FRAPPÉ - Air Quality Research as a Key to Addressing Societal Needs

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NSF

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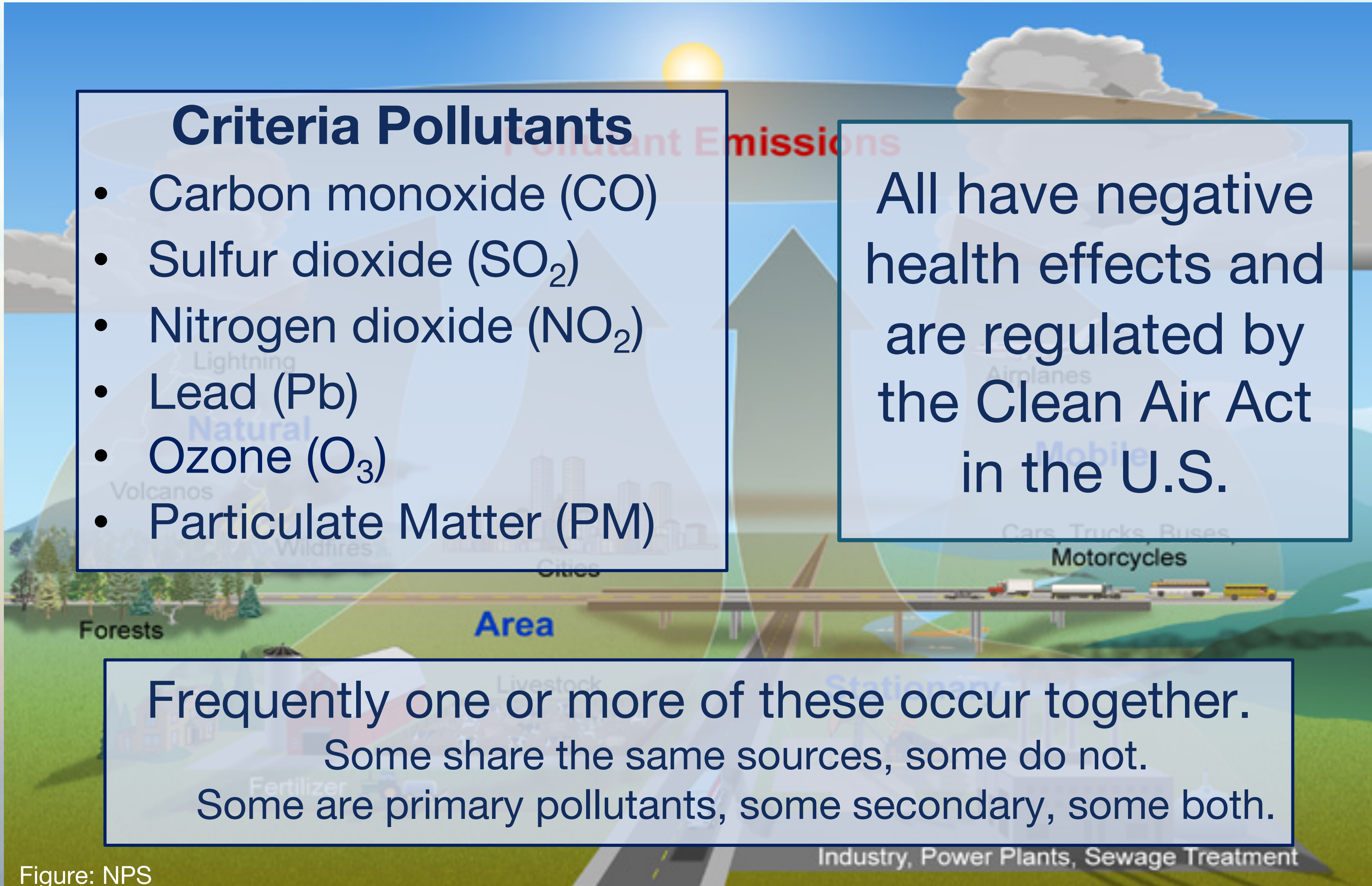
Air Quality – Why care?



Criteria Pollutants

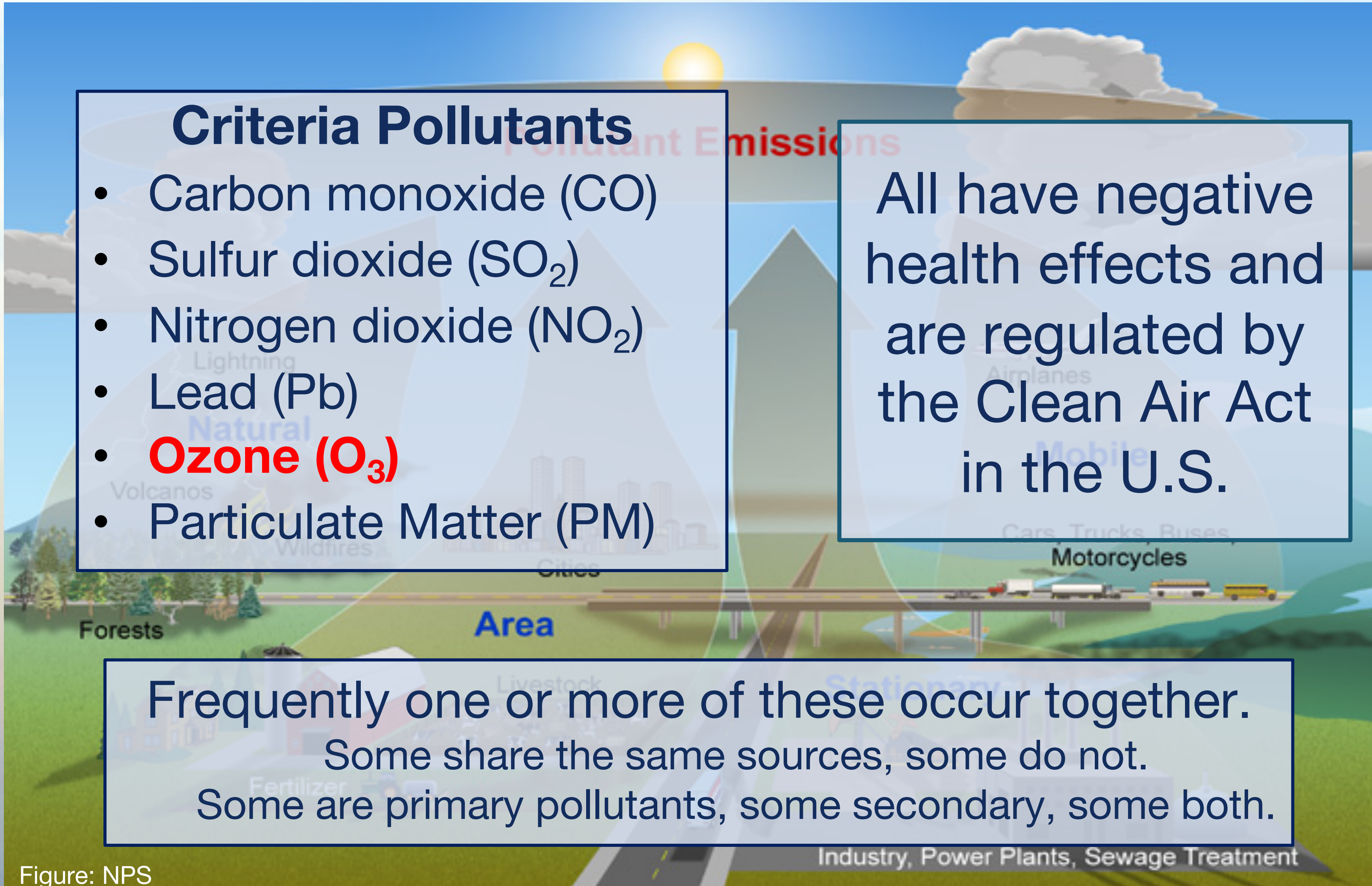
- Carbon monoxide (CO)
- Sulfur dioxide (SO_2)
- Nitrogen dioxide (NO_2)
- Lead (Pb)
- Ozone (O_3)
- Particulate Matter (PM)

All have negative health effects and are regulated by the Clean Air Act in the U.S.

Frequently one or more of these occur together.
Some share the same sources, some do not.
Some are primary pollutants, some secondary, some both.

