to raise long inlet lines to obtain continuous measurements of ozone, oxides of nitrogen, and methane and non-methane hydrocarbons at four levels (4, 33, 67, 100 meters) during daytime hours of IOP days.

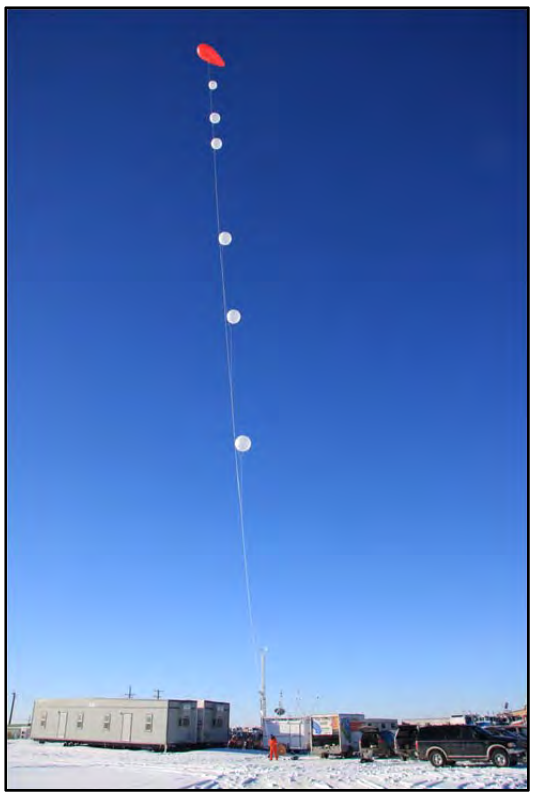


Figure 2.13 Tethered Balloon/Mobile Trailer

Figure 2.14 Mobile Trailer

In addition to sampling air quality parameters, temperature and relative humidity were monitored at each level using small, lightweight temperature and relative humidity dataloggers. These meteorological parameters were measured at one-minute intervals. The same long line sampling methods and level switching equipment used at the tall tower were used for the tethered balloon system. When vertically extended, the sample inlet lines were positioned at 100, 67, 33, and 4 meters above ground. Inlet tubing, switching valves and sample timing and averaging were identical to those used for the tall tower. The tethered balloon inlet tubing was configured with access ports to allow drawing VOC canister grab samples. Samples were typically taken in pairs – one from an upper level and one from a lower level within a five-minute period. A total of 12 valid samples were collected during UGWOS 2011 usually triggered by elevated TNMHC concentrations during tethered balloon operations.

2.2.4 Boulder Monitoring Complex: HONO

During UGWOS 2011, specialized measurements were performed from a monitoring shelter positioned adjacent to the Boulder monitoring station. The University of Houston again provided nitrous acid (HONO) measurements to further explore the role of hydroxyl (-OH) radicals in wintertime ozone formation. MSI's in-field technician provided calibration, maintenance and troubleshooting services for the HONO measurement system. Data were collected using a moving inlet which at times cycled between sampling just above the snow surface to approximately the 1.8-meter level. Figure 2.15 shows the Boulder monitoring complex with the HONO measurement system in the foreground. The permanent Boulder monitoring station is positioned behind the HONO system with the specialized measurement shelter to the right.

Figure 2.15 Boulder Complex (HONO Equipment in Foreground)

2.2.5 mini-SODAR

The AQD Wind Explorer mini-SODAR was maintained and operated adjacent to the Boulder monitoring station and continuously measured surface and winds aloft and provided mixing height information up to approximately 250 meters. Figure 2.16 shows the mini-SODAR at its Boulder monitoring complex location.

Figure 2.16 mini-SODAR

2.2.6 Ozonesondes

AQD released ozonesondes or rawinsondes 3-4 times per day during intensive operational periods from a base of operations adjacent to the Boulder monitoring site. Sounding data provided vertical profiles of ozone, temperature and winds and information about inversion height and depth. A photo taken during one of the releases is shown in Figure 2.17.

Figure 2.17 Ozonesonde Release from the Boulder Monitoring Site

2.2.7 Other Specialized Measurements: Speciated PM, VOC, and NO_y

Speciated $PM_{2.5}$ samples were collected during UGWOS 2011 on the EPA one-in-three day schedule at the Boulder monitoring complex. Additional samples were collected during elevated ozone periods and 20 samples were selected for analysis based on a review of local conditions.

Speciated VOC measurements were performed using the TO-15 canister sampling method at the Boulder monitoring station. Canister samples were triggered manually during elevated ozone events or automatically when continuously monitored NMHC levels exceeded 1.5 parts per million (ppm).

Trace level NO, NO_2, and NO_y measurements were performed at the Boulder complex by Air Quality Design, Inc. using a high performance 2-channel chemiluminescent analyzer. Results of these other specialized measurements will be available through AQD.

2.3 Elevated Ozone Events (IOPs)

This section describes the weather and ozone development outlooks issued daily to forecast elevated ozone episodes as well as the synoptic weather summaries of conditions during the two IOP's during UGWOS 2011.

2.3.1 Forecasts for Elevated Ozone Events

To assist in the planning of Intensive Operational Period (IOP) events, a daily forecast/extended outlook was issued and posted on the UGWOS web site each morning by 10 AM MST.

The forecast/extended outlook issued for the project contained four sections. The first section provided a synopsis of current general weather conditions over the study area. It described what the expected changes to these conditions would be for the following few days. The second section provided a short term forecast that covered expected weather and ozone conditions for the day of the forecast and the following two days. The third section was a longer range outlook that covered the period from four to seven days after the issuance date. This section provided expected weather conditions as well as what ozone concentrations were expected to develop during this period. The fourth section provided a brief statement indicating the status of IOP events and what the possibilities of future events were. Figure 2.18 shows an example of the forecast/outlook issued during an IOP event.

2011 **U**pper **G**reen **W**inter **O**zone **S**tudy

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, FEBRUARY 28, 2011 AT 1000 MST/0900 PST**

SYNOPSIS

The next seven days will see high and low pressure systems moving rapidly through the western US. A weak high pressure ridge will be over the state today. A storm system will swing through a low off the Pacific Northwest coast, and the nearly zonal flow over Wyoming will turn more southwesterly with time beginning Tuesday night as the low moves inland. The low will cross into the Rockies Wednesday night and Thursday. High pressure will move in behind this storm and will push into the Wyoming Friday night and Saturday. Another rapidly moving storm system is expected to take the ridges place on Sunday.

SHORT TERM FORECAST (THRU DAY 3)

Today will be partly to mostly cloudy with higher level clouds. Tuesday will be fair to partly cloudy and a little warmer. Wednesday will see partly cloudy skies becoming mostly cloudy late. Winds will be southerly and possibly breezy at times.

OZONE: Elevated readings this afternoon through Wednesday afternoon are possible.

LONG RANGE OUTLOOK (DAY 4 TO 7)

For Thursday and Friday it will be mostly cloudy with snow showers at times. By late Friday and Friday night there will be clearing skies with showers ending. Saturday will be fair to partly cloudy early becoming mostly cloudy late. Saturday night and Sunday will see increasing clouds with snow showers developing.

OZONE: There will continue to be a chance for elevated ozone readings Wednesday. Low readings are currently expected Thursday, Friday and Sunday with a chance for elevated readings on Saturday afternoon.

IOP: An IOP is currently in progress.

T&B Systems MSI ENVIRON

Figure 2.18 Example Weather Outlook

2.3.2 Synoptic Weather Summaries of IOP's

There were two IOP events during the 2011 UGWOS study. The first IOP was a three day event that occurred from February 28 through March 2, 2011. The second IOP was a four day event that occurred from March 9 through March 12, 2011.

In the days leading up to the first IOP, the outlook was for a zonal pattern to develop with weak ridging at the 700 mb level (10,000 ft). From past experience, this type of pattern would not normally produce elevated ozone since the amount of sunlight is reduced due to increased cloudiness and higher surface winds because of weak high pressure at the surface and aloft. However, it appears that the deep snow cover that was present over much of the study area (see Section 4.1.2 for a detailed snow cover discussion) during this first IOP caused stronger inversion development resulting in lighter surface winds which was conducive to elevated ozone development during the February 28 through March 2 period.

At 700 mb, the flow was west-southwesterly over western Wyoming during the first IOP. A weak ridge of high pressure progressed along this flow over the first two days of the IOP. On the third day a weak shortwave trough moved along this flow and over the state. The surface maps for the period indicate that there was a weak surface high pressure centered over western Wyoming between 1018 mb and 1022 mb MSL on February 28 and March 1. On March 2 as the trough of low pressure aloft moved over the study area, surface low pressure moved into the eastern half of the state from the north, pushed into position by a cold high pressure system that traveled south into the northern plains and upper mid-west. Light winds both aloft and at the surface occurred during this IOP and the surface inversion continued through the daytime hours. Despite the weak storm system that moved into the state on March 2, the highest ozone readings of the IOP were recorded this day. Figure 2.19 presents the 700 mb level chart on the afternoon of March 2; Figure 2.20 shows the surface weather chart, obtained from the National Centers for Environmental Prediction, Hydrometeorological Prediction Center, from the morning of March 2.

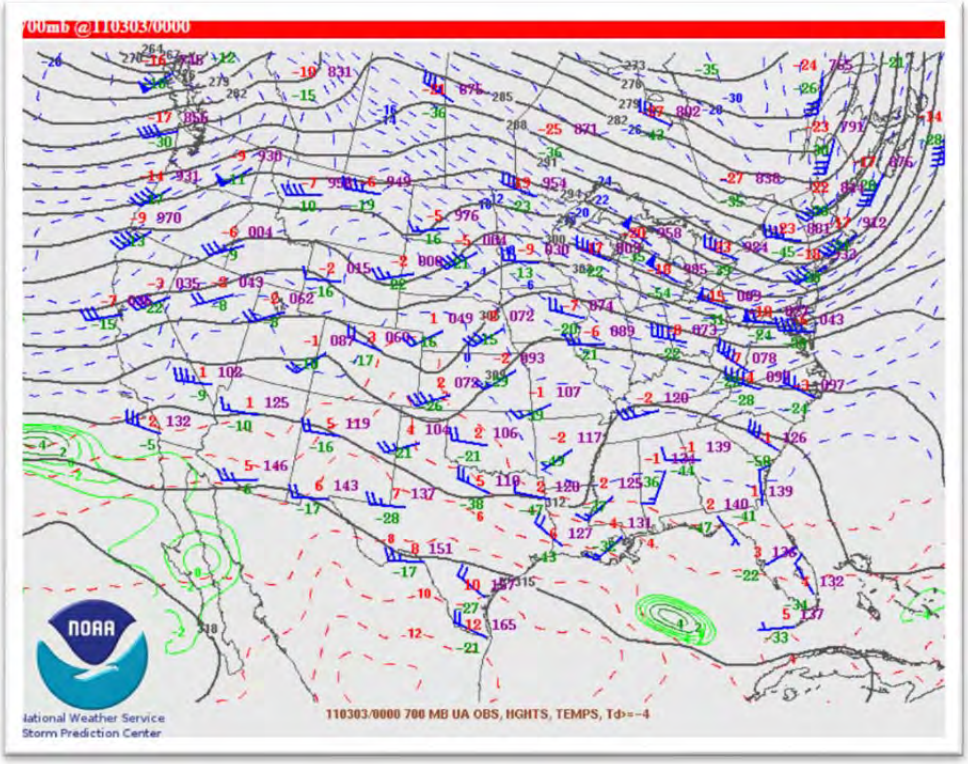


Figure 2.19 700 mb Chart at 1700 MST March 2, 2011

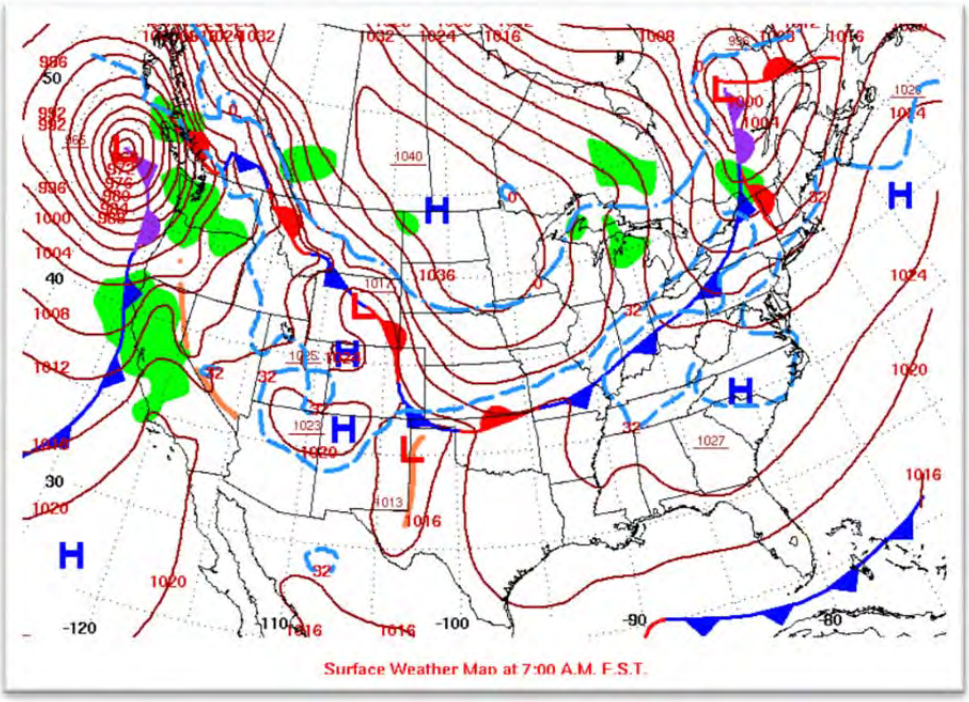


Figure 2.20 Surface Chart at 0500 MST March 2, 2011

For the second IOP, the forecasts leading up to the event indicated that higher pressure would build over the study area on March 9 and 10, but that a weak storm would cross over Wyoming March 11, and another weak system would move over the state March 12. Despite these storms moving through the area and as with the first IOP, the winds remained light allowing inversions to persist, and elevated ozone readings were very high. The highest ozone levels occurred on Saturday March 12 when seven sites recorded 8-hour ozone readings above 65 ppb and three sites were above 90 ppb. Figure 2.21 shows the 700 mb weather chart on the afternoon of March 12 when the highest ozone readings occurred during this IOP. As can be seen in this figure, winds at this level were light at around 10 knots (5 mps) and this would mean little mixing was occurring over the study area. Figure 2.22 shows the surface weather chart during the morning of March 12.

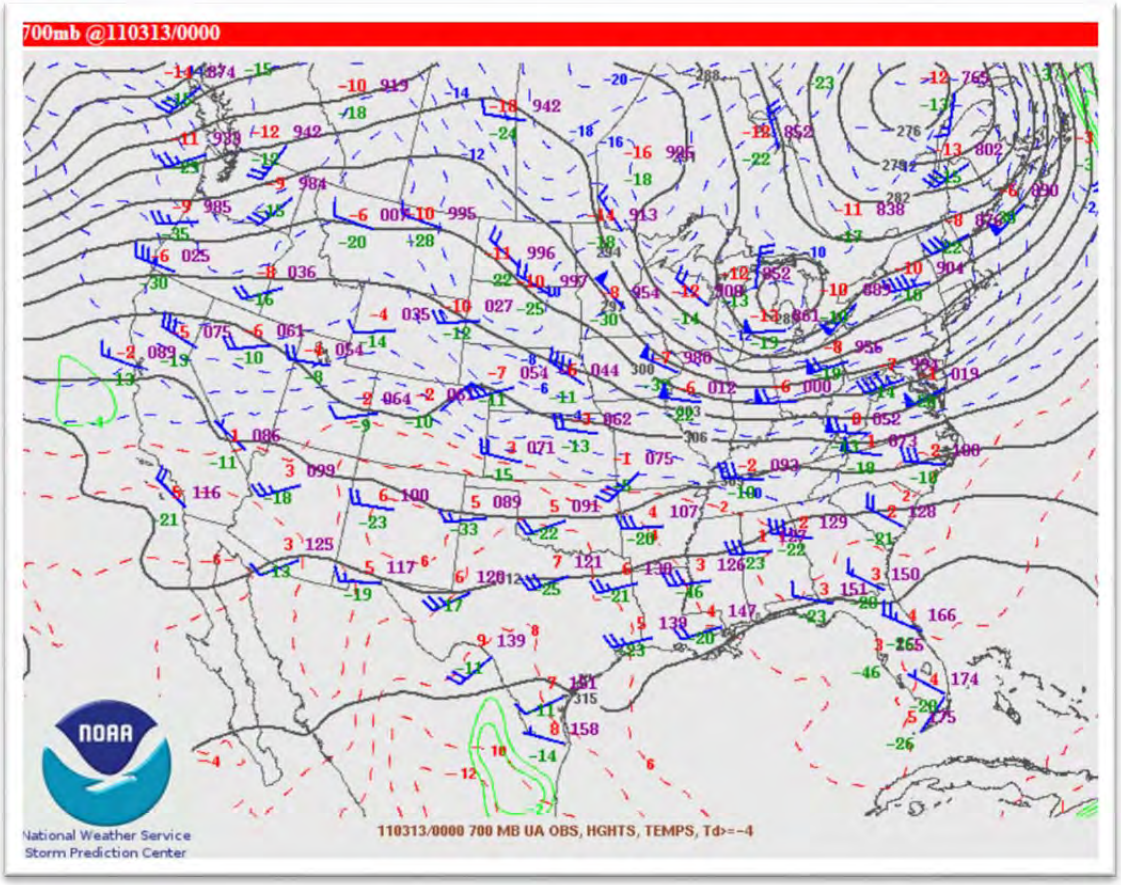


Figure 2.21 700 mb Chart at 1700 MST March 12, 2011

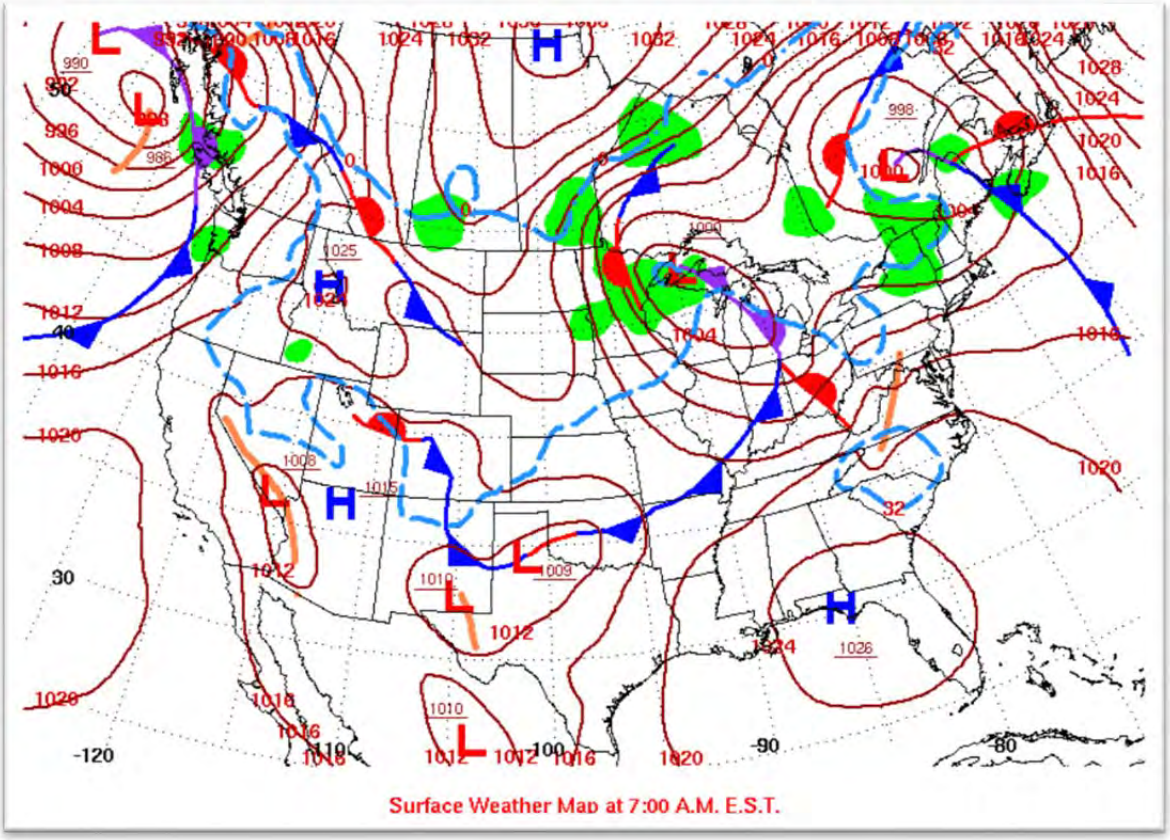


Figure 2.22 Surface Chart at 0500 MST March 12, 2011

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, Microsoft Access, was designed to be straightforward and easy for users to obtain data and provide updates. All data were quality-assured and submitted to MSI's UGWOS Data Manager for entry to the project database. A brief summary of procedures used is provided below.

3.1 Database Management

The overall goal of the data management effort was to create a well-documented system such that data could be readily input and easily accessed from the database. A Monitoring and Quality Assurance document was prepared and approved by all the project participants and can be found on the AQD website.

Each of the participants that provided data was responsible for reviewing and validating their respective data to Level 1 as described in "The Measurement Process: Precision, Accuracy, Validity" (Watson, 2001). This included flagging data during instrument downtime and performance tests, applying any adjustments for calibration deviation, investigating extreme values, and applying appropriate flags. Quality control (QC) codes used for the UGWOS data set are presented in Table 3-1. QC codes include simple validation codes as well as AQS null codes developed by the EPA.

Table 3-1

Data Quality Control Codes Used in UGWOS Database

QC	Description
V	Valid Data
M	Missing Data
I	Invalid Data
S	Suspect Data. Data appears to be a data spike or outside normal data range
U	Data which has not been validated - User is responsible for validation.
N	Instrument Noise detected in sub hourly data used to create hourly average
B	Below Detection Limit
AA	Sample Pressure out of Limits
AB	Technician Unavailable
AC	Construction/Repairs in Area
AD	Shelter Storm Damage
AE	Shelter Temperature Outside Limits
AF	Scheduled but not Collected
AG	Sample Time out of Limits
AH	Sample Flow Rate out of Limits
AI	Insufficient Data (cannot calculate)
AJ	Filter Damage
AK	Filter Leak
AL	Voided by Operator
AM	Miscellaneous Void
AN	Machine Malfunction
AO	Bad Weather
AP	Vandalism
AQ	Collection Error
AR	Lab Error
AS	Poor Quality Assurance Results
AT	Calibration
AU	Monitoring Waived
AV	Power Failure
AW	Wildlife Damage
AX	Precision Check
AY	Q C Control Points (zero/span)
AZ	Q C Audit
BA	Maintenance/Routine Repairs
BB	Unable to Reach Site
BC	Multi-point Calibration
BD	Auto Calibration

Table 3-1 Continued

Data Quality Control Codes Used in UGWOS Database

QC	Description
BE	Building/Site Repair
BF	Precision/Zero/Span
BG	Missing ozone data not likely to exceed level of standard
BH	Interference/co-elution/misidentification
BI	Lost or damaged in transit
BJ	Operator Error
BK	Site computer/data logger down
BL	QA Audit
BM	Accuracy check
BN	Sample Value Exceeds Media Limit
B	Below Detection Limit

Once the data were validated to Level 1, the data were prepared for submittal to the database in a form that clearly defined the time reference, averaging period, parameter names and units. The time reference for the database was in local standard time (Mountain Standard Time) and the averaging period reference was standardized to hour beginning (0 – 23). Standards for time reference, averaging period, parameter names and units 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 marked with the AQS Null code value or the value –999. Suspect data or data that haven't been validated (one-minute Mobile Trailer data) to Level 1 standards 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 AQD 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 UGWOS 2011 analyzers were routinely checked using a traceable transfer standard following operating procedures consistent with EPA guidelines. Automatic zero/span checks were conducted on all air quality analyzers used for this study. Automatic zero/span checks on the tall tower and tethered balloon analyzers were conducted nightly.

The status of the mini-SODAR was checked daily via remote access of the data. When problems were noted, AQD field staff was called upon to assist in correcting them. In addition, the mini-SODAR data were available in real time so that team members were able to use these 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 concentrations and adjusting the instrument to respond accurately to those concentrations. The calibration method for each of the air quality and meteorological variables is detailed in the Monitoring and Quality Assurance Plan (Appendix A).

Calibrations of the air quality analyzers used at the tall tower were performed upon initial installation and at the end of the study period. Additional calibrations were performed on an as-needed basis in the event of equipment repair or replacement. Calibrations of the analyzers at the tethered balloon site were conducted by ARS using their established operating procedures. All calibrations were performed in accordance with the manufacturer's recommendations and were consistent with US EPA guidelines. The linear regression slopes and intercepts from the calibrations performed on each analyzer during the course of the study were reviewed and used as necessary to adjust the raw data.

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 on the tall tower were calibrated using a water bath. The four portable temperature and humidity sensors used on the tethered balloon were compared with each other over the course of several days, to establish consistency between the sensors.

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 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.

3.2.2.1 Performance Audits

Performance audits were conducted during T&B Systems' 1st Quarter 2011 auditing effort for the AQD. Audit procedures and detailed results were included in the T&B Systems' report "First Quarter 2011 Quality Assurance Report for the Wyoming Department of Environmental Quality Air Monitoring Network." This included performance audits of the tall tower and tethered balloon analyzers. A summary of the results for the UGWOS-specific instrumentation is presented in Table 3-2.

Table 3-2

UGWOS 2011 Performance Audit Results for Tall Tower and Tethered Balloon Analyzers

	Parameter	Max. Diff. (%)	Response Slope	Response Intercept	Response R^2
Tower	Ozone	-0.5	0.994	0.000	1.0000
	NO	13.2	1.131	-0.001	0.9999
	NOx	13.1	1.126	0.000	1.0000
	NO_2	13.8	1.102	0.002	0.9999
	THC	2.5	1.030	-0.060	1.0000
Balloon	Ozone	-1.2	0.988	0.000	1.0000
	NO	-1.7	0.987	0.000	1.0000
	NO_x	-1.7	0.990	0.000	1.0000
	NO_2	-1.6	0.981	0.001	1.0000
	THC	6.9	1.019	0.061	0.9999

Access to the Tall Tower was limited, requiring a representative of the tower owner to be at the tower during all activities. Consequently, there was limited time to integrate the gas monitoring system, which included verifying the certification of the calibration system supplied by ARS. Rather than adjust the already stable response of the NO_x analyzer, it was decided to correct any inaccuracies in the response during processing and validation of the data. Further testing and review revealed that the NO_x analyzer was reading 5% high based on the calibrations. Consequently, NO, NO_2 and NO_x values were adjusted by dividing the values by 1.05. This brings the agreement with the audits to within 10%.

3.2.2.2 System Audits

A system audit of the field operations was conducted by Bob Baxter of T&B Systems at the start of the first Intensive Operational Period. The audit addressed the following field related elements:

- Siting of the equipment used for the intensive measurements
- Adherence of the field personnel to the Standard Operating Procedures
- Quality assurance and Quality Control procedures implemented
- Documentation of the field activities
- Data collection and chain of custody procedures

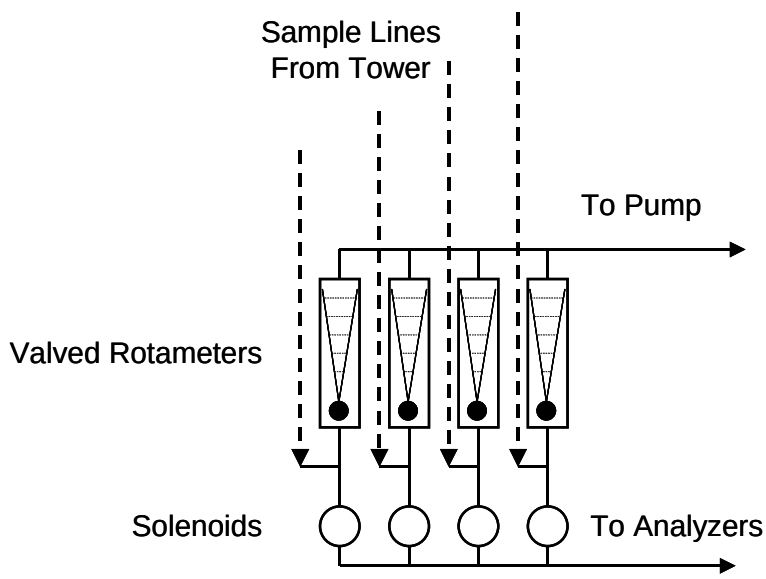
Observations from the system audits are presented below:

Tall Tower Air Quality and Meteorological Measurements

The exposure of the tower was excellent with no obstructions or local sources that could interfere with the measurements. Findings from the system audit review were as follows:

- The orientation of the wind sensor boxes for the bottom three levels was verified as 179°. The height of the top level was too high to accurately view.

- The long lines coming down from the tower were color coded to help prevent any confusion as where the lines terminated on the tower. The flow through the valve switching systems was then reviewed to determine if there were any portions of the systems that could contaminate or otherwise alter the sample before it entered the sample manifold leading to the analyzers. All tubing and connecting systems "touching" the sample were FEP Teflon® or stainless steel. The flow control and metering valves were located after a Tee assembly so that these components never contacted the sample that entered the analyzers. A simple schematic of the flow system is shown below.



- The calibration gas used in the calibration system was provided by ARS and was current with a recertification date of 12/19/2012.
- It was indicated that the entire system was checked just after installation to verify no vacuum leaks.
- All sample lines up to the termination points on the tower are solid with connection points. This minimizes any chance of leaks from the wrong levels.
- The programming of the data logging system and valve switching was observed during multiple cycles. The system does overlap the levels for about 5 seconds during a cycle to the next level to help minimize the chances for vacuum pulses to the analyzer inlets.

- The setting of the flows for each of the lines was quite sensitive, but once set, was stable.
- As a recommendation, one change to the system that could help monitor the performance is to add a data logger recorded vacuum gauge to the common manifold that runs to the analyzers. This would provide a measure of the variations during the system cycling and help determine if a flow issue or leak may be present. (Note that a vacuum recording system was not implemented, but routine checks included documenting the vacuum for each line using the NO_x analyzer sample pressure sensor.)

Tethered Balloon Air Quality and Meteorological Measurements

The tethered balloon site was located at a Shell Exploration facility adjacent to the M&N equipment yard and used one of the AQD mobile monitoring trailers built by ARS. The site is in the mix of a variety of surface and elevated sources and can be considered in one of the major source regions. Operators of the system were Dave Bush and Bill Knuth. The results of the audit are described below. Each of the observations was discussed with the field personnel during the course of the system audit.

- The tethered balloon system consisted of an 800 ft^3 tethered blimp that did not have the tail fin assembly attached to help maximize the lifting capacity. A sample tube bundle was attached to the tether line with pre-cut lengths of FEP Teflon® tubing to sample from pre-determined altitudes. The tether line and tube bundle was measured and marked to determine the altitude of the sample inlet. As the system was raised, additional 100-gram type weather balloons were attached to the sample line to provide additional lift for the inlet bundle. At the time of the audit, the system was near vertical as winds were light. There is a potential for these heights to lower if winds increase and the balloon train leans.
- It was indicated by the operator that an initial leak test of the system was performed and a minor leak was found and corrected before the data collection began.

- The valve switching, pump and data logging system were similar to the system at the tall tower system.
- The time on the data logging system used to control the system was set to PST rather than MST. This was noted by the operator and the data was adjusted to the correct time zone.
- A solenoid switching system had been provided by ARS to switch between the sampling through an intake on the roof of the trailer and the balloon sampling system. It was decided by the operator to not use the solenoid and connect directly to the analyzer manifold using a Teflon union to minimize any potential of leaks.
- The temperature/relative humidity sensors at each level were placed inside Styrofoam cups to minimize the solar radiation effects on the measurements. There does, however, remain the potential for a sensor to be exposed to sunlight if the cups rotate to the right direction. A review of the data on each sample day should help confirm if there was any interference.

Ozonesonde Preparation

The sonde preparation process was reviewed in the office area at the rear of the BLM building. Within the office, an area had been dedicated for the preparation, conditioning and testing of the ozonesondes. The preparation process was under the management of Jennifer Frazier. Key findings of the review are as follows. Each of these findings was discussed with the project personnel at the conclusion of the audit.

- The sonde preparation process followed detailed Standard Operating Procedures with the great apparent care in each of the steps. Results of the preparation were recorded in standard log sheets.
- The thermostat in the room used for preparation and storage of the samplers was set to about 10°C. The SOP and manufacturers recommendation for the storage of prepared sondes is to maintain them at 20 – 25°C. It was recommended to raise the room temperature to the sonde-specified range.

- The general procedure was to prepare a single sonde and deliver it to the field prior to each launch. It was recommended that at least two sondes be transferred to the field for each scheduled launch to allow for a backup sonde in the event that the first one failed, or for some other reason, a second sonde was needed.

Ozonesonde Launch

The first launch of the IOP was observed from the Boulder site and as with every first time, there are usually some associated minor issues. These issues encountered were resolved and changes made to the associated procedures to make the execution of the subsequent launches smoother. Key findings of the review are summarized below. As with all of the reviews performed, the findings were discussed with the project personnel at the conclusion of the audit. Personnel performing the launches were Ryan McCammon and Kirk Billings.

- Some minor issues were encountered in preparing the system for launch. These were resolved after talking with the system manufacturer and adding a step to the launch SOPs that was not included in the version followed at the site.
- It was recommended that a series of ground truth checks be performed by comparing sonde readings to the ozone values at the adjacent Boulder ozone monitor prior to launch. This check would indicate if the sonde was operating properly prior to the launch.
- The delivery of the sondes to the site was only a few minutes prior to the scheduled launch time. It was recommended that the schedule be changed so that the sondes are at the site at least 45 minutes prior to the scheduled time to allow for unforeseen issues that may arise.
- The first launch had a very rapid ascent rate (10-15 m/s). The manufacturer was contacted for a recommended change in the weigh-off device to bring the ascent rate down to a rate to achieve a one-second data point every 3 to 5 meters. With the new weight, the subsequent launch had an ascent rate closer to 5 m/s.

- The sonde software was not yet complete to integrate both the meteorology (winds, temperature, and humidity) and the ozone values. This was deemed not an issue, as all the data were complete and the merging could occur later when the software was finished.

mini-SODAR

The mini-SODAR has been operational at the site for over a year with good data recovery. Prior to arrival at the site the data were reviewed for internal consistency. While at the site a review of the level of the antenna was conducted. The results of all reviews are summarized below.

- The operational frequency of the mini-SODAR had been set to 4,500 Hz. A review of the data on Saturday 2/26 showed a spurious signal at about 4,375 Hz that occasionally showed up as higher winds in the upper reporting range gates. The frequency of the mini-SODAR was moved to 4,600 in an attempt to move out of the affected range. A subsequent review showed that the interfering frequency was moving in the range about 4,300 Hz ±300 Hz, with no real temporal pattern. For the most part the data are unaffected, but there are some periods when spurious data will need to be invalidated.
- The level of the mini-SODAR was verified.
- The array system monitor board did show two faulty speakers, but it was decided that the effect on the data will be negligible. The faulty speakers will be replaced at a future date.

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.

3.3 Data Validation

Each study participant was responsible for reviewing and validating their collected data. As described by Watson, et. al. (2001), these data were validated to Level 1 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.

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 billion for O_3, NO, NO_2, and NO_x
- Parts per trillion for HONO
- Micrograms per cubic meter for PM_{10}, $PM_{2.5}$, and speciated particulate
- Parts per million for methane, non-methane hydrocarbons, and total hydrocarbons
- Micrograms per cubic meter, parts per billion by volume, and parts per billion by Carbon for VOC data,
- SITE = Alpha-numeric site code identifier
- DATE = (MM/DD/YYYY)
- HOUR= Nearest whole begin hour (HH) (MST)
- TIME, START_TIME or END_TIME = Time stamp of data (HHMM) (MST)
- HEIGHT = Elevation in meters above MSL
- QC_CODE, (WS_QC, WD_QC, O3_QC, etc.) = As described in Table 3-1
- 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 discusses the results of meteorological and air quality measurements collected during the UGWOS 2011 field effort.

4.1 Summary of 2011 Meteorological and Air Quality Conditions and Comparison with Prior Years

This section describes meteorological and air quality conditions and measurements recorded during UGWOS 2011 and how they compared with previous UGWOS studies.

4.1.1 Upper Level Pressure Differences: 2011 vs. 2007-2010

This section will look at how the upper level pressure pattern during the 2011 UGWOS study differed from the previous four studies. During 2011, synoptic conditions leading up to elevated ozone episodes did not follow what had become the expected weather criteria seen in the previous four years. A more detailed study discussing this aspect will be performed in a separate report to the AQD[2] and will include an analysis of all weather parameters that have been studied and used to forecast elevated ozone since 2007.

Since the 700 mb pressure level at 10,000 feet is relatively close to the surface conditions over the study area where much of the surface elevation is at or above 7000 feet, this pressure level will be the focus of this comparison.

Prior to the first UGWOS study, objective criteria for forecasting elevated ozone episodes were developed based on several weather parameters. These criteria were developed after studying high ozone periods that occurred prior to 2007 and have been used as guidance in forecasting elevated ozone in the UGWOS study area since that time. The 700 mb criteria that have been used for forecasting elevated ozone are as follows:

[2] *Comparison of Weather Conditions During the 2011 Upper Green Winter Ozone Study to Past Study Seasons*, Meteorological Solutions, Inc., September 2011.

- Pressure level is 3060 meters or higher
- Temperature is between 0° and -8°C
- Wind speeds at less than 20 knots (~10 mps)

Table 4-1 contains the average 700 mb criteria for each of the study years (February and March only). These data were taken from maps developed from reanalysis data[3] provided by NOAA's Earth System Research Labs (ESRL).

Table 4-1

Averaged 700mb Parameters during UGWOS 2007-2011

February/March Period	Average700 mb Height (m)	Average 700 mb Temperature (^{0}C)	Average 700 mb Wind Speed (mps)
2007	3042	-5.1	10.4
2008	3018	-8.2	10.1
2009	3024	-6.5	9.6
2010	3023	-7.0	6.8
2011	3008	-8.2	10.8

This table shows that on average the height of the 700 mb level in 2011 was lower in the atmosphere than in any other study year. This is not unexpected as there were no strong high-pressure periods this year during these two months. With lower heights you could also expect temperatures to be colder and wind speeds to be stronger, and for 2011 the average 700 mb temperature was the coldest (equaling 2008) while the winds were the strongest of the five years.

During the 2007 through 2011 UGWOS study periods there were a total of thirty two days when IOP's occurred. UGWOS 2010 was the only year that did not see higher ozone levels develop. Table 4-2 provides the number of IOP's each year.

[3] *NCEP Reanalysis data provided by the NOAA/OAR/ESRL PSD, Boulder, Colorado, USA, from their Web site at http://www.esrl.noaa.gov/psd/*

Table 4-2

Intensive Operational Periods by Year

Year	Number of IOP's	Number of IOP Days	Number of Sites with 8-hour Ozone > 75 ppb	IOP dates
2007	1	6	0	March 14-19
2008	3	10	3 (for all Feb. Dates) 2	Feb.18 - 21 Feb. 27 - 29 March 10 - 12
2009	3	9	0	Feb. 3 - 5 Feb. 21 - 22 Feb. 28 – Mar. 3
2010	0	0	0	-
2011	2	7	7	Feb. 28 – Mar. 2 Mar. 9 - 12
Total	9	32	-	-

Using reanalysis data and incorporating only IOP days reveals the following averaged results for the 700mb criteria parameters in Table 4-3.

Table 4-3

Averaged 700mb Parameters during IOP Days 2007-2011

February/March Period	Average700 mb Height (m)	Average 700 mb Temperature (°C)	Average 700 mb Wind Speed (mps)
2007	3061	-1.9	11.2
2008	3064	-7.2	6.5
2009	3104	-4.8	7.7
2010	-	-	-
2011	3053	-9.1	10.7

Comparing the values to the criteria shown previously, it can be seen that each of the values for the 2011 study were outside of the suggested range. Heights were lower, temperatures colder and wind speeds higher than established criteria levels. Other years also had some of these criteria exceeded. During UGWOS 2007, averaged wind speeds were not only higher than the criteria of 10 mps but also higher than the averaged winds in the 2011 study. Elevated ozone forecasting criteria have only been established using a limited number of cases and need to be continually reviewed and refined.

4.1.2 Snow Cover in 2011 versus 2007-2010

Over the past five years of UGWOS studies it has become apparent that the snow cover that accumulates in the Upper Green River Basin during the winter and early spring months plays an important role in the development of elevated ozone.

The 2011 study appears to be a strong case in point. During January 15 through March 31, the weather pattern was progressive with the storm track bringing multiple storm systems into the western US. This persistent pattern did not allow stable, strong, high pressure features to develop or weaker high pressure to remain in place for more than a day or two over western Wyoming. Additionally this pattern allowed storms and thus unstable conditions, to bring frequent snowfall to much of the UGWOS study area. This lack of stability would normally mean weaker inversions and a lower probability that elevated ozone would develop. However, evidence would suggest that with significant snow cover in place during 2011, inversions were able to strengthen enough to remain intact during periods when the upper atmosphere was more unstable.

Figures 4.1 and 4.2 show the snow depth[4] for mid-January at the beginning of the 2011 study and for mid-March near the end of the study. Only the last few days of March showed significant melting and bare ground. Images showing the modeled snow depth over the UGWOS study area at the middle and end of each month can be found in Appendix C.

[4] Modeled Snow cover data provided by the NOHRSC, Chanhassen Minnesota, USA, from their Web site at http://www.nohrsc.noaa.gov/interactive/html/map.html.

The 2011 snow cover was the deepest of the five years at the beginning of the study period. The January 15, 2011 image (Figure 4.1) shows 4 to 8 inches over much of the lower basin (7100 feet and lower), with up to 30 to 40 inches in the higher foothills (8000 feet and above) including around the AQD Wyoming Range site. By February 15, 2011 the snow cover had decreased to below what was observed in other years, with some bare spots showing up south of La Barge. Elsewhere in the lower basin amounts ranged from a trace to 8 inches. The foothills remained similar in depth to January 15, at up to 30 to 40 inches. Only the 2009 study period had less snow with much of the basin indicating a trace to 2 inches or less that year. The foothills showed similar amounts in 2009 to 2011. In fact all the years except 2010 which showed lower snow depths had similar amounts of snow in the foothills on this date. By March 15 (Figure 4.2) the snow cover was again at a level which was the deepest of the five study years for mid-March. There were wide spread amounts between 4 and 12 inches in the lower basin except south of La Barge where bare areas were common. The higher foothills, including around the Wyoming Range site had depths of 40 to 50 inches, and these areas had the deepest snow cover of the five study periods as well.

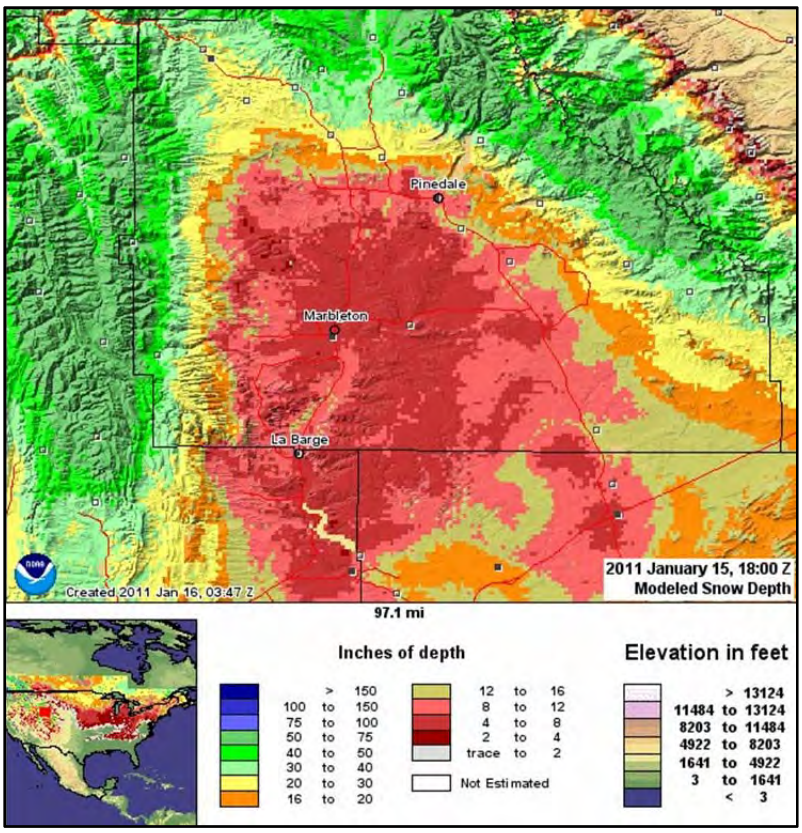


Figure 4.1 January 15, 2011 UGWOS Area Snow Cover

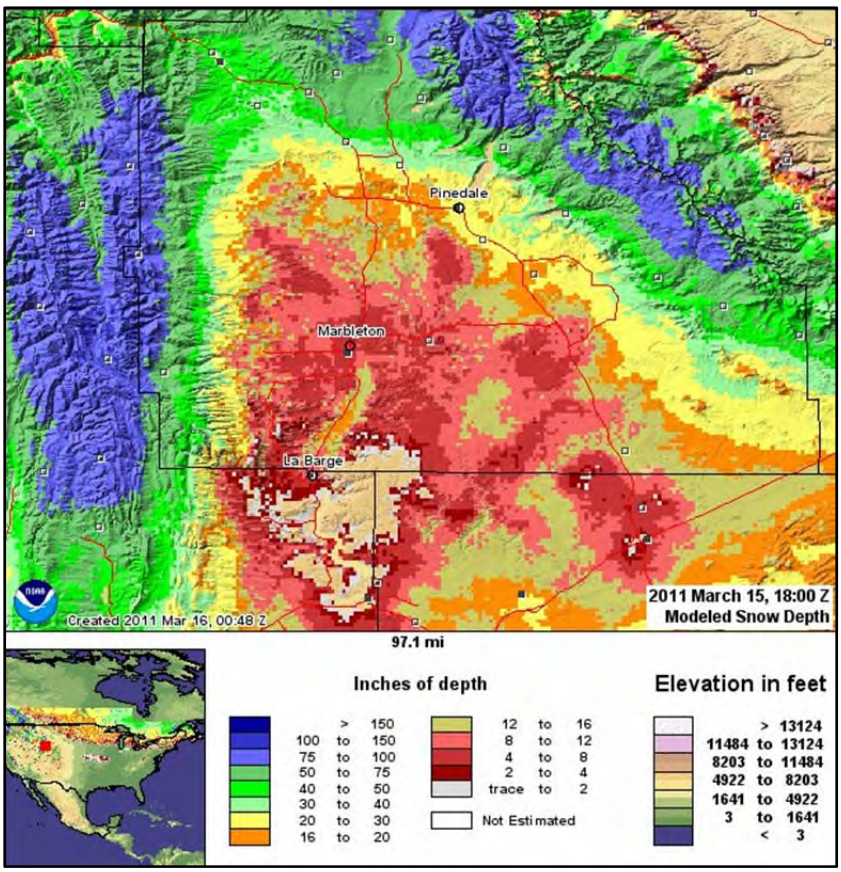


Figure 4.2 March 15, 2011 UGWOS Area Snow Cover

In summary, the snow pack in 2011 was generally the deepest of the five year period although this was not consistently so as there were times, especially in February when other years had as much or more, particularly in the lower basin elevations. The deepest snow cover in the lower basin occurred during the first few days of the study around January 15 to 17 and then again from February 20 through about March 15, 2011. Snow depths during these periods were at 4 to 16 inches on the ground over most of the lower elevations while the higher foothills had 30 to 50 inches on the ground. It is interesting to note that some of the deepest snow cover was in place when the two IOP's occurred.

4.1.3 Comparison of Ozone in 2011 with 2005-2010

Ozone data have been recorded at permanent monitoring sites in the UGRB since 2005. The Jonah, Boulder (BD), Daniel (DN), Pinedale (PD), Juel Springs, and Wyoming Range (WR) sites utilize Federal Equivalent Method (FEM) air quality monitors. After the conclusion of the 2009 UGWOS campaign, the monitoring equipment at Jonah was dismantled and moved to its current location at Juel Springs. Eight-hour ozone averages and maxima 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, Boulder, Daniel, Pinedale, Juel Springs, and Wyoming Range

January	**Average 8-Hour Ozone (ppb)**						**Maximum 8-Hour Ozone (ppb)**					
Year	**Jonah**	**BD**	**DN**	**PD**	**Juel**	**WR**	**Jonah**	**BD**	**DN**	**PD**	**Juel**	**WR**
2005	35	NA	NA	NA	NA	NA	78	NA	NA	NA	NA	NA
2006	33	41	43	NA	NA	NA	49	67	53	NA	NA	NA
2007	27	43	40	NA	NA	NA	57	71	53	NA	NA	NA
2008	29	39	42	NA	NA	NA	47	58	56	NA	NA	NA
2009	24	34	37	NA	38*	NA	52	55	48	NA	64*	NA
2010	34†	38	39	36	40	NA	57	69	49	61	55	NA
2011	NA	39	41	40	42	45	NA	69	59	62	63	54
February	**8-Hour Ozone (ppb)**						**8-Hour Ozone (ppb)**					
Year	**Jonah**	**BD**	**DN**	**PD**	**Juel**	**WR**	**Jonah**	**BD**	**DN**	**PD**	**Juel**	**WR**
2005	42	51	NA	NA	NA	NA	98	89	NA	NA	NA	NA
2006	39	48	49	NA	NA	NA	93	71	82	NA	NA	NA
2007	29	42	40	NA	NA	NA	46	59	57	NA	NA	NA
2008	40	54	50	NA	NA	NA	102	122	76	NA	NA	NA
2009	33	42	43	NA	40*	NA	69	67	64	NA	62*	NA
2010	44†	51	46	42	46	NA	54	62	52	57	53	NA
2011	NA	46	47	44	47	51	NA	87	74	59	68	80
March	**8-Hour Ozone (ppb)**						**8-Hour Ozone (ppb)**					
Year	**Jonah**	**BD**	**DN**	**PD**	**Juel**	**WR**	**Jonah**	**BD**	**DN**	**PD**	**Juel**	**WR**
2005	40	48	NA	NA	NA	NA	58	71	NA	NA	NA	NA
2006	44	48	50	NA	NA	NA	68	67	71	NA	NA	NA
2007	32	44	40	NA	NA	NA	44	65	55	NA	NA	NA
2008	39	53	50	NA	NA	NA	98	102	75	NA	NA	NA
2009	39	46	43	NA	42*	NA	63	70	67	NA	67*	NA
2010	48†	53	48	41	49	NA	55	66	54	57	53	NA
2011	NA	54	52	51	53	55	NA	123	85	89	94	83

* Temporary Mesonet site with 2B ozone analyzer prior to permanent site.
† BAM trailer with FEM monitor after permanent site equipment moved to Juel Springs
NA – Data not available

With the exception of Boulder, the average eight-hour ozone level for each month in 2011 was greater than or equal to the average of the previous years for the corresponding month. The maximum eight-hour ozone concentration for each site in March 2011 was higher than any previous March - the highest being 123 ppb at Boulder.

4.1.4 Comparison of NO_x and PM during UGWOS 2011 with 2006-2010

Average monthly NO and NO_2 concentrations at AQD monitoring sites in the UGRB are presented in Table 4-5. The average NO_2 concentrations measured at Boulder and Daniel in March 2011 were higher than those observed in any previous March.

Table 4-5

Monthly Average One-Hour NO and NO_2 Concentrations by Year for Jonah/BAM, Boulder, Daniel, Pinedale, Juel Springs, and Wyoming Range

Jan.	1-Hour NO (ppb)						1-Hour NO_2 (ppb)					
Year	**Jonah/ BAM**	**BD**	**DN**	**PD**	**Juel**	**WR**	**Jonah/ BAM**	**BD**	**DN**	**PD**	**Juel**	**WR**
2006	11.2	1.7	0.04	NA	NA	NA	16.9	7.2	0.5	NA	NA	NA
2007	24.6	0.9	0.05	NA	NA	NA	22.6	4.5	0.7	NA	NA	NA
2008	27.2	NA	0.01	NA	NA	NA	26.2	NA	0.2	NA	NA	NA
2009	20.6	2.5	0.01	NA	NA	NA	24.4	5.6	0.2	NA	NA	NA
2010	4.9*	2.1	NA	0.8	1.3	NA	11.2*	8.0	0.7	4.3	2.9	NA
2011	NA	1.7	0.02	1.6	0.6	0.1	NA	7.0	0.1	3.9	3.3	0.3
Feb.	**1-Hour NO (ppb)**						**1-Hour NO_2 (ppb)**					
2006	16.3	0.9	0.04	NA	NA	NA	18.1	4.8	0.7	NA	NA	NA
2007	19.6	0.4	0.01	NA	NA	NA	16.8	1.7	0.1	NA	NA	NA
2008	24.0	NA	0.00	NA	NA	NA	19.0	NA	0.1	NA	NA	NA
2009	10.6	1.9	0.00	NA	NA	NA	16.2	5.7	0.4	NA	NA	NA
2010	8.1	1.3	NA	0.4	1.3	NA	10.4	4.6	0.3	2.6	2.9	NA
2011	NA	0.8	0.02	1.8	0.5	0.1	NA	4.8	0.6	5.5	2.5	1.0
Mar.	**1-Hour NO (ppb)**						**1-Hour NO_2 (ppb)**					
2006	0.3	0.01	4.4	NA	NA	NA	9.0	1.8	0.4	NA	NA	NA
2007	0.2	0.00	20.3	NA	NA	NA	16.1	0.7	0.05	NA	NA	NA
2008	0.03	0.00	13.1	NA	NA	NA	14.6	0.9	0.02	NA	NA	NA
2009	0.3	0.00	2.6	NA	NA	NA	6.9	2.0	0.2	NA	NA	NA
2010	0.2	NA	7.0	0.9	1.3	NA	6.6	1.7	0.4	1.9	1.2	NA
2011	0.9	0.00	NA	2.4	0.4	0.1	NA	4.9	0.5	7.4	2.5	0.8

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

Average monthly PM_{10} and $PM_{2.5}$ concentrations at AQD monitoring sites in the UGRB are presented in Table 4-6. Levels of PM_{10} in February and March 2011 were higher at Boulder than those during any previous year. Concentrations of $PM_{2.5}$ at Pinedale were higher for each month in 2011 than the same corresponding month in previous years.

Table 4-6

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

January	**Average PM_{10} (µg/m^3)**			**Average $PM_{2.5}$ (µg/m^3)**	
Year	**Boulder**	**Daniel**	**Wyoming Range**	**Pinedale**	**Wyoming Range**
2006	7.1	5.0	NA	NA	NA
2007	NA	5.2	NA	NA	NA
2008	6.9	6.4	NA	NA	NA
2009	6.7	4.9	NA	4.1	NA
2010	6.7	4.3	NA	4.1*	NA
2011	6.7	4.4	1.6	4.4	0.8
February	**Average PM_{10} (µg/m^3)**			**Average $PM_{2.5}$ (µg/m^3)**	
2006	7.4	6.1	NA	NA	NA
2007	5.0	4.8	NA	NA	NA
2008	7.4	5.7	NA	NA	NA
2009	6.9	6.6	NA	3.6	NA
2010	6.3	4.4	NA	2.4	NA
2011	10.3	6.4	4.4	5.1	2.1
March	**Average PM_{10} (µg/m^3)**			**Average $PM_{2.5}$ (µg/m^3)**	
2006	7.7	6.8	NA	NA	NA
2007	8.5	6.7	NA	NA	NA
2008	7.5	6.7	NA	NA	NA
2009	10.9	11.2	NA	4.3	NA
2010	8.2	6.6	NA	3.0	NA
2011	11.1	7.3†	5.7	5.5	3.1

* January 15-31, 2010.
† March 1-20, 2011.
NA – Data not available

4.1.5 Methane/Total Non-Methane Hydrocarbons

Methane/THC measurements using a continuous analyzer were made at three locations during UGWOS 2011: the Tall Tower, the tethered balloon/Mobile Trailer, and the Boulder site. Only the Boulder site made these measurements during prior years to 2011, and then only during 2010 when very little ozone activity was observed. Figure 4.3 presents a comparison of the NMHC and ozone concentrations for 2010 and 2011 for a period of common days for the two years showing 24-hr NMHC average concentrations and peak 8-hour ozone concentrations. NMHC concentrations for 2011 are considerably higher than those for 2010. (This may be due to stronger inversions and the corresponding lower mixing heights that were likely created by the more extensive snow cover during 2011 compared to 2010). In 2010, the snow cover had effectively ended by March 5, and the lack of any significant NMHC concentrations after March 5, 2010 is notable, especially when compared with 2011. Furthermore, ozone concentrations appear highly correlated to NMHC, though NMHC is likely a good surrogate for all ozone precursors. The plot clearly demonstrates the relationship between ozone precursors (NMHC) and ozone formation.

In reviewing the Boulder 2011 hydrocarbon data, a strong linear correlation between NMHC and THC was noted on high ozone days. To illustrate this relationship, Figure 4.4 compares hourly average NMHC and THC data for all hours associated with the IOPs (daytime hours when ozone formation was typically occurring). As discussed later in the report, this relationship is important in interpreting some of the continuous NMHC data obtained by the tethered balloon. In addition, it supports observations later in the report that the composition of hydrocarbons within the mixing layer may be fairly uniform.

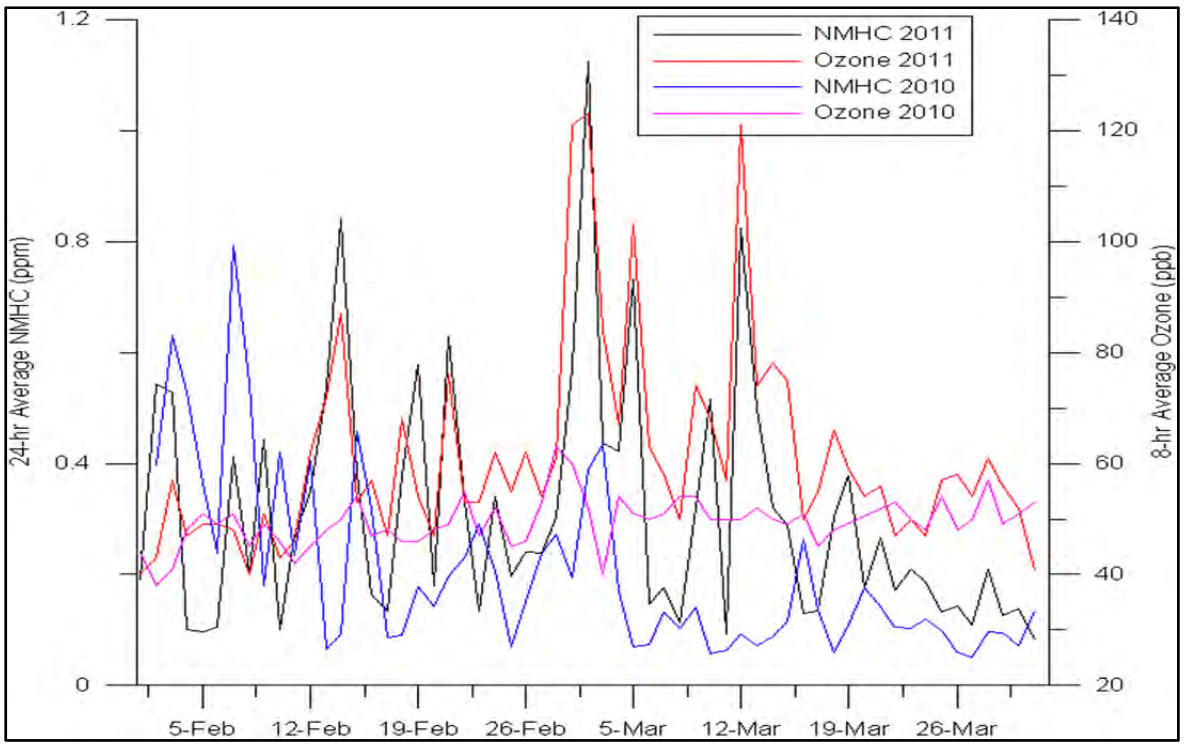


Figure 4.3 Comparison of 2010 and 2011 NMHC

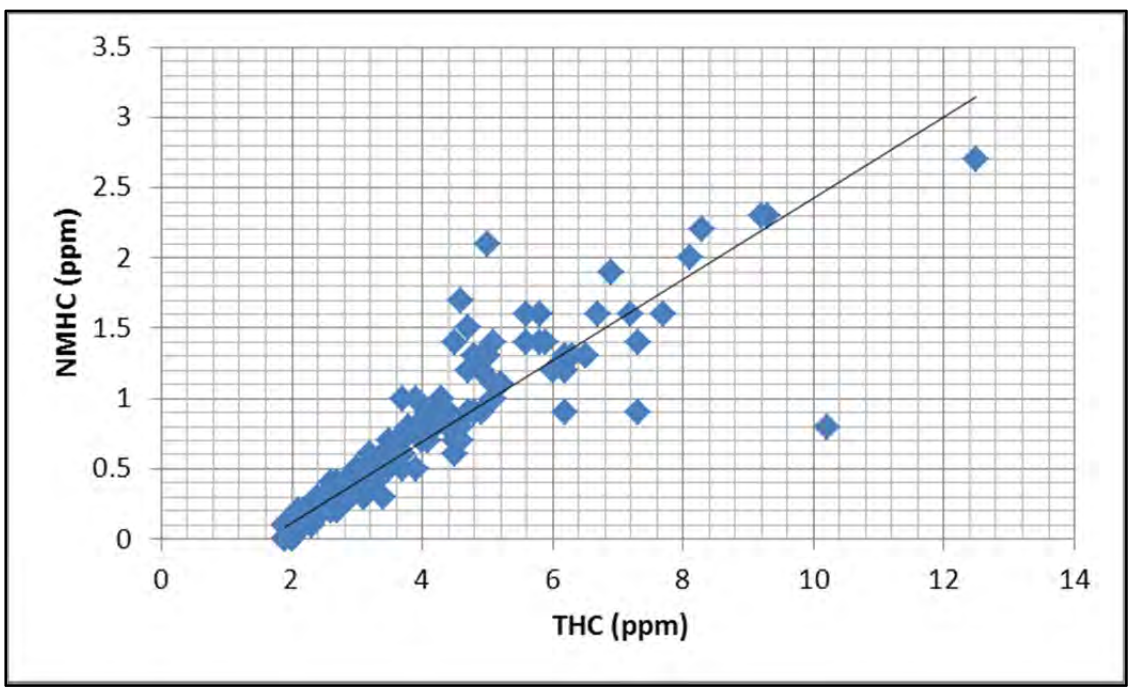


Figure 4.4 Boulder One-Hour Average Hydrocarbon Concentrations During UGWOS 2011 IOP Hours

4.2 Ozone Spatial and Temporal Distribution

There were 13 days during the UGWOS 2011 campaign that the US EPA ozone eight-hour standard (75 ppb) was exceeded at any air quality monitoring station in the UGRB. There were 25 days during UGWOS 2011 when eight-hour ozone concentrations exceeded 65 ppb. The maximum eight-hour and one-hour ozone concentrations at all UGWOS 2011 monitoring sites presented in Figure 4.5.

