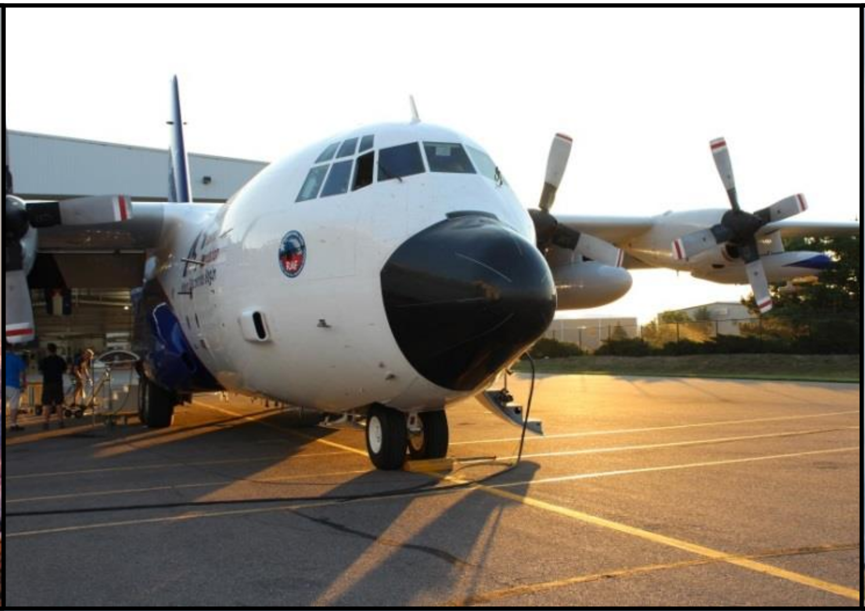
Existing VOC Measurements from the Colorado Front Range's Oil and Natural Gas Region: Availability, Value, and Limitations

Dr. Rebecca Hornbrook, NCAR, Boulder, Colorado

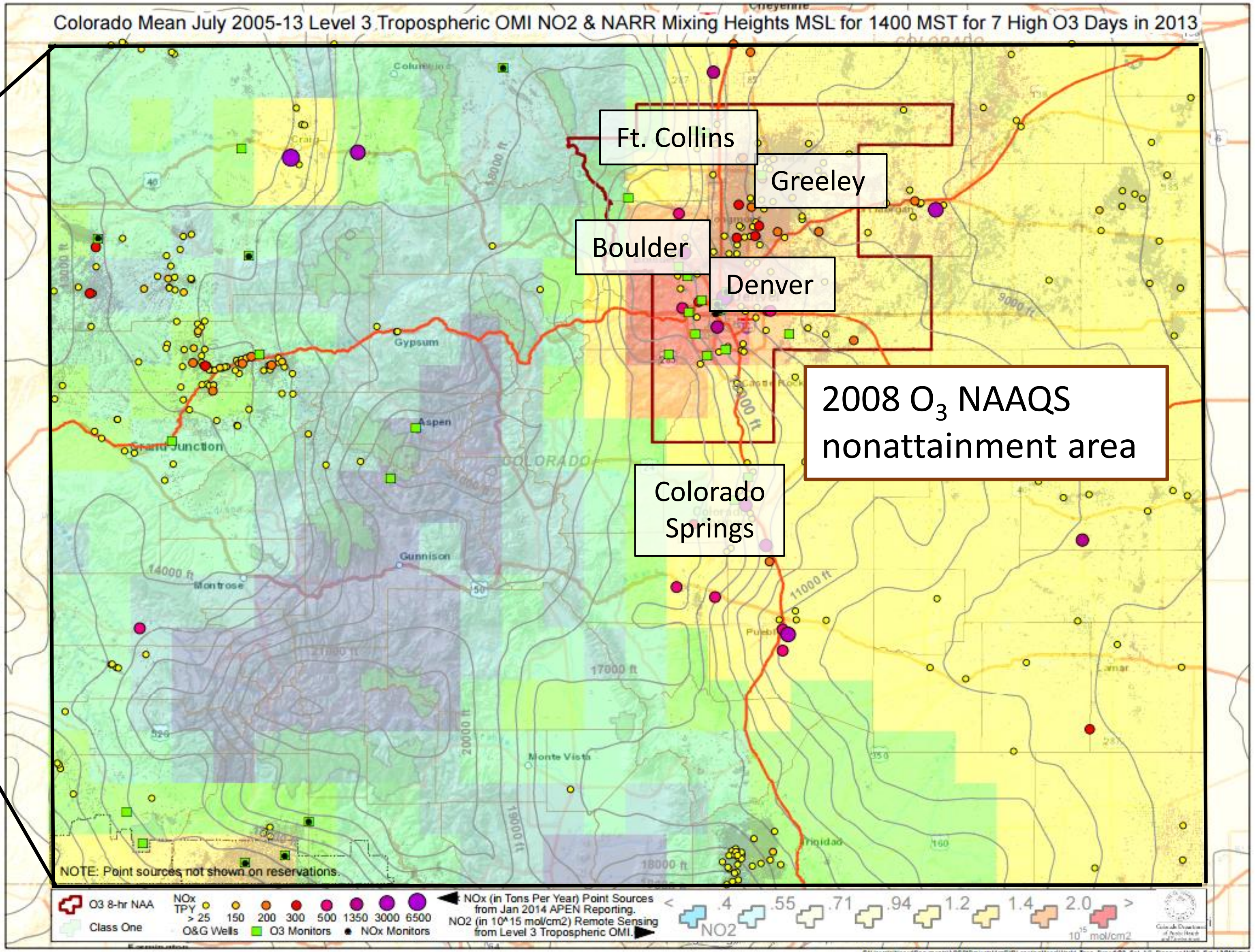
Dr. Eric Apel, Dr. Gabi Pfister, Dr. Lizzy Asher, Dr. Frank Flocke, NCAR
and the FRAPPÉ and DISCOVER-AQ science teams



Western North America Shale Plays

Source: Energy Information Administration based on data from various published studies.
Updated: May 9, 2011

Colorado: OMI NO_2; O_3 nonattainment (8-hour 75 ppbV) area



Front Range Air Pollution and Photochemistry Experiment, Summer 2014

Designed to answer the questions:

- What and where are the relevant sources and processes that lead to the Colorado Front Range exceeding ozone standards in the summer?
- How much pollution comes into Colorado from the outside (what is it we can do something about)?
- What are the best ways to improve air quality?

- ❖ Funded by the Colorado Department of Public Health and Environment (CDPHE), NSF, NOAA, National Park Service (NPS), EPA
- ❖ Joint project with NASA's **DISCOVER-AQ** (*Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality*)
- ❖ Four research aircraft (NSF/NCAR C-130, NASA P-3B, NASA B-200 King Air, NASA Falcon)
- ❖ Mobile vans, tower sampling, numerous ground sites, balloons, sondes, satellite data

All data are publicly available at https://www-air.larc.nasa.gov/missions/discover-aq/discover-aq.html
Project Field Catalog: http://catalog.eol.ucar.edu/frappe

NCAR TOGA (Trace Organic Gas Analyzer)

Instrument Specifications:

- fast online GC/MS
- 35-second samples every 2 minutes
- samples processed in flight
- analyzed post-flight for 60+ VOCs
- wide dynamic range
- detection limits at low pptv to sub-pptv range

Quantifies VOCs from several sources/types:

- Biogenic VOCs and oxidation products
- **Anthropogenic VOCs**
- **Oil & Gas Tracers** →
- Long-lived Halogenated VOCs
- Short-lived Halogenated VOCs
- OVOCs, including HCHO
- Alkyl Nitrates
- Biomass Burning tracers (HCN, CH_3CN)
- Sulfur-containing compounds (DMS, OCS)

Benzene
Toluene
Ethylbenzene
***m*-/*p*-Xylene**
***o*-Xylene**

i.e., BTEX

Also, O&G relevant alkanes
Propane
Isobutane
n-butane
Isopentane
n-Pentane
2-Methylpentane
3-Methylpentane
***n*-Hexane**
n-Heptane

+ OVOCs (**CH_2O**, **CH_3CHO**, **CH_3OH**, Ethanol, Acetone, MEK, …)

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- c … e

TOGA routinely quantifies 34 of 187 EPA Hazardous Air Pollutants listed under the Clean Air Act

Q

- B
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***n*-Hexane**
n-Heptane

+ OVOCs (**CH_2O, CH_3CHO, CH_3OH**, Ethanol, Acetone, MEK, …)

TOGA installed on the C-130

C-130 inlets

Other VOC measurements

NSF/NCAR C-130

- *Picarro* (CH_4)
- *CAMS* (Ethane, CH_2O)
- *UCI Canisters* (NHMC, alkyl nitrates, HVOCs, CH_4 isotopes)
- *PTR-MS* (Isoprene, Terpenes, Aromatics, OVOCs)
- *CIMS* (PAN, PPN)
- *PCIMS* (Peroxides, Acids)

NASA P-3B

- *DACOM* (CH_4)
- *TILDAS* (Ethane)
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- *PTR-TOF* (Propene, Isoprene, Terpenes, Aromatics, OVOCs)

Boulder Foothills Lab

- *NCAR FTS* (column HCN, Ethane, Ethyne, CH_2O)

CU Mobile Lab

- *DOAS* (column Ethane and CH_2O)

NOAA Mobile Lab

- *UCI Canisters* (NHMC, HVOCs, alkyl nitrates, CH_4 isotopes

Aerodyne Mobile Lab

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- *QCL_TILDAS* (Methane, Ethane, Ethyne)

Platteville

- *UCI Canisters* (NHMC, alkyl nitrates, HVOCs)

BAO Tower

- *Picarro* (CH_4)
- *CIMS* (PAN)

Other

- *CU Canisters* (NMHC)
- *UCI Canisters* (NMHC)
- *NPS canisters* (NMHC) *and PTR-MS* (OVOCs, aromatics)
- *RMNP CIMS* (PAN)