Figure: NPS

Figure Credit NPS



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Ozone Chemistry & Budget

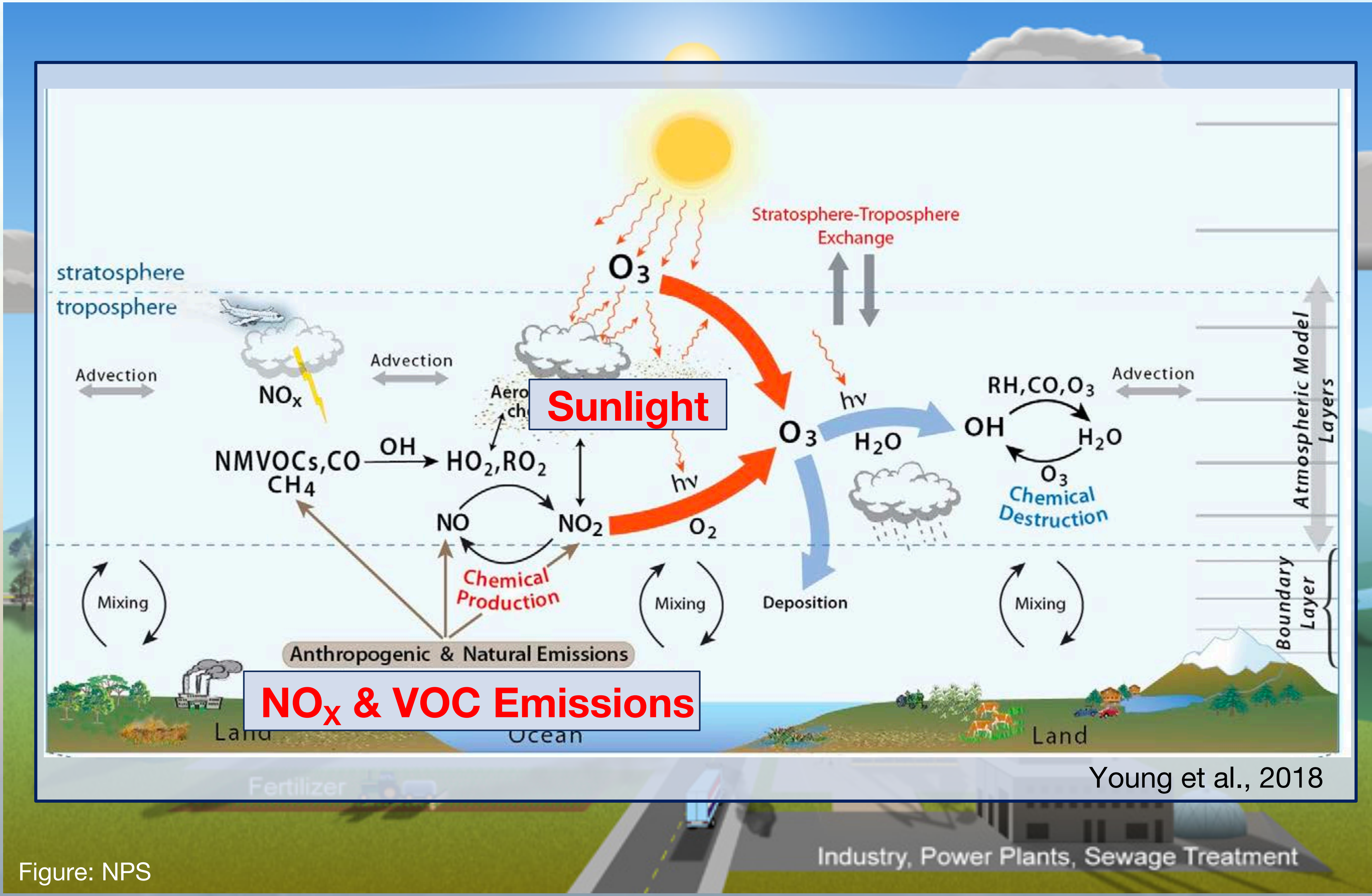


Figure: NPS

Ozone Chemistry & Budget

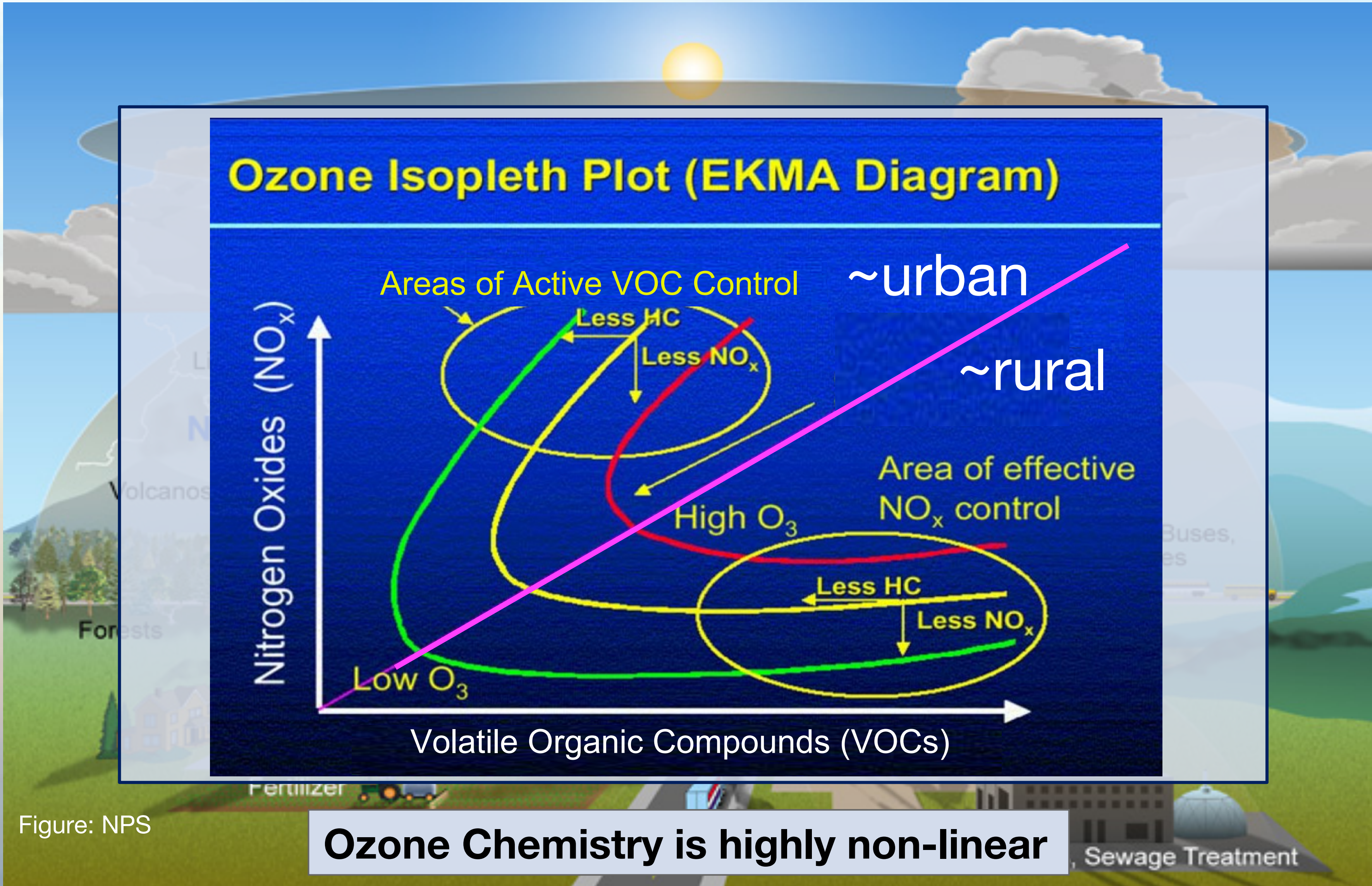
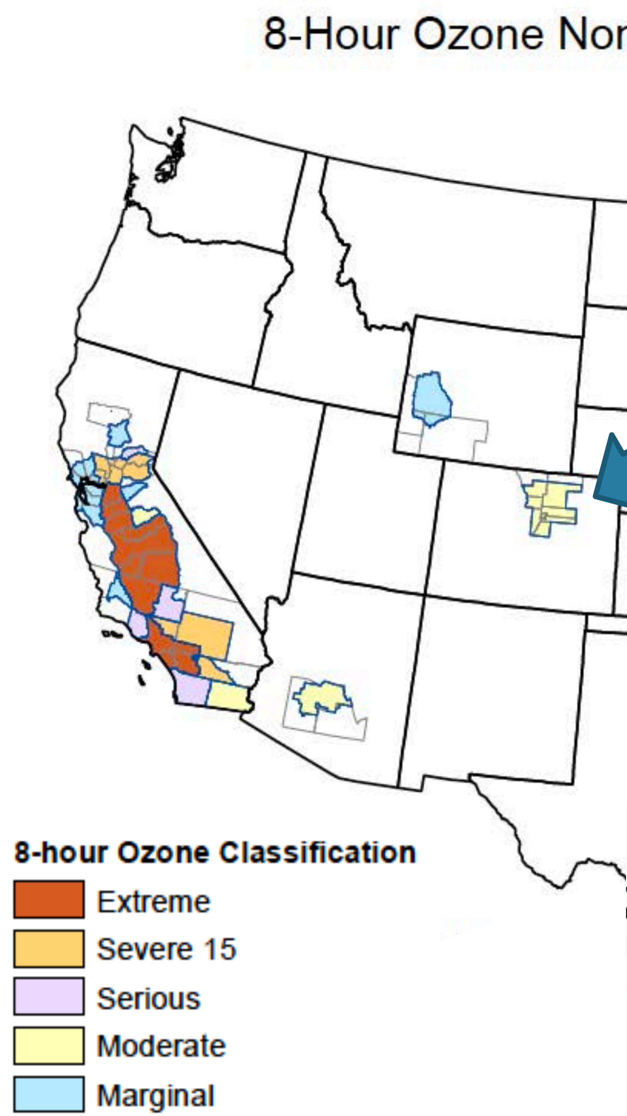


