## **Operations on BAO Tower during FRAPPÉ / DISCOVER**



Steve Brown, NOAA Earth System Research Laboratory

Brown

Farmer

Murphy

Gordon

### **Profiling Instrument Shelter with Amenities**

- 300 m tower "PISA Hut"
- Ascent / descent rate 0.6 m s<sup>-1</sup>, One vertical profile = 9 min
- Usable payload of approximately 1 ton
- Temperature-controlled enclosure, 5-15 kW available power, real time communication with ground

#### Measurements planned for summer 2014

NO, NO <sub>2</sub> , NO <sub>v</sub> , O <sub>3</sub>	CRDS
(instrument also has NO <sub>3</sub> ,	N <sub>2</sub> O <sub>5</sub> )
Organic / Inorganic Acids	CIMS
NH <sub>3</sub>	TLDS
Open Path Aerosol Extinction	CRDS



## (Some) Scientific Goals

1. Investigate relationships between  $NO_x$ ,  $NO_y$  and  $O_3$  as a function of wind direction and height to differentiate between various sources (e.g., urban, oil and gas) in local  $O_3$  production



NO<sub>x</sub> wind rose from the NACHTT study at BAO, winter 2011

Urban (from south) and "other" (from northeast) NO<sub>x</sub> sources appear spatially distinct

> Pict Collins-West Veid Co. Tower Veid Co. Tower Platteville parkland Airstrip BAO Tower Boulder Iats - N - RMMA CAMP 270 te Mtn. Denver-LaCasa 225 Weich

2. Augment aircraft measurements of  $NO_x$ ,  $O_3$  and other species through vertical profiling in the lowest 300 m of the boundary layer

- Currently expect to run continuous vertical profiles during periods when either the P-3 or C 130 is flying
- May run vertical profiles during other periods, depending on investigator interest in these data

• Open to suggestions re: instrument payload or tower operation. Contact: steven.s.brown@noaa.gov

# Observational constraints on the impact of oil and gas exploration on $O_3$ production in the Northern Colorado Front Range Metro Area as part of FRAPPÉ

Delphine K. Farmer and Emily V. Fischer, Colorado State University

**Measurements Proposed for BAO Tower Ground site:** 

	*		
Measurement	Instrument/Technique	Frequency	Expected Uncertainty (u), Precision (p), LOD
J(NO <sub>2</sub> )	Filter Radiometer	1 min avg	<2% (p)
CO, CO <sub>2</sub> , CH <sub>4</sub>	Picarro G4201	5 min avg	CO: (p) 2 ppbv (when CO > 100ppbv); CO <sub>2</sub> : (p) 50 ppbv CH <sub>4</sub> : (p) 0.7 ppbv
OH reactivity	Comparative Reactivity	40 min pt	(u) 25% above 8 s <sup>-1</sup>
SO <sub>2</sub>	Thermo Sci Model 43i	1 min	(u) 1 ppbv or 1%
0 <sub>3</sub>	2B Technology	1 min	(u) 1 %
Hydrocarbons (C <sub>2</sub> -C <sub>8</sub> )	GC-FID; Rt <sup>®</sup> -Alumina BOND/Na <sub>2</sub> SO <sub>4</sub> (Restek)	20 min avg	<ul><li>(u) 10% at mixing ratios &gt;&gt; detection</li></ul>
PAN	NCAR GC-ECD	5 min pt	(u) 10% at mixing ratios >> LOD
Aerosol size distributions (60nm – 1µm)	DMT Ultra High Sensitivity Aerosol Spectrometer (UHSAS)	1 s pt, avg to 5 min	Detection efficiency ~100% for particles between 100-1000 nm

#### Measurements on BAO Tower (PISA, vertical profiling):

Measurement	Instrument/Technique	PI / Institution
NO, NO <sub>2</sub> , O <sub>3</sub> , NO <sub>y</sub> , N <sub>2</sub> O <sub>5</sub>	Diode laser cavity ring down spectroscopy	Steve Brown, NOAA
Oxidized VOCs (carboxylic acid, organic nitrates), HONO (?)	I <sup>-</sup> / Acetate CIMS	Delphine Farmer, CSU
NH <sub>3 (g)</sub>		Jennifer Murphy, UofToronto

### NOAA TOPAZ Ozone Lidar (1)

- Tunable UV ozone differential absorption lidar (DIAL)
- Truck-based, scanning instrument
- Ozone and aerosol backscatter profiles from ~15 m up to 3 km AGL





Composite vertical profiles every 5 min

### NOAA TOPAZ Ozone Lidar (2)



12-hour time-height cross sections of ozone (top) and aerosol backscatter (bottom) observed with TOPAZ on 25 September 2013 at La Porte, TX during DiscoverAQ Houston. Light winds and sunny skies combined with high levels of  $O_3$  precursors advected from the Houston Ship Channel led to very high afternoon  $O_3$  concentrations.