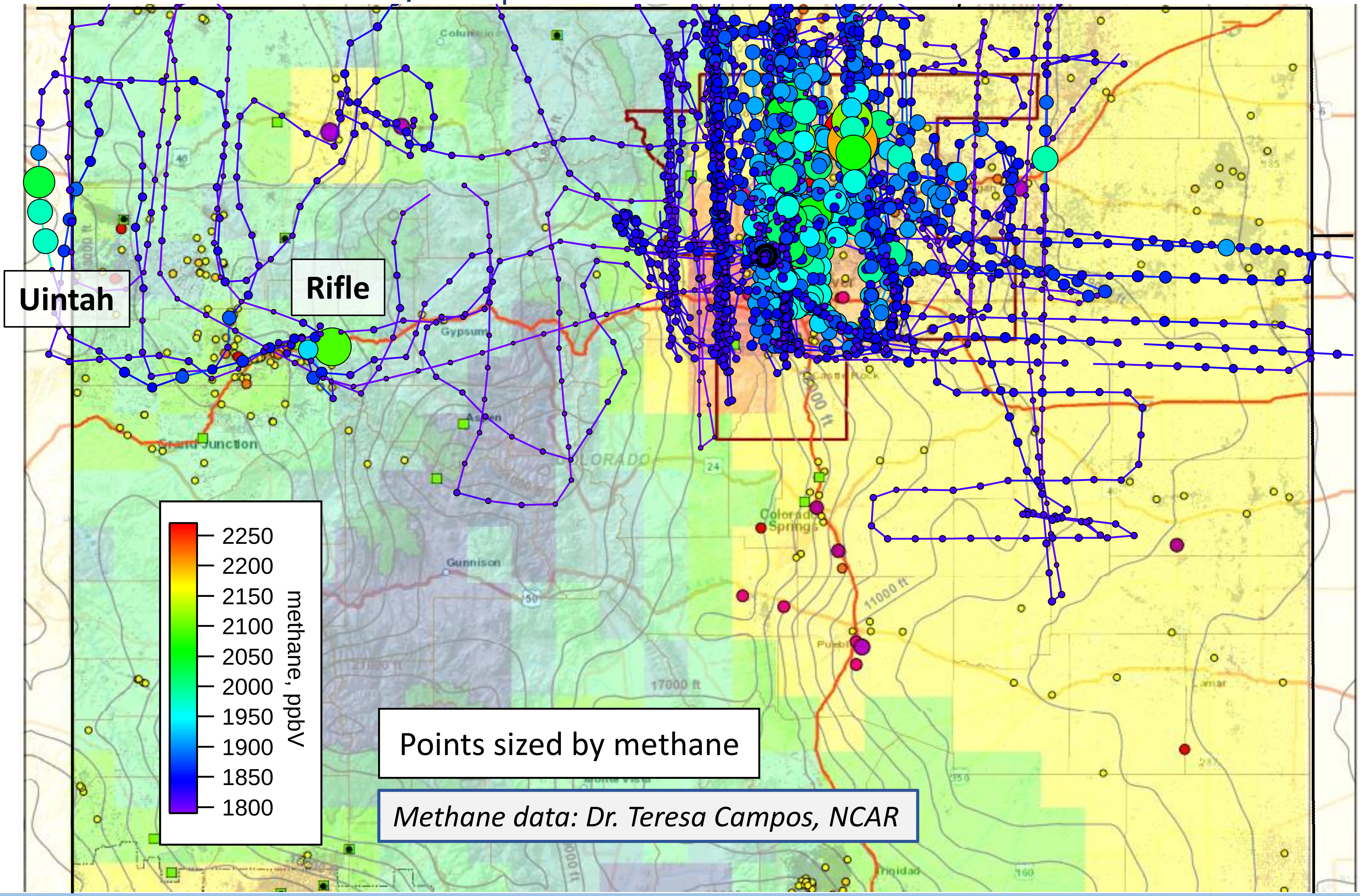



FRAPPÉ C-130 Observations – Methane, CH_4

(1-s observations averaged over the TOGA timescale)

Uintah – Uinta Basin
Rifle – Piceance Basin

Denver-Greeley – Denver-Julesberg Basin



FRAPPÉ C-130 Observations – Ethane, C_2H_6

(1-s observations averaged over the TOGA timescale)

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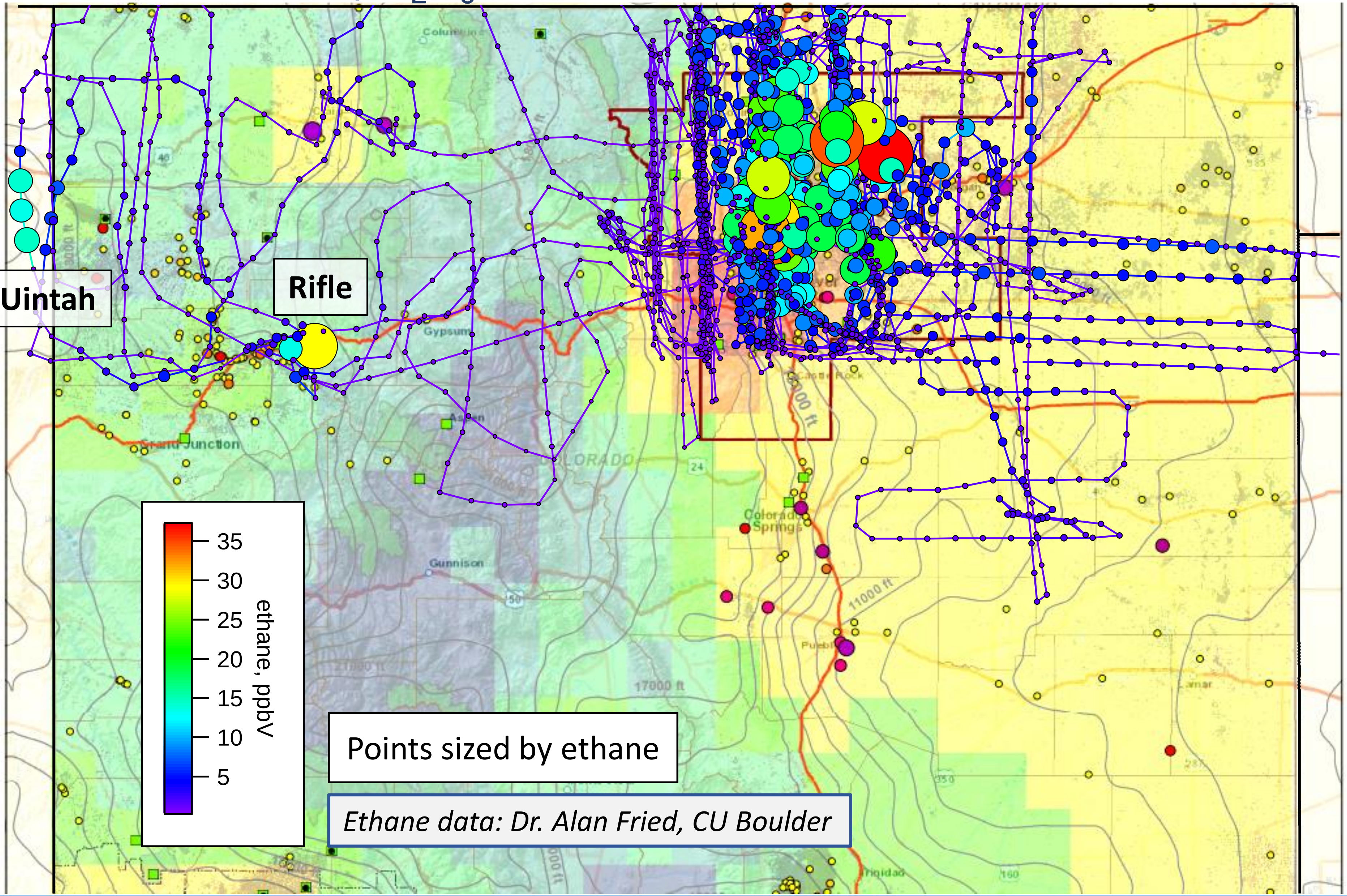
Rifle – Piceance Basin