The eight-hour ozone concentration at Boulder exceeded 65 ppb on more days than any other site. Boulder also led in the number of days that eight-hour ozone levels exceeded 75 ppb. For all sites, the median number of days that the eight-hour ozone exceeded 65 ppb was 10 days and the median number of days that the eight-hour ozone exceeded 75 ppb was 3 days. Figure 4.6 illustrates the count of days that each site experienced elevated ozone during UGWOS 2011.

Table 4-7 shows maximum eight-hour average ozone concentrations on any day where it exceeded 65 ppb at any site in the UGRB. The UGRB network daily maximum is indicated in the right-most column of the table. Table 4-7 shows that elevated ozone levels were often observed at multiple sites on the same day. On March 2, eight-hour average ozone concentrations exceeded 65 ppb at all nine UGWOS 2011 monitoring sites.

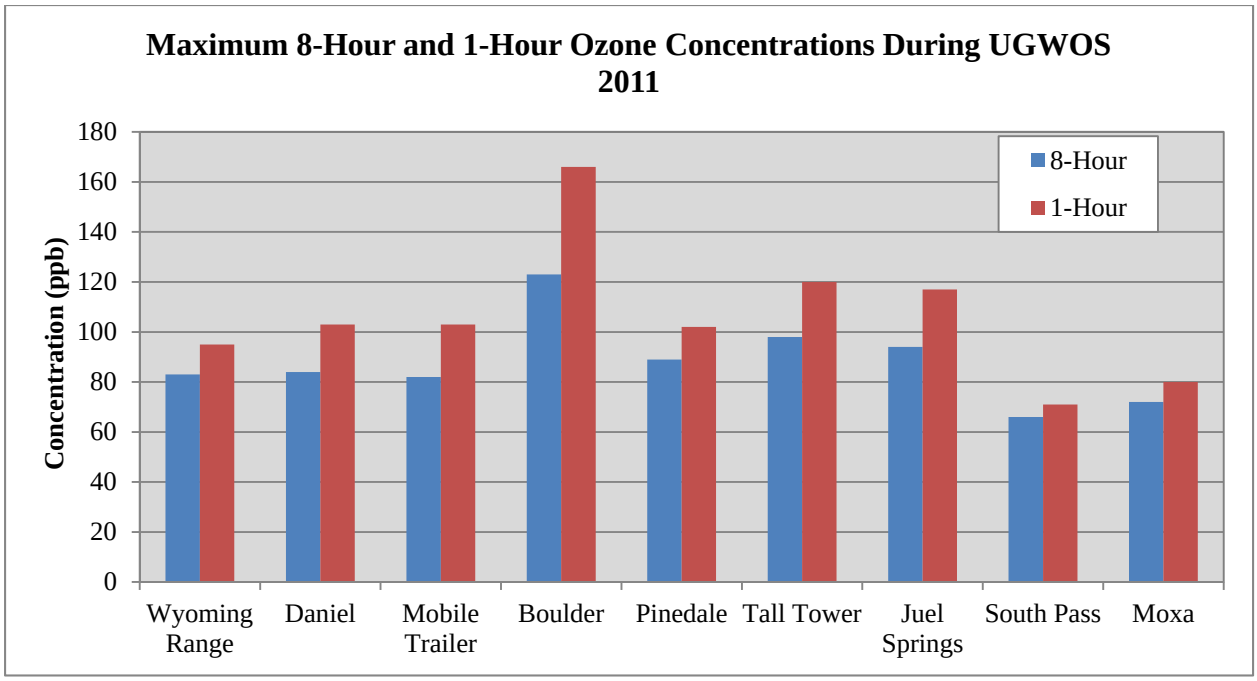


Figure 4.5 Maximum Eight-Hour and One-Hour Average Ozone Concentrations in the UGRB during UGWOS 2011

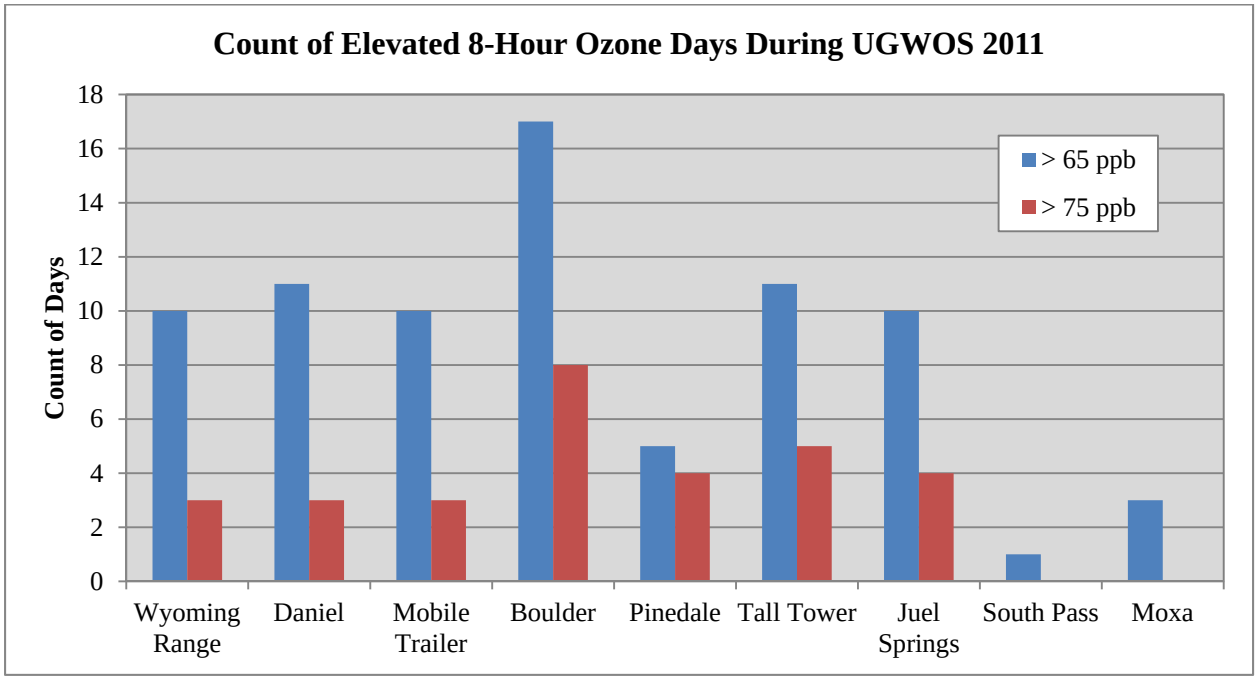


Figure 4.6 Count of Days when the Eight-Hour Ozone Concentration Exceeded 65 ppb and 75 ppb at all Sites during UGWOS 2011

Table 4-7

Maximum Eight-hour Average Ozone Concentrations (ppb)

for Wyoming Range, Pinedale, Juel Springs,

Daniel, Boulder, Mobile Trailer, Moxa, South Pass, and Tall Tower on Days

When at Least One Site Recorded Concentrations > 65 ppb

Station	Wyo Range	PD	Juel	DN	BD	Mobile Trailer	Moxa	South Pass	Tall Tower	Network Max
Jan 29	50	62	63	44	69	61	43	52	71	**71**
Feb 12	52	56	57	60	62	71	51	53	58	**71**
Feb 13	53	53	63	66	72	64	48	53	61	**72**
Feb 14	64	59	67	63	87	82	58	57	67	**87**
Feb 15	80	51	59	74	53	50	54	57	59	**80**
Feb 16	67	57	57	62	57	56	53	62	59	**67**
Feb 18	64	55	56	64	68	68	47	59	59	**68**
Feb 21	50	45	52	46	77	72	45	50	51	**77**
Feb 26	58	53	68	53	62	57	56	57	68	**68**
Feb 28	72	56	61	68	61	46	56	59	63	**72**
Mar 1	66	83	73	69	121	51	71	64	77	**121**
Mar 2	79	89	94	75	123	66	72	66	98	**123**
Mar 3	66	70	65	71	85	82	50	54	65	**85**
Mar 4	53	48	53	49	67	51	48	53	57	**67**
Mar 5	66	80	76	63	103	79	55	57	82	**103**
Mar 6	61	57	59	77	63	61	53	53	61	**77**
Mar 9	55	76	67	56	74	49	52	54	67	**76**
Mar 10	83	62	69	84	68	52	63	60	70	**84**
Mar 12	57	56	85	56	121	54	67	60	91	**121**
Mar 13	54	55	57	53	74	56	53	55	59	**74**
Mar 14	57	65	68	79	78	75	51	55	70	**79**
Mar 15	63	65	85	67	75	71	51	55	80	**85**
Mar 18	64	64	59	70	66	67	54	60	62	**70**
Mar 23	69	57	60	60	50	54	53	56	62	**69**
Mar 24	66	61	59	62	47	63	53	61	61	**66**

Values > 65 in Yellow
Values > 75 in Red

Figure 4.7 presents the rolling eight-hour average ozone levels for all monitoring sites during UGWOS 2011. Elevated ozone concentration maximums occurred most frequently at Boulder and the Tall Tower.

Figure 4.8 presents the daily maximum eight-hour average ozone concentrations for all sites during UGWOS 2011. The Moxa monitoring site observed the lowest daily maximum eight-hour average ozone concentration 53% of the time.

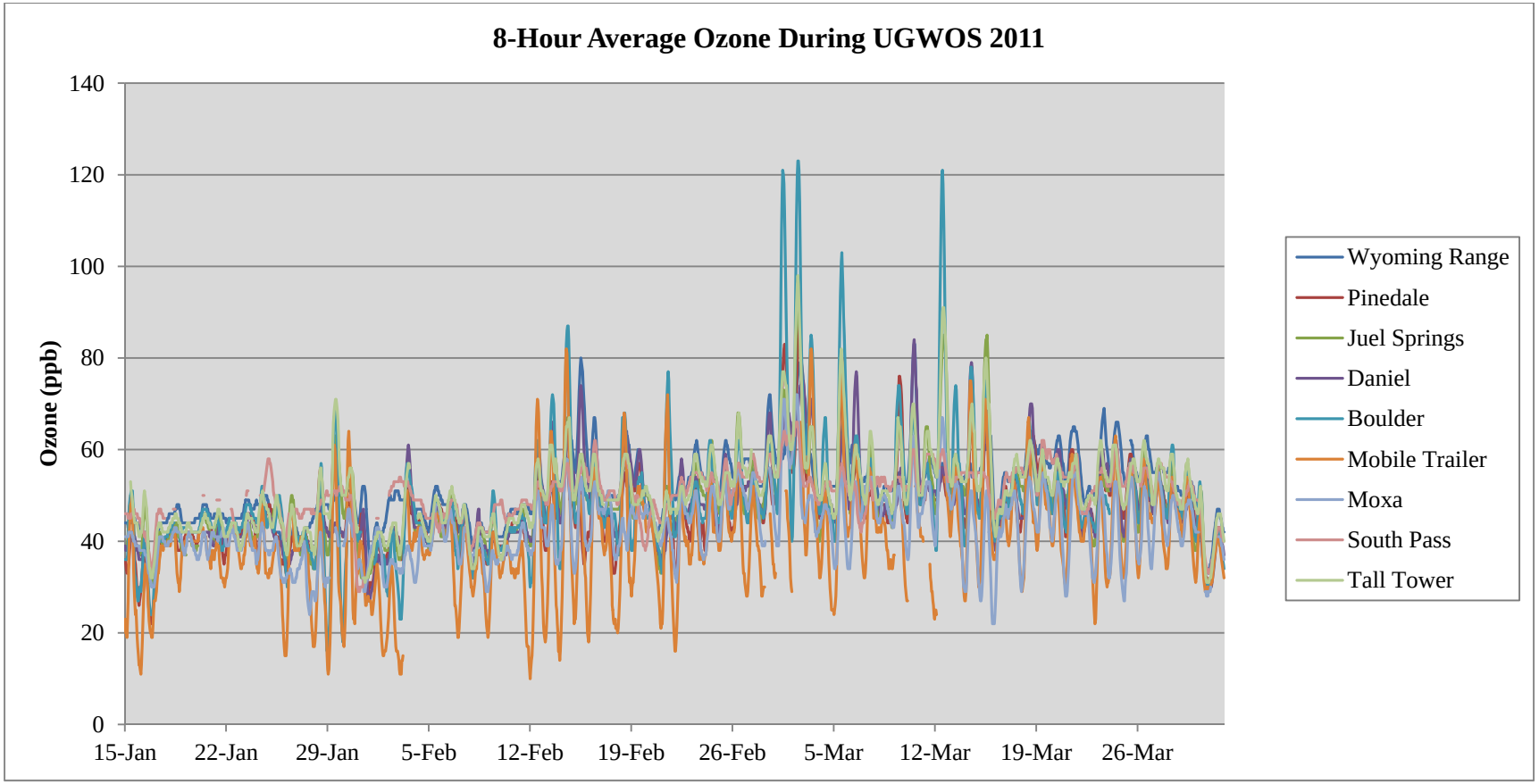


Figure 4.7 Running Eight-Hour Ozone Concentrations during UGWOS 2011

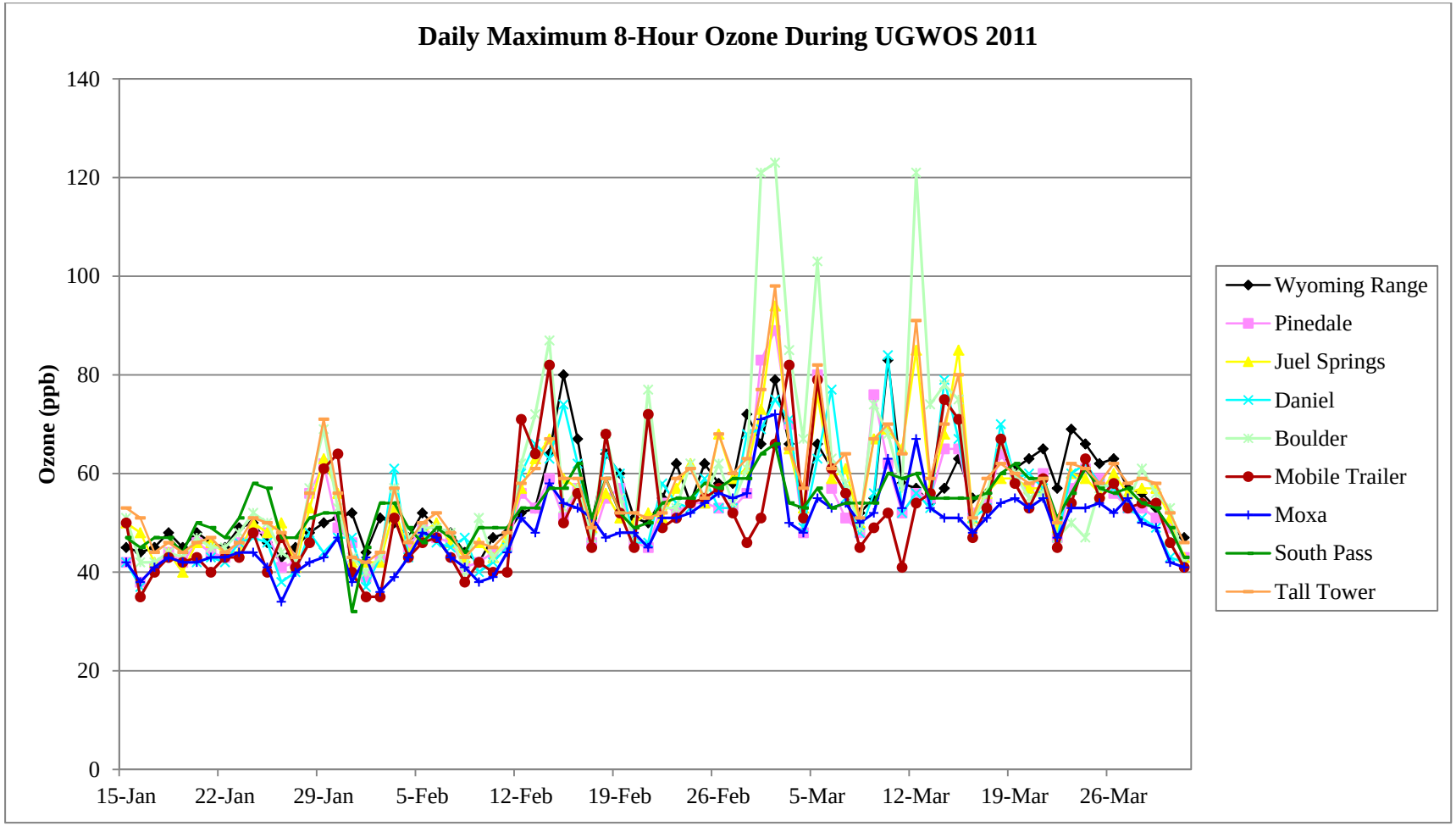


Figure 4.8 Daily Maximum Eight-Hour Ozone Concentrations, UGWOS 2011

4.2.1 Diurnal Ozone Patterns during Intensive Operational Periods

For each IOP, plots of the composite one-hour average ozone from each site were created and are presented in Figure 4.9 and Figure 4.10. Early morning ozone minimums were usually in the 40-60 ppb range, except for the Mobile Trailer site, which likely experienced significant NO_x scavenging due to its location within an area of heavy industrial support. Morning ozone production generally started between 0800 and 1100 and peaked in the mid-afternoon or early evening between 1400 and 1900. Ozone maximums ranged from 60-90 ppb except for Boulder which averaged a peak one-hour ozone level in excess of 120 ppb during IOP 1.

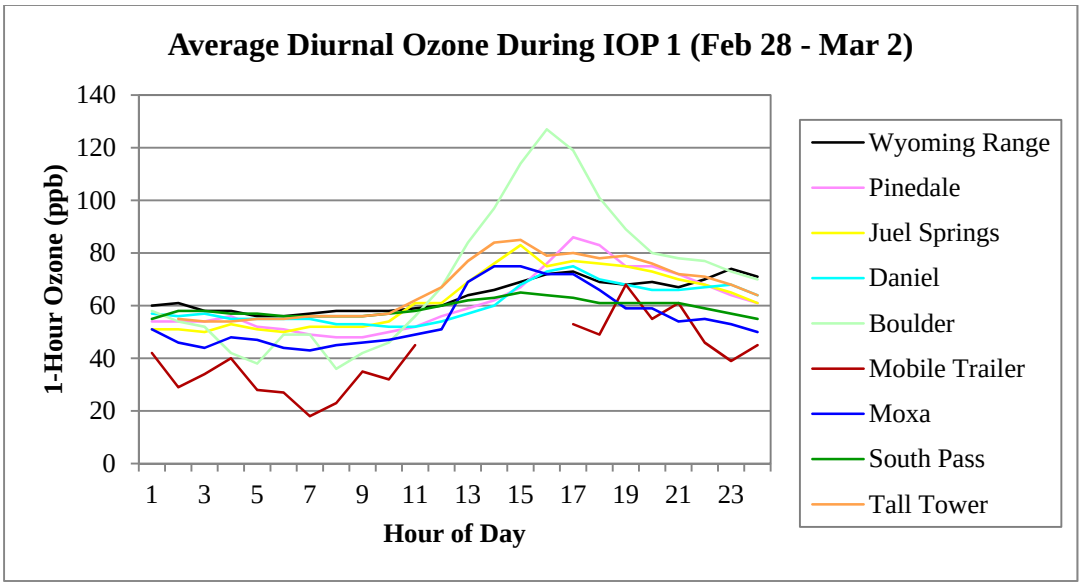


Figure 4.9 Average Diurnal One-Hour Ozone during IOP 1 (February 28 – March 2)

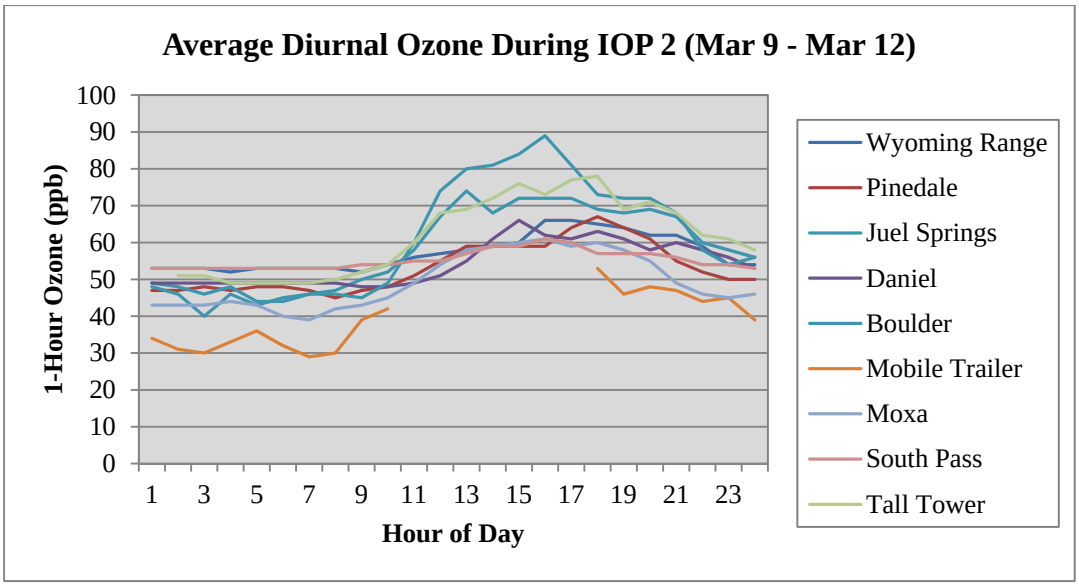


Figure 4.10 Average Diurnal One-Hour Ozone during IOP 2 (March 9 – March 12)

4.2.2 Discussion of Spatial and Temporal Distribution of O_3 during Intensive Operational Periods

The first IOP occurred from February 28 to March 2, 2011 and a time series of one-hour average ozone concentrations from all sites is shown in Figure 4.11. The first day of IOP 1 was characterized by elevated ozone levels in the northwest portion of the UGWOS domain at Daniel and Wyoming Range with modest levels of ozone elsewhere. Ozone development was more pronounced in the eastern portion of the domain on the second and third days of IOP 1 at Boulder, Pinedale, the Tall Tower, and Juel Springs. Ozone levels on the third day of IOP 1 were generally the highest of the three days with Boulder recording a one-hour average ozone concentration of 166 ppb.

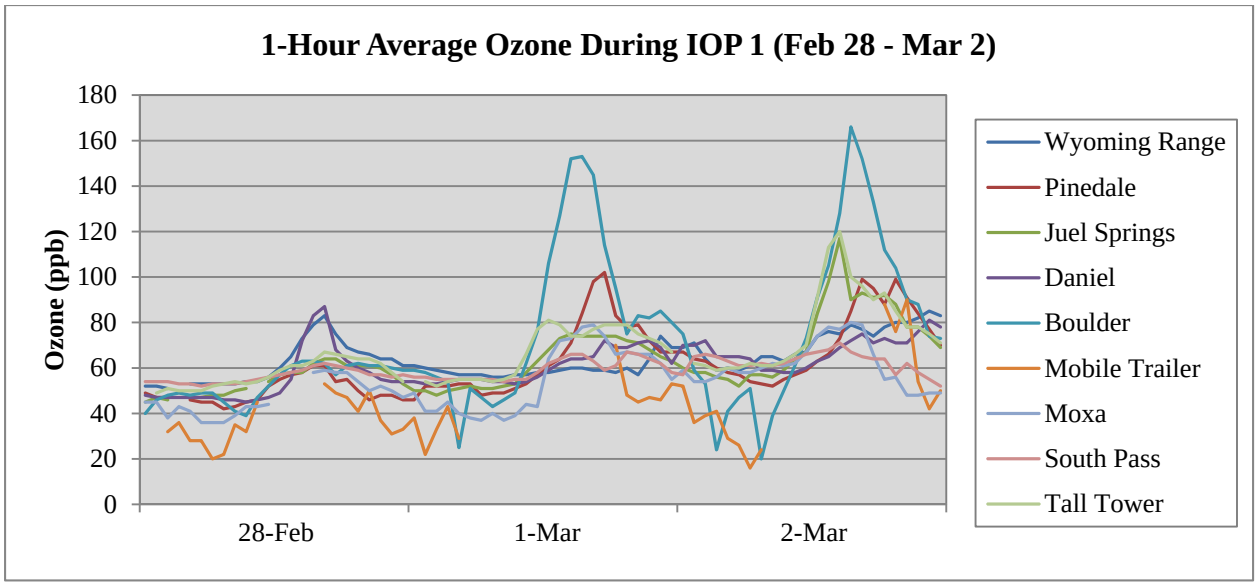


Figure 4.11 One-Hour Average Ozone during IOP 1 (February 28 – March 2)

The morning minimum ozone levels generally increased slightly each of the three mornings during IOP 1, suggesting that residual ozone from the previous day was gradually accumulating during the period. Sharp drops in ozone at the Mobile Trailer and Boulder suggest evidence of NO_x scavenging occurring in the early morning hours during IOP 1.

"Scavenging" occurs when oxides of nitrogen react with ozone to produce nitrogen dioxide effectively reducing the ambient concentration of ozone. Boulder and the Mobile Trailer are located near areas with NO_x-emitting facilities, which could contribute to possible NO_x scavenging of the ambient ozone measured at these sites.

The second IOP occurred from March 9 to March 12, 2011. One-hour average ozone concentrations at all sites during this period are shown in Figure 4.12. The first day of IOP 2 was characterized by elevated ozone located in the eastern portion of the domain at Pinedale, Boulder, and the Tall Tower. On the second day of IOP 2, elevated ozone occurred first at Daniel, then at Wyoming Range. Wind data from these sites confirms that southeast flow was transporting ozone and ozone precursors up the western slope of the UGRB. Only modest rises in ozone levels were seen in the eastern portion of the domain on the second day of IOP 2.

The third day of IOP 2 was the least active ozone day during the period, with Juel Springs ant the Tall Tower recording levels of ozone slightly less than 80 ppb. The fourth day of IOP2 saw the highest levels of ozone during the period, with Boulder observing a one-hour ozone concentration of 143 ppb. The Tall Tower and Juel Springs also observed significantly elevated levels of ozone on the fourth day of IOP 2. Winds during this day were generally light and variable.

As in IOP 1, there is evidence of NO_x scavenging at Boulder and the Mobile Trailer. However, there is less evidence of nighttime residual ozone carryover than there was during IOP 1.

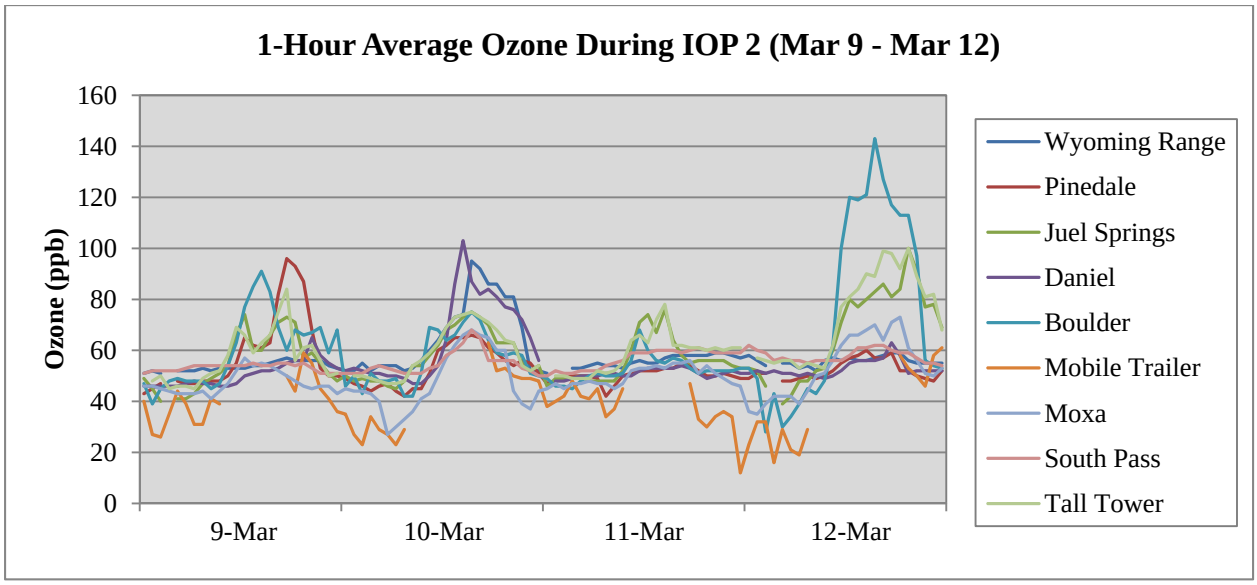


Figure 4.12 One-Hour Average Ozone during IOP 2 (March 9 – March 12)

4.2.3 Vertical Distribution of Ozone, Ozone Precursors, and Mixing Height

This section provides information about the vertical distribution of ozone, ozone precursors, and mixing height based on data from the tall tower, tethered balloon, ozonesondes, and mini-SODAR primarily during intensive operational periods.

4.2.3.1 Tethered Balloon

Two very successful IOPs provided additional insight into the vertical structure of ozone and ozone precursors during high ozone episodes. Time/height cross-sectional plots are presented for each of the IOP days. These plots present contoured isopleths of ozone, NO, NO_x, NMHC, and THC concentrations, as well as delta temperature readings, reported at the 12-minute frequency described in Section 2.2.2. In viewing the tethered balloon plots, the following should be noted:

- All data are shown as "period beginning".
- Heights on the left hand axis are in meters.
- In displaying the temperature profile, plotting delta temperature (delta-T) rather than temperature (T) was determined to be easier to interpret when evaluating the stability of the layer. Delta T is calculated as the temperature at a given level minus the temperature at the surface. For example, at the balloon site the delta-T value for the 67-meter level was calculated as $T_{67m} - T_{4m}$. Thus, greater than zero delta-T values represent a well-defined inversion and stable conditions.
- In reviewing the NMHC data, it is important to remember the methodology used by the hydrocarbon analyzer to produce the NMHC data, which involves taking 30 seconds to measure methane, followed by 30 seconds to measure THC, during which NMHC is calculated as the difference between THC and methane. In the highly fluctuating near-source environment of the balloon measurements, it is entirely possible for the measured methane concentration to be higher than the measured THC concentration for a given cycle, causing the reported NMHC concentration to be reported as a negative value.

Conversely, THC values may be high compared to the corresponding methane readings, causing unrepresentatively high NMHC readings. Both NMHC and THC concentrations are presented in the plots. The NMHC data provide information on the concentration levels of VOCs associated with ozone development. However, in some cases, these THC data may actually better represent the vertical structure of the VOC ozone precursors, due to the high correlation between NMHC and THC as noted above (Section 4.1.5).

- The wind data presented for the tethered balloon is from the mini-SODAR located at the Boulder site. While the Boulder site is located about 7 km from the balloon site on a ridge that is 40 meters higher than the balloon site base, a comparison of surface winds between the balloon and mini-SODAR sites shows relatively good agreement even under the light wind conditions encountered during the IOPs. Figure 4.13 shows a comparison of 10 meter wind speed and direction for all daytime IOP hours, with a prevailing one-to-one relationship apparent. To hypothetically account for the difference in elevation, 30 meters has been added to the mini-SODAR level heights (e.g. data reported for 30 meters is displayed as 60 meters.
- Estimated hourly average mixing heights from the mini-SODAR fax displays are shown as "+" on the plots. Again, 30 meters has been added to the heights to partially account for the difference in elevation between the balloon and mini-SODAR (Boulder) sites.

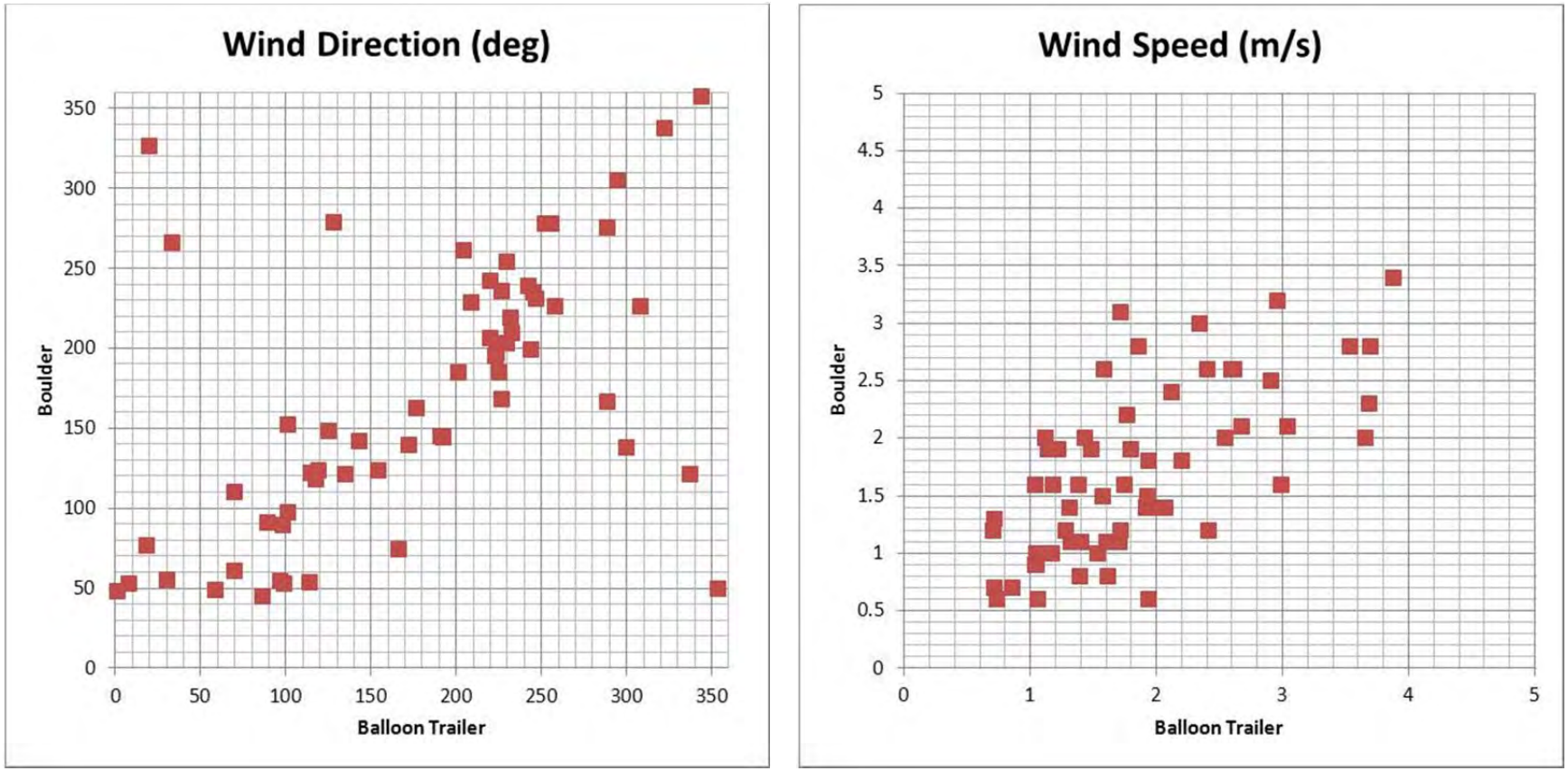


Figure 4.13 Comparisons of Boulder and Balloon Site Winds during IOPs

February 28, 2011 (Figure 4.14)

- Sustained winds from the ESE of the tethered balloon site with good mixing result in low, uniform concentrations of precursors and ozone.
- The mini-SODAR does not identify a mixing height after 13:00, emphasizing good mixing and a relatively deep mixing layer.

March 1, 2011 (Figures 4.15, 4.16, and 4.17)

- Light and variable winds persist throughout day, allowing buildup of ozone. Despite temperature profiles that would indicate good mixing in the afternoon, the mini-SODAR continues to show a lower mixing height throughout the day (Figure 4.16), indicating fairly stable conditions.
- A strong elevated inversion trapped precursor emissions in the morning. This elevated plume can be seen drifting in and out of the upper levels.
- The mini-SODAR fax chart indicates an elevated plume as evidenced by the stronger returns highlighted in Figure 4.16.
- High concentrations of NMHC impact the site at 13:30-14:00 under very stable NO_2 concentrations. NO concentrations during this period remain near zero. Despite the NMHC plume, ozone concentrations remain high but stable during this period, consistent with a NO_x limited scenario. However, beginning around 14:00, there is a notable correlation between ozone and NMHC. Since the Pinedale Anticline is considered NO_x limited, with an over-abundance of VOCs, it seems contradictory that this correlation is actually due to a direct relationship between NMHC and ozone. A possible explanation is that the higher NMHC concentrations are indicative of ozone precursors in general, including the original presence of NO_x precursors. However, by the afternoon hours, NO and NO_2 concentrations have been consumed by the traditional sinks associated with ozone chemistry, leaving only the NMHC. NMHC concentrations are at this point less than 6 ppm. Further analysis of the data will be required to understand the relationship between the measured precursor concentrations and ozone.

- Note the apparent lack in NMHC at 13:00, most likely a consequence of potential errors due to the hydrocarbon measurement methodology discussed above.
- The following vertical structure details are more apparent when looking at conventional time series plot (Figure 4.17)
    - Note first the lack of any drop in hydrocarbons at 13:00 as well as the consistent near zero NO readings beginning at 13:00, both referenced above.
    - The bottom three levels have relatively consistent ozone concentrations, while the 100-m level can be seen responding to excess NO at that level. However, in the the morning when NO is low, ozone at the 100-m level is at times notably higher than at other levels – possible evidence of ozone carry over from a prior time.
    - The increases in ozone also appear to be correlated to hydrocarbon concentrations, and thus the higher ozone concentrations are more likely due to the availability of more precursors. The correlation between NMHC and ozone is more apparent in these plots.

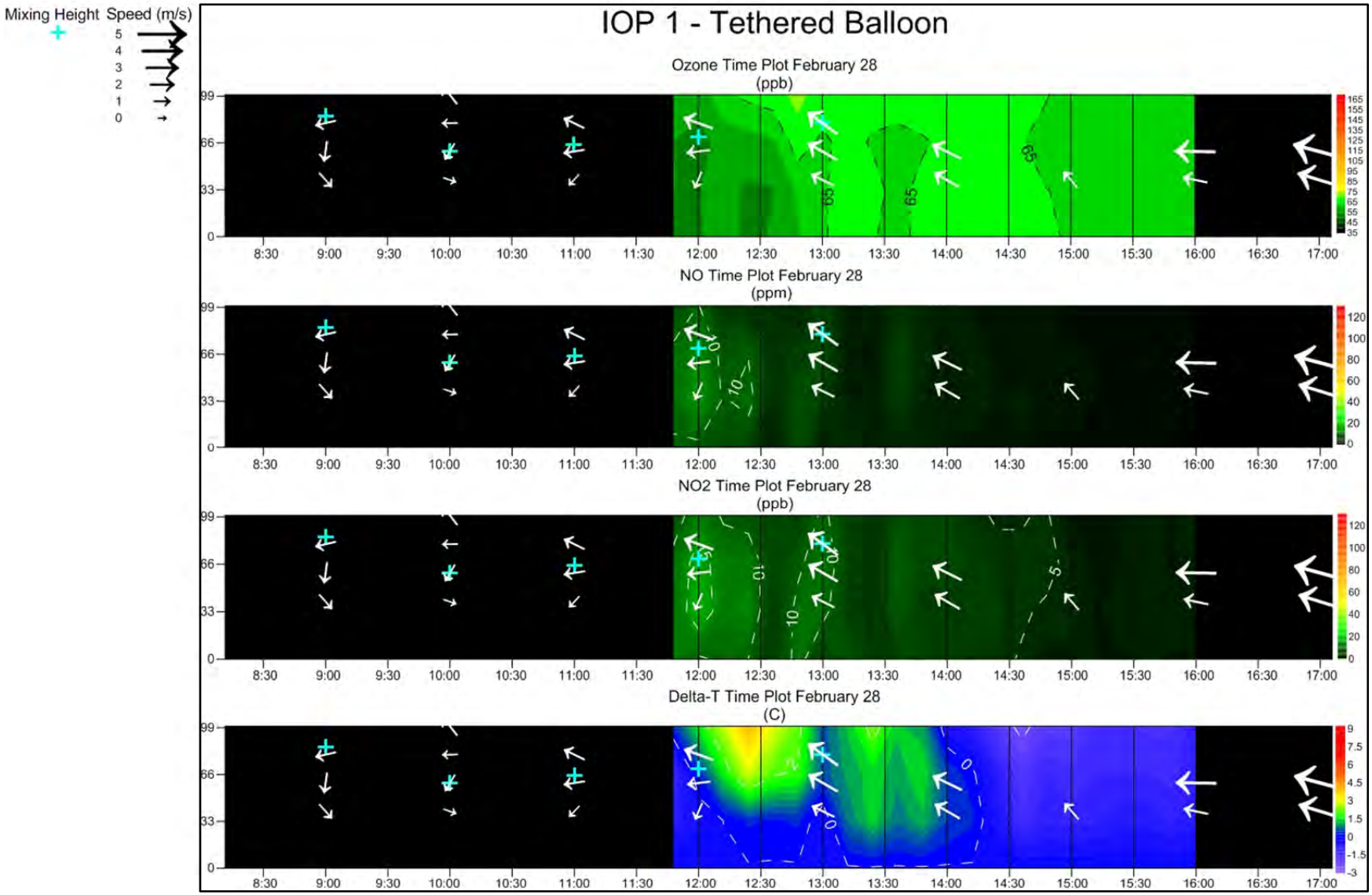


Figure 4.14 Tethered Balloon – February 28, 2011

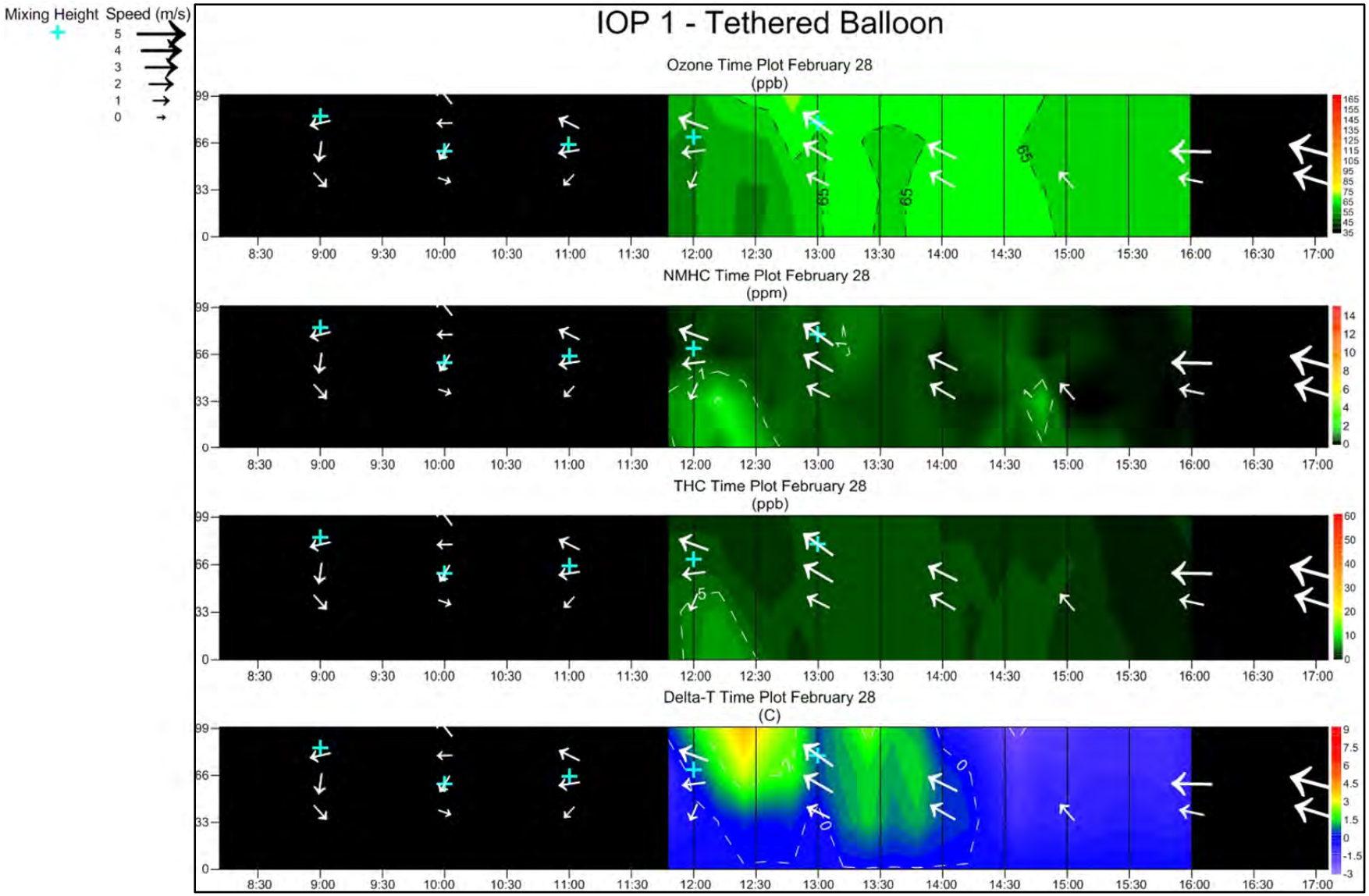


Figure 4.14 Tethered Balloon – February 28, 2011 (Continued)

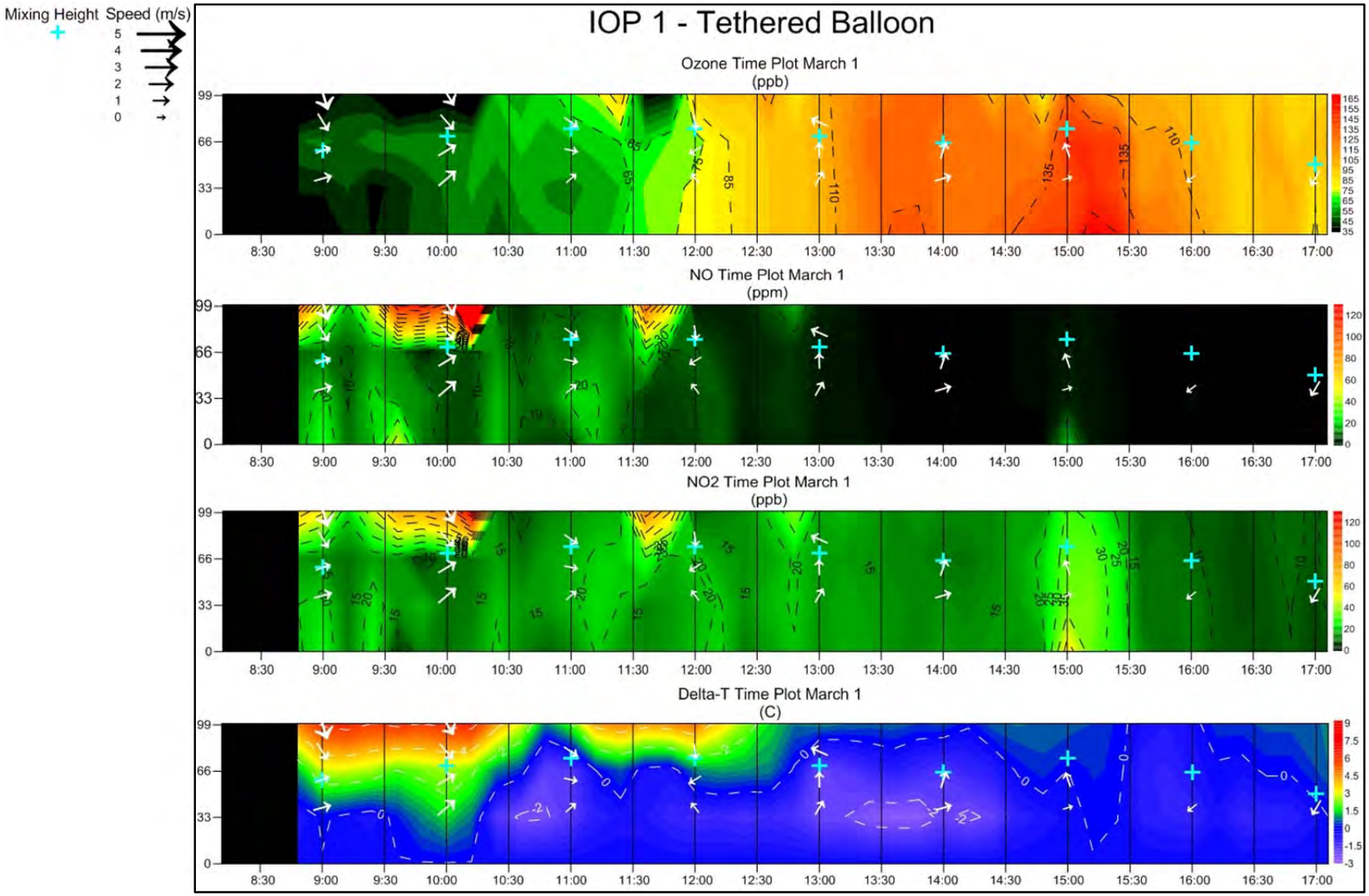


Figure 4.15 Tethered Balloon – March 1, 2011

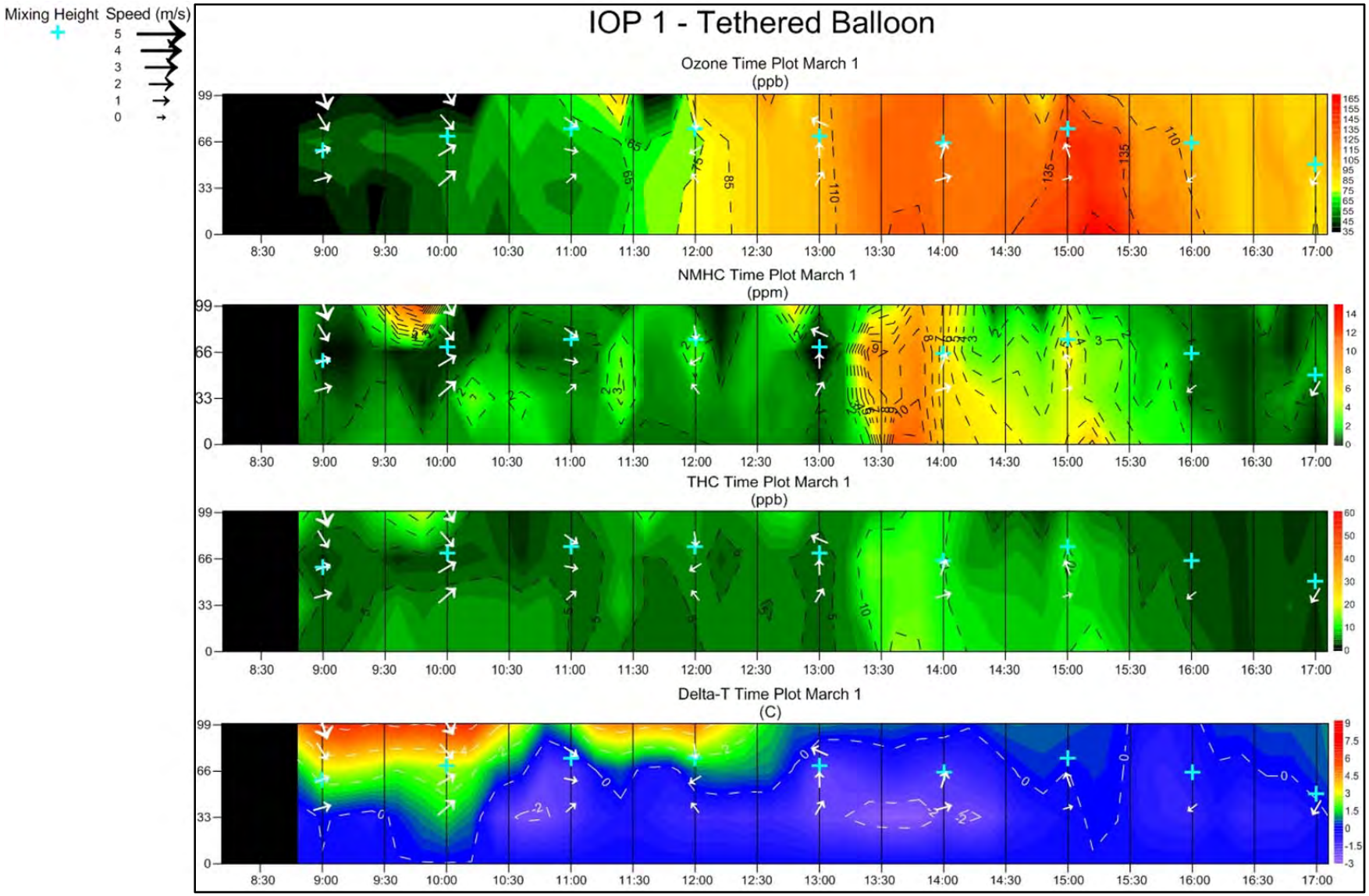


Figure 4.15 Tethered Balloon – March 1, 2011 (Continued)

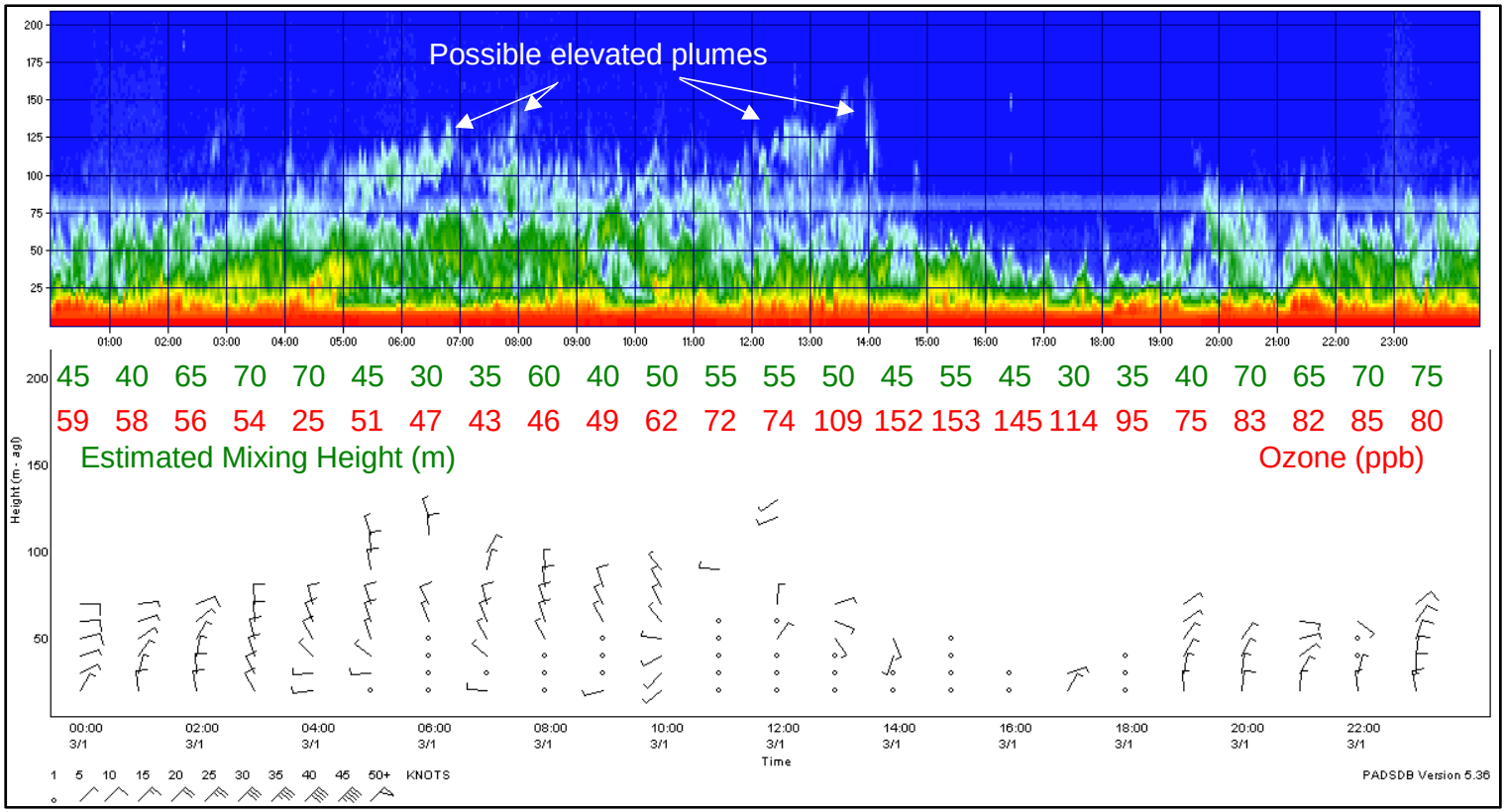


Figure 4.16 March 1, 2011 mini-SODAR Mixing Heights

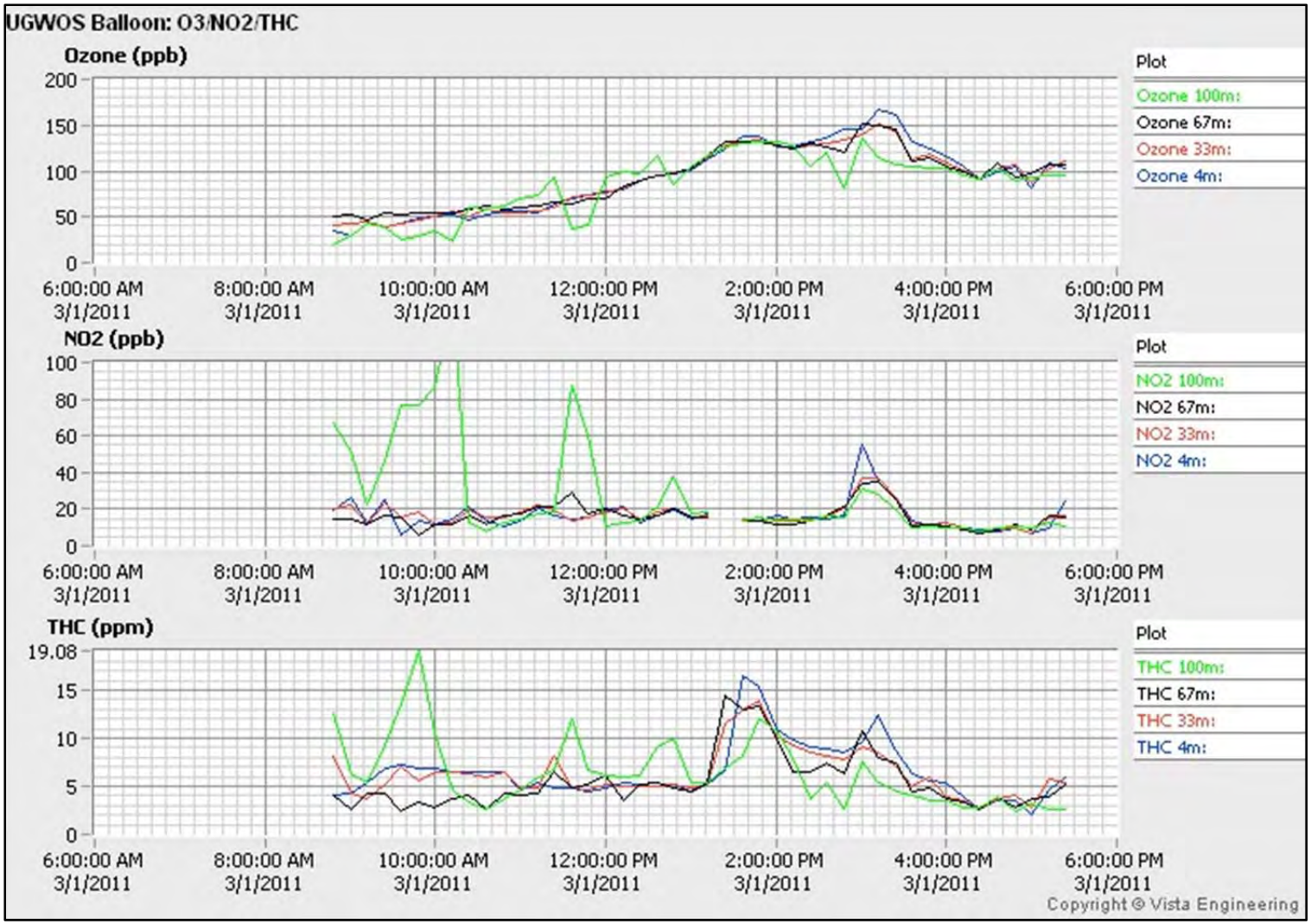


Figure 4.17 March 1, 2011 Time Series Plot

March 2, 2011 (Figures 4.18, 4.19, and 4.20)

- March 2 is similar in all respects to March 1, except that the higher morning ozone at the 100-meter level does not occur (Figure 4.18).
- The correlation between THC and ozone concentrations in the afternoon is even more apparent (see Figure 4.19 for a more detailed time series plot). NMHC concentrations during the peak ozone period are less than 5 ppm.
- The 16:00 ozonesonde data (Figure 4.20) show a strong slightly elevated temperature inversion persisting into the afternoon that caps the surface layer allowing ozone concentrations to accumulate.