## Ozone Chemistry and Dynamics in the Colorado Front Range

D. Helmig (P.I.), Institute of Arctic and Alpine Research, University of Colorado

G. Pfister (Co-P.I.), Atmospheric Chemistry Division, NCAR



**Figure 1** One of the proposed flight patterns for FRAPPÉ, investigating the mountain-plains air circulation patterns. The extension of the surface sites network proposed in this study is indicated by the red area. (Figure adapted from the NCAR FRAPPÉ LAOF white paper).



**Figure 2** a) Map of the study area showing the seven sites on an east-west transect from which data will be collected. b) Graphical representation of the elevation cross-section. Abbreviations used stand for Tundra Lab (TL), Soddie (SD), C1 (Mountain Research Station), Coughlin (CO), Sugarloaf (SL), Betasso (BE), and Boulder (BO). Also included for reference are the sites that were included within the framework of the Boulder County Air Toxics Study, i.e. Lyons, South Boulder, Longmont, and Rocky Mountain National Park.



**Figure 3** Average diurnal ozone profiles at each site for winter and summer seasons in the 2007-2008 study.

#### Frappe Experimental Plan:

- 1. Continuous Monitoring of Ozone
  - eight elevation gradient sites
  - May August
  - one hour time resolution
- 2. Methane and Volatile Organic Compounds on FRAPPE and DISCOVER-AQ flight days
  - five elevation gradient sites
  - 72 in-situ samples in Boulder
  - 72 flask/canister samples
- 3. WRF Chem Transport and Chemical Modeling

#### UW-Madison Space Science and Engineering Center (SSEC) High Spectral Resolution Lidar (HSRL)

- Ground based measurements of aerosol backscatter cross section, depoloarization, and extinction at 532nm
- Backscatter cross section measurements are robust more then one order of magnitude below molecular backscatter

Recent deployments: Norman, OK (2012, DC3), Huntsville, AL (2013, SEAC4RS)

HSRL aerosol extinction near the surface is historically difficult due to narrow field of view of the system and need for large overlap corrections at altitudes below 4km asl.

Instrument now has improved temperature stability and additional molecular wide field channel that allows direct measurement of overlap correction.

Wide field of view overlap correction is applied down to ~400m and then the lidar ratio measured above 400m (but within BL) is used to extend the overlap correction to ~100m (lowest measurement altitude)

Contact: Edwin Eloranta (eloranta@ssec.wisc.edu)



HSRL cross-sections for August 20, 2013 over Huntsville, AL

#### UW-Madison Space Science and Engineering Center (SSEC) Atmospheric Emitted Radiance Interferometer (AERI)



Temperature, ozone, and methane Jacobians

#### **ARM Facility Instrument:**

Deployed at North Slope, Southern Great Plains, Tropical Western Pacific, and ARM Mobile Facility ARM sites. Trace gas retrieval developed by Bill Smith (HU/

#### Contact:

Jonathan Gero jonathan.gero@ssec.wisc.edu

- Ground-based measurements of downwelling atmospheric radiance from 3.3 to 18.2 μm (550–3000 cm<sup>-1</sup>) with a spectral resolution of 0.5 cm<sup>-1</sup> and an absolute calibration accuracy <1% of the ambient radiance
- Vertical profile retrievals of temperature (T), humidity (Q), carbon monoxide (CO), ozone (O3), methane (CH4), and nitrous oxide (N2O).
- AERI accuracy of 1K and 10% for T and Q, respectively, most accurate in the boundary layer.



Retrieval cross-sections for April 19, 2013 over Moody Texas.

### **NOAA Tethered Ozone and Met Profiles in FRAPPE**

Russ Schnell for NOAA Tethersonde Group

russell.c.schnell@noaa.gov



- NOAA will operate a profiling ozone/met tethersonde at one site.
- Profiles from the surface to 1,000/2,000 ft. depending on FAA clearance and wind speed.
- A profile can be completed every 30 minutes.
- Ozone and met available in real time.
- Surface ozone will be measured continuously at the tethersonde site and at Niwot Ridge.
- The tethersonde will operate on 10 selected days, 16 profiles/day.

#### **Tethersonde specifications:**

Ozone Absolute accuracy:	± 2ppbv
Temperature accuracy:	± 0.2 C
Humidity accuracy	± 3%
Pressure accuracy	± 0.5 mb
GPS Altitude	± 5 m
Data Frequency:	± 1 hz







Figure Legends for Tethersonde Data: A. Individual ozone and temperature profiles, three different locations, Utah. B. Ozone profiles, winter day, Uintah Basin, Utah. C. Ozone contours showing rapid, low altitude ozone production in mid-day (red) and ozone removal later in the day (blue).



