

# **Uintah Basin Winter Ozone Study Plan and Budget**

**Draft Version 3.0**

**Prepared for Utah Department of Environmental Quality**

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## Table of Contents

1. Introduction .....	5
1.1. Proposed Statement of Needs and General Approach .....	5
1.2. Discussion of Needed Uintah Basin Winter Study Components .....	5
2. Study Components.....	8
2.1 Study Components 1 and 2. Long-Term Trends and Distributed Monitoring for Wintertime Ozone: .....	8
2.2 Study Component 3. Wintertime Ozone Formation Chemistry, Vertical Mixing and 3-Dimension Structure Data Collection and Analysis: .....	9
2.3 Study Component 4. Oil and Gas Development Activity and Emission Inventory: .....	9
2.4 Study Component 5. Targeted Source Chemical Characterization, Attribution, and 3-Dimension Vertical Profile Ozone Distributions and Meteorology Studies: .....	10
2.5 Study Component 6. Ozone, Nitrogen Oxides, and Hydrocarbons in the Lower Boundary Layer:.....	11
2.6 Study Component 7. Analysis of Collected Air Quality Data: .....	11
2.7 Further Discussion of Costs.....	12
3. Roles and Responsibilities.....	12
4. Deliverables and Schedule .....	14
4.1 Project Schedule .....	14
4.2 Report Schedule.....	14
5. Project Timeline .....	15
APPENDIX I Study Component 1 - Long-Term Trends Wintertime Monitoring for Ozone, and Key Precursor Species .....	16
Purpose and Need:.....	16
Approach:.....	16
Deliverables: .....	18
Schedule:.....	18
APPENDIX II Study Component 2 – Distributed Basin-Wide Winter Ozone, Limited Precursors, and Meteorological Monitoring Program.....	20
Purpose and Need:.....	20
Approach:.....	20
Deliverables: .....	21
Schedule:.....	21
APPENDIX III Study Component 3 - Wintertime Ozone Formation Chemistry, Vertical Mixing and 3-D Structure.....	23
Objective .....	23
Project Management and Data Reporting.....	23
Acid CIMS .....	24
Snow Composition .....	25
Fluxes .....	26
Aerosol Surface Area.....	26
Aerosol Chemical Composition.....	27
Schedule.....	27

Deployment of the NOAA/ESRL/CSD TOPAZ Ozone Lidar at the Uintah Basin Experiment in February 2012 .....	27
Background .....	28
TOPAZ Lidar at Uintah Basin Experiment.....	28
Schedule and Deliverables .....	28
HRDL: High-Resolution Doppler Lidar Measurement of Winds and Turbulence During the Uintah Basin 2012 Study .....	29
Schedule and Deliverables .....	29
APPENDIX IV Study Component 4 - Emissions Inventory and Activity Data .....	30
Purpose and Need.....	30
Approach.....	30
Deliverables.....	31
Schedule.....	31
APPENDIX V Study Component 5 - Source Characterization, Attribution and Ozone Distribution in the Uintah Basin Using Mobile Measurement Platforms and Balloon Borne Ozonesondes ...	32
Purpose and Need.....	32
Approach.....	32
A. High frequency multi-species mobile laboratory measurements.....	32
B. Atmospheric ozone profiles and 3 dimension ozone and meteorology structure.....	36
Sources and distributions of gases in the Uintah Basin.....	40
Deliverables.....	41
Schedule.....	41
Budget:     A) Chemical Concentrations and Sources; B) 3-Dimensional Atmospheric and Ozone Structure .....	42
APPENDIX VI Study Component 6 - Continuous Vertical Profiling of Meteorological Variables, Ozone, Nitrogen Oxides, Methane, and Total Hydrocarbons from a Tethered Balloon during the 2012 Uintah Basin Ozone Study.....	43
Purpose and Need.....	43
Previous Results .....	43
Approach.....	45
Broader Impacts.....	48
Deliverables.....	48
Schedule.....	49
APPENDIX VII Study Component 7 - Analysis of Collected Air Quality Data and Mitigation Efforts.....	50
Purpose and Need.....	50
Approach.....	50
Deliverables.....	51
Schedule.....	51
APPENDIX VIII References .....	52



# 1. Introduction

## ***1.1. Proposed Statement of Needs and General Approach***

High winter ozone levels were first observed in the Upper Green River Basin, Wyoming in 2005. Since that time, the Uintah Basin in Utah has also seen high ozone in the winter months. Neither of these cases is well understood and further information and evaluation are needed to understand the processes that cause formation of winter ozone and determine its sensitivity to changes in VOC and NO<sub>x</sub>. The 2011 - 2012 Uintah Basin winter ozone study must include specific new air quality and meteorological measurements to provide a better understanding of the local, unique formation of ambient ozone. Ambient monitoring at multiple sites of key species, and meteorological measurements (described below) are needed to understand emissions, dispersion and chemical reactions of ozone and its precursors. The study must also build on what has been learned from the Wyoming experience.

Seven key Study Components, along with their estimated costs are listed and discussed below. Study Components 1 and 2 provide critical information needed to characterize ozone long-term trends and distribution within the Uintah Basin. Study Components 3, 4, 5 and 6, will provide valuable information needed to understand ozone formation chemistry as they provide unique NO<sub>x</sub> and VOC concentration measurements. Study Component 7 will be a report detailing the interim analysis of data collected from this and previous related studies to better understand the winter ozone problem. Table 1 summarizes these activities.

## ***1.2. Discussion of Needed Uintah Basin Winter Study Components***

Since understanding the basis of this problem is critical to air quality planning in the area, this work needs to begin as soon as possible, with information developed at each step used to inform subsequent data collection and analysis. More specifically and immediately, we need to establish long-term trends monitoring of ozone, speciated VOC, CH<sub>4</sub>, speciated NO<sub>x</sub> and meteorological data for use in evaluating trends in ozone precursors and to characterize the climatology of winter ozone (identified in Study Component 1 in Table 1 below). We will eventually use these data to evaluate the response of ambient ozone primarily to future changes in oil and gas production activity as well as future emission mitigation measures. For example, if winter ozone levels increase after adoption of NO<sub>x</sub> emissions reductions, these data will be used to determine if the increase in ozone is caused by changes in meteorology or changes in photochemistry. These measurements will also be used to evaluate the relative benefits of VOC versus NO<sub>x</sub> emission controls for reducing ambient ozone.

Additionally, chemical processes need to be studied to understand unique aspects of winter photochemistry that affect the formation of ozone and its sensitivity to VOC and NO<sub>x</sub>. The National Oceanic and Atmospheric Administration (NOAA) has committed internal funding to study chemical processes in the Uintah Basin in winter 2011- 2012. Study Component 3 of Table 1 summarizes the tasks that will be performed by NOAA making use of both internal and external funding. The NOAA research site will be co-located with the Utah State University Research Foundation Energy Dynamics Laboratory (EDL) air research trailer at the Horse Pool

site, and the combined data from both of these studies will increase the interpretive power of the data collected.

In Table 1, we have identified the Study Components we propose to accomplish next winter. These study components will help us understand winter ozone formation and ultimately develop effective ozone precursor emissions reductions strategies in the Uintah Basin. Additional descriptions of the seven study components are provided below and in the attached appendices, however some elements of the tasks could be modified depending on peer review by the Science Steering Committee.

Study Components	Purpose	Participating Agencies	Funding
<p>1. Long-Term Trends Wintertime Monitoring for Ozone, and Key Precursor Species - two "Super Sites".</p> <p>a. Source Site (Horse Pool)</p> <p>b. Receptor Site (Roosevelt)</p>	<p>Obtain data beginning this winter to evaluate trends in ozone and precursors (precursor trends: speciated VOC: aromatics, alkanes, alkenes, carbonyls, etc., and for speciated NO<sub>x</sub>: NO, true NO<sub>2</sub> and total NO<sub>y</sub>). These measurements would extend over several winter seasons to capture baseline trends.</p>	<p>UDEQ EDL/USU</p>	<p><u>Total: \$1,347,000</u></p> <ul style="list-style-type: none"> <li>• \$422,000– UDEQ: in-kind</li> <li>• \$400,000 – UIMSSD/DOE: purchase EDL-BRC air research trailer</li> <li>• \$300,000 UIMSSD: purchase equipment for Roosevelt site</li> <li>• \$125,000 – UIMSSD: labor</li> <li>• \$100,000– EPA</li> </ul>
<p>2. Distributed Basin-Wide Winter Ozone, Limited Precursors, and Meteorological Monitoring Program.</p>	<p>Basin-wide program to monitor ozone at up to 20 locations with co-located passive (survey level) monitoring of VOCs and NO<sub>x</sub> up to 10 locations. Co-located meteorological data at up to 20 selected locations.</p>	<p>UDEQ EDL/USU</p>	<p><u>Total: \$480,000</u></p> <ul style="list-style-type: none"> <li>• \$100,000– UDEQ: in-kind</li> <li>• \$380,000 – UIMSSD: labor and equipment</li> </ul>
<p>3. Wintertime Ozone Formation Chemistry, Vertical Mixing and 3-D Structure – Horse Pool.</p>	<p>Understand core chemical processes, which control the formation of winter ozone and its sensitivity to VOC and NO<sub>x</sub>. These measurements would be conducted this winter with possible follow-up next winter.</p> <p>Additional measurements of 3-D ozone distribution and chemical formation measurements, rapid measurements of gas-phase acids and their fluxes, snow surface chemistry, aerosol chemistry, are important to understanding ozone formation in the Basin, but funding is needed.</p>	<p>NOAA</p>	<p><u>Total: \$2,215,000 total</u></p> <ul style="list-style-type: none"> <li>• \$1,650,000 – NOAA: in-kind for core measurements</li> <li>• \$565,000 – WEA</li> </ul>
<p>4. Emissions Inventory and Activity Data</p>	<p>Compile and update specific emissions inventory data to be used in modeling and determining potential mitigation options. This would include specific information related to factors, activities, location, and speciation.</p>	<p>EDL/USU</p>	<p><u>Total: \$60,000</u></p> <ul style="list-style-type: none"> <li>• \$60,000 UIMSSD</li> </ul>

<p>5. Source Characterization, Attribution, and 3-Dimensional Vertical Ozone Distribution and Meteorology Using Mobile Measurement Platforms (2), Balloon Borne Ozone sondes and Radiosondes, and Tethersonde.</p>	<p>A. Source specific air sampling for multispecies chemical analysis, and analytical comparison w/bottom up emissions inventory (Task 4). B. Basin wide measurements of balloon borne ozone and meteorological profiles, especially at the boundaries of the Uintah Basin to provide a 3-dimensional picture of the ozone transport and formation processes invaluable in modeling and chemical balance calculations.</p>	<p>NOAA</p>	<p><u>Total: \$897,000</u></p> <ul style="list-style-type: none"> <li>• \$337,000 NOAA: in-kind for core Source Attribution and 3-D Basin Wide Mobile Measurements of Ozone and Meteorology.</li> <li>• \$560,000 - WEA</li> </ul>
<p>6. Continuous Vertical Profiling of Meteorological Variables, Ozone, Nitrogen Oxides, Methane, and Total Hydrocarbons using Tethered Balloon</p>	<p>Study sources, sinks, and distribution of ozone, nitrogen oxides, and hydrocarbons in the Uintah Basin by vertical profiling these gases using a tethered balloon vertical profiling platform. Meteorological variables will also be monitored to understand effects of micrometeorological and boundary layer conditions.</p>	<p>CU</p>	<p><u>Total: \$382,000</u></p> <ul style="list-style-type: none"> <li>• \$260,000 CU in-kind for Tethered Balloon System, NOx and O3 monitors</li> <li>• \$122,000 BLM</li> </ul>
<p>7. Analysis of Collected Air Quality Data and Mitigation Efforts (developed by above tasks)</p>	<p>Detailed analysis of mitigation efforts and air quality, meteorological and source emissions data collected in the Uintah Basin and Wyoming Upper Green River Basin to understand potential ozone formation mechanisms, sources of ozone precursors, and potential mitigation options.</p>	<p>EDL/USU</p>	<p><u>Total: \$115,000</u></p> <ul style="list-style-type: none"> <li>• \$115,000 UIMSSD</li> </ul>
<p><b>Total Funding</b></p>	<p><b>In-cash        \$2,727,000</b> <b>In-kind         \$2,769,000</b></p>	<p><b>Agency totals includes both in-cash and in-kind contributions.</b></p>	<p><b>NOAA        \$1,987,000</b> <b>UIMSSD     \$1,380,000</b> <b>WEA         \$1,125,000</b> <b>UDEQ        \$522,000</b> <b>CU Boulder  \$260,000</b> <b>BLM         \$122,000</b> <b>EPA           \$100,000</b> <b><u>Total        \$5,496,000</u></b></p>

Table 1. Summary of Proposed Uintah Basin Winter 2011-12 Ozone Studies

## 2. Study Components

### 2.1 Study Components 1 and 2. Long-Term Trends and Distributed Monitoring for Wintertime Ozone:

The long-term trends monitoring will include operating two “super sites” to gather high resolution speciated VOC, photolytic NO<sub>2</sub>, NO<sub>y</sub> and meteorological data. In addition, up to 20 distributed monitoring sites with ozone, passive VOC and NO<sub>x</sub> and meteorological data will be located throughout the Uintah Basin as presented in Figure 1. The two super sites would mirror each other in capabilities and be located at Horse Pool and Roosevelt, selected to represent source and receptor locations, respectively.