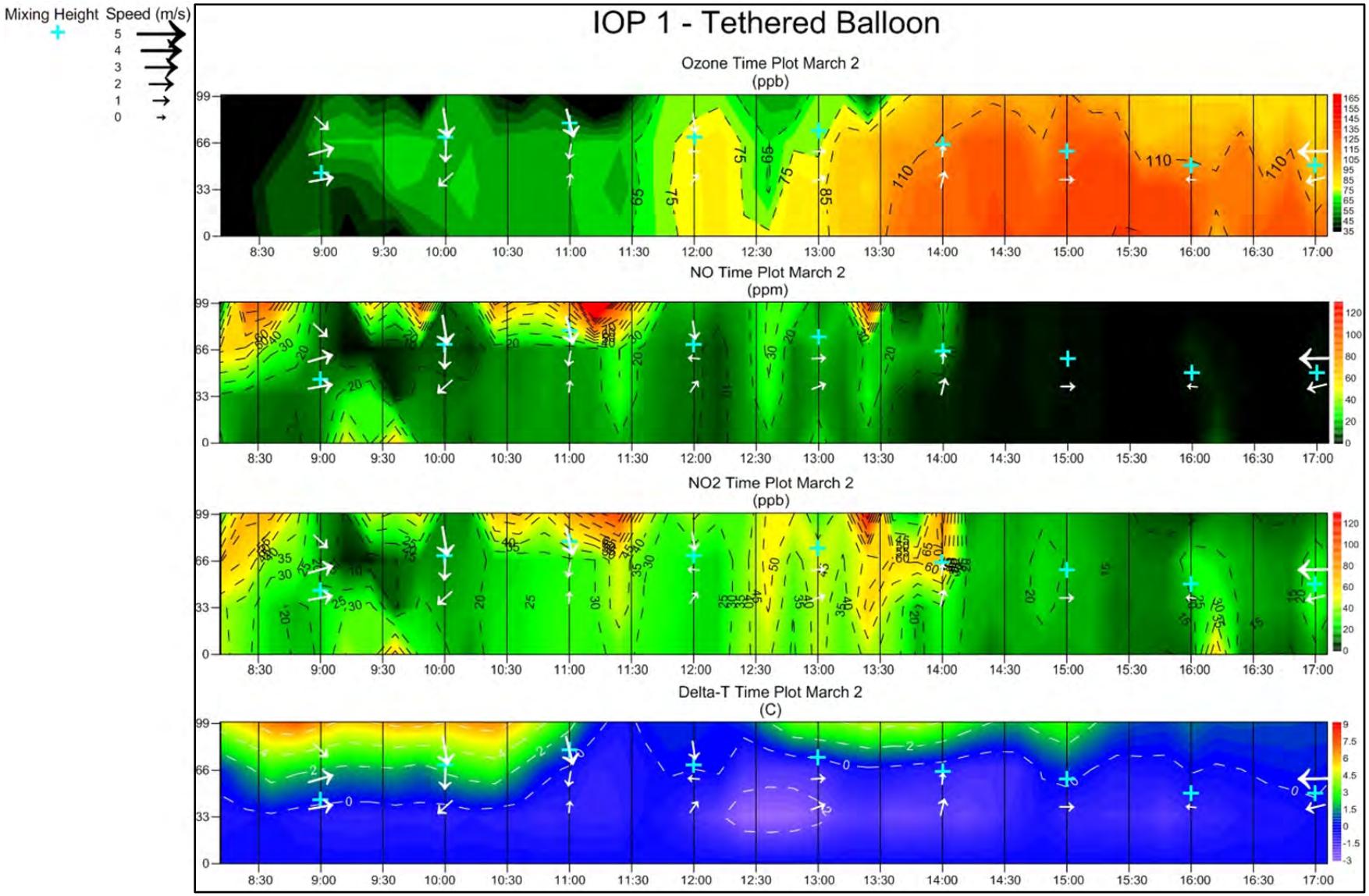


Figure 4.18 Tethered Balloon – March 2, 2011.

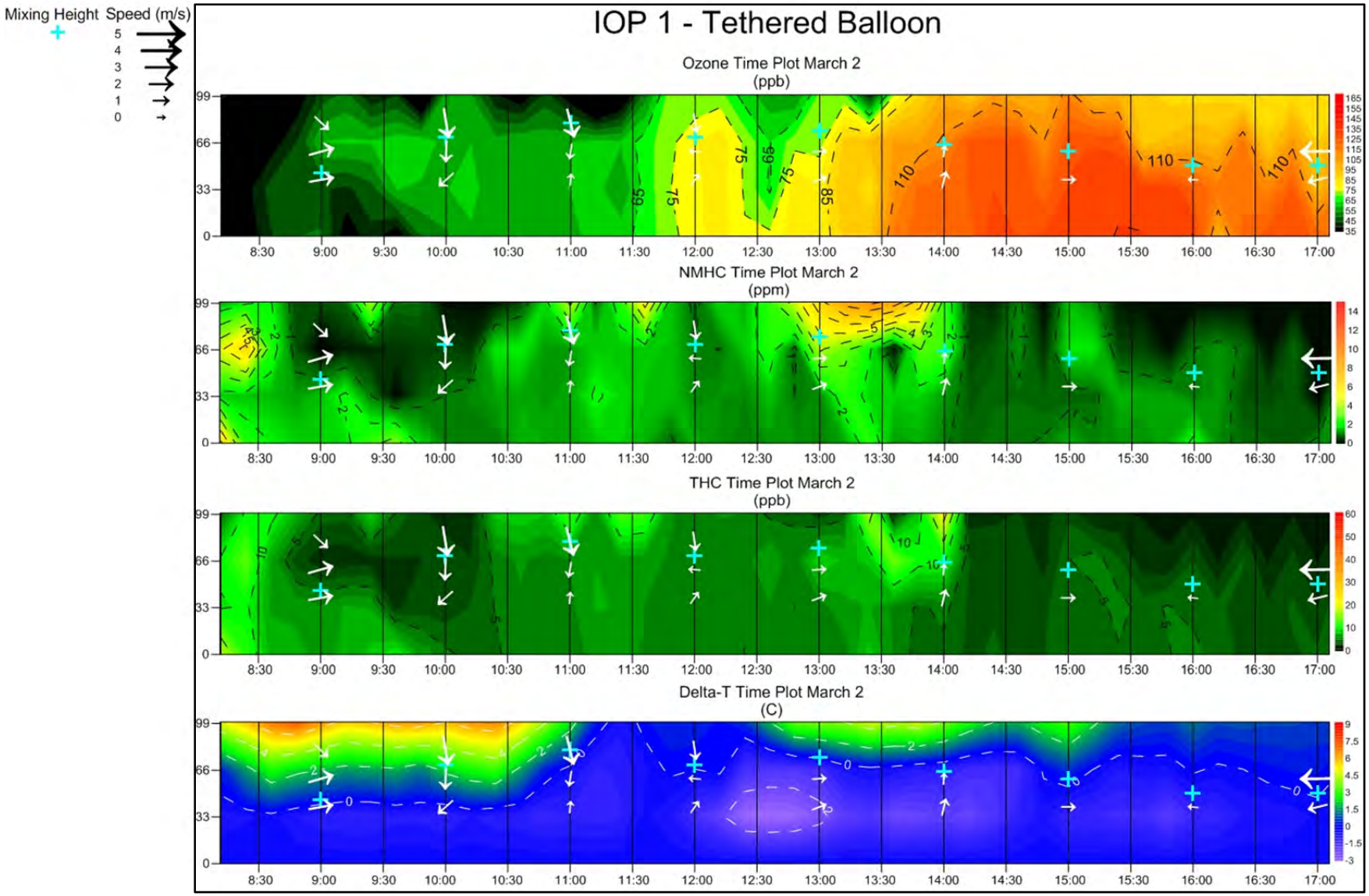


Figure 4.18 Tethered Balloon – March 2, 2011 (Continued)

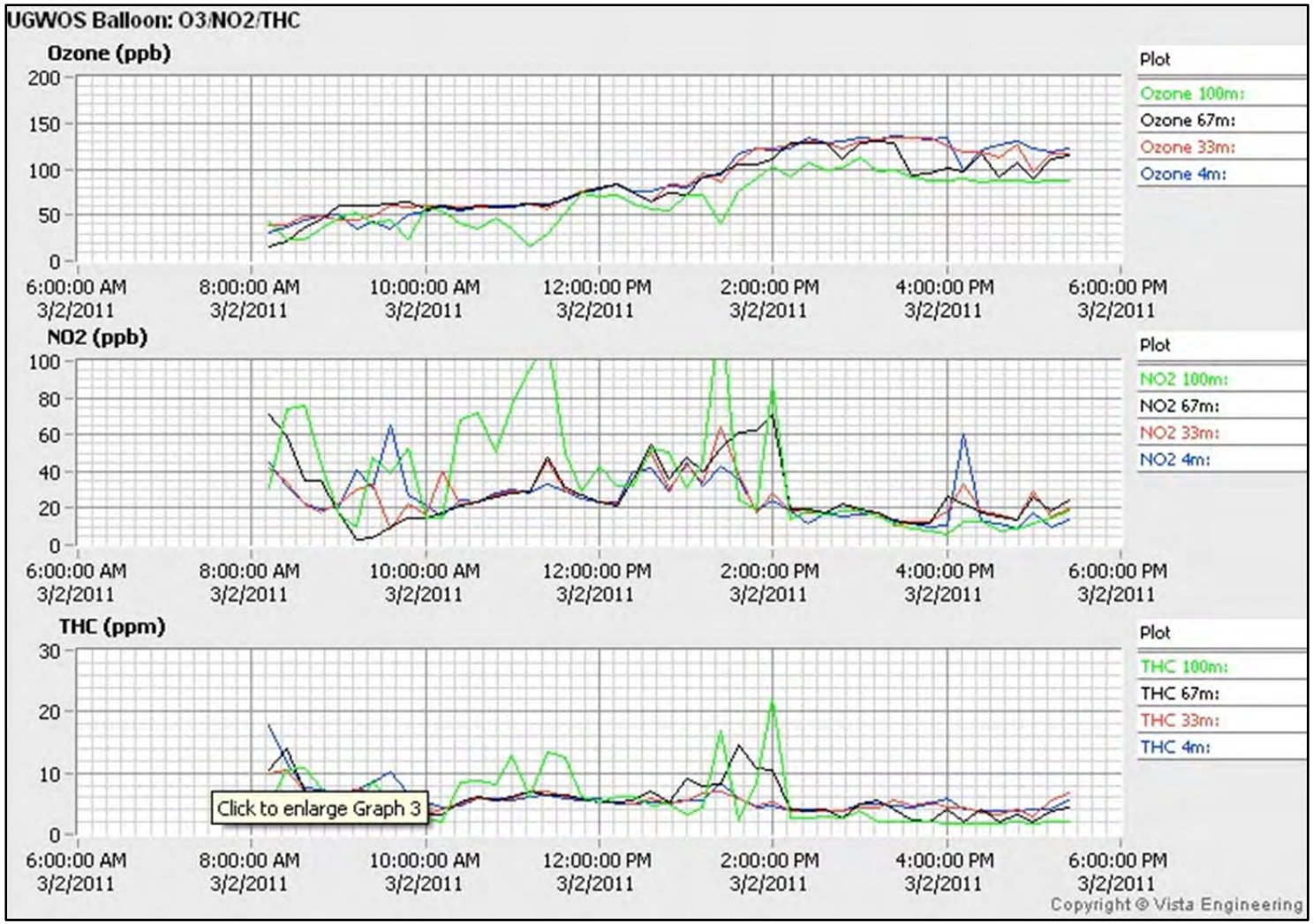


Figure 4.19 Tethered Balloon Time Series Plot for March 2, 2011

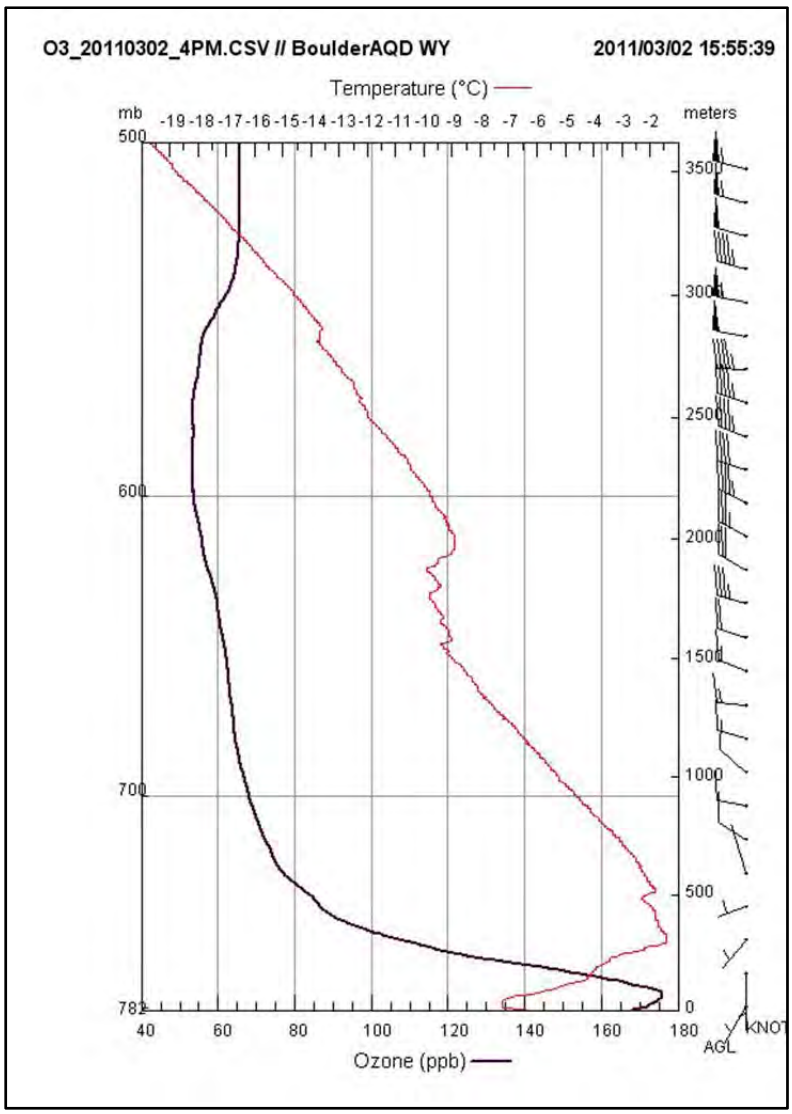


Figure 4.20 March 2, 2011 Ozonesonde (1600 MST)

March 9, 2011 (Figure 4.21)

- This day shows an absence of strong inversion and a fairly well mixed scenario. The mini-SODAR could not identify top of mixing height in the afternoon.
- Precursor concentrations are relatively low and uniform.
- Winds are consistently from the southwest and steady at around 2 mps. This is a wind direction not associated with nearby precursor sources – consistent with the low precursor concentrations.
- Ozone concentrations are uniform across all levels, but despite the lack of any evidence of source precursor contributions, a notable buildup of higher ozone concentrations occurs, peaking at 14:00. This possibly implies an older plume. The high ozone events on March 1 and 2 showed a varying vertical ozone structure that correlated with well-defined temporal and vertical precursor gradients. In contrast, the vertical structure of the ozone concentrations on March 9 is much more uniform at all levels and not associated with any notable precursor gradients since little precursor activity is noted. This possible implies an air mass that has undergone more dispersion, which given the still relatively low wind speeds implies a greater age. However, it may be that better mixing on March 9, based on the delta-T and mini-SODAR data, neither of which shows a well-defined top of the mixing layer, the surface layer is thicker on this day than on other high ozone IOP days.

  The presence of elevated ozone implies capping of the layer by an elevated inversion inhibiting the dispersion of ozone concentrations, with the elevated inversion above the 100-meter balloon height or the mini-SODAR measurement range. This cannot be definitely confirmed, as there was no ozonesonde released during this period. However, an earlier sounding at 12:00 shows an inversion that is notably weaker than those for the same period on March 1 and 2, consistent with likely improved mixing conditions. By the time of the next sounding at16:00 the temperature profile shows no elevated inversion and much lower ozone concentrations. Further analysis will be required to resolve these issues.

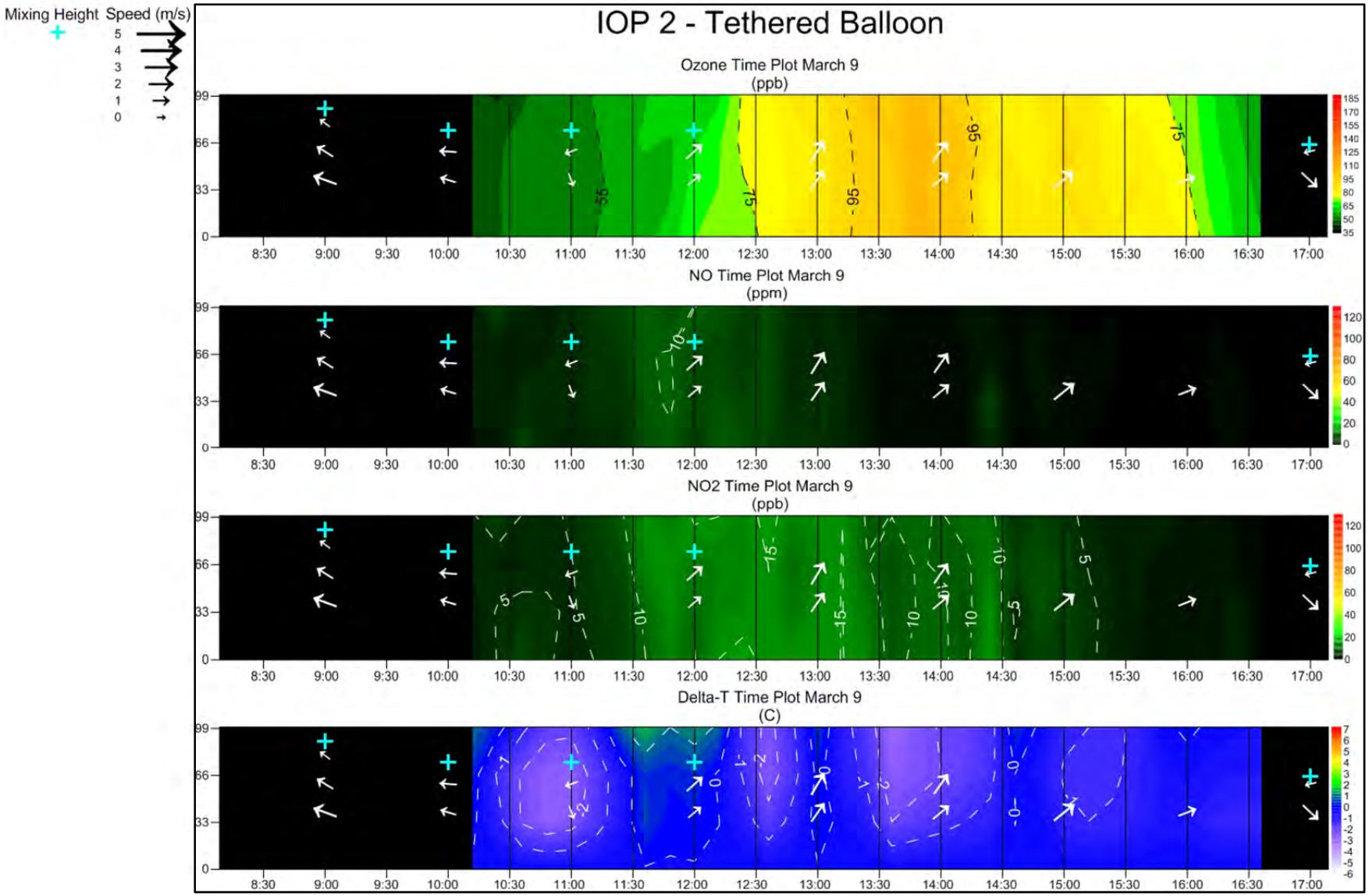


Figure 4.21 Tethered Balloon – March 9, 2011

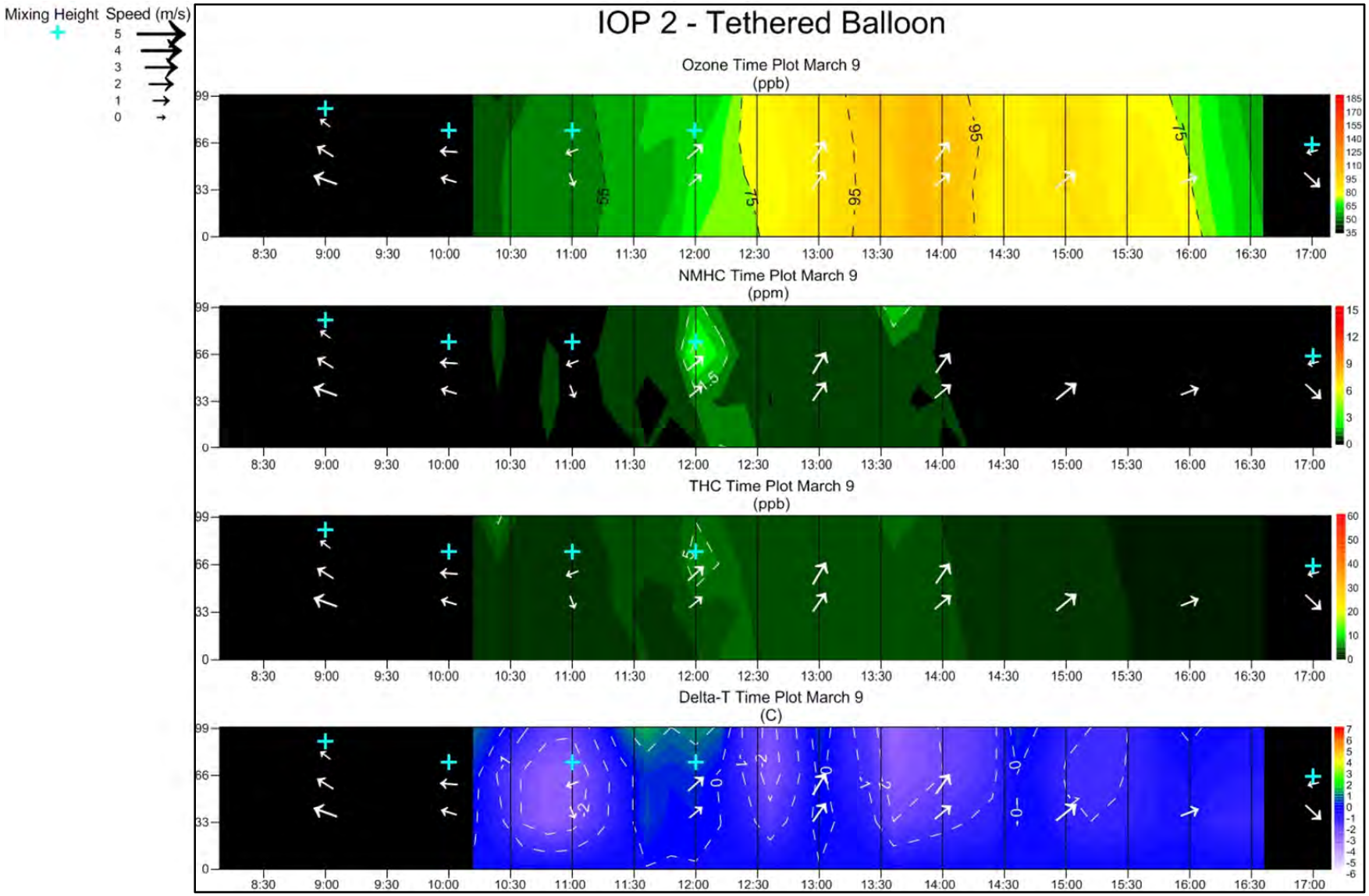


Figure 4.21 Tethered Balloon – March 9, 2011 (Continued)

March 10, 2011 (Figure 4.22)

- The day started off similar to March 1 and 2, with a strong morning inversion, light winds at the surface, evidence of an elevated plume of precursors (also observed on the mini-SODAR fax charts), and rapid buildup of ozone prior to 12:00.
- Based on the NO_x plots, it appears that the top of the elevated plume can be seen during the morning, with higher concentrations associated with the plume at the 67-meter level, and much cleaner air above it at the 100-meter level. This is consistent with the wind data, which shows a notable amount of shear between these levels, with notably higher winds at the 100-meter level. This observation substantiates to a large degree the height-adjusting assumptions regarding the mini-SODAR data that were discussed at the beginning of this section.
- After 12:00, buildup of ozone concentrations ceases due to good mixing and relatively strong winds from the southeast, though ozone concentrations rise somewhat after 14:30 when winds lighten. Note that the one location in the study area that experienced 8-hour average ozone concentrations greater than 75 ppb was the Wyoming Range site, located to the northwest of the balloon site. This episode is discussed later in the report.

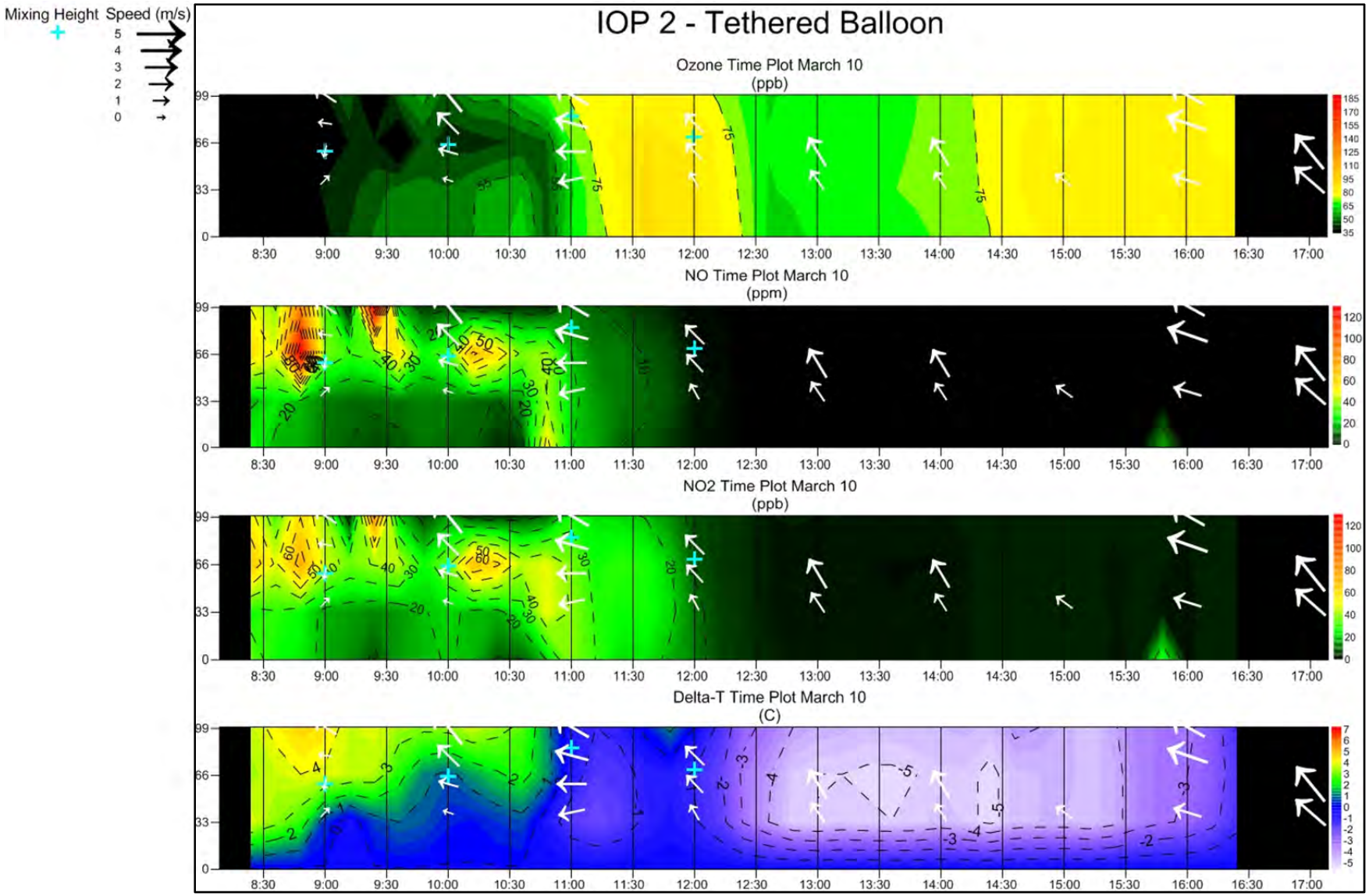


Figure 4.22 Tethered Balloon – March 10, 2011

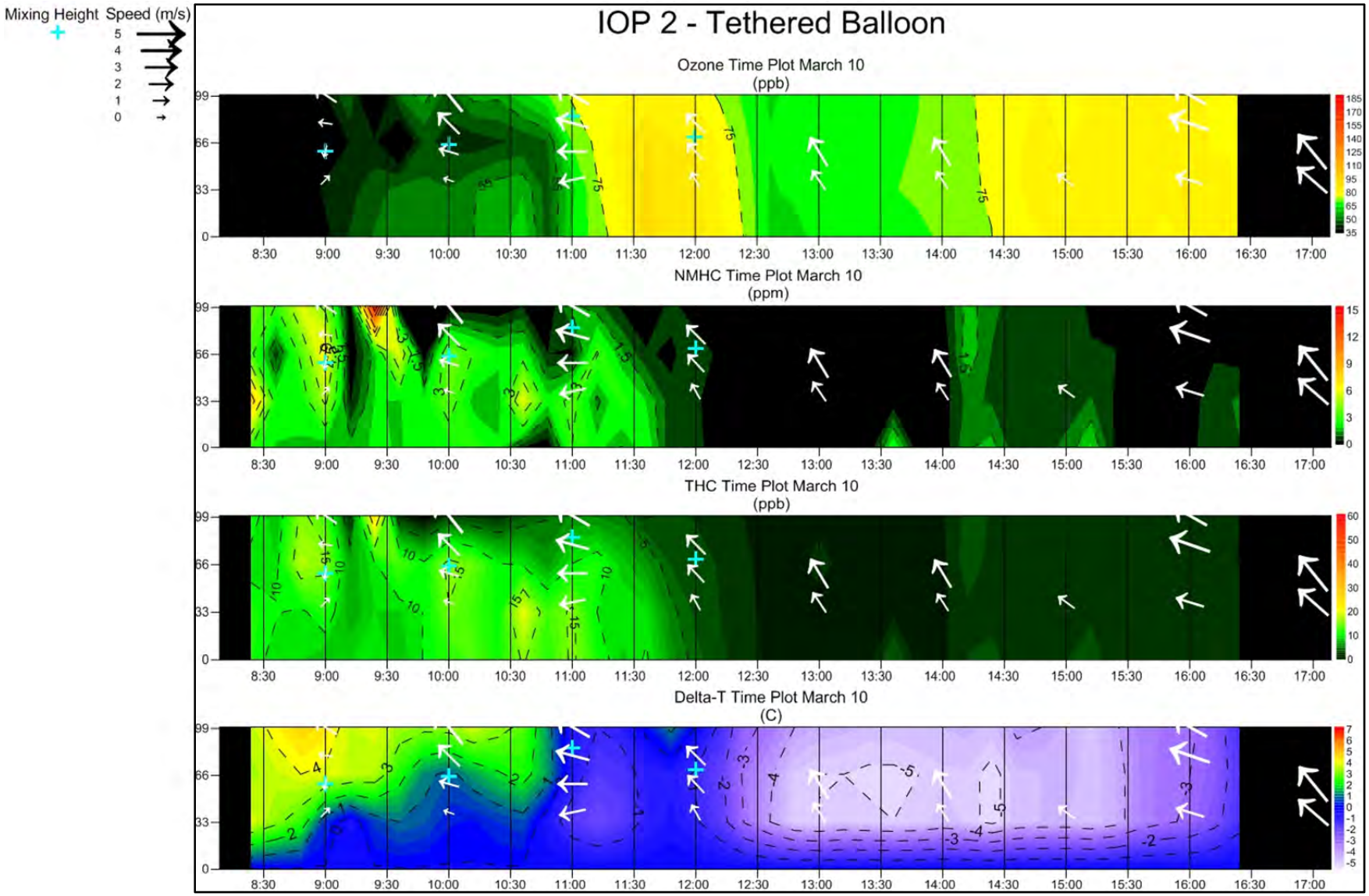


Figure 4.22 Tethered Balloon – March 10, 2011 (Continued)

March 11, 2011 (Figure 4.23)

- 10 to 15 mps winds from the WNW persisted through 6:00, providing good ventilation and preventing the buildup of precursor concentrations.
- Moderately light winds and a weak inversion allowed brief periods of higher precursor concentrations. NO_x concentrations peak in the 100-meter level, while hydrocarbon concentrations peak nearer to surface. This is a likely indication of fresher emissions, with sharp, well-defined temporal and vertical gradients, consistent with likely sources (cooler VOC sources, more buoyant NO_x sources) which have not yet had an opportunity to disperse, even under the relatively good dispersion conditions.
- The day remains well-mixed, with essentially no ozone development.

March 12, 2011 (Figures 4.24 and 4.25)

- This day is very similar to March 1 and 2, with a strong morning inversion, elevated plumes of precursors, NMHC plumes at the surface in the morning, and low mixing heights indicated by the mini-SODAR throughout day.
- At about 15:15, the boundary layer is compressed, to the point where it appears the top level was actually above the surface mixed layer, based on the 60 ppb ozone concentration reported at this level, which is typical of "clean" air during the UGWOS studies. This is the only high ozone period during the study when this situation occurred. Figure 4.25 shows the ozonesonde sounding obtained during this period and confirms an extremely low top to the mixing layer. The highest surface ozone concentrations reported at the tethered balloon site for this study are noted during this period, with an hourly average of 166 ppb reported for the hour ending 16:00.

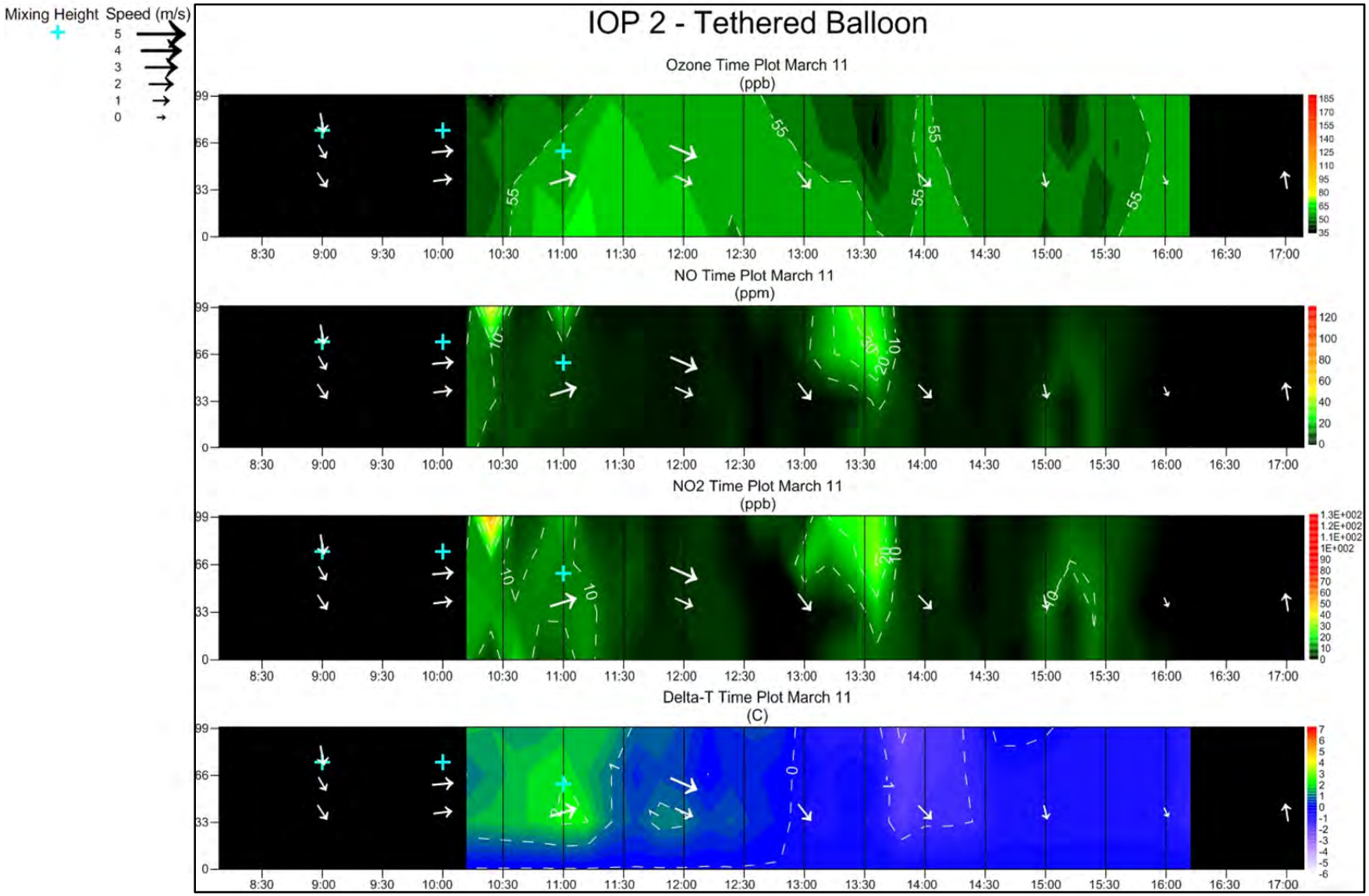


Figure 4.23 Tethered Balloon – March 11, 2011

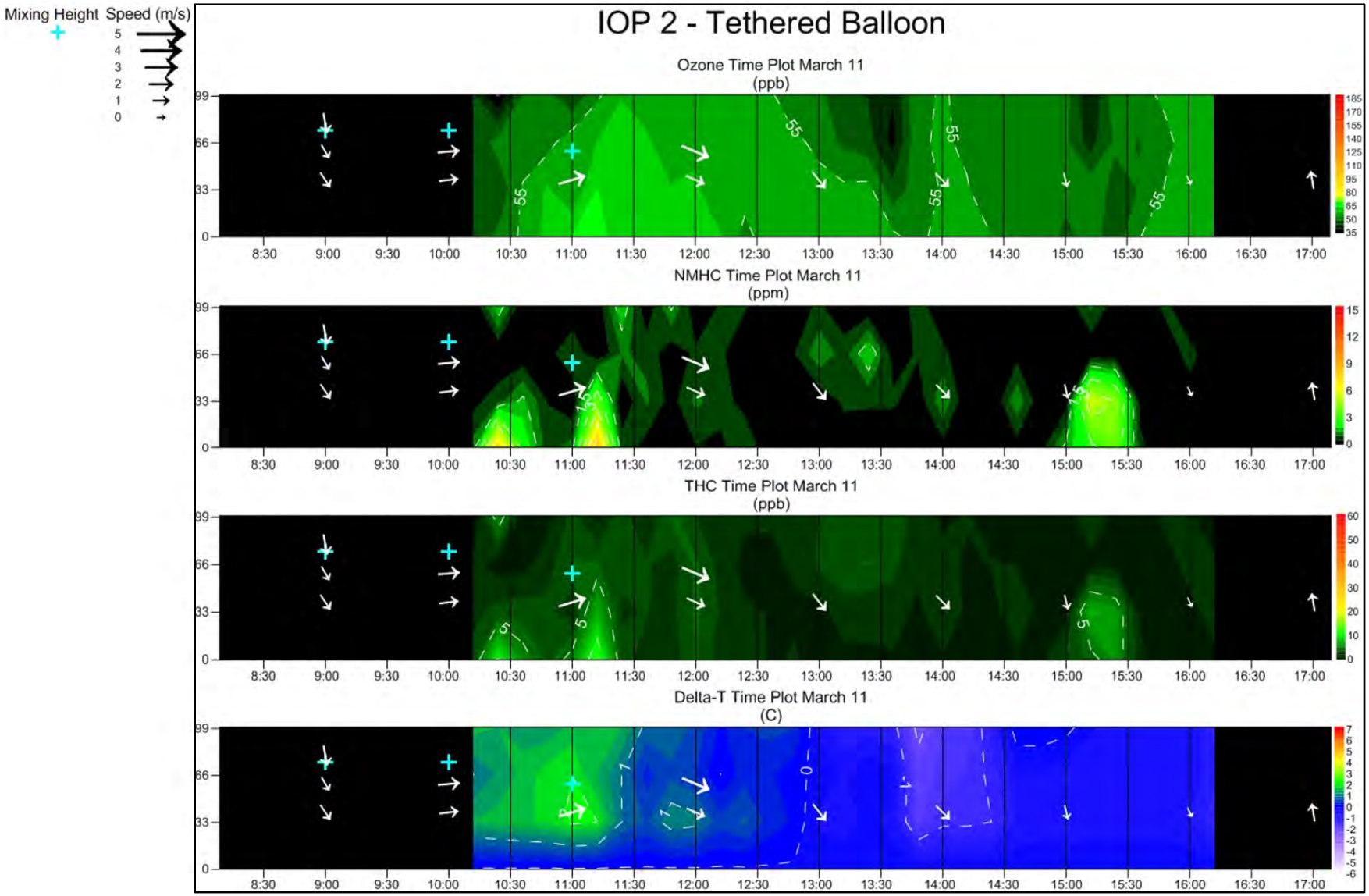


Figure 4.23 Tethered Balloon – March 11, 2011 (Continued)

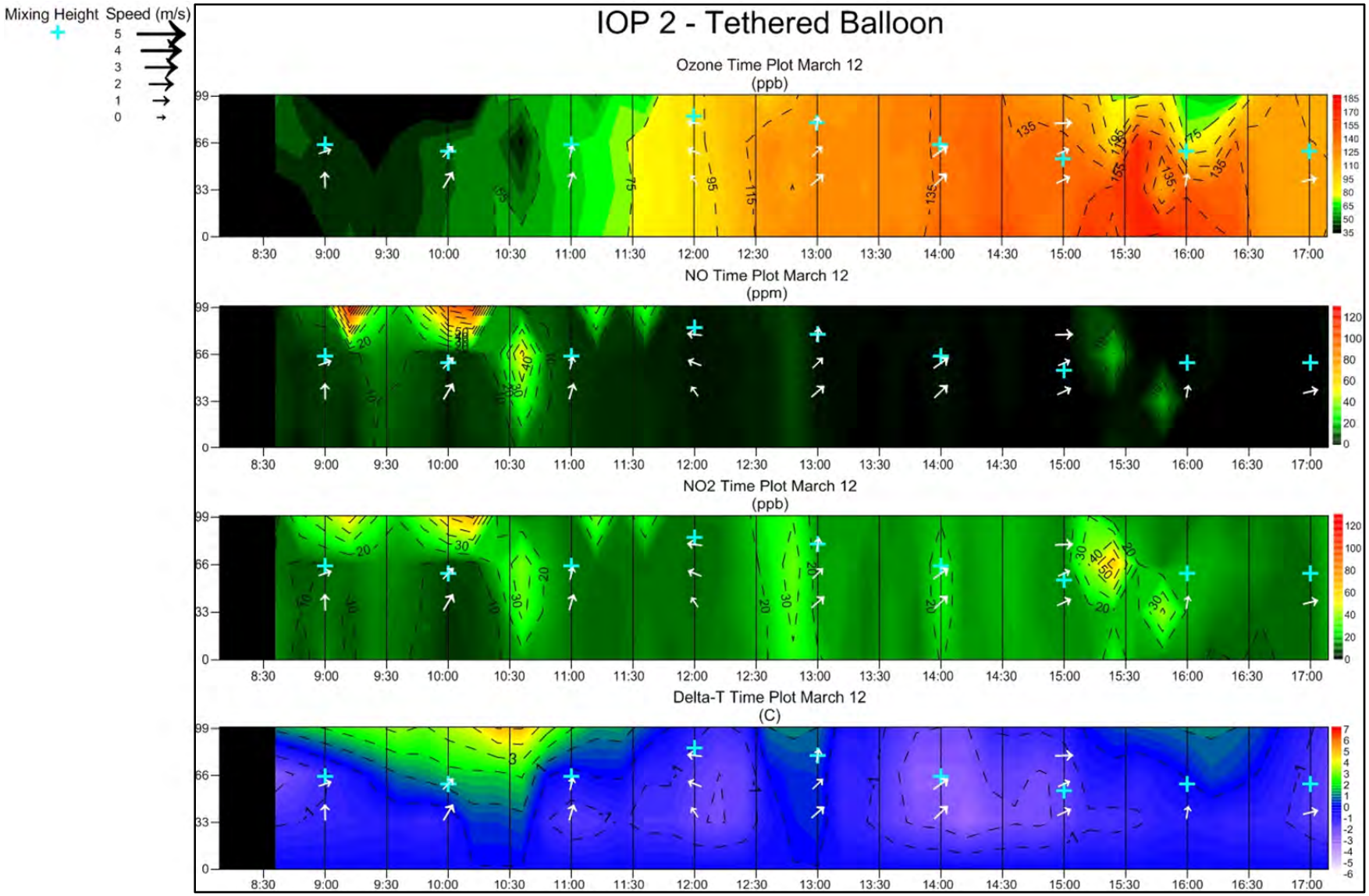


Figure 4.24 Tethered Balloon – March 12, 2011

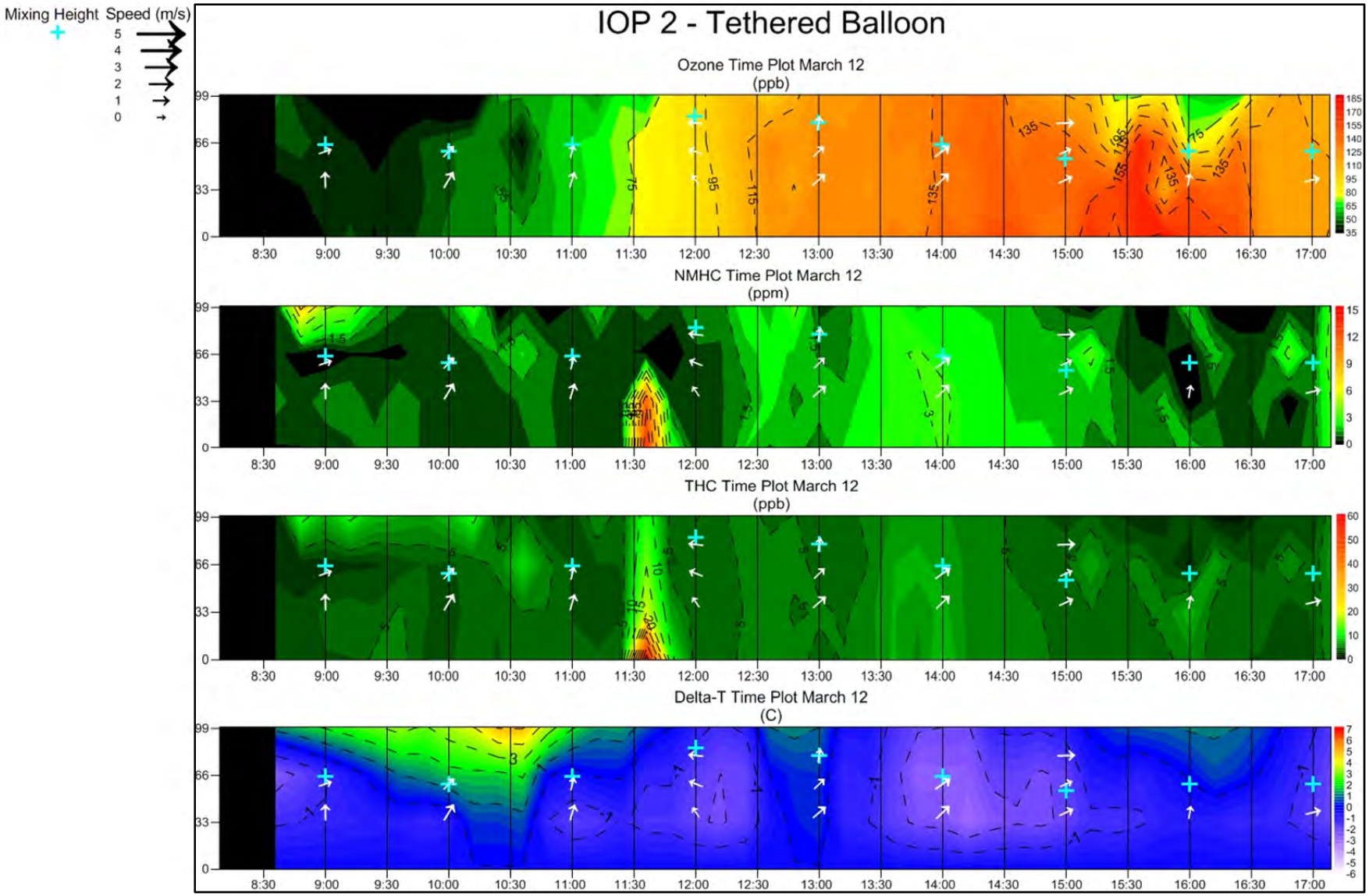


Figure 4.24 Tethered Balloon – March 12, 2011 (Continued)

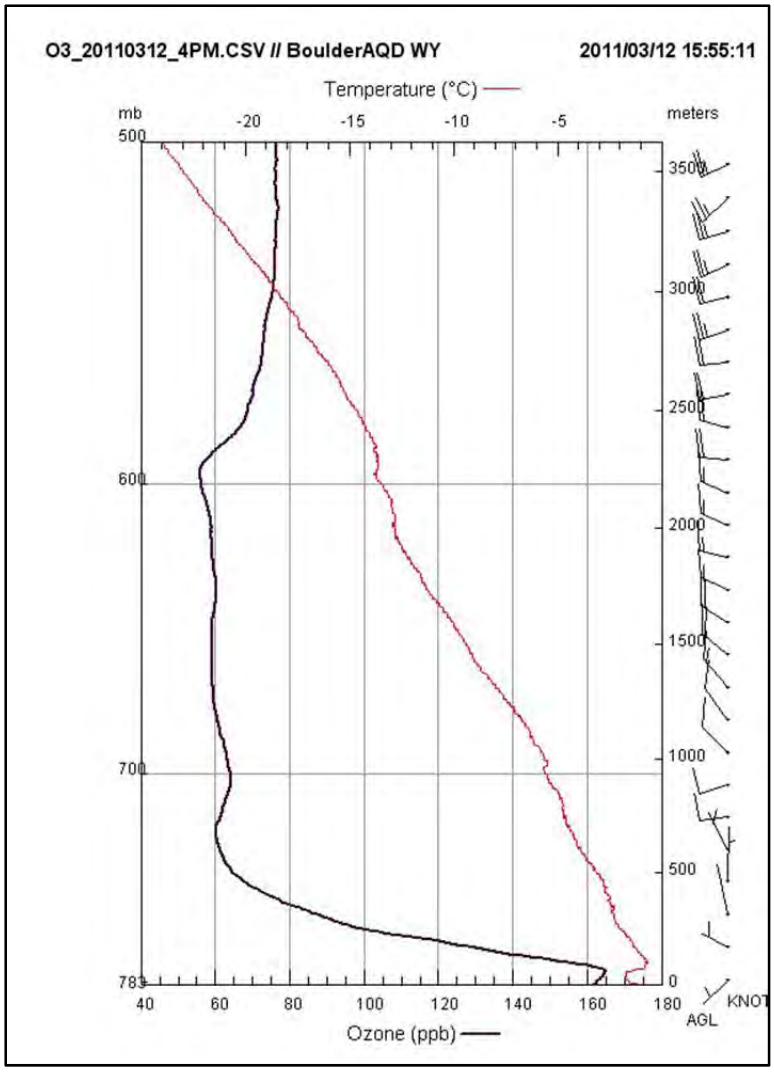


Figure 4.25 March 12, 2011 Ozonesonde (1600 MST)

Figure 4.26 is a compilation of all of the data obtained during the IOPs, presented as a vertical profile of the study-averaged data. On average, NO_x concentrations increase with altitude, while hydrocarbon concentrations are highest at the surface. No substantial ozone gradient is noted within this range of altitudes, other than that cause by increased titration by NO.

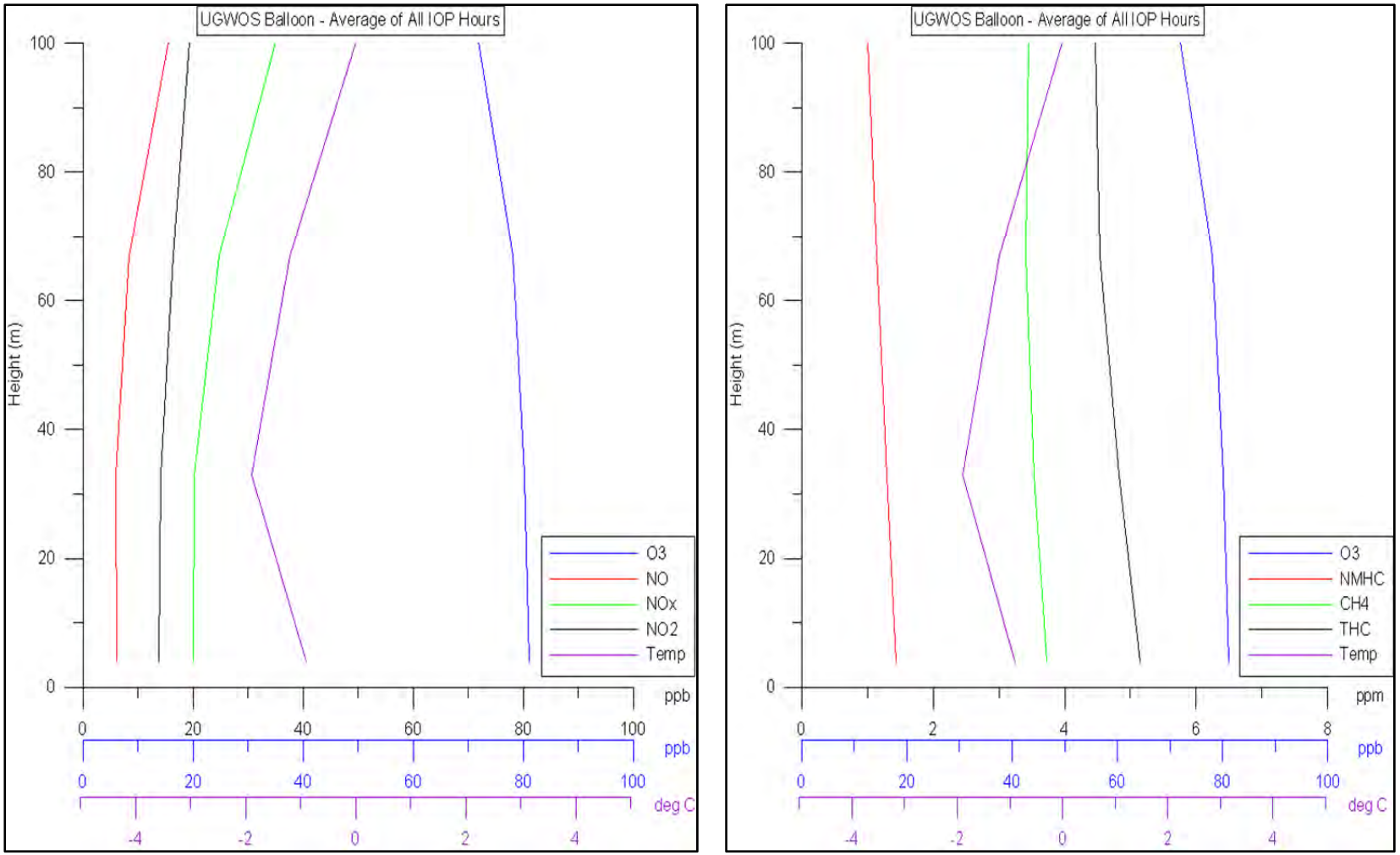


Figure 4.26 Vertical Profiles of Averaged Tethered Balloon Data

4.2.3.2 Tall Tower

Plots of the Tall Tower data are for the most part identical to those for the tethered balloon. The only exceptions are that the wind data are obtained directly from the tower, and there are no mixing height data.

In contrast to the balloon data, the tall tower data is located away from nearby sources, and consequently measures ambient air quality and meteorological conditions away from source locations. In addition, they provide a continuous record of conditions, including nighttime hours, providing additional insight into the development and destruction of ozone episodes. The tall tower data shows many of the same characteristics leading to higher ozone concentrations as the balloon data: light winds, the presence of higher precursor concentrations, and strong inversions near the surface. The following addresses key characteristics noted during the two IOPs, during which most of the high ozone activity occurred. Three additional periods are presented during which significant ozone activity was noted: two periods that are basically expansions of the IOPs, and one period that occurred earlier in the study.

It is worth noting that, due to the greater distance from emission sources, the Tall Tower NMHC data is not affected to nearly the same degree by the sampling methodology issues discussed above for the tethered balloon NMHC data.

IOP1 – February 28 through March 2 (Figure 4.27)

- There is a general increase in ozone concentrations over this three-day period, which may be an indication of regional building of concentrations on the previous day's concentrations. However, the data show that ozone concentrations are clearly associated with higher precursor concentrations, so a buildup of precursors is likely the critical component.

- Wind patterns are also likely a factor. A reversal in wind direction during the late morning on March 1 appears to have recirculated pollutants back into the region, resulting in some ozone development in the afternoon. Precursor concentrations are relatively uniform both in time and vertical structure during the afternoon, which is a likely indication of a more aged plume. In contrast, westerly winds around noon on March 2 bring in higher precursor concentrations, most likely from the nearby Jonah Field, resulting in higher ozone concentrations.
- The correlation between ozone precursors (particularly hydrocarbons) and afternoon ozone development is very apparent on the afternoon of March 2.

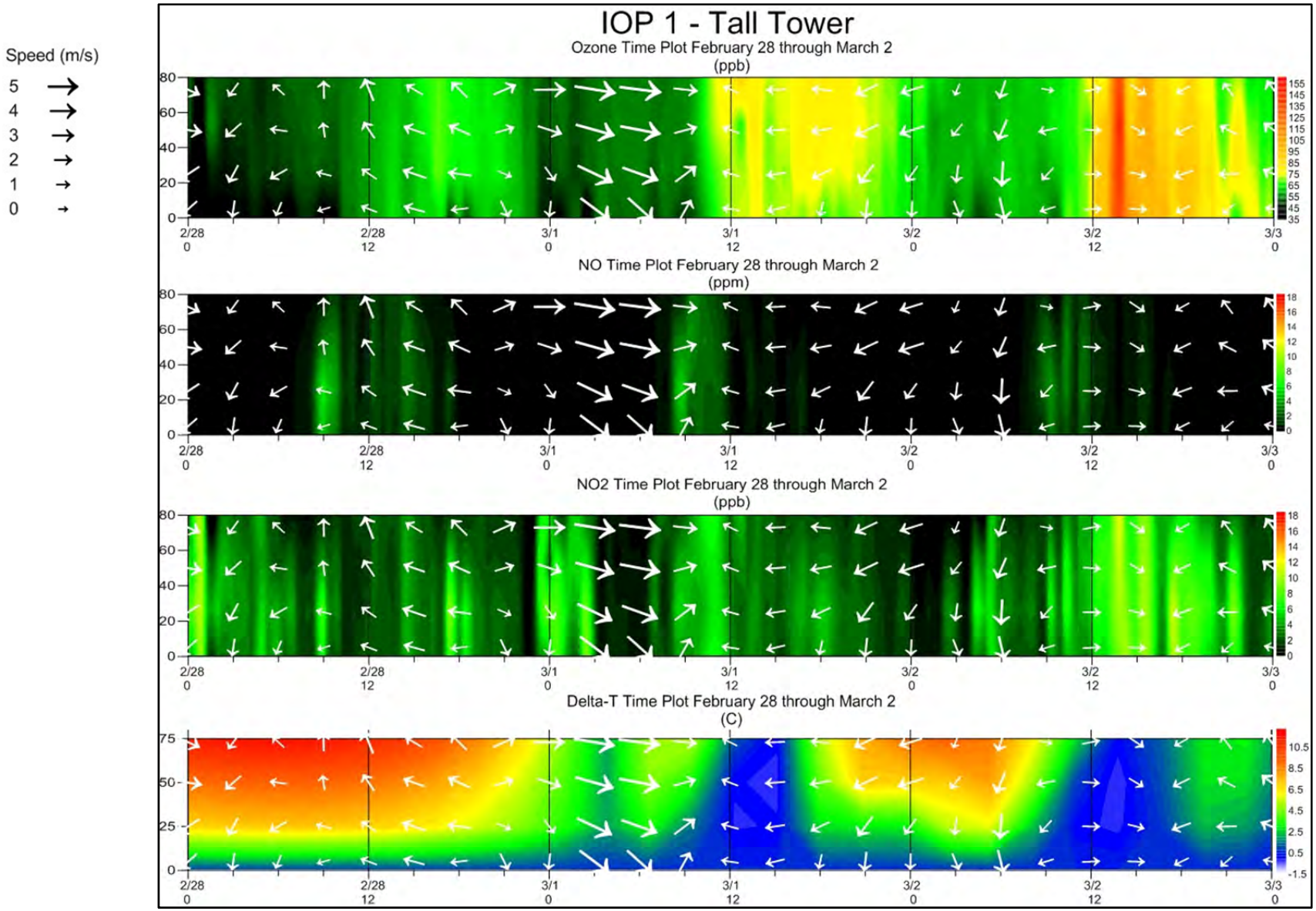


Figure 4.27 Tall Tower – February 28 through March 2, 2011

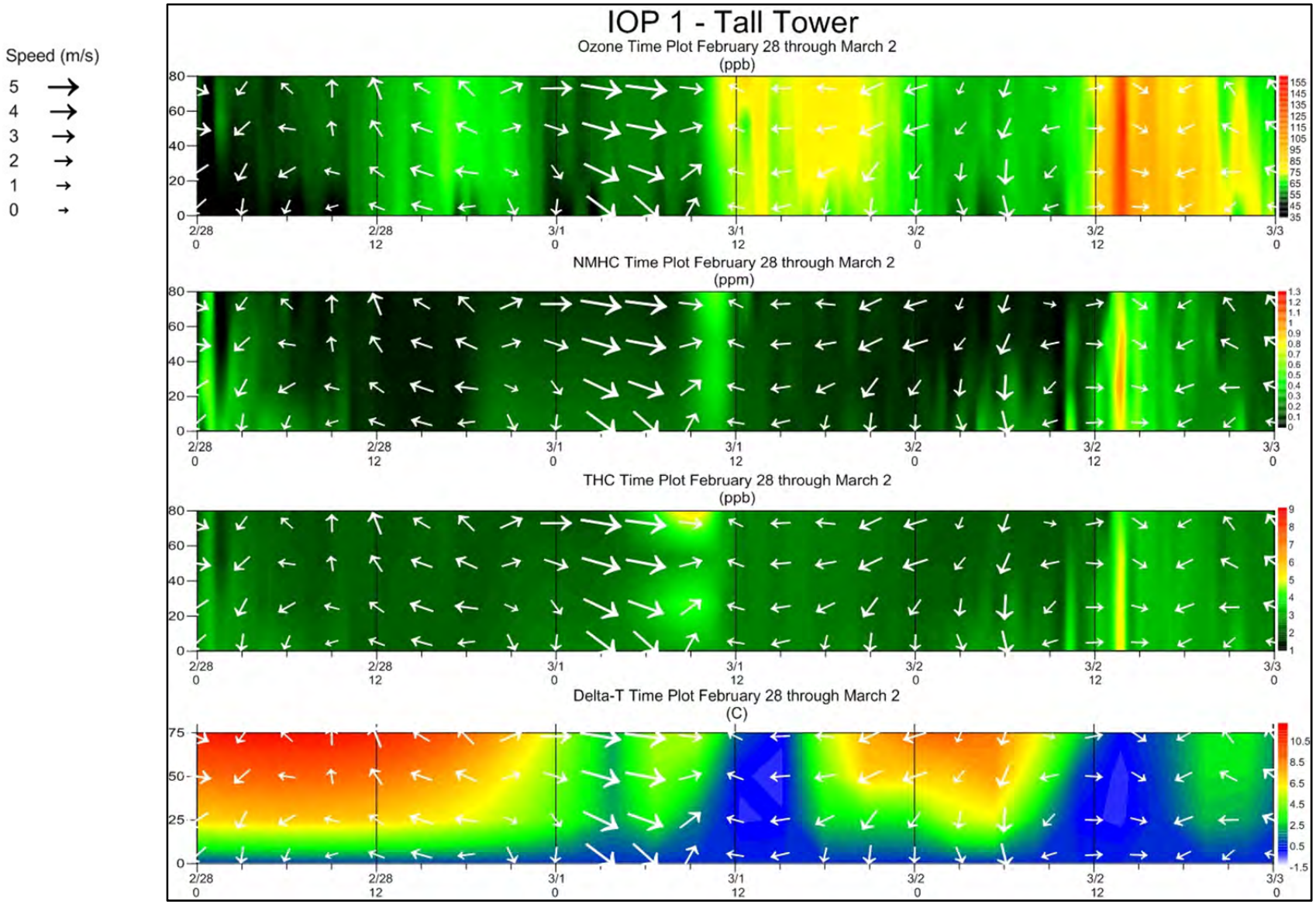


Figure 4.27 Tall Tower – February 28 through March 12, 2011 (Continued)

IOP2 – March 9 through March 12 (Figures 4.28, 4.29, and 4.30)

- Once again winds are critical to the development of high ozone concentrations. The highest ozone concentrations occur during the lowest wind speeds. Wind reversals and winds with a northerly component again coincide with higher ozone concentrations. March 10 is similar to March 1, with a reversal in wind direction recirculating morning precursors back into the region, likely portraying a more aged plume. March 12 is similar to March 2, with notably higher, likely fresher precursor concentrations from the west in the afternoon that correlate well with the resulting ozone concentrations (see Figures 4.29 and 4.30). Again, the time-series plots presented in Figure 4.30 illustrate well the correlation between NMHC and ozone, with the peaks and valleys in the ozone concentrations closely matching those for NMHC for all levels.
- During this period NMHCs are more frequently concentrated at the surface, whereas NO_2 concentrations are more uniformly distributed across all levels. The near-surface plumes of NMHC may likely be a function of fresher, nearby sources, as evidenced by the sharp, well-defined plume vertical and temporal gradients. All such NMHC plumes noted during this period are associated with northwesterly to westerly winds – direct from the nearby Jonah Field. In contrast, a plume which impacted the tower during the period from 10:00 to 12:00 on March 12 shows much weaker and less defined gradients, with concentrations evenly dispersed over all reported levels. Winds during this period initially have a more northerly component and then shift to easterly, implying more distant source and longer time during which concentrations can disperse.
- Ozone and NMHC concentrations on March 12 show an unusual vertical gradient in late afternoon and high concentrations lingering into the late night. The vertical structure appears to be evidence that the upper levels of the tower are monitoring air above the mixing layer. Though not apparent in the delta T data, this is entirely consistent with the observations on this day by the tethered balloon and confirmed by the ozonesonde and mini-SODAR data, which showed a compression of the surface layer that was uniquely strong for the study. As with the tethered balloon site, ozone concentrations during this period are the highest of this IOP. This may provide evidence that such events affect a regionally large area.