INSTAAR, University of Colorado Stable Isotope Lab Supporting Regional Assessments of CH<sub>4</sub> Emissions with Ground-Based Isotopic Measurements and FLIR (Forward Looking InfraRed) Imaging

> Bruce H. Vaughn & Owen Sherwood, Andrea Sack Contact: Bruce.Vaughn@colorado.edu

### Combining Real-Time Mobile CH<sub>4</sub> Measurements with Infrared Imaging Leak Verification and Isotopic Fingerprinting

### Mobile Picarro Isotopic CH<sub>4</sub> Analyzer





- 4-wheel drive platform
- GPS
- Sonic Anemometer
- Wireless package
- Cloud Computing
- Real-time air and Mega-Core measurements

#### **FLIR Camera**



Thermal Infrared gas leak detection using the Regional Air Quality Council Optical Gas Imaging (OGI) Camera Loan Program (as available)

### **Examples of Outputs**

Las an reaction because the suggestion of the	pre - sension easy tenne news -	
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Select your run:		Location
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Tuesday, November 5th, 2013 : 3		A QUILDIN R
Wednesday, November 6th, 2013 : 3		
Thursday, November 7th, 2013 : 3		the star
Friday, November 8th, 2013 : 3		RARE CON
Saturday, November 9th, 2013 : 2		
Tuesday, November 26th, 2013 : 1		and the states of the
Tuesday, December 3rd, 2013 : 3		Plume Man
Wednesday, December 4th, 2013 : 1		Trans map
Thursday, December 5th, 2013 : 3		and the second sec
Friday, December 6th, 2013 : 1		
Saturday, January 18th, 2014 : 1		
▼ FDDS2036 : 07:13 PM : 3hrs 30mins Stare Download	Investigate	
4		

Real-Time analysis of ambient air and collection of 'Mega-Core', samples of transects that can be analyzed in detail for  $\delta^{13}$ C of CH<sub>4</sub> in post processing.



Use 'Keeling-plot' identification of isotopic source signatures to distinguish methane from natural gas and oil from landfills, feedlots, wetlands, etc. and use mass spectrometer analysis for air flask samples for  $\delta^{13}$ C and  $\delta$ D of CH<sub>4</sub>



Generate maps with measured  $CH_4$  concentration over study area along accessible roads. All data are archived and KML files aid visualization.



Use RAQC FLIR Camera to detect and verify point sources as found with infrared imagery.

### NOAA GMD & CU BAO and Mobile Sampling

Gaby Pétron, Jon Kofler, Audra McClure, Ben Miller, Steve Montzka, Ed Dlugokencky, Arlyn Andrews et al. Contact: Gabrielle.Petron@noaa.gov

#### Main goal: Characterizing hydrocarbon sources in the region



GMD Mobile Lab - In situ: CO<sub>2</sub>, CH<sub>4</sub>, CO, H<sub>2</sub>O (Picarro) Ozone (2B) - Flasks - Met



NOAA BAO Tower GMD CO<sub>2</sub>, CH<sub>4</sub>, CO (3 levels) Ozone (10m, 300m) Flasks at 300m PSD Met Fields (3+ levels)

http://www.esrl.noaa.gov/psd/technology/bao/

#### Methane time series at BAO



Example of survey (day and nighttime data)









## AML Goals at Frappe

- Characterization of oil and natural gas facilities near the Denver Julesburg Area (DJA)
- Emission measurements of feed lots and large scale dairy operations
- Explore particle and gaseous emissions from the commercial vehicle fleet
- Understand photochemical aging and daily transport of the urban plume



## Dual Tracer Release Example



- One second time response on every species.
- Better than 1 ‰ sensitivity on all species while mobile.









NW Wind

Natural Gas Liquid Tanks



Yacovitch, et al. (Submitted)



## Source Attribution Cont.





# Herd CH<sub>4</sub>/CO<sub>2</sub> Emission Ratio



- Given adequate dispersion and advection, one can sample a mixed herd plume.
- Herd emissions were monitored between 0 and 60M
- The herd plume represents the average emission ratio (Similar cattle)
- The results below are from 67 Beef Cattle



### Methane / CO<sub>2</sub>





## Vehicle Chase



#### AMS Profile:

Particle Phase: G

- BC
- Organics
- Gas Phase:
  - NO<sub>x</sub>
  - CO
  - CO<sub>2</sub>
  - VOC's
  - Hydrocarbons



## **Photochemistry - VOC Ratios**





 $\Delta t = [OH] / (1/(k_{VOC} - k_{benzene}) [In{VOC_0/Benzene_0} - In{VOC_t/Benzene_t}])$ 

### **Rocky Mountain National Park (ROMO)**

**Objective:** Supplement continuous monitoring occurring at ROMO during campaign intensive period.

Key areas of NPS interest: Oil and gas impacts, N deposition, O<sub>3</sub>

Ongoing measurement programs:

IMPROVE, AMoN, NADP, CASTNet (O<sub>3</sub>, met, filter packs)

CSU will play a significant role in supplemental measurements at ROMO.