Denver-Greeley – Denver-Julesberg Basin



FRAPPÉ C-130 Observations – n-Butane, C_4H_{10}

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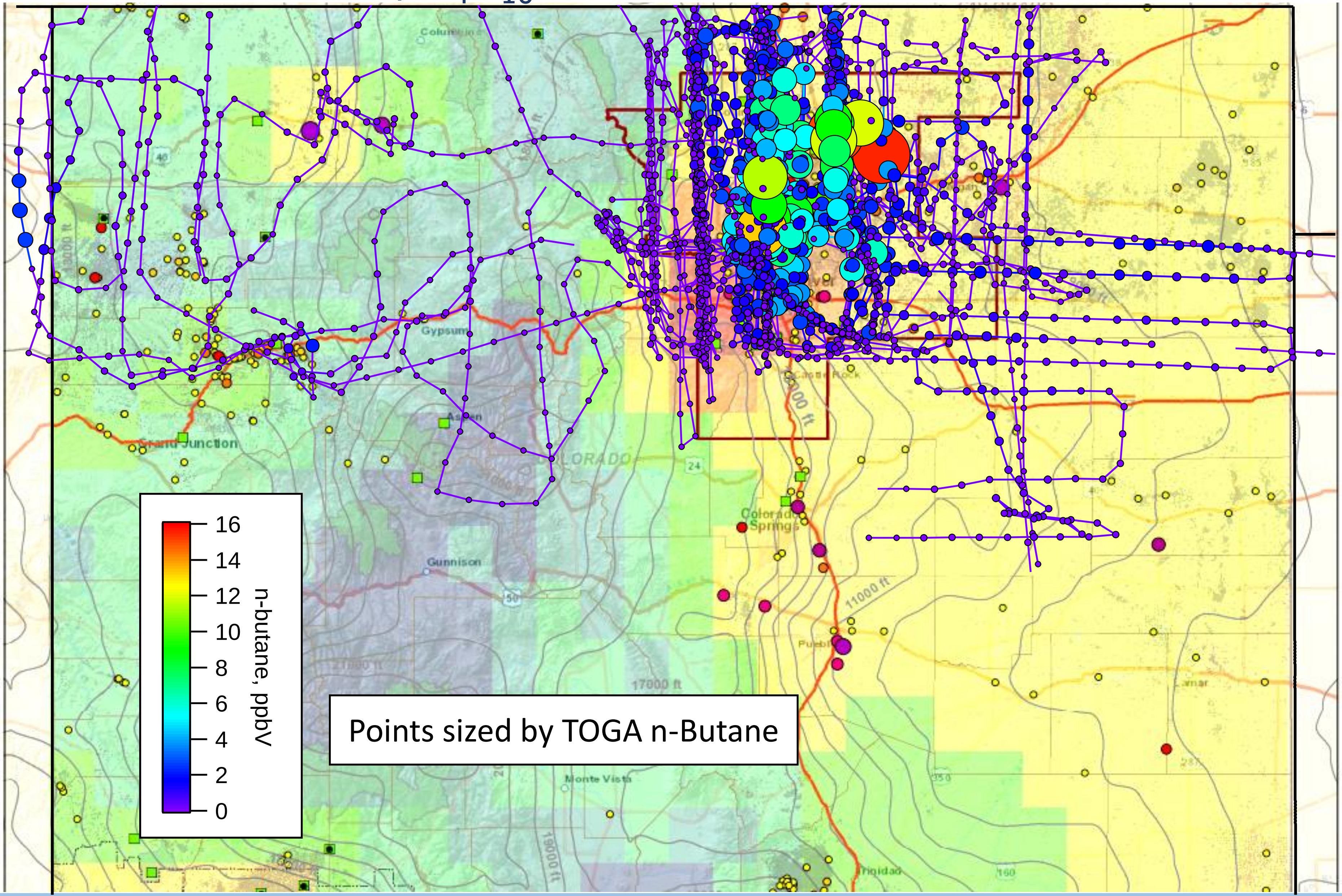
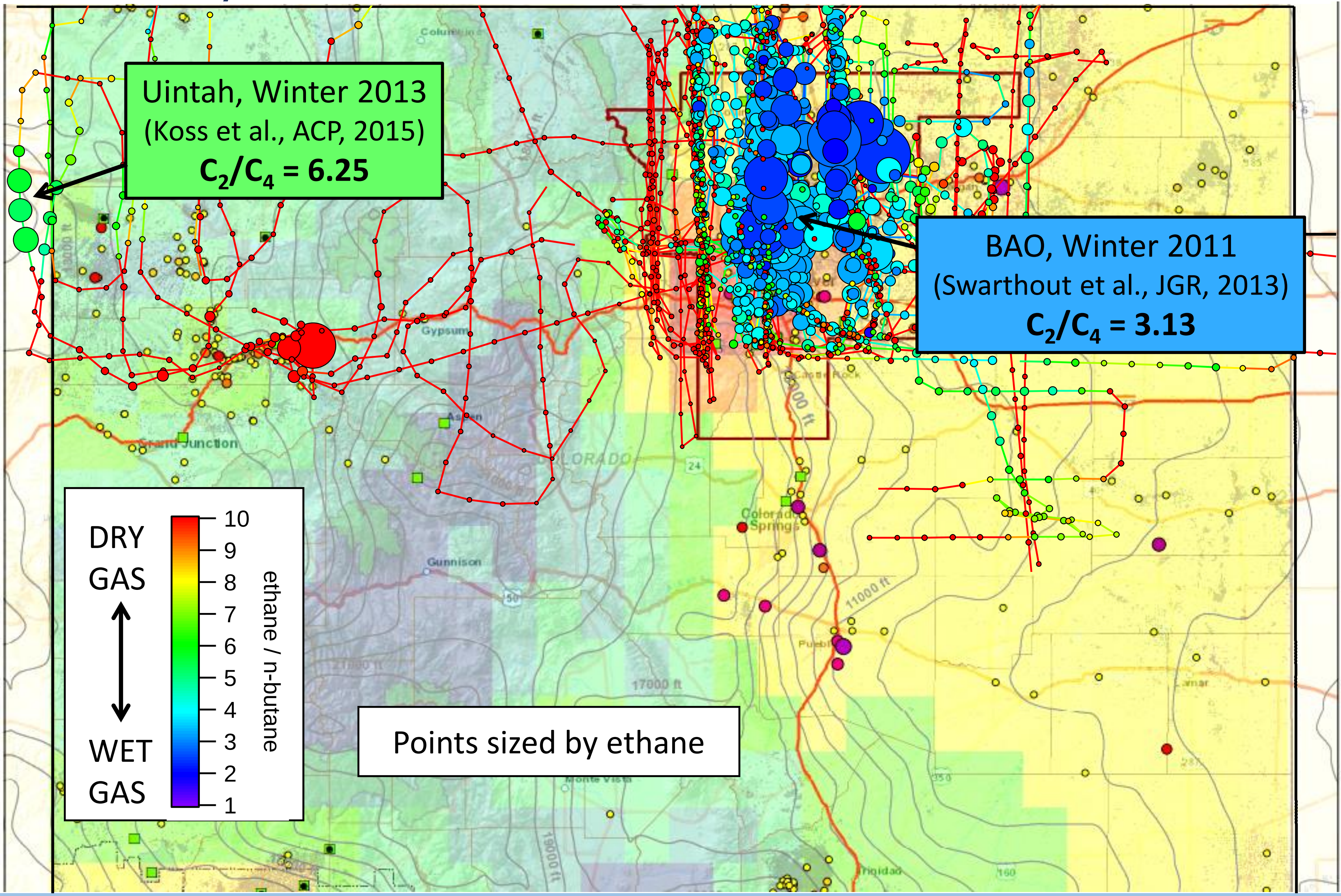
Rifle – Piceance Basin