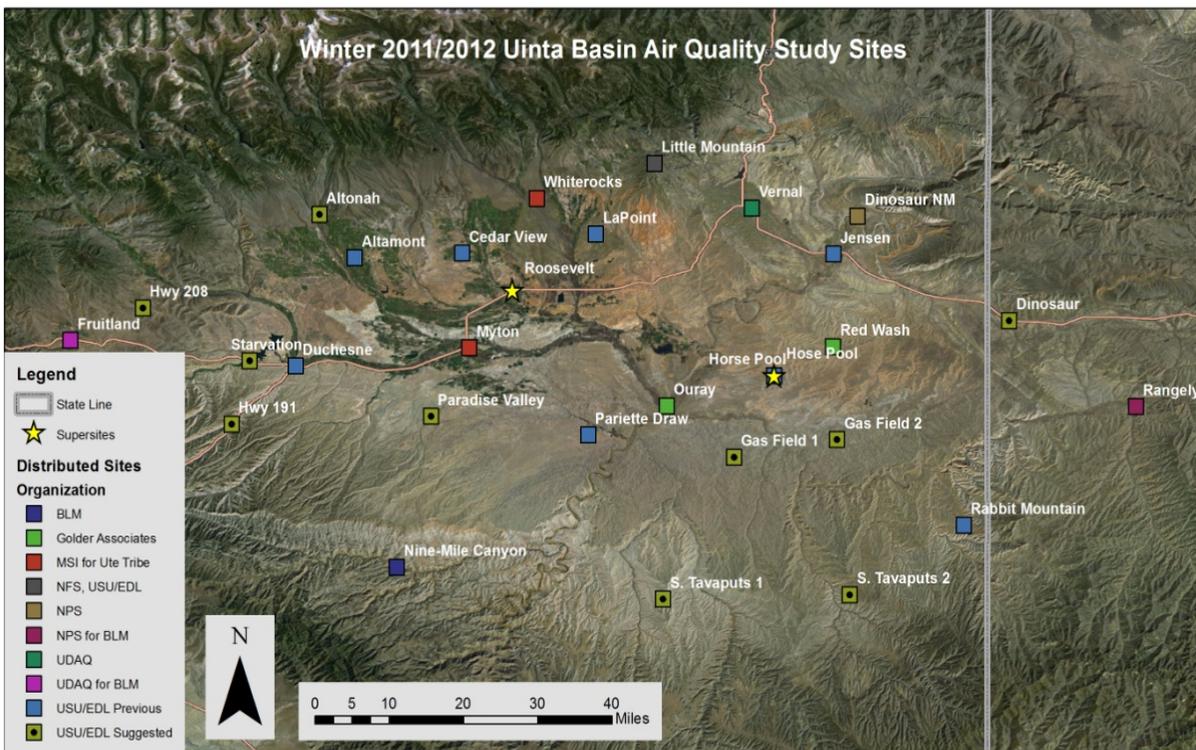


Figure 1. Winter 2011-2012 Uintah Basin Air Quality Study Sites

The primary purpose of these two study components is to provide baseline trend information for ozone and its precursors and build on the initial survey data collected in 2010-2011. These data can be used to evaluate the response to future oil and gas production growth and to analyze the benefits of potential mitigation measures. The distributed sites will also provide continuity to the measurements collected in last winter’s study as well as validation of the study results.

The Energy Dynamics Laboratory (EDL)/Utah State University (USU) and the Utah Department of Environmental Quality (UDEQ) will operate these sites. Some of the equipment for the super

sites is already available from the 2010 Uintah Basin study while some is located in a new research trailer at EDL funded by the Uintah Impact Mitigation Special Services District (UIMSSD) and the Department of Energy (DOE). Some additional equipment needs to be purchased for the Roosevelt super site.

The estimated 2011-2012 costs for EDL/USU to operate these two super sites (Study Component 1) with support from UDEQ (including purchasing the remaining equipment for the Roosevelt site, preparation, and labor) is \$1,347,000. The funding is being provided by UIMSSD - \$425,000 in-cash funding, UIMSSD/DOE - \$400,000 in-kind funding, UDEQ - \$422,000 in-kind funding, and EPA-\$100,000 in-cash funding. Future annual costs to operate these two super sites are estimated at \$250,000 per year.

## ***2.2 Study Component 3. Wintertime Ozone Formation Chemistry, Vertical Mixing and 3-Dimension Structure Data Collection and Analysis:***

The purpose of this component is to advance an understanding of the chemical processes that control winter ozone formation and its sensitivity to VOC and NO<sub>x</sub>. This includes measuring radical species that initiate the formation of ozone and heterogeneous processes, including snow photochemistry that might produce radical precursors. The results of these measurements will be compared to the data gathered in Study Component 1 to quantify the sources of free radicals that catalyze winter ozone formation.

This study would also evaluate the vertical transport of ozone and its precursors. This is needed to understand the possible contributions of emissions sources well above the surface. The goal is to determine if tall stack and buoyant sources of NO<sub>x</sub> from electric utility steam generating units (EGUs), drill rigs, or compressor stations contribute to the formation of winter ozone. This knowledge will offer insight into whether emissions reduction should be considered for elevated NO<sub>x</sub> sources. It will also evaluate background ozone and precursor levels.

This effort would include the NOAA-planned Uintah Basin chemical processes research study, to be conducted during winter 2011-12 using \$1,650,000 of internal funding. The NOAA research site will be co-located with the Horse Pool super site. An additional \$565,000 is budgeted to fully fund NOAA's chemical processes study. These additional research measurements are needed to understand critical processes that affect winter ozone formation and characterize ozone's 3-dimensional structure.

## ***2.3 Study Component 4. Oil and Gas Development Activity and Emission Inventory:***

This component will characterize activity levels in the Uintah Basin and provide data needed for the compilation of emissions inventories. An accurate, up-to-date emissions inventory is needed to understand the sources of precursor gases that result in wintertime ozone formation. This study would include operator surveys to build on the WRAP Phase III emissions inventory studies. We estimate the cost of this study to be \$60,000. The data collected for this task will be

critical for possible future photochemical modeling and will include speciation, location, and temporal data specific to a winter ozone episode. This Study Component will also provide insights and direction for future mitigation efforts.

#### **2.4 Study Component 5. Targeted Source Chemical Characterization, Attribution, and 3-Dimension Vertical Profile Ozone Distributions and Meteorology Studies:**

This Study Component is needed to document the emissions characteristics of point, mobile and area sources using mobile laboratories that measures ambient CO<sub>2</sub>, CH<sub>4</sub>, CO, NO<sub>x</sub>, and O<sub>3</sub>. This information can be used to verify the bottom-up emissions inventory developed in Study Component 4 as well as coordinate measurements with the fixed, super site at Horse Pool by measuring in real time, sources and concentrations of chemicals upwind, surrounding and downwind of the fixed base facility.

The research team proposes to A) document the ozone precursors emissions characteristics of point, mobile and area sources in the Uintah Basin during an intensive study period lasting two to three weeks with an instrumented mobile platform, and B) to measure the ozone formation and dissipation in three dimensions during the winter intensive period using Electrochemical Concentration Cell (ECC) ozonesondes carried aloft with free floating balloons to provide high quality, high resolution vertical profiles of ozone in the Uintah Basin.

These measurements will be planned and coordinated with the EDL/USU tethersonde measurements, the NOAA TOPAZ ozone lidar and the INSTAAR tethered balloon measurements to provide some overlap for QA/QC and verification. Some of the ozone and met profiles will be conducted in regions of interest not covered by other instruments.

The goal of the NO<sub>x</sub> and VOC Mobile Lab measurements is to characterize the important source processes for both precursors and to document the composition and patterns of the emissions in space and time.

The O<sub>3</sub> sondes and Mobile Lab O<sub>3</sub> measurements in the Basin will provide a 3-D view of the evolution of ozone in and out of the region and will provide key data to link the fixed surface site ozone measurements and to help constrain the modeling of the ozone budget for the region.

Each in situ instrument and ozonesonde used in this project will be rigorously calibrated and records of the calibrations maintained for open inspection. NOAA GMD has state-of-the art facilities for preparing standards for most trace gases proposed in this study. They maintain the World Meteorological Organization, Global Atmosphere Watch primary standards for CO<sub>2</sub>, CH<sub>4</sub>, CO, N<sub>2</sub>O, and SF<sub>6</sub> and maintain a NIST standard calibration facility for in situ ozone measurements.

NOAA has submitted a “Source Characterization, Attribution and Ozone Distribution in the Uintah Basin Using Mobile Measurement Platforms and Balloon Borne Ozonesondes” proposal that addresses the two studies above: A) Chemical Concentrations and Sources Study - \$330,000 and B) Atmospheric Structure and Ozone Profiles and Distributions Study - \$230,000, both

funded. NOAA has committed \$337,000 of in-house in-kind funding for Study Component 5, Parts A and B. NOAA and EDL/USU would both be involved in this Study Component.

### ***2.5 Study Component 6. Ozone, Nitrogen Oxides, and Hydrocarbons in the Lower Boundary Layer:***

The purpose of this study component is to investigate the vertical distribution and temporal behavior of ozone, nitrogen oxides, and hydrocarbons in the lower part of the atmosphere. This experiment will focus on the lowest 500 feet of the atmosphere. This is the layer where ozone production chemistry is expected to be the most prominent under the frequently encountered strongly stable boundary layer conditions over snow.

The experiment will build upon deployment of the INSTAAR CU Boulder tethered balloon vertical profiling platform. A 20-foot diameter Sky Doc balloon will be used as a 'sky hook' for raising a series of long sampling lines to three distinct heights above the ground (150, 300, 450 feet). Air pulled from the balloon-borne inlets will be subjected to analysis of ozone, nitrogen oxides, and methane and non-methane hydrocarbons. A second type of experiment entails the raising and lowering of a movable inlet with a second tether system. These measurements will yield continuous vertical profile data at 2 m height resolution. A meteorological instrument package will be deployed with the moving sample inlet for measurement of wind speed, wind direction, temperature, and humidity. A set of 40 canister samples will be collected for speciation of total hydrocarbon measurement in the balloon profiles. Combined, these meteorological and chemical measurements will provide high resolution data on the temporal and vertical dynamic behavior and coupling of meteorological and chemical conditions. The CU tethered balloon atmospheric profiling system will be deployed. This equipment, including two Sky Doc balloons, tether lines, two winches, flagging, strobe lights, and meteorological sondes and sounding system has an estimated in-kind value of \$80,000. In addition, CU Boulder will provide in-kind five UV absorption ozone monitors, one TEI 42TL NOx Monitor, one custom-built fast response ozone chemiluminescence instrument, and a whole air (canister) sampling package. This equipment is estimated at \$180,000. All of these equipment items will be made available at no cost for this project. The CU Boulder budget of \$129,000 covers salary and benefits for participating project personnel, project administration, travel, and expenses for consumables and supplies.

### ***2.6 Study Component 7. Analysis of Collected Air Quality Data:***

An important part of this overall effort is to analyze and report on the collected data to provide information regarding the formation of winter ozone. An analysis of the field measurements will aid the ultimate goal of developing a plan for reducing winter ozone formation. Analyses of Sublette County, Wyoming winter ozone studies may also provide insights into winter ozone formation in the Uintah Basin. Elements of this effort include:

- Analyses of meteorological data to determine the extent to which meteorology plays a role in increasing levels of winter ozone. Sufficient information has been gathered for Wyoming to conduct such analyses and these may provide insights into winter ozone

issues in the Uintah Basin. Additionally, as a result of this study, there may be enough information to perform these analyses for the Uintah Basin.

- Reconciliation of ambient measurements with emission inventories needs to be performed. It is important to compare the speciation of source characterization hydrocarbon measurements with the speciation of hydrocarbon in emission inventories. If possible, it is also important to verify the source emissions rates and activity data. These analyses will provide confirmation of the emission inventories.
- Analyses of ambient measurements coupled with emission density can provide information regarding the spatial representative nature of the measurements.
- Analyses of the chemistry measurements to determine the VOC /NO<sub>x</sub> regime and relative benefit of VOC versus NO<sub>x</sub> emissions reductions for ozone mitigation.
- Identify potential ozone pathways unique to the Uintah Basin, e.g., snow surface chemical pathways.
- Develop a list of potential mitigation strategies based on the conceptual model of ozone formation in the Uintah Basin.

## **2.7 Further Discussion of Costs**

Significant contributions to the cost of this winter ozone study are being provided by in-cash and in-kind contributions from the UIMSSD, in-kind contributions from UDEQ, and internal funding from NOAA and EPA. The UDEQ in-kind contribution is estimated to be \$422,000. NOAA's internal funding contribution for staff and equipment for the chemical processes study is estimated by NOAA to be \$1,987,000. The EDL air research trailer was funded by a \$400,000 grant from the UIMSSD. USU will provide additional instruments and EDL will provide instrumentation that was funded by the UIMSSD for the 2010-11 winter ozone study. The Western Energy Alliance (WEA) has contributed \$1,125,000. EPA Region 8 will contribute \$100,000 for the study, and additional funds have been contributed by BLM. The UDEQ has also committed a dedicated FTE to coordinate winter ozone research. UDEQ and EPA Region 8 staff will also advise and participate in the planning and data analysis for the study. BLM has committed personnel to assist in the monitoring efforts during the winter months.

## **3. Roles and Responsibilities**

Overall study management and coordination will be by UDEQ with support from BLM. The Oversight Team will be responsible for making high level study decisions and receiving periodic updates and reports from the Science Steering Committee. The membership will be made up of the Study funding agencies. The Science Steering Committee will be responsible for coordinating the Study Component

research, maintaining the study scope and schedule, and reporting progress. The membership will consist of representatives from each of the research groups and will be lead by EPA.

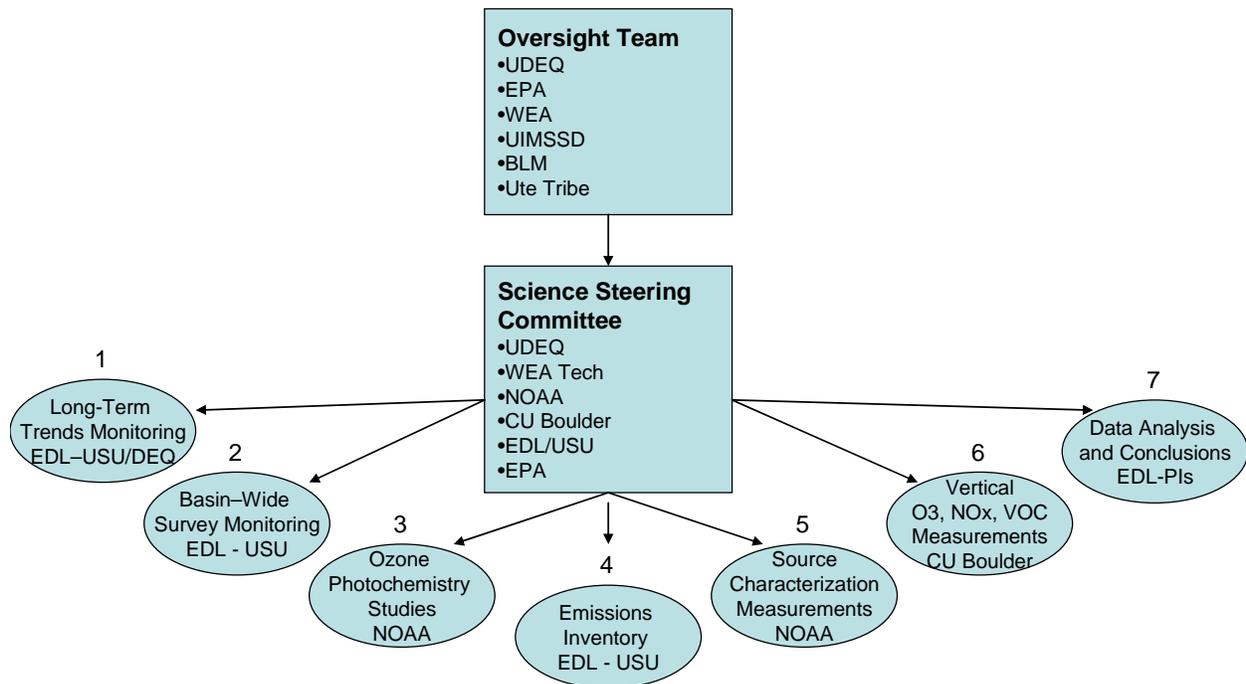
Oversight Team

- UDEQ
- WEA
- UIMSSD
- BLM
- EPA
- Ute Tribe

Science Steering Committee

- EPA
- WEA Tech
- NOAA
- CU Boulder
- EDL/USU
- UDEQ

## Study Organization



## 4. Deliverables and Schedule

### 4.1 Project Schedule

Study Plan Finalized (PIs)	October 1, 2011
Stake Holders/Funding Agencies Review Meeting	October 12, 2011
Pre-study meeting in Uintah Basin at BRC	November 3, 2011
Instrumentation Deployed, Start of Study Window	December 15, 2011
Begin Bi-Monthly Status Calls	January 15, 2012
Mid-Study Assessment Meeting at BRC	February 15, 2012
End of Study Window	March 15, 2012
Preliminary Datasets Available	April 15, 2012
Individual Study Components Conclusion/Results Available	May 15, 2012
Post-Study Technical Meeting-Overall Conclusions (PIs)	June 1, 2012
Draft of Overall Study Conclusions/Recommendations	July 31, 2012
Draft Final Report with Study Conclusions/Recommends (EDL)	August 1, 2012
Draft Report Review Period	Aug-Sept 2012
Final Datasets Available	September 1, 2012
Final Report	October 1, 2012