#### **POTENTIAL MEASUREMENTS**

**VOC GC**: 4 channel cryoless GC-FID-ECD system

 $C_2$ - $C_{10}$  NMHCs,  $C_1$ - $C_5$  alkyl nitrates  $C_1$ - $C_2$  halocarbons, OVOCs, hourly measurements

Proton Transfer Reaction-Mass Spectrometer (PTR-MS): VOCs, OVOCs, CH<sub>3</sub>CN, DMS

6 minute cycle time (44 channels)

**GHG GC**: 2 channel GC FID-ECD system,  $CH_4$ ,  $CO_2$ , CO,  $N_2O$ ,  $SF_6$ , 10 minute cycle time **PAN GC**: GC-ECD, 10 minute cycle time

NO<sub>x</sub>, NO<sub>v</sub>: 1 minute data

**MARGA:** hourly gas (NH<sub>3</sub>, HNO<sub>3</sub>, SO<sub>2</sub>) and PM<sub>2.5</sub> (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>) **URG annular denuder system:** 24 hr gas and PM2.5 ions (levoglucosan if smoke impacts occur); possibly an additional system deployed in Fort Collins

#### Additional spatial sampling:

Portable ozone (2B Technologies) VOCs with canisters

 $NH_3$ 

## Typical data from the VOC GC, canisters and the PTR-MS Similar data products are expected from the other measurements



Cryoless VOC GC system (hourly) and daily canister samples

Cryoless VOC GC system (hourly) and PTR-MS

a)

b)

c)

7/22/04

# GO3 Project – Student Measurement of Ozone and Black



# **Colorado Monitoring Locations**



## Data Quality



### Mapping Methane Sources in the D-J Basin Using Airborne and Ground Measurements (proposed) NOAA/CIRES/INSTARR/Aerodyne/Scientific Aviation

- NOAA and Scientific Aviation would fly an instrumented light aircraft in a regular gridded pattern across the D-J to map methane and ethane sources.
- Three mobile labs (NOAA, INSTARR and Aerodyne) would drive a gridded patter across the basin similarly mapping methane "hot spots".
- Vans would have a combination of methane, ethane, Flask packs, and FLIR cameras.
- The aircraft and vans would interact to check each others observations and to check on persistence of the "hot spots".

Instrument	Measurement	Precision
Picarro 2301f	CO <sub>2</sub>	150 ppb (5 sec)
Picarro 2301f	Methane	1 ppb (5 sec)
Picarro 2301f	Water	6 ppm (5 sec)
Aerodyne	Ethane	0.06 ppb (1 sec)
2B Model 205	Ozone	1 ppb (10 sec)
Vaisala HMP60	Temperature	±0.5C
Vaisala HMP60	Relative Humidity	±3%
Airplane	Horizontal Wind	±0.3 m s <sup>-1</sup>
LGR	NO <sub>2</sub>	0.05 ppb (1 sec)

Table 1. Instruments that would fly on the Mooney light aircraft .



**Figure Legends**. **A.** Light aircraft proposed for use in the D-J successfully used by NOAA in Texas and Utah methane studies. **B.** Methane survey in the Uintah Basin, Utah flying above a strong temperature inversion. **C.** Methane measured beneath the temperature inversion.



## Supplemental Slides

# Intrinsic CO<sub>2</sub> Tracer



- Figure right shows strong correlation of CH<sub>4</sub> and CO<sub>2</sub> during HERD tracer release studies (single emission rate)
- One can estimate CO<sub>2</sub> flux from metabolic weight of the animal
- Mean CO<sub>2</sub> flux = 70±30 L kg<sup>-1</sup> BW<sup>0.75</sup> d<sup>-1</sup>
- BW <sup>0.75</sup> = Metabolic weight

• 
$$CH_{4(SLPM)} = CO_{2(SLPM)} * \frac{CH_{4(ppbv)}}{CO_{2(ppmv)}} * \frac{1}{1000}$$

Stewart et al.(2008) Kinsman et al. (1995) Boadi et al. (2002)





Ethane measurement assists methane source attribution