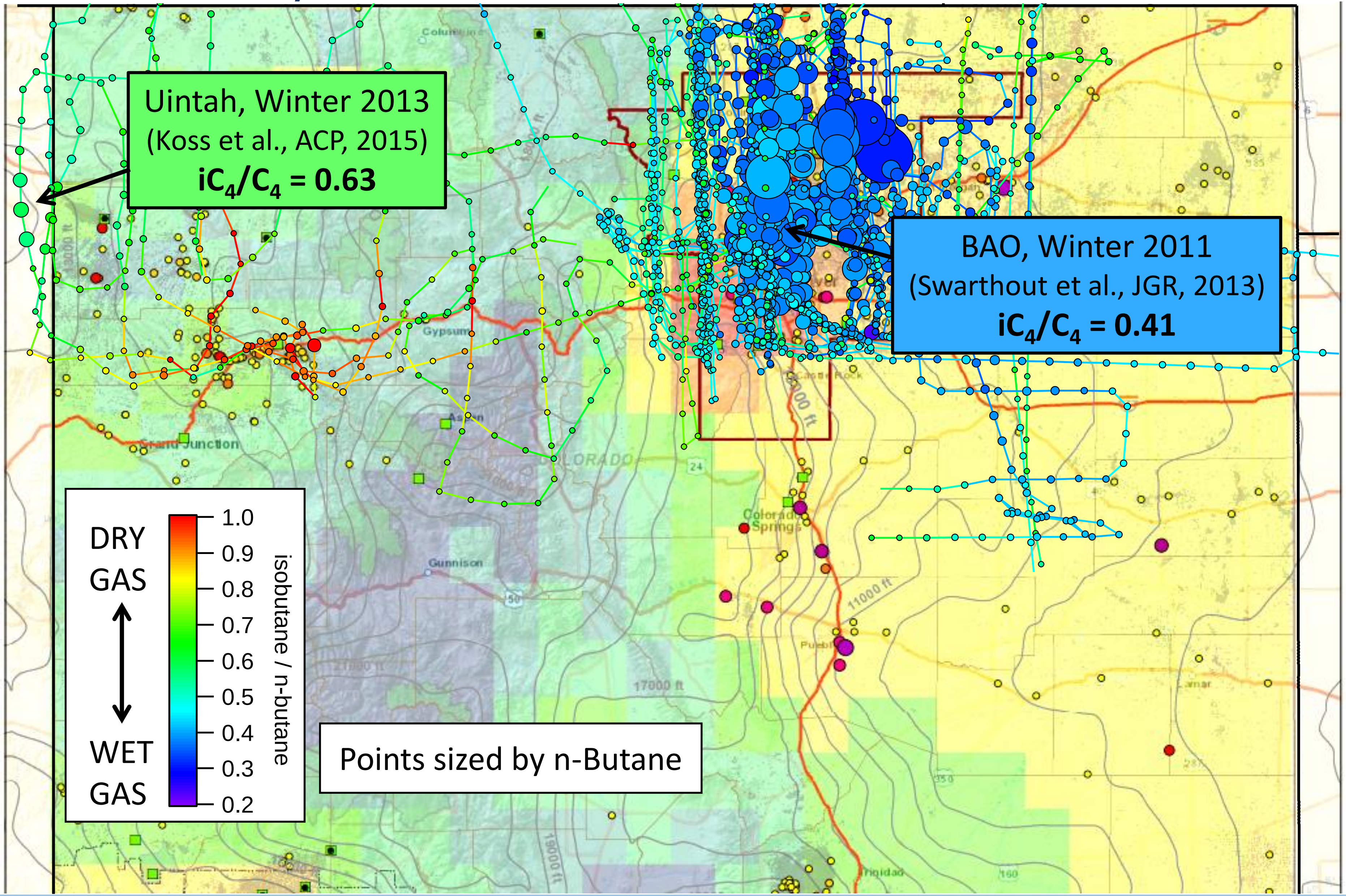
Denver-Greeley –
Denver-Julesberg Basin



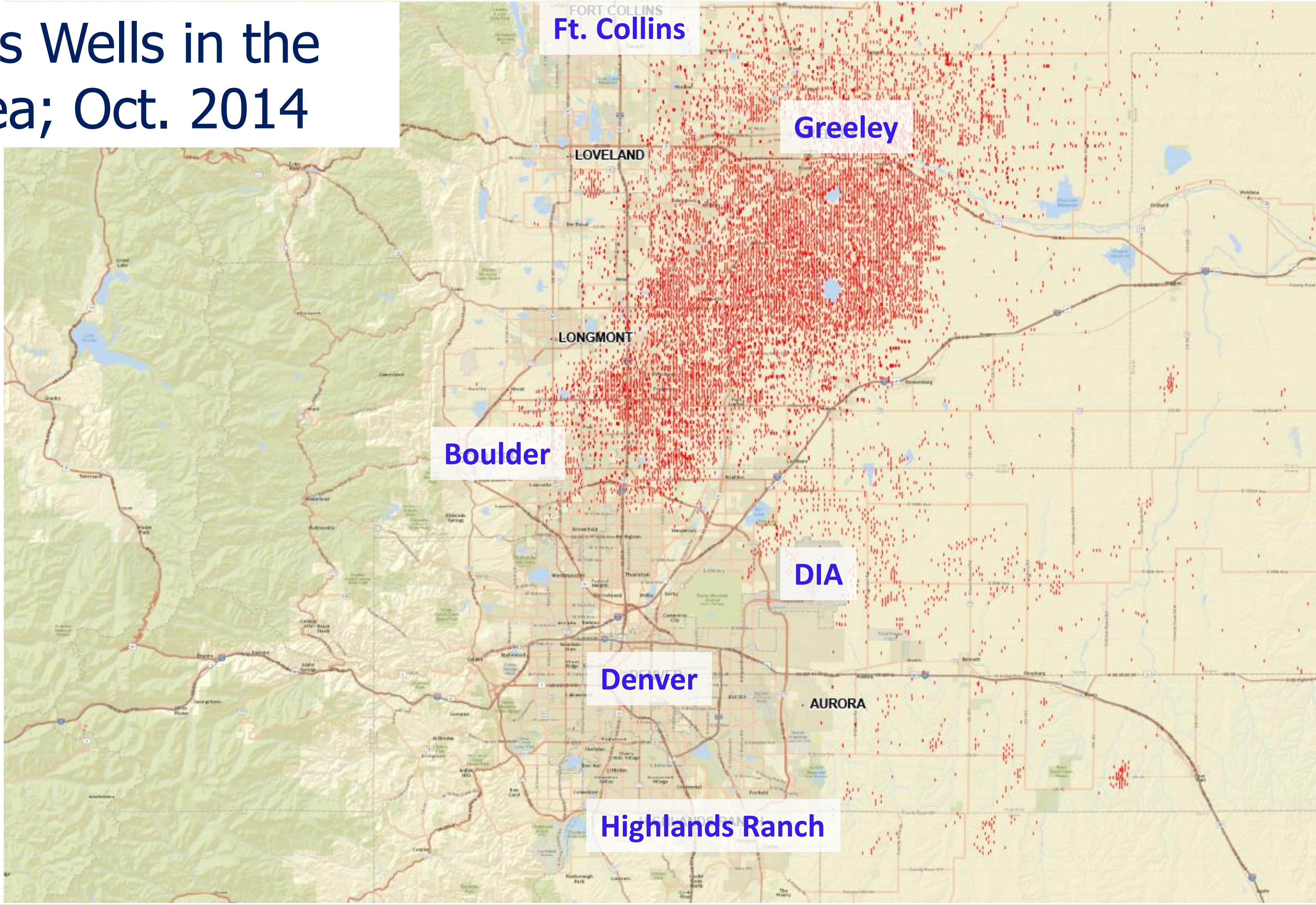
Ratios of Ethane/n-Butane - Dry vs. Wet Shale Gas



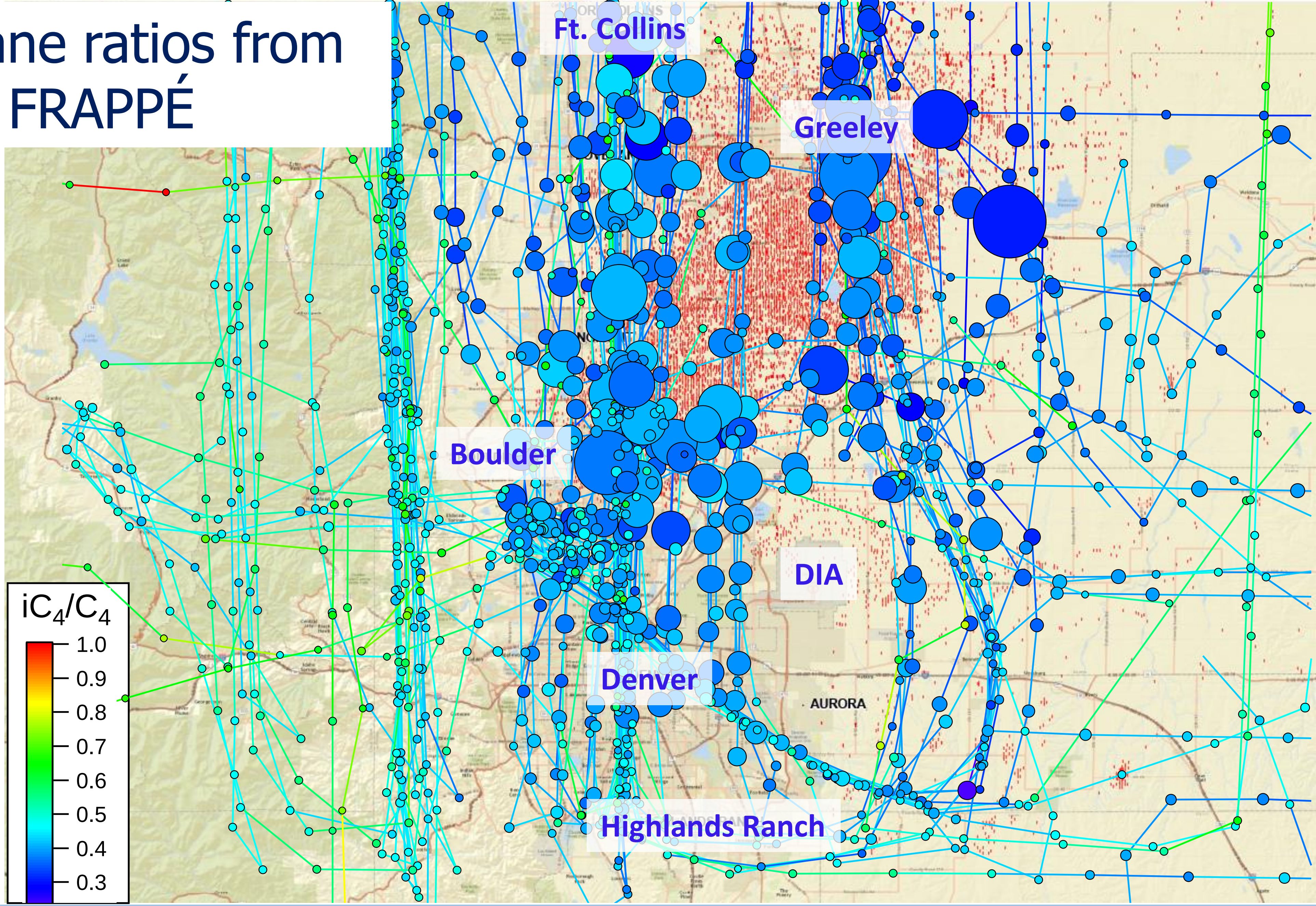
Ratios of Isobutane/n-Butane – Dry vs. Wet Shale Gas



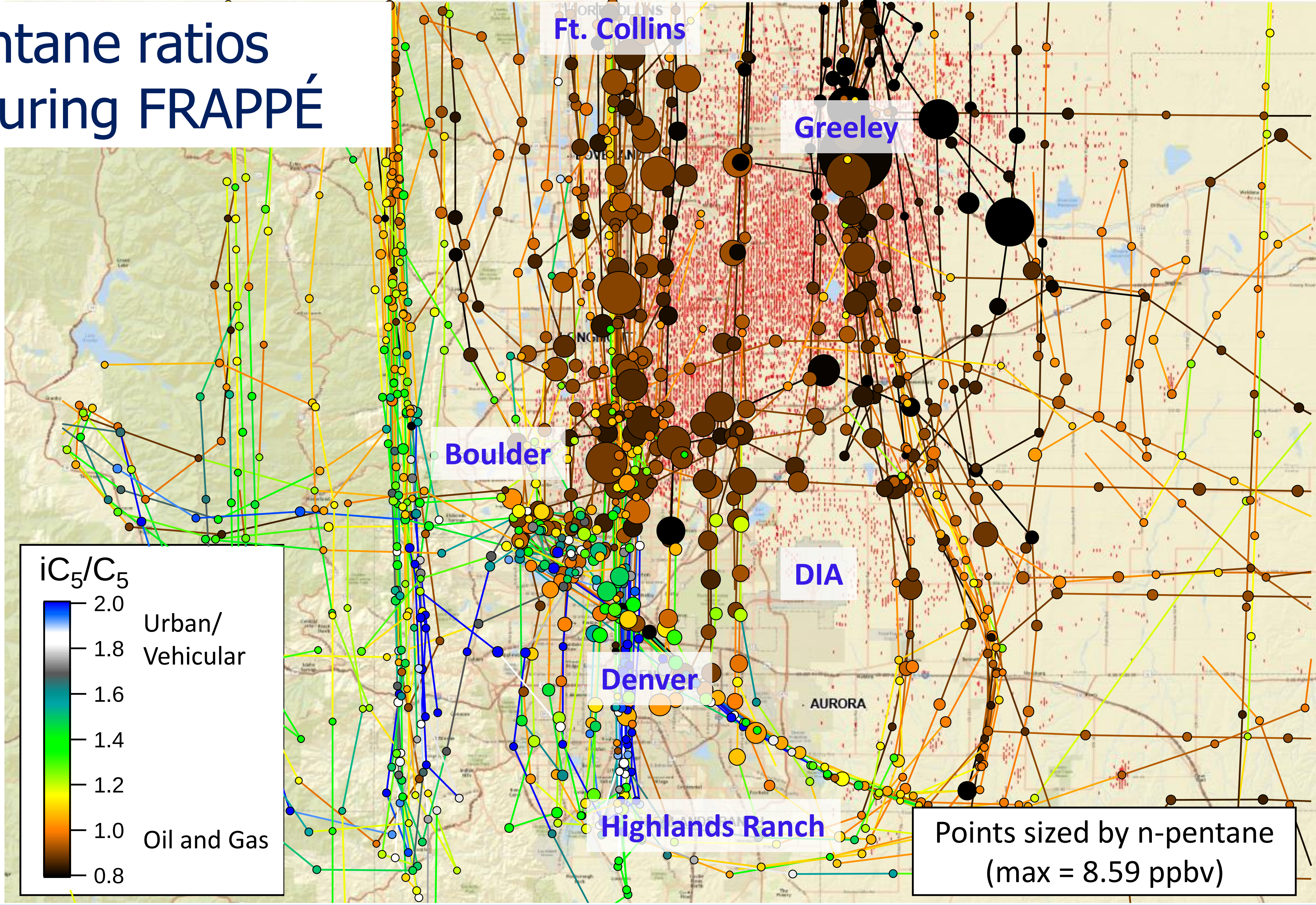
Active Oil and Gas Wells in the Denver Metro Area; Oct. 2014