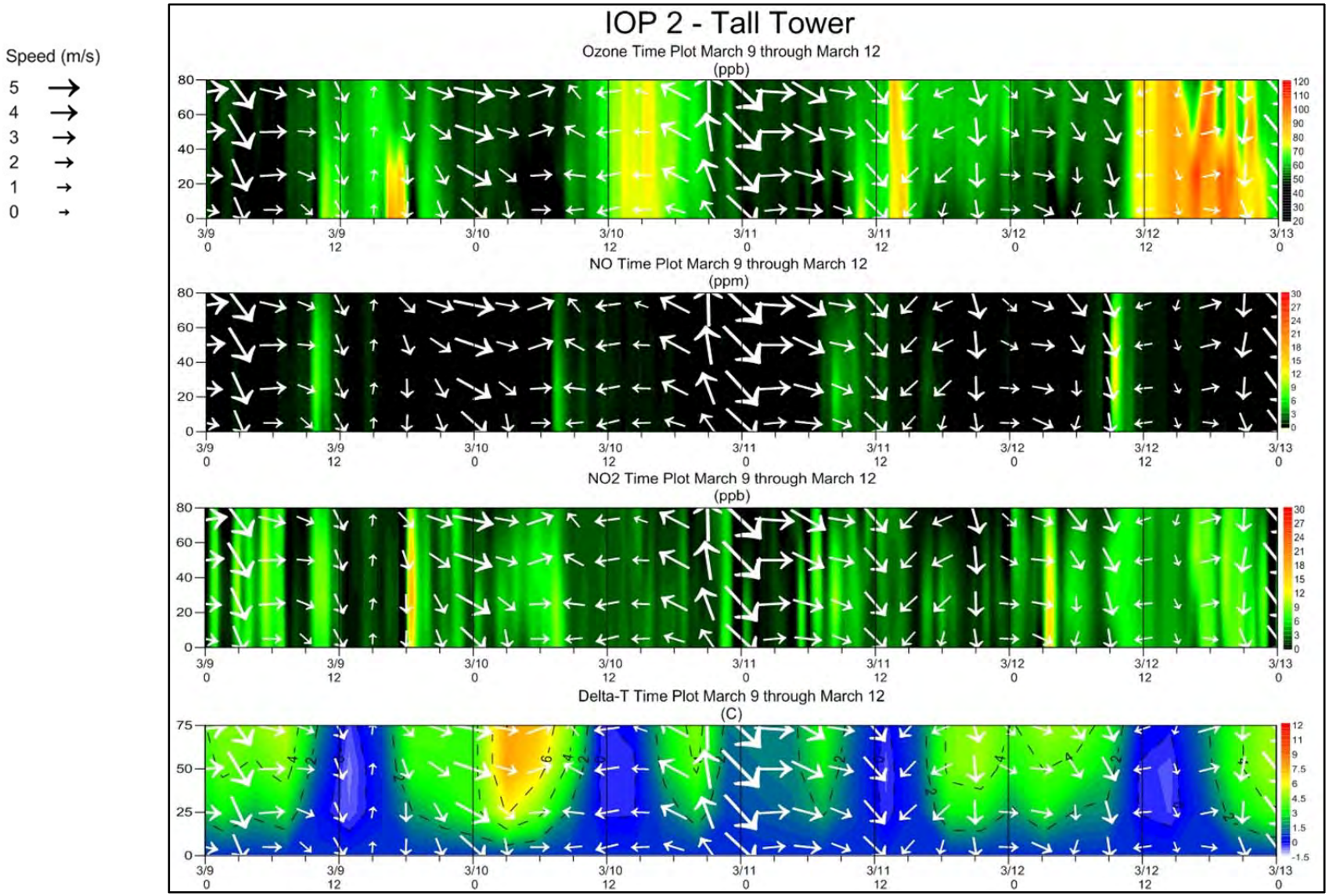


Figure 4.28 Tall Tower – March 9 through March 12, 2011

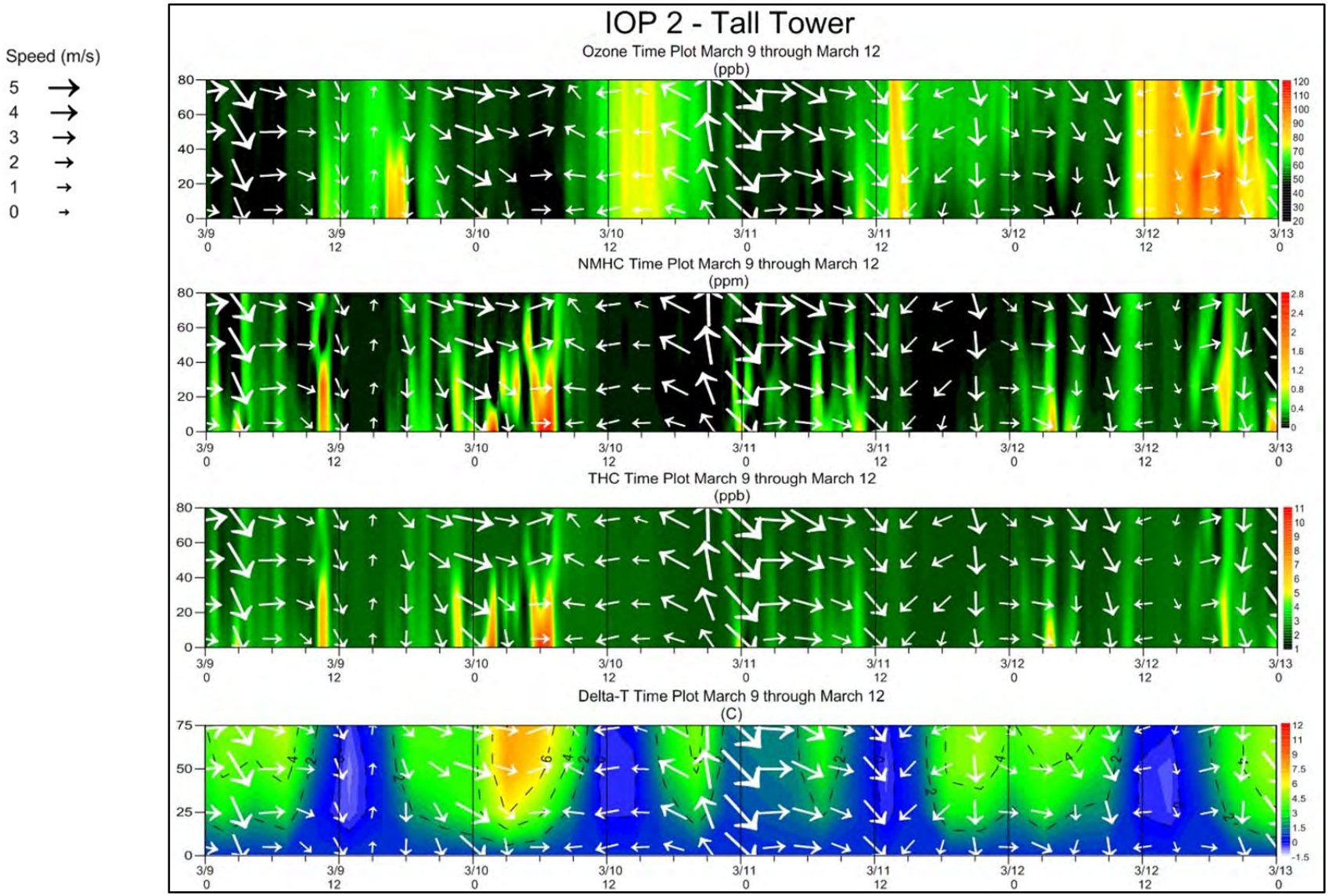


Figure 4.28 Tall Tower – March 9 through March 12, 2011 (Continued)

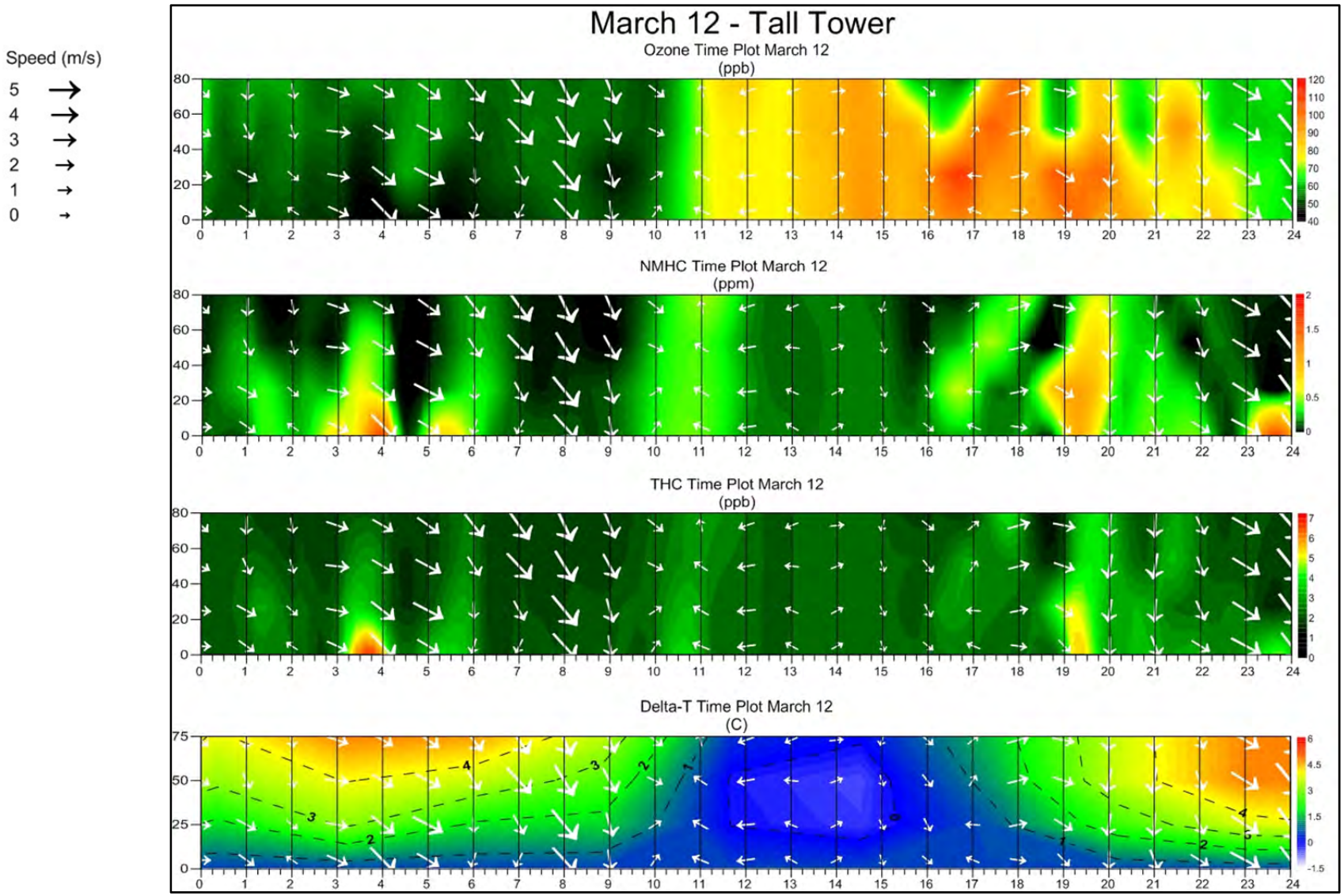


Figure 4.29 Tall Tower – March 12, 2011

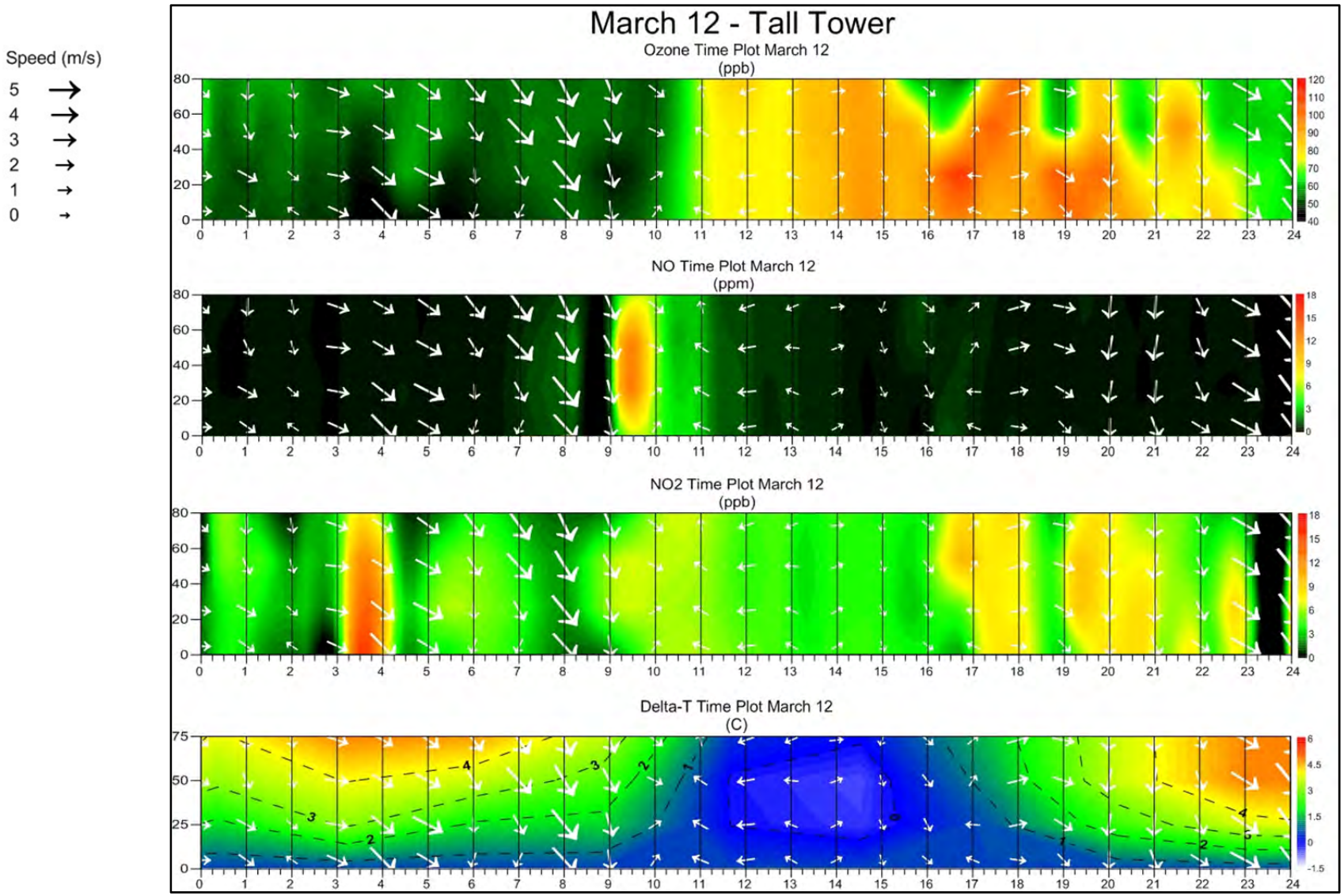


Figure 4.29 Tall Tower – March 12, 2011 (Continued)

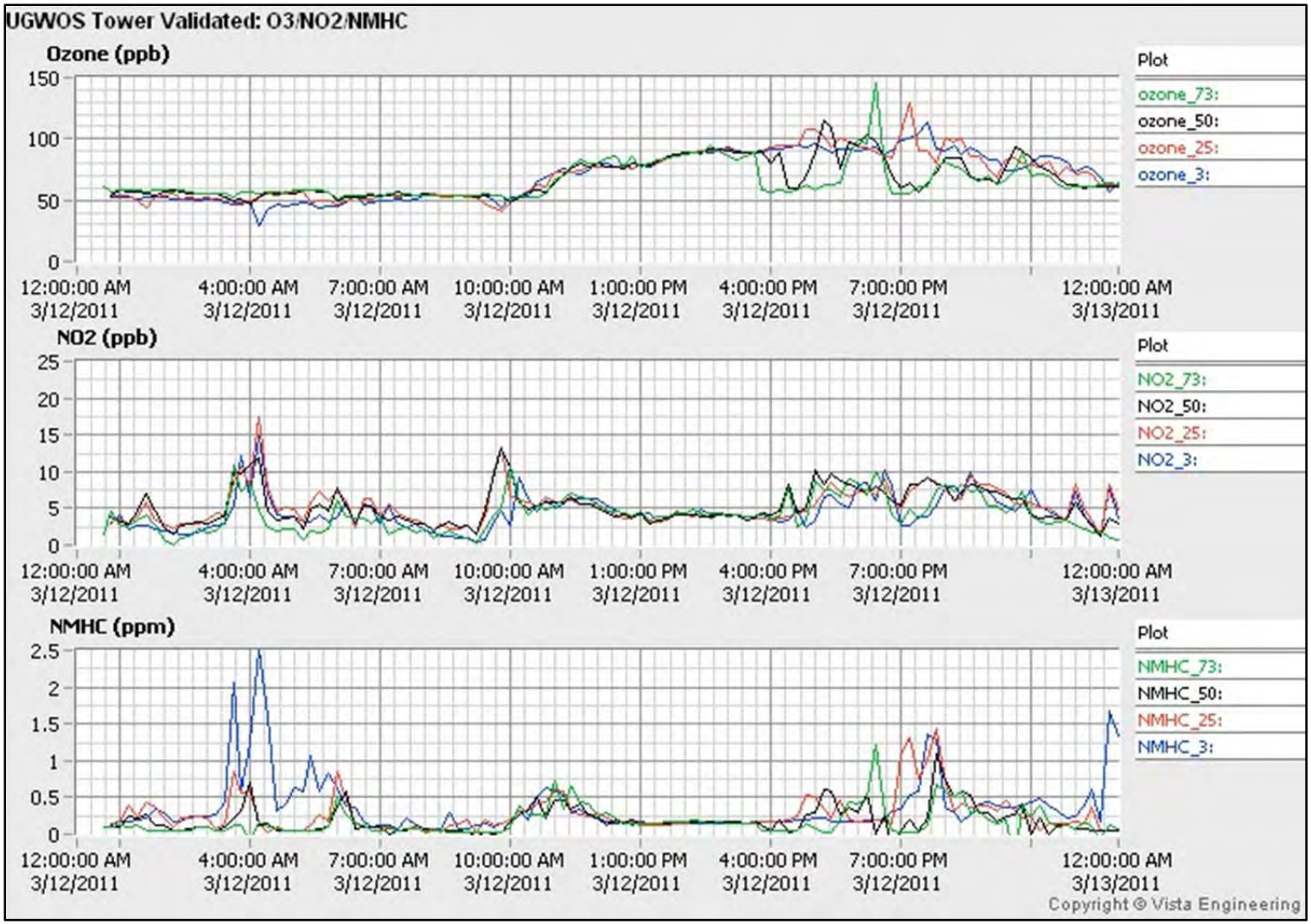


Figure 4.30 Tall Tower Time Series Plots for March 12, 2011

February 12 – February 15 (Figure 4.31)

This period was the first period during the study during which notable development of higher ozone concentrations occurred. Some minor increases in ozone concentrations are noted on February 12 and 13 during the mid-afternoon. However, a much more significant ozone episode occurs around 18:00 on February 14, coinciding with a very rapid increase in precursor concentrations, particularly NMHC concentrations. This event is unusual when compared with other 2011 events for two reasons. First, it occurs relatively late in the day (around 18:00 MST). This would tend to imply an aged plume. Second, the winds preceding the event have a consistent easterly component, bringing in air from directions that are not typically associated with precursor sources. However, the near-surface NMHC concentrations and the appearance of what looks like a rather narrow plume with sharp boundaries (note both the rapid increase and decrease of ozone and precursor concentrations) imply local sources. Further investigation of this event is warranted.

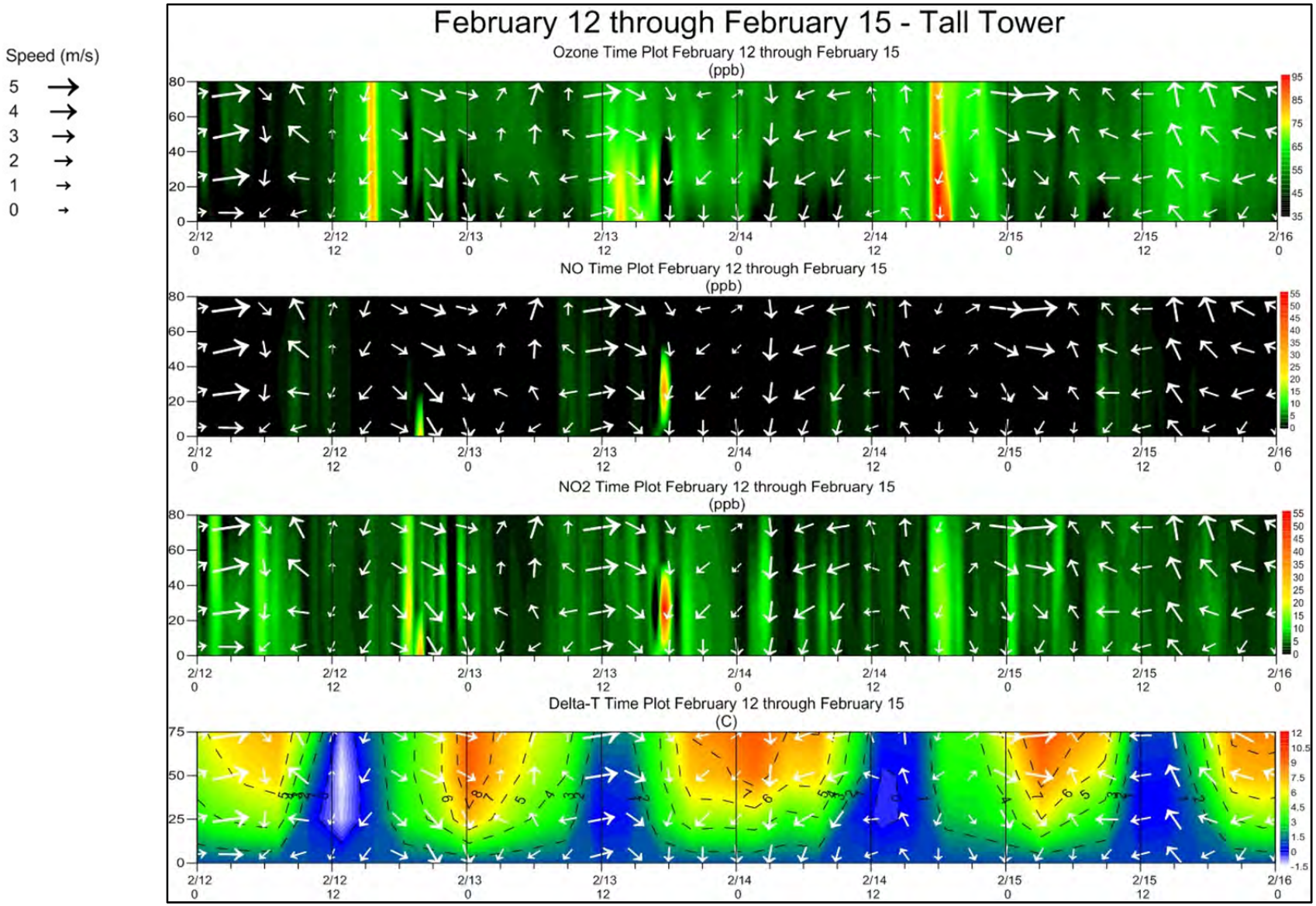


Figure 4.31 Tall Tower – February 12 through February 15, 2011

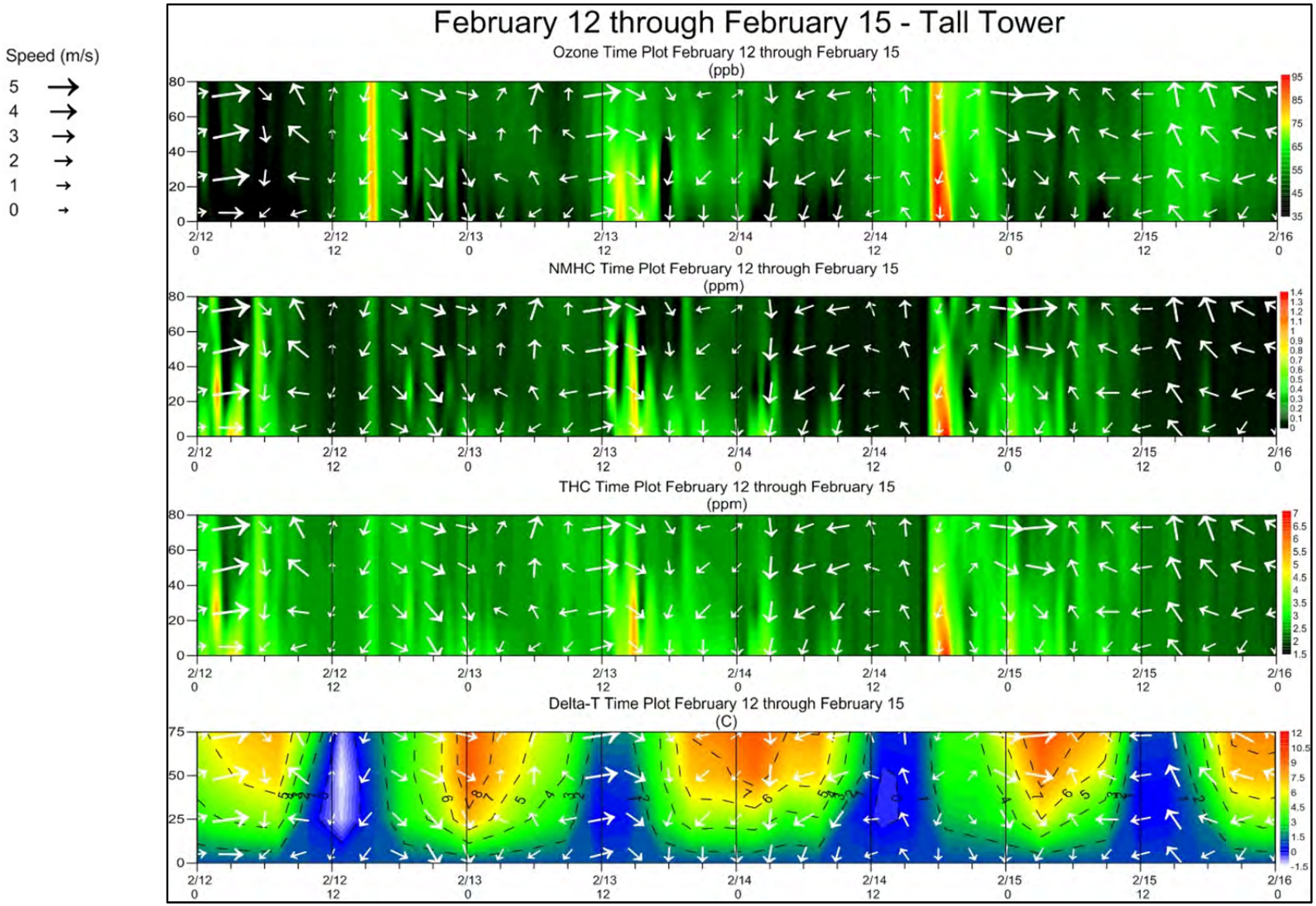


Figure 4.31 Tall Tower – February 12 through February 15, 2011 (Continued)

March 1 – March 5 (Figure 4.32)

This period is an extension of the first IOP that shows the termination of the initial ozone episode, followed by a brief ozone episode that occurred on March 5. The light winds, strong temperature inversion and presence of precursors that lead to the high ozone readings on March 2 are again apparent. However, the temperature inversion on the morning of March 3 is notably weaker – almost nonexistent at levels measured by the tower. This implies a much higher mixing height than that of the previous morning, and afternoon delta T readings similarly show less stable conditions. Thus, ozone concentrations are notably lower than during the previous days. Strong wind on the evening of March 3 and most of March 4 effectively flush out the area and prevent the buildup of precursors. However, by the morning of March 5, a strong temperature inversion has again been established accompanied by light winds, allowing ozone precursor concentrations to rise, with activity peaking around noon. This is followed by moderately high ozone concentrations during the afternoon of March 5. The winds leading up to these higher ozone concentrations are again associated with a northwesterly trajectory.

March 9 – March 15 (Figure 4.33)

This is an expansion of the second IOP. Strong northwest winds during the morning of March 13 flush out the area and end high ozone readings of the previous days during the IOP. However, lighter winds again prevail during March 14 and 15, and ozone precursors again accumulate. Some ozone formation on March 14 is noted, with increased activity on March 15. The correlation between afternoon ozone formation and precursors is particularly evident on March 15.

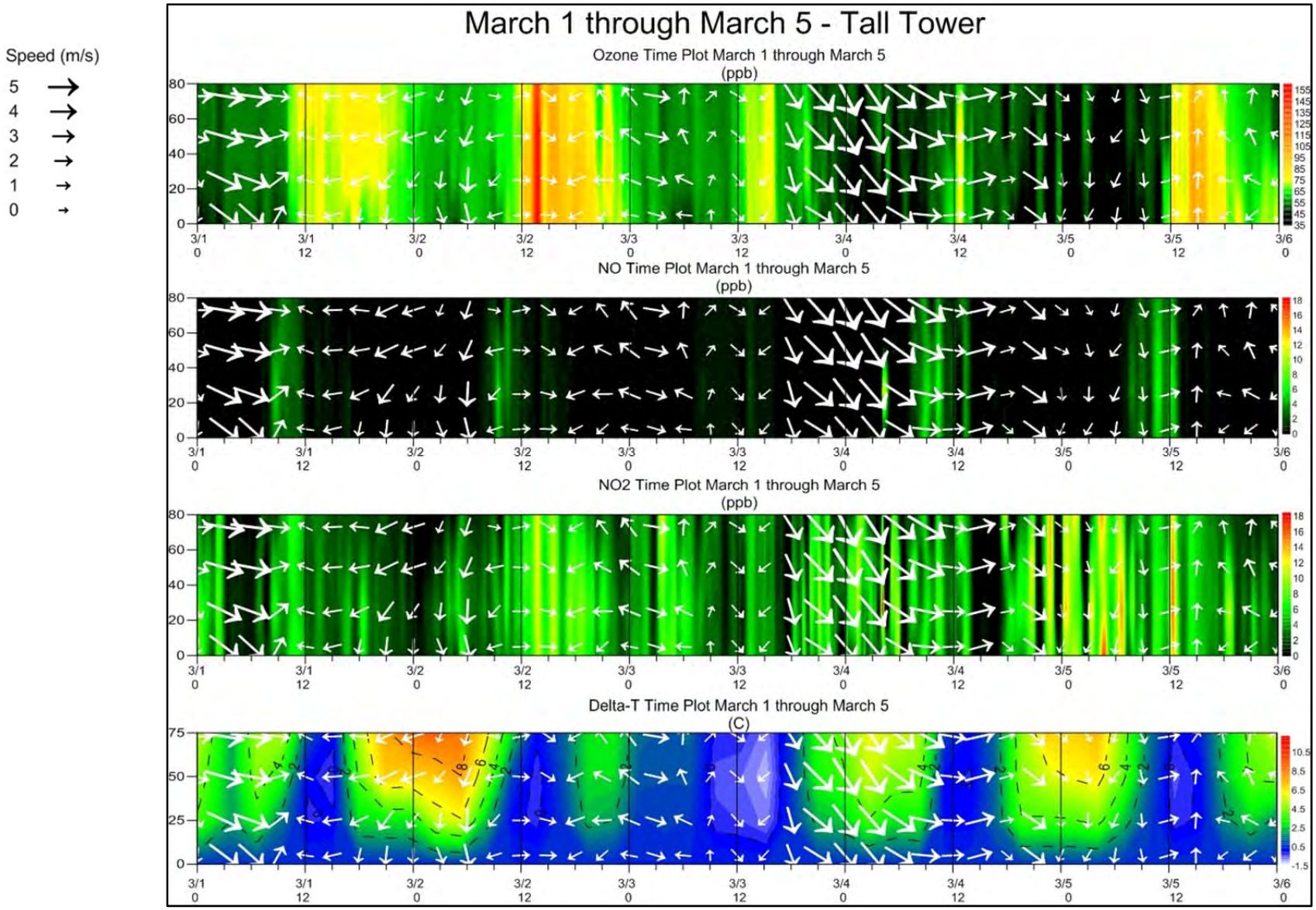


Figure 4.32 Tall Tower – March 1 through March 5, 2011

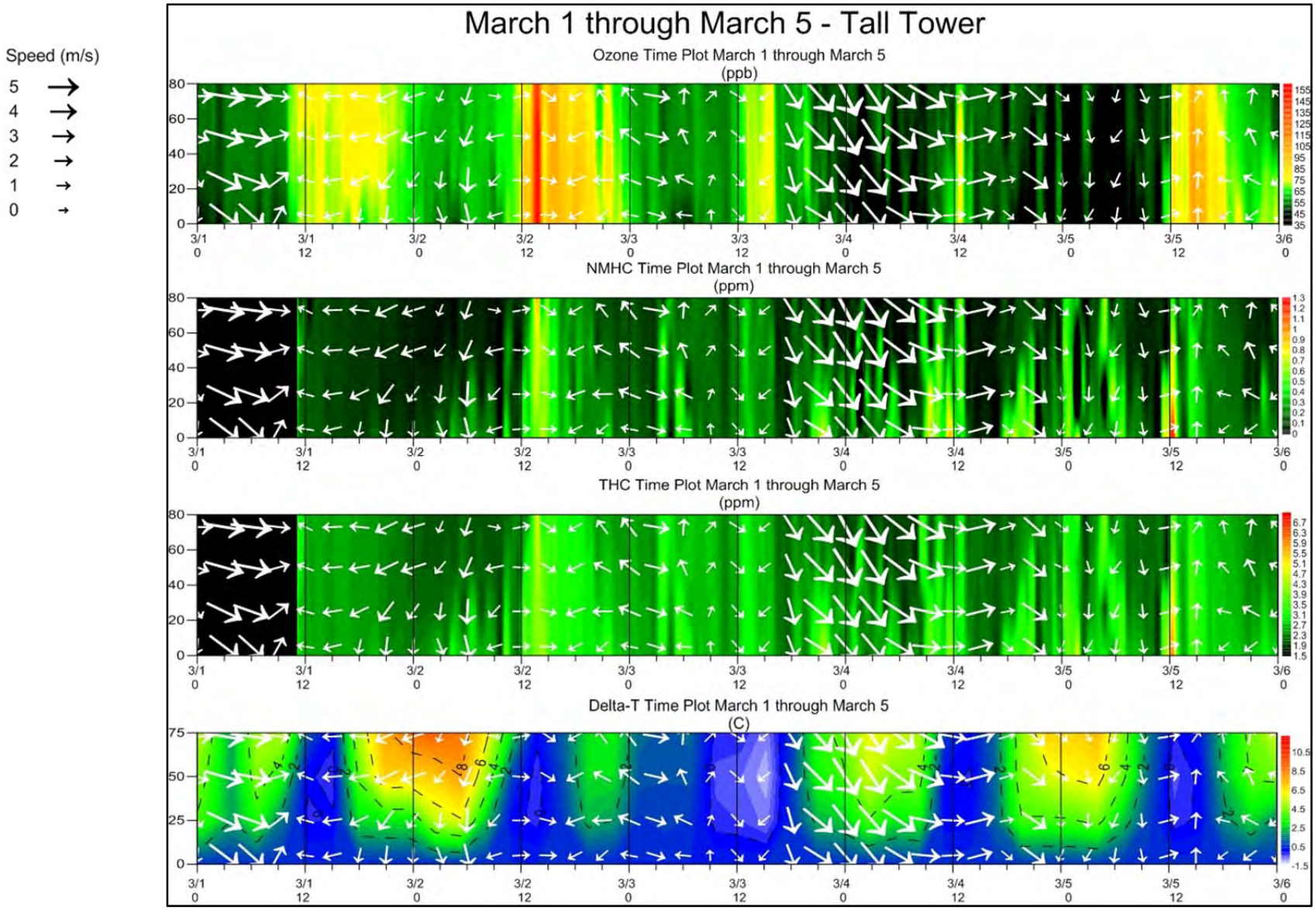


Figure 4.32 Tall Tower – March 1 through March 5, 2011 (Continued)

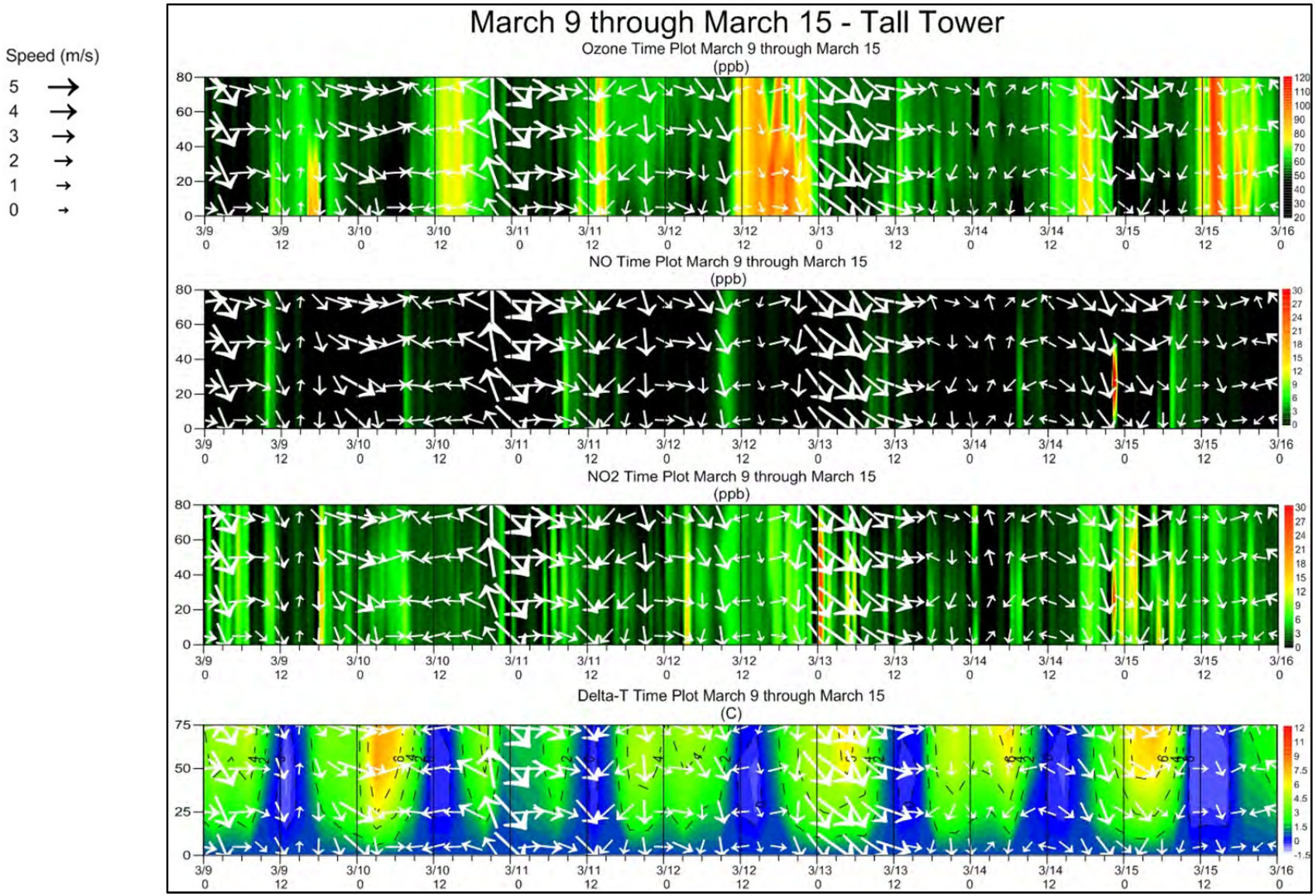


Figure 4.33 Tall Tower – March 9 through March 15, 2011

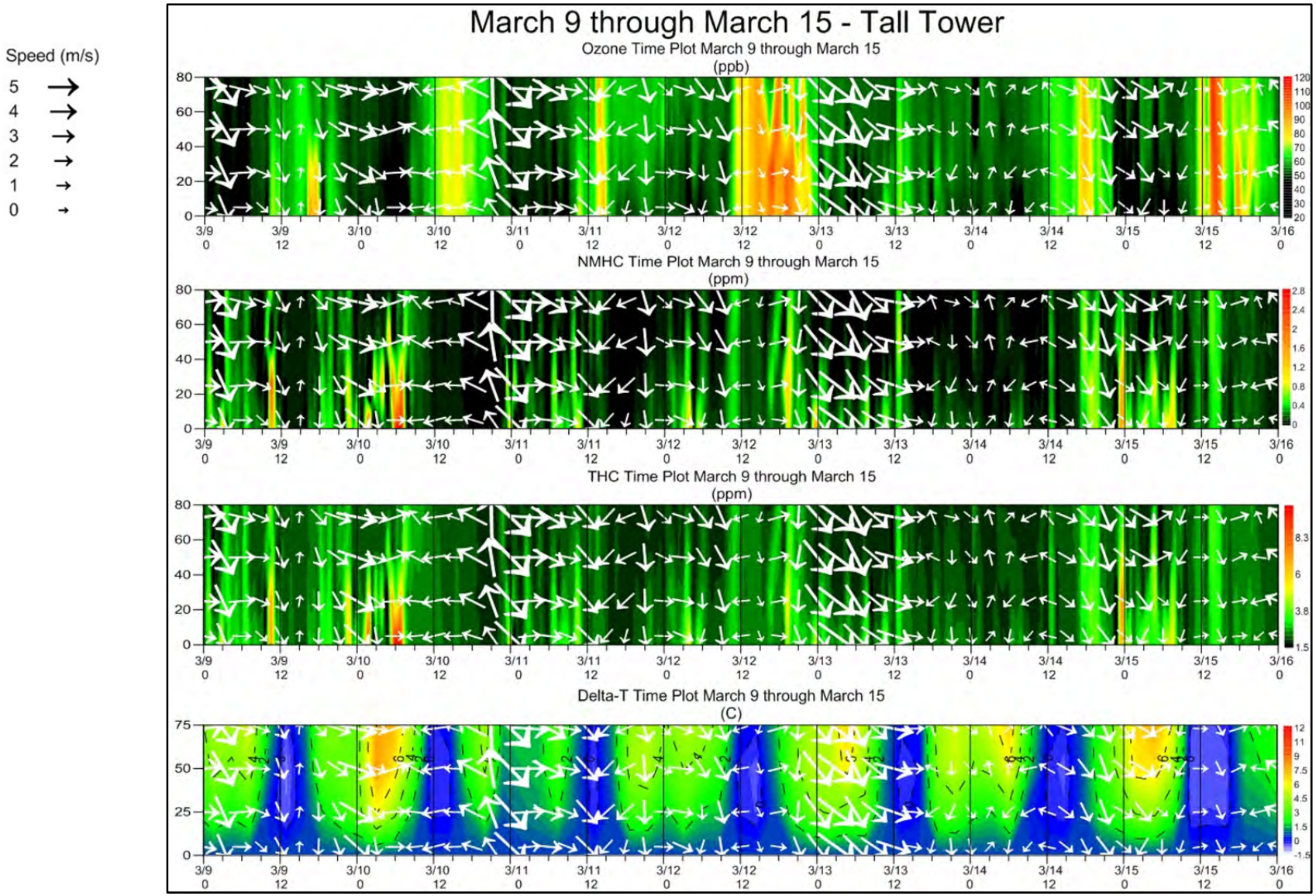


Figure 4.33 Tall Tower – March 9 through March 15, 2011 (Continued)

Tower Profiles

Similar to the balloon data presented above, the tall tower data were averaged together to produce generalized profiles. Given that snow was present throughout the 2011 study period, the remaining meteorological condition that has been repeatedly shown necessary for ozone formation is low wind speeds. Figure 4.34 presents averaged hourly data for all low wind speed days (sustained winds less than 3 mps) during which data were available for all parameters. The low wind speed days were divided into two categories: days when ozone concentration were greater than or equal to 75 ppb for at least one hour, and days that did not meet this criteria. This division resulted in fourteen elevated ozone days and three low ozone days. The goal was to visualize precursor and meteorological conditions that resulted in ozone development. For this presentation, hourly averages for four hours are presented: 05:00, 09:00, 13:00, and 17:00 MST.

The following general characteristics in the vertical profiles are noted:

- Slight scavenging of ozone occurs at surface during morning and evening hours due to the presence of NO.
- Strong inversions exist in the early morning (07:00) that break down over the course of the morning and linger as only a slightly elevated inversion at 15:00, at which point the vertical structure is essentially uniform due to good mixing conditions.
- NMHC concentrations are highest at the surface, while NO_x concentrations peak at the 25-m level.

Days with elevated ozone concentrations are further characterized by the following:

- The morning inversions are notably stronger.
- The NMHC gradient much stronger, though the top two levels remain basically constant throughout the day.
- Precursor concentrations in general are significantly higher.
- The NO_2/NO ratio at time of maximum ozone (15:00) is significantly higher.

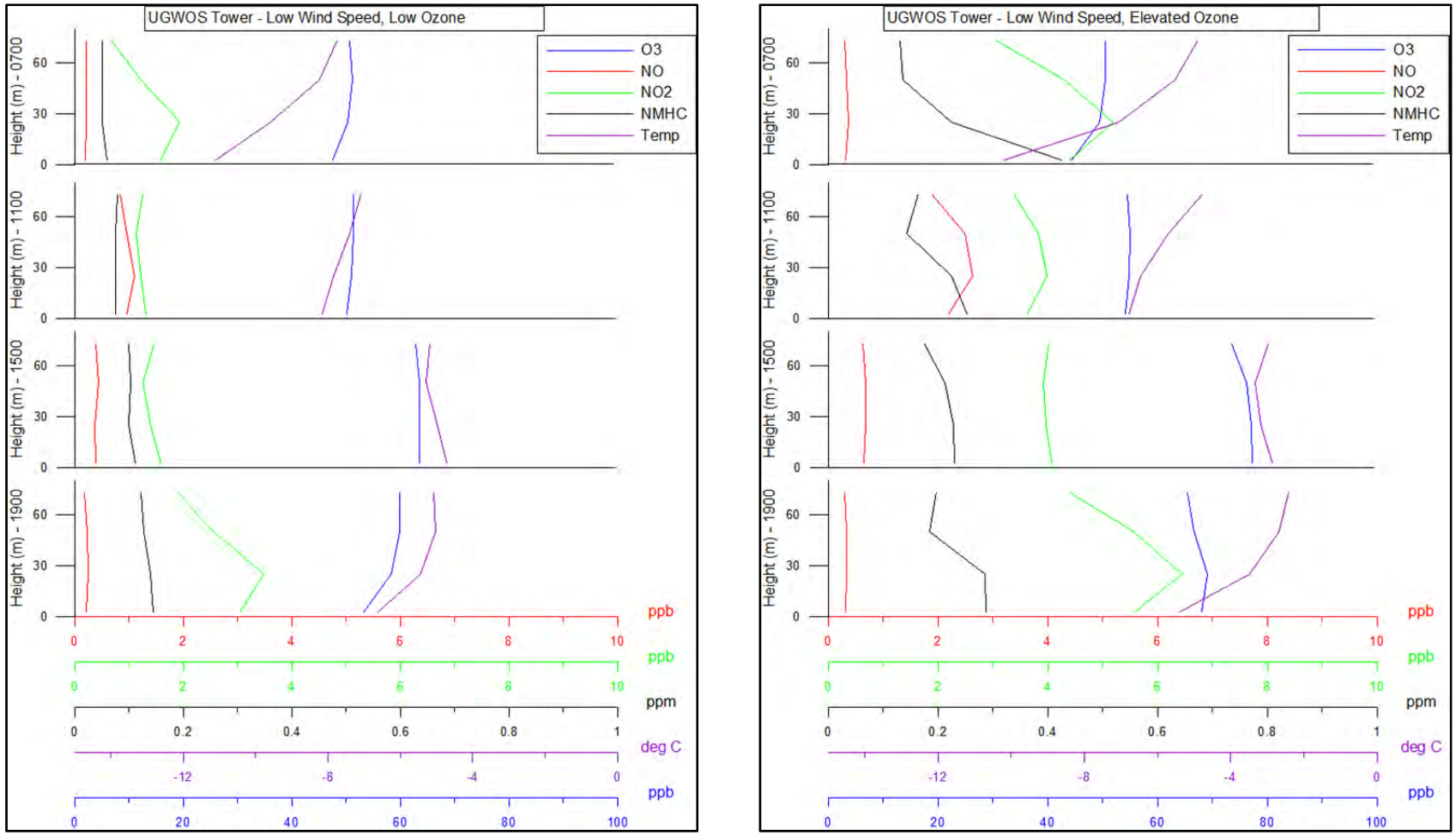


Figure 4.34 Vertical Profiles at the Tall Tower during Low Wind Speed Days

4.2.4 Summary of Observations Regarding Vertical Structure

While the Tall Tower and tethered balloon measurements were limited to at most 100 meters above the surface, which was nearly always below the top of the mixed layer, several general observations can be made regarding the vertical structure of wintertime ozone and ozone precursors in the UGWOS study area:

- A shallow inversion and low mixing height is critical for initial development of high ozone.
- Trapping of precursors at the base of elevated inversions is common.
- There is no evidence of ozone carryover aloft in either the tethered balloon or tall tower data, consistent with the aircraft data findings from the 2008 study.
- Furthermore, during UGWOS 2011, there is no significant evidence of ozone consistently developing in layers aloft and then being mixed down to the surface during the afternoon. In general, the layer above the surface becomes relatively well mixed early in the day and ozone concentrations are fairly uniform vertically, on average. There is, however, evidence of ozone development within a plume of precursors at any given level. A correlation between ozone and NMHC concentrations is frequently noted at all levels, particularly in the afternoon/evening, when NMHC < 6 ppm.
- VOC concentrations are highest at the surface, while NO_x concentrations are highest slightly above the surface. This is likely due to the buoyancy of the consistently hot NOx emissions.
- The NMHC/NO_x ratio is higher near the surface during the morning.
- In the balloon data, this appears to be due primarily to higher NO_x in the aloft stable layer.
- In Tall Tower data, this appears to be associated with low level NMHC sources.
- No NO_x plumes were noted aloft in the stable layer at Tall Tower, whereas NO_x plumes aloft were frequently noted at the balloon site. This is likely due to the distance of sources from each of the sites, with the tower seeing older, dispersed plumes, and the balloon seeing newer, still well defined plumes. VOC plumes were noted at both the Tall Tower and balloon site. Fresher plumes typically showed up closer to the ground.

4.2.5 Ozonesonde Data

Ozonesonde data have been presented in the above discussions as further information regarding the vertical structure of the surface mixing layer and ozone concentrations aloft. The ozonesonde data for 2011 in general show key features similar to those noted in 2008. The 2011 soundings once again demonstrate that the high ozone concentrations occur in a well-defined surface layer, with concentrations dropping off to values of about 50 to 60 ppb once above this surface layer. However, in reviewing the ozonesonde data for 2011, a significant difference in the typical ozone vertical profile was noted between 2011 and 2008. Figure 4.35 presents three ozonesonde soundings obtained during high ozone episodes in 2011. The plots show a consistent peak-to-background transition interval of about 400 to 500 meters. In contrast, the 2008 ozonesonde data consistently showed about a 100m peak-to-background transition depth (Figure 4.36). The 2008 profiles show ozone concentrations dropping off very quickly at the base of the elevated inversion, consistent with the highly stable air associated with the inversion.

In contrast to the 2008 profiles, the 2011 profiles show elevated concentrations persisting through the inversion layer and even into the well-mixed layer above the inversion, which is surprising.

The tethered balloon data provides some data that are useful in resolving this discrepancy. March 12 was unique in that it appears the tethered balloon was actually above the mixing layer during the late afternoon, with a very notable drop in ozone concentrations around 16:00 at the 100-meter level, and decreasing to the 60 ppb concentrations typically noted above the surface layer (Figure 4.37). This occurrence is consistent with the notably lower base of the inversion on March 12 compared to previous ozone episode days, as shown in Figure 4.35. The tethered balloon data shows a drop from about 145 ppb to 60 ppb in 67 meters, whereas the ozonesonde takes about 400 meters to make the same transition. The 67-meter tethered balloon transition interval is consistent with the 100-meter interval seen in the 2008 data.

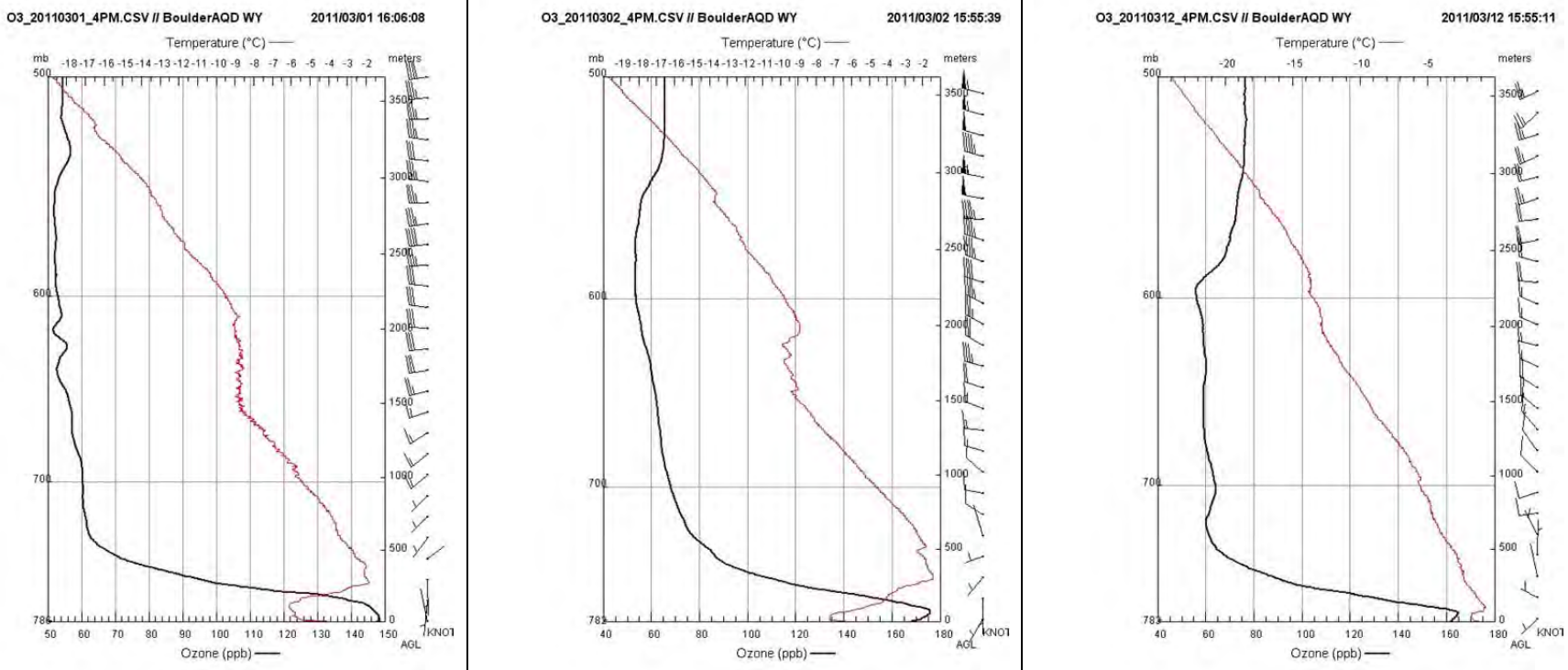


Figure 4.35 Ozone Soundings during Peak Ozone Episodes

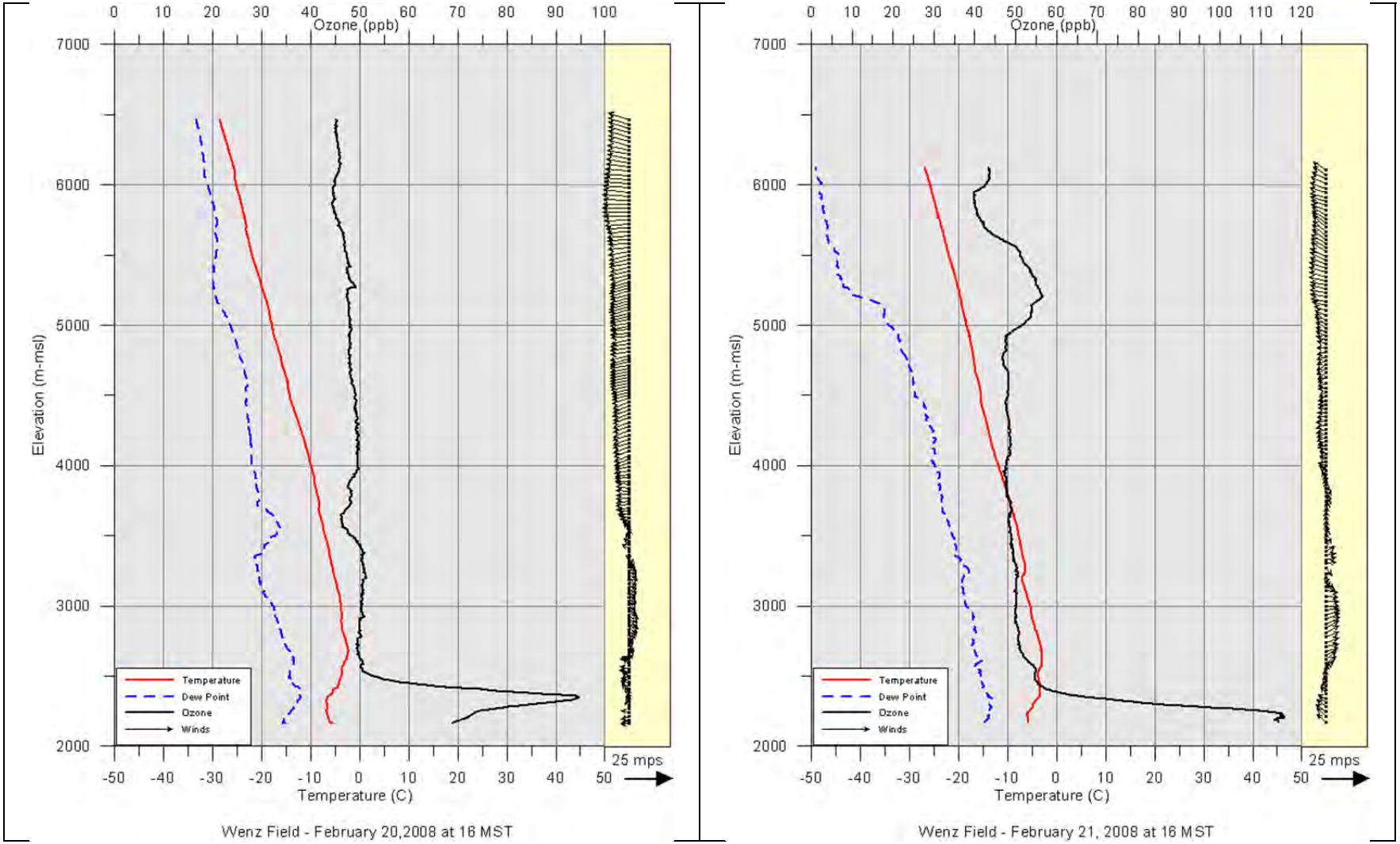


Figure 4.36 100 Meter Ozone Peak to Transition Depth

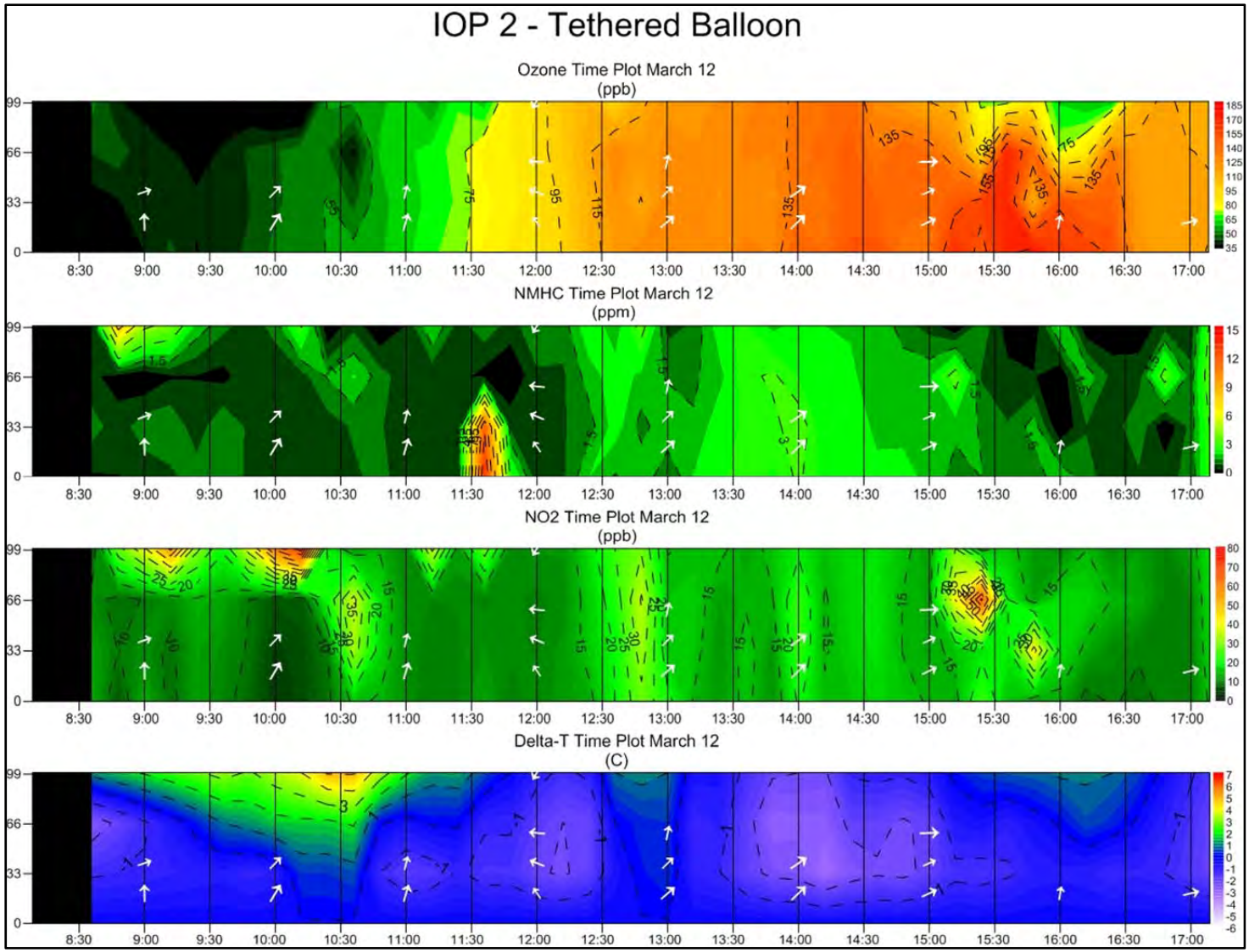


Figure 4.37 Typical Ozone Background Concentrations

With the tethered balloon data substantiating the 2008 profiles, it therefore seems likely that some sort of time constant or smoothing is being applied to the 2011 data. A different rawinsonde/ozonesonde system was used during 2011 than during the other UGWOS studies, including 2008. For 2011, an iMet-3050 System was used. The original system was configured to only receive and process rawinsonde data or ozonesonde data, but not both at the same time.