Figure: NPS

Ozone Chemistry is highly non-linear

Ozone in the U.S.



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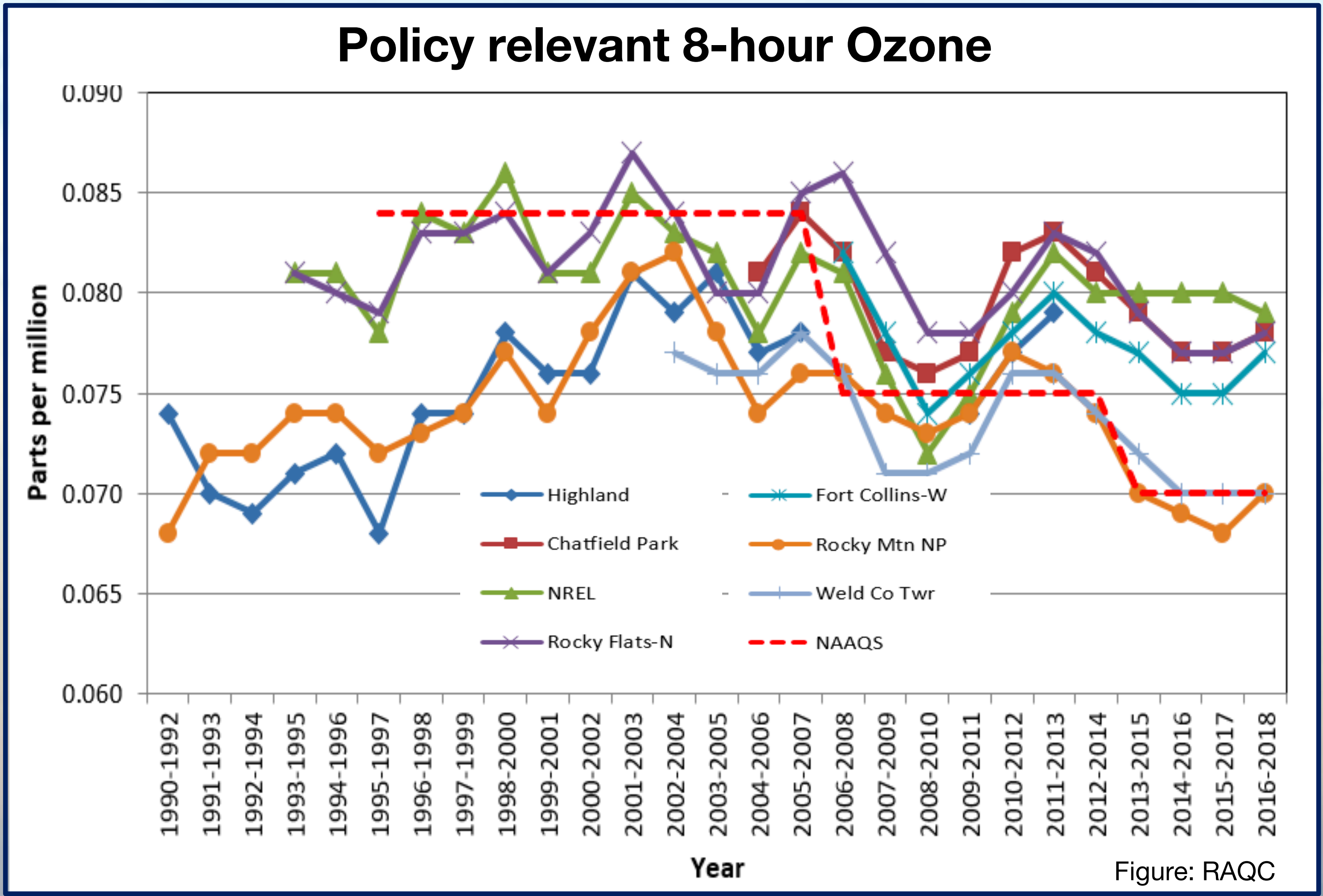
NEWS › ENVIRONMENT

EPA declares Colorado a "serious" violator of federal air quality standards, forcing stricter efforts to reduce pollution

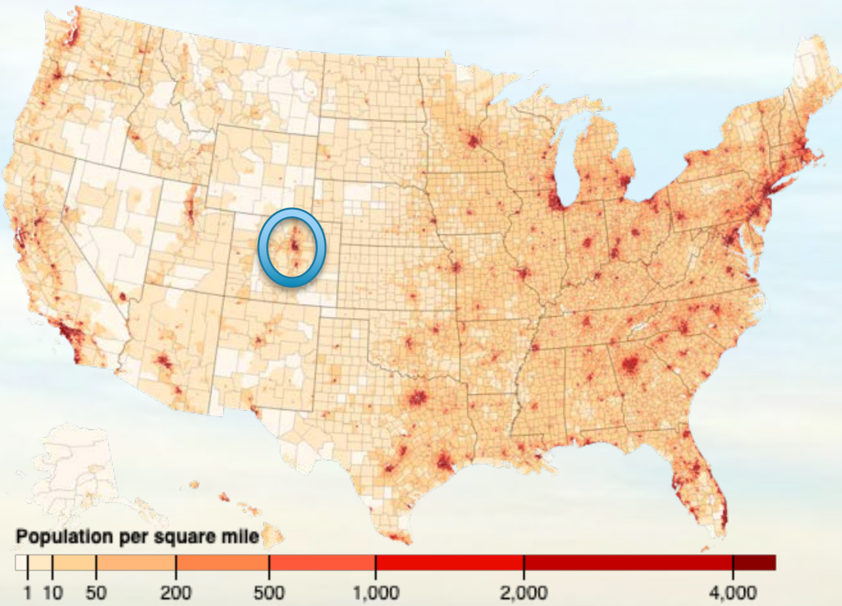
Colorado must reduce pollution by 2021

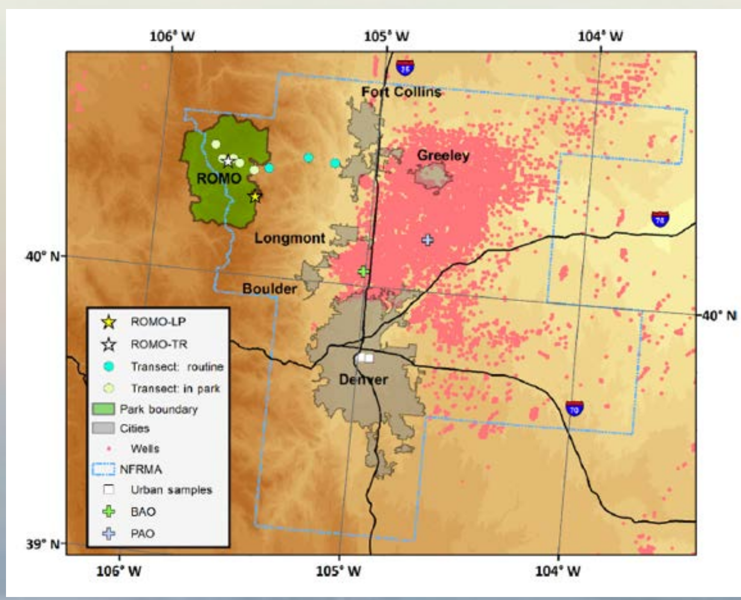
Ozone in Colorado



Policy relevant = fourth-highest daily 8-hour maximum, averaged across three consecutive years