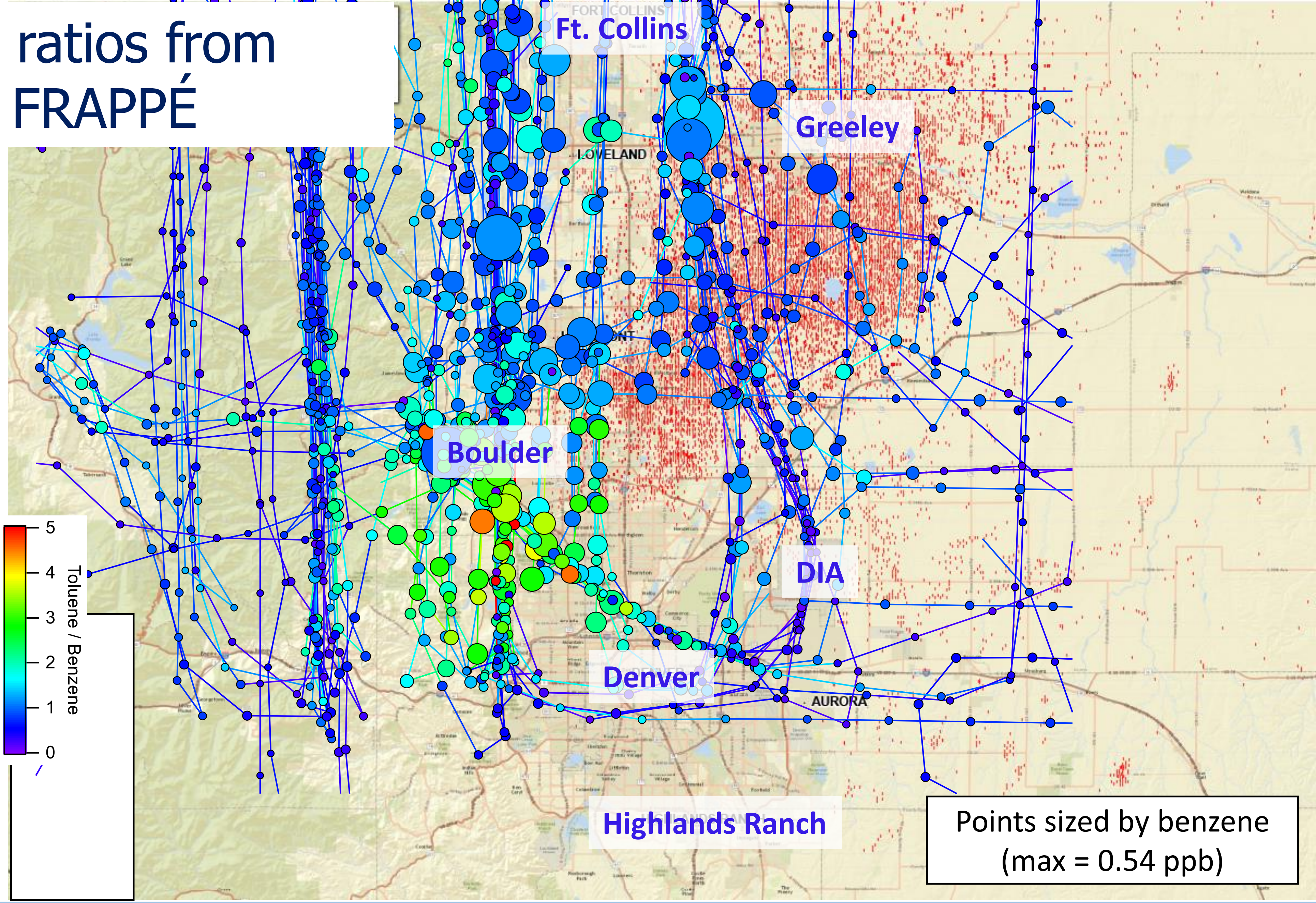
Isobutane/n-Butane ratios from the C-130 during FRAPPÉ



Isopentane/n-Pentane ratios from the C-130 during FRAPPÉ

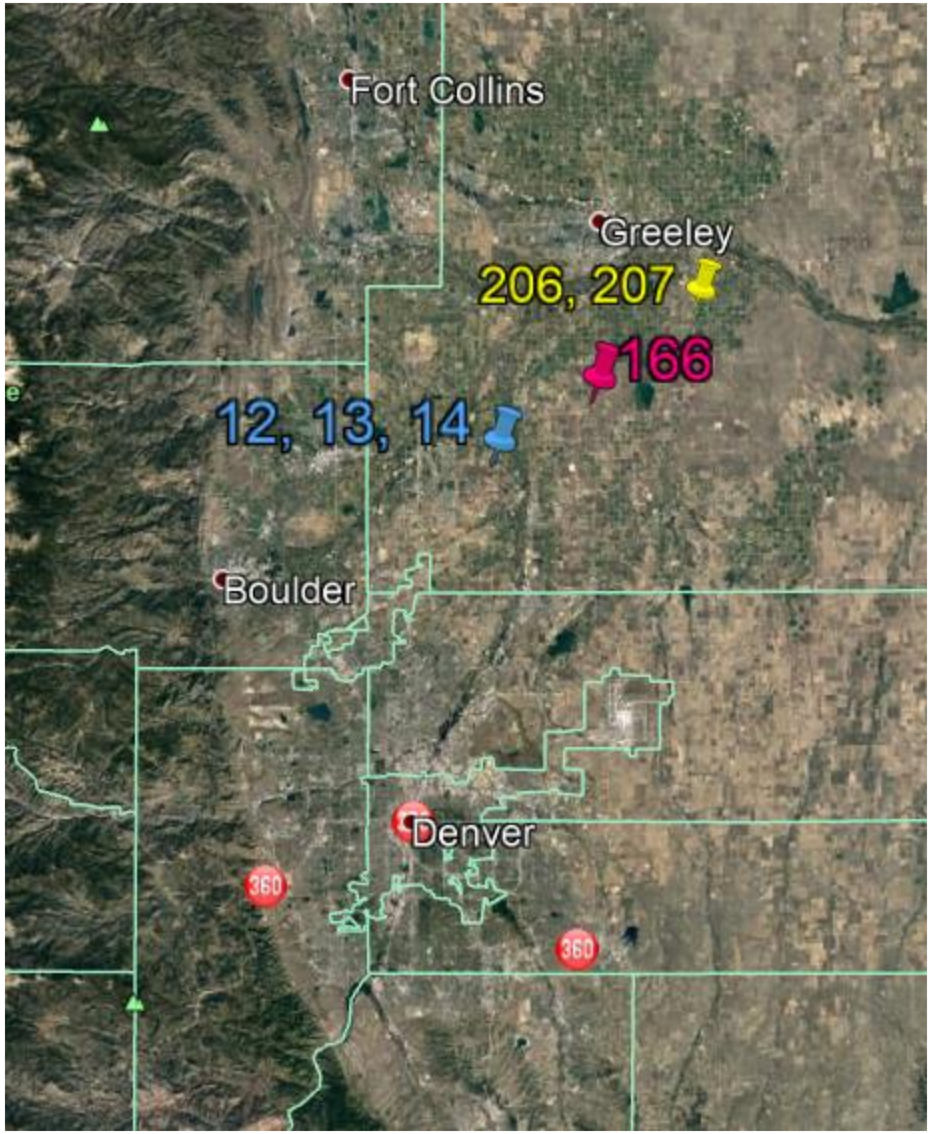


Toluene/Benzene ratios from the C-130 during FRAPPÉ



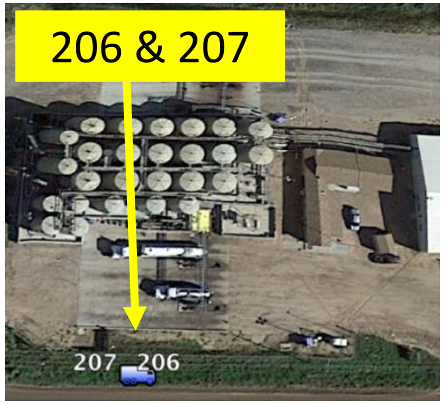
Points sized by benzene (max = 0.54 ppb)

Ground-based Canister Sampling



The ratios of the VOCs in the ground-based whole air samples can be compared to the aircraft measurements, connecting near-field and regional data.

index	latitude	longitude	CH4_ppmv	Ethane_pptv	Ethyne_pptv	Propane_pptv	Benzene_pptv	Toluene_pptv
166	40.2169	-104.7206	1.93	21,810	259	55,296	120,807	105,708
206	40.3197	-104.5678	2.19	60,643	406	158,469	62,666	48,405
14	40.1453	-104.8694	3.45	141,901	144	92,304	42,686	55,206
207	40.3197	-104.5678	2.17	61,376	347	128,046	36,780	37,423
13	40.1453	-104.8694	3.53	353,178	302	198,842	33,673	92,257
12	40.1453	-104.8694	3.41	335,157	277	190,545	30,864	82,111
25	40.2467	-104.8144	3.10	828,036	313	793,001	24,278	29,512
24	40.2467	-104.8144	3.07	538,869	327	635,712	23,564	28,111
68	40.3647	-104.8328	2.34	303,854	134	399,946	11,668	8,046
5	40.0147	-104.8972	2.84	258,838	641	505,596	8,637	7,194