Modifications were made by iMet and by the start of the 2011 study the system had been modified to process both simultaneously through a virtualization technique and sharing of the iMet ground station data stream. Thus, two independent software interfaces were used in the system – one for the rawinsonde data stream and one for the ozonesonde data stream, with the ozonesonde interface provided by the ozonesonde manufacturer (Droplet Measurement Technologies, previously EnSci). Data streams were then combined into one file. In contrast, the 2008 system, a Sippican W-9000, had an integrated software interface designed by the manufacturer that handled both rawinsonde and ozonesonde data simultaneously. Thus, there is a very real probability of inherent differences between the years in the way that the data are received and processed, though both iMet and Droplet Measurement Technologies have to-date not revealed any data smoothing issues.

Figure 4.38 provides plots comparing the raw ozone data for 2008 and 2011. For this comparison two pairs of high ozone days were chosen, concentrating on the portion of the sounding about (3500 – 4500 meters MSL), where the readings are similar in magnitude for the two years, as well as relatively steady. One-second ozone partial pressure data from the original ozonesonde files are plotted. They demonstrate a fundamental difference between the 2008 and 2011 data. The 2008 data are allowed to change rapidly, showing the inherent but entirely expected (and basically insignificant) "noise" in the ozonesonde signal. In contrast, the 2011 data is completely smooth. This would seem to imply some sort of filtering or smoothing of the 2011 ozone data in the measurement cell, cell to rawinsonde interface, or in the software used to process the ozonesonde data received from the ground station. This inherent difference was noted in every 2008 and 2011 sounding.

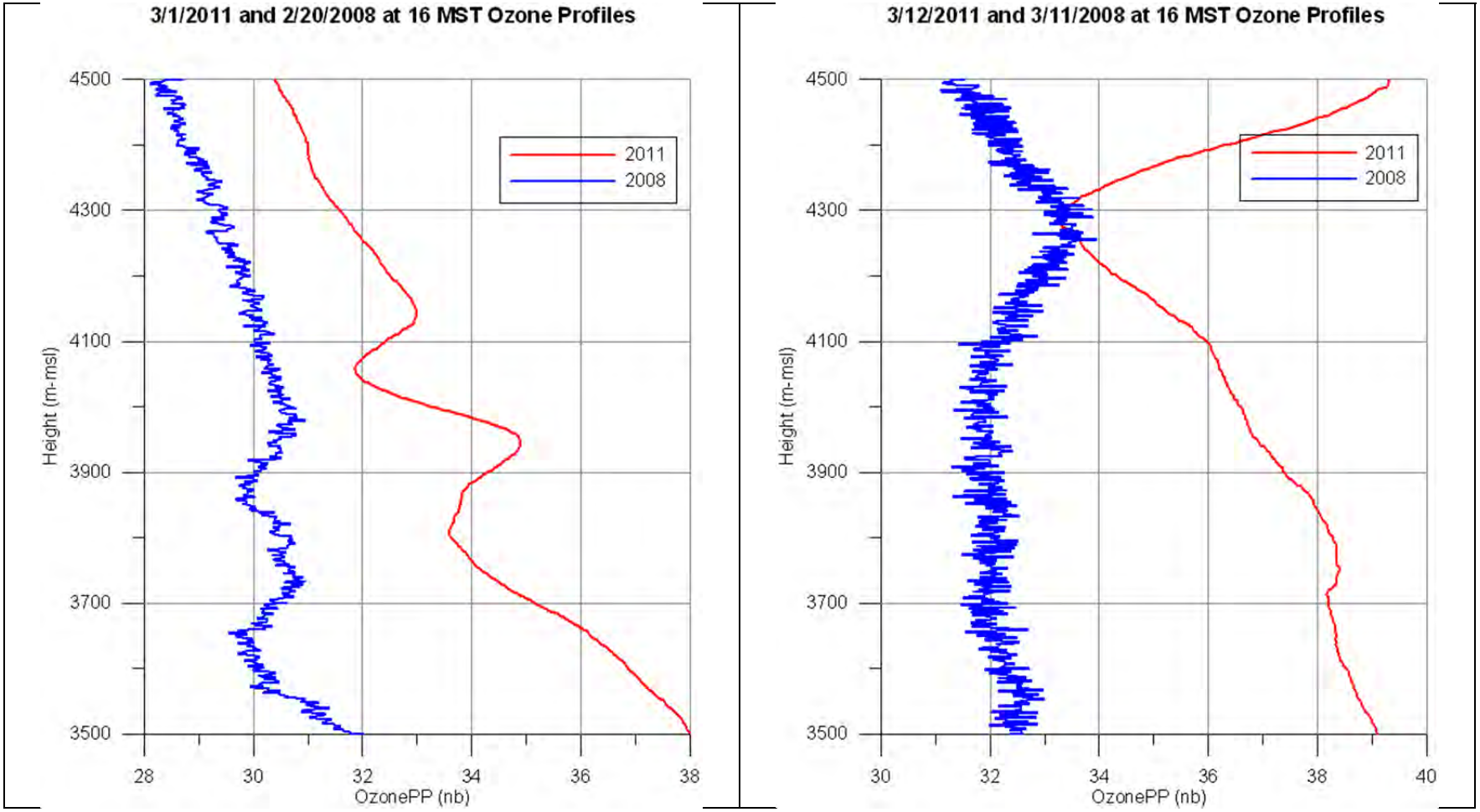


Figure 4.38 Comparison of 2008 and 2011 Ozonesonde Profiles

Note that the rawinsonde data from the 2011 soundings are not in question and the ozonesonde data still provide valuable information regarding ozone concentrations above and below the inversions. However, based on the discussion above, it does not appear that the 400 to 500 meter region above the inversion is impacted by ozone in the manner shown by the 2011 soundings, and that the ozone profiles observed in 2008 are more representative of the wintertime ozone episode conditions and in particular, the vertical structure of the ozone profile and rapid decrease in ozone concentrations above the shallow surface layer. If the AQD plans to use ozonesonde data for future modeling purposes, it may be prudent to clarify this issue.

4.2.6 Transport to Wyoming Range

Several days of elevated ozone were measured at the Wyoming Range site during the UGWOS field study. Since this site is on the far western edge of the Green River Basin at a relatively high elevation, it was unexpected that 11 days during UGWOS recorded an 8-hour ozone concentration above 65 ppb and two days recorded an 8-hour concentration over 80 ppb. AQD requested further analysis of the monitoring data in an attempt to better understand the meteorology associated with the high ozone episodes. The analysis focused on the weather conditions conducive to high ozone formation and the transport times of the ozone laden air mass from the source region to the Wyoming Range site. In addition, the vertical structure of the atmosphere was analyzed to determine the height associated with the top of the inversion, the inversion strength and depth and the wind speeds and directions within the transport layer.

On March 10, 2011, an eight-hour ozone concentration of 83 ppb and a 5-minute concentration of 102 ppb were measured at the Wyoming Range site. The meteorology present during this episode was near optimal for transport of higher ozone concentrations and became the primary focus of this analysis. The following section reviews the meteorology associated with this high ozone period.

Figures 4.39 through 4.42 present ozone pollutant roses for the Wyoming Range Site. Pollutant rose arms containing darker orange segments indicate the wind direction associated with higher ozone values. Figure 4.39 shows the ozone rose for the entire four day intensive operational period from March 9 through March 12. The Figure indicates that higher ozone concentrations occurred during southeast flow. The daily variability is very striking however as the vast majority of the ozone transport occurred during March 10 with very little ozone on either March 9 or March 11. This variability highlights how ozone can be formed and transported to outlying areas in the Basin.

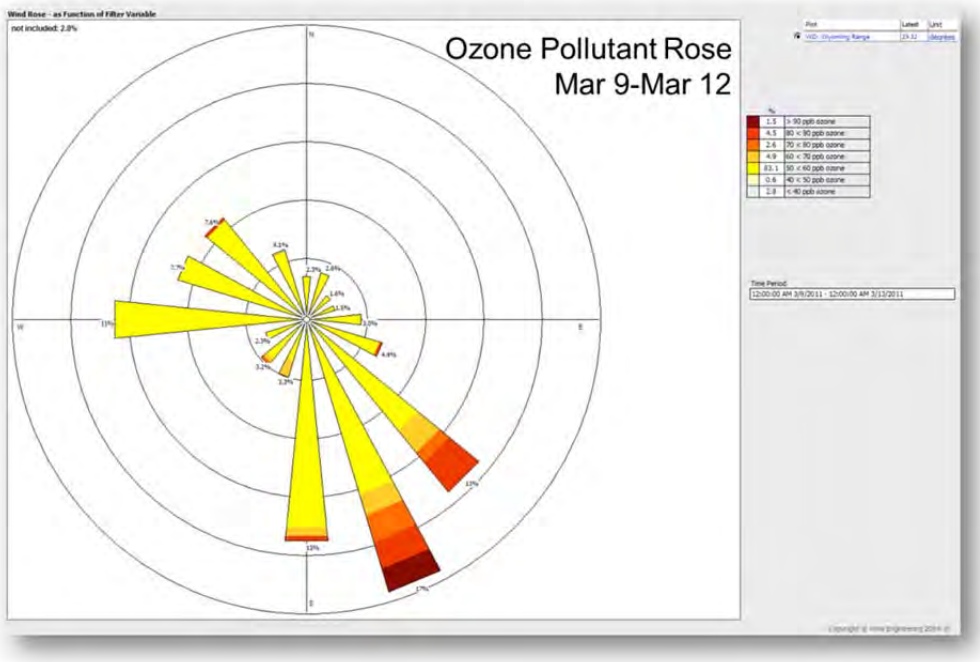


Figure 4.39 Ozone Pollutant Rose for Intensive Operational Period #2 (March 9 - March 12, 2011) at Wyoming Range Site

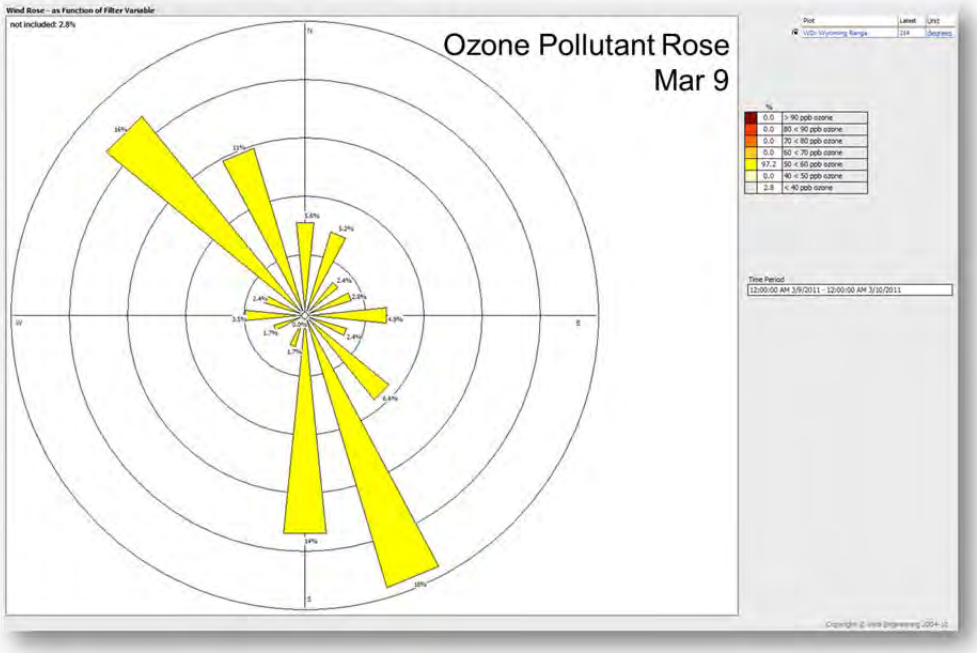


Figure 4.40 Ozone Pollutant Rose for March 9, 2011 at Wyoming Range Site

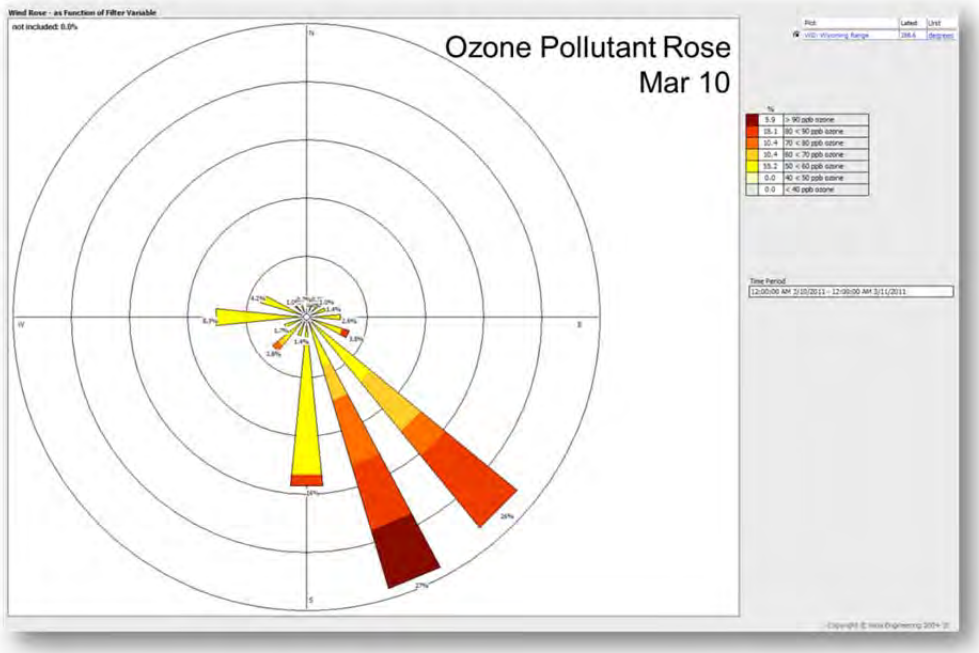


Figure 4.41 Ozone Pollutant Rose for March 10, 2011 at Wyoming Range Site

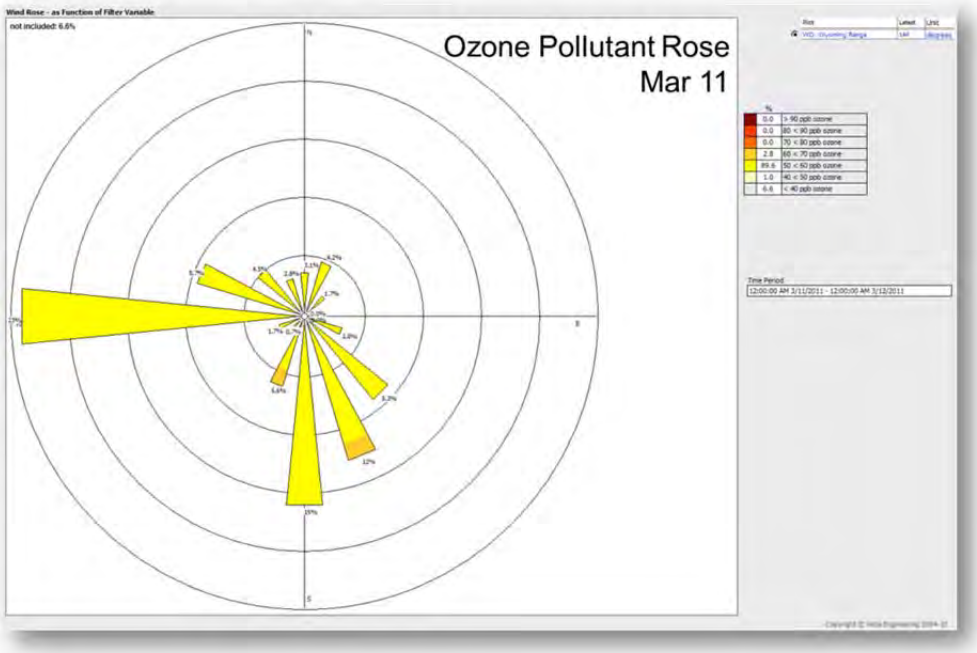


Figure 4.42 Ozone Pollutant Rose for March 11, 2011 at Wyoming Range Site

Figure 4.43 presents the 24-hour duration time series plots of ozone, wind direction and wind speed measured on March 10, 2011 at the Wyoming Range site. The ozone concentrations gradually trended upward starting at approximately 9:00 a.m. in the morning, reaching a peak at 16:00 in the afternoon. Ozone continued to stay elevated at approximately 90 ppb until 10:00 p.m. at which point a frontal passage occurred scouring the elevated ozone air mass from the area.

During the period from 9:00 a.m. until 10:00 p.m. the wind direction was fairly consistent out of the southeast associated with a strong, well developed upslope flow. This type of upslope pattern typically starts later in the morning or early afternoon. The duration of this event was particularly long and was reinforced by a cold front moving in from the west. The magnitude of the winds speeds averaged 5 to 6 mps during the 12-hour period. Normal upslope flow tends to be lighter in magnitude but again this was reinforced by the cold front to the west. As soon as the cold front moved through at approximately 10:00 p.m. ozone concentrations dropped to background values.

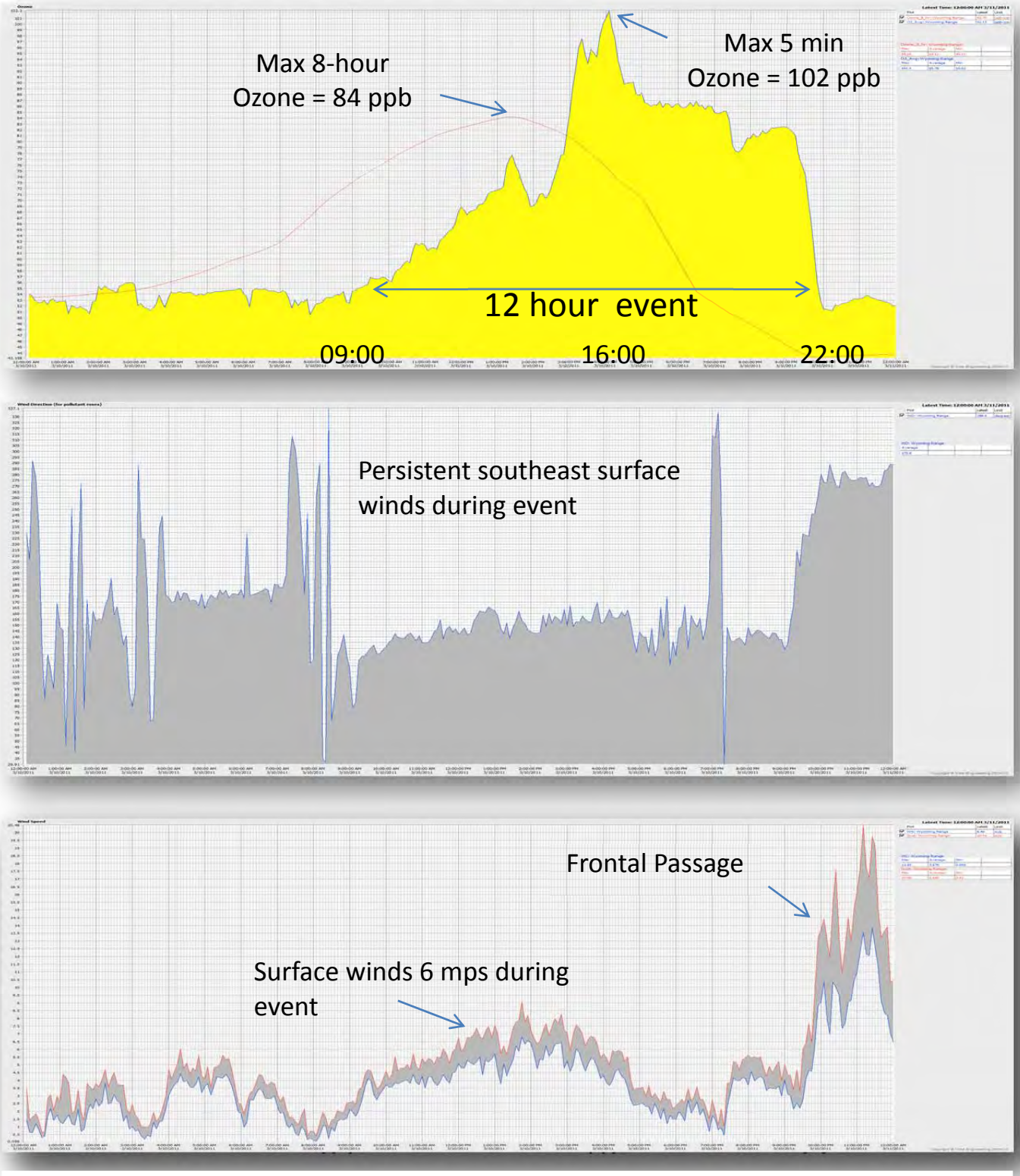


Figure 4.43 Time Series Plots from March 10, 2011 at Wyoming Range Site

Conditions aloft during the elevated ozone episode were also examined. The ozonesondes released from the Boulder site were used to determine the top of the inversion, depth of the inversion and relative strength of the inversion. In addition, the transport winds within the inversion associated with the higher ozone concentrations were examined.

The sounding taken at 8:00 a.m. on March 10 showed a strong (14° C) inversion with a depth of approximately 200 meters (Figure 4.44). The elevation difference between the sounding site and the Wyoming Range site is approximately 450 meters. A southeast wind flow pattern with light winds (below 10 mps) was forming in the lower levels but was still somewhat unorganized. By noon (Figure 4.45), the southeast wind flow was well developed and the inversion depth had increased to 460 meters, the approximate base elevation of the Wyoming Range site. Winds were still fairly light in speed and surface ozone concentrations had started to climb at the Wyoming Range site. The 14:00 sounding (Figure 4.46) continued to show a very organized southeast flow aloft with the base of the inversion rising another 50 meters (well above the elevation of the Wyoming Range site). At this time, ozone concentrations began to rise rapidly at the Wyoming Range site. By 16:00 (Figure 4.47) southeast flow continued and turned more southerly aloft, likely due to the approaching cold front. The inversion base had lowered to approximately the elevation of the Wyoming Range site while surface ozone concentrations peaked over 100 ppb. There were no additional soundings taken that day. Figure 4.43 shows that at approximately 10:00 p.m. on March 10, a cold front with wind speeds greater than 10 mps out of the west-northwest, passed over the location of the Wyoming Range site. As a result, the site ventilated and ozone concentrations dropped back to near background values (approximately 50 ppb). Figure 4.48 shows the sounding taken at 8:00 a.m. on March 11. Winds aloft were now northwesterly behind the cold front but a shallow inversion remained at the sounding site. Wyoming Range was above the inversion.

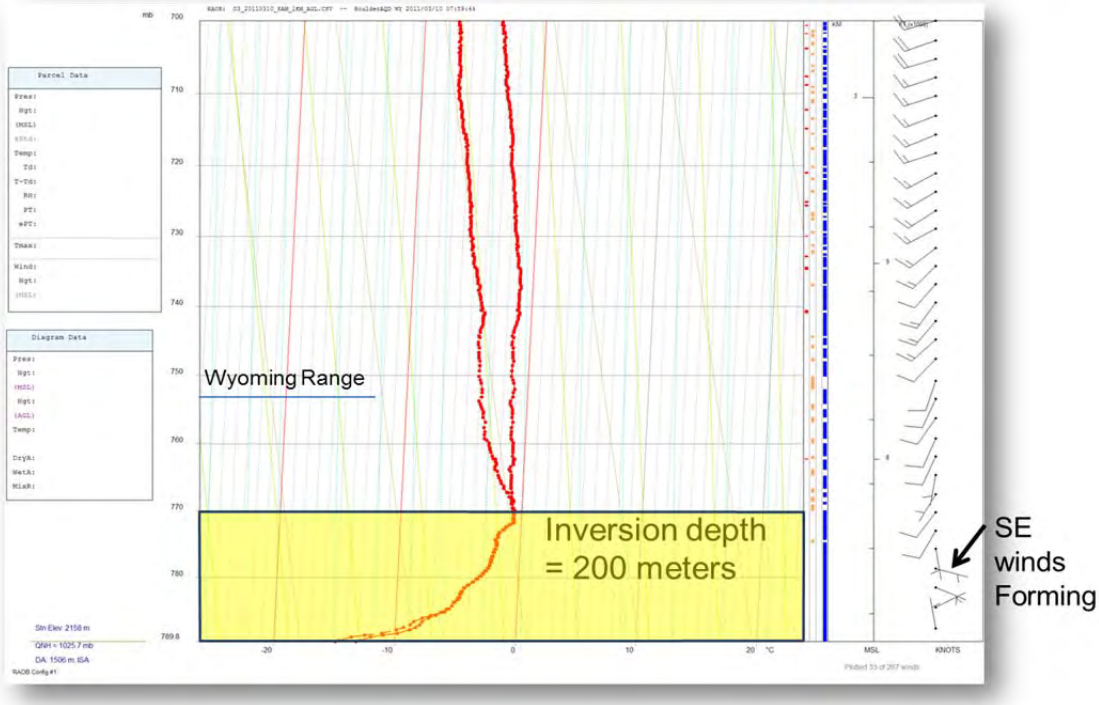


Figure 4.44 Ozonesonde from 08:00 on March 10, 2011

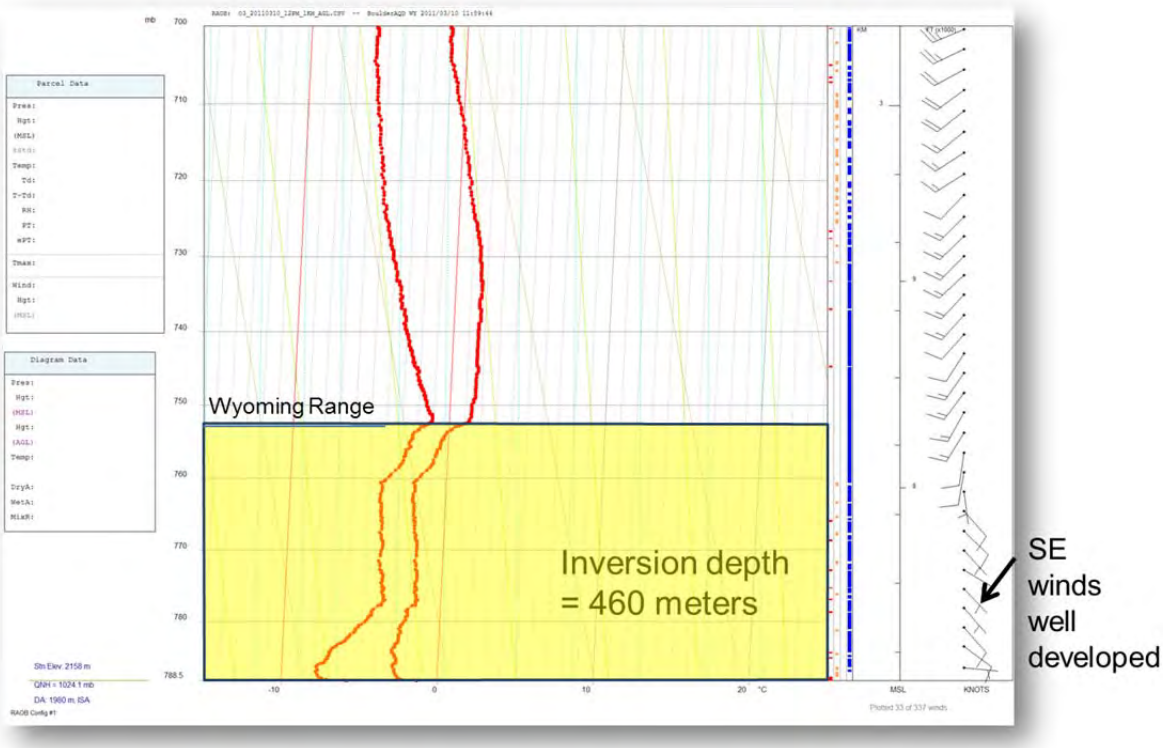


Figure 4.45 Ozonesonde from Noon on March 10, 2011

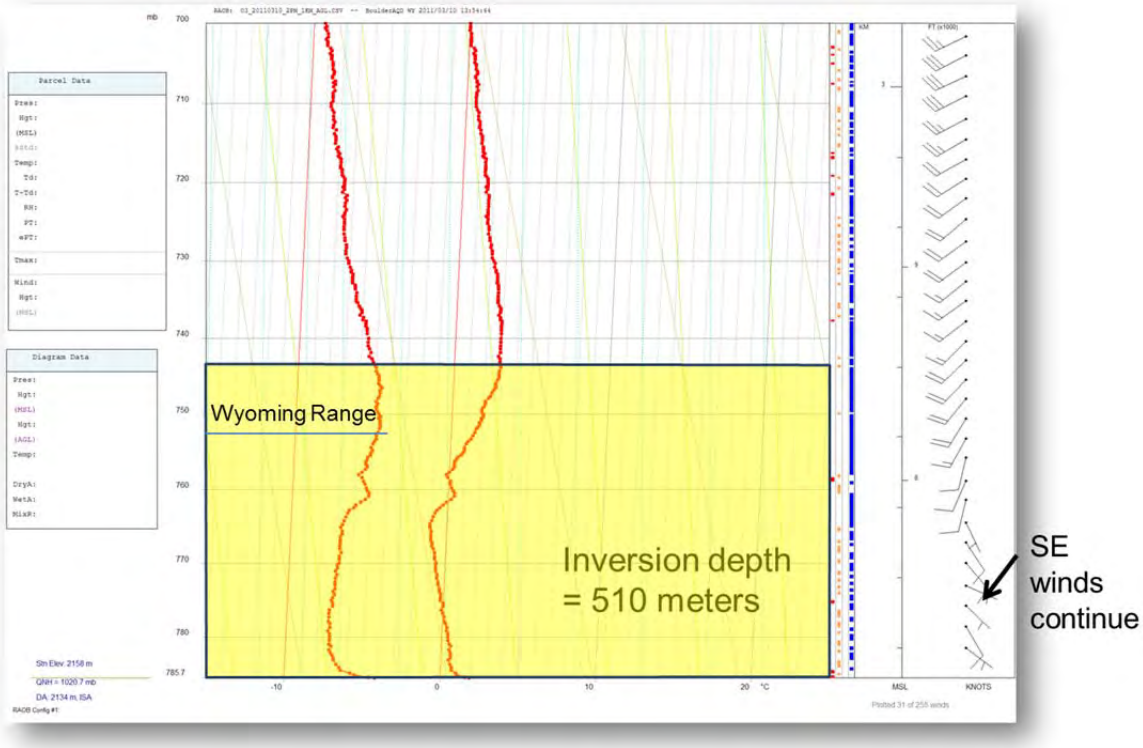


Figure 4.46 Ozonesonde from 14:00 on March 10, 2011

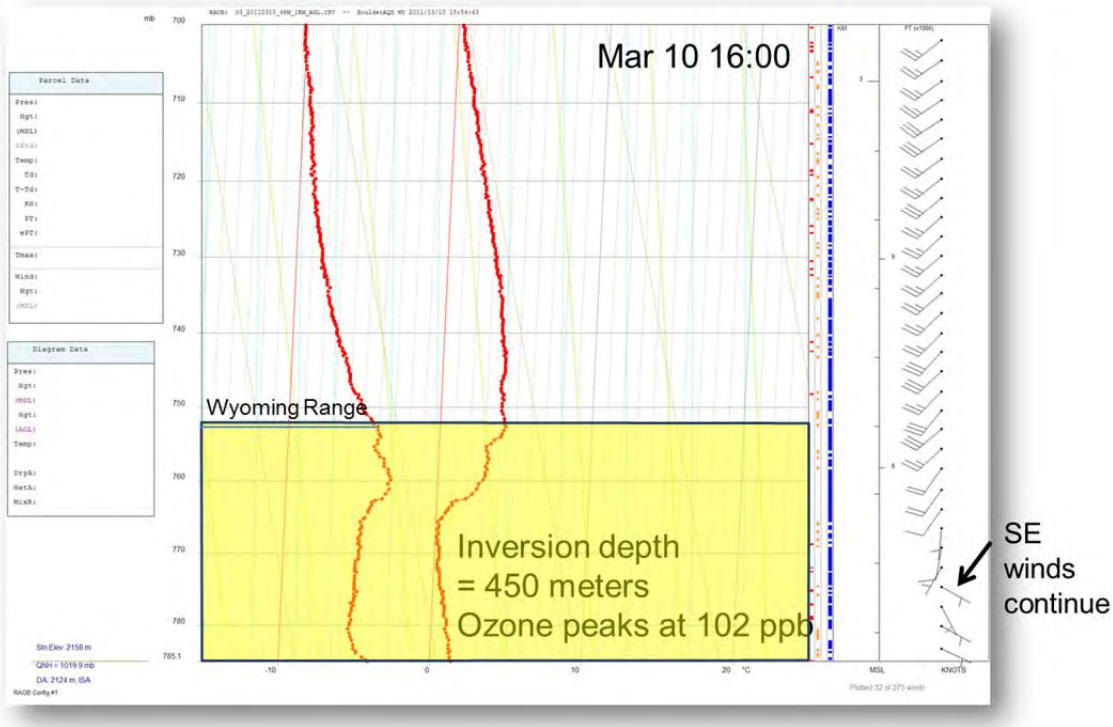


Figure 4.47 Ozonesonde from 16:00 on March 10, 2011

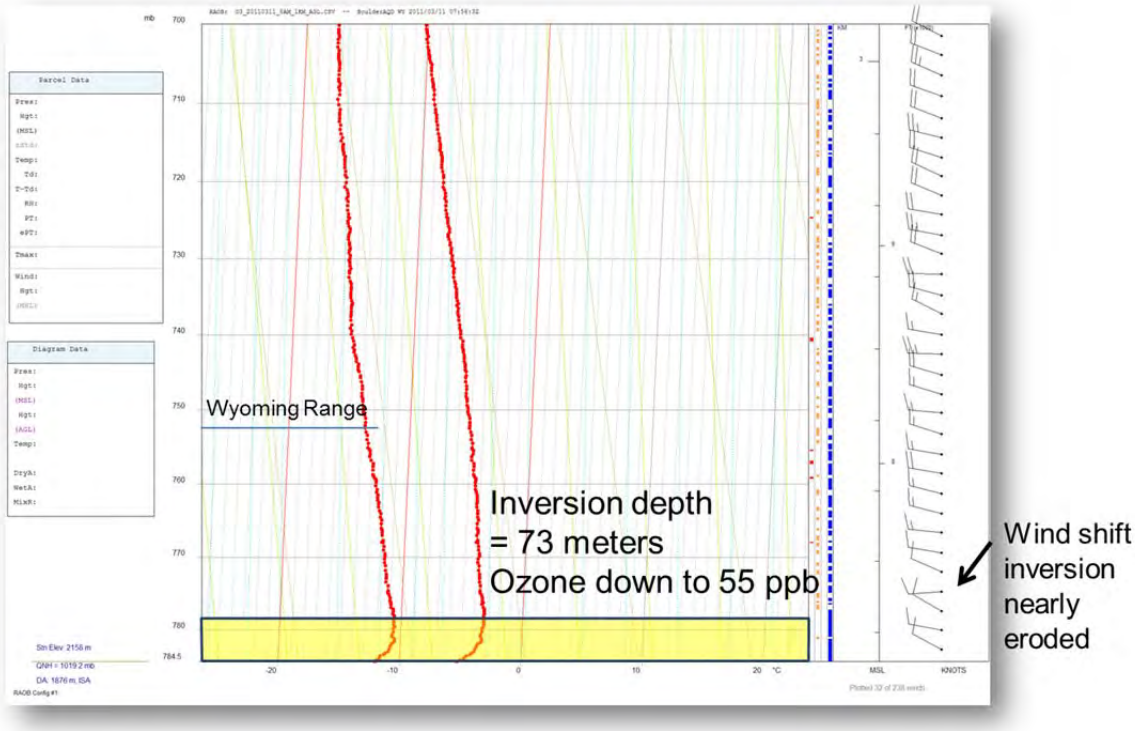


Figure 4.48 Ozonesonde from 08:00 on March 11, 2011

Figures 4.49 through 4.52 show a sequence of observations at the Wyoming Range, Daniel, Pinedale, Boulder, and Juel sites on March 10, 2011. The transparent yellow areas on these plots are an approximation of the inversion top elevation throughout the Upper Green Basin. The white numbers below the station names are ozone concentrations in ppb, the blue arrows indicate wind direction and the numbers within the arrows indicate the wind speed in mps. On the bottom left of each of the figures is a tabular listing of hourly ozone concentrations at the Wyoming Range and Daniel sites. The ozone concentrations are plotted as a color gradient with light green being the lowest concentrations and dark blue the highest. This is done to show the temporal progression of the ozone laden air mass as it transports northwestward embedded in the southeasterly flow. It is evident that the high ozone concentrations that move through the Daniel area move through the Wyoming Range location approximately 3-hours later with little in the way of dispersion or enhanced chemistry is producing new ozone at a rate which essentially offsets the ongoing dispersion.

Figure 4.49 contains the data from 08:00 in the morning corresponding to the approximate time of the sounding in Figure 4.44. At this point surface ozone concentrations are low throughout the network and surface wind patterns show very light southeasterly flow. By noon (Figure 4.50) surface ozone is on the rise throughout the network but especially evident at Daniel. Surface winds at Wyoming Range are from the southeast at 5 mps. The base of the inversion is now high enough that the Wyoming Range site is within the inversion. By 2:00 p.m. (Figure 4.51) the highest ozone concentrations have moved past the Daniel site and are approaching the Wyoming Range site. Surface winds continue to be southeasterly and are increasing in velocity and the Wyoming Range site remains within the inversion. Figure 4.52 shows that by 16:00 the peak ozone has reached the Wyoming Range Site and the southeasterly flow continues.

Figure 4.53 shows the data from March 12 at 16:00. Wyoming Range is above the inversion and the resulting winds from the cold front place the site upwind of the basin. Hourly ozone concentrations have dropped to background levels and the inversion base has retreated to the east. The most interesting residual data is the extraordinary horizontal ozone gradient between Pinedale (57 ppb) and Boulder (127 ppb). The ozone concentrations at Boulder are high due to the very shallow inversion overhead while Pinedale is above the inversion top with a northwesterly wind ventilating air at the site. This underlies the extreme importance of documenting and measuring the depth and strength of the inversion base in prediction of ozone concentrations.

Figure 4.49 Surface Ozone, Winds, and Estimated Inversion Top at 08:00 on March 10, 2011

Figure 4.50 Surface Ozone, Winds, and Estimated Inversion Top at Noon on March 10, 2011

Figure 4.51 Surface Ozone, Winds, and Estimated Inversion Top at 14:00 on March 10, 2011

Figure 4.52 Surface Ozone, Winds, and Estimated Inversion Top at 16:00 on March 10, 2011

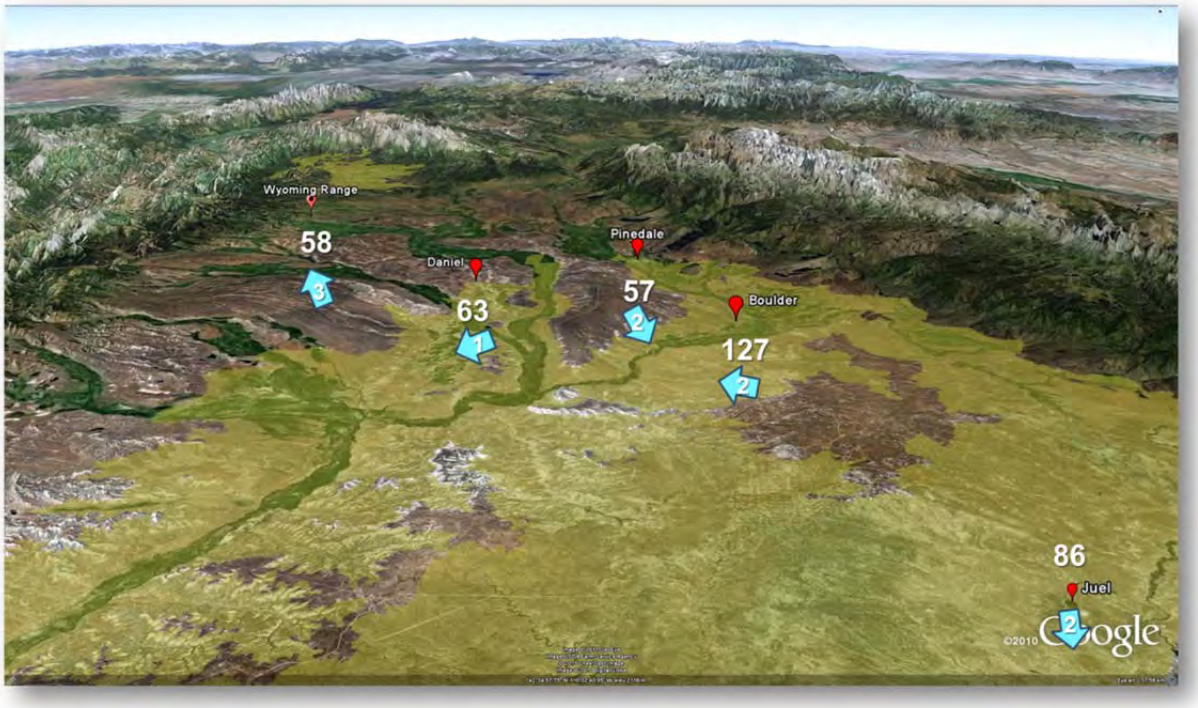


Figure 4.53 Surface Ozone, Winds, and Estimated Inversion Top at 16:00 on March 12, 2011

The analysis of the March 10, 2011 ozone event at Wyoming Range brings us to several conclusions/observations:

- Persistent southeast transport winds within lower levels of the inversion are important for ozone transport. These winds are not necessarily light (winds during highest ozone episode > 5 mps).
- High ozone at Wyoming Range typically develops 6-24 hours after peak values are measured at lower elevation sites.
- As the inversion strengthens and deepens, the air mass with higher ozone / precursor concentrations is transported northwestward on the western half of the Upper Green River Basin.
- Strengthening inversions can on occasion be deep enough to build over the Wyoming Range site allowing for transport of ozone laden air mass with minimal dispersion. The rapid development and significant depth of the inversion were not anticipated.

- Abundant snow cover enhances these episodes due to reflective incoming radiation and also near surface cooling which strengthens the inversions.
- These episodes also occurred during periods of clear skies with abundant radiation to enhance the atmospheric chemistry needed to produce the high ozone values.
- There are likely no areas in the Upper Green River basin isolated from potential transport of these ozone laden air masses. In addition to ozone transport northwest to Wyoming Range, it is also anticipated upslope flow and associated southwest flow has the potential to transport ozone laden air northeast to the west slope of the Wind River Mountain range under optimal conditions.
- This daily variability in ozone concentrations highlights how quickly the ozone can be formed and transported to outlying areas in the Basin.

4.3 Precursors

4.3.1 Nitrous Acid (HONO) Measurements

As a subcontractor to MSI, the University of Houston performed continuous measurements of nitrous acid (HONO) at the Boulder II site during the 2011 UGWOS field program. The LOPAP instrument started collecting data on January 11, 2011 and ran almost continuously until March 31, 2011. Unfortunately, some electronic units of the instrument were severely damaged in mid February due to a power outage. As a consequence data loss for about 2 weeks occurred.

For the 2011 campaign the sampling unit was attached to a small tower (height 1.80 m). The sampling unit stayed at the surface for 15 min, then moved to the top of the tower, where it stayed for another 15 minutes. Afterwards, the unit returned back to the surface and resumed a new cycle. The purpose was to explore whether HONO gradients close to the surface could be detected.

Based on one-minute values, 10-minute and one-hour average values were calculated and merged with other data sets available at the Boulder site. However, only the times when the HONO sampling unit was at the top of the small tower were compared to other data obtained at the Boulder site.

Figure 4.54 presents a time-series plot of 10-min HONO data for the period January 11-March 31, 2011. The gap in February is due to damage to electronic units in the HONO instrument.

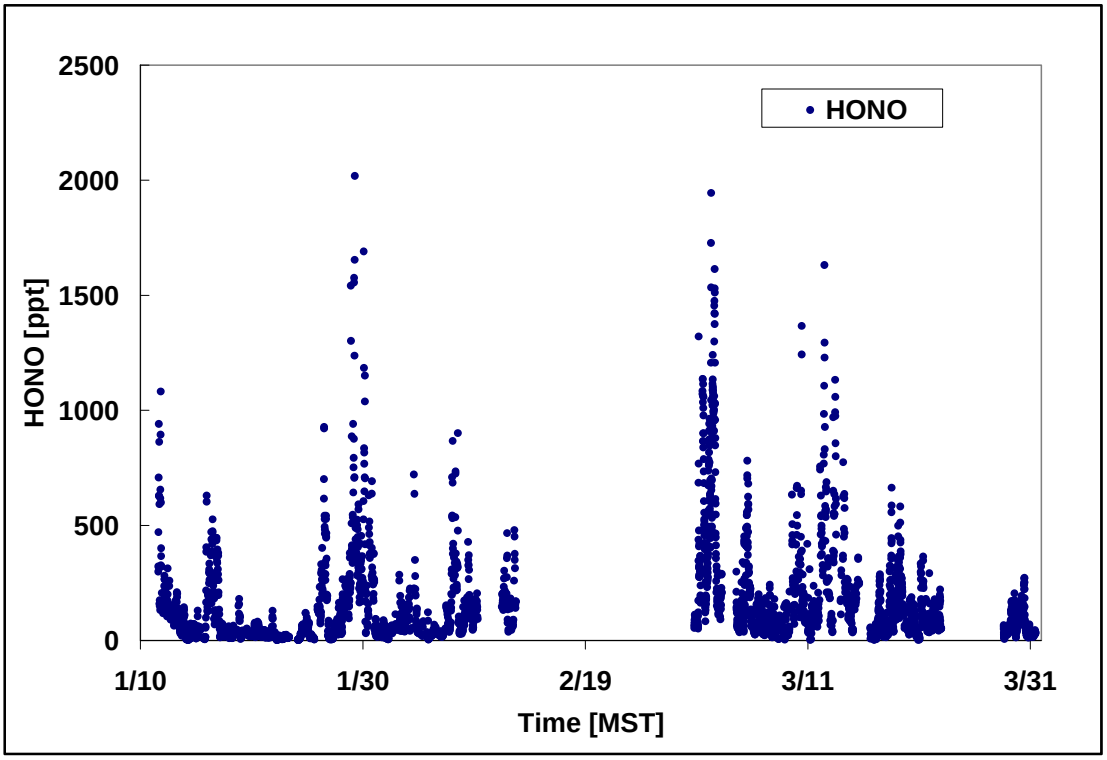


Figure 4.54 10-Minute HONO Data for the Period January 11 - March 31, 2011

Based on the data set obtained from January 11 - March 31, 2011, the main findings include the following:

- HONO levels are well correlated with NO_2, NO_x, and HNO_3. Best correlation occurs with HNO_3. 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 southwest through west-southwest wind conditions. During daytime periods HONO mixing ratios are generally higher than nighttime values, which is a different observation compared with the previous 2010 campaign. Similar to nighttime conditions, daytime HONO levels continue to show enhanced values under southwest through west-southwest conditions, but also generally occur under southeast through west-southwest wind directions.
- HONO levels at 1.8 meters above ground are quite similar to those at the surface level. Both levels also show the morning HONO peak around 10 am MST. However, afterwards high HONO levels persist at the surface, while at 1.8 meters above ground HONO depletes faster than at the surface.
- 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. This is also supported by very good correlations of HONO with HNO_3 (and NO_y).
- HONO formation may occur through NO_x conversion (also potentially associated with primary organic aerosol) in highly polluted air masses that are transported to the Boulder site.
- HONO accumulation is favored in a very shallow daytime mixing layer.
- 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. HONO also correlates with HNO_3 and NO_y during daytime.
- Data collected in this study indicate that high values of relative humidity favor the presence of high levels of HONO.

[5] Kleffmann (2007)

- $HONO/NO_x$ ratios tend to have minimum values when nitrogen oxides are at a diurnal maximum in the morning. This ratio increases as 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. When the $HONO/NO_x$ ratio is at a maximum in the afternoon, O_3 shows the daytime maximum.

The University of Houston's report on HONO monitoring during the UGWOS 2011 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, NMHC and PM_{10}.

4.3.2 VOC Canisters from Tethered Balloon Operations

A total of 12 VOC canister samples were obtained using the tethered balloon during the IOPs. With this relatively small number of canisters budgeted for the 2011 study, sampling schedule strategies were limited. As the overall goal of the 2011 study was to investigate vertical structure of precursor concentrations, it was decided to obtain sample pairs when a noticeable gradient in the hydrocarbon concentrations was noted, based on the readings from the continuous methane/non-methane analyzer. A total of five such pairs were thus obtained, in addition to two non-paired samples.

Table 4-8 summarizes the total identified NMHC (ppmC) for each of the canisters, compared with corresponding data from the continuous analyzer (essentially one-minute averages obtained every 12 minutes). As pointed out previously, NMHC values reported by the analyzer can exhibit inaccuracies when concentrations in this near-source environment change rapidly. Furthermore, canister samples were never drawn during the period when the one-minute analyzer average was being collected.

Thus, the temporally closest and second closest one-minute ozone averages are presented to provide a range of likely concentrations during which the canister was drawn. As can be seen, there is relatively good agreement between the canisters and the analyzer.

Figure 4.55 summarizes analytical results for each of the canister samples, broken down by species groups, and Figure 4.56 presents the relative contribution of each species group. The time and date of each sample can be found in the sample label, as well as the vertical level from which the sample was obtained (L1, L2, L3, L4 equals 4m, 33m, 67m, and 100m, respectively). Sample pairs are presented with the lower level first to aid in the evaluation of vertical structure.

An initial review of the data reveals no obvious conclusion related to the vertical structuring of non-methane hydrocarbons. The only consistent observation when looking at the pairs is that the paraffins for the upper level sample always constitute a higher percentage of the measured hydrocarbons than the lower sample (see Figure 4.56). However, looking at Figure 4.56, the conclusion could be made that the composition of the upper level and lower level samples are generally consistent. The one exception to this conclusion is the noontime sample on March 2 (030211), and once again it is the paraffins that show a significant change in relative composition, though the lack of any aromatics in the upper level sample is also notable. The March 2 pair is unique in that it is the only pair where the hydrocarbon plume was in the upper levels, rather than the lower levels. This could be an indication that the source of this plume was from hot combustion sources that rose to the base of the inversion, rather than cooler emissions that stayed closer to the surface. Thus, the notable change in composition may be an actual differentiation between plume sources. Again, it should be emphasized that the very limited number of samples makes it difficult to conclusively draw any conclusions.

Table 4-8

Total Identified NMHC in ppmC

Time	Level	Canister (ppm)	Analyzer 1st-closest time (ppm)	Analyzer 2nd-closest time (ppm)
03/01/11 14:55	4m	7.4	7.3	5.0
03/01/11 15:00	100m	2.8	3.8	1.4
03/02/11 08:14	100m	2.3	1.3	1.8
03/02/11 08:16	4m	3.6	2.4	6.2
03/02/11 11:23	4m	1.2	1.4	1.7
03/02/11 11:25	100m	3.2	2.4	1.0
03/10/11 08:38	33m	2.3	2.4	2.2
03/10/11 08:39	100m	2.6	5.7	3.0
03/10/11 11:22	67m	1.9	1.6	3.1
03/11/11 11:09	4m	2.3	8.6	1.3
03/11/11 11:14	67m	0.6	1.0	0.0
03/12/11 13:30	4m	2.5	3.0	2.3

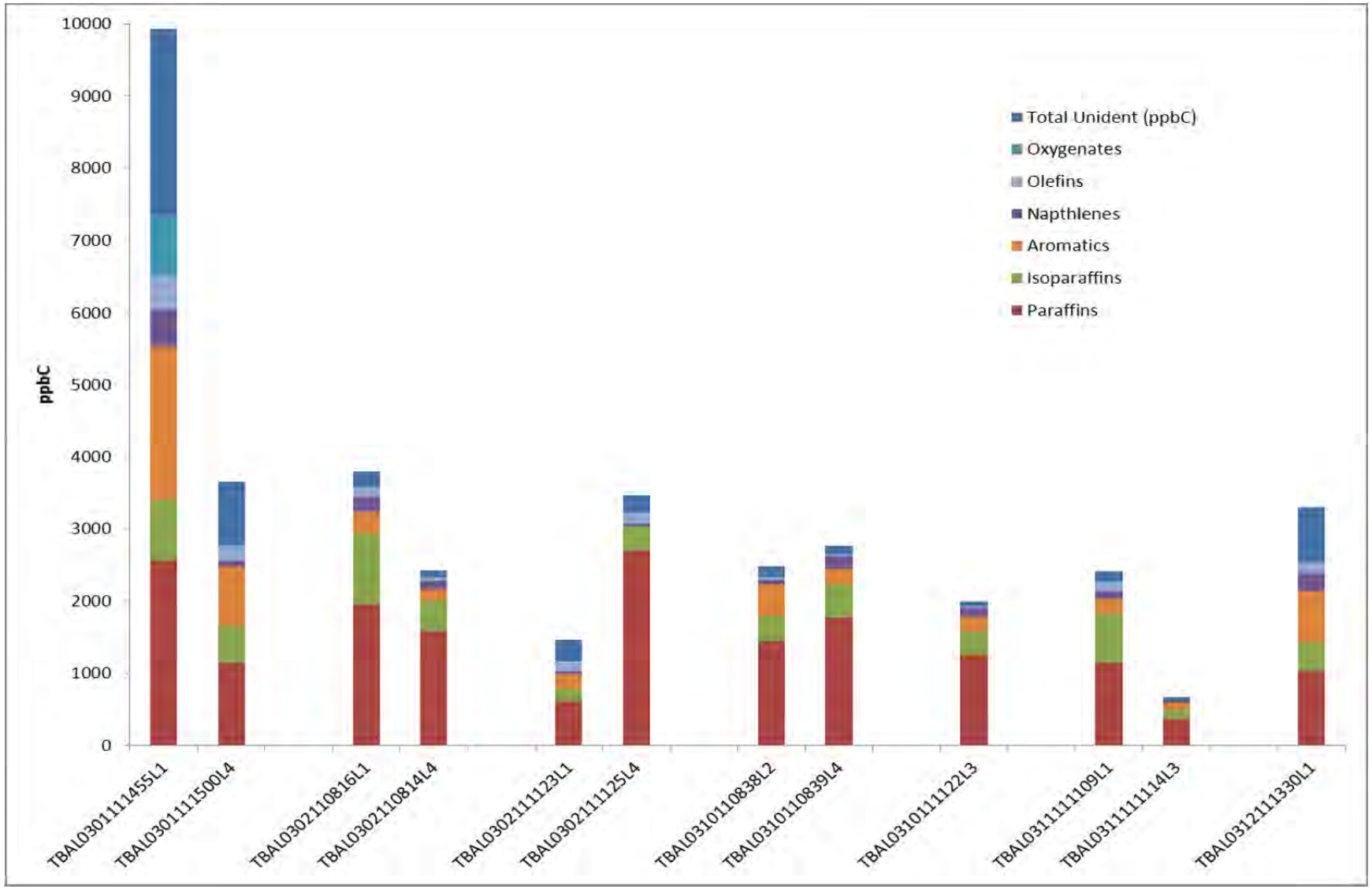


Figure 4.55 VOC Concentrations from Canisters Collected Using the Tethered Balloon

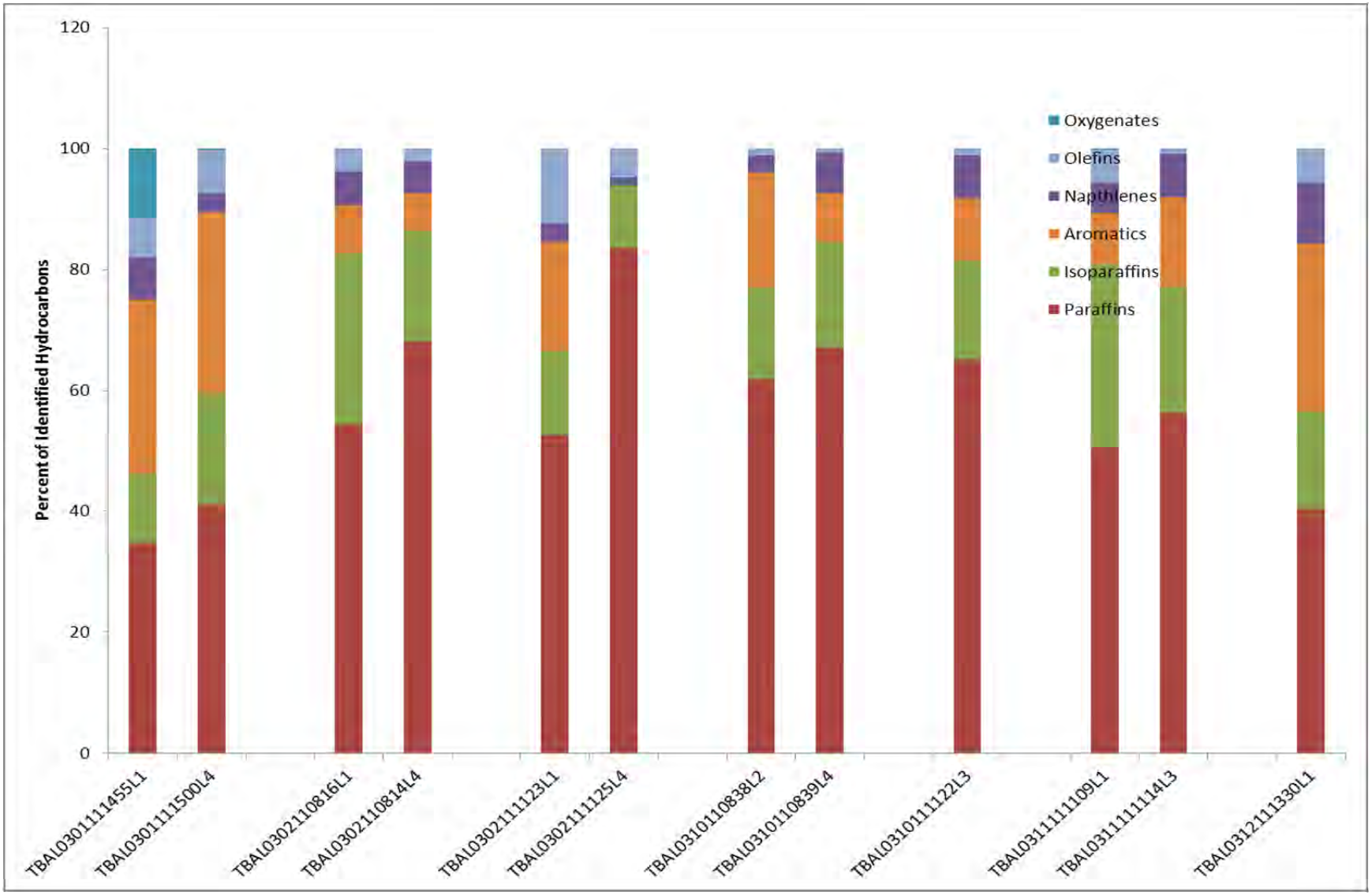


Figure 4.56 Relative Composition of Canisters Collected using the Tethered Balloon

5.0 SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

Presented below is a summary of the UGWOS 2011 field campaign, observations and conclusions drawn from the data obtained during the study, and recommendations for future measurements.