Ozone in Colorado





Benedict et al., 2019

Diverse sources of air pollutants

- Urban, traffic, oil and gas development, industry,…
- Separated spatially/temporally in some cases, co-located in others
- Emissions difficult to assess due to variability and high number of individual sources

Unique, mountain-driven local meteorology

- Drives local mixing and transport
- Recirculation of pollutants
- Plenty sunshine and warm summers
- A challenge for chemical-transport models

Needs for Research

- What and where are the relevant sources?
- How do these emissions get transported?
- How do they get chemically processed?
- How much pollution comes into Colorado?
- Which are the best ways to improve air quality?

FRAPPÉ

State of Colorado and NSF

PIs: Gabriele Pfister and Frank Flocke (NCAR)

PI: James Crawford (NASA)

Colorado Front Range, Summer 2014

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Funding: FRAPPÉ (State of Colorado / CDPHE, NSF), DISCOVER-AQ (NASA)

FRAPPÉ

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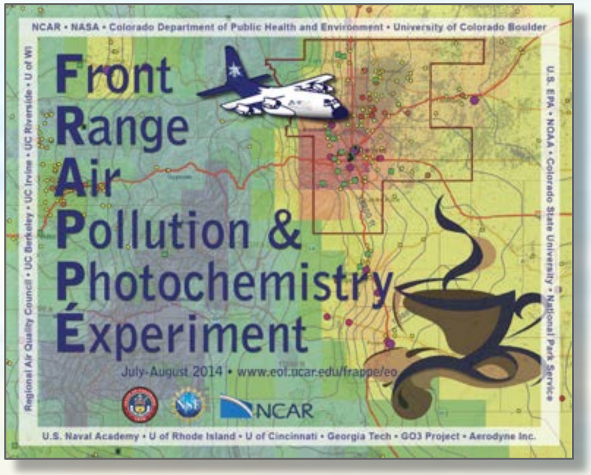

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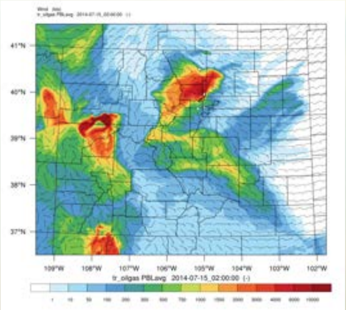

Colorado Front Range, Summer 2014

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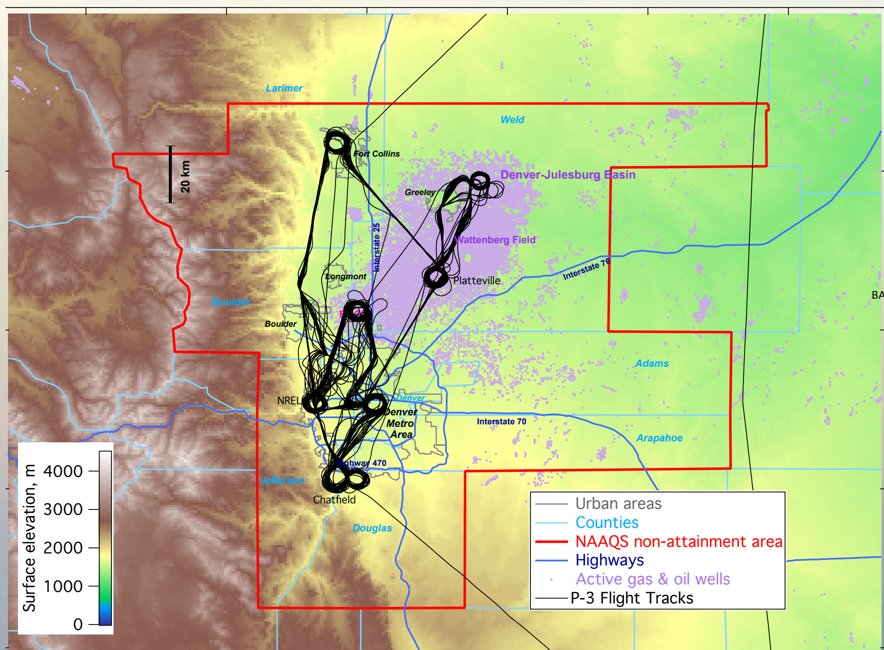
Measurement Strategy

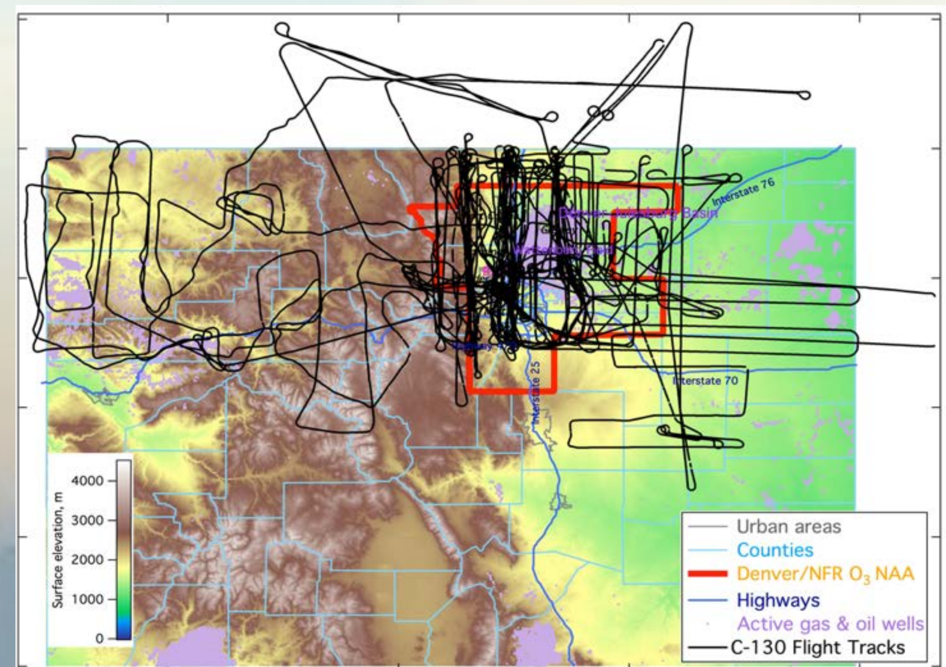
NASA aircraft: Examine relationships between remotely-sensed columns, and surface air quality.

- **NASA P-3 -** repeated vertical sampling during cloud-free conditions, spirals over six ground super-sites.
- **B-200 and Falcon**: higher altitudes to optimize vertical coverage of remote sensing payloads.

NCAR C-130 : Targeted flights to address scientific objectives based on conditions

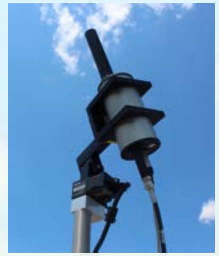
- Local, terrain-driven (upslope) air mass chemistry
- Transport, local emissions, and large scale inflow of pollution
- Outflow into the eastern plains and injection of polluted air into the free troposphere.