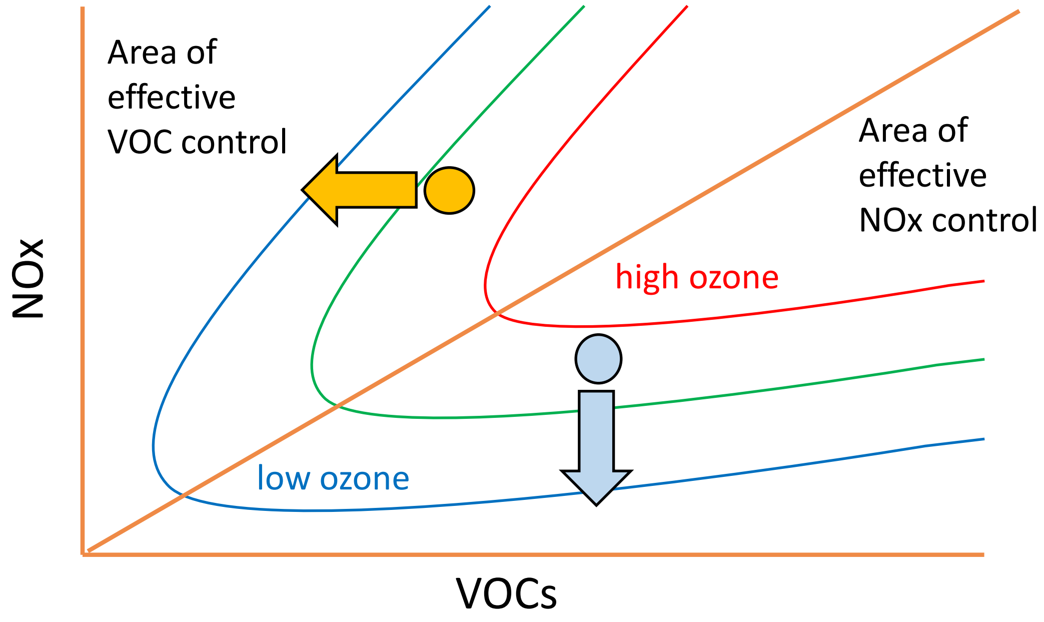
Pollutant Mitigation Strategies

Mitigation Strategies for **<u>Primary Pollutants</u>** are clear: Reduced Emissions = Reduced concentrations*

Mitigation Strategies for **<u>Secondary Pollutants</u>** are much more complex:

The chemical processes producing Secondary Pollutants are non-linear, e.g. ozone

- They depend on emissions of precursors

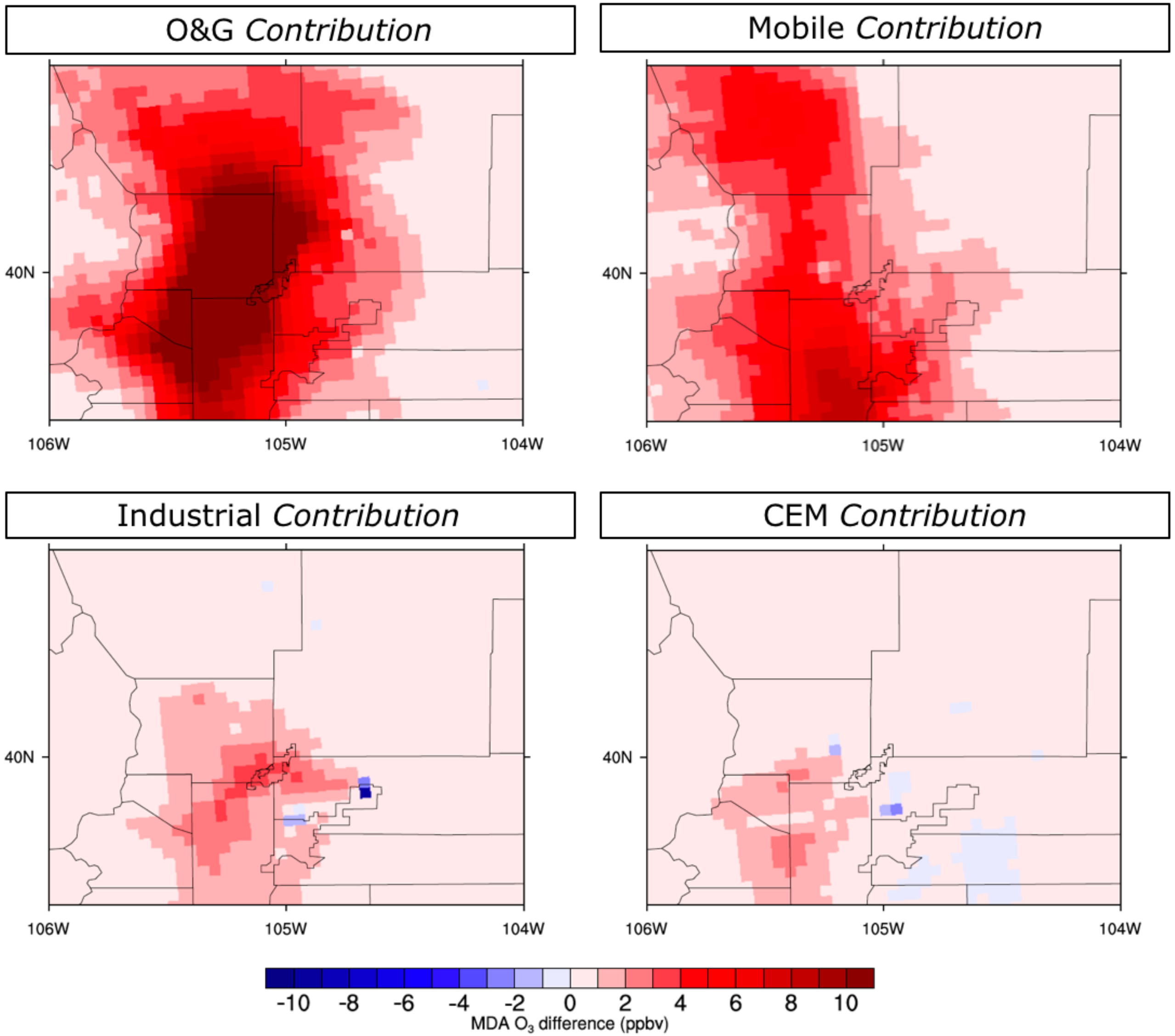


Ozone Production is limited by the **availability of VOCs**
⇒ **Reducing VOC emissions** most effective

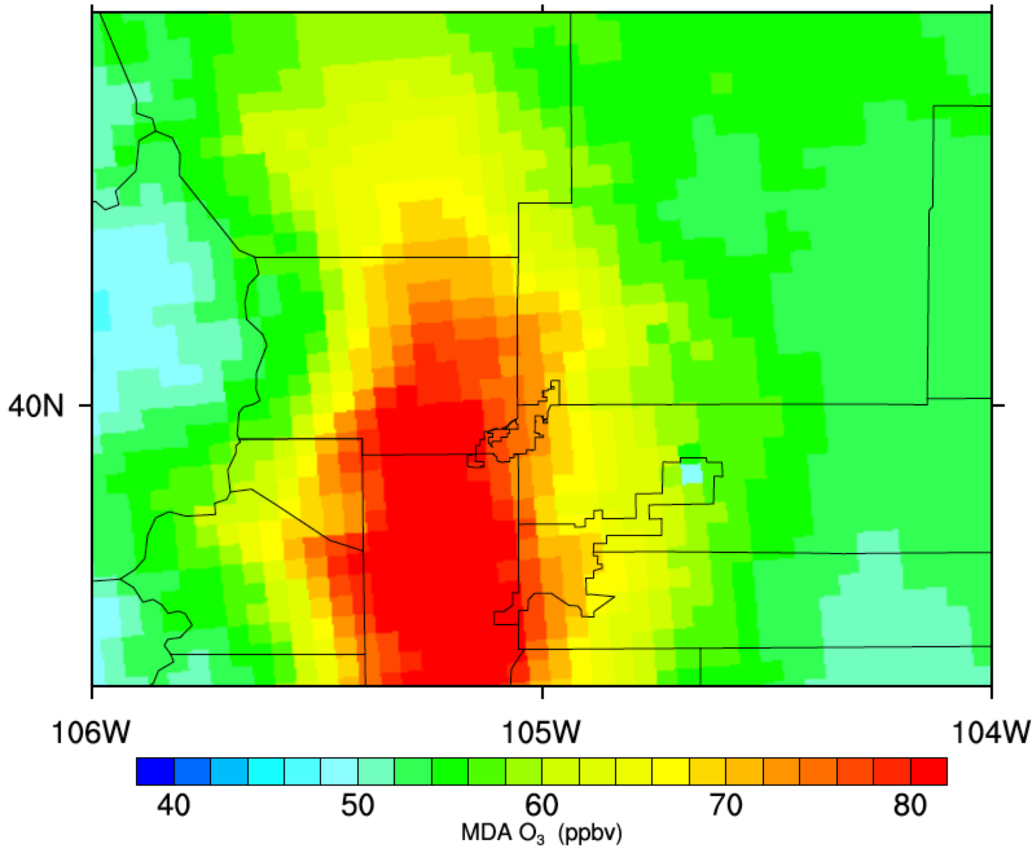
Ozone Production is limited by the **availability of NOx**
⇒ **Reducing NOx** emissions most effective

* non-local transport of pollution could counteract local mitigation strategies!