### 4.2 Report Schedule

A comprehensive final report will be issued for the Uintah Basin 2011-12 Winter Ozone Study. The report is scheduled for release on October 1, 2012. The report will integrate the six Study Components discussed previously, and will be edited by personnel from EDL/USU and UDAQ. The organizations responsible for submitting the contributions for each Study Component are listed below:

#### Responsible Organization:

Study Component 1	EDL/USU
Study Component 2	EDL/USU
Study Component 3	NOAA
Study Component 4	EDL/USU
Study Component 5	NOAA/EDL/USU
Study Component 6	EDL/USU/UDAQ

In order to complete the final report on schedule, it is necessary that the various sections be contributed in a timely manner. The schedule for submitting the various sections of the report is shown below:

#### Submission Schedule:

Objectives	October 1, 2011
Approach	December 1, 2011
Implementation	April 1, 2012
Study Component Conclusions/Results	May 15, 2012



# APPENDIX I Study Component 1 - Long-Term Trends Wintertime Monitoring for Ozone, and Key Precursor Species

## ***Purpose and Need:***

Evaluate the detailed relationships between ozone formation and precursor species availability and reactivity at near-source (oil/gas field) and receptor (city/urban) locations. These measurements would extend over several winter seasons to capture baseline trends and observe the effects of related activities in the region.

## ***Approach:***

Two sampling locations have already been identified (see Figure 1): (1) the Horse Pool Injection site located in the southwestern section of the Uintah Basin within one of the densest areas of well development and (2) Roosevelt, a population center in the central part of the Basin which is moderately distant from concentrated oil/gas development.

The pollutants and related parameters (e.g. meteorology) that will be monitored include species significant to ozone formation and behavior characterization. All instruments will be calibrated, audited, and serviced according to manufacturer and EPA protocols, as appropriate. Data will be archived and compiled nominally on one-hour (1-hr) averages unless otherwise specified. The measurements at each site are planned to include:

- Ozone (O<sub>3</sub>)
  - Monitored using the Federal Equivalent Method (FEM) of UV photometry, nominally configured for 1-hr averaging times, but may be configured for faster averaging times
- NO<sub>x</sub> (NO + NO<sub>2</sub>)
  - Measurements will be made using a modified Federal Reference Method (FRM) photolytic NO<sub>2</sub> reducer (UV), to derive “true” NO<sub>2</sub>. Archival times will be similar to the O<sub>3</sub> system.
- NO<sub>y</sub>, (NO<sub>x</sub> plus all other reactive oxides of nitrogen: HNO<sub>3</sub>, HONO, PAN, etc.)
  - Measurements will be made using a FRM system modified with both catalytic (molybdenum) and photolytic (UV) to sequentially quantify and NO<sub>x</sub> and other tropospherically reactive oxides of nitrogen (NO<sub>y</sub>). Archival times will be similar to the O<sub>3</sub> and the NO<sub>x</sub> systems.
- Methane (CH<sub>4</sub>) and Total Non-Methane Hydrocarbons (NMHC)
  - Measurements quantified using a specifically designed CH<sub>4</sub>/total NMHC miniature gas chromatograph (GC), which can be set for dwell times of 5 to 60 minutes.
- Speciated NMHC (C<sub>2</sub>-C<sub>12</sub> Alkanes, Alkenes, Alkynes, and Aromatics)
  - Measurements will be monitored on 30-60 minute averaging times using American EcoTech’s *airmOzone Ambient Air Volatile Organic Compound Analyzer* (PAMS 56 List) at both the Horse Pool and the Roosevelt locations. The systems collects ambient air on a sorption tube for the specified dwell time,

then automatically injects the sample onto two different, parallel GC columns, one for C2-C6 and one for C6-C12 hydrocarbons. Detection is by separate flame ionization detection (FID).

- Low Molecular Weight Carbonyl Compounds (Acetone, Formaldehyde, Acetaldehyde, etc.)
  - Ambient carbonyls will be assessed using collection by DNPH-impregnated cartridges, followed by subsequent HPLC quantification at USU's Utah Water Research Laboratory (UWRL). The detection limit of the carbonyl protocol requires longer sampling times (3-6 hours), as such, it is currently planned to collect 3-4 samples per day over the duration of the intensive test period. Actual samples will be collected using a specifically designed, time valving and pump system.
- Particulate Matter: PM<sub>2.5</sub> Real-Time and PM<sub>2.5</sub> and PM<sub>10</sub> 24-hr Averaged
  - Real-time (5-60 min) PM<sub>2.5</sub> concentrations will be monitored using an FEM  $\beta$ -attenuation gauge.
  - 24-hr averaged ( $\pm$ 1-hr) PM<sub>2.5</sub> and PM<sub>10</sub> filter-based concentration will also be determined using FRM/FEM samplers. PM will be collected on preconditioned and pre-weighed 47 mm Teflon filters.
  - Partisol 2300 PM<sub>2.5</sub> speciation samplers or similar will also be deployed at each site to collect parallel filters for chemical compositional analysis
    - TFE and nylon filters for ionic analysis (at USU-UWRL or USU-BRC)
    - TFE filters for crustal elemental (XRF) analysis via commercial laboratory
    - Quartz filters for carbon (elemental and organic) analysis via commercial laboratory
- Meteorology
  - Typical surface parameters (WS, WD, T, P, %RH, precipitation dT/dz, snow depth) will be measured using standard met stations.
  - Incoming and reflected solar radiation (allows albedo determination)
    - Kipp and Zonen CNR4 net radiometers (300-2800 nm and 4500-42000 nm) will be deployed at each site. Additionally, for further spectrum delineation, separate up and down welling UVA and UVB radiometers will be deployed at the Horse Pool site.
  - Vertical meteorology
    - Measurements at both sites will be made using a balloon-borne tethersonde package. Furthermore, it is planned to deploy a USU-modified 2B Technologies portable O<sub>3</sub> sampler, coupled with the winched balloon system to obtain vertical O<sub>3</sub> profiles to approximately 300 m. It should also be noted that the NOAA task listed as Study Component 3 will include some vertical meteorological data collection at the Horse Pool site using SoDAR techniques.

Individuals from USU-Logan, EDL-Logan, USU/EDL-BRC, Utah Division of Air Quality (UDAQ), and likely the regional Bureau of Land Management (BLM) will fulfill support roles throughout the duration of the project, including fulltime M.S. level graduate student and part-time undergraduate students from USU-Logan and field technicians from USU/EDL-BRC.

UDAQ personnel will also be very important to the integration of the instruments into the Roosevelt sampling trailer and initial deployment and activation of that site.

***Deliverables:***

Most of the measured parameters will be compiled and available within one to two months after the conclusion of the test period. Samples that require post-test analysis will not be available as quickly, especially for samples, which require analysis via commercial laboratories. It is anticipated that the final data analysis and report for this task would be completed within 4-6 months of the final sampling period. It is not planned to have the data for the Roosevelt or Horse Pool sites publicly available in near-real time.

***Schedule:***

The schedule for this task is shown in Figure A1-1. Although this plan is specifically directed toward the winter of 2011-12, it is anticipated that this task, the Supersites Studies, would continue for multiple, consecutive years. Briefly, the schedule for the 2012 Supersites Study will include equipment deployment in mid-January, followed by the intensive field measurements for three-four weeks centered in February, and equipment recovery and refurbishment in mid-March. February is targeted as the focus of the study as the probability of a wintertime inversion and O<sub>3</sub> episode is high (increasing sunlight, likely snow cover, and expected stagnant high pressure systems).

Detailed Photochemical (Supersite) Study		Month	Aug	Sept	Oct	Nov	Dec	Jan	Feb	March
1 Site Preparation	Documented Site Permission Footprint preparation Power		█	█	█	█				
2 Equipment Preparation & Initial Testing	Horse Pool Site Trailer Delivery to Logan, UT (Sept. 30) Vendor-provided training Integrate Radiometer systems Side-by-side comparison with NOAA system (Boulder, CO) Data analysis NOAA comparison Preparation for field deployment Roosevelt Site Purchase Ambient VOC Gas Chromatograph Identify and prioritize remaining equipment needs Purchase remaining equipment Training, initial testing, and deployment preparation			█	█	█	█	█		
3 Installation & Field Testing and Calibration	Horse Pool Site Roosevelt Site Equipment integration into UDAQ sample trailer Field testing and calibration				█	█	█	█		
4 Sample Collection and Analysis	Intensive sampling period Data collection & on-site analysis Off-site analysis Extended sampling period (real-time systems) Limited data collection and on-site analysis								█	█
5 Field removal of equipment for repair and refurbishment	Horse Pool Site Transfer to Logan for service, repair, and adjustment Roosevelt Site Removal of selected equipment for service and repair									

Figure A1-1. Schedule for Study Component 1 – Long-Term Wintertime Monitoring for Ozone and Key Precursor Species

## **APPENDIX II Study Component 2 – Distributed Basin-Wide Winter Ozone, Limited Precursors, and Meteorological Monitoring Program**

### ***Purpose and Need:***

Expand and further verify winter 2010-11 basin-wide spatial and temporal trends in ozone, as well as survey trends in NO<sub>x</sub>, VOCs, and meteorological data at selected distributed sites.

### ***Approach:***

Establish up to 20 ozone-monitoring sites, in addition to permanent/semi-permanent sites established by other organizations, throughout the Basin. These will include most of the 2011 locations and additional sites targeting periphery areas, especially locations near the more dense gas/oil fields in the southeast Basin area (see Figure 1). The distributed sites will be monitored from late December 2011 through mid-March 2012 at most of the sites. At the sites under the jurisdiction of the USU-EDL sampling team, the ozone will be measured using portable 2B Technology UV photometric Model 205 O<sub>3</sub> analyzers. The systems will be initially calibrated in a laboratory setting either at USU in Logan or the USU/EDL-BRC facility in Vernal using 2B Technologies Model 306 ozone calibrators, which will have been previously calibrated against the Utah Division of Air Quality (UDAQ) /Air Monitoring Center's (AMC) EPA-certified ozone calibration system. Following deployment, the field O<sub>3</sub> systems will be serviced and audited (precision, zero, span checked and recalibrated, as needed) nominally every two weeks.

In order to develop a broad survey of precursor source areas, passive monitors will be deployed at 10-12 of the distributed locations to assess the spatial concentrations of NO<sub>x</sub> and VOCs. The passive samplers are not being deployed at all the sites nor for the entire three month duration because they require limited term exposures (up to a week) and ideally should all be deployed (exposed) for as close to the same time period as possible (i.e. all start and stop at approximately the same times). The initial plans call for distributed NO<sub>x</sub>/VOC sampling for one week in January, two weeks in February (to roughly overlap the parallel "supersite" studies), and one week in March. The NO<sub>x</sub> will be sampled using Ogawa samplers, commercially purchased sorption pads, two per sampler, one for NO<sub>x</sub> and one for NO<sub>2</sub>. By differencing these two measurements NO concentrations can be derived. The recovered sorption pads will be analyzed within 28 days of collection via ion chromatography at USU-Vernal's Bingham Research Center (USU-BRC). At present, the VOCs are planned be collected using Radiello passive VOC samplers and analyzed via a commercial laboratory, as such the turn around time is not yet known.

Additionally, the locations will be assessed as to whether local meteorologically data are available, and if not, additional, portable meteorological systems will be deployed. UDAQ has offered to loan several POM III portable meteorological systems for this project. Additional systems may be purchased and deployed if necessary.

During the servicing portion of the distribution study, two 2-man teams will be deployed on an every two-week schedule, one from USU-Logan/EDL and one from USU/EDL-BRC. UDAQ personnel may augment the USU/EDL-Logan team. Based on the successful 2011 project, servicing the ozone samplers is anticipated to take two to three days each time. Owing to the planned exposure times of the passive samplers (5-7 days) and the need to have them deployed and recovered at specific times, two-to-four separate teams, most likely from USU-Vernal will be tasked with this operation. Additionally, a part-time undergraduate at USU-Logan will be hired to develop scripts for optimizing the data analysis and keep the data compilations completed in a timely manner. Furthermore, a fulltime graduate student from USU-Logan will be assigned to this effort, as well as the “Supersites” study described in Study Component 1.

***Deliverables:***

Data from the distributed O<sub>3</sub> network will not be available for at least one month after initial recovery (for every two week sampling period, each sampler collects roughly 4032 lines of data). The data will be QA'd and compiled into one hour (1-hr) and eight hour (8-hr) averages for each location. The parallel data at sites operated through cooperating partners (e.g. UDAQ, BLM, NPS, etc.) has not historically been available for up to one month after collection. It should be noted that some of the cooperating partners already web-post non-QA'd data for near real-time assessment. There are no plans to have the distributed data available in near-real time, however all draft data will be available to the cooperating partners by April 15, 2012.

The NO<sub>x</sub> and NO<sub>2</sub> data will also require at least a month after sample collection to quantify, compile, and the analyze concentration data. Owing to as yet unknown vendor response times, VOC data availability times cannot be given at this time. It is anticipated that the final data analysis and report would be completed within 4-6 months of the final sampling period.