5.1 Summary

In response to wintertime exceedances of the current EPA 8-hour ozone standard, AQD has sponsored the Upper Green Winter Ozone Study (UGWOS) every year since 2007 in order to better understand ozone formation in Wyoming's Upper Green River Basin. Ozone formation mechanisms were the focus during the 2007-2009 studies. The 2010 study focused on monitoring spatial and temporal patterns of ozone and meteorology. Thus far, the only attempts to investigate the vertical distribution of ozone and ozone precursors took place during the 2008 field studies when a light aircraft instrumented with ozone, particulate and temperature monitoring equipment made airborne measurements over the UGRB study domain.

During UGWOS 2011, the synoptic weather pattern was very active. The jet stream brought several cold, wet storms into the western United States which translated into deep snow cover in the UGRB that persisted until approximately mid-March. During the UGWOS 2010 field season, there were no days when 8-hour ozone concentrations above the current EPA standard of 75 ppb were observed at monitoring stations in the UGRB. During UGWOS 2011, there were 13 days when at least one monitoring station measured 8-hour ozone concentrations above 75 ppb.

5.1.1 UGWOS 2011 Measurement Platforms

In response to unanswered questions about whether or not ozone developed in layers above the surface and with the recommendation of the AQD-sponsored ozone Technical Advisory Group, AQD again sponsored an UGWOS field campaign in 2011. The focus of this year's study was the vertical distribution of ozone and ozone precursors. The UGWOS team utilized an existing 73-meter tall tower instrumented at four levels to provide continuous measurements of ozone, ozone precursors, and meteorology. During IOP's, a tethered balloon system instrumented at four levels similar to the tall tower was utilized to collect ozone, ozone precursor, and meteorological measurements up to the 100-meter level. An AQD mobile trailer provided the instrumentation base for tethered balloon operations and its air quality analyzers and 10-meter meteorological station operated continuously when not used as a tethered balloon base.

Forecasts were issued daily to alert measurement crews when elevated ozone episodes were expected so they could prepare for more intensive measurement operations. During UGWOS 2011, two (2) intensive operational periods (IOP's) were declared during the periods February 28-March 2 and March 9-12. In addition to the 100-meter tethered balloon, an AQD team released three to four ozonesondes or rawinsondes during each IOP day.

The AQD permanent seven station monitoring network provided surface air quality and meteorological measurements during the UGWOS field effort. The Boulder Monitoring Complex, an expansion of the Boulder monitoring station, provided specialized measurements to further characterize the role of ozone precursors during ozone formation. Specialized measurements included nitrous acid (HONO), trace level NO, NO_2, and NO_y, and speciated VOC and particulate matter. The AQD Wind Explorer mini-SODAR operated adjacent to the Boulder monitoring station for the duration of the UGWOS study period.

As a subcontractor to MSI, the University of Houston performed continuous measurements of HONO at the Boulder Monitoring Complex during the 2011 UGWOS field program. The Long Path Absorption Photometry (LOPAP) instrument started collecting data on January 11, 2011 and ran almost continuously until March 31, 2011. For this campaign the sampling unit was attached to a small tower (height 1.8 meters). The sampling unit stayed at the surface for 15 minutes, and then moved to the top of the tower, where it stayed for another 15 minutes. Afterwards, the unit returned back to the surface and resumed a new cycle. The purpose of these measurements was to explore whether HONO gradients close to the surface could be detected.

5.2 Conclusions/Observations

The following conclusions/observations are made based on an analysis of the UGWOS 2011 field study results:

- Meteorology once again proved to be the decisive factor in the development of ozone episodes. Snow cover clearly played a very important role. The tower data showed that, with snow on the ground, temperature inversions formed at or near the surface nightly. When wind speeds remained low (less than 10 mps), these inversions persisted into the afternoon hours, capping ozone precursor concentrations as well as the generated ozone. The height of this cap appeared to play a part both in the concentration and regional extent of ozone episodes.

- Ambient ozone concentrations during IOP's were highly variable from one day to the next. This daily variability in ozone concentrations highlights how quickly the ozone can be formed and transported to outlying areas in the Basin. The newly installed Wyoming Range Site measured elevated ozone on several occasions during the UGWOS field study even though it is situated 50 kilometers to the northwest of the primary ozone development area and at a significantly higher elevation (elevation between Wyoming Range and Boulder site is approximately 450 meters).

Since this site is on the far western edge of the Green River Basin it was unexpected that 3 days during UGWOS recorded an 8-hour ozone concentration above 75 ppb.

- While the tethered balloon and tall tower platforms provided very useful data, it became evident that the typical inversion base was much higher than the 100-meter measurement limit. The lack of collocated wind data at the tethered balloon site limited the ability to make conclusive observations using the tethered balloon data.

- The database of ozone measurements are currently skewed toward high ozone days. We think it would be important to make measurements on all days so that conditions that are not favorable to ozone formation are also documented.

- HONO concentrations were well correlated with HNO_3. Nighttime HONO correlated well with NO_2/NO_x while daytime HONO correlated well with NO_y. To a lesser extent, HONO was also correlated with non-methane hydrocarbons (NMHC) and methane (CH_4). No correlation was found with particulate matter (PM_{10}). Snow cover lead to enhanced UV radiation and UV radiation correlated with HONO levels. This finding suggested photo-induced formation of HONO. This was also supported by very good correlations of HONO with HNO_3 (and NO_y).

- On average, the $HONO/NO_x$ ratio peaked in the afternoon; ozone was at the daytime maximum also in the afternoon. HONO formation may occur through NO_x conversion (also potentially associated with primary organic aerosol) in highly polluted air masses. Under SW-WSW wind conditions, HONO levels were generally enhanced.

5.3 Recommendations

Recommendations for future measurements/objectives are proposed and presented below.

5.3.1 Tethered Balloon and Tall Tower Measurements

Data collected from the tethered balloon and tall tower platforms are useful for identifying trends in the vertical structure that can be used for forecasting purposes. Both measurement systems perform well with minimal downtime. A common observation from project participants was that the tethered balloon sampling site appeared to have been optimally placed at a location with consistently high ozone readings while the tall tower sampling location seemed to be south of the highest ozone reading on most days.

We recommend considering the installation of a permanent 100-meter tower, instrumented with meteorological sensors, and sample tube inlets every 20 meters. As noted above, the 73-meter tower provided useful data, but its proximity from ozone precursor sources and lower height limited its usefulness in studying ozone formation mechanisms. While the 100-meter tethered balloon did not typically get above the mixed layer, it did so on the day during which the surface layer was most compressed and ozone concentrations were highest. During other periods, it appeared that the top level was at least measuring concentrations within the trapped plume at the top of the mixing layer, based on mixing height data from the mini-SODAR. We recommend placing the tower at the Boulder air quality site. In addition to having numerous surface measurements that would be collocated with the tower measurements, the elevation at the Boulder site would place the top level about 35 meters higher than the top level of the tethered balloon, increasing the likelihood of being able to better define the surface layer. The meteorological measurements would provide continuous temperature profiles from this critical layer, with the sample lines leading to each level providing the capability of a number of both continuous and instantaneous air quality sampling strategies to investigate specific questions regarding ozone formation chemistry.

5.3.2 Radiometer or Ceilometer

The use of a radiometer or ceilometer to assist in identifying atmospheric structure could be beneficial. In particular, a radiometer has the potential to provide continuous temperature profile data with sufficient resolution to identify vertical structure characteristics such as the base of elevated inversions and inversion strength, both of which likely play a part in the development of ozone episodes.

Currently, a 25 meter vertical resolution is possible using radiometers and collection of data in climates and environments similar to wintertime conditions in the UGRB will be needed to confirm this potential. Another cold climate study using a single channel radiometer (not the one we proposed earlier) demonstrated the ability to detect low level inversions, but had some issues with the structure above the surface layer. There is still a question if the issues noted were related to the specific instrument, or to the measurement technology as a whole.

Therefore, we recommend that the AQD lease a unit to verify the performance of a radiometer relative to forecasting and modeling goals. Performance of the radiometer can be quantified by comparison with rawinsonde releases using AQD equipment and personnel. Leasing plans exist that will allow a large portion of the lease amount to be applied to a purchase of the equipment once performance in verified. Again, it is important that the temperature data be collocated with continuous wind data, such as that provided by a SODAR.

5.3.3 Ozonesonde/Rawinsonde System

Because of the variability of ambient ozone concentrations from one day to the next and the relative speed at which ozone can be formed and transported, a continuous measurement of inversion strength, base depth, and winds within the inversion would be very helpful tools for understands elevated ozone events.

AQD already owns an ozonesonde/rawinsonde system which might also be used in a tethered mode to be able to utilize ozonesondes more than once if soundings took place on a daily basis. To better understand the chemistry and structure within the inversion, measurements should be systematically made which extend through the top of the inversion collecting continuous wind and temperature data. Several profiles could be made with a single sonde before the sonde's chemistry is expended. Since this measurement is continuous it would provide much more vertical resolution and detail. This data would not only be valuable for forecasting purposes but also for regional modeling efforts and associated model validation efforts.

5.3.4 HONO Measurements

Based on the above conclusions/observations, the University of Houston offers two recommendations for obtaining more conclusive information about processes which determine air quality in the Upper Green River Basin. They include: (1) Analysis of the data obtained in this project with speciated particle data may elucidate potential HONO formation processes through HNO_3 conversion according to findings by Ziemba et al., 2010, and (2) Chemistry-transport modeling including an advanced HONO chemistry module [Czader and Rappenglück, 2009; Czader et al., 2010; Czader et al., 2011] may help to explain the findings in the UGRB.

5.3.5 Drainage Monitoring

Although not performed during UGWOS 2011, we believe that the addition of NO_x monitoring in one or more low lying drainage areas could be beneficial. Mobile monitoring stations configured to measure oxides of nitrogen and meteorology should be located in areas which experience nighttime drainage flows to better understand NO_x and ozone interactions and transport. Better understanding of these transport corridors could help to refine/validate dispersion modeling simulations and may provide critical information of ozone precursor transport and potential ozone development for the coming day. In addition to NO_x measurements, it would be important to have collocated meteorological measurements to document the actual flow conditions.

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Appendix A
Monitoring and Quality Assurance Plan

MONITORING AND QUALITY ASSURANCE PLAN

for the

UPPER GREEN RIVER WINTER OZONE STUDY - 2011

Prepared for

State of Wyoming
Department of Environmental Quality, Air Quality Division
122 West 25th Street
Herschler Building, 2nd Floor East
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February 15, 2011

Prepared by

Meteorological Solutions Inc.

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ENVIRON

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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 2011, 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 through 2010. While meteorological conditions unfavorable to ozone formation encountered during the 2007 study period resulted in only limited monitoring, more favorable meteorological conditions during 2008, and to a lesser degree during 2009 and 2010, resulted in several days of high ozone concentrations, including a large number of days in 2008 when the 0.075 ppm Federal ozone standard was exceeded. Additional measurements have been planned for the winter of 2011. This QA plan addresses the 2011 monitoring effort.

Data from the 2011 study will be used to refine a conceptual model of ozone formation developed on the basis of prior year's 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

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

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 2011 will run from January 15, 2011 through March 31, 2011. Sampling that will be conducted for UGWOS during this period is described below.

2.1 Forecasting Protocol

The UGWOS effort for 2011 will have an intensive operating period (IOP) component. As in prior years, 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.

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.

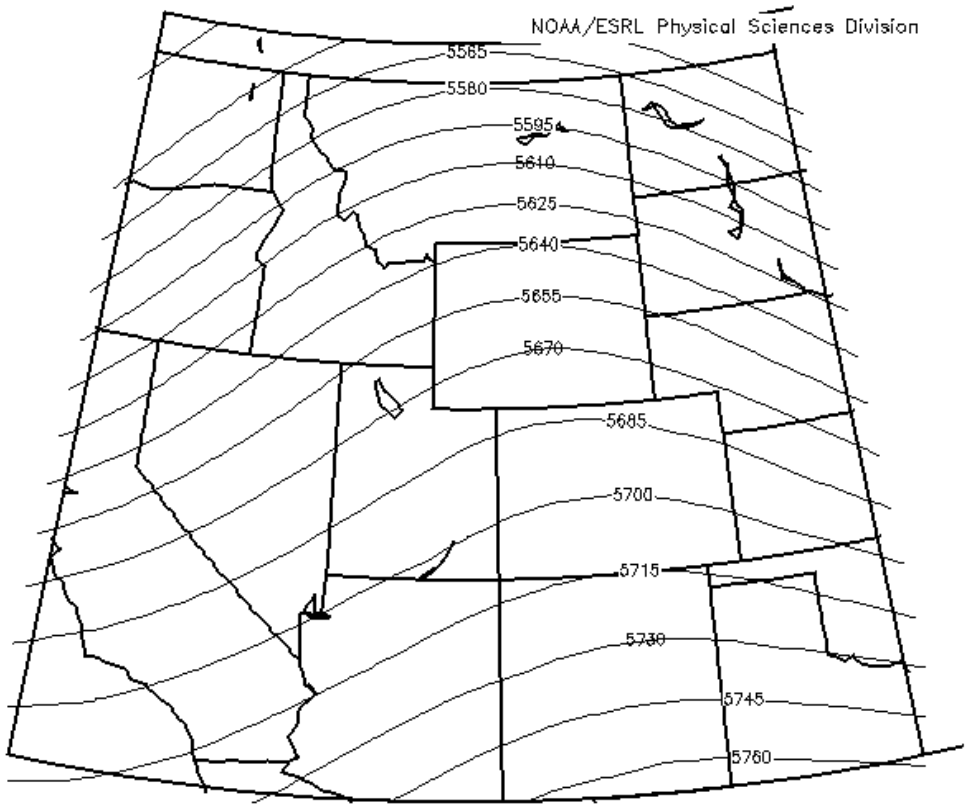

Figure 2-1 Composite 500 mb Heights During High Ozone Periods

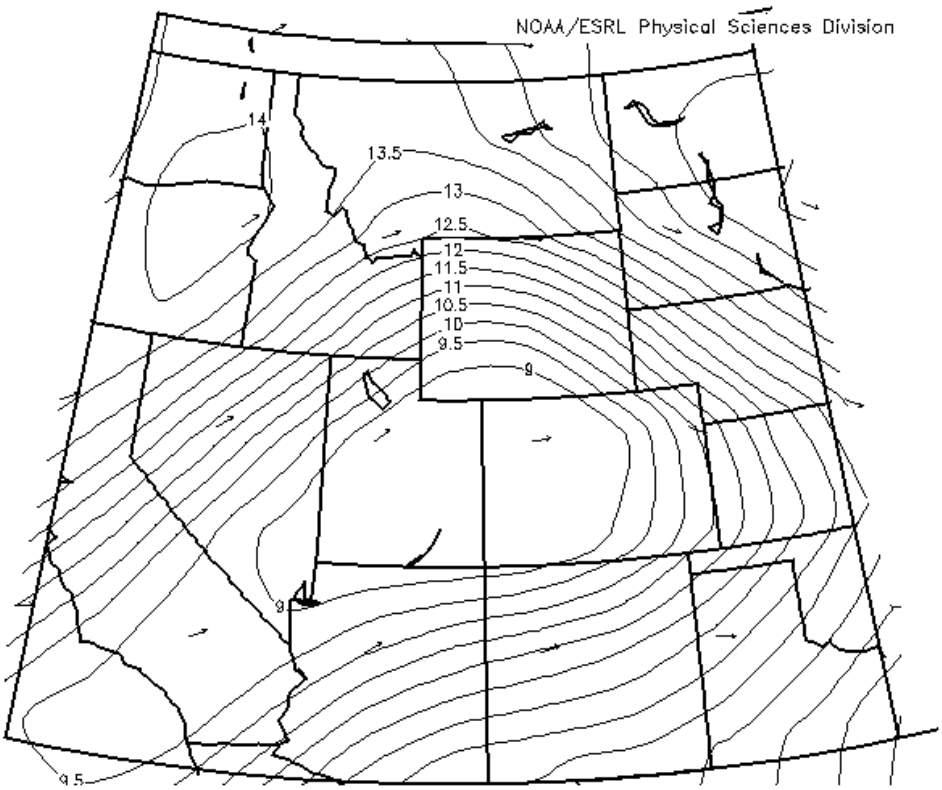

Figure 2-2 Composite 500 mb Winds During High Ozone Periods

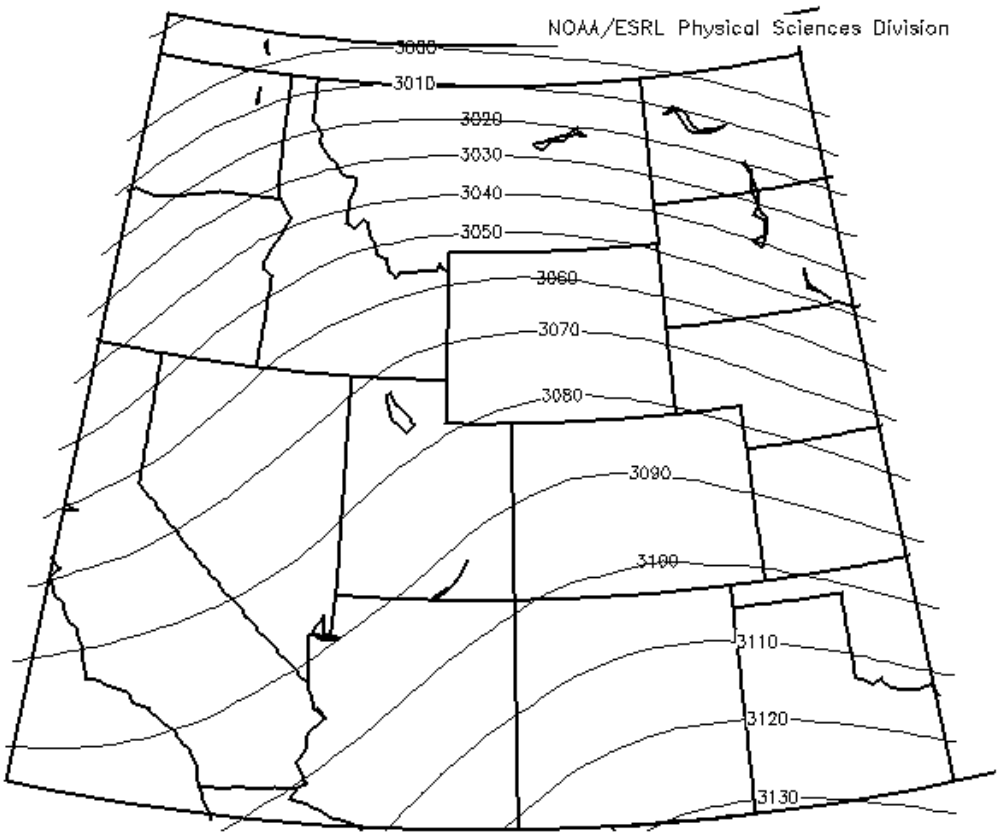

Figure 2-3 Composite 700 mb Heights During High Ozone Periods

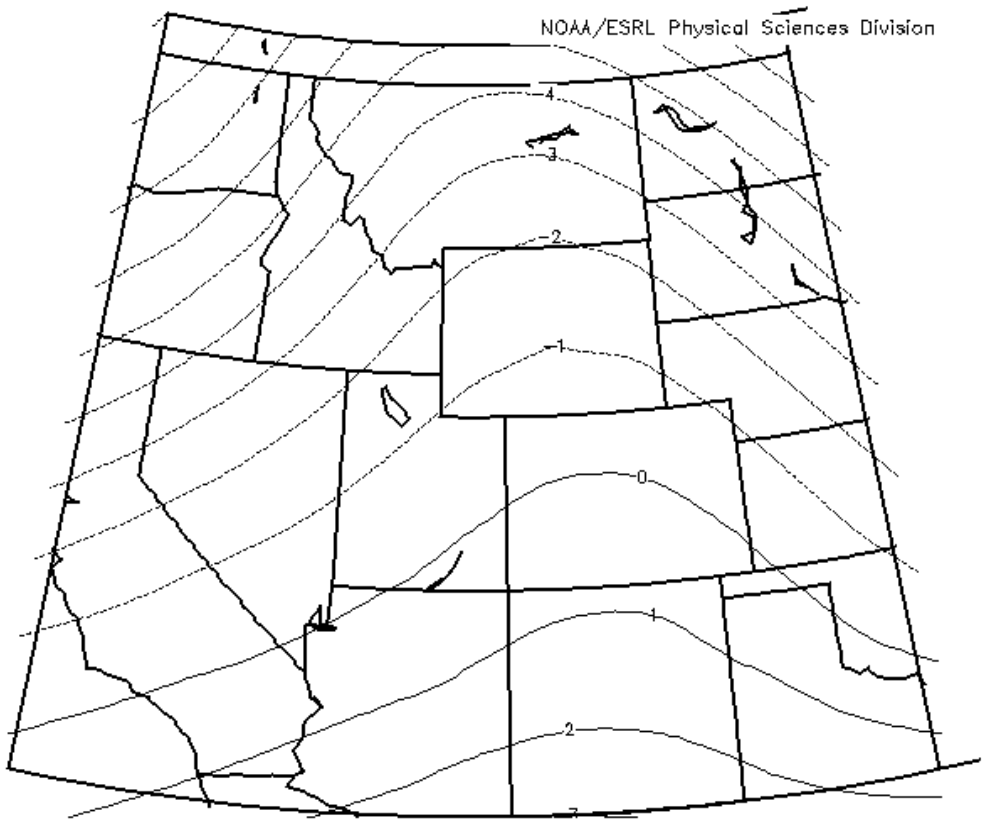

Figure 2-4 Composite 700 mb Temperature During High Ozone Periods

2.2 Continuous Measurements

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

2.2.1 Long-line Tower Measurements

Continuous measurements of ozone, NO/NOx, and methane and non-methane hydrocarbons will be made on an existing 73-meter tower using long line sampling. Long lines will be installed to four levels on the tower (73, 50, 25, and 5 meters), through which air will be continuously drawn down to the surface. The lines consist of 3/8" OD / 5/16" ID Teflon tubing. Air will be drawn down the tubing at a rate of 4 lpm, resulting in only a slight vacuum in the sample lines while maintaining a residence time of less than 20 seconds. Air from each of these levels will be directed to analyzers located at the

surface using a switching mechanism that will sequentially sample each line for 3 minutes over a 12-minute cycle. For each 3-minute sample, the first 2.5 minutes will be used to allow the analyzers to equilibrate to concentrations from the sampled line (in particular the hydrocarbon analyzer which must go through several cycles to obtain good data). Thus, for any given sampling level, each hour will consist of five 0.5-minute averages. The collection of both total hydrocarbon and methane (for calculating non-methane hydrocarbon) will be reviewed, but will depend on how the operational timing of the hydrocarbon analyzer matches the line switching described above. The sample lines will be configured to allow the drawing of canister samples, if desired.

In addition to the air quality sampling, meteorological monitoring will be conducted at each of the four levels. Wind speed, wind direction, and temperature will be monitored continuously at all levels, and relative humidity will be monitored at the 5-meter and 73-meter levels.

T&B Systems will be responsible for the air quality measurements, and MSI will be responsible for the meteorological measurements. Routine checks of the entire system will be conducted by MSI.

2.2.2 SODAR Upper Level Winds

For the 2011 monitoring effort, the WY DEQ MiniSodar (sodar) will be maintained at 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, validate the wind data, and reduce mixing height data for key periods during the study.

2.2.3 HONO

The existing WY DEQ Boulder site will be expanded to included measurements of HONO. For the 2011 study, Dr. Bernhard Rappenglueck of the University of Houston will provide equipment and setup for the measurements. Routine oversight of the equipment will be conducted remotely by University of Houston personnel. MSI will be conducting regular visits to the Boulder site, including routine checks and calibrations.

2.3 Intensive Measurements

During periods when high ozone levels are forecast, additional intensive measurements will be initiated. Two three-day IOPs will be conducted, weather permitting. The key components of the intensive monitoring periods (IOPs) are:

- Tethered balloon measurements of ozone and ozone precursors

- Ozone/rawinsonde operations

2.3.1 Tethered Balloon Long-line Measurements

A tethered balloon will be used to raise long-lines to obtain continuous measurements of ozone, NO/NOx, and methane (CH4) and non-methane (NMHC) hydrocarbons at four levels during daytime hours of IOP days. The four levels will be 100 meters, 67 meters, 33 meters and 4 meters. The balloon consists of a blimp similar to those used for advertising. The balloon will be raised each morning and brought down in the late afternoon. The blimp will be secured inflated during the night between IOP days.

The monitoring methodology for the air quality parameters will be identical to that used at the tall tower, described in Section 2.2.1. In addition to sampling the air quality parameters, temperature and relative humidity will be monitored at each of the levels using small, lightweight temperature and relative humidity data loggers. The loggers will be set to record data at a 1-minute interval.

VOC samples will be collected using SUMMA canisters at the tethered balloon site during long-line sampling. A total of eight samples will be obtained during the course of the study, with the exact sample strategy determined during the study, based on real-time NMHC data. Research team technicians will be responsible for collecting the samples and filling out the affiliated documentation. Exposed sample media will be collected at the end of each intensive study day and brought to Pinedale for packaging and shipment to EAS laboratory for analysis. Field sample sheets will accompany samples and the required chain-of-custody documentation will accompany each shipment.

2.3.2 Ozone/rawinsonde Operations

Concurrent to the tethered balloon free ascending balloon-borne measurements of ozone, temperature, relative humidity, and winds will be made during each IOP from the Boulder air quality monitoring site by WY DEQ personnel using equipment maintained by the WY DEQ. The sampling schedule will be determined by the WY DEQ.

A T&B Systems technician will travel out to Pinedale for 3 days of training. The training will begin with the preparation of the ozonesondes. This will use much of the first day for the testing and conditioning process. Many of the study's ozonesondes can be prepared during this time to the point where the cells can be activated for use. At least one or two of the sondes will be activated for the training flight. The second and third day will concentrate on training for launches, culminating in at least one two actual practice launches. Tips on processing and validating the collected data will be discussed.

2.4 Supplemental Monitoring and Data Collection

<u>Archiving of NOAA Products</u>

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 twice per day. (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. Table 3-1 presents coordinates 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, both past and present, in the study region.

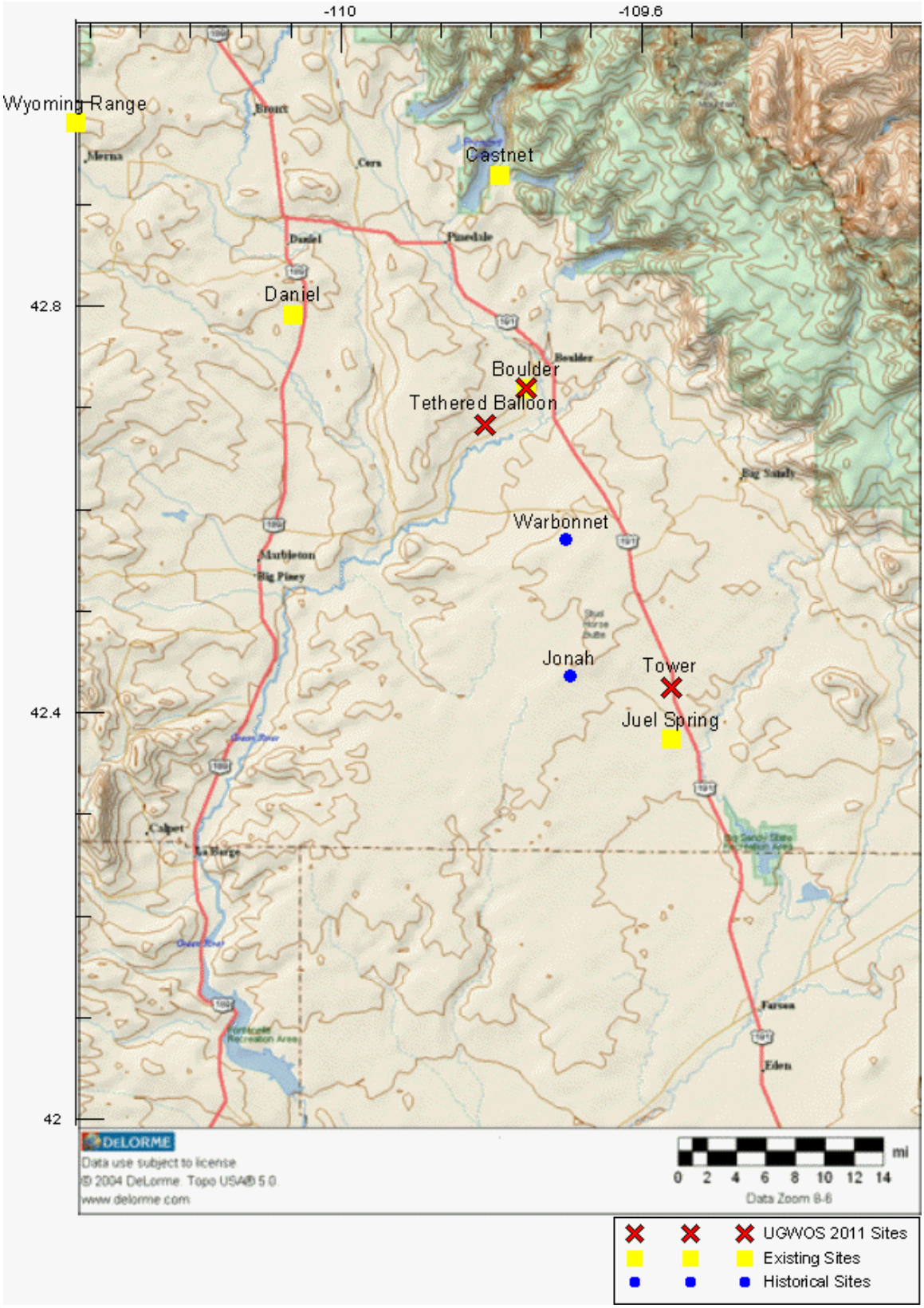

Figure 3-1. Map of UGWOS and Additional Ozone Monitoring Site Locations

Table 3-1. Network Locations and Identifiers

	Latitude	Longitude	Elev.
SODAR / HONO SITE			
Boulder	42.7188	-109.7529	7078’
LONG-LINE MONITORING TOWER SITE			
Tower	42.4240	-109.5609	7051’
TETHERED BALLON SITE			
M&N Yard	42.6825	-109.8090	6966’
ADDITIONAL MONITORING SITES OF INTEREST			
Pinedale (WY DEQ)	42.8698	-109.8707	7186’
Juel Spring (WY DEQ)	42.3735	-109.5605	7020’
Daniel (WY DEQ)	42.7910	-110.0650	7084’
Castnet	42.9284	-109.7880	7853’
Wyoming Range	42.9801	-110.3530	8123’

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 LONG-LINE MONITORING – AIR QUALITY

The equipment and sampling methodology used for the long-line monitoring are identical for both the tall tower and the tethered balloon monitoring efforts. **Figure 4-1** shows the line-switching mechanism used for both efforts.

Figure 4-1. Line-switching mechanism.

The basic flow through the mechanism is as follows:

Air is drawn into the box from each of the four sampling lines and through the rotameters, which are used for setting and monitoring the sampling flow rate at 4 lpm. Below each rotameter is normally closed solenoid, which is sequentially opened to allow the air to enter a manifold, which leads to the analyzers. The solenoids are controlled by a Campbell Scientific A6REL-12 relay drive, located on the upper half of the box door. The A6REL-12 is designed to drive up to 6 internal relays to control up to 12 external AC or DC devices. Each relay set can be controlled manually or by a datalogger control port. During routine operations, the relay drive is controlled by a programmable Campbell Scientific CR10X data logger (located on the lower half of the box door), but each solenoid can be opened or closed manually for testing or to override the CR10X sampling program. In addition to controlling the relay drive, the CR10X stores all air quality data and the station temperature data. 12-minute averages will be stored following the sample methodology discussed in Section 2.2.1. The CR10X can operate for a period in excess of four weeks before it is necessary to download data. However, the datalogger will be polled every hour and data transferred to the T&B Systems and MSI servers through the Internet.

Air quality parameters will be monitored using the following equipment:

Teledyne/API Model 200E NO/NO_2/NOx Analyzer – EPA Approval RFNA-1194-099

The Model 200E uses the chemiluminescence detection principle, coupled with state-of-the-art microprocessor technology to provide the sensitivity, stability and ease of use needed for ambient monitoring requirements. The analyzer uses multi-tasking software, which allows complete control of all functions while providing online indication of important operating parameters. Measurements are automatically compensated for temperature and pressure changes. Stability is enhanced by an Auto-Zero circuit that continuously provides a true zero reference.

Accuracy (performance checks)	±5%
Precision (performance checks)	±5%
Resolution	1 ppb
Lower Quantifiable Limit	2 ppb

Teledyne/API Model 400E Ozone Analyzer – EPA Approval EQOA-0992-087

The Model 400E UV Absorption Ozone Analyzer is a microprocessor-controlled analyzer that uses a system based on the Beer-Lambert law for measuring low ranges of ozone in ambient air. A 254 nm UV light signal is passed through the sample cell where it is absorbed in proportion to the amount of ozone present. Every three seconds, a switching valve alternates measurement between the sample stream and a sample that has been scrubbed of ozone. The result is a true, stable ozone measurement.

Accuracy (performance checks)	±5%

Precision (performance checks)	±5%
Resolution	1 ppb
Lower Quantifiable Limit	2 ppb

Baseline-Mocon Series 9000 NMHC Methane/Non-Methane Analyzer

The Series 9000 NMHC is designed to provide continuous, fully automated gas analysis of total, methane, and non-methane hydrocarbon content of gas samples over a broad range of concentrations. The analyzer is based on a flame ionization detector (FID) with FlowGuard electronic control that delivers a small portion of the sample gas to the detector flame. During the combustion process, organic or hydrocarbon-based gases in the sample are ionized and then detected by the instrument and reported as a concentration.

Accuracy (performance checks)	±5%
Precision (performance checks)	±5%
Resolution	0.1 ppm
Lower Quantifiable Limit	0.1 ppm

Teledyne/API Model 700E Calibrator

The Model 700E is a microprocessor based calibrator for precision gas analyzers. Using a combination of highly accurate mass flow controllers and compressed sources of standard gases, calibration standards are provided for multipoint span and zero checks. Up to 4 gas sources may be used. In addition, the Model 700E is equipped with an optional built-in, programmable ozone generator for accurate, dependable ozone calibrations and to produce NO_2 when blended with NO gas in the internal GPT chamber. As many as 50 independent calibration sequences may be programmed into the M700E, covering time periods of up to one year. These sequences may be actuated manually, automatically, or by a remote signal.

4.2 LONG-LINE MONITORING – METEOROLOGY

RM Young Model 05305 Wind Monitor AQ

For monitoring of wind speed and wind direction on the tall tower, a RM Young 05305 Wind Monitor AQ wind speed and direction sensor will be employed. These sensors use a propeller-type anemometer. The sensor will be mounted on a 2-meter boom extending from the tower. The direction vane will be oriented to true north using either a compass or the GPS walkoff method.

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

RM Young 41342 Temperature Sensors

The temperature and delta temperature for the four levels on the tower will be measured using matched calibration sets of RM Young model 41342 Platinum RTDs. The temperature sensors will be mounted in RM Young model 43408 aspirated radiation shields.

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

Vaisala HMP45AC Temperature / Relative Humidity Sensor

Relative humidity on the tall tower will be measured at the 5- and 73-meter level using Vaisala HMP45AC sensors.

Accuracy (performance checks)	±5% RH
Precision (performance checks)	±1% RH
Resolution	0.1% RH

Onset HOBO U23 Pro v2 Temperature/Relative Humidity Data Logger

The HOBO Pro v2 Temperature/Relative Humidity data logger is a weatherproof data logger with built-in high accuracy temperature and relative humidity sensors.

Temperature

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

Relative Humidity

Accuracy (performance checks)	±5% RH
Precision (performance checks)	±1% RH
Resolution	0.1% RH

4.3 HONO MEASUREMENTS

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%

4.4 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 4-2**. 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

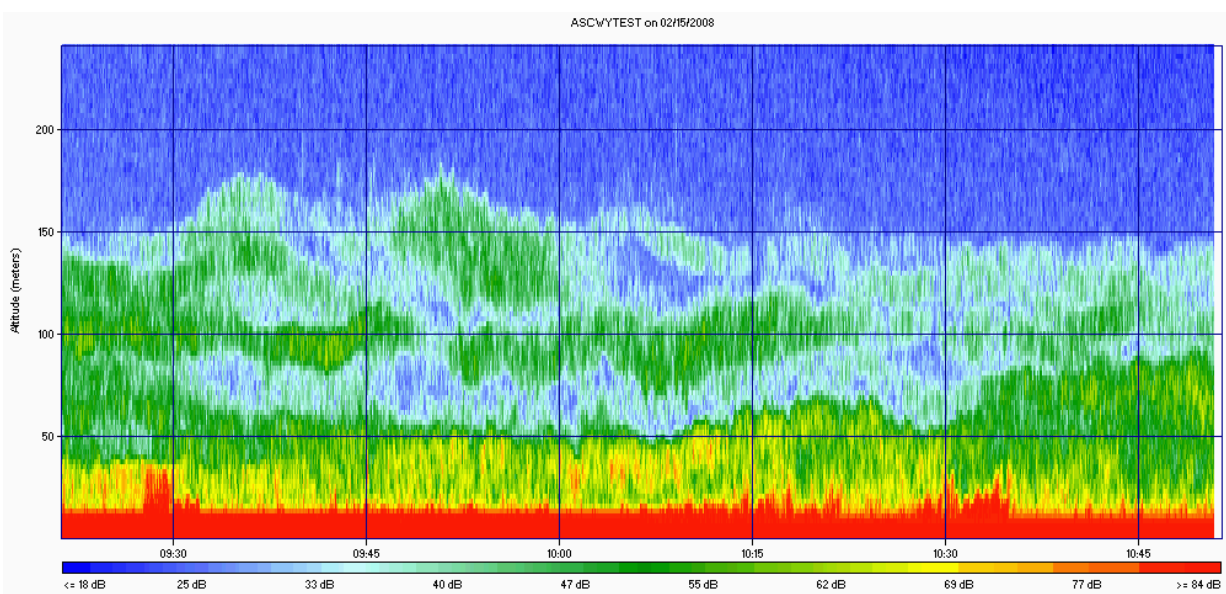

Figure 4-2. Example of sodar backscatter data capturing the daytime mixing height layers under cold wintertime conditions.

4.5 OZONE/RAWINSONDES

To profile ozone concentrations from the surface to the tropopause, we will use balloon-borne ozonesondes, with measurements placed at the Boulder air quality site. The ozonesonde systems has three primary components, described below:

Sippican W-9000

The Sippican W-9000 system consists of a SIPPICAN ZEEMET W-9000 GPS based navaid receiver/data system for measuring winds and the SIPPICAN Mark II Microsondes radiosonde packages.

The SIPPICAN ZEEMET W-9000 receiving station interfaces with a personal computer and printer. This is a state-of-the-art wind finding system employing GPS technology. The UHF receiver operates in the 400 MHZ range. SIPPICAN software enables the interface with the SIPPICAN W-9000 receiver and reduces the thermodynamic pressure, temperature and humidity (PTU) and navaid/wind data. During each flight, the technician is able to monitor both raw and reduced data in near real time. The software also includes graphics and plotting capabilities that allow the technician to review results during and at the end of each flight. Both raw and reduced data are stored on the hard disk in subdirectories identified by the flight name. All data files are copied to both primary and backup diskettes immediately after each flight.

SIPPICAN Mark II Microsondes

The SIPPICAN Mark II Microsondes are 10 x 19 x 15 cm and weigh 250 grams with a water-activated 18V battery. The radiosonde UHF transmitter sends its modulated signals in the 400 MHZ range. The Microsondes are calibrated at the factory in a computer-controlled environmental chamber. Calibration coefficients are stored in read-only-memory (ROM) within each sonde and are automatically transmitted to the receiver in 1.5 sec intervals. Temperature is measured using a bead thermistor and relative humidity using a carbon hygristor. The SIPPICAN W-9000 is an automatic wind finding system that is based on tracking the sonde using the GPS satellite network. The Microsonde incorporates a low-noise integrated circuit GPS receiver. Winds aloft are calculated from the change in balloon position (determined from navaid) with time. Height is obtained directly from GPS positioning and, unlike older systems, pressure is now a derived parameter, calculated from the hydrostatic equation, using measured height, temperature, and humidity.

Accuracy (instrument specifications)	
Horizontal Wind Speed	± 0.5 ms^{-1}
Horizontal Wind Direction	Unknown
Temperature	± 0.2° C
Relative Humidity	± 2.0%
Output Resolution	

Horizontal Wind Speed	0.1 m/s
Horizontal Wind Direction	1.0°
Temperature	0.1° C
Relative Humidity	1.0%

EN-SCI Corporation KZ-ECC Ozonesondes

EN-SCI Corporation KZ-ECC ozonesonde system will be used in conjunction with the radiosonde package described above. Ozone is measured with an electrochemical concentration cell (ECC) ozonesonde coupled through an electronic interface to the radiosonde.

The ECC ozonesonde is of a simple design consisting of a rigid mainframe on which is mounted a motor-driven Teflon/glass air sampling pump, a thermistor for measuring pump temperature, an ozone sensing ECC, and an electronics box containing interface circuitry which couple the ozone sensor to the radiosonde. The mainframe is mounted in a lightweight weatherproof polystyrene flight box that is taped and wired to the radiosonde during flight.

The ozone-sensing cell is made of two bright platinum electrodes immersed in potassium iodide (KI) solutions of different concentrations contained in separate cathode and anode chambers. The chambers are linked with an ion bridge that, in addition to providing an ion pathway, retards mixing of the cathode and anode electrolytes thereby preserving their concentrations. The electrolytes also contain potassium bromide (KBr) and a buffer whose concentrations in each half-cell are the same. The driving electromotive force for the cell, of approximately 0.13 V, is provided by the difference in potassium iodide concentrations in the two half cells. Sample air is forced through the ECC sensor by means of a non-reactive pump fabricated from TFE Teflon impregnated with glass fibers. The pump is designed to operate without ozone-destroying lubricants. Pumping efficiency for each pump varies from pump to pump and is also dependent on ambient air pressure. The sampling flow rate is calibrated at the factory and checked in the field before launch. The ECC ozone concentration calibration is also determined prior to launch.

When ozone in air enters the sensor, iodine is formed in the cathode half cell according to the relation

$$2KI + O_3 + H_2O \rightarrow 2KOH + I_2 + O_2. \qquad (1)$$

The cell converts the iodine to iodide according to

$$I_2 + 2e \rightarrow 2I^- \qquad (2)$$

during which time two electrons flow in the cell's external circuit. Measurement of the electron flow (i.e., the cell current), together with the rate at which ozone enters the cell per unit time, enables ozone concentrations in the sampled air to be derived from

$$p_3 = 4.307 \times 10^{-3}(i_m - i_b)T_p t \quad (3)$$

where p_3 is the ozone partial pressure in nanobars, i_m is the measured sensor output current in microamperes, i_b is the sensor background current (i.e., the residual current emanating from the cell in the absence of ozone in the air) in microamperes, T_p is the pump temperature in Kelvin, and t is the time in seconds taken by the sonde gas sampling pump to force 100 ml of air through the sensor.

Sensitivity	2-3 ppb by volume ozone in air
Response Time	15 seconds for 67% of change; 60 seconds for 85% of change
Noise	less than 1% of full scale
Estimated Measurement Uncertainty	less than ± 10% of indicated value

As an integral part of the ozonesonde operations, the ozone analyzer readings at the Boulder site will provide ground-truth data.

4.6 VOC SAMPLING

VOC samples will be collected using SUMMA canisters at the tethered balloon site during long-line sampling. A total of eight samples will be obtained during the course of the study, with the exact sample strategy determined during the study, based on real-time NMHC data. VOC samples will be analyzed using Method TO-14 with an expanded PAMS list of compounds (see Table 4-1). Analysis will be performed by Environmental Analytical Services, Inc., Santa Barbara, CA.

Table 4-1. Target compound list for EPA Method TO-14 Toxics in Air (Expanded for PAMS).

Ethene	Cyclohexane	Total Petroleum Hydrocarbons:
Acetylene	2-Methylhexane	Total Non-Methane Hydrocarbons
Ethane	2,3-Dimethylpentane	Total Gas Non-Methane Organics
Propene	3-Methylhexane	Total Volatile Organic Compounds
Propane	2-Methyl-1hexene	TPH (gasoline)
i-Butane	Tert amyl methyl ether	TPH (diesel)
Methanol	2,2,4-Trimethylpentane	TPH (hexane)
1-Butene	n-Heptane	TPH (toluene)
1,3-Butadiene	Methylcyclohexane	TPH (methane)
n-Butane	2,5-Dimethylhexane	TPH (Jet A Fuel)
t-2-Butene	2,4-Dimethylhexane	TPH (Mineral Spirits)
c-2-Butene	2,3,4-Trimethylpentane	c6+ (hexane)
Ethanol	Toluene	Sample: Composition
3-Methyl-1-butene	2,3-Dimethylhexane	Total Identified
Acetone	2-Methylheptane	Paraffins
i-Pentane	4-Methylheptane	Isoparaffins
1-Pentene	3-Ethyl-3-methylpentane	Aromatics
Isopropanol	3-Methylheptane	Napthlenes
2-Methyl-1-butene	2-Methyl-1-heptene	Olefins
n-Pentane	n-Octane	Oxygenates
Isoprene	Ethylbenzene	Carbon Ranges:
t-2-Pentene	m,p-xylene	C2 (ethane)
c-2-Pentene	Styrene	C3 (propane)
Tert butyl alcohol	o-xylene	C4 (Butane)
2-Methyl-2-butene	1-Nonene	C5 (Pentane)
2,2-Dimethylbutane	n-Nonane	C6 (Hexane)
Cyclopentene	i-Propylbenzene	C7 (Heptane)
n-Propanol	n-propylbenzene	C8 (Octane)
Cyclopentane	a-Pinene	C9 (Nonane)
Methyl tert butyl ether	3-Ethyltoluene	C10 (Decane)
2,3-Dimethylbutane	4-Ethyltoluene	C11+ (Undecane)
2-Methylpentane	1,3,5-Trimethylbenzene	
3-Methylpentane	2-Ethyltoluene	
1-Hexene	b-Pinene	
n-Hexane	1,2,4-Trimethylbenzene	
Diisopropyl ether	n-Decane	
3-Methylcyclopentene	1,2,3-Trimethylbenzene	
Ethyl tert butyl ether	Indan	
Methylcyclopentane	d-Limonene	
2,4-Dimethylpentane	1,3-Diethylbenzene	
Benzene	1,4-Diethylbenzene	
	n-Butylbenzene	
	1,4-Dimethyl-2-ethylbenzene	
	1,3-Dimethyl-4-ethylbenzene	
	1,2-Dimethyl-4-ethylbenzene	
	Undecane	
	1,2,4,5-Tetramethylbenzene	
	1,2,3,5-Tetramethylbenzene	
	Napthalene	
	Dodecane	

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/ugwos11/index.htm. Both sub-hourly and hourly averages will be collected. The data loggers are all equipped with internal memory that can store data. 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 are 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 1, 2011.

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. Time-height cross sections of ozone, ozone precursors, winds, and mixing heights;
4. Wind roses at the surface;
5. Pollution roses at the surface; and
6. 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 provided to WY DEQ by June 1, 2011. 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.

An organizational chart for UGWOS 2011 is provided in Figure 6-1. Study personnel responsibilities and contact information are 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/ugwos11/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.

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, 2011. 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 developed for key monitoring activities. SOPs can be found in Appendix B.

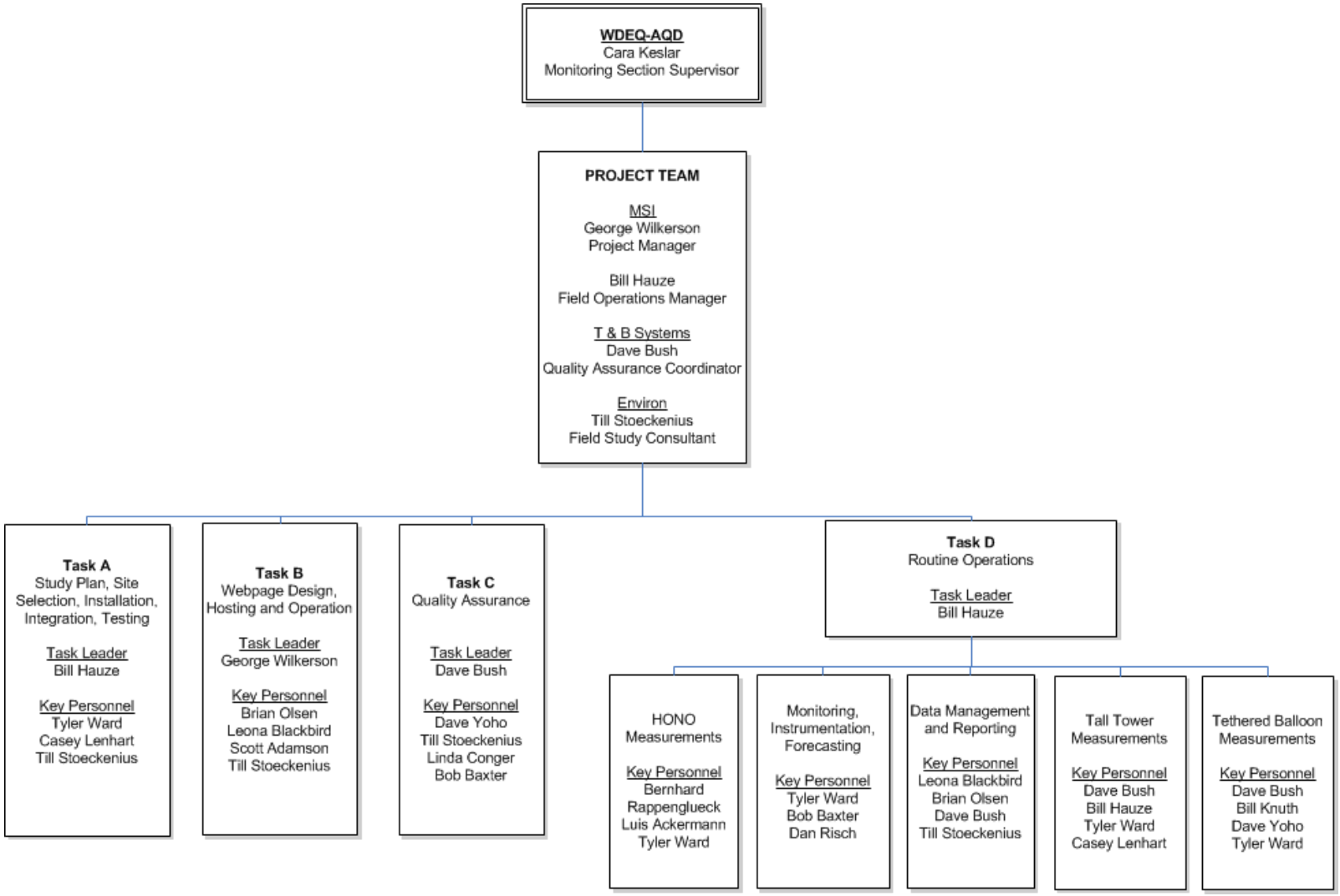

Figure 6-1. Project organization.

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	General study support Daniel site operations	(307) 231-2387 (cell)
Ryan McCammon	Wyoming DEQ	Forecasting, ozonesonde operations	(307) 777-7104
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
Brian Olsen	MSI	Data polling Data processing and validation	(801) 272-3000
Tyler Ward	MSI	Full-time onsite field support	(928) 814-3926 (cell)
David Bush	T&B Systems	Quality Assurance Tower and tethered balloon measurements QAPP	(530) 647-1169 (530) 903-6831 (cell)
Bob Baxter	T&B Systems	Measurements support Quality Assurance audits Sodar operations	(661) 294-1103 (661) 645-0526 (cell)
Bill Knuth	T&B Systems	Ozonesonde training Tethered balloon measurements support	(707) 279-1661 (707) 975-4413 (cell)
David Yoho	T&B Systems	Quality Assurance audits Tethered balloon measurements support	(661) 294-1103 (661) 212-3008 (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
Bryan Bibeau	ARS	ARS support	(970) 219-8546

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

Station Checks

Performance of all UGWOS 2011 equipment will be checked daily using the data website listed in Section 6.1. In addition, the Boulder site will be visited at least twice a week to service and check the HONO measurements. Access to the tall tower is restricted, requiring Questar personnel to accompany UGWOS personnel during any visit to the site. Thus, physical site checks of the tall tower operations will initially be limited to once every two weeks. In addition, a physical check off the tall tower will be conducted immediately before the beginning of any IOP in order to verify that all systems are operating. If this schedule is insufficient for maintaining data recoverability, it will be modified.

ARS is responsible for the performance of the analyzers in the WY DEQ trailer being used for the tethered balloon. Quality control procedures for the trailer are covered under ARS's quality assurance program and QAPP.

Ozone, NO/NOx, and CH4/NMHC Analyzers

Analyzers for the tall tower and the tethered balloon will be checked using a certified transfer standard, following operating procedures consistent with EPA guidelines. This will consist of zero and span checks conducted nightly. Certified transfer standards are being supplied by Air Resource Specialists, Inc. (ARS) in Fort Collins, CA. A pass/fail criterion of +/-10% will be used when evaluating the span and calibration data, after which corrective measures will be implemented.

MiniSodar

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/.

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, NO/NOx, and methane/non-methane hydrocarbon analyzers 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).

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.

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, CH4/NMHC	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, including the tall tower, tethered balloon measurements, and HONO measurements, as well as a review of WY DEQ ozonesonde measurements. System audits will address the following:

- Siting
- Adherence to SOPs
- QA/QC procedures
- Documentation

- Data collection and chain of custody

Mr. Bob Baxter will conduct the system audits. Mr. Baxter is independent of all UGWOS 2011 measurements. He will conduct the audits during an IOP in order to witness operations for the tethered balloon and ozonesonde operations.

In addition to the system audits, performance audits of the gaseous analyzers will be conducted at tall tower and tethered balloon sites. Performance audits will be conducted using equipment and standards independent of those used in the field. The ozone analyzers 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. The nitrogen oxide and methane/non-methane hydrocarbon analyzer will be audited using a certified dilution system and a certified cylinder of NO and methane. The standards used for the UGWOS audits will be the same as those used for the Wyoming state-wide audit program conducted by T&B Systems for the WY DEQ.

Mr. David Yoho will conduct the performance audits of all measurement platforms. 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

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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.

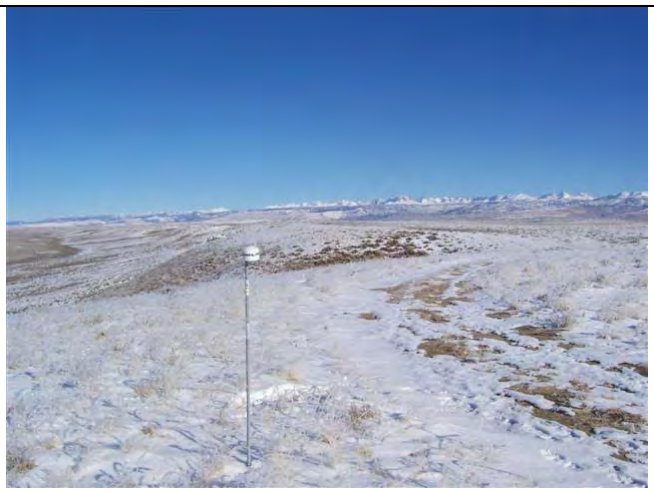
United States Environmental Protection Agency (2000). Meteorological Monitoring Guidance for Regulatory Modeling Applications. Document EPA-454/R-99-005. Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina.

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 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

View of Site Interior

Tethered Balloon Site

View to North

View to East

View to South

View to West

View of Site

View of Site Interior

Tower Site

APPENDIX B

STANDARD OPERATING PROCEDURES

4525 Wasatch Blvd. Suite 200 SLC, UT 84124 MSI Meteorological Solutions Inc. P: 801.272.3000 F: 801.272.3040	**STANDARD OPERATING PROCEDURE**	Title: HONO LOPAP Analyzer Cleaning Procedure	
		Number: SOP 74	Page: 1 of 1
		Revision Number: 0	Effective Date: 02/18/2010
Approval:	Date:		Concurred By:

HONO Cleaning Procedure

1. Turn air and liquid pumps off.

2. Detach ABS inlet tubes and connect to cleaning tubing. Insert other end of cleaning tubes into ultra pure water.

3. Join other end of ABS inlet tubes together with knotted tubing.

4. Turn pumps back on.

5. After 10 minutes replace water with pre-mixed solution of NaOH (12 g NaOH with 100 ml H_2O) and wait 10-15 minutes.

6. Again, replace NaOH with ultra pure water for 10 minutes.

7. Alternate NaOH and water as necessary ensuring that the process ends with water.

8. Turn pumps off.

9. Reconnect ABS inlet tubes.

10. Turn pumps on, which allow Reagent 1(R1) to re-enter the analyzer. Wait 10-20 minutes.

11. Adjust lamp intensities and integration time so that spectra are between 2000 and 4000 photon counts.

12. Conduct calibration (See MSI SOP 75).

Meteorological Solutions Inc. P: 801.272.3000 F: 801.272.3040 **STANDARD OPERATING PROCEDURE**	Title: HONO LOPAP Analyzer Calibration Procedure	
	Number: SOP 75	Page: 1 of 1
	Revision Number: 0	Effective Date: 02/18/2010
Approval:	Date:	Concurred By:

HONO Calibration Procedure

1. This calibration procedure must be preceded by the HONO LOPAP analyzer cleaning procedure (See MSI SOP 74).

2. Check Liquid flow using smallest volumetric flasks (5 ml). Disconnect the liquid flow tubing and allow the liquid to fill the volumetric flask to the 5 ml line. Note fill times in excel logbook.

3. Check air flow at the inlet using a flow standard. Note the value in the excel logbook.

4. Start zero air using the LOPAP analyzer menu.

5. Wait 20-30 minutes or until spectra become stable at zero. Replace R1 with liquid calibration standard.

6. Wait 20-30 minutes or until spectra rise and reach a stable plateau. Replace liquid standard with R1 and wait 10 minutes until the calibration plateau returns to zero.

7. Set Auto zero air schedule to 30 minutes active and 10 hours inactive.

SOP - UGWOS TALL TOWER AIR QUALITY MEASUREMENTS

Site Check

- Record all information of the checklist spreadsheet (see attached).
- Record the cylinder pressures and regulator settings on the checklist, verifying that they have not changed unpredictably.
- Verify that the pressure of the active hydrogen cylinder is above 500 psi.
- Verify that the rotameters are all reading 8 ± 0.5 SCFH. Record values and adjust as necessary.
- Using the TST keys on the NOx analyzer, toggle through until the sample pressure is displayed. Record the sample pressure for each level. They should be around 22" Hg, and within 0.5" Hg of each other. At the same time, verify that the solenoids are cycling. It takes three minutes to cycle from one solenoid to the next.
- Check the analyzers for any fault lights. If fault lights are visible, determine the problem and record the issue in the site log.

Zero Check

- On the calibrator display, press GEN, AUTO, and toggle through the pollutants to ZERO.
- Toggle through the pollutant key to NO (if not already present).
- Make sure that the concentration is 0000.0 and the units are PPB, and press ENTR.
- Set the Total Flow to 7.000 LPM and press ENTR.
- Wait at least 5 minutes or until concentrations of all analyzers have stabilized.
- Record the zero values on the checklist spreadsheet.
- Press STBY to end the zero check and place the calibrator in Standby mode.

Precision Check

- On the calibrator display, press GEN, and then AUTO.
- Toggle through the pollutants and select O3.
- Select an O3 concentration of 090.0 PPB and press ENTR.
- Select a Total Flow of 7.000 LPM and press ENTR.
- Wait at least 10 minutes or until the ozone concentration has stabilized.
- Record the precision value for O3 on the checklist spreadsheet, along with the photometer ozone concentration (toggle through the TST choices until the photometer concentration is displayed).

- On the calibrator display, press GEN, and then GPT.
- Select an NO concentration of 090.0 PPB and press ENTR.
- Select an O3 concentration of 000.0 PPB and press ENTR.
- Select a Total Flow of 7.000 LPM and press ENTR
- Wait at least 10 minutes or until concentrations of all analyzers have stabilized.
- Record the precision values for NO, NOx, Methane, NMHC, and THC on the checklist spreadsheet.

- On the calibrator display, press GEN, and then GPT.
- Select an NO concentration of 090.0 PPB and press ENTR.
- Select an O3 concentration of 080.0 PPB and press ENTR.
- Select a Total Flow of 7.000 LPM and press ENTR
- Wait at least 10 minutes or until concentrations of NOx analyzer have stabilized.
- Record the precision value for NO2 on the checklist spreadsheet.
- Press STBY to put the calibrator in the Standby mode.

Resetting Analyzer Responses

We do not anticipate needing to recalibrate the ozone and NOx analyzer during the course of the study. If either of these analyzers needs calibration, use existing MSI SOPs for conducting the calibrations. The response of the THC analyzer, however, has been know to drift, and resetting the analyzer response may be necessary.

- Initiate a zero calibration point using the Zero Check procedures above.
- On the THC analyzer, press the left or right arrow to get to the CALIBRATION menu.
- Use the down arrow to select Calibrate Now. The display should show "Calibration Methane Zero". The Target value should show 0.000 ppm.
- Wait at lease five minutes or until the actual concentration and detector current have stabilized.
- Press the left arrow to set the actual to the target (0.000 ppm). If the change appears successful, press Enter to accept.
- The display should now show "Calibration Methane Span".
- On the calibrator display, press GEN, and then AUTO.
- Toggle through the pollutants and select NO.
- Select an NO concentration of 200.0 PPB and press ENTR.
- Select a Total Flow of 7.000 LPM and press ENTR.
- Wait at least 5 minutes or until the methane concentration has stabilized.
- Press the left arrow to set the actual to the target (20.0 ppm). If the change appears successful, press Enter to accept.
- Repeat the above steps for "Calibration Non-Methane Zero" and "Calibration Non-Methane Span". The target value for the Non-Methane Span will be 6.0 ppm.
- After accepting the final value, the display on the THC analyzer should return to showing Methane, Non Methane, and Total Hydrocarbon.
- Press STBY to put the calibrator in the Standby mode.

Note that manuals are available at the site for the analyzers and calibrator, and they provide detailed presentations of procedures and menu choices. For the THC analyzer response adjustment, refer to Section 4.11 Performing a Manual Calibration.

Before Leaving Site . . .

- Verify that all switches on the relay board are in the Auto position.