WRF-chem Modeling at NCAR

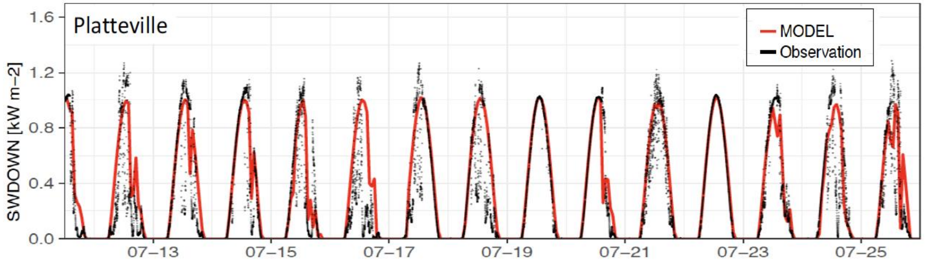


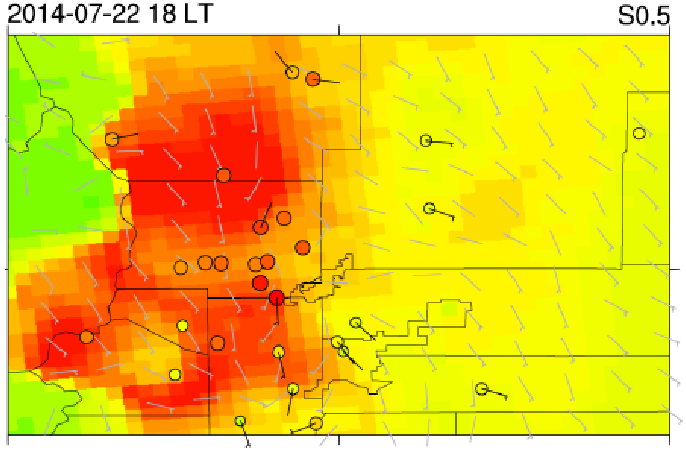
Modeled Ozone MDA8 (28 July)

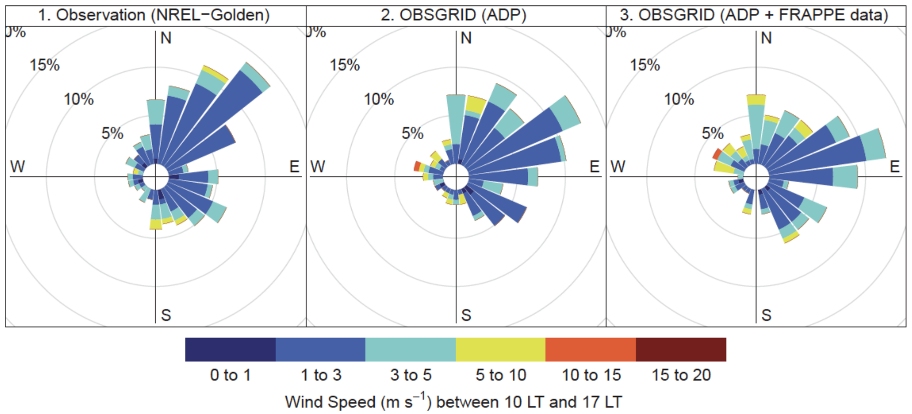


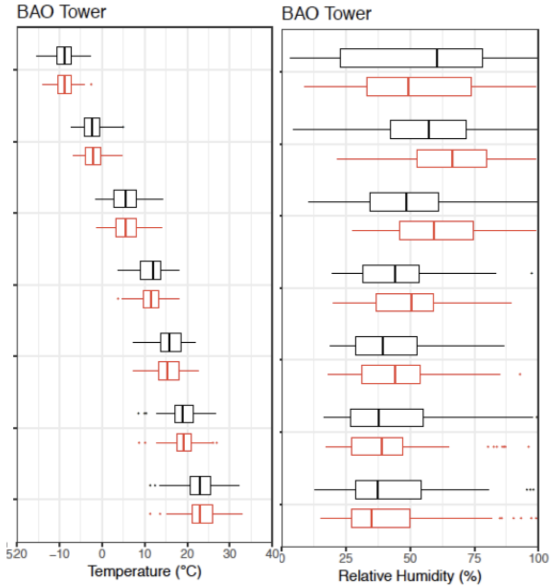
The NCAR FRAPPÉ report is publicly available at: https://www2.acom.ucar.edu/frappe

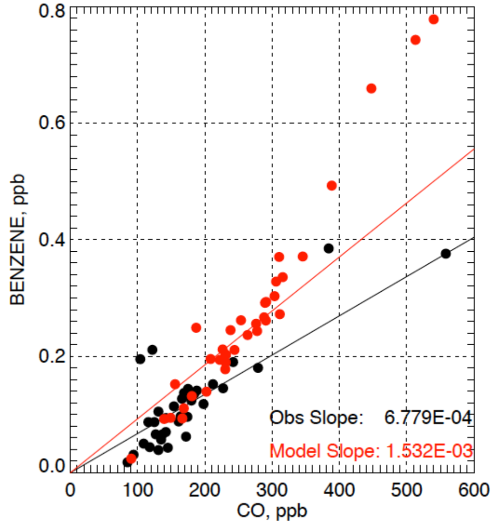
O_3 modeling efforts have involved an ensemble of available data

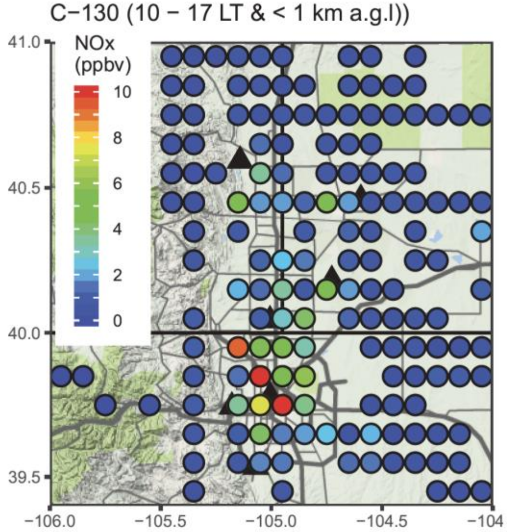


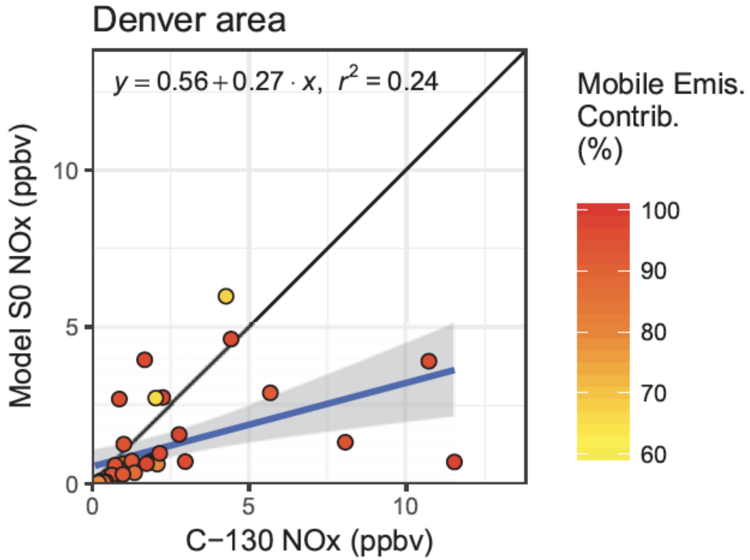


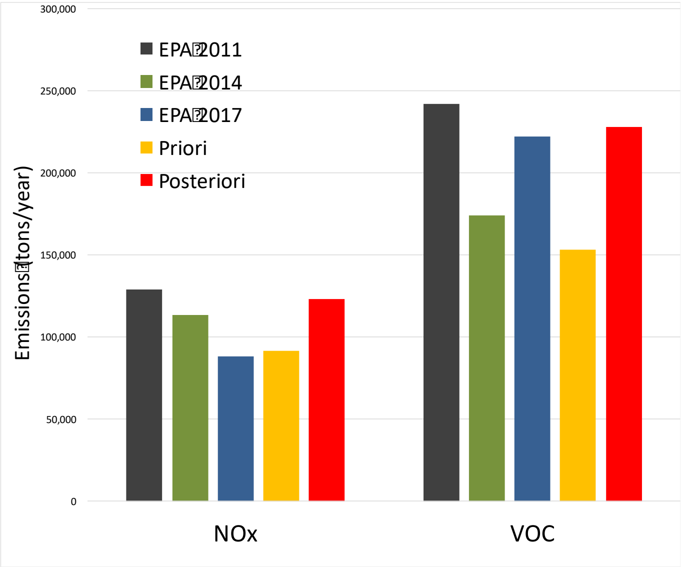












Selected publications using FRAPPÉ data

- Baier *et al*., Higher measured than modeled ozone production at increased NOx levels in the Colorado Front Range, *Atmos. Chem. Phys.*, 2017.
- **Bahreini *et al*., Sources and characteristics of summertime organic aerosol in the Colorado Front Range: perspective from measurements and WRF-Chem modeling, *Atmos. Chem. Phys.*, 2018.**
- Battye *et al*., Evaluating ammonia (NH_3) predictions in the NOAA National Air Quality Forecast Capability (NAQFC) using *in situ* aircraft, ground-level, and satellite measurements from the DISCOVER-AQ Colorado campaign, *Atmos. Environ*., 2016.
- Benedict *et al*., Volatile Organic Compounds and Ozone in Rocky Mountain National Park during FRAPPÉ, *Atmos. Chem. Phys. Disc*., 2018.
- Cheadle *et al*., Surface ozone in the Colorado northern Front Range and the influence of oil and gas development during FRAPPE/DISCOVER-AQ in summer 2014, *Elementa*, 2017.
- **Dingle *et al.*, Aerosol optical extinction during the Front Range Air Pollution and Photochemistry Éxperiment (FRAPPÉ) 2014 summertime field campaign, Colorado, USA, *Atmos. Chem. Phys*., 2016.**
- Evans and Helmig, Investigation of the influence of transport from oil and natural gas regions on elevated ozone levels in the northern Colorado front range, *J. Air Waste. Manag. Assoc*., 2017.
- **Halliday *et al.*, Atmospheric benzene observations from oil and gas production in the Denver-Julesburg Basin in July and August 2014, *J. Geophys. Res. Atmos.*, 2016.**
- McKenzie *et al*., Ambient Nonmethane Hydrocarbon Levels Along Colorado's Northern Front Range: Acute and Chronic Health Risks, *Environ. Sci. Technol.*, 2018.
- Sullivan *et al.*, Quantifying the contribution of thermally driven recirculation to a high-ozone event along the Colorado Front Range using lidar, *J. Geophys. Res. Atmos.*, 2016.
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FRAPPÉ data has not been fully exploited to explore the impact of air toxics emissions and population exposure.