***Schedule:***

Figure 1 shows a chronology Gantt chart of the sampling and preparation tasks. Briefly, the schedule for the 2011-12 Distributed Monitoring Study will include site identification, permissions, preparation, etc. from September through October, equipment identification and acquisition from October through December, site setup and monitor installation in December, ozone data collection and monitor servicing from mid-December through March, NO<sub>x</sub> and VOCs sample collection from mid-January through mid-March, and equipment collection and tear down from mid-February through mid-March.

<b>Distributed Site Project Schedule</b>									
<i>Task</i>	<i>Month</i>	<i>Aug</i>	<i>Sept</i>	<i>Oct</i>	<i>Nov</i>	<i>Dec</i>	<i>Jan</i>	<i>Feb</i>	<i>March</i>
<i>1 Site Selection</i>									
<i>General</i>									
<i>Previous Site Review</i>		█	█	█					
<i>New Site Identification</i>			█	█	█				
<i>Site Permission</i>									
<i>Passive NOx, VOC sample locations</i>			█	█	█				
<i>Meteorology</i>									
<i>Acceptability of established sites</i>		█	█						
<i>Identify gaps filled collocated sites</i>		█	█	█					
<i>2 Equipment Acquisition, Servicing &amp; Initial Calibration</i>									
<i>2B Ozone Monitors</i>				█	█				
<i>Meteorology</i>									
<i>Passives (NOx and VOCs)</i>				█		█			
<i>3 Site Setup and Installation (by Dec. 20)</i>									
<i>2B Ozone Monitors</i>						█			
<i>Meteorology</i>									
<i>HOBO Temperature sensors</i>						█			
<i>Selected sites for meteorological station</i>						█			
<i>Identify passive sampler deployment location</i>						█			
<i>4 Sample Season Ozone Monitor Service Schedule</i>									
<i>2 week service calls to each site</i>						█	█	█	█
<i>5 Passive NOx and VOC Sample Collection</i>									
<i>Deployment and collection passive samples</i>							█	█	█
<i>- 4 total: Jan - 1, Feb - 2, March - 1</i>							█	█	█
<i>6 Recovery and tear down</i>									
<i>DAQ Samplers (Due: March 1st)</i>								█	
<i>EDL Samplers</i>									█

Figure A2-1. Schedule for Study Component 2 – Distributed Basin-Wide Winter Ozone Monitoring Program

## **APPENDIX III Study Component 3 - Wintertime Ozone Formation Chemistry, Vertical Mixing and 3-D Structure**

### ***Objective***

The objective of this study is to make a comprehensive set of measurements of NO<sub>y</sub> compounds and speciated VOCs, both primary and photochemically produced, along with the three major possible radical sources: formaldehyde, HONO and ClNO<sub>2</sub>. In addition to ambient measurements, we will examine surface interactions such as deposition to snow, and flux measurements of HONO by the gradient and eddy-covariance, methods. The results of our intensive study will provide much more chemical detail than has previously been available, and will be amenable to box-model level analysis that will identify the species and processes responsible for rapid ozone formation in this environment. The measurements performed in this study will also be used in future photochemical grid modeling and will aid in determining whether VOC or NO<sub>x</sub> controls are more effective for reducing winter ozone. This study will also make 3-dimensional measurements of ozone and meteorological data, and this research will be integrated with our on-going research in source characterization (both stationary and mobile), and numerical modeling of tropospheric photochemistry. The following sections provide details concerning the measurements, project and data management, and budget for the proposed project.

### ***Project Management and Data Reporting***

The CSD and GMD groups at NOAA/ESRL collectively have several decades of experience in organizing and conducting ground-based research of the kind proposed here (<http://www.esrl.noaa.gov/csd/tropchem/>; <http://www.esrl.noaa.gov/gmd/>). We propose an informal management structure for this project consisting of an Advisory Council comprising people from the major stakeholder parties, and a Science Team, comprising the PIs who are performing the measurements and analysis. The Science Team will be headed by a Project Scientist (to be named later) and will designate a Site Manager (also to be named later) who will be responsible for coordinating the site planning and logistics.

Data generation and reporting during field projects of this nature have generally two stages. The individual measurement teams make every effort to produce “first-look” data within a few days of acquisition to provide a near-real time guide to experiment planning. These data are available to everyone on the Science Team (and Advisory Council if desired) and are for internal use only. We often call informal data meetings during the field mission to discuss interesting and important new findings and to make decisions about the course of the experiment.

Preliminary data will be available to study participants and sponsors during the study when possible, but by April 15, 2012 at the latest. Final data will be available to participants and sponsors on September 1, 2012, 6 months after conclusion of the study. During this time, the data are put through a QA/QC process that is somewhat idiosyncratic given that many of these experiments are one-of-a-kind, and have been invented by the PI. Several of the measurements, such the UV O<sub>3</sub> photometer, are essentially the same as the instruments used for ambient

monitoring, and their data QA/QC looks very much like the process specified by regulatory agencies. At, or about the time that final data are reported, it has been customary to host a data workshop to report and discuss findings.

The data typically are archived on the NOAA/ESRL/CSD or GMD websites and are initially available on a collaborative basis, i.e. the relevant PI is consulted and involved in whatever analysis process is being contemplated. The data will be released to the public one year after completion of the study, March 1, 2013. The NOAA/ESRL laboratories cannot accept any limitations on the publication or dissemination of data beyond that described above.

### **Acid CIMS** [1, 2]

Gas phase acids will be measured by Negative Ion Proton Transfer Chemical Ionization Mass Spectrometry (NI-PT-CIMS). This system uses acetate ions to react with a wide range of species that we readily recognize as acids, such as nitric acid,  $\text{HNO}_3$ , hydrochloric acid,  $\text{HCl}$ , nitrous acid,  $\text{HONO}$ , and carboxylic acids (aside from acetic acid) and a number of compounds that are typically not considered acids but may be important in a highly impacted atmosphere such as Uintah Basin. This instrument can provide high sensitivity (detection limits of  $<20$  pptv) of many acid species on a 1-minute timescale. The acids of most interest to this project are  $\text{HONO}$ ,  $\text{HCl}$  and organic acids. Nitrous acid is a radical source, that is formed on both ground and particle surfaces, from  $\text{NO}_x$  and  $\text{NO}_y$  species. Measurements in the Upper Green River during the winters of 2010 and 2011 (B. Rappengluck, UGWOS Studies 2010, 2011) have indicated mid-day  $\text{HONO}$  levels that were well above 1 ppbv, a range at which that source is a significant contributor to radical production. It is not clear at this point where that  $\text{HONO}$  is coming from, but a leading candidate is snow-pack photochemistry[3]. Hydrochloric acid is a key intermediate in the surface conversion of oxides of nitrogen to nitryl chloride ( $\text{ClNO}_2$ ) an active chlorine compound[4]. We will be measuring  $\text{ClNO}_2$  and the parent oxides of nitrogen ( $\text{NO}_3$ ,  $\text{N}_2\text{O}_5$ ) as part of our core measurements, so gas-phase  $\text{HCl}$  and soluble particle chloride (see below) would complete the chloride/chlorine budget. The reason active chlorines compounds might be very important in this environment is that chlorine atoms react approximately 200 times faster with simple alkanes such as ethane and propane, than do OH radicals. Formic acid ( $\text{HC(O)OH}$ ), and the other organic acids we would also measure, are important intermediates in VOC oxidation and will yield valuable diagnostic information on that process.

The other valuable features of this instrument are that it can make rapid measurements of a few species at high sensitivity, making eddy flux measurements possible. In addition, the inlet for this instrument is moveable, and could be used to make gradient measurements of acidic species in the height range between 0 and 20 meters. (see Figure 2) This height range should yield reasonable gradients given that the snow-cover during the highest ozone periods reduces vertical mixing. Examples of  $\text{HONO}$  vertical gradient measurements that are possible with the Acid-CIMS are shown in the following figure. These measurements were made from a moveable tower carriage over mixed grassland/dirt during a recent experiment at the Boulder Atmospheric observatory. The measurements proposed for the Horse Pool/Uintah site will be made with a moveable inlet, attached to a small instrument tower. Surface flux measurements of  $\text{HONO}$  will provide definitive evidence of the presence or absence of a surface source.

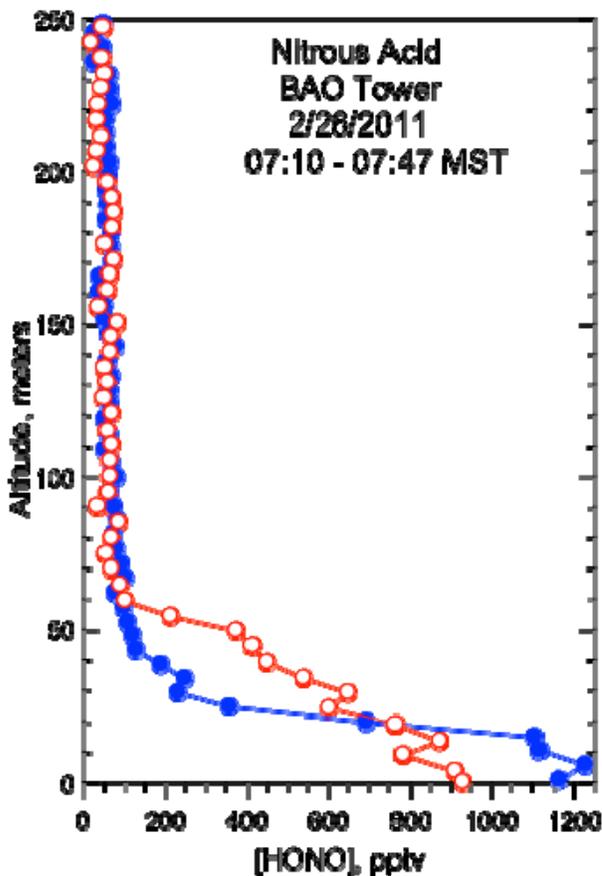


Figure 2. Nitrous acid profiles from tall tower measurements near Boulder, Colorado, February 26, 2011.

The deliverables for this part of the project will be a set of high sensitivity, high time-resolution measurements of HONO, formic acid and other organic acids, made both at single heights and in gradient mode at two or more heights. In addition short periods of the experiment will be devoted to characterizing the strong acids HNO<sub>3</sub> and HCl, using a short inlet appropriate for the transmission of those compounds. Fast measurements of HONO, and formic acid will also be made in conjunction with the eddy flux measurements that are proposed below, if those measurements are supported.

### ***Snow Composition***

Snow composition could have a significant impact on the ozone production chemistry if the snow surface turns out to be a source of HONO. The mechanism for this chemistry appears to be photochemical conversion of nitrate in the presence of humic substances[3]. Measurements of the major cations and anions in snow will define the starting materials available for this chemistry and, if snow chemistry turns out to be important, the likely sources of this material. Bulk and surface layer snow samples will be taken on a daily or semi-daily basis, depending on the spatial and temporal variability that is observed. Horizontal distances to be sampled can be

gauged by the effective “footprint” that the ambient air measurements sample during stable daytime periods and are on the order of a kilometer or less surrounding the site. The samples will be preserved on ice or dry ice and transported weekly for analysis by ion chromatography. Typical detection limits, 5-20  $\mu\text{g}/\text{l}$ , should be sufficient to measure ions in snow that has been impacted by pollution sources.

The deliverables for these measurements are spatial and temporal profiles of surface and bulk cations and anions in snow. The data from this experiment will not be subject to the same data availability as the other measurements (see below) due to the extra step required for ion chromatographic analysis.

## ***Fluxes***

Chemical flux measurements will provide the needed information on the direction and magnitude of exchange processes between the atmosphere and snow surfaces. The two methods proposed here are gradient and fast-eddy correlation. The gradient method involves measurement of chemical species at two different heights, typically a few to a few tens of meters, apart in conjunction with fast measurements of heat, momentum and water gradients and fluxes. The fluxes are measured by fast sensors in combination with fast 3-dimensional winds, and the gradients are measured at the same heights at which the chemical measurements are being made. If chemical sensors are fast enough (typically 1 Hz or faster) then eddy flux measurements can be made directly by calculating the average co-variance of the wind and chemical vectors. The Acid CIMS measurement of the common inorganic and organic acids is fast enough to provide gradient measurements. In addition, the Acid-CIMS measurements of HONO and several of the organic acids is fast enough to permit eddy correlation flux measurements, provided the instrument inlet can be properly characterized.

The deliverables for this measurement will be measured chemical gradients and fluxes for HONO and formic acids, and gradient measurements for other inorganic and organic acids of opportunity, for example HCl, and HNCO. These measurements will focus on the daytime periods of snow cover and high stability that typify high ozone days, but will also be made on days on which the ground is clear or the PBL is unstable for comparison purposes.

## ***Aerosol Surface Area***

Aerosol surface represents a fundamental measurement that is required for any quantitative assessment of chemical reactions that might be happening on particles. The measurement proposed here involves a commercial instrument, owned, maintained and calibrated by NOAA/ERSL/CSD. The basic instrument is described on the manufacturer’s website [6].

The deliverables from this measurement are 1 sec measurements of total particle surface area on a 1-sec time scale for the entire campaign.

## ***Aerosol Chemical Composition***

Aerosol particle composition is an important measurement in instances where significant aerosol surface chemistry is taking place. There are at least two possible areas in which this might be important in the wintertime ozone chemistry; formation of HONO from reaction of NO<sub>x</sub> on particles, and formation of ClNO<sub>2</sub> from reaction of N<sub>2</sub>O<sub>5</sub> with aerosol chloride. Each process has particular chemical signatures or requirements. For example, HONO formation should leave a detectable amount of aerosol nitrite ion and ClNO<sub>2</sub> production requires a certain amount of aerosol chloride. The measurement proposed here is sampling of soluble species by a Particle into Liquid Sampling (PiLS) with analysis by ion chromatography [7]. PiLS samples will be acquired with a dedicated sampler, preserved on ice, transported to the laboratory and analyzed for the major cations and anions. The time resolution of this measurement is somewhat dependent on the desired detection limit and sampler capacity, but will be on the order of 15 to 30 minutes.

The deliverables from this experiment The data from this experiment will not be subject to the same data availability as the other measurements (see below) due to the extra step required for ion chromatographic analysis.

## ***Schedule***

Completion of Study Plan and QA/QC Procedures – September 15, 2011.

### Site Selection and Preparation

Site selection is done

Site prep - power installation and testing - ? (Scott Hill)

Tower Installations- November 15, 2011- January 15, 2012

Trailer and Sea Container Installation- January 15, 2012

Measurement Period: January 15, 2012 – March 1, 2012

### Data Availability-

First look data – 2 days following acquisition, password protected website

Mid-Experiment Data Meeting – week of Feb 15, 2012 (this is open for discussion). To be held at the Bingham Energy Research Center, Vernal, UT.

Final QA/QC'd data - September 1, 2012.