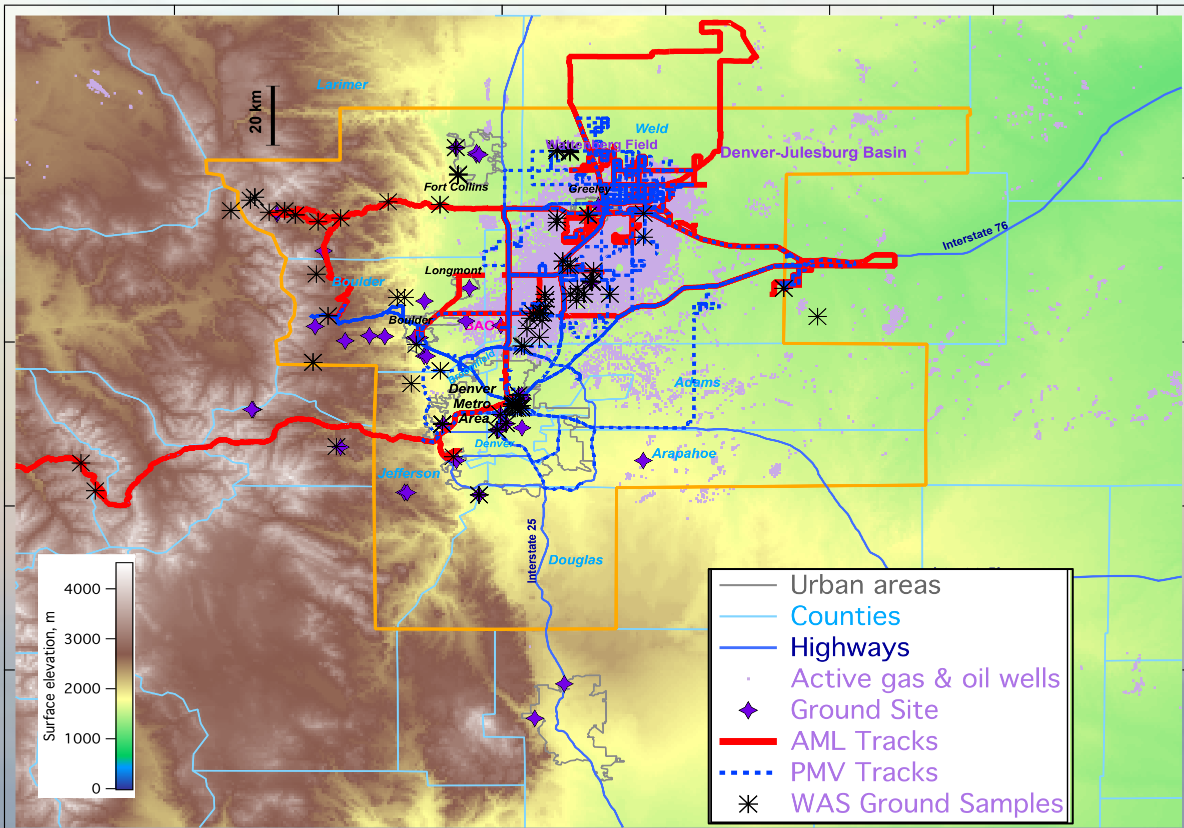




Measurement Strategy

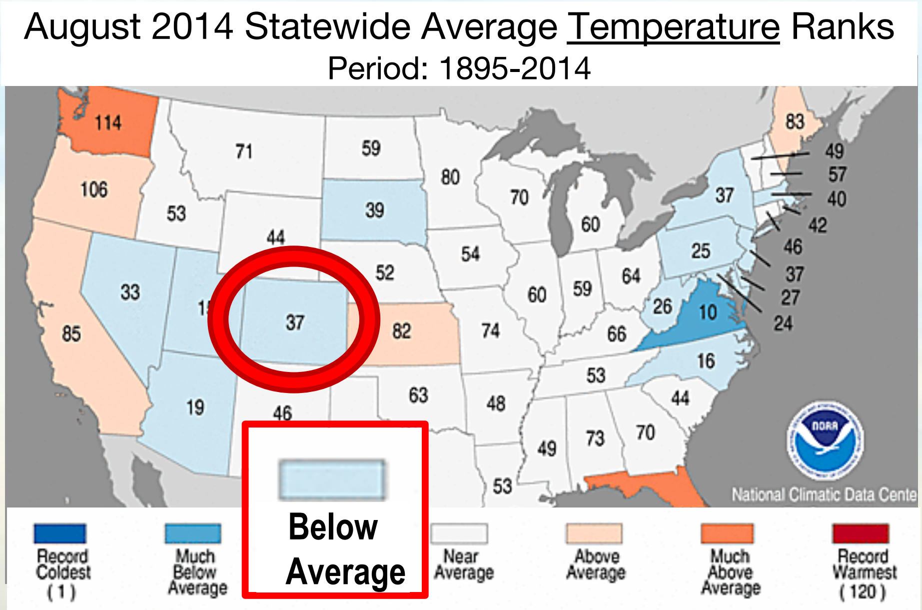
Ground Sites & Mobile Vans

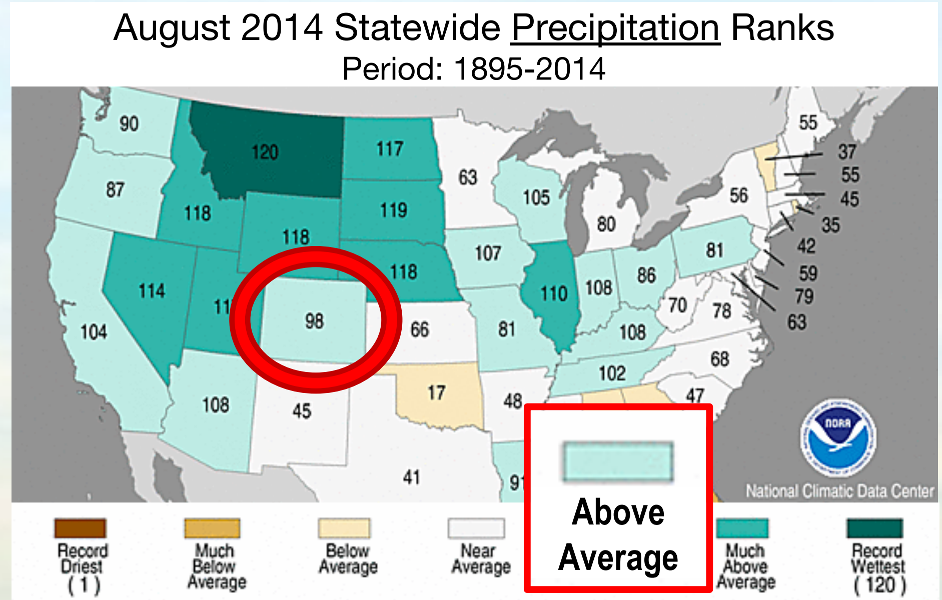


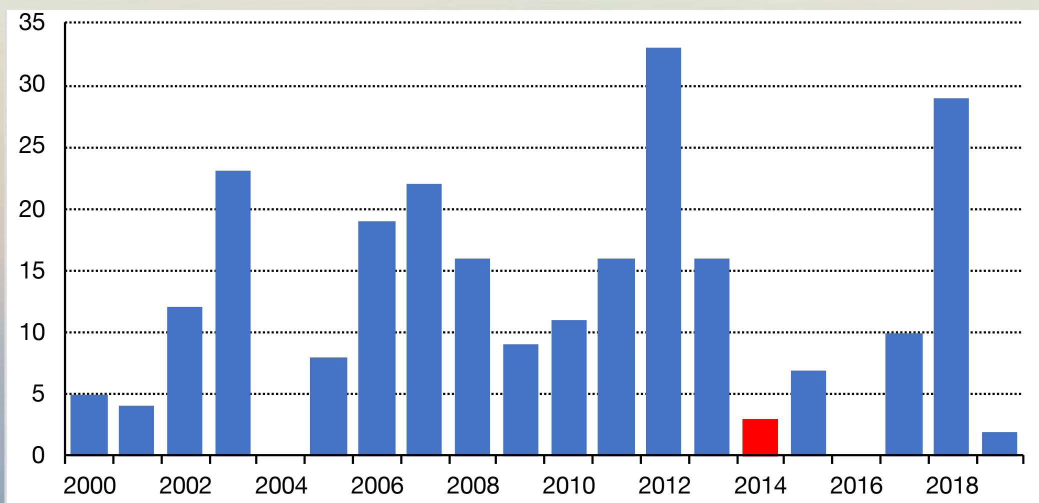


Name	Elev.(m asl)	Measurements
BAO Tower[a,b,c]	1580	O_3, NO_{xy}, CO, CO_2, CH_4, SO_2, VOC[d], N_2O, NH_3, F OH reactivity, aerosol param., LIDAR, wind pr N_2O_5, org. acids, $RONO_2$, met, ceilometer
Chatfield Park[a,b,c]	1676	O_3, NO_2, met, VOC, CH_4
Denver-LaCasa[a,b,c]	1601	O_3, NO_2, NOy, SO_2, VOC, PM
Fort Collins-West[a,b,c]	1572	O_3, NO_2, met, VOC, CH_4, TOLnet O_3, MPL
NREL-Golden[a,b,c]	1833	O_3, NO_{xy}, CO, CO_2, SO_2, CH_4, VOC, tether sond tower, nephelometer, LIDAR, wind profiler, ceilometer, TOLnet O_3
Platteville[a,b,c]	1523	O_3, NO_{xy}, CO, CO_2, SO_2, CH4, VOC[d], wind profil profiler, radiation
Aurora East/DU[c]	1802	O_3, met
CAMP (Denver)	1594	O_3, NO_2, NO_y, SO_2, CO, VOC, PM
I-25 Denver[b]	1587	O_3, NO_2
Niwot Ridge C1[b,c]	2886	O_3, met
Rocky Flats - N [b,c]	1803	O_3, NO_2, met
Squaw Mtn [b,c]	3492	O_3