- Verify that the calibrator is in the Standby mode.

Date	1/15/2011					
Hydrogen cylinder left	1980					
Hydrogen cylinder right	2000					
Hydrogen fuel	20					
Cal cylinder (psi)	1900					
Zero air (psi)	22.5					
Cal gas (psi)	22.5					
Level 1 flow (SCFH)	8					
Level 2 flow (SCFH)	8					
Level 3 flow (SCFH)	8					
Level 4 flow (SCFH)	8					
Level 1 NOx sample P	22.2					
Level 1 NOx sample P	22.1					
Level 1 NOx sample P	22					
Level 1 NOx sample P	21.9					
Any fault lights on?	no					
Solenoids cycling	yes					
O3 zero (ch 1)	0					
NO zero (ch 6)	0					
NOx zero (ch 11)	0					
NMHC zero (ch 16)	0					
THC zero (ch 21)	0					
O3 precision	90					
NO precision	90					
NOx precision	90					
NMHC precision	2.7					
THC precision	11.7					
NO GPT	10					
NOx GPT	90					
NO2 precision	80	0	0	0	0	0
Raven connected	yes					
Calibrator on Standby	yes					
All switches in "Auto"	yes					

Tall Tower Checklist

Appendix B
Microsoft Access Database Description

The Upper Green Winter Ozone Study (UGWOS) 2011 Database

1. Introduction

This document describes the Upper Green Winter Ozone Study (UGWOS) database for 2011. 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. Overview of Measurements and Field Study Participants

The 2011 UGWOS field study included hourly measurements of surface air quality and meteorological data during the period of January through March 2011 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 during the two Intensive Operating Periods (IOPs). Measurements of HONO were conducted at an additional shelter located at the Boulder site.

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

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

- WDEQ runs an ambient air quality network throughout the state of Wyoming. Air Quality sites included in UGWOS 2011 were located in or near Sublette County in southwestern Wyoming. The stations include:
    - Boulder (including 1-minute and 1-hour data collection),
    - Campbell County,
    - Cheyenne,
    - Cloud Peak,
    - Daniel,
    - Juel Springs,
    - Moxa,
    - Murphy Ridge,
    - Pinedale,
    - South Pass,
    - Thunder Basin,
    - Wamsutter, and
    - Wyoming Range.

- The WDEQ Monitoring network data consisting of some or all of the parameters presented below:
    - Ozone
    - PM_{10}
    - $PM_{2.5}$
    - 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
    - Methane, Non-methane Hydrocarbons, Total Hydrocarbons

<u>T&B Systems</u>

- SODAR measurements (Boulder site)
    - Wind speed
    - Wind direction
    - Mixing heights
- Tethered Balloon/Mobile Trailer (four levels)
    - Ozone
    - $NO/NO_2/NO_X$
    - Methane, Non-methane Hydrocarbons, Total Hydrocarbons
    - Wind speed
    - Wind direction
    - Ambient Temperature
    - Additional met parameters (relative humidity, barometric pressure, solar radiation, sigma theta)
- Tall Tower (four levels)
    - Ozone
    - $NO/NO_2/NO_X$
    - Methane, Non-methane Hydrocarbons, Total Hydrocarbons

<u>Meteorological Solutions, Inc.</u>

- Tall Tower (four levels)
    - Wind speed
    - Wind direction
    - Ambient Temperature
    - Relative Humidity
- Canister Data
    - VOCs

<u>University of Houston</u>

- Second shelter at Boulder
    - HONO

Supplemental data included hourly surface ozone and meteorological data from three CASTNET (Clean Air Status and Trends Network) sites, 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 and any adjustments for calibration deviations were applied. Appropriate flags were assigned for extreme values, instrument downtime and performance tests. A description of the Quality Control (QC) codes used are given in Table 1 and also listed in the table **QC_flags** in the UGWOS 2011 database.

Table 1 - Data Flags

QC	Description
V	Valid Data
M	Missing Data
I	Invalid Data
S	Suspect Data - Data appears to be a data spike or outside normal data range
U	Data which has not been validated - User is responsible for validation.
N	Instrument Noise detected in sub hourly data used to create hourly average
B	Below Detection Limit
AA	Sample Pressure out of Limits
AB	Technician Unavailable
AC	Construction/Repairs in Area
AD	Shelter Storm Damage
AE	Shelter Temperature Outside Limits
AF	Scheduled but not Collected
AG	Sample Time out of Limits
AH	Sample Flow Rate out of Limits
AI	Insufficient Data (cannot calculate)
AJ	Filter Damage
AK	Filter Leak
AL	Voided by Operator
AM	Miscellaneous Void
AN	Machine Malfunction
AO	Bad Weather
AP	Vandalism
AQ	Collection Error
AR	Lab Error
AS	Poor Quality Assurance Results
AT	Calibration
AU	Monitoring Waived
AV	Power Failure
AW	Wildlife Damage

Table 1 Continued - Data Flags

QC	Description
AX	Precision Check
AY	Q C Control Points (zero/span)
AZ	Q C Audit
BA	Maintenance/Routine Repairs
BB	Unable to Reach Site
BC	Multi-point Calibration
BD	Auto Calibration
BE	Building/Site Repair
BF	Precision/Zero/Span
BG	Missing ozone data not likely to exceed level of standard
BH	Interference/co-elution/misidentification
BI	Lost or damaged in transit
BJ	Operator Error
BK	Site computer/data logger down
BL	QA Audit
BM	Accuracy check
BN	Sample Value Exceeds Media Limit
B	Below Detection Limit

3. UGWOS Database Design

Meteorological Solutions Inc. assimilated the submitted data into an ACCESS 2011 database called UGWOS_2011_Database_Version?.?.mdb (where ?.? indicates version number). 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 as well as dates of said modifications. The name of the database includes a version number to help users identify the most current 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 adverse AQS Null code values or 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.

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. One minute air quality data were collected at the Boulder and Mobile trailer sites. These data are presented in the **1-minute Air Quality** data table. Boulder data went through quality assurance with valid data marked with a “V” in the QC flag field. The Mobile Trailer did not get validated and is associated with a “U” in the data QC flag filed as specified in Table 1 as data which has not been validated.

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. One minute meteorological data were collected at the Boulder and Mobile trailer sites. These data are presented in the **1-minute Meteorology** data table. Boulder data went through quality assurance. The Mobile Trailer did not get validated and the data has a QC flag of “U” as specified in Table 1 as data which has not been validated.

The **8-Hour Ozone** table includes the leading 8-hour average of ozone for each of the sites.

Data included in the **Hourly HONO** table represent hourly HONO data collected in a separate shelter at the Boulder site. HONO data are also available in the **1-minute HONO** data table. Parameters measured include HONO in parts per trillion by volume, confidence, and the position of the sample inlet.

The HONO sample inlet was attached to a two meter tower which adjusted from slightly above ground level (above the snow) to two meters. The position parameter indicates it is near ground level with a “G”, at the top of the tower with a “T” or mirrors the quality control flag to the right of the data.

The data from the SODAR is included in the **Sodar** and the **Mixing Height** data tables. Sodar data were only collected during intensive operating periods (IOPs).

Upper air data was collected during IOPs. These data are assembled in **Sonde Data (met)** and **Sonde Data (ozone)** data tables. GPS coordinates and elevation (by altimeter and GPS reading) as well as meteorological and ozone readings are available in these tables.

Surface VOC data collected during IOPs at the tethered balloon site are presented in the **VOC** table. A summary of the canister data collected at the tethered balloon site is also available in **VOC Summary** table. VOC data were also collected at the Boulder site and are presented in the **VOC at Boulder** data table

Particulate data collected every three days at the Boulder site were analyzed for content. The **Speciated Mass** data table presents the particulate data in various chemical species and heavy metals.

Additional upper air pollutant data was collected via tethered balloon and a 73 meter communications tower (referred to as Tall Tower) at four different heights above ground level. The samplers used during the study had twelve minute resolution data for pollutants. These data have been posted in the **12-minute Tethered Balloon Air Quality, 12-minute Tethered Balloon Met** and **12-minute Tall Tower Air Quality** data tables. The Tall Tower has hourly average data for both pollutant and meteorological data in **Tall Tower Hourly Air Quality** and **Tall Tower Hourly Meteorology** data tables.

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 2011 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 in chronological order 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.

The data have the following general unit configurations:

- Parts per billion for O3, NO, NO_2, and NO_X
- Parts per trillion for HONO
- Micrograms per cubic meter for PM_{10}, $PM_{2.5}$, and speciated particulate
- Parts per million for methane, non-methane hydrocarbons, and total hydrocarbons
- Micrograms per cubic meter, parts per billion by volume, and parts per billion by Carbon for VOC data,
- 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
- Percent for relative humidity

The 2011 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, 2011 and March 31, 2011. 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.

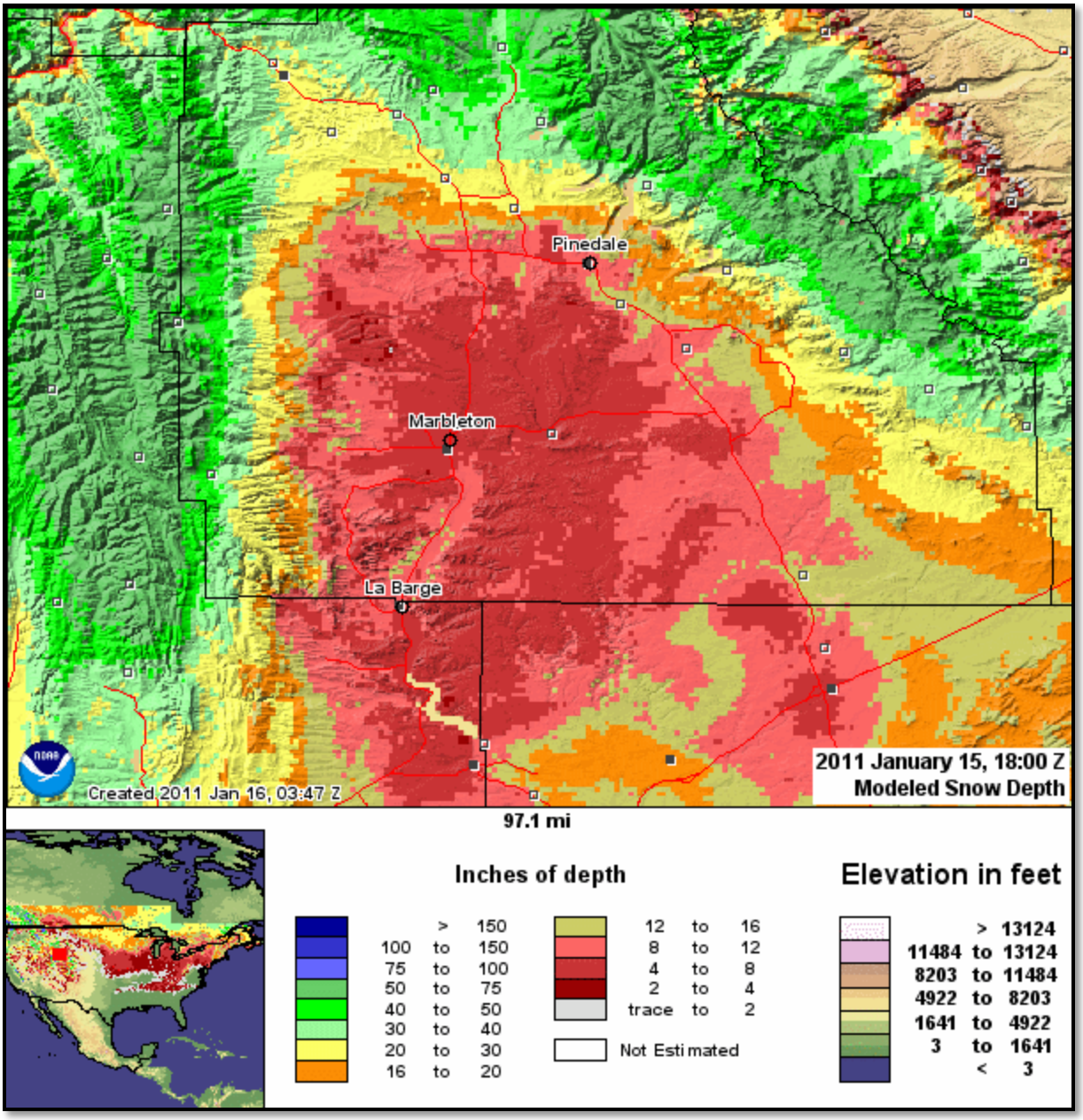
Sort 1-hour Ozone Data- the purpose of this query and the **Sort 8-hour Ozone Data** query are to sort any data above a user specified threshold. The user will be asked to provide a level of which no data records with an ozone level below that threshold will be displayed. Common parameters are displayed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

This document describes the 2011 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
Snow Depth Images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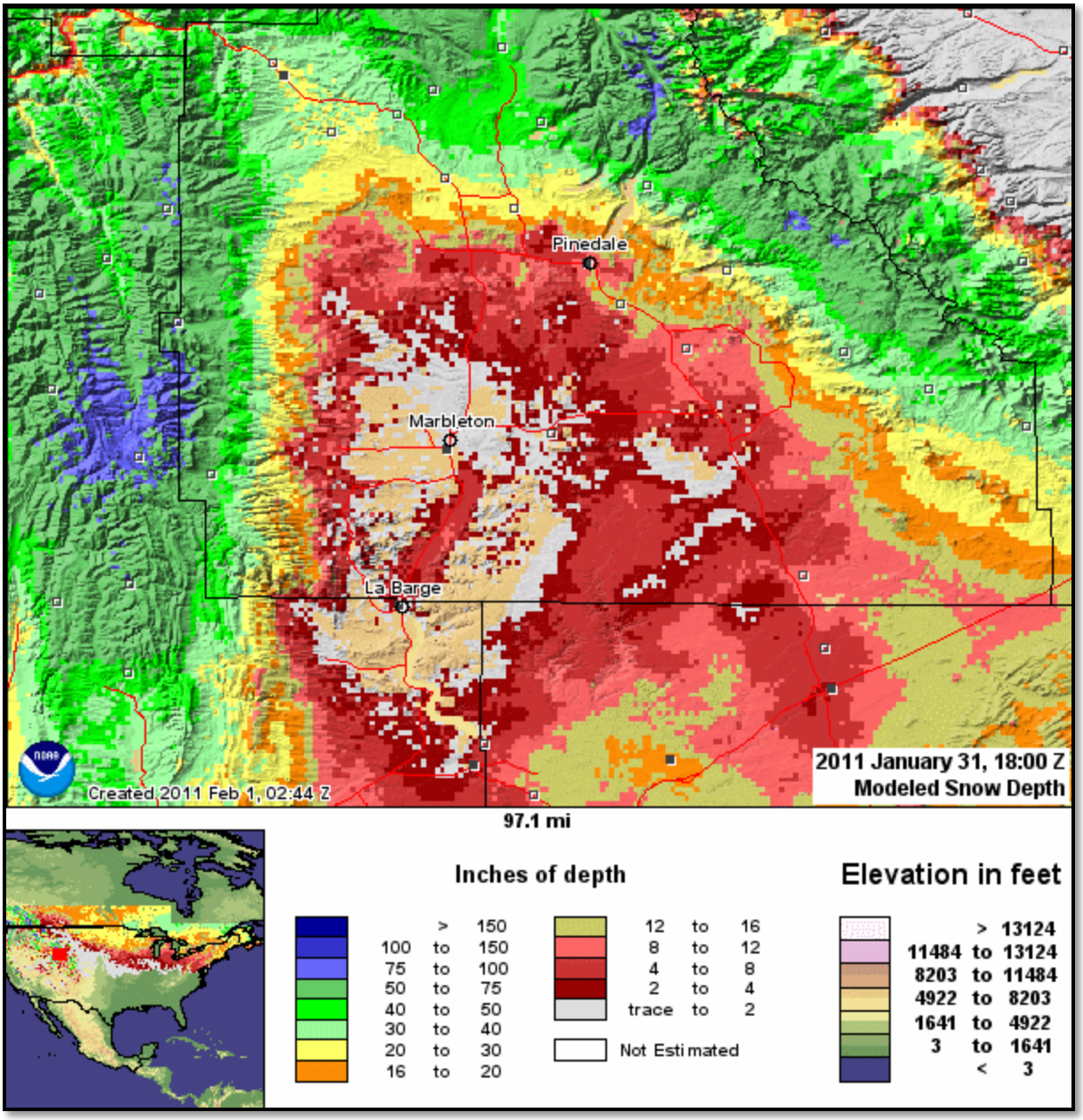
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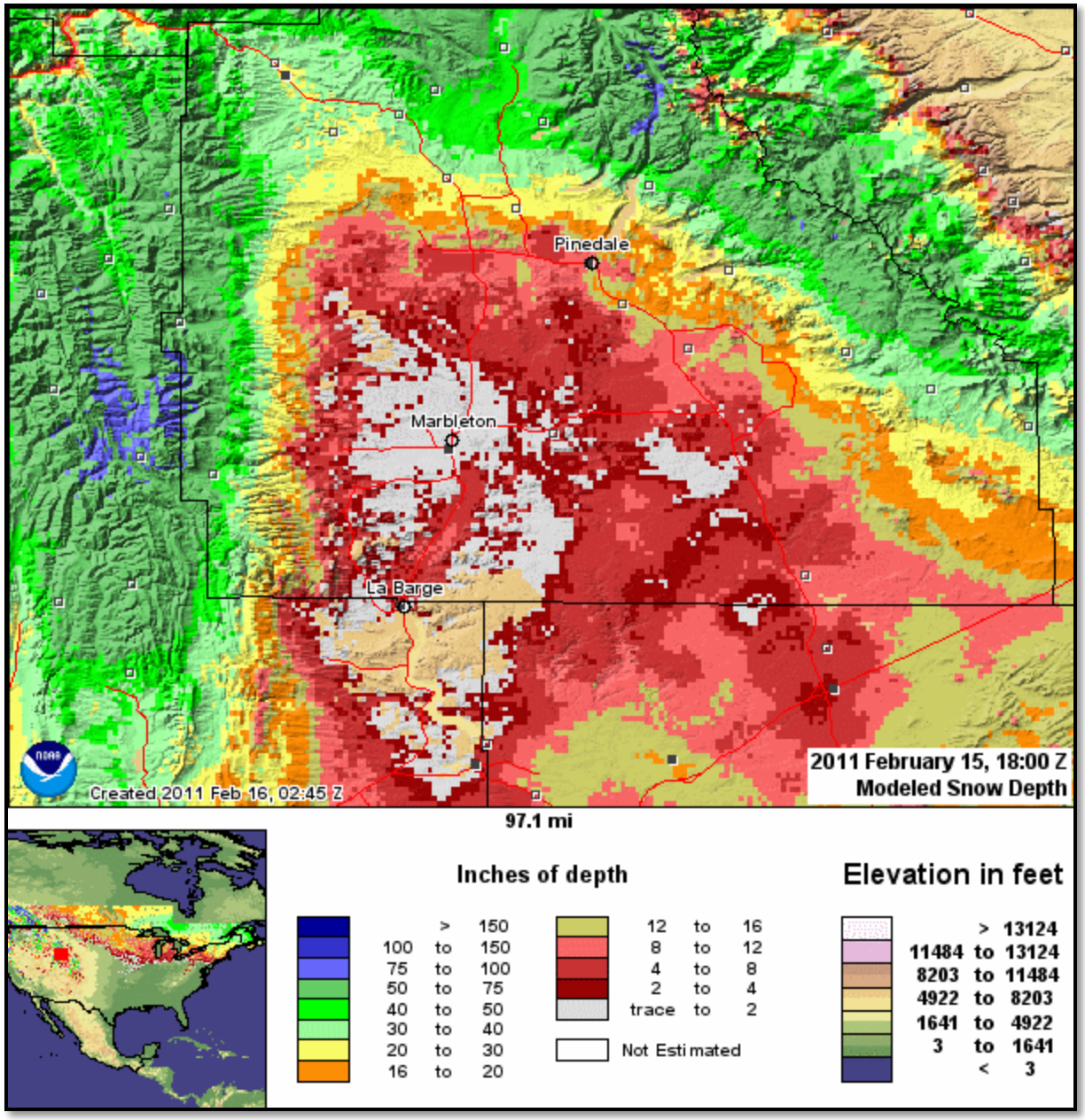
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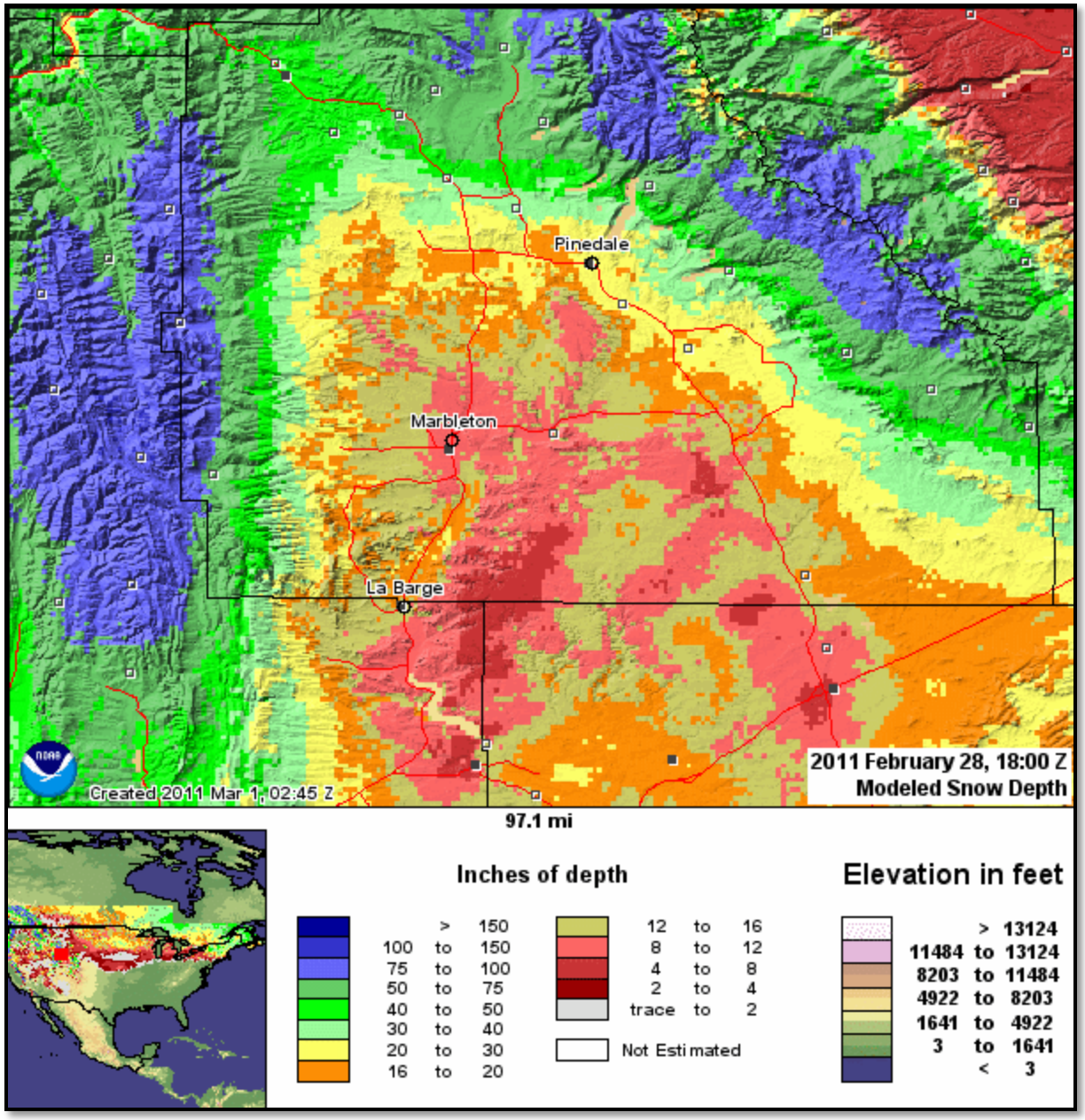
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40 to 50
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20 to 30
16 to 20
12 to 16
8 to 12
4 to 8
2 to 4
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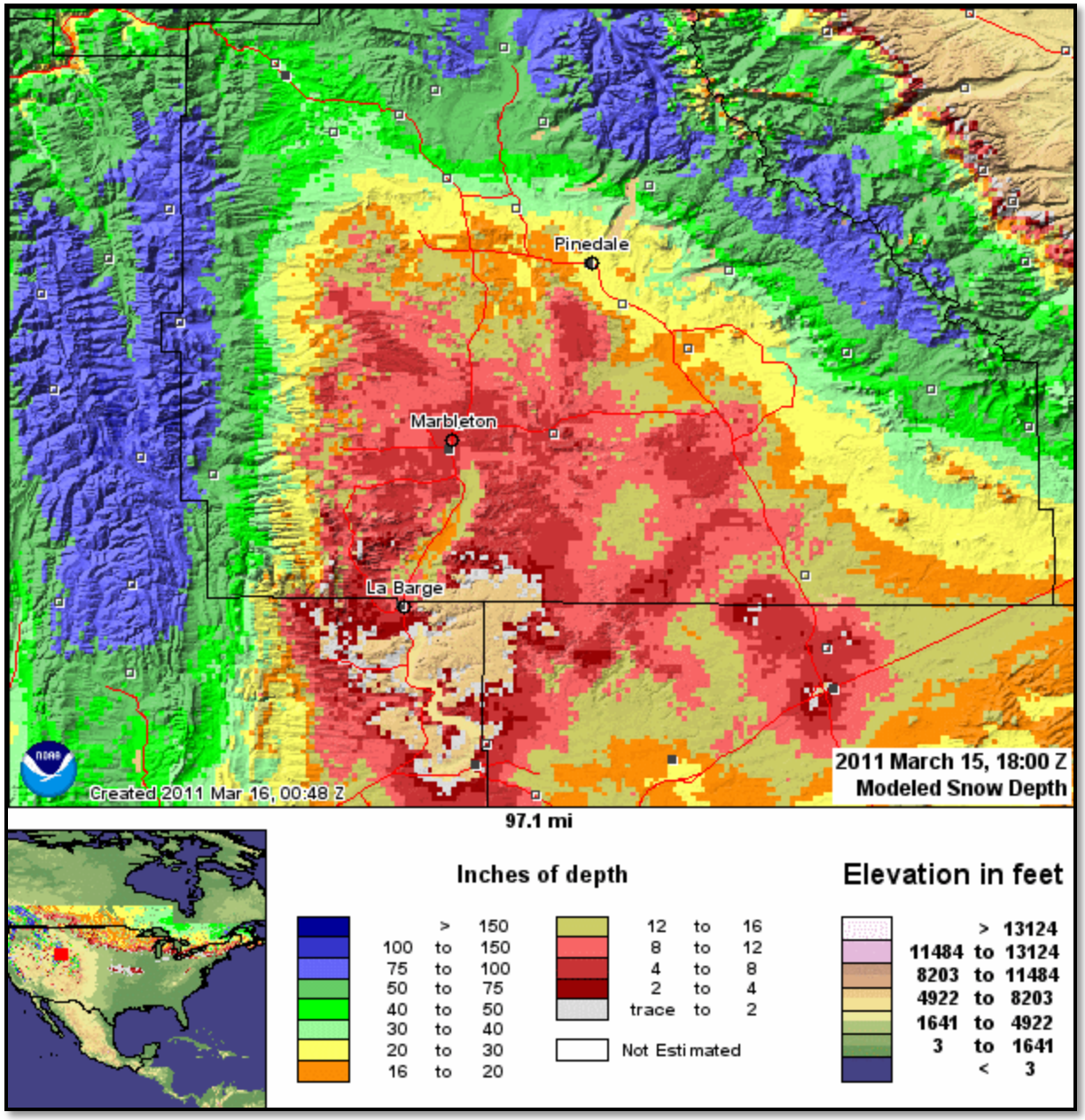
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16 to 20
12 to 16
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8203 to 11484
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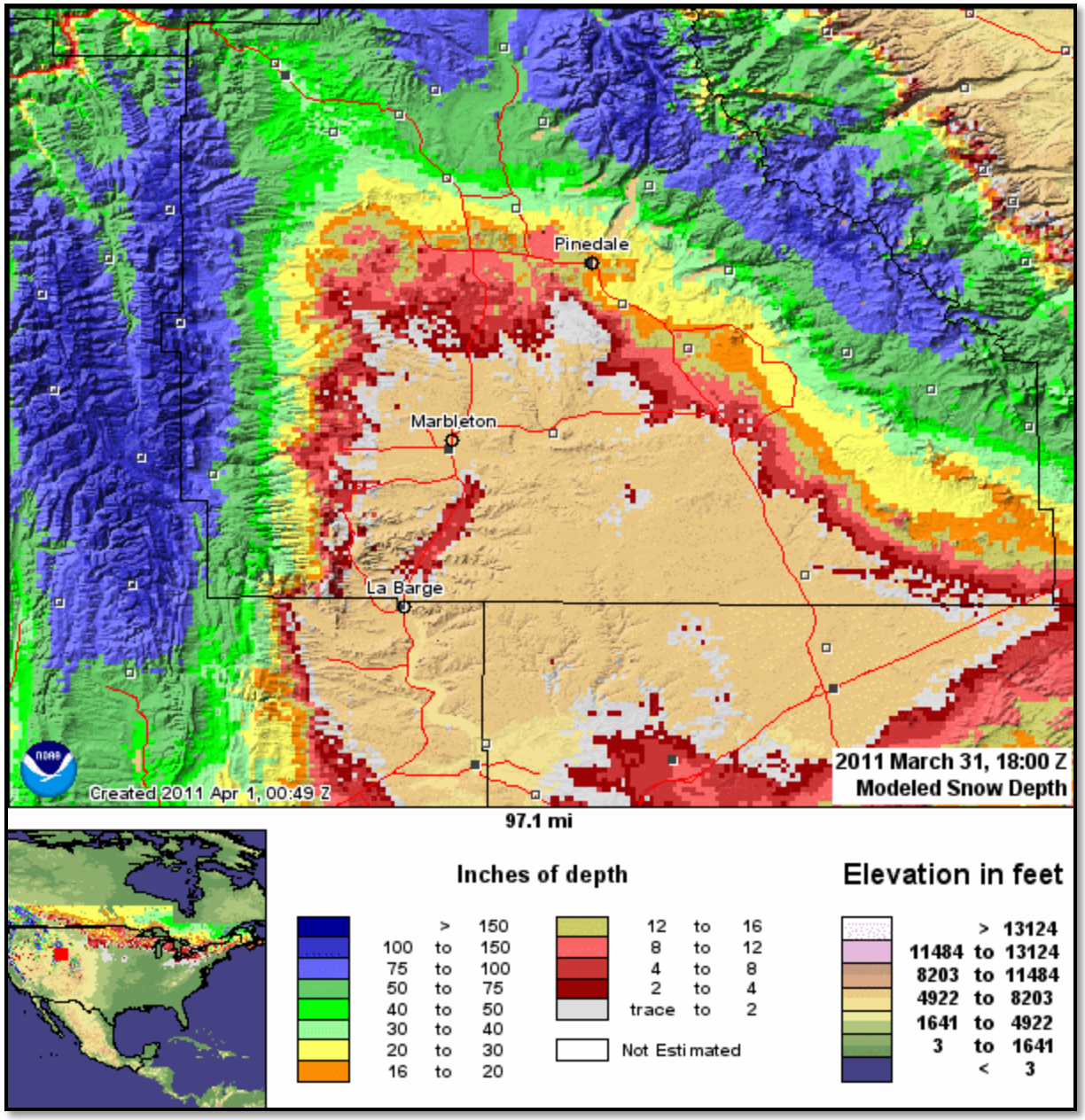
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8 to 12
4 to 8
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trace to 2
Not Estimated
Elevation in feet
> 13124
11484 to 13124
8203 to 11484
4922 to 8203
1641 to 4922
3 to 1641
< 3

Appendix D
HONO Report

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

WDEQ UGWOS 2011 HONO Measurements

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3.2 Conditions associated with elevated HONO readings; relationships with other parameters 10

4. Findings and Recommendations 12

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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 11 - March 31, 2011, 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, NO_x, and HNO_3. Best correlation occurs with HNO_3. 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 SW-WSW wind conditions. During daytime periods HONO mixing ratios are generally higher than nighttime values, which is a different observation compared with the previous 2010 campaign. Similar to nighttime conditions, daytime HONO levels continue to show enhanced values under SW-WSW conditions, but also generally occur under SE-WSW wind directions.
- HONO levels at 1.80 m above ground are quite similar to those at the surface level. Both levels also show the morning HONO peak around 10 am MST. However, afterwards high HONO levels persist at the surface, while at 1.80 m above ground HONO depletes faster than at the surface.
- Snow cover leads to enhanced UV radiation and UV radiation correlates with HONO levels. This finding suggests photo-induced formation of HONO. This is also supported by very good correlations of HONO with HNO_3 (and NO_y).
- HONO formation may occur through NO_x conversion (also potentially associated with primary organic aerosol) in highly polluted air masses that are transported to the Boulder site.
- HONO accumulation is favoured in a very shallow daytime mixing layer.
- 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. HONO also correlates with HNO_3 and NO_y during daytime.
- 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. While the $HONO/NO_x$ ratio is at a maximum in the afternoon, also O_3 shows the daytime maximum.

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.

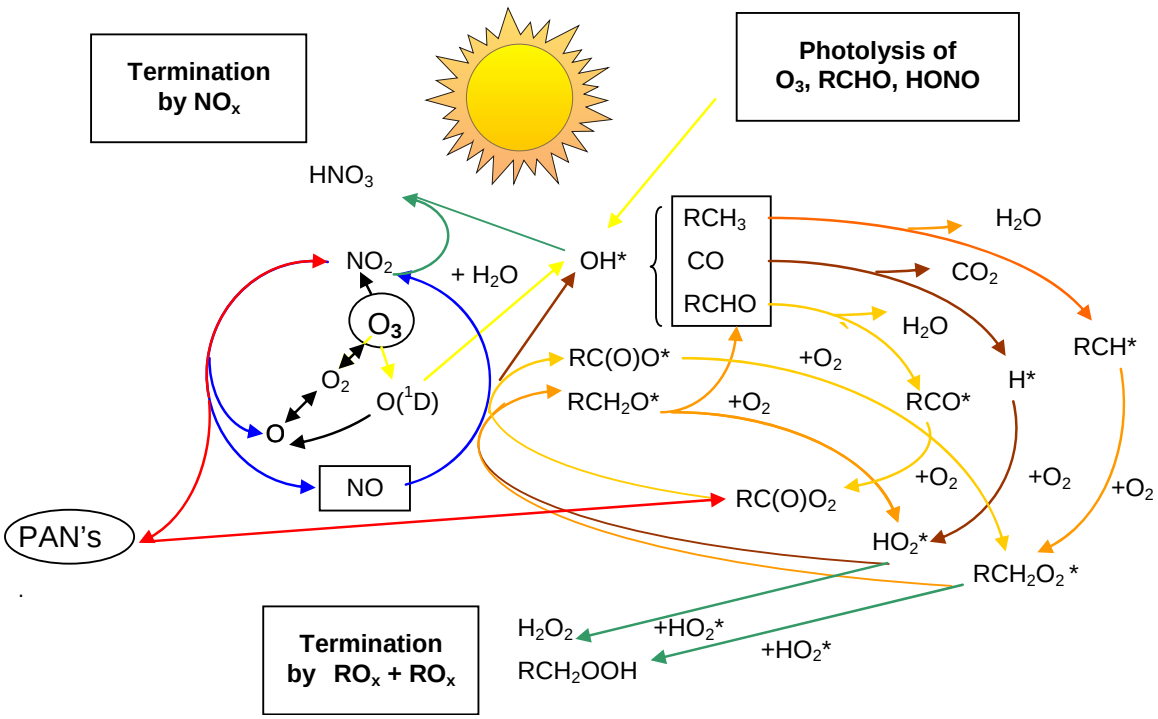


Figure 1: Daytime photochemical Processes.

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 [Rappenglück et al., 2011]. 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; Czader et al., 2010; Czader et al., 2011], which have been found frequently, in particular urban studies [e.g. Wong et al., 2011, Villena et al., 2011].

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. The UH LOPAP instrument recently participated in a large intercomparison chamber instrument [Ródenas et al., 2010; Ródenas et al., 2011].

3.1 Summary Statistics

The LOPAP instrument started collecting data on January 11, 2011 and ran almost continuously until March 31, 2011. Unfortunately, some electronic units of the instrument were severely damaged in mid February due to a power outage. As a consequence data loss for about 2 weeks occurred.

For the 2011 campaign the sampling unit was attached to a small tower (height 1.80 m). The sampling unit stayed at the surface for 15 min, then moved to the top of the tower, where it stayed for another 15 min, afterwards the unit returned back to the surface and resumed a new cycle. The purpose was to explore whether HONO gradients close to the surface could be detected.

Based on 1-min values also 10- min and 1-hour average values were calculated and merged with other data sets available at the Boulder site. However, only the times when the HONO sampling unit was at the top of the small tower were compared to other data obtained at the Boulder site.

Table 1 provides an overview of data statistics for the campaign split into the times when the HONO sampling unit was at the surface and times when it was at the top of the sampling tower. According to table 1 there were only small differences observed between the two sampling locations. However, the maximum HONO value was observed close to the surface.

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

Parameter	Surface (January 11 - March 31, 2011)	Top (1.80 m above ground) (January 11 - March 31, 2011)
Number of measurements above DL (DL=2 pptv)	24,955	33,970
Mean [pptv]	151	163
Median [pptv]	78	82
Maximum [pptv]	4938	3078

Figure 2a shows HONO levels and their dependence on wind direction during the entire field campaign split into day- and nighttime periods, and also split into the two main HONO sampling locations (surface; 1.80 m above ground). The daytime/nighttime 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 SW-WSW flow conditions. During daytime periods HONO mixing ratios are generally higher than nighttime values, which is a different observation compared with the previous 2010 campaign. Similar to nighttime conditions, daytime HONO levels continue to show enhanced values under SW-WSW conditions, but also generally occur under SE-WSW wind directions. No significant differences could be observed between the two different locations of the HONO sampling instrument (surface; 1.80 m above ground). However, there is a tendency that during day- and nighttimes HONO values are slightly higher at 1.80 m under WSW (and SW winds), while during daytime HONO levels are higher at the surface under S-SSW winds. The higher values towards SW-WSW are probably due to transport of pollutant air masses which contain significant amount of precursors including reactive nitrogen compounds (see Figure 7).

Similar plots for ozone (Figure 2b) show that elevated HONO under night time SW-WSW winds is associated with slightly lower ozone, indicative of ozone titration by fresh NO emissions. This is likely due to NO_x sources (compressors and drill rigs) in the Boulder area operating during January – March 2011 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.

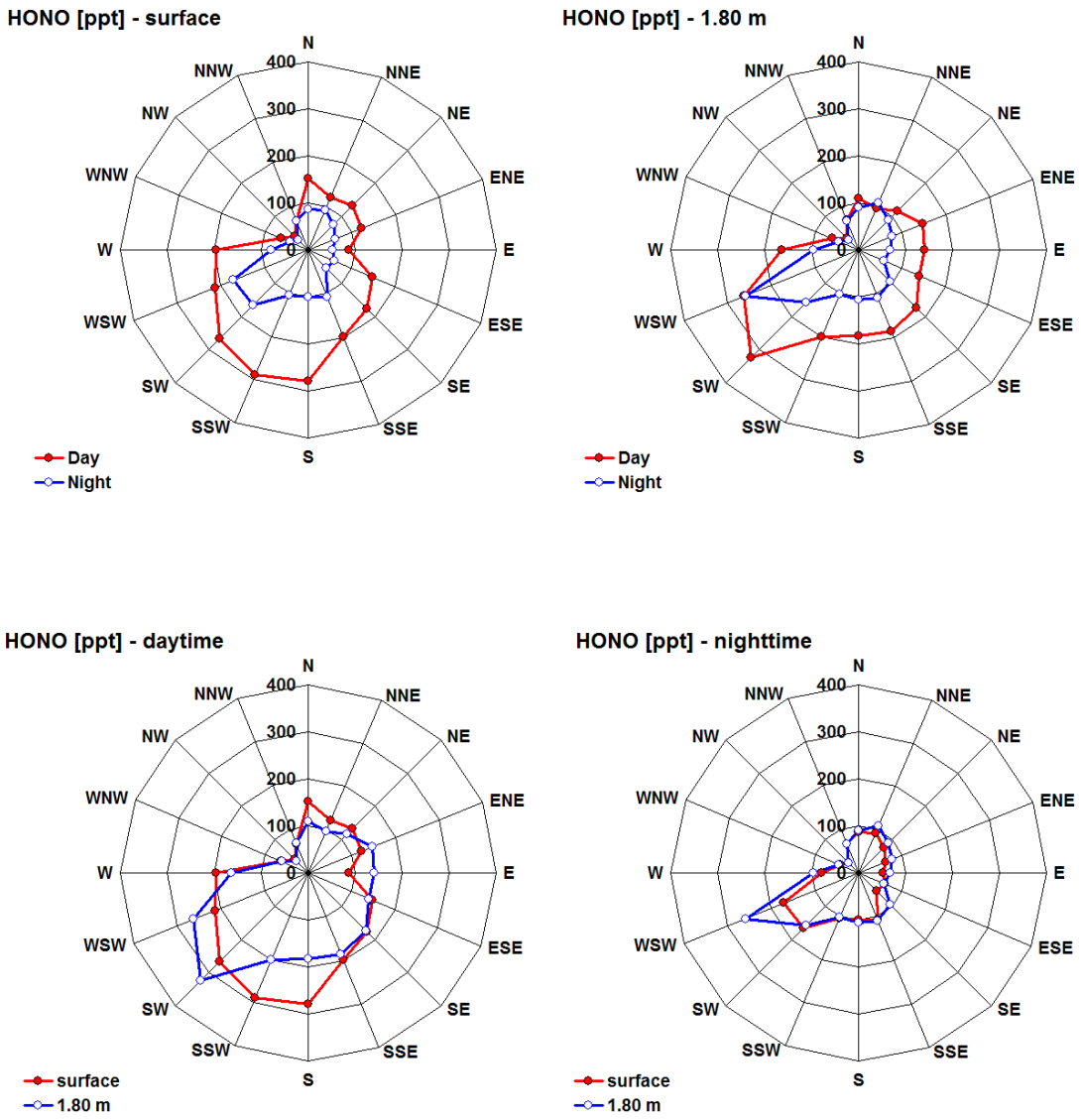


Figure 2a: Median of 1-min HONO levels and their dependence on wind direction and HONO sampling location (surface; 1.80 m above ground) during the time period January 11 - March 31, 2011. Daytime was assumed when solar radiation values were above 1 W m^{-2}.

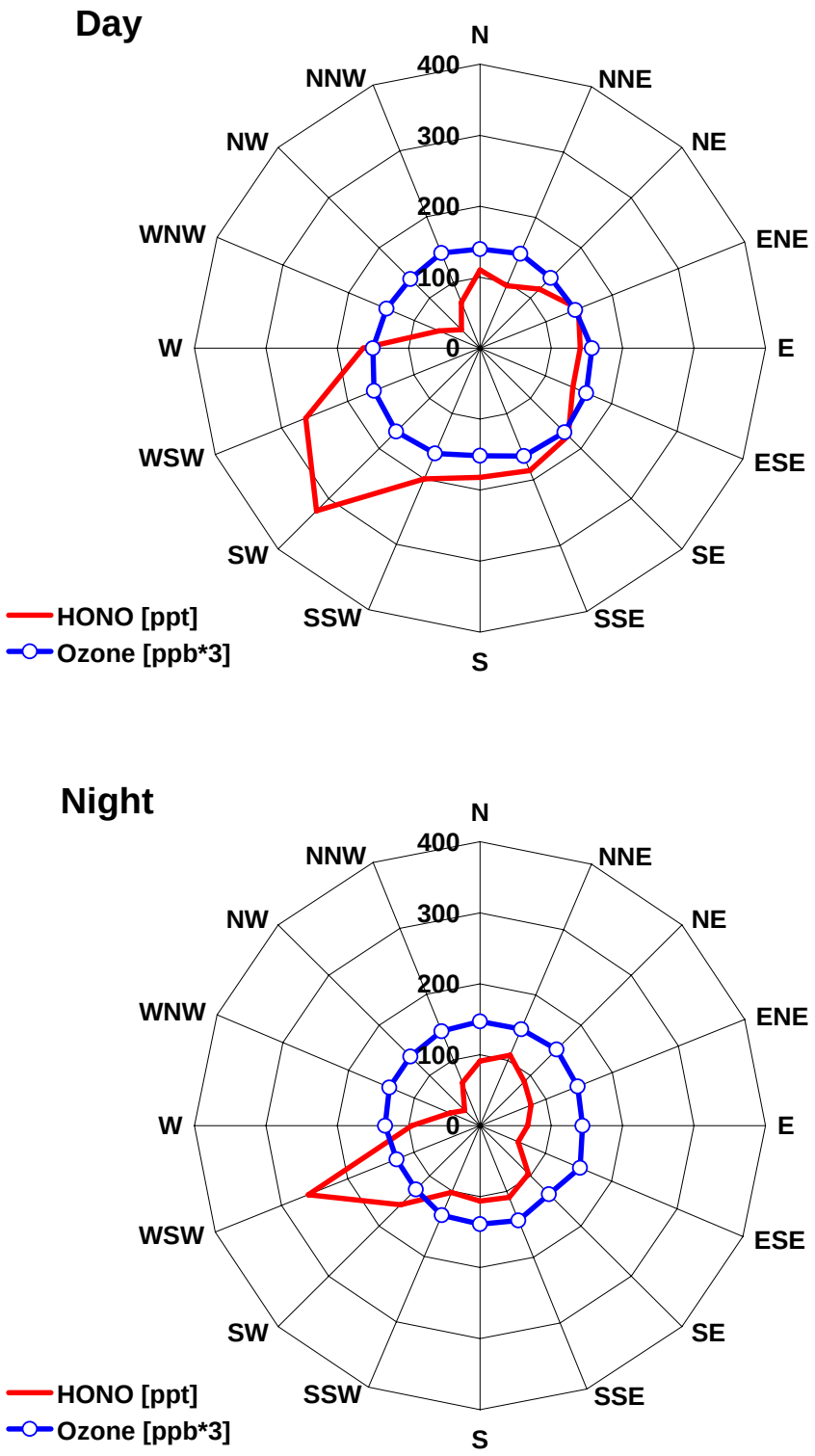


Figure 2b: As in Figure 2a but for HONO and ozone during daytime hours (top) and night time hours (bottom).

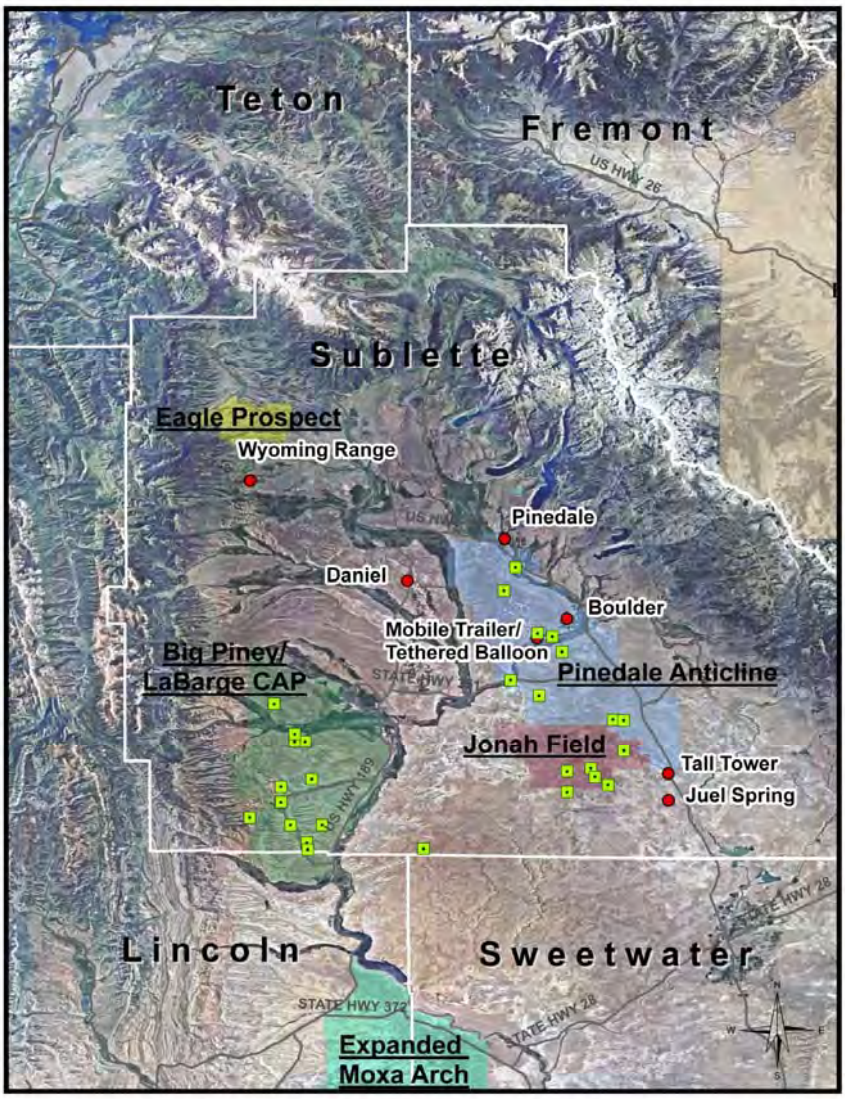


Figure 3: Locations of compressors (green rectangles) operating during January – March 2011 relative to the Boulder monitoring site.

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 (NMHC, PM-10) and 10-min (NO, NO_2, NO_x) values for the entire field campaign. Apart from PM-10, all other compounds are usually well correlated with HONO. Figure 6 shows correlations between HONO, NMHC, NO_2, NO_x, and HNO_3 for nighttime conditions. Figure 6 clearly shows the close relationship between HONO and $NO_2/NO_x./HNO_3$.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 HONO and PM-10 at this site.

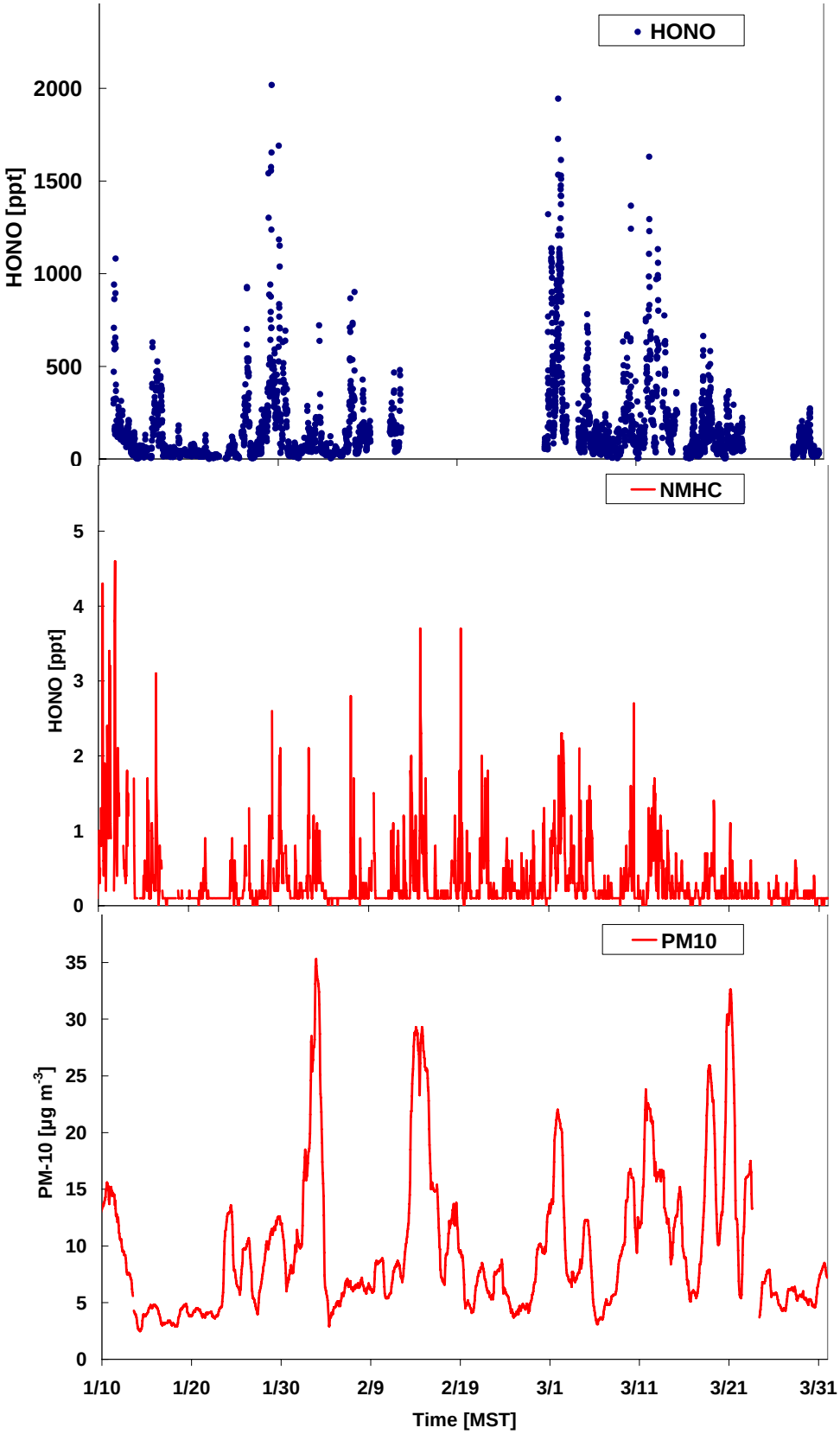


Figure 4: Time series of HONO, NMHC and PM-10 from January 11 - March 31, 2011. For NMHC and PM-10 hourly values and for HONO 10-min values are shown.

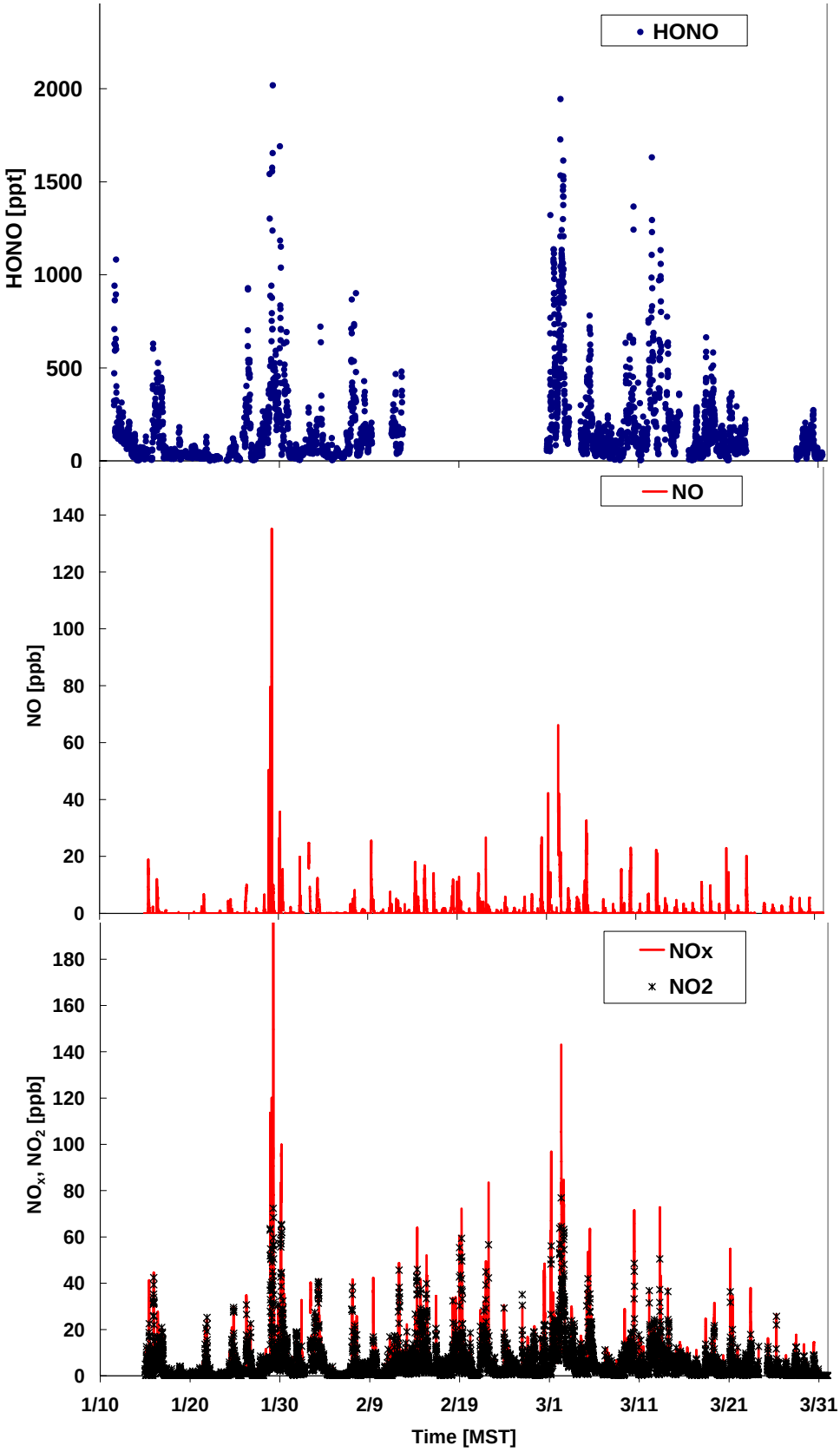


Figure 5: Time series of HONO, NO, NO_2 and NO_x from January 11 - March 31, 2011. 10-min values are shown.

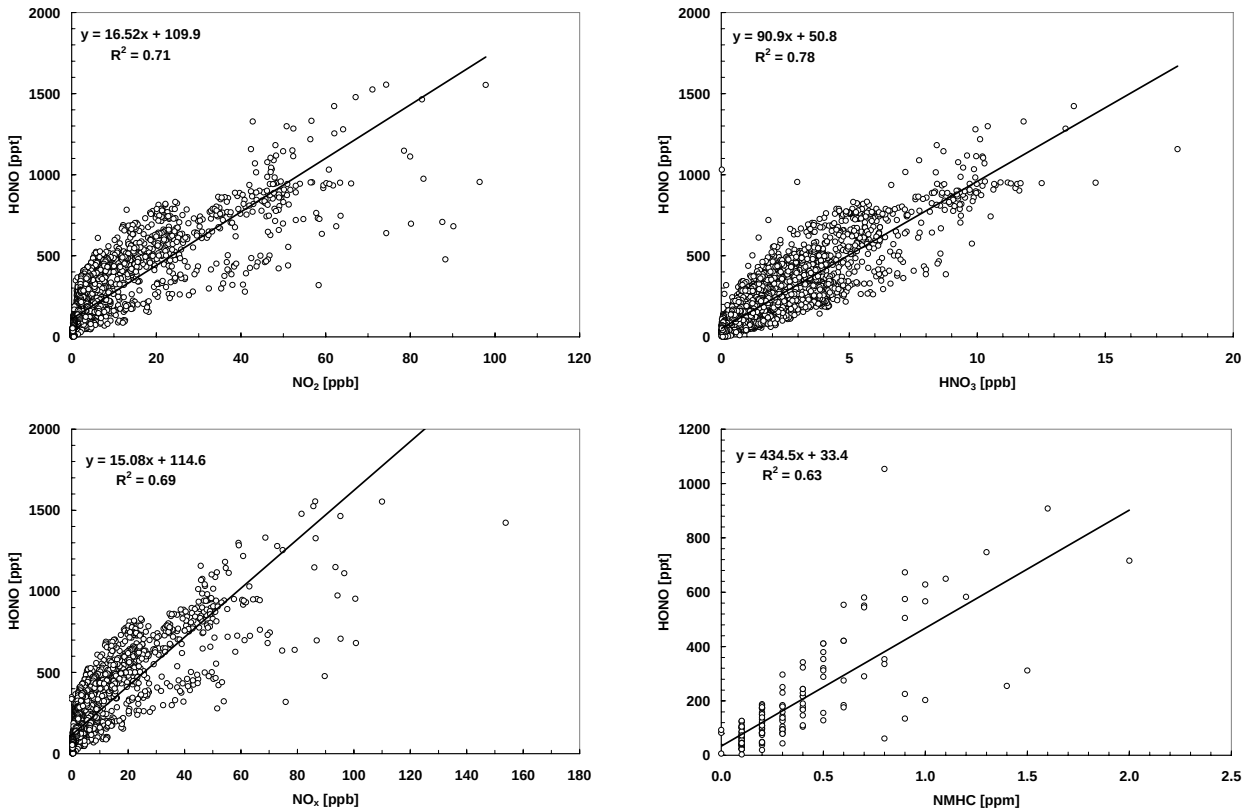


Figure 6: Correlations of HONO vs. NO_2 (top left), HNO_3 (top right), NO_x (bottom left) and NMHC (bottom right) during night. All data 10-min values, with the exception of HONO vs NMHC which is based on hourly data.

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 eliminates daytime photochemical processes. Interestingly, it seems that CH_4 is also enhanced under SW-WSW conditions indicating sources which emit nitrogen oxides, NMHC and CH_4 or different sources located in the same area which may overlap. This is likely consistent with locations of compressors and drill rigs operating during January – March 2011 (which emit primarily NO_x) relative to well head equipment (which emits primarily CH_4 and NMHC). 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 8 shows reactive nitrogen compounds and their dependence on wind direction split into day- and nighttime. Higher levels during nighttime occur under WSW directions, whereas during daytime higher levels occur under SW directions. Interestingly NO levels show significantly higher mixing rations during daytime.