Final report on supported measurements – October 1, 2012

## ***Deployment of the NOAA/ESRL/CSD TOPAZ Ozone Lidar at the Uintah Basin Experiment in February 2012***

## **Background**

NOAA/ESRL/CSD has been deploying airborne, ship-borne, and ground-based ozone lidars since 1995, primarily as part of large, multi-agency field campaigns that were aimed at studying the transport, chemical transformation, and sources and sinks of air pollutants including ozone. The ozone lidar measurements provide a unique 2-D or 3-D (in case of airborne lidar) picture of the distribution of ozone in the lower atmosphere, which is particularly useful to characterize pollutant transport patterns and to provide a vertical context for collocated in situ measurements (e.g. Senff et al., 1998; Banta et al. 1998, Banta et al., 2005). The latest incarnation of CSD's airborne ozone lidar is TOPAZ (Tunable Optical Profiler for Aerosols and oZone), which is typically flown in a nadir-looking configuration on a Twin Otter aircraft a several kilometers altitude. TOPAZ provides highly resolved ozone profile measurements at 10 s (600 m horizontal) and 90 m vertical resolution over a range of a few kilometers (Alvarez et al., 2011). The precision of the ozone measurements achievable with TOPAZ is several ppbv. TOPAZ has been validated against high-quality airborne in situ ozone measurements and compared to ozone sondes (Langford et al., 2011). In recent years, TOPAZ has been deployed at the TEXAQS 2006 study, the Front Range Air Quality Study in 2008, and the CALNEX 2010 experiment. Results from these campaigns obtained with TOPAZ have been reported in Langford et al. (2009), Senff et al. (2010), and Langford et al. (2010).

## **TOPAZ Lidar at Uintah Basin Experiment**

For the proposed deployment of the TOPAZ lidar at the Uintah Basin Experiment in February 2012 we plan to convert TOPAZ to a zenith-looking configuration. In addition, we envision including a scanner which would allow us to point the TOPAZ laser beam at several shallow elevation angles at a fixed azimuth angle. By splicing together the shallow elevation angle and zenith-pointing measurements we will be able to provide profiles of ozone concentration extending from near the surface to several kilometers above ground. TOPAZ will be mounted in a truck in order to facilitate easy deployment at multiple measurement sites. We envision that we will be able to provide composite ozone profiles with a time resolution of several minutes on a continuous basis during Intensive Operational Periods (IOPs). These observations will provide important information on the height, thickness and evolution of surface-based and elevated ozone and aerosol layers. Availability of the ozone profiles will enable characterization of how much, if any, ozone is being transported downward from the free troposphere, the degree of homogeneity within the surface-based boundary layer, and the influence of transport of ozone from residual layers on surface ozone measurements.

We also anticipate being to investigate horizontal variability of surface ozone over ranges extended to about 4 or 5 km from the lidar. For these measurements, we will point the lidar beam horizontally just above the surface and observe spatial and temporal variability of surface ozone.

## **Schedule and Deliverables**

09/2011 – 01/2012: Modify TOPAZ to allow truck-based zenith-looking and scanning operation.  
Fall 2011: Site survey to identify multiple sites from which the truck-based TOPAZ lidar could be operated.

02/2012: Deploy TOPAZ. Provide continuous ozone profiles from near the surface to several kilometers altitude during IOPs. Post first-look ozone profile data on a dedicated web site within 24 hours.

09/1/2012: Post final TOPAZ data.

09/2012-12/2013: Present results at additional workshops and international conferences. Publish results in a scientific journal.

### ***HRDL: High-Resolution Doppler Lidar Measurement of Winds and Turbulence During the Uintah Basin 2012 Study***

In the strongly stable atmospheric conditions that will lead to high ozone concentrations during this study, temporal and spatial variability—and in particular, strong vertical layering—make point measurements difficult to interpret, and often unrepresentative of the wider area. In a field program using high-precision state-of-the-art chemistry measurements, it should be desirable to pair these data with the best available meteorological measurements, which provide insight into transport pathways and therefore the locations of source activity, as well as the vertical extent of flow and turbulent layers. These kinds of measurement are especially needed in highly variable stable conditions, which are the most challenging and most poorly understood conditions in the atmosphere.

The current state of the art in wind velocity measurements in the lowest few hundreds of meters of the atmosphere is NOAA/ESRL CSD's High-Resolution Doppler Lidar (HRDL). The effectiveness of this system in revealing atmospheric structure in stable conditions has been well documented in numerous journal articles over the past several years (Banta et al. 2003, 2006, 2007, Pichugina et al. 2008, 2010). For example, one revealing study showed that Doppler lidar could be used to determine the depth of the stable boundary layer to better than 10%, a measurement that previously carried an uncertainty of 30-40% or more, using available technologies such as surface measurements or sodar. Deploying a Doppler lidar will allow ambiguities in the inference of source locations and other transport issues to be addressed, and will extend the usefulness of the dataset into time periods where the chemistry data alone are impossible to interpret.

### **Schedule and Deliverables**

Fall 2011: Site survey

02/2012: Deploy HRDL to chosen site in Uintah basin; obtain datasets. Provide continuous profiles of wind velocity, aerosol backscatter from the surface to several hundred meters AGL . Post raw profiles to dedicated web site within 24 h.

09/2012: post final HRDL velocity, turbulence, and aerosol data

09/2012-12/2013: Present results at workshops and international conferences. Publish results in a scientific journal.

## **APPENDIX IV Study Component 4 - Emissions Inventory and Activity Data**

### ***Purpose and Need***

Initiate development of a comprehensive, winter episode specific, air resources emission inventory data set of the Uintah Basin. The emissions inventory is needed to understand the sources of precursor gases that result in wintertime ozone formation. The emissions inventory will be used in conjunction with the results of the monitoring studies to examine ozone mitigation scenarios focused on various combinations of effective emissions reductions.

### ***Approach***

The emission inventory data set will be prepared for an area encompassing the Uintah Basin to be used in future modeling analyses. The inventory will be episodic, i.e., tied to the meteorological inversion periods when high ozone levels are observed. It will be both spatially and temporally resolved to provide an understanding of where and when the precursor gases are released into the atmosphere. Speciation of the VOC and NO<sub>x</sub> gases is also needed to understand their potential chemical reactivity.

Special attention will be given to existing and proposed oil and gas development, mobile emissions (including unpaved road emissions), electric generating units, biogenic emissions, and other area sources. The spatially allocated emissions inventory will include all criteria air pollutants (with the exception of lead) and volatile organic compounds (VOCs). This study would include operator surveys and would be similar to the WRAP Phase III emissions inventory studies.

Previous emission inventories that have been performed recently will be reviewed and integrated to provide the basis for the proposed emissions inventory in this task. Recent photochemical modeling studies of Eastern Utah and surrounding regions that have been performed over the last five years will also be reviewed to provide direction and input for this task.

Inventories previously developed for the Western Regional Air Partnership (WRAP) will be used as the main starting point for this task. Emissions outside of the study area from anthropogenic sources will be based on the WRAP III inventories with linear interpolation to 2011, and will follow WRAP's projection calculation methods for determining future year emissions. Consistency with other inventories currently in development or planning, such as the Southwest Wyoming Oil and Gas Inventory under development by the Wyoming Department of Environmental Quality, will also be sought. Spatial and temporal allocation of oil and gas emissions, mobile source emissions (including unpaved road emissions), electric generating units (based on actual emissions), and area source emissions will also be included. Base case oil and gas emission inventory projection work will be verified with industry, the Utah Oil and Gas Commission, the Utah Department of Environmental Quality, and the Uintah and Ouray Tribes to ensure accuracy.

## ***Deliverables***

- A detailed report of the results, which will include a discussion of: data sources used to obtain the inventory, research work (including method and results), maps of significant emission sources, and the spatially allocated emission inventory.
- An updated oil and gas emissions inventory for Duchesne and Uintah counties based on the WRAP Phase III inventory
- Reviewed, updated, and quality assured spatial surrogate file for oil and gas activity in the two counties. This will include oil/gas mobile emissions.
- Reviewed, updated, and quality assured temporal profiles for oil and gas activity in the two counties.
- Review and if necessary update speciation profiles for oil/gas sources.

## ***Schedule***

Initiate obtaining previously developed inventories	September 1, 2011
Initiate operator surveys	September 1, 2011
Complete review of previously developed inventories	December 31, 2011
Complete operator surveys	March 1, 2012
Finalize emissions inventory maps and report	April 15, 2012

# **APPENDIX V Study Component 5 - Source Characterization, Attribution and Ozone Distribution in the Uintah Basin Using Mobile Measurement Platforms and Balloon Borne Ozonesondes**

## ***Purpose and Need***

We propose to A) document the emissions characteristics of point, mobile and area sources in the Uintah Basin during intensive study periods lasting one to two weeks with an instrumented mobile platform, and B) to measure the ozone formation and dissipation in three dimensions during the winter intensive period using an additional mobile van to release Electrochemical Concentration Cell (ECC) ozonesondes carried aloft with free floating balloons to provide high quality, high resolution vertical profiles of ozone throughout the Uintah Basin, especially on the upwind and downwind sides of the basin. These ozonesondes can be released and tracked from a vehicle independent of surface power sources. These measurements will be planned and coordinated with the EDL/USU tethersonde measurements and the NOAA TOPAZ ozone lidar to provide some overlap for QA/QC and verification. The balance of the balloon profiles will be conducted in regions of interest not covered by other instruments.

The goal of the NO<sub>x</sub> and VOC Mobile Lab measurements is to characterize the important source processes for both precursors and to document the composition and patterns of the emissions in space and time.

The extensive mobile measurements in the Basin will provide a 3-D view of the evolution of ozone in and out of the region and will provide key data to link the fixed surface site ozone measurements and to help constrain the modeling of the ozone budget for the region. Each instrument and ozonesonde used in this project will be rigorously calibrated and records of the calibrations maintained for open inspection. NOAA GMD has state-of-the art facilities for preparing standards for most trace gases proposed in this study. They maintain the World Meteorological Organization, Global Atmosphere Watch primary standards for CO<sub>2</sub>, CH<sub>4</sub>, CO, N<sub>2</sub>O, and SF<sub>6</sub> and maintain a NIST standard calibration facility for in situ ozone measurements.

## ***Approach***

### **A. High frequency multi-species mobile laboratory measurements**

High-frequency measurements of ambient CO<sub>2</sub>, CH<sub>4</sub>, CO, NO<sub>x</sub>, and O<sub>3</sub> will be recorded with the "Mobile Lab" and used to detect pollution plumes. Discrete air samples will be collected downwind of point or area sources for more extensive chemical analysis of dozens of VOCs later on at the NOAA and INSTAAR Boulder labs. Previous work in the Denver Julesburg Basin has shown that methane can reliably be used as a tracer to track natural gas and condensate tanks leaks.

The Mobile Lab instrumentation will include:

- a four species CRDS instrument (Picarro): CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O vapor, CO (all at 2.5 second frequency)
- four 2B ozone analyzers (10 second frequency)
- T, wind speed and direction, RH met box (10 sec frequency)
- a NO<sub>x</sub> diode laser cavity ring down instrument (NO<sub>x</sub>CaRD): NO, NO<sub>2</sub> at 1 second frequency
- GPS units for plotting positions of the mobile vans and the discrete air samplers

The ozone analyzers will be calibrated before and after each 2-week deployment in the Uintah Basin. The Picarro will be calibrated every 4 hours with two standards. The 2B and Picarro instruments have proven to be very stable during previous Mobile Lab surveys. The measurement reproducibility and accuracy against World Meteorological (WMO) standards are presented in Table 2.

**Table 2..** Measurement accuracy and reproducibility for mobile laboratory instrumentation.

<u>Species</u>	<u>Accuracy</u>
O <sub>3</sub>	1 ppb
CO <sub>2</sub>	0.1 ppm
CH <sub>4</sub>	1 ppb
CO	5 ppb
NO <sub>2</sub>	3% (22 ppt, 2 sigma, 1 second measurement)
NO <sub>x</sub>	5% (50 ppt, 2 sigma, 1 second measurement)
Ozonesondes	2 ppb

### ***VOC analysis in discrete air samples***

Discrete air samples will be collected downwind of selected point sources and in and out of regional plumes to further characterize the composition of emissions and the evolution of polluted air masses. For each deployment, we will collect samples in a minimum six Programmable Flask Packages (PFP), which contain twelve 0.7L glass flasks each (total of 72 flasks) (<http://esrl.noaa.gov/gmd/ccgg/aircraft/sampling.html>). The air samples will be analyzed at NOAA for the following species outlined in Table 3. The NOAA MAGICC instrument will provide the only flask analysis of CH<sub>4</sub> and CO and will allow us to link the flask measurements with the fast response CH<sub>4</sub> and CO measurements in the Mobile Lab. Half of the flasks will also be analyzed at INSTAAR for the species listed in Table 4.

**Table 3.** Species analyzed in the NOAA PFP Flasks on the A. NOAA MAGICC analysis system ([http://esrl.noaa.gov/gmd/ccgg/images/magicc\\_flow.png](http://esrl.noaa.gov/gmd/ccgg/images/magicc_flow.png)) and B. for VOCs on a GC-MS system reported as dry gas mole fractions in parts per trillion on the NOAA/ESRL/GMD scale.