Table Mountain[b,c]	1687	O_3
Welch	1743	O_3, met
Weld Co. Tower[b,c]	1484	O_3, NO_2, met
Aspen Park-RTD	2477	O_3, met
Fort Collins-CSU	1525	O_3, met
South Boulder Creek	1671	O_3
Welby	1556	O_3, NO_{xy}, met, SO_2, CO
Fritz Peak	2681	O_3
Squaw Mtn [b,c]	3492	O_3
Mines Peak	3797	O_3
Daniels Park	1978	O_3
Golden Gate Fire	2452	O_3
North Fork Fire St.	2323	O_3
Jackson Res. SP	1361	O_3
NCAR Mesa Lab	1862	O_3
Briggsdale	1481	O_3
Pawnee Buttes	1600	O_3
INSTAAR Boulder	1610	O_3, VOC canisters
Dawson School	1562	O_3, VOC canisters
Betasso	1981	O_3, VOC canisters
Sugar Loaf	2396	O_3, VOC canisters
Coughlin Meadows	2530	O_3, VOC canisters
Niwot Ridge C1[b,c]	2880	O_3
Niwot Ridge Soddie	3359	O_3, VOC canisters
Niwot Ridge Saddle	3527	O_3
Rocky Mountain NP[d]	2743	O_3, NO_{xy}, SO_2, met, VOC, NH_3, PANs, HNO_3, H_2 aerosol composition
Rocky Mountain NP High Alt.	3545	O_3, met
Foothills Lab	1615	FTIR integrated Column Measurements

How "typical" was 2014



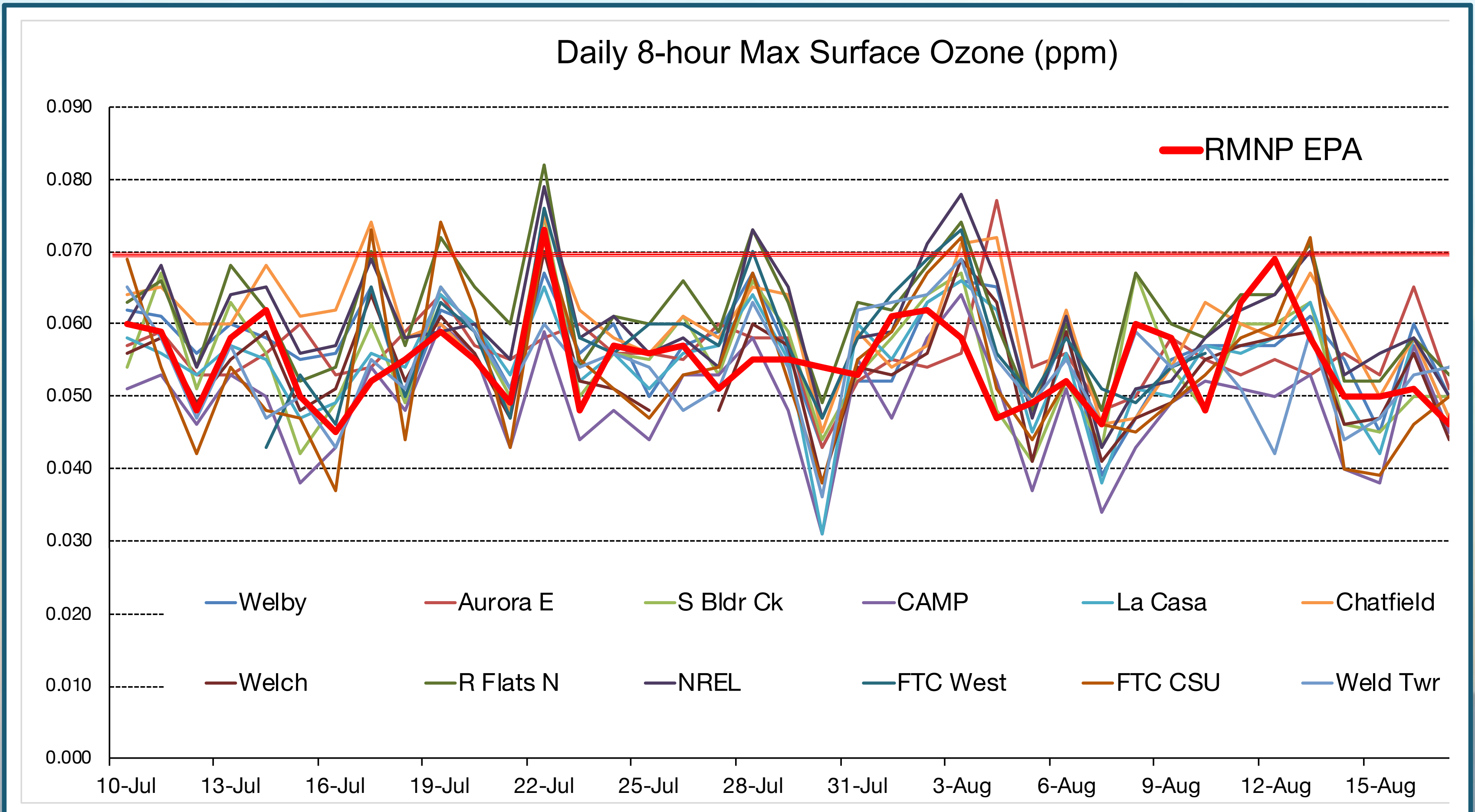




Data Source: https://www.epa.gov/outdoor-air-quality-data/air-data-ozone-exceedances