Unmanned Whole Air Sampling System (UWASS)

Drone-platform whole air canister sampling system

Dr. Lizzy Asher, NCAR

- Collects up to 15 canisters per flight
- Sample size sufficient for duplicate TOGA subsamples
- Filters particles > 2 µm
- Logs ambient T, RH, P, wind speed and wind direction using the onboard Trisonica Mini anemometer, as well system P, system flow, and GPS at a sampling resolution of 1 Hz,
- PID sensor for plume detection
- Computer programmed or piloted flights
- 0'– 400' AGL without FAA clearance

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Drone-platform whole air canister sampling system

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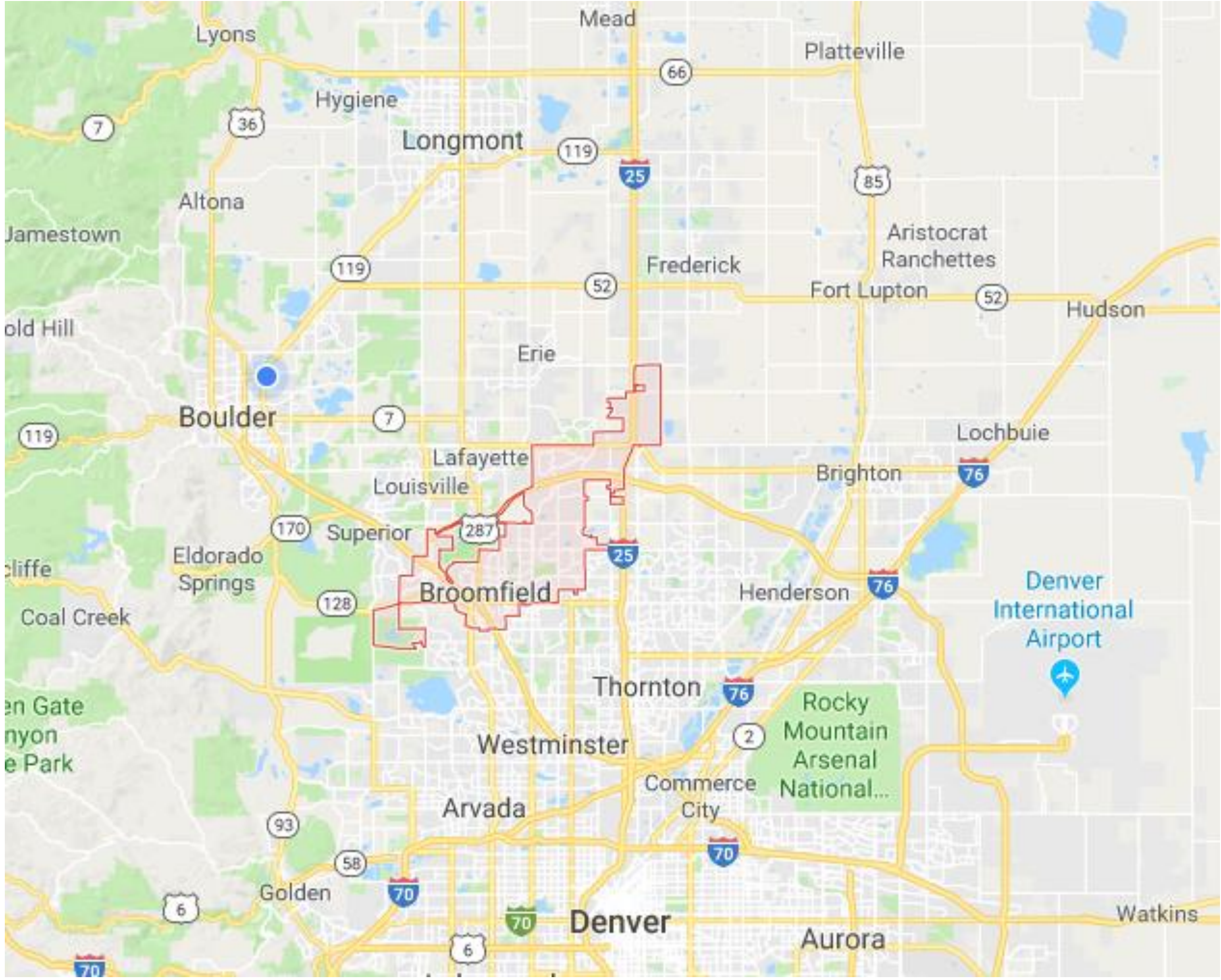
In cooperation with the City of Broomfield, Colorado and the CDPHE mobile lab (Daniel Bon)

UWASS field testing planned for October 2018:

- sampling in the vicinity of a new drilling site
- 3D mapping of air toxics emissions
- sampling at different times of the day to explore boundary layer and meteorological impacts
- potential for additional sampling dependent on funding



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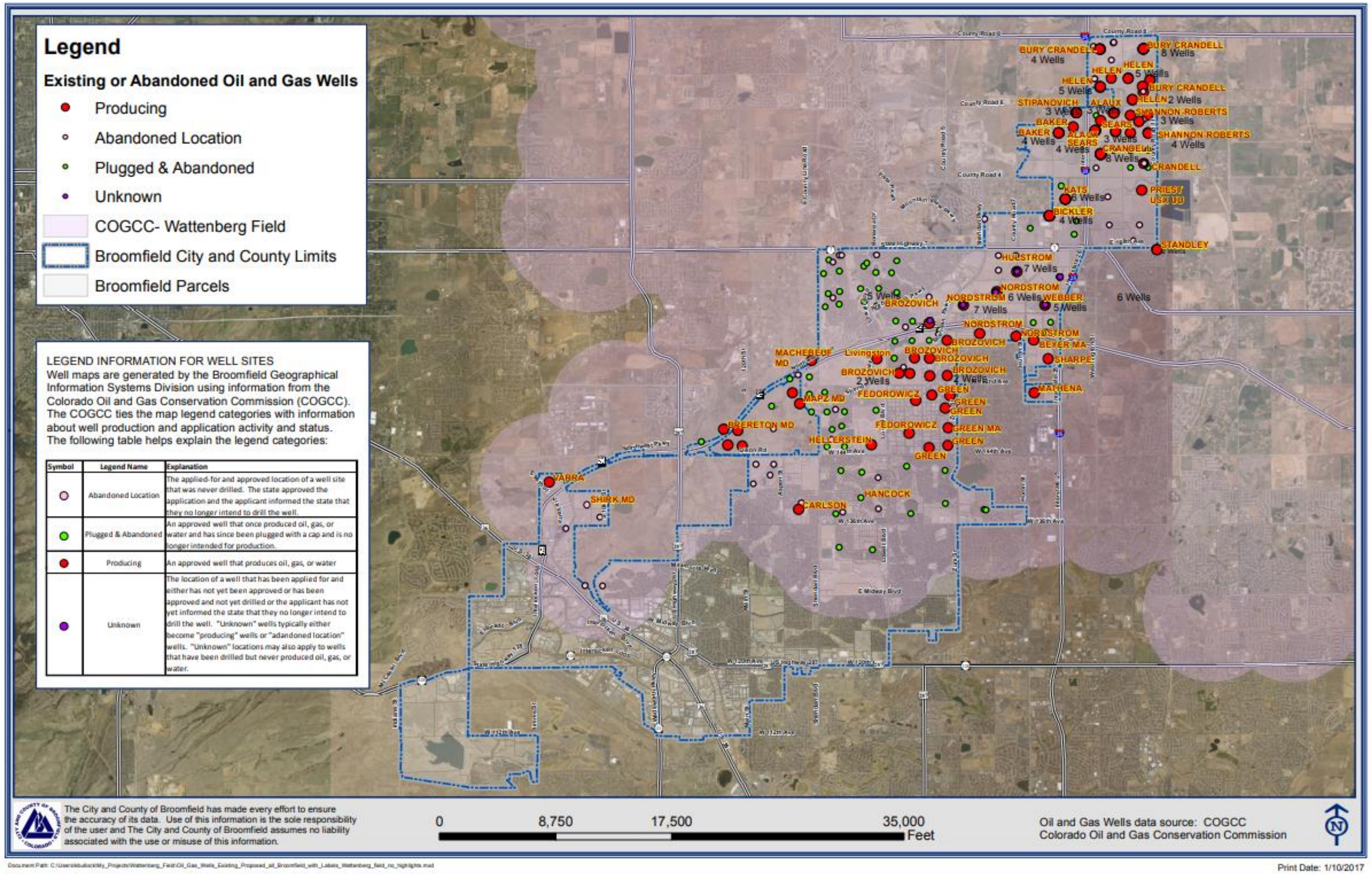

Summary

- FRAPPÉ provided an extensive atmospheric chemistry data set in the Colorado Front Range, including extensive VOC data.
- Several peer-reviewed papers have been published using the FRAPPÉ and DISCOVER-AQ data, but the primary focus thus far has been on O_3 production and air quality.
- The VOC data set has not been fully exploited as an ensemble with respect to population exposures and impacts of air toxics
- UWASS drone sampling adds a unique capability for quantifying the spatial extent and dispersion of air toxics emissions from unconventional oil and gas development.

NCAR TOGA (Trace Organic Gas Analyzer)

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Isobutane	**Toluene**
n-butane	**Ethylbenzene**
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n-Pentane	***o*-Xylene**
2-Methylpentane	
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***n*-Hexane**	**CH_3CHO, CH_3OH**,
n-Heptane…	Ethanol, Acetone, …)

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