A. Species                      Accuracy

CO <sub>2</sub>	0.1 ppm
CH <sub>4</sub>	1 ppb
N <sub>2</sub> O	0.4 ppb
CO	1 ppb
H <sub>2</sub>	0.3 ppb
SF <sub>6</sub>	0.04 ppt

B. Species	Accuracy
acetylene	2% on all species
propane	
benzene	
carbon tetrachloride	
CFC-113	
CFC-114	
CFC-115	
CFC-11	
CFC-12	
CFC-13	
dibromomethane	
dichloromethane	
methyl bromide	
methyl chloroform	
methyl chloride	
methyl iodide	
bromoform	
chloroform	
carbon disulfide	
Halon-1211	
Halon-1301	
Halon-2402	
HCFC-141b	
HCFC-142b	
HCFC-22	
HFC-227ea	
HFC-125	
HFC-134a	
HFC-143a	
HFC-152a	
HFC-23	
HFC-32	
HFC-365mfc	
i-pentane	
n-butane	

n-pentane  
 carbonyl sulfide  
 perfluoropropane

**Table 4.** Species analyzed in the NOAA PFP Flasks on the INSTAAR analysis systems.

AIRS No.	Abbr.	Compound	Class	INSTAAR (* see Note below)	Levels < 250 pptv Uncertainty	Levels > 250 pptv Uncertainty
43206	acety	Acetylene	Olefin	Y	<20%	<10%
43203	ethyl	Ethylene	Olefin	Y	<40%	<20%
43202	ethan	Ethane	Paraffin	Y	<10%	<5%
43205	prpyl	Propylene	Olefin	Y	<20%	<10%
43204	propa	Propane	Paraffin	Y	<20%	<5%
43214	isbta	Isobutane	Paraffin	Y	<20%	<5%
43280	1bute	1-Butene	Olefin	Y	<20%	<10%
43212	nbuta	n-Butane	Paraffin	Y	<20%	<5%
43216	t2bte	trans-2-Butene	Olefin	Y	<20%	<10%
43217	c2bte	cis-2-Butene	Olefin	Y	<20%	<5%
43221	ispna	Isopentane	Paraffin	Y	<20%	<10%
43224	1pnte	1-Pentene	Olefin	Y	<20%	<10%
43220	npnta	n-Pentane	Paraffin	Y	<20%	<10%
43243	ispre	Isoprene	Olefin	Y	<20%	<10%
43226	t2pne	trans-2-Pentene	Olefin	Y	<20%	<10%
43227	c2pne	cis-2-Pentene	Olefin	Y	<20%	<10%
43244	22dmb	2,2-Dimethylbutane	Paraffin	Y	<20%	<5%
43242	cypna	Cyclopentane	Paraffin	Y	<20%	<5%
43284	23dmb	2,3-Dimethylbutane	Paraffin	Y	<20%	<5%
43285	2mpna	2-Methylpentane	Paraffin	Y	<20%	<5%
43230	3mpna	3-Methylpentane	Paraffin	Y	<20%	<5%
43246	2m1pe	2-Methyl-1-Pentene	Olefin	Y	<20%	<10%
43231	nhexa	n-Hexane	Paraffin	Y	<20%	<5%
43262	mcpna	Methylcyclopentane	Paraffin	Y	<20%	<5%
43247	24dmp	2,4-Dimethylpentane	Paraffin	Y	<20%	<15%
45201	benz	Benzene	Aromatic	Y	<20%	<10%
43248	cyhxa	Cyclohexane	Paraffin	Y	<20%	<5%
43263	2mhxa	2-Methylhexane	Paraffin	Y	<20%	<5%
43291	23dmp	2,3-Dimethylpentane	Paraffin	Y	<20%	<5%
43249	3mhxa	3-Methylhexane	Paraffin	Y	<20%	<5%
43250	224tmp	2,2,4-Trimethylpentane	Paraffin	Y	<20%	<5%

43232	nhept	n-Heptane	Paraffin	Y	<20%	<5%
43261	mcyhx	Methylcyclohexane	Paraffin	Y	<20%	<5%
43252	234tmp	2,3,4-Trimethylpentane	Paraffin	Y	<20%	<10%
45202	tolu	Toluene	Aromatic	Y	<20%	<10%
43960	2mhhep	2-Methylheptane	Paraffin	Y	<20%	<10%
43253	3mhhep	3-Methylheptane	Paraffin	Y	<20%	<10%
43233	noct	n-Octane	Paraffin	Y	<20%	<10%
45203	ebenz	Ethylbenzene	Aromatic	Y	<20%	<10%
45109	m/pxy	m/p-Xylene	Aromatic	Y	<20%	<10%
45220	styr	Styrene	Aromatic	Y	<20%	<10%
45204	oxyl	o-Xylene	Aromatic	Y	<20%	<10%
43235	nnon	n-Nonane	Paraffin	Y	<20%	<10%
45210	ispbz	Isopropylbenzene	Aromatic	Y	<20%	<15%
45209	npbz	n-Propylbenzene	Aromatic	Y	<20%	<15%
45208	124tmb	1,2,4-Trimethylbenzene	Aromatic	Y	<20%	<15%
45207	135tmb	1,3,5-Trimethylbenzene	Aromatic	Y	<20%	<15%
45211	oetol	o-Ethyltoluene	Aromatic	Y	<20%	<15%
45212	metol	m-Ethyltoluene	Aromatic	Y	<20%	<15%
45213	petol	p-Ethyltoluene	Aromatic	Y	<20%	<20%
45218	mdeben	m-Diethylbenzene	Aromatic	Y	<20%	<20%
45219	pdeben	p-Diethylbenzene	Aromatic	Y	<20%	<20%
45225	123tmb	1,2,3-Trimethylbenzene	Aromatic	Y	<20%	<20%
43238	ndec	n-Decane	Paraffin	Y	<20%	<20%
43954	nundc	n-Undecane	Paraffin	Y	<25%	<25%
43502	form	Formaldehyde	Carbonyl	N		
43551	acet	Acetone	Carbonyl	N		
43503	aceta	Acetaldehyde	Carbonyl	N		

\*Note: 5% of the compounds listed above may not be captured individually because of GC co-elution problems. Uncertainty figures are all best estimates with a 95% confidence level.

## B. Atmospheric ozone profiles and 3 dimension ozone and meteorology structure.

To be able to put the mobile and fixed based measurements (including the ozone lidar measurements) into perspective and to allow for calculations of the total mass balances of gases involved in the ozone forming reactions, a detailed determination of the spatial, temporal, depth and horizontal distribution of the ozone formation reactions along with associated meteorology across the Uintah Basin will be required. This will be assisted by using a second NOAA vehicle equipped with in situ continuous 2B ozone analyzer to track the diurnal ozone formation reaction as it is occurring across the basin and to tie these measurements to those of the fixed base measurements where the high speed chemical reactions will be conducted. This vehicle will be

equipped to release and monitor balloon borne ozonesondes that are capable of measuring vertical ozone concentrations from the surface into the stratosphere along with temperature, pressure and humidity. The depth of the mixing layer and strength of the inversions will be determined with each ascent and descent of the combined ozonesonde/radiosonde packages. The ozonesonde/radiosonde packages will have balloon cut-offs so that the ozonesondes can be parachuted back to the ground on command to provide a second profile on descent and to allow for recovery of some of the ozonesondes if they land in accessible locations. The majority of the ozonesonde/radiosonde launches will be designed to provide high resolution in the lowest 1 km by using low-rise balloons, as shown in Figure 4, while a smaller number of launches will be designed to measure ozone profiles in the troposphere to characterize background and possible transport of ozone during winter.

These ozonesondes can be launched anywhere in the Uintah Basin on short notice by NOAA crews experienced in launches at the South Pole and Greenland in cold temperatures, high winds and darkness. Ozonesonde operations will be available any time of day as planned for or requested by the steering group (more on this below) during high ozone production events. For example, it has been discussed that it might be desirable to obtain up to four simultaneous profiles at different locations at different diurnal times throughout the Basin. If so, multiple teams will be assembled, with NOAA personnel training and guiding USU/EDL personnel to operate additional ozonesonde stations.

The basin wide ozone data will aid in providing a three dimensional picture of the ozone formation process which in turn will be crucial in modeling studies and as input for chemical dynamics and chemical balance determinations.

**Table.5.** Operational specifications for A. 2B Ozone Monitors, B. ECC ozonesonde and C. Radiosonde released with the Ozonesondes.

**A. 2B Ozone Monitors**

Principle: Dual path UV Absorption at 254 nm

Accuracy: 1.0 ppb

Precision: 1.0 ppb

Range: 1-250 ppb

Calibration: NIST Traceable

Data rate: 2 s

Data Availability: Basic data in near real-time, error checked and reprocessed data with 24 hours.

**B. ECC Ozonesonde Measurement Specifications:**

Principle: Electrochemical Concentration Cell

Accuracy Troposphere:  $\pm 2$  ppbv (parts per billion by volume)

Accuracy Stratosphere:  $\pm 4\%$  of reading.

Precision:  $\pm 3\%$

Vertical Resolution: 50 meters

Altitude Range: surface to 35 km

Time per ascent 240 meters per minute rise rate

Data frequency: one second

Calibration: Absolute measurement method prior to launch. Regular instrument checks done at GMD ozone laboratory using UV calibrator traceable to NIST ozone instrument.

Data Availability: Real time to 95 % accuracy, reprocessed final data within 4 hours.

Number of ozonesondes per day: up to 6.

Number of ozonesondes per study period: up to 60

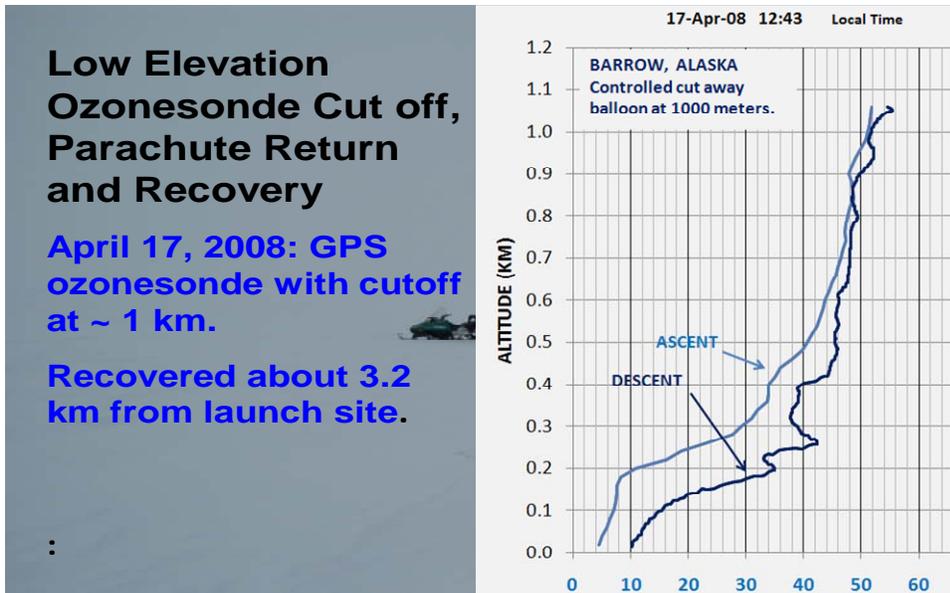
### C. Radiosonde Specifications :

Temperature accuracy/precision:  $\pm 0.2 \text{ C} / 0.2 \text{ C}$

## Launch of a combined NOAA ozonesonde/radiosonde in spring at Barrow, Alaska



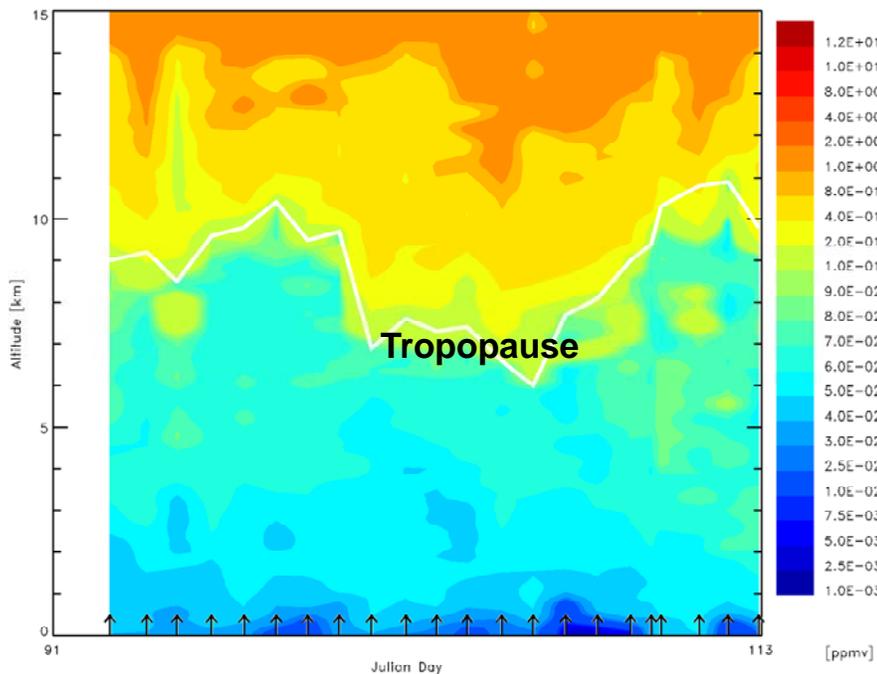
**Figure 3.** NOAA plans on launching up to 70 combined ozonesonde/radiosondes during the intensive study period. Many of these will be on the perimeter of the Uintah Basin to allow for initiating models and verifying model results.



**Figure 4.** As in the Barrow ozone study, many of the ozonesondes will be parachuted back to the surface from 1-2 km altitudes which will be above the surface inversion layer. This allows for rapid dual soundings during period of rapid ozone fluctuations as shown above. The sondes will carry GPS transmitting tracking devices for recovering sondes (where possible) for reuse.

## BARROW, ALASKA April, 2008

Ozone mixing ratio contour plot: 0-15 km



**Figure 5.** A representative cross section of ozone concentrations over a 3 week period for Barrow, Alaska from an ozone study intensive. Similar cross sections will be produced for the Uintah Basin at much higher resolution in the lowest 2 km by using low-rise balloons and remote low altitude ozonesonde cut-offs and parachutes.

## **Sources and distributions of gases in the Uintah Basin**

Targeted surveys with the NO<sub>x</sub> and VOC Mobile Lab will include sampling downwind of drilling rigs, compressor stations, truck exhaust, oil and gas well pads in various stages of development/operations, oil and condensate tanks, natural gas processing plants, power plants, and wastewater ponds. The data collected will be used to characterize the chemical composition of emissions from different source types. NO<sub>x</sub> and VOC point sources in the region have not been sampled in the region yet. A deployment of the Mobile Lab in the Fall will provide much needed information on the VOC speciation of various source types and on the relative source strengths of various emission processes. A deployment in the winter time when the boundary layer is not well mixed will make the interpretation of surface measurements more challenging. The source characterization work could be done later in the spring or summer of 2012 if Fall of 2011 is not possible.

Prior to the first deployment of a single instrumented van in the Fall of 2011, we will work with local agencies to acquire maps of important point and area sources in the region, discuss past studies results and on-going measurements and plan the site specific and area sampling surveys. The Mobile Lab is an independent unit that is configured to have instruments run uninterrupted for close to ½ day before batteries will need to be swapped. Survey areas will be based on accessibility and the particular meteorological and chemical conditions the day of the survey. The Mobile Lab provides a lot of flexibility in terms of adapting to changing planned routes and sampling strategies.

The second (winter) deployment will coincide with the chemical measurements at the NOAA fixed laboratory deployed at (most likely) Horse Pool in January/February 2012 and the basin wide ozone monitoring and ozonesonde measurements. We will have all the instruments, crews and van ready to go and wait to hear from the steering committee for the evolution of the conditions in the field. Once in Utah, the Mobile Lab and other ozone vehicle will coordinate measurements with the staff at the fixed base laboratory to measure in real time sources and concentrations of chemicals upwind, surrounding and downwind of the fixed base facility. In addition if necessary, the instrumented vehicles can be in near continuous operation day and night for a few days crossing the Uintah Basin to do a complete inventory of effluent concentrations beneath the wintertime inversion layer constraining the ozone production zone. This will be accomplished by two crews of scientists driving shifts on a rotating basis. These intensive studies will be conducted prior to (before snow on the ground), leading into and during a major winter ozone event, and post-event. From this data it will be possible to see how various ozone precursor gases are distributed and collect prior to, during and subsequent to a major ozone production event. More than two deployments could be considered if additional measurements were necessary to assess sources and pollution dynamics and to reach more definitive conclusions.