Number of Days with 8-hour Max. Surface Ozone > 70 ppb

How "typical" was 2014



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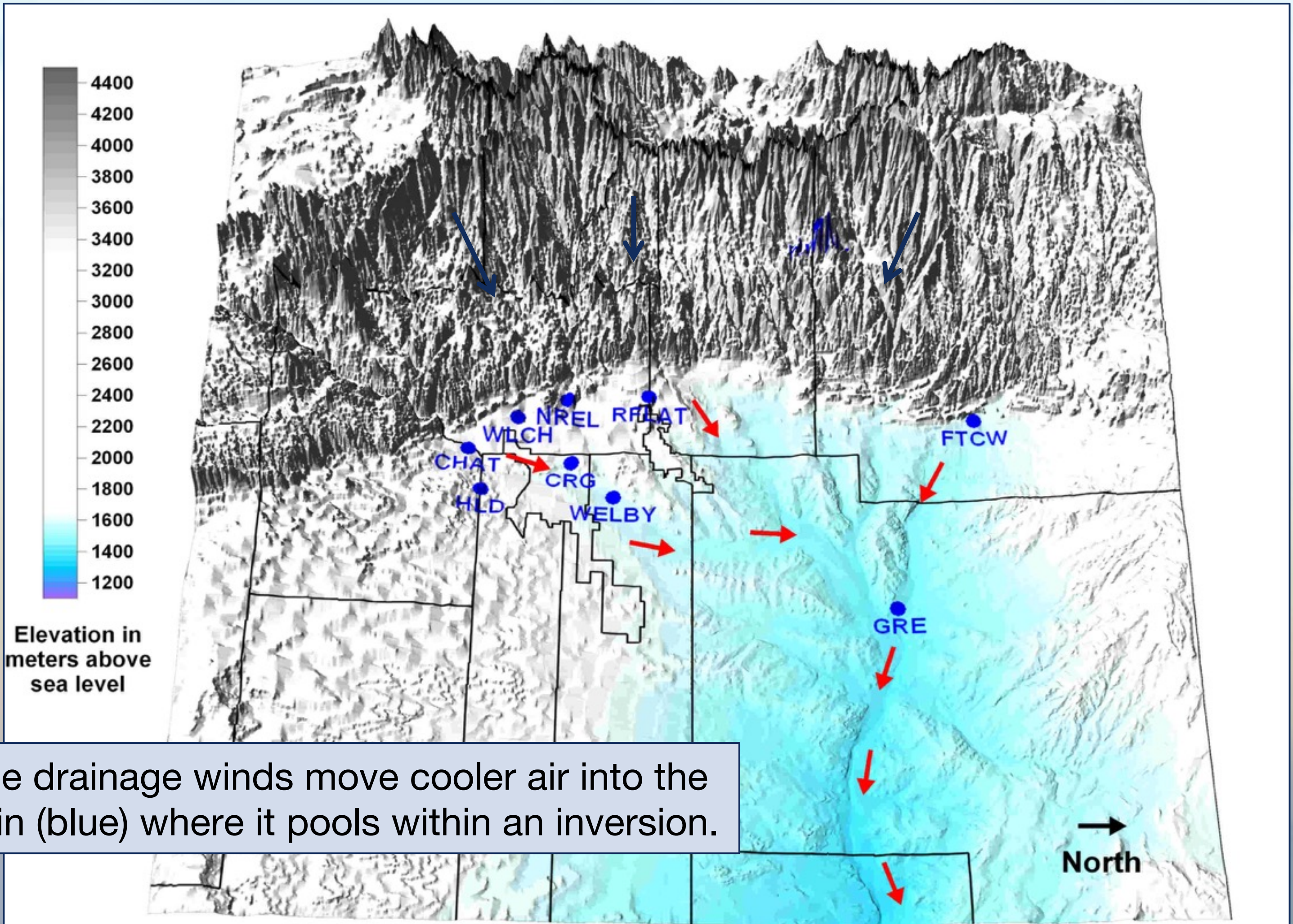
Mountain-Valley Flows

Nighttime



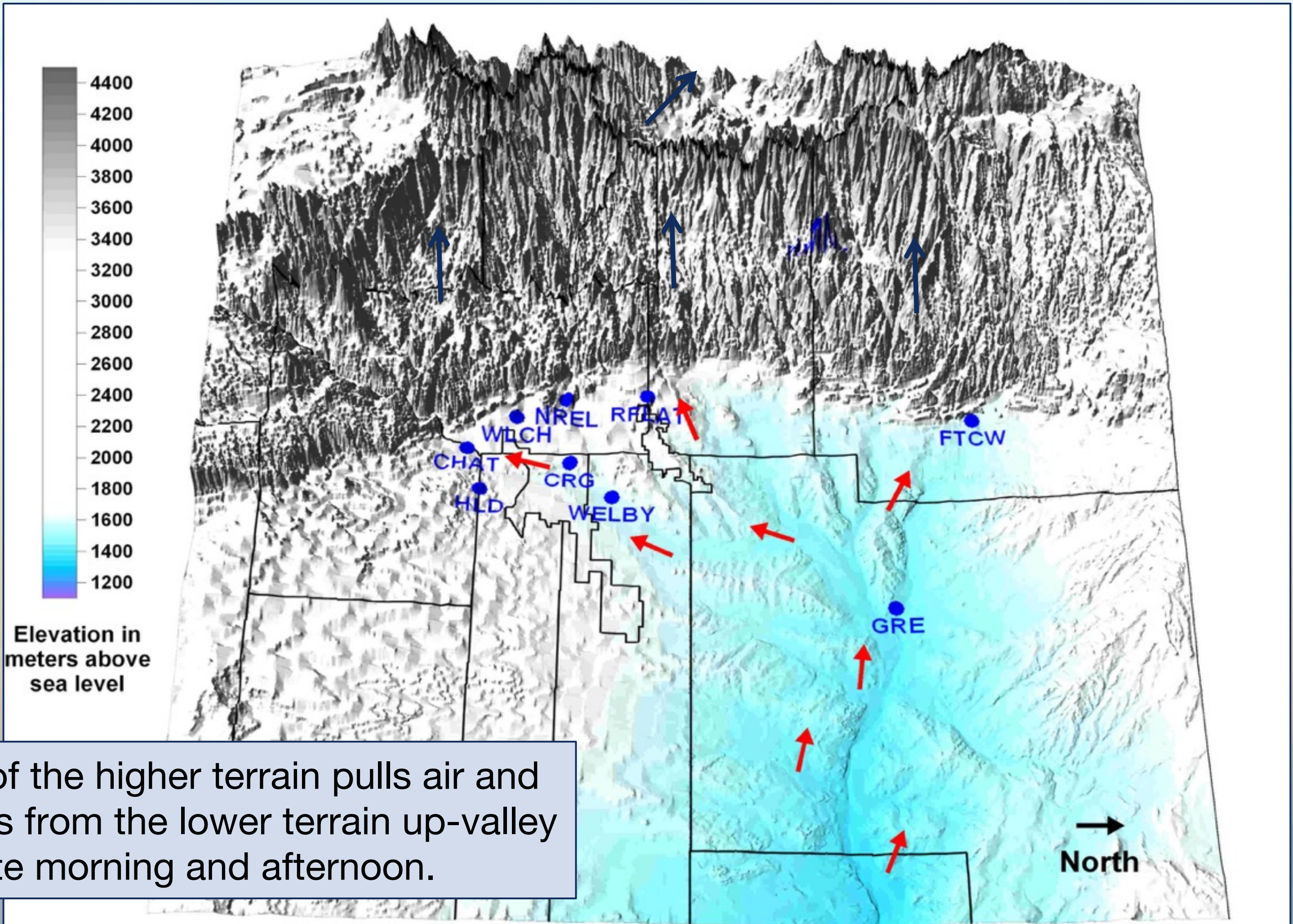
Reddy and Pfister, JGR 2016; Pfister et al., JGR, 2017

Nighttime drainage winds move cooler air into the low terrain (blue) where it pools within an inversion.