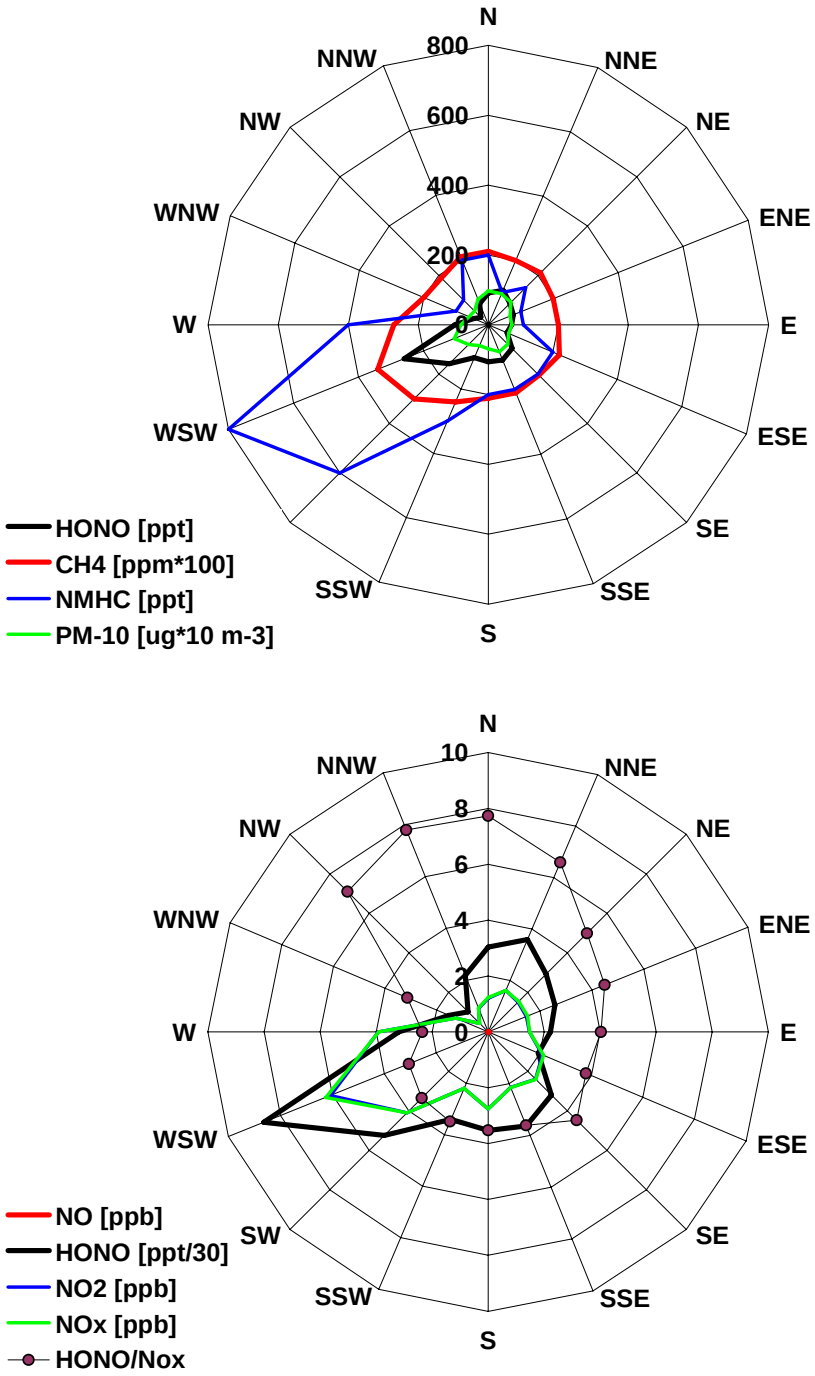
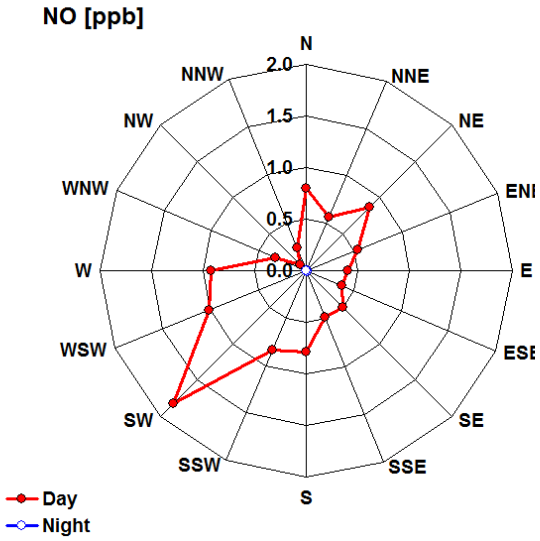
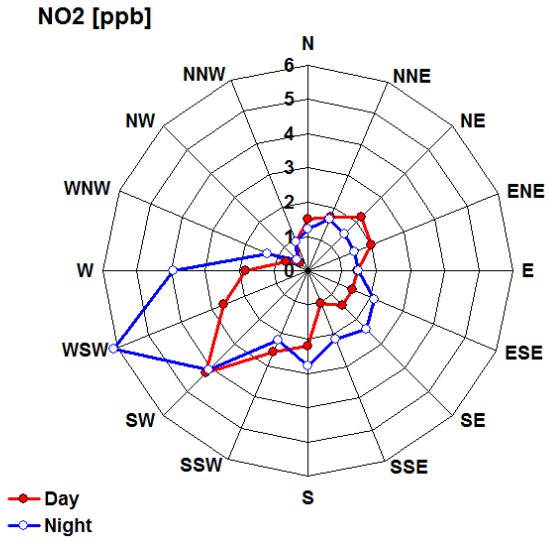
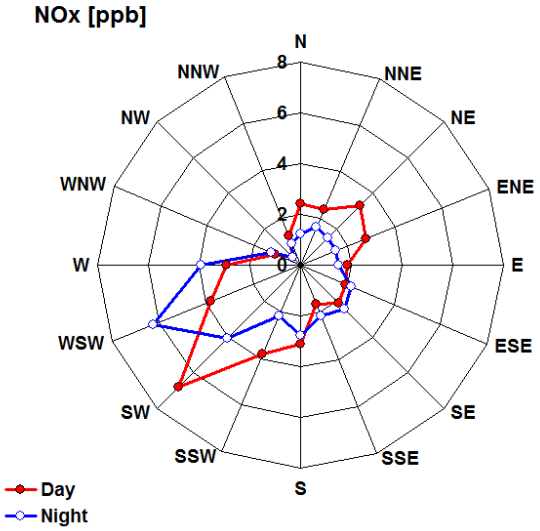
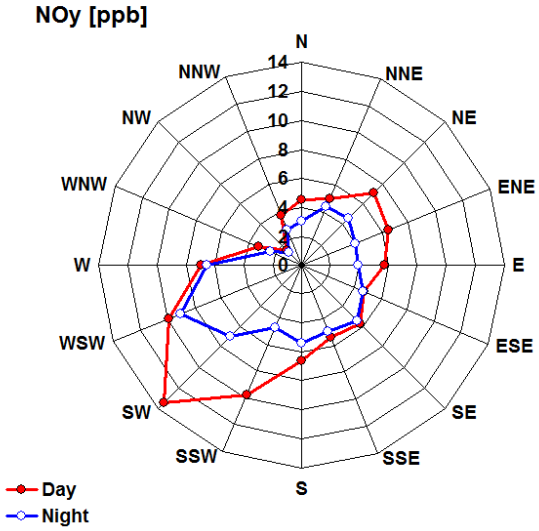


Figure 7: Wind directional dependence of HONO, CH_4, NMHC, PM-10, NO_2, NO_x, and the HONO/NO_x ratio for the time period January 11 - March 31, 2011 for night-time conditions (defined as time periods with solar radiation less than 1 W/m^2). NO did not show appreciable values. Note: most NO_x consists 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.









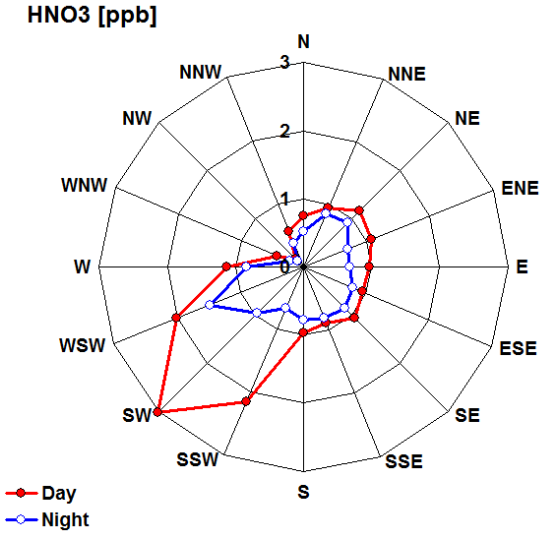


Figure 8: Wind directional dependence of NO, NO_2, NO_x, NO_y, and HNO_3 for the time period January 11 - March 31, 2011 for night-time conditions (defined as time periods with solar radiation less than 1 W/m^2).

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.

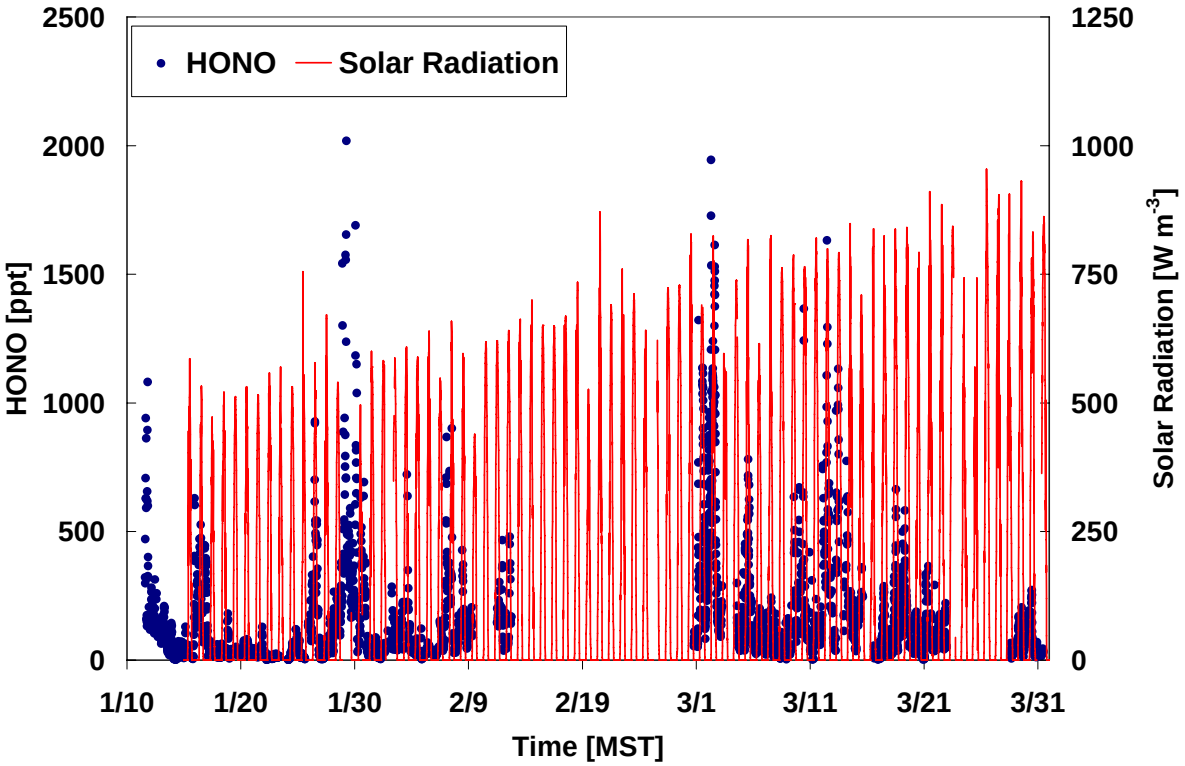


Figure 9: HONO and solar radiation time series for the time period January 11 - March 31, 2011. 10-min values are shown.

The picture is different when UV radiation is considered, in particular if both incoming and outgoing UV radiation are taken into account. Contrary to the preceding year there was snow cover almost throughout the entire 2011 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 10 together with the HONO time series. There appears to be a good correlation between HONO the total UV radiation, in particular in the first two weeks of March, when actually all the IOPs occurred. The correlation between total UV and HONO indicate the potential presence of photo-induced HONO formation.

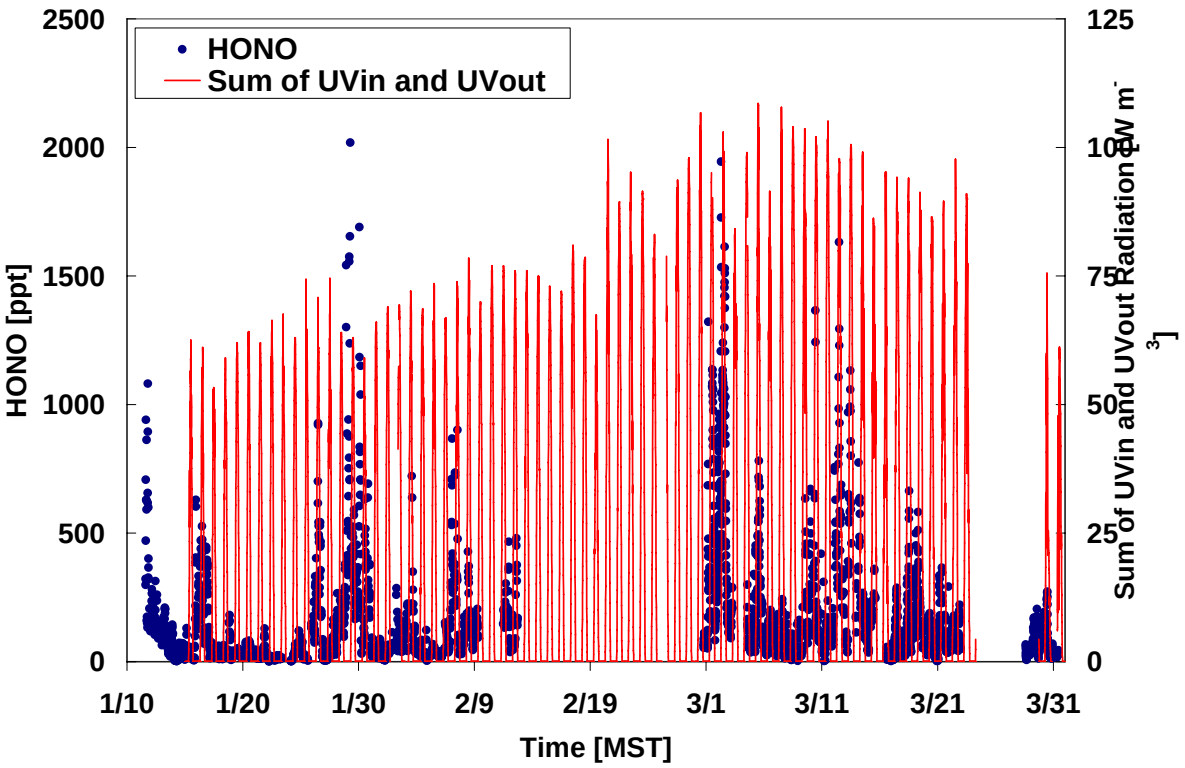


Figure 10: HONO and total UV radiation time series for the time period January 11 - March 31, 2011. 10-min values are shown.

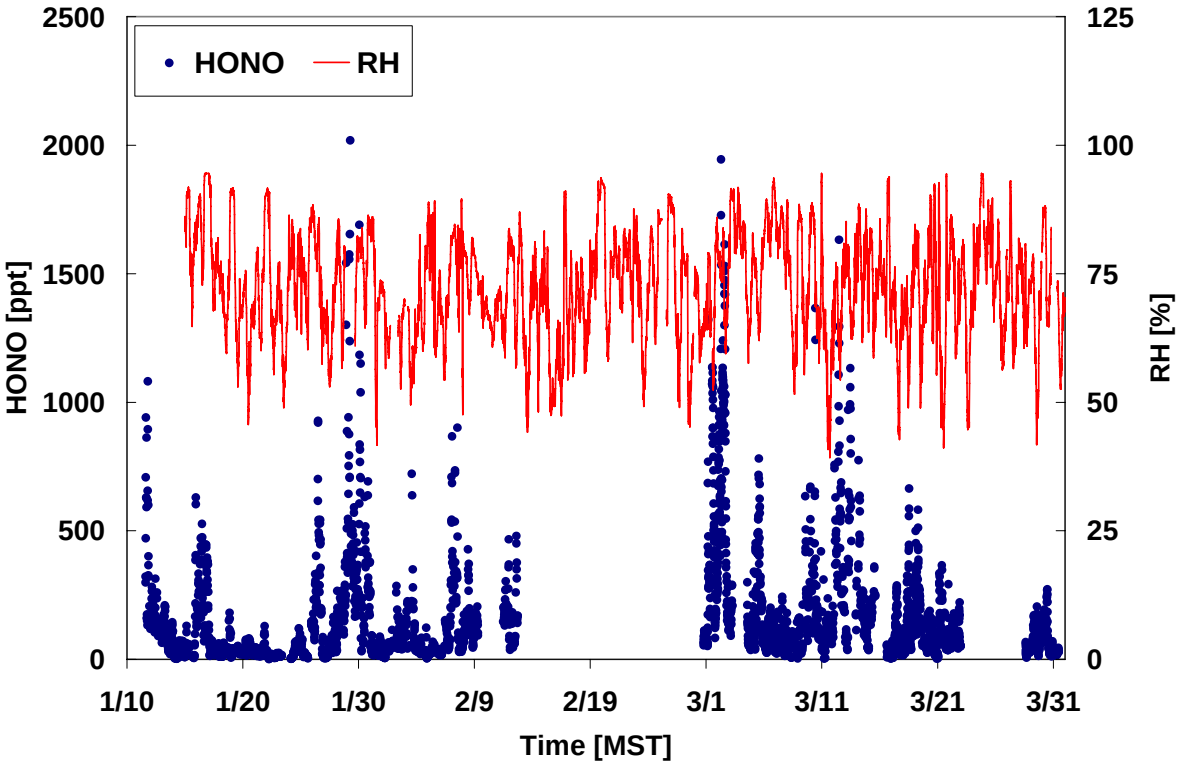


Figure 11: Time series of HONO and relative humidity for the time period January 11 - March 31, 2011. 10-min values are shown.

As pointed out by Stutz et al. (2004) relative humidity may be favorable for HONO formation, at least in urban environments. Figure 11 shows that contrary to the 2010 campaign overall higher relative humidity values persisted throughout March due to the continued presence of the snow cover. Further support for the impact of relative humidity is shown in figure 12: nighttime data of HONO vs relative humidity indicates that strongly elevated HONO levels only occur at relative humidities above 80%. The data suggests that this humidity effect is likely even more important at the surface.

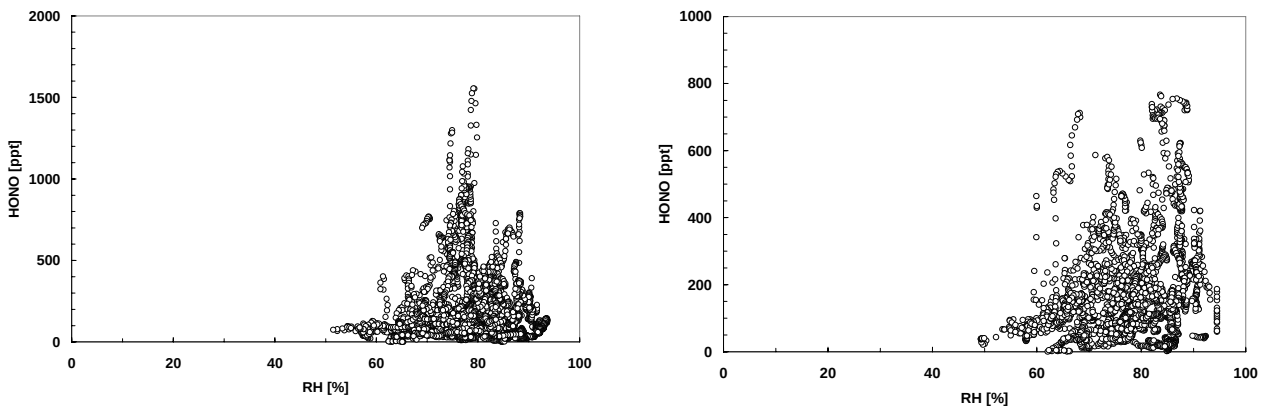


Figure 12: Dependence of HONO on relative humidity during nighttime conditions for the time period January 11 - March 31, 2011. Left: figure shows data when the HONO sampling unit was at 1.80 m above the ground, while right figure shows data when the HONO sampling unit was at the surface. 1-min values are shown.

Diurnal variation:

Figures 13-22 display composite diurnal variations of pollutant species and incoming UV radiation. As a data base the time period March 01-15, 2011 was chosen. This time period includes all IOPs and thus represents the most interesting features. In all Figures the mixing height layer [MLH], incoming UV radiation [UVin] and HONO measurements at 1.80 m above ground are taken as a reference. It is important to note that the mixing layer height is very low (between 50-60 m above ground), even during the daytime and certainly helps to accumulate trace gases in this shallow layer.

Data in Figure 13 shows that HONO increases while incoming 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. Figure 13 shows that HONO displays 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 (Figure 13) are around 400-600 pptv, which is around 50-75% of HONO levels observed at highly frequented Houston highway junction [Rappenglück et al., 2010]. The HONO/NO_x ratio (Figure 18) is between 2-5%, which is similar to other locations. However, it increases significantly increases in the afternoon, which indicates that more HONO is being formed through NO_x conversion. During the same time period also O_3 increases (Figure 14). HONO levels at 1.80 m above ground are quite similar to those at the surface level (Figure 13). Both levels also show the morning HONO peak around 10 am MST. However, afterwards high HONO levels persist at the surface, while at 1.80 m above ground HONO depletes faster than at the surface.

Both, primary and secondary compound reach maximum values during daytime. Earliest peaks show NO shortly after sunrise around 6:00 am MST (Figure 15). Good correlation of NO_x, CH_4 and NMHC (Figures 17, 21, 22) indicate that during daytime polluted air masses are transported to Boulder. Interestingly HONO does not decrease during daytime. Apart from a strong early morning peak around 10 am MST, HONO nicely correlates with HNO_3 and NO_y (Figures 19 and 20), indicating

secondary formation processes for HONO while reactive nitrogen compounds are present. It appears likely that HONO is being produced through photo-enhanced formation processes which are most efficient when snow cover is present. While the early morning HONO peak around 10 am is not reflected in the reactive nitrogen compounds, CH_4 and NMHC tend to coincide with the HONO peak (Figures 21 and 22). It is also the time, when HONO/NO_x ratios (Figure 18) tend to have minimum values. It may be possible that primary organic aerosol that accompanies CH_4 and NMHC may lead to HNO_3 to HONO [Ziemba et al., 2010], since these air masses persistently contain appreciable amounts of HNO_3. This HONO/NO_x ratio increases while nitrogen oxide levels decrease (Figure 17).

These observations suggest that multiple processes may occur that help to accumulate HONO:

- Photo-enhanced HONO formation during daytime while snow cover present.
- HONO formation through NO_x conversion (also potentially associated with primary organic aerosol) in highly polluted air masses that are transported to the Boulder site.
- Accumulation in a very shallow daytime mixing layer.

Subsequent photolysis of HONO may yield OH radicals which in turn will oxidize NMHCs eventually leading to an increase in ozone.

Case Studies:

Figures 23-24 display two case studies (3/2 and 3/12, 2011), which were observed during IOP days in the first weeks of March when all IOPs occurred. Both case studies have some common features: very low mixing layer heights, winds from SW-WSW, strong accumulation of precursors during the daytime and high ozone peaks in the afternoon. In most cases HONO levels coincides with presursor peaks, but also actually coincided quite often with the peak ozone levels. HONO maximum levels during daytime reached appreciable values. Here some specific features on the individual days are listed:

03/02/2011:

- Steady O_3 increase until 13:45 MST
- Strong O_3 peak around 14:00-16:45 MST
- Wind during daytime: ~WSW
- ~7:00 MST: strong increase in nitrogen oxides
- Late morning: HONO increase
- First part of O_3 afternoon peak coincides in particular with HONO
- HONO around 1.6 ppbv!

03/12/2011:

- Strong increase of O_3 between 10:00-12:00 MST
- Maximum around 14:30-16:30 MST
- Wind during daytime: SW-WSW
- Lower levels of NO_2, HNO_3, NO_x, NO_y compared with 3/2/2011
- HONO around 1.6 ppbv!
- HONO coincides with O_3

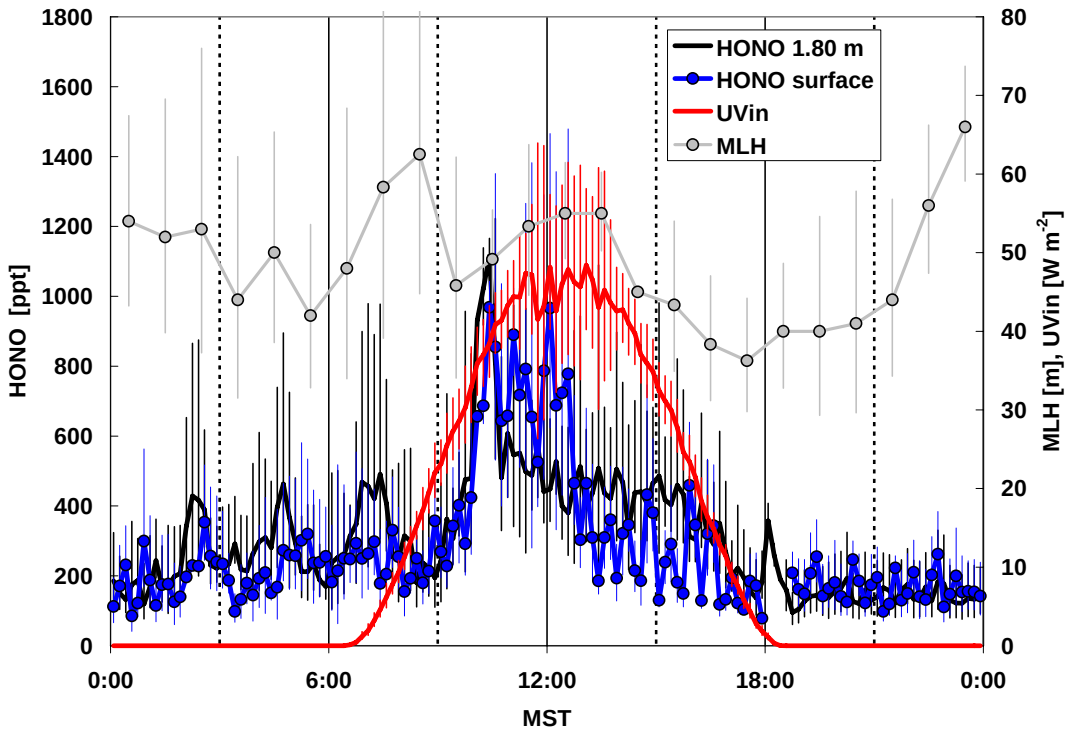


Figure 13: Composite diurnal variation of Mixing Layer Height [MLH], incoming UV radiation [UVin] and HONO measurements taken at 1.80 m above ground and at the surface for the period March 01-15, 2011. Bars indicate standard deviation of the measurements. Hourly values are shown for MLH, apart from UVin and HONO, which are 1-min values.

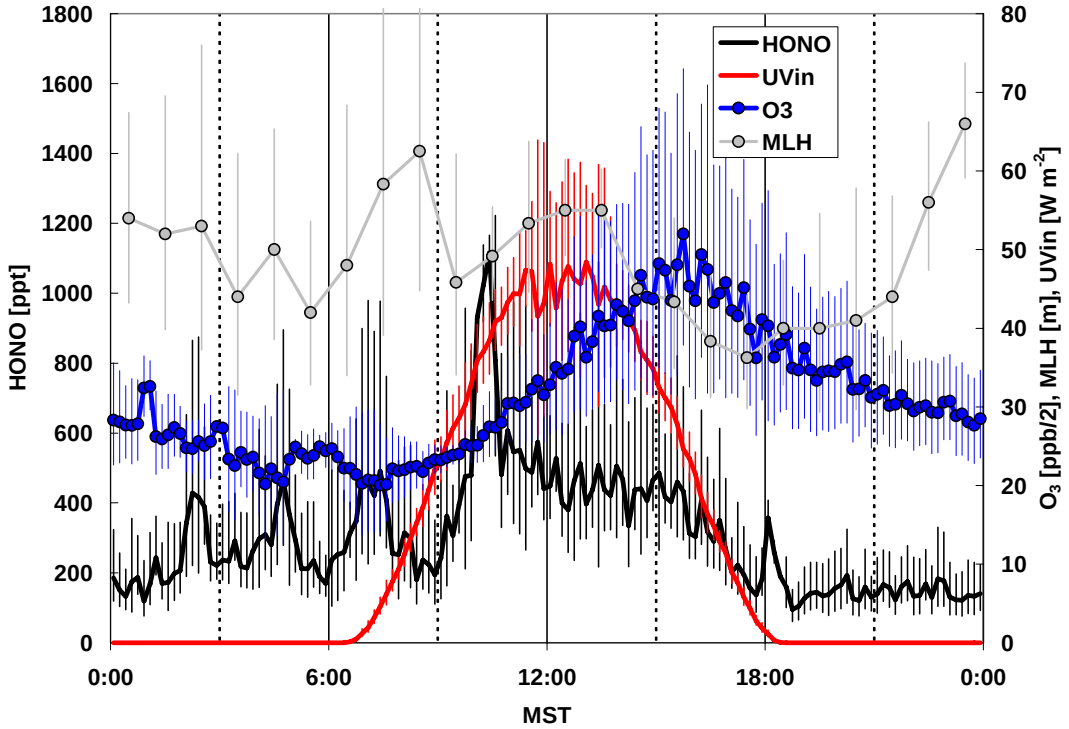


Figure 14: Composite diurnal variation of Mixing Layer Height [MLH], incoming UV radiation [UVin] and HONO and O_3 for the period March 01-15, 2011. Bars indicate standard deviation of the measurements. Hourly values are shown for MLH, apart from UVin and HONO, and O_3, which are 1-min values.

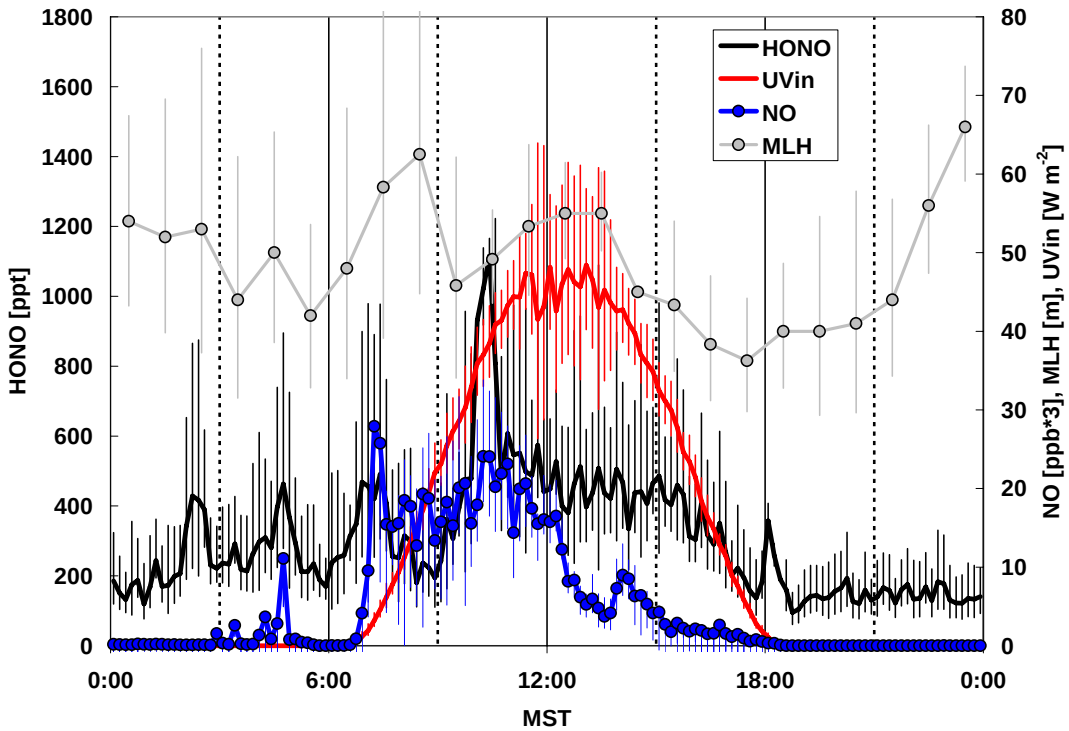


Figure 15: Composite diurnal variation of Mixing Layer Height [MLH], incoming UV radiation [UVin], HONO and NO for the period March 01-15, 2011. Bars indicate standard deviation of the measurements. Hourly values are shown for MLH, apart from UVin, HONO, and NO, which are 1-min values.

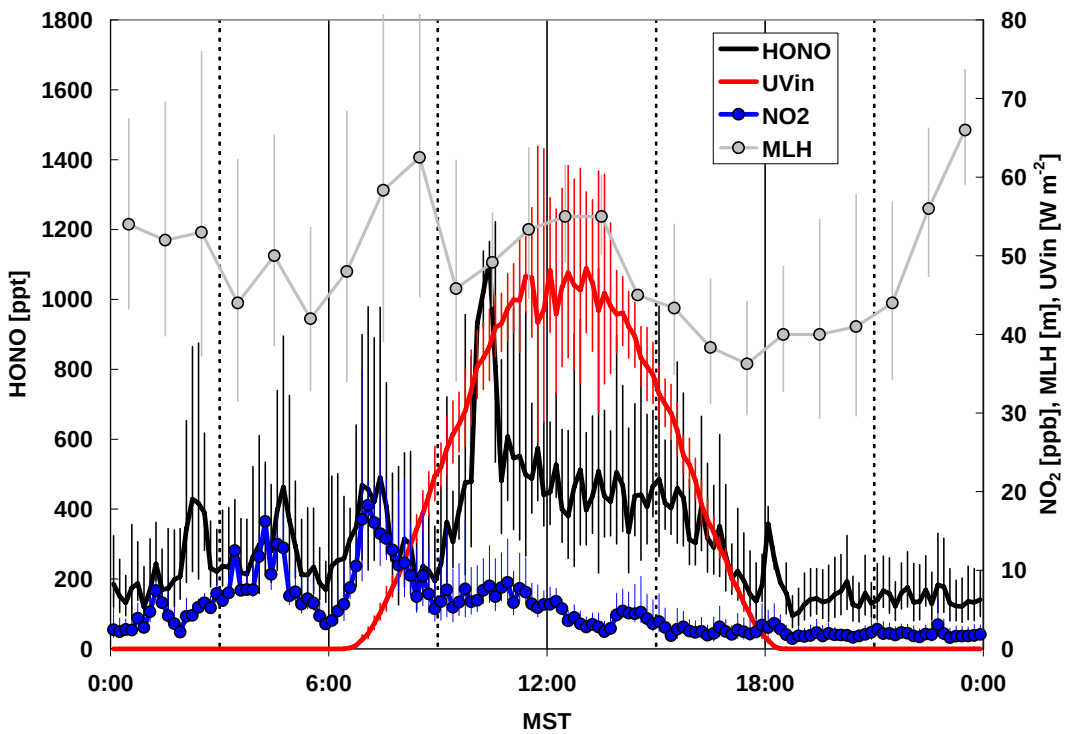


Figure 16: Composite diurnal variation of Mixing Layer Height [MLH], incoming UV radiation [UVin], HONO and NO_2 for the period March 01-15, 2011. Bars indicate standard deviation of the measurements. Hourly values are shown for MLH, apart from UVin, HONO, and NO_2, which are 1-min values.

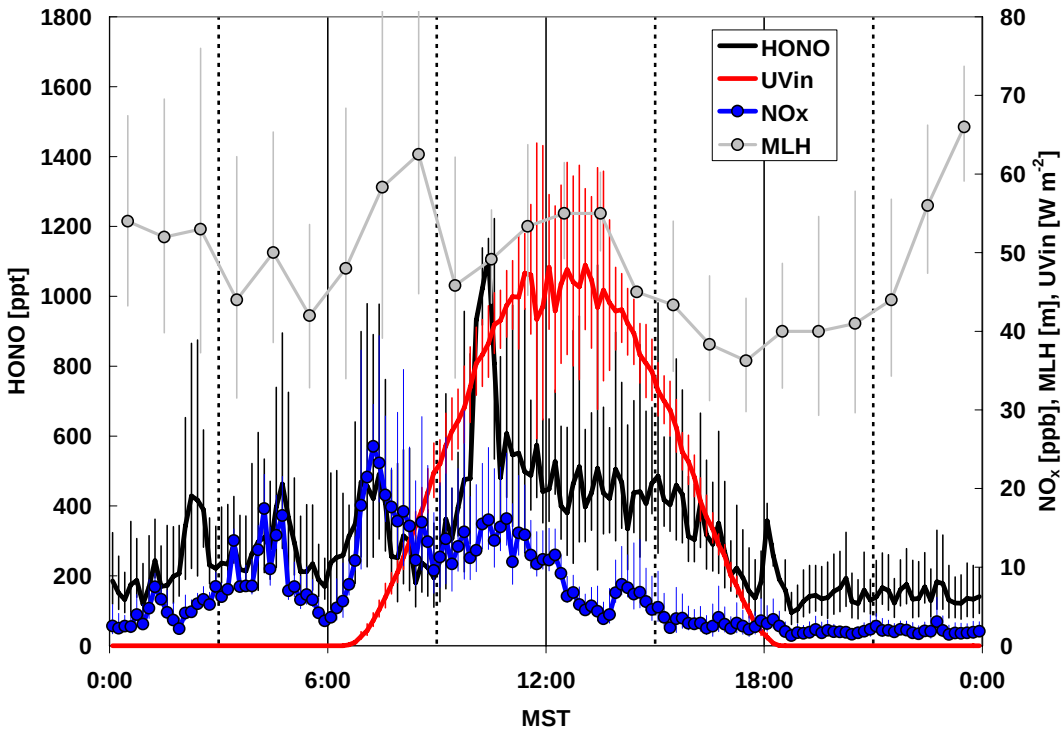


Figure 17: Composite diurnal variation of Mixing Layer Height [MLH], incoming UV radiation [UVin], HONO and NO_x for the period March 01-15, 2011. Bars indicate standard deviation of the measurements. Hourly values are shown for MLH, apart from UVin, HONO, and NO_x, which are 1-min values.

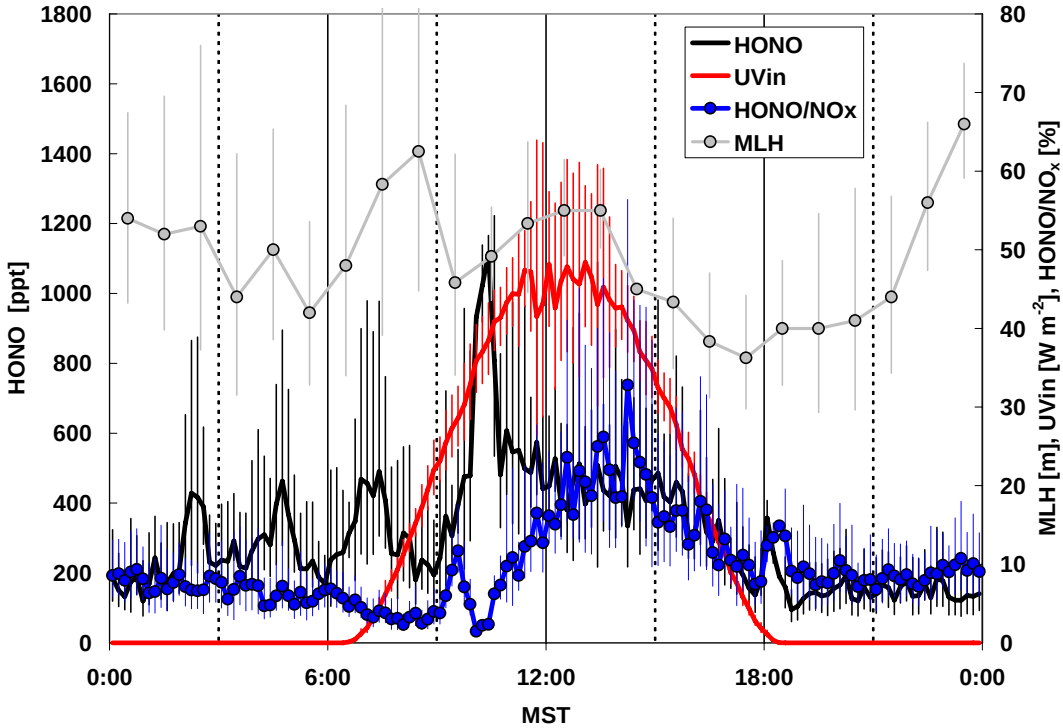


Figure 18: Composite diurnal variation of Mixing Layer Height [MLH], incoming UV radiation [UVin], HONO and HONO/NO_x for the period March 01-15, 2011. Bars indicate standard deviation of the measurements. Hourly values are shown for MLH, apart from UVin, HONO, and HONO/NO_x, which are 1-min values.

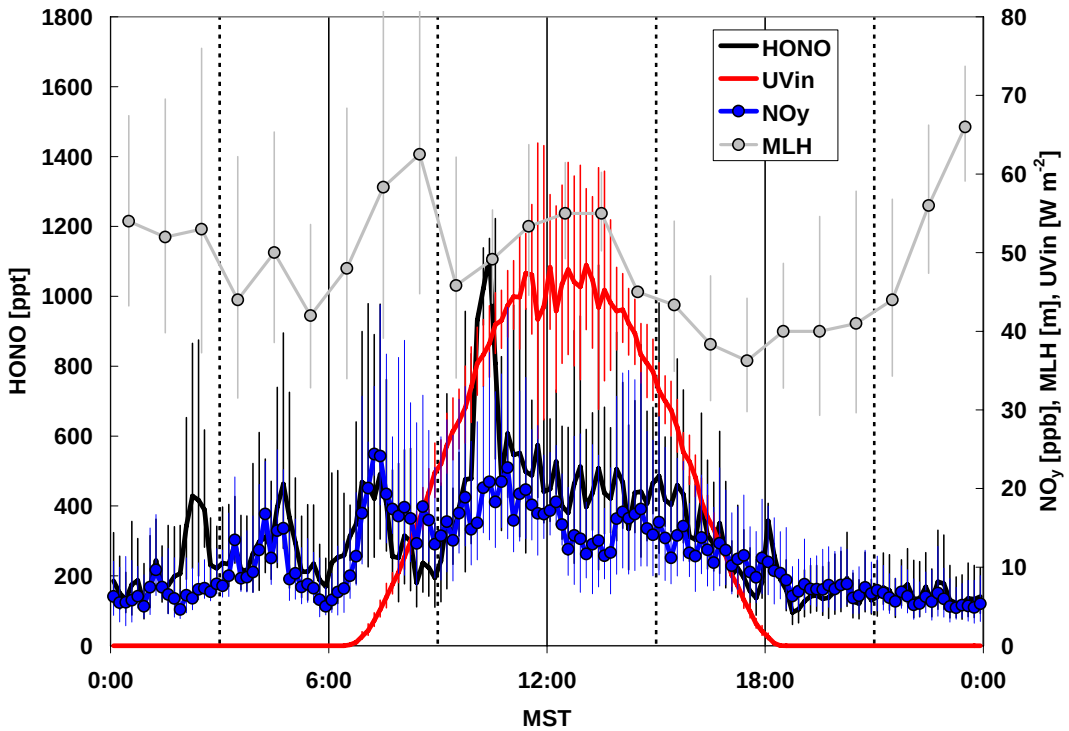


Figure 19: Composite diurnal variation of Mixing Layer Height [MLH], incoming UV radiation [UVin], HONO and NO_y for the period March 01-15, 2011. Bars indicate standard deviation of the measurements. Hourly values are shown for MLH, apart from UVin, HONO, and NO_y, which are 1-min values.

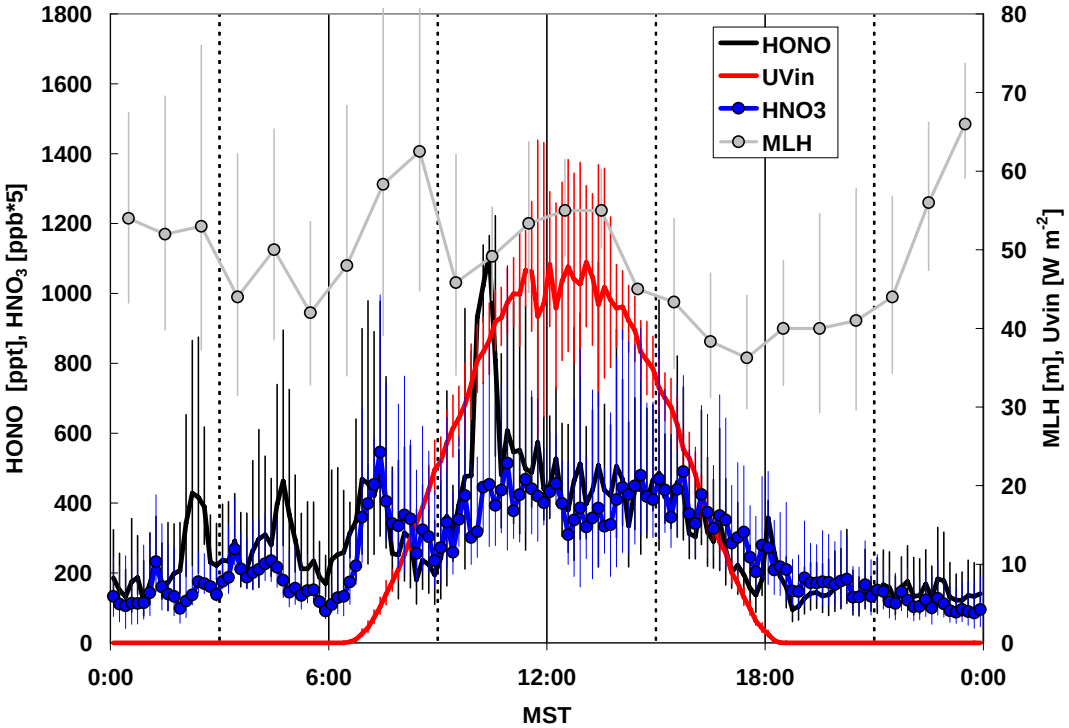


Figure 20: Composite diurnal variation of Mixing Layer Height [MLH], incoming UV radiation [UVin], HONO and HNO_3 for the period March 01-15, 2011. Bars indicate standard deviation of the measurements. Hourly values are shown for MLH, apart from UVin, HONO, and HNO_3, which are 1-min values.

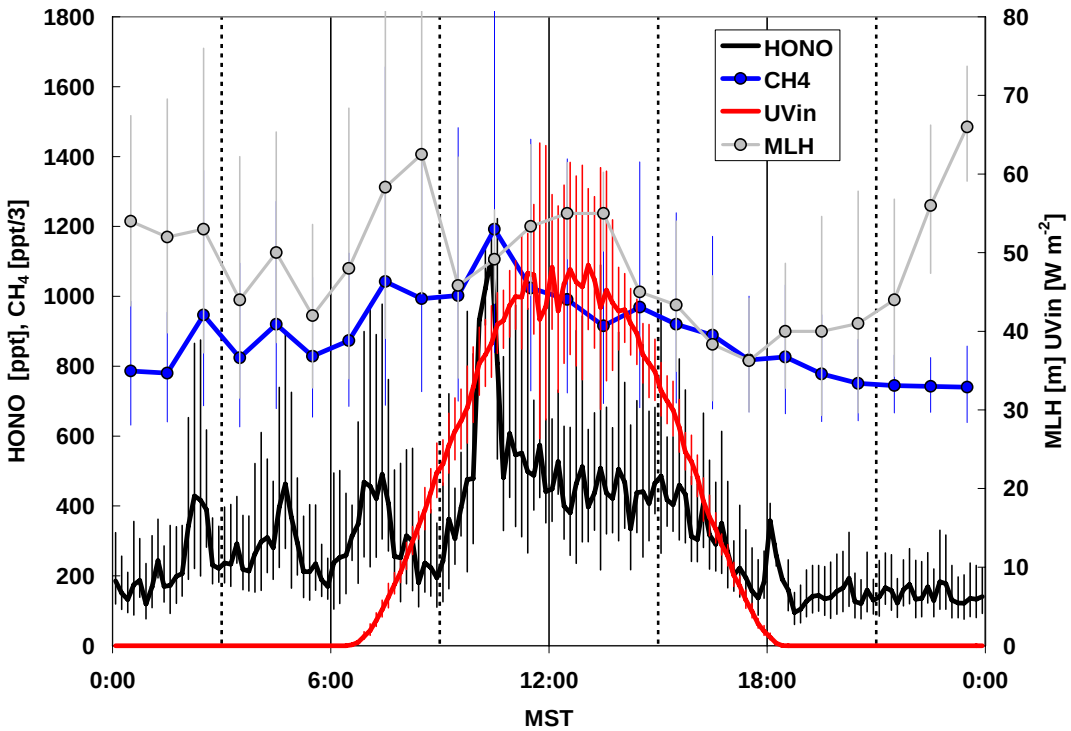


Figure 21: Composite diurnal variation of Mixing Layer Height [MLH], incoming UV radiation [UVin], HONO and CH_4 for the period March 01-15, 2011. Bars indicate standard deviation of the measurements. Hourly values are shown for MLH and CH_4, apart from UVin, and HONO, which are 1-min values.

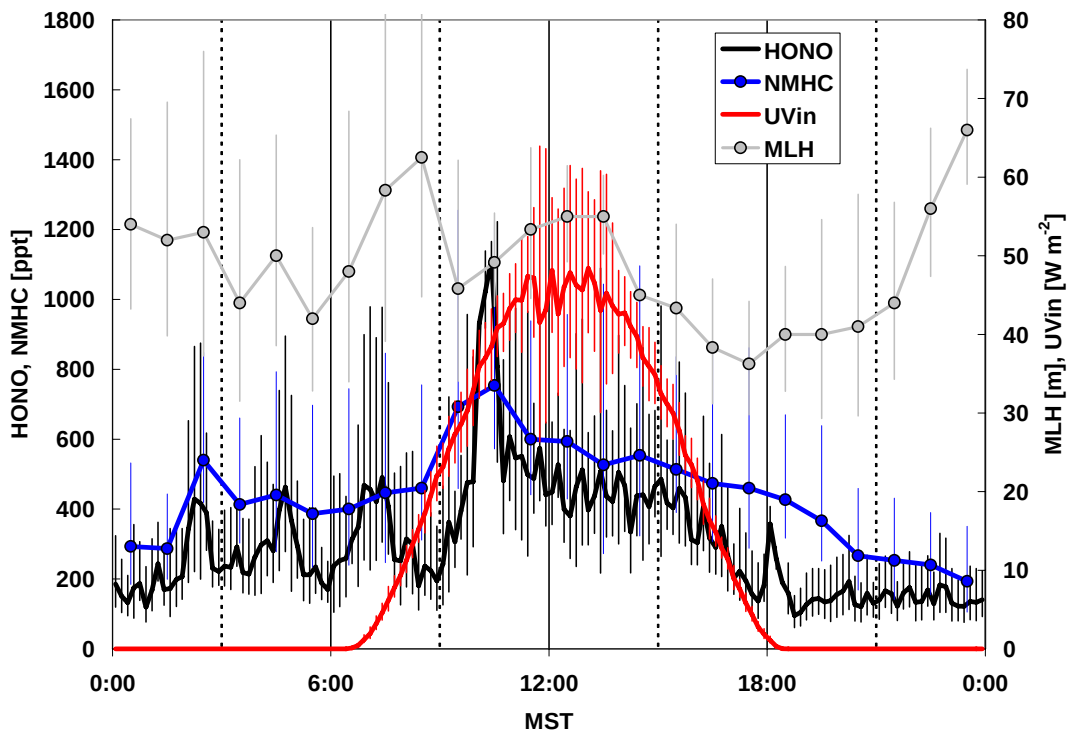


Figure 22: Composite diurnal variation of Mixing Layer Height [MLH], incoming UV radiation [UVin], HONO and NMHC for the period March 01-15, 2011. Bars indicate standard deviation of the measurements. Hourly values are shown for MLH and NMHC, apart from UVin, and HONO, which are 1-min values.

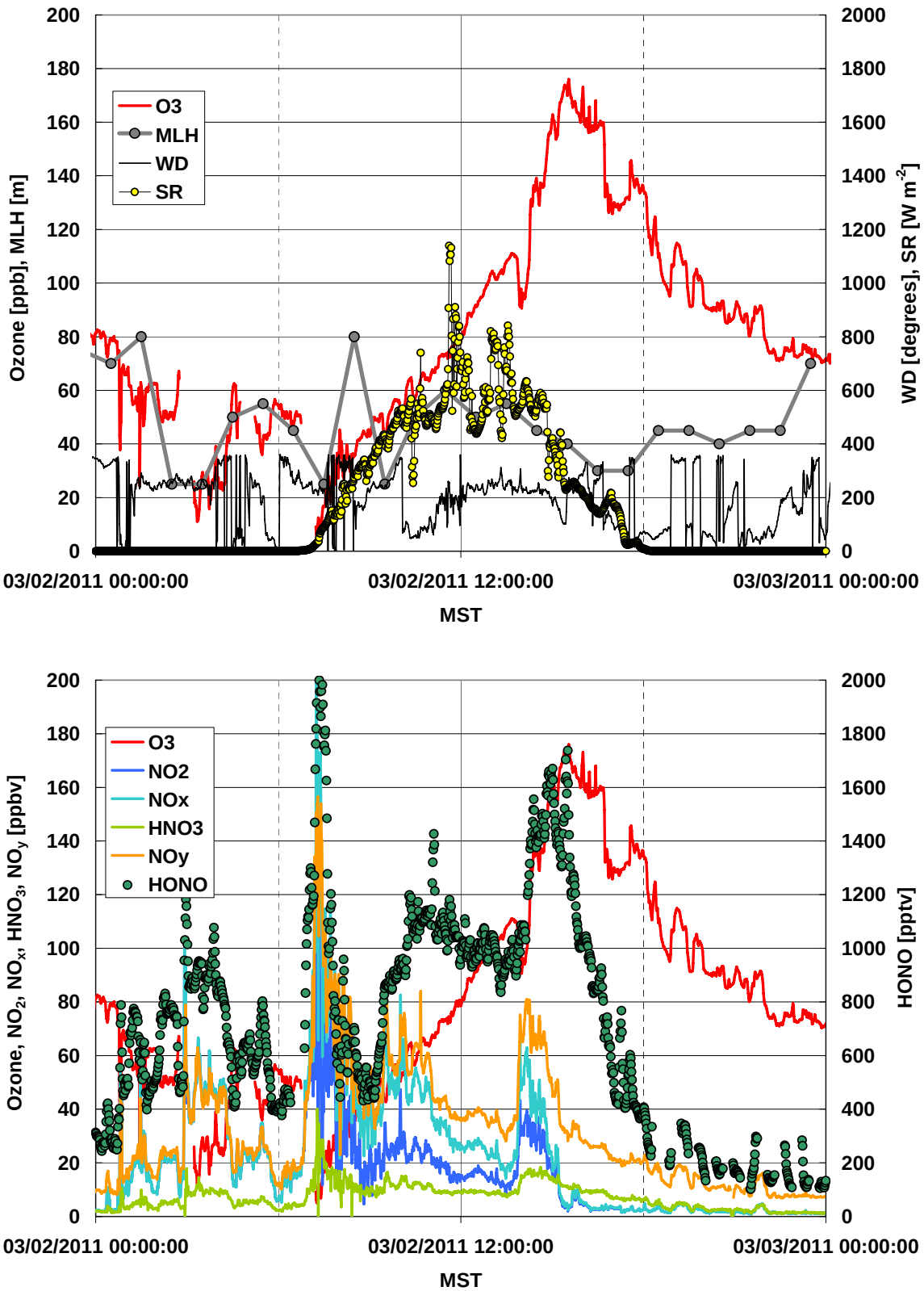
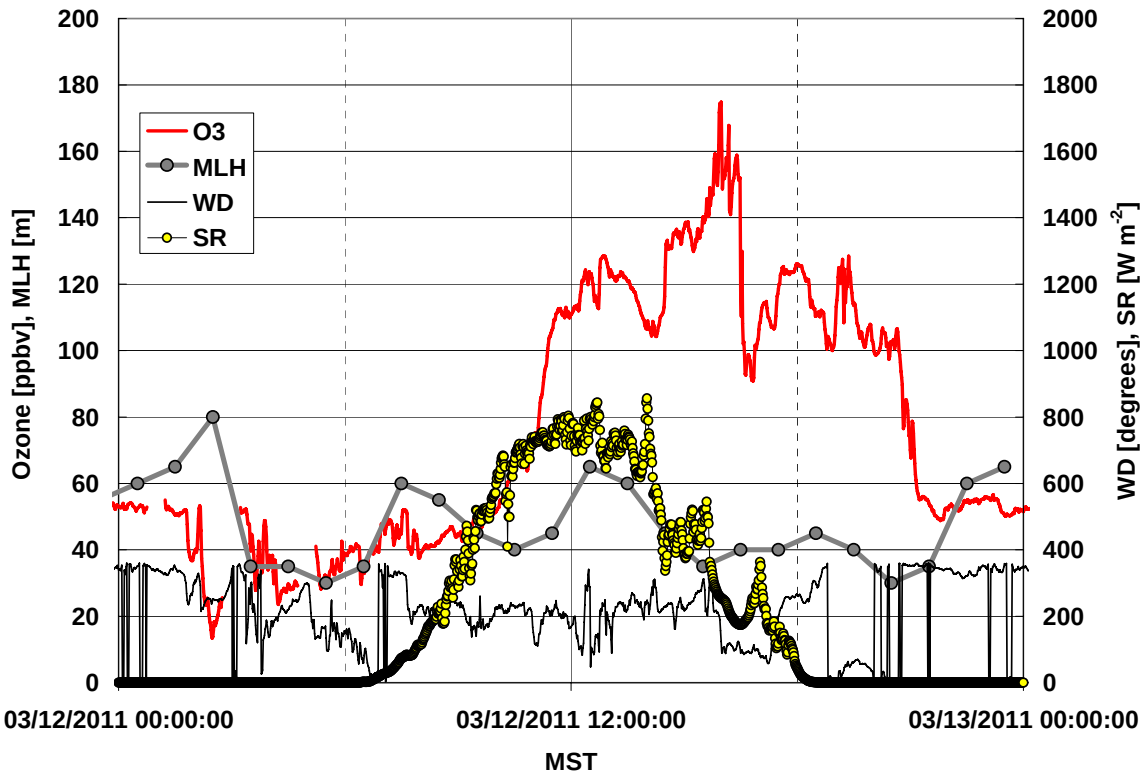


Figure 23: Case study 03/02/2011. Apart from mixing height layer (hourly values), all other parameters shown as 1-min values.



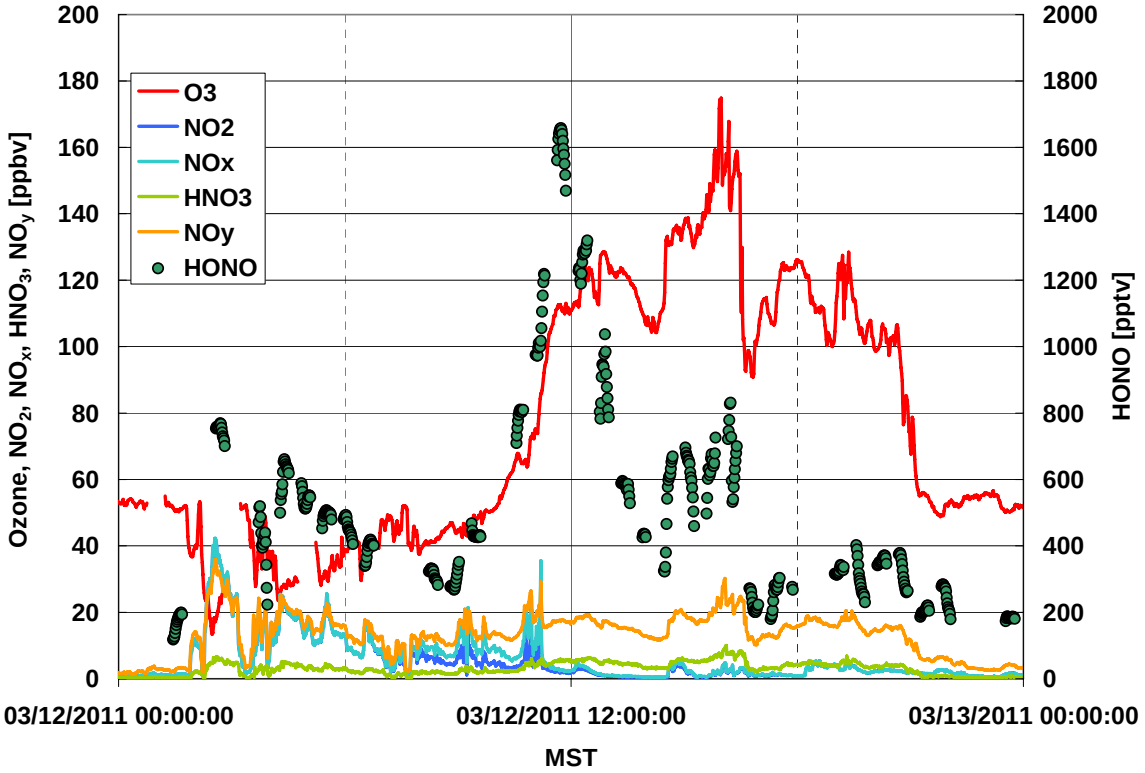


Figure 24: Case study 03/12/2011. Apart from mixing height layer (hourly values), all other parameters shown as 1-min values.

4. Findings and Recommendations

HONO measurements performed by UH during UGWOS 2011 yielded some interesting results:

- Nighttime HONO levels are well correlated with NO_2, NO_x, and HNO_3. Best correlation occurs with HNO_3. 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 SW-WSW wind conditions. During daytime periods HONO mixing ratios are generally higher than nighttime values, which is a different observation compared with the previous 2010 campaign. Similar to nighttime conditions, daytime HONO levels continue to show enhanced values under SW-WSW conditions, but also generally occur under SE-WSW wind directions.
- HONO levels at 1.80 m above ground are quite similar to those at the surface level. Both levels also show the morning HONO peak around 10 am MST. However, afterwards high HONO levels persist at the surface, while at 1.80 m above ground HONO depletes faster than at the surface.
- Snow cover leads to enhanced UV radiation and UV radiation correlates with HONO levels. This finding suggests photo-induced formation of HONO. This is also supported by very good correlations of HONO with HNO_3 (and NO_y).
- HONO formation may occur through NO_x conversion (also potentially associated with primary organic aerosol) in highly polluted air masses that are transported to the Boulder site
- HONO accumulation is favoured in very shallow daytime mixing layer
- 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. HONO also correlates with HNO_3 and NO_y during daytime.
- 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. While the HONO/NO_x ratio is at a maximum in the afternoon, also O_3 shows the daytime maximum.

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:

- Analysis of the data obtained in this project with speciated particle data may elucidate potential HONO formation processes through HNO_3 conversion according to findings by Ziemba et al., 2010.
- Chemistry-Transport modeling including an advanced HONO chemistry module [Czader and Rappenglück, 2009; Czader et al., 2010; Czader et al., 2011] may help to explain the findings in the Upper Green River Basin

5. Acknowledgements

Support by MSI, especially Bill Hauze and Tyler Ward is greatly appreciated. NO, NO_2, NO_x, NO_y, and HNO_3 data is courtesy Martin Buhr (Air Quality Design).

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