It is expected that during ozone intensive period we will be able to make two to four transects of the basin per vehicle per day so as to characterize the basin wide concentrations of the species

bring studied. These transects will pass by as many of the continuous monitoring installations operated by various agencies as possible.

## ***Deliverables***

We propose to measure the sources, sinks and concentrations of trace, reactive gases and VOCs involved in/associated with winter time photochemical ozone production in the Uintah Basin along with ozone concentration cross-sections over time. Balloon borne ozone and meteorological profiles, especially at the upwind side of the Uintah Basin will be invaluable for model initiation. When combined with fixed base laboratory measurements, an unprecedented three dimension picture of the ozone formation process and production rates will be forthcoming. These data should provide a unique set of tools with which to determine the fine details of the ozone formation processes and their relationships to snow cover, meteorology and chemical precursors. Together, the data should then be useable to develop a new model of winter time photochemical ozone production.

The measurement program will focus on the winter of 2011-2012 with a preliminary scoping study in the fall of 2011 to determine gas source strengths in the Uintah Basin. Preliminary analyses and results will be available within days of the measurements and more detailed data and analyses following the timetable in Section *4.1 Project Schedule*.

## ***Schedule***

### **A. Availability of Mobile Lab and VOC Flask (Canister) Data**

Data from the Mobile Lab fast response instruments and GPS will be combined and plotted every day to provide the steering committee with information for making decisions regarding future surveys and to assess the evolution of pollution events. The preliminary data sets and analysis plots can be shared with the group daily while the final data sets should be processed within a few weeks after returning to the lab when more extensive tests on the instruments will be performed. We do not expect however the final data to differ from the preliminary data substantially.

The initial data from the discrete air samples will be available within a week and QA/QC'd data should be available within 4-5 weeks after returning to the lab. Once we have a better idea of the VOC levels in the air samples from the preliminary study in October and how they may affect the performance of the analysis instruments, the calibration pattern of the GC-MS will be adjusted to minimize the measurement errors. Each individual flask sample analysis on the GC-MS requires approximately 30 min.

### **B. Availability of Ozonesonde and Radiosonde Data**

The sonde data will be available in preliminary form within 30 minutes of collection and final form within 1 day of acquisition. The amalgamated data sets and Basin wide cross sections will be available within 2 weeks of the end of the field collection period.

**Budget: A) Chemical Concentrations and Sources; B) 3-Dimensional Atmospheric and Ozone Structure**

The above measurements are labor intensive and conducted by specialized scientists covering a 24 hours a day schedule up to 14 days in a row in the winter over large regions of the Uintah Basin. NOAA will contribute most instrumentation, management and much of the time and resources of senior personnel for data analysis at an in-kind contribution of \$337,000 over one year. NOAA will need to recover the costs of flask analyses, standard gases, some minimal additional instrumentation, ozonesondes, helium, expendables, vehicle mileage, transportation, per diem and salaries for the field staff. It is expected that NOAA will field 12 staff for the mobile lab and ozone profile and distribution measurements for a total of no less than 400 person days in the winter of 2011-2012. Sample and data analysis costs will also have to be partially covered.

**A) Chemical Concentrations and Sources**

Salaries, benefits and overheads	\$200,000
Travel and per diem	24,000
Commercial Transportation and shipping	6,000
Gas flask analyses (NOAA)	37,000
VOC analyses (INSTAAR)	57,000
Equipment	6,000
Sub-Total	<b>\$330,000</b>

**B) 3-Dimensional Atmospheric and Ozone Structure**

Salaries, benefits and overheads	\$136,000
Travel and per diem	19,000
Transportation and telecommunications	1,000
Ozonesondes, radiosondes, balloons and helium	70,000
Equipment	4,000
Sub-Total	<b><u>\$230,000</u></b>
<b>Total</b>	<b>\$560,000</b>

NOAA GMD In-kind contributions for salaries, benefits and overheads:	<b>\$337,000</b>
NOAA GMD Charges for instrument use and depreciation:	<b>\$0</b>

# **APPENDIX VI Study Component 6 - Continuous Vertical Profiling of Meteorological Variables, Ozone, Nitrogen Oxides, Methane, and Total Hydrocarbons from a Tethered Balloon during the 2012 Uintah Basin Ozone Study**

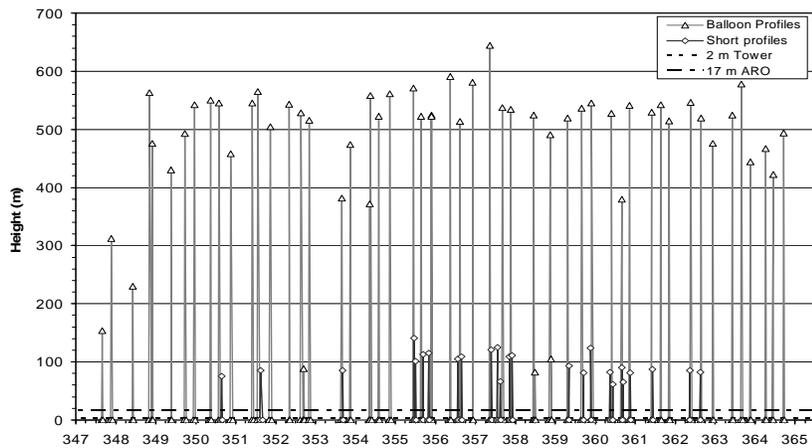
## ***Purpose and Need***

The objective of this project is to study the sources, sinks, and distribution of ozone, nitrogen oxides, and hydrocarbons in the Uintah Basin by continuous vertical profiling of these gases using the CU Boulder/INSTAAR tethered balloon vertical profiling platform. Meteorological variables that will be monitored in concert of the chemical observations will allow linking the chemical behavior of these important photochemical gas species to synoptic, micrometeorological, and boundary layer conditions and upwind source regions. All instrumentation for meteorological, ozone, and nitrogen oxides measurements and the tethered balloon profiling platform are already available and will be provided by CU researchers. A methane and total hydrocarbon analyzer provided by Utah DEQ will be integrated into the profiling system. Non-methane hydrocarbons will be specified by whole air sampling and subsequent chemical analysis on a laboratory gas chromatography-flame ionization instrument.

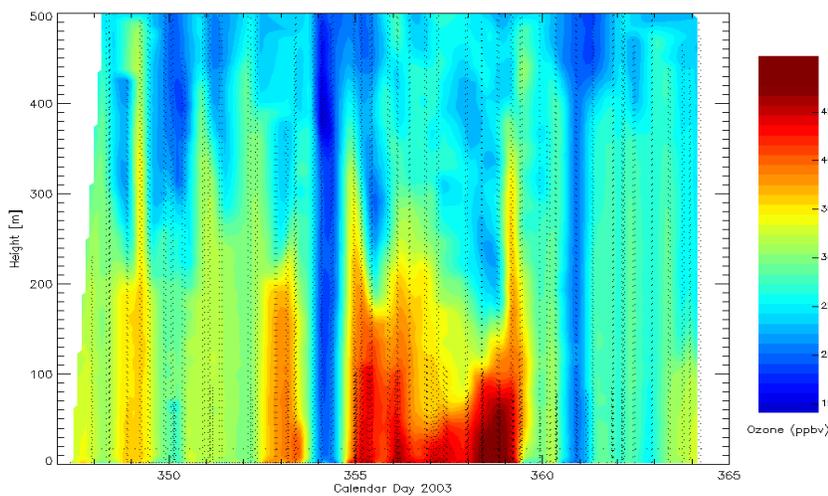
## ***Previous Results***

This experiment will build upon our experience using tethered balloons for investigating the vertical and temporal distribution of trace gases in the atmosphere [Guenther *et al.*, 1996] [Helmig *et al.*, 1998] [Greenberg *et al.*, 1999] [Helmig *et al.*, 2002] [Helmig *et al.*, 2008a] [Helmig *et al.*, 2008b]. An emphasis of this work has been the development of techniques and research applications over snow-covered landscapes. In this context we have developed novel approaches for the particular requirements of chemical measurements from tethered balloon platforms and conducted extensive experiments at Summit, Greenland, South Pole, Antarctica, and Barrow, Alaska.

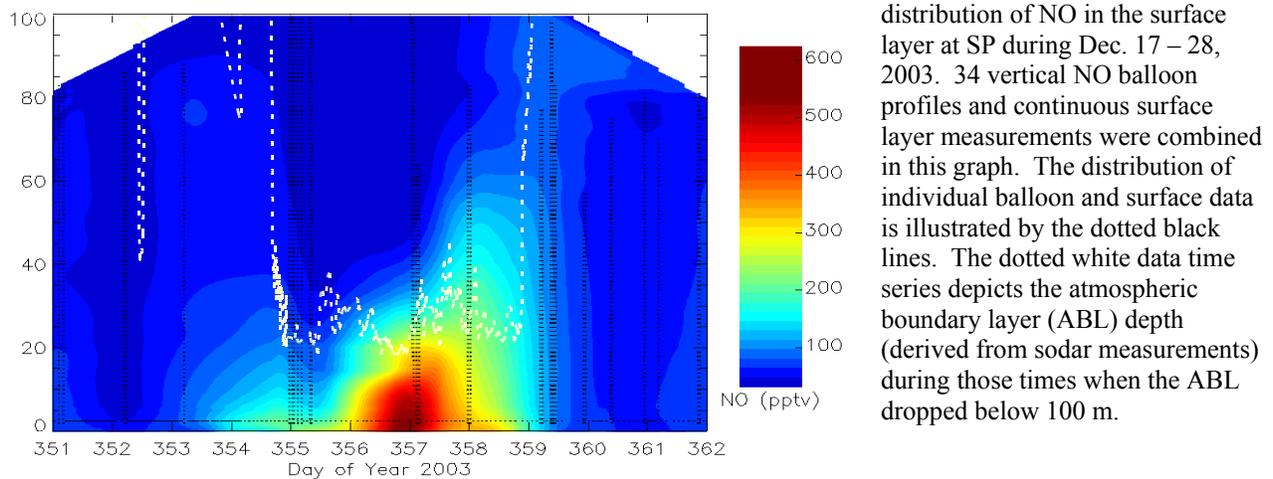
An experiment that resembles in many respects this proposed study was conducted at South Pole (SP), Antarctica, in 2003. More than 50 vertical profiles were accomplished during the 20-day experiment. Not a single day was missed, and we were able to conduct balloon profiling and obtain data during all encountered weather conditions despite the harsh conditions at this site (Fig. 1). The density and resolution of these measurements allowed for the generation of contour displays that depict the temporal and vertical behavior of measured parameters. These images (Figs. 2, 3) proved to be highly valuable for defining the chemical and meteorological behavior of the lower atmosphere at SP. Highly variable and strong vertical gradients of nitric oxide (NO) and ozone were found, with up to 5 ppbv (~20%) and 200 pptv (300%) enhancements of ozone and NO, respectively, in the lowest 20 m of the atmosphere (Figs. 3, 4). The meteorological measurements from the balloon illustrated the dependency of chemical gradients on boundary layer (BL) conditions. Strong ozone and NO gradients developed under conditions of increased atmospheric stability and light winds. This situation promoted active



**Figure 1:** Distribution of tethered balloon profiles during the December 2003 experiment at South Pole. Balloon apex height is plotted against the day of year (DOY) 2003 (Dec. 13–31). High profiles (to ~500 m) were conducted using the balloon-borne radiosonde instruments (ozone sonde, tether sonde). Profiles to ~100 m were done with the long Teflon sampling line attached to the balloon.



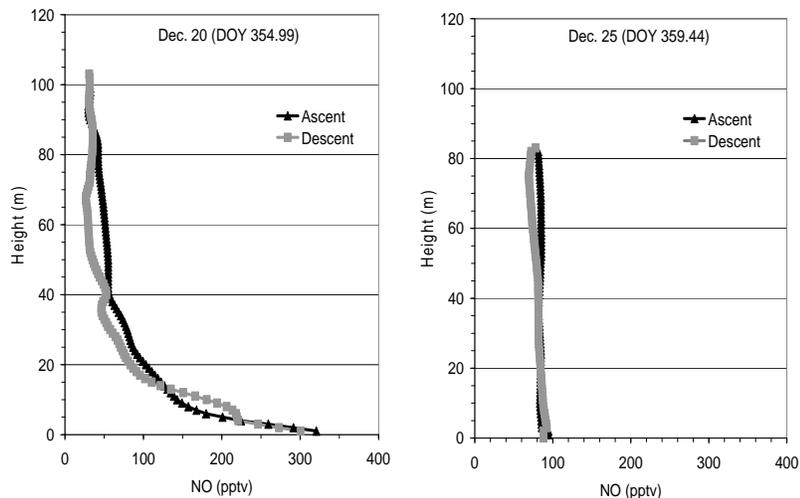
**Figure 2:** Ozone at South Pole between the surface and 500 m during 2003 (dates are listed as day of year (DOY) with data from all available balloon (up to 179 vertical profile data sets) and surface measurements. The black dots indicate the distribution of data from the tethered balloon.



**Figure 3:** Vertical and temporal distribution of NO in the surface layer at SP during Dec. 17 – 28, 2003. 34 vertical NO balloon profiles and continuous surface layer measurements were combined in this graph. The distribution of individual balloon and surface data is illustrated by the dotted black lines. The dotted white data time series depicts the atmospheric boundary layer (ABL) depth (derived from sodar measurements) during those times when the ABL dropped below 100 m.

photochemistry with resulting ozone production in the atmospheric boundary layer region. The depth of the layer with enhanced NO was shallower than for ozone, which reflects the much different lifetimes of these two gases. The balloon measurements point towards ozone

production rates that are in the upper range of previous calculations. Given the non-linearity of ozone production with [NO], maximum ozone formation is not expected right above the surface, but within a distinct height layer where [NO] = 100–300 pptv [Davis *et al.*, 2008].



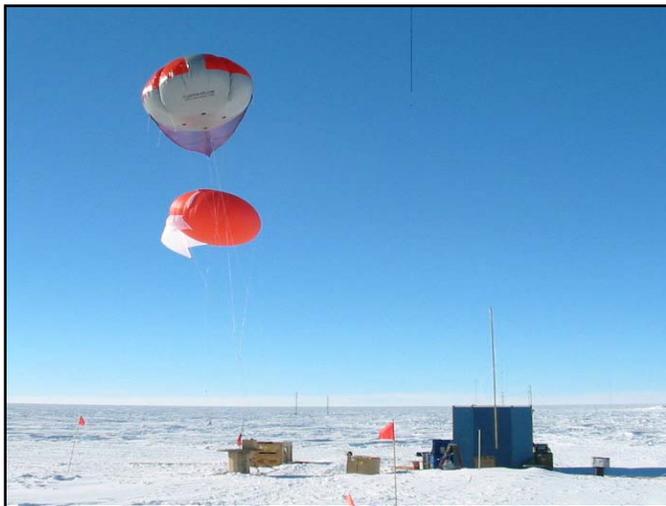
**Figure 4:** Vertical profiles (illustrated profiles are 5-point running means) of NO as measured with the tethered balloon long sampling line experiment during a period of enhanced NO buildup at South Pole (left, DOY 354.99, Dec. 20) in comparison to an episode when NO surface layer mixing ratios were much lower (right, DOY 359.44, Dec. 25). Both graphs show data from the balloon ascent and descent, which were on the order of 30 min apart.

## Approach

Federal Aviation Administration (FAA) approval: The proposed experiment will focus on the study of the surface/boundary layer over snow, which typically is rather shallow, many times on the order of <100-200 m. Therefore, the experiment will entail profiling within the 500 feet-above ground ceiling that is set by the FAA for balloon operation without requirement of special FAA permits and waivers. For operation to 500 feet, notification of the regional FAA flight operations office for placing a note is the only requirement. We will follow this procedure and fully apply with FAA regulations in all aspects of the tethered balloon operation.

Balloon platform: Our mobile equipment trailer will be deployed at the site for use as a field laboratory and instrument shelter adjacent to the balloon launch site. We will again use helium-filled Sky-Doc balloons (Fig. 5), which have a proven track record for polar field research. Sky-Doc balloons combine properties of both blimps and kites, and can be flown in much higher winds (>30 miles per hour) than blimp-type systems (<http://www.skydocballoon.com>). Two Sky-Doc balloons that were used at SP are illustrated in Fig. 4. Because of their kite-like properties, Sky-Doc balloons develop stronger lift in winds. Since there is usually at least some moderate air motion in the boundary layer, Sky-Doc balloons do not need to be as large as conventional blimps for achieving the required lift. We have used Sky-Doc balloons in six experiments, three of which were in polar locations, at Summit, Greenland ([Helmig *et al.*, 2002], SP [Helmig *et al.*, 2008a][Neff *et al.*, 2008][Helmig *et al.*, 2008b], and Barrow, AK [Boylan *et al.*, 2011]. We will be equipped with two complementary balloon systems, sized at 12 and 20 feet in diameter. This approach will have a number of advantages over working with a single platform as we will be able to: 1. operate an array of meteorological and chemical

sensors on two balloons flown in parallel, 2. work under a wider range of wind conditions, 3. have a backup system, in case there is failure or accidental loss of one of the balloons.



**Figure 5:** 12-foot and 18-foot Sky-Doc balloons during their previous deployment at South Pole. These same balloons will be used during the Uintah ozone study. Their deployment will be alternated depending on wind conditions and payload requirements. This picture also shows the hydraulic winch, which is contained in the insulated, heated wooden box below the airborne balloons.

Balloon ascent and descent will be controlled with a hydraulic winch that is contained in a heated container and engineered for use in cold environments. This winch has previously proven to work well in the extreme conditions encountered at Summit, SP, and Barrow. Balloons will be equipped with strobe lights and flags along the tether line according to FAA regulations

Meteorological parameters: TSP-5A-SP Vaisala tethersondes and RS-80 Vaisala radiosondes will be used for the measurement of meteorological parameters along vertical profiles with the balloon (Fig. 6). The TSP-5A-SP tethersonde measures pressure (electronic aneroid capacitance sensor), temperature (fast response bead thermistor), relative humidity (fast response capacitance polymer sensor), wind speed (three-cup anemometer with light-chopper tachometer), and wind direction (electronically-controlled magnetic compass). The RS-80 radiosonde measures



**Figure 6:** Meteorological and chemical tethered balloon instrument package. The TSP-5A-SP tethersonde (top) records wind speed, wind direction, relative humidity, and temperature. Below the tethersonde is the ECC ozonesonde with the RS-80 radiosonde attached on the side.

pressure (aneroid capacitor), temperature (bead capacitor), and relative humidity (thin film capacitor). Both sondes radio-transmit ~2 s data to a ground receiver, which is interfaced to a laptop computer for data acquisition.

Ozone: Ozone will be measured using EN-SCI Model 2Z (EN-SCI Corporation, Boulder, CO) electrochemical concentration cell (ECC) sondes, which are based on the principle that ozone and iodide react within an electrochemical cell. The ECC ozonesondes are interfaced to the RS-80 (Vaisala, Helsinki, Finland) radiosonde, with data being transmitted to the ground receiver (Fig. 6). We have spent a considerable amount of effort on characterizing the quality of this measurement; results from an intercomparison experiment at SP were reported by [Johnson *et al.*, 2008].

Long sampling line measurements: Besides the balloon-borne sondes for measurement of ozone, we will deploy long sampling lines with inlets lifted above ground by the balloon. There will be two different types of long sampling line experiments.

1. Three stationary inlets at fixed heights.

Similar to the experiment we conducted during OASIS at Barrow, AK, sampling inlets will be attached to the balloon tether line, for pulling air from up three heights to ground level for chemical gradient measurements. These sampling lines will be operated in parallel, with the SkyDoc providing a 'sky hook', keeping these inlets at a constant height. The balloon will be raised to 500 feet above ground, with sampling line inlets attached to the primary tether line at heights of 450, 300, and 150 feet. All three sampling lines will be of equal length, at 600 feet, and made of thin-wall PFA Teflon. Lines will be continuously purged with air drawn from the inlet aloft. The other end of the sampling lines will be directed into an instrument trailer to a manifold from where chemical analyzers collect sequentially for 5 min sample air from each line. The sampling sequence will be automated, allowing for around-the-clock vertical gradient concentration measurements. This experiment will be operated during day and night.

Chemical analyses will be performed with continuously operated monitors located inside the instrument trailer parked near the balloon winch.

NO<sub>x</sub>: A Thermoenvironmental (TEI) Model 42C-TL will be used for measurement of nitrogen oxides. This monitor has a 50 pptv detection limit, which is well suitable for the conditions anticipated in Uintah Basin. The TEI 42C-TL has 2 channels. The first channel measures nitric oxide (NO) via NO + O<sub>3</sub> chemiluminescence. The second channel measures nitrogen dioxide (NO<sub>2</sub>) by redirecting air through a heated (325°C) molybdenum converter, which causes NO<sub>2</sub>—including other oxidized nitrogen compounds—to be converted to NO. NO<sub>2</sub> is then determined by subtracting NO (obtained by the first channel) from the resulting NO<sub>x</sub> signal. We have thoroughly investigated the concern that NO might be reduced by wall losses or reaction with ozone during the ~2 min transport time from the inlet to the instrument. Comparison measurements by parallel sampling through a short (10 m) sampling line showed that such losses were on the order of ~ 5%, which the long line data were subsequently corrected for. We will implement one change to further reduce the sample residence time in the tubing by using a stronger, secondary pump (scroll pump) to purge the sampling line at a higher rate (10 l min<sup>-1</sup>).

Ozone: Ozone will be monitored in the air stream from the balloon inlets using a TEI Model 49C UV absorption instrument. A second TEI monitor will be deployed for the continuous

monitoring of ground level (2 m) ozone at the launch site. All monitors to be used will be calibrated prior and after the field experiment against a NIST standard located at Boulder NOAA ESRL laboratory.

Total Hydrocarbons: These measurements will be performed with a Baseline8900 GC-FID Total Hydrocarbon (THC) analyzer to be provided by the Utah Department of Environmental Quality (DEQ). This analyzer provides data for both methane and non-methane hydrocarbons by directing an air flow through a flame ionization detector. Measurements are continuous, at ~120 s time intervals.

Speciated Non-Methane Hydrocarbons: During events when the THC analyzer indicates elevated hydrocarbon levels whole air samples will be filled from the tethered balloon inlet lines into whole air sampling flasks. We have three different sampling systems that will be employed, depending on sampling situation. These include a series of 2.5 l glass flasks (these are the same flasks as used by NOAA in the Cooperate Flask Sampling Network), programmable flask packages (PFP, see [http://www.aosinc.net/prod\\_pfp\\_pcp.html](http://www.aosinc.net/prod_pfp_pcp.html)), and 6 l Summa stainless steel flasks. These samples will be transported to our NMHC trace analysis laboratory on the CU campus. Samples will be subjected to gas chromatography analysis with flame ionization detection (FID). C2-C10 NMHC will be identified and quantified against a series of standards that are referenced against the Global Atmospheric Watch (GAW) volatile organic compound calibration scale.

2. A moving inlet will be raised and lowered with a secondary tether line.

A second tether line will run over a pulley mounted below the balloon and a fifth sampling inlet attached to a 600-foot sampling line will be attached to it. The ascent and descent of this inlet will be controlled with a smaller second winch. Air will be continuously drawn through this line and analyzed with the same analyzers as mentioned above. This experiment requires attendance by project personal and will primarily be conducted during daytime hours. Each run will deliver two profiles, one during ascent and one during descent. A complete set of profiles will take 20 min. A minimum of six profiles are planned for each day.

Data analyses: Data from the balloon-borne sondes will be thoroughly quality controlled, analyzed and interpreted by CU scientists, and be shared with all other collaborating study participants. We will provide individual flight vertical profiles for each measured parameter as well as color contour plots (see Figs. 2, 3) that depict the vertical and temporal behavior of ozone and NO<sub>x</sub> under all encountered atmospheric mixing and synoptic transport conditions.

### ***Broader Impacts***

This experiment will be in close collaboration with other groups participating in the Uintah Basin Winter Ozone Study. It will bring together scientists, including students, from the University of Colorado, and NOAA-ESRL, the State of Colorado and Utah federal agencies as well as from other participating institutions.

### ***Deliverables***

This project will deliver high spatial and temporal resolution meteorological data and chemical data for ozone, nitrogen oxides, methane, and total non-methane hydrocarbon concentration

between the surface and 500 feet height above ground for a full one-month period. We will provide continuous time series of the measurements performed from three stationary sampling inlets at 6, 150, 300, and 450 feet above ground. Secondly, this experiment will provide a minimum of six daily vertical ozone and NO<sub>x</sub> profiles from instruments and long sampling line being moved up and down to the balloon ceiling altitude. A total of 40 canister samples will be collected from the balloon and surface inlets for speciated NMHC analysis on the CU-INSTAAR trace analysis NMHC gas chromatography system. All data will be quality controlled and reported in tabular format and graphical outputs, similar to those depicted in Figs. 2 and 3.

### ***Schedule***

The field schedule will be coordinated with the other institutions participating in this study. Our current plan is somewhat flexible, but is based on a 3-day setup period during late January 2012, a full one-month continuous operation of the tethered balloon experiment, a 1-day takedown, and 3-9 months of data analyses and interpretation, and preparation of a final project report. During the field experiment, 1-2 project personnel will be present at the site at all times for the 24/7 balloon operation.

## **APPENDIX VII Study Component 7 - Analysis of Collected Air Quality Data and Mitigation Efforts**

### ***Purpose and Need***

The purpose of this component is to bring together all of the study results and draw conclusions about why high values of winter-time ozone are observed in the Uintah Basin. Based on this “conceptual model”, develop a set of mitigation strategies that would be effective for reducing ozone. Compare the conclusions of this study with those from past studies in Wyoming’s Upper Green River Basin.

### ***Approach***

One of the main objectives of this 2011-12 Winter Ozone Study is to develop a “conceptual model” for wintertime ozone formation in the Uintah Basin and identify mitigation strategies that could be implemented based on this model. This Study Component will analyze and integrate the results from the respective investigators participating in the other Study Components in developing this model. Results from past studies in Wyoming’s Upper Green River Basin will also be examined and possibly included in the development of the conceptual model. In analyzing the results from the other Study Components and the Wyoming study, the emphasis will be on developing a better understanding of winter ozone and relevant mitigation efforts. A scheduled review period will allow all of the technical participants, stake holders and funding agencies the opportunity to review and comment on the resulting document.

An important part of this overall effort is analyzing the collected data to provide information regarding the formation of winter ozone and to help focus field measurements with the ultimate goal of developing a plan for reducing winter ozone formation. Analyses of Sublette County, Wyoming winter ozone studies may also provide insights into winter ozone formation in the Uintah Basin. Elements of this effort include:

- Analyses of meteorological data to determine if meteorology or changes in precursor emissions result in increasing levels of winter ozone. There is currently sufficient information for Wyoming to conduct such analyses, and these analyses may provide insights into winter ozone issues in the Uintah Basin. Additionally there may be enough information to perform these analyses for the Uintah Basin.
- Reconciliation of ambient measurements with emission inventories needs to be performed. It is important to compare the speciation of hydrocarbon measurements with the speciation of hydrocarbon in emission inventories. These analyses will provide confirmation of the emission inventories. This analysis needs to incorporate engineering input to identify emissions from different source types.

- Analyses of ambient measurements coupled with emission density can provide information regarding the spatial representative nature of the measurements.
- Analyses of the chemistry measurements to determine the VOC /NO<sub>x</sub> regime and relative benefit of VOC versus NO<sub>x</sub> emissions reductions for ozone mitigation.
- Identify potential ozone pathways unique to the Uintah Basin, e.g., snow surface chemical pathways.
- Develop a list of potential mitigation strategies based on the conceptual model of ozone formation in the Uintah Basin.

### ***Deliverables***

The comprehensive final report for the 2011-12 Winter Ozone Study will be the deliverable from this Study Component. The report will integrate all of the Study Components into one report, and the discussion and analysis of study results will include input from all of the investigators.

### ***Schedule***

The final report for this project is scheduled for release on October 1, 2012. The report will integrate the six Study Components discussed previously, and will be edited by personnel from EDL/USU and UDAQ. The organizations responsible for submitting the contributions for each Study Component are listed below:

#### Responsible Organization:

Study Component 1	EDL/USU
Study Component 2	EDL/USU
Study Component 3	NOAA
Study Component 4	EDL/USU
Study Component 5	NOAA/EDL/USU
Study Component 6	EDL/USU

In order to complete the final report on schedule, it is necessary that the various sections of the report be received for each Study Component in a timely manner. The schedule for submitting the various sections of the report is shown below:

#### Submission Schedule:

Objectives	October 1, 2011
Approach	December 1, 2011
Implementation	April 1, 2012
Conclusions/Results	May 15, 2012

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