View to the west

Mountain-Valley Flows

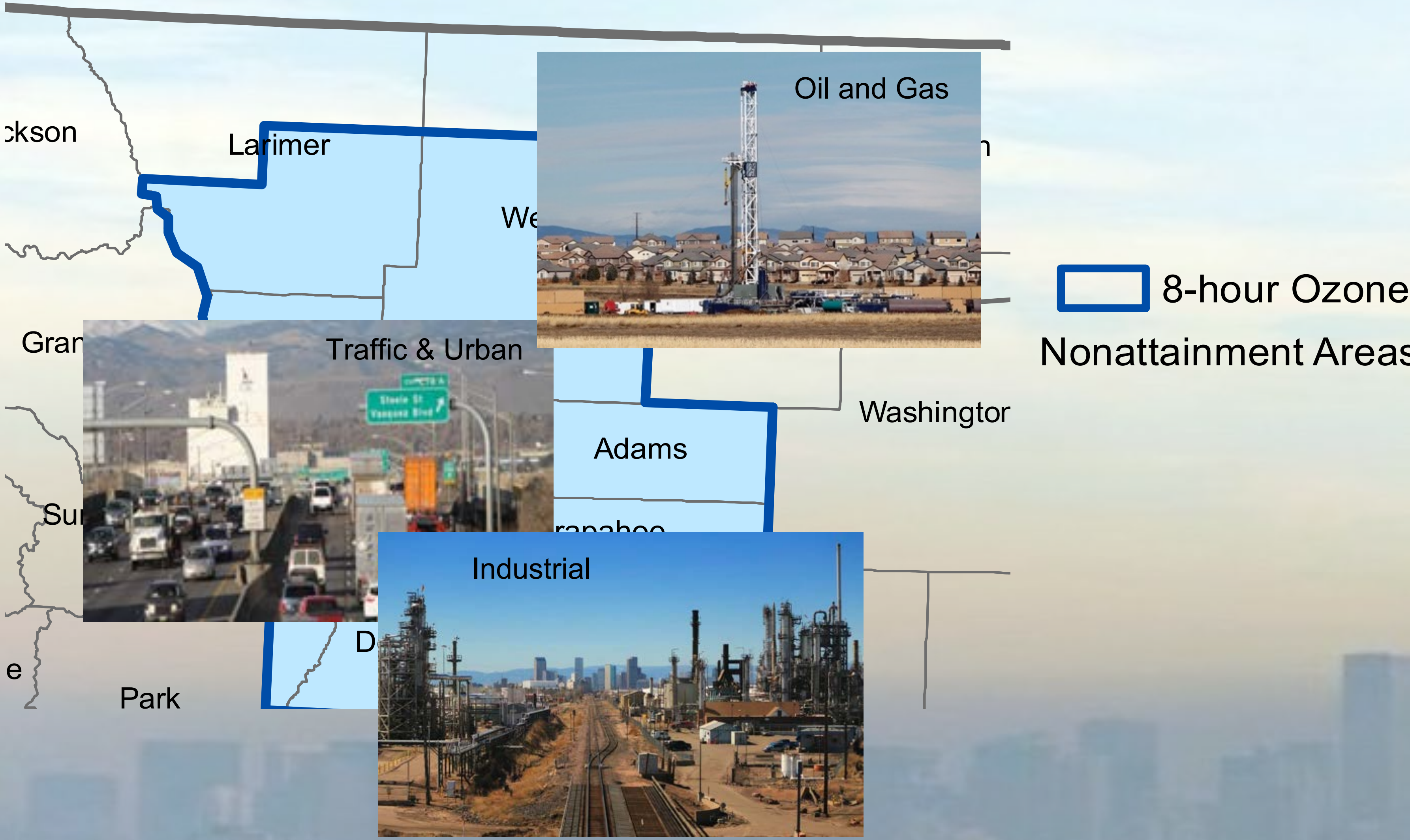
Daytime



Heating of the higher terrain pulls air and emissions from the lower terrain up-valley during late morning and afternoon.

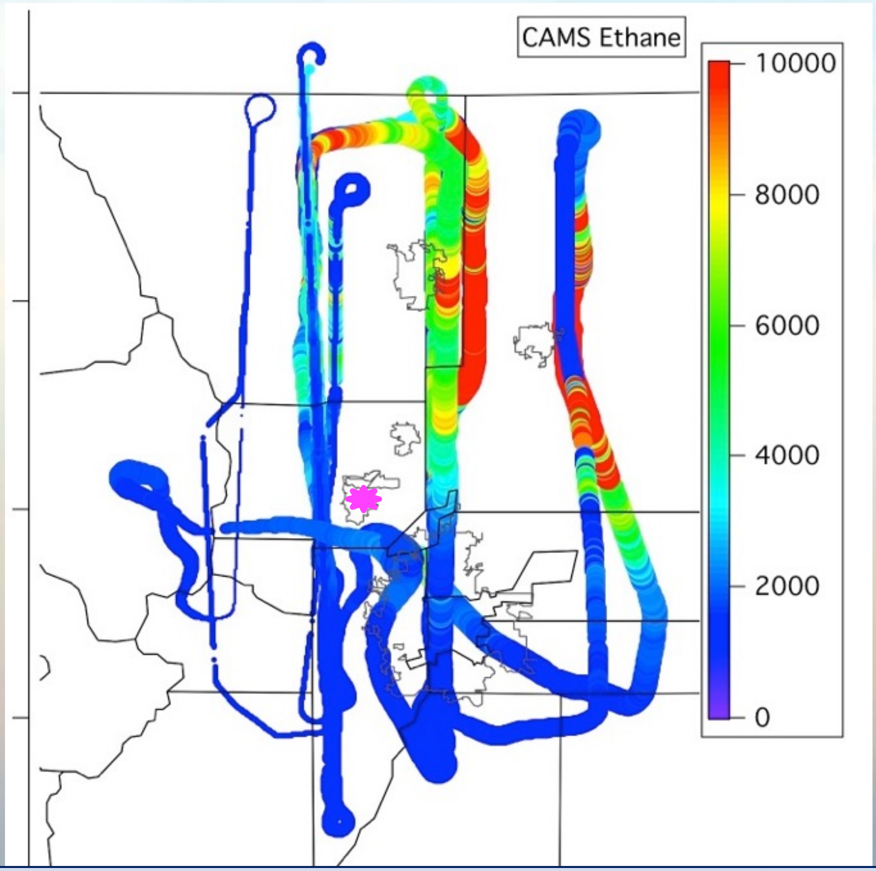
Reddy and Pfister, JGR 2016; Pfister et al., JGR, 2017

View to the west

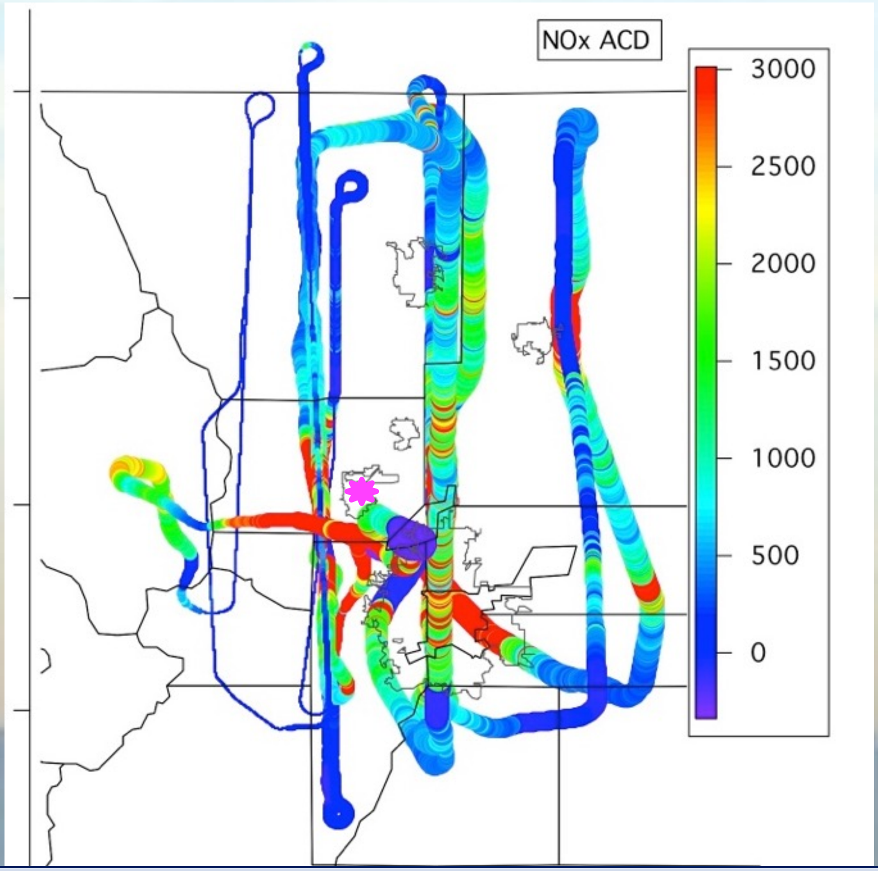

Larimer
Oil and Gas
Traffic & Urban
Adams
Industrial
Park
8-hour Ozone
Nonattainment Areas

Emissions & Transport

C-130 Ethane (~VOCs)



C-130 NO_x

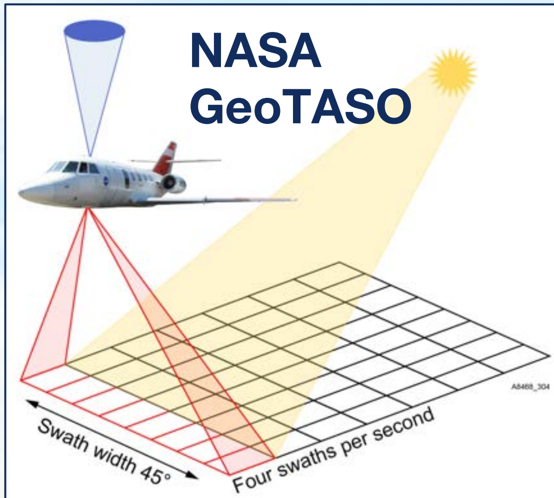


Highest VOCs in Weld County (O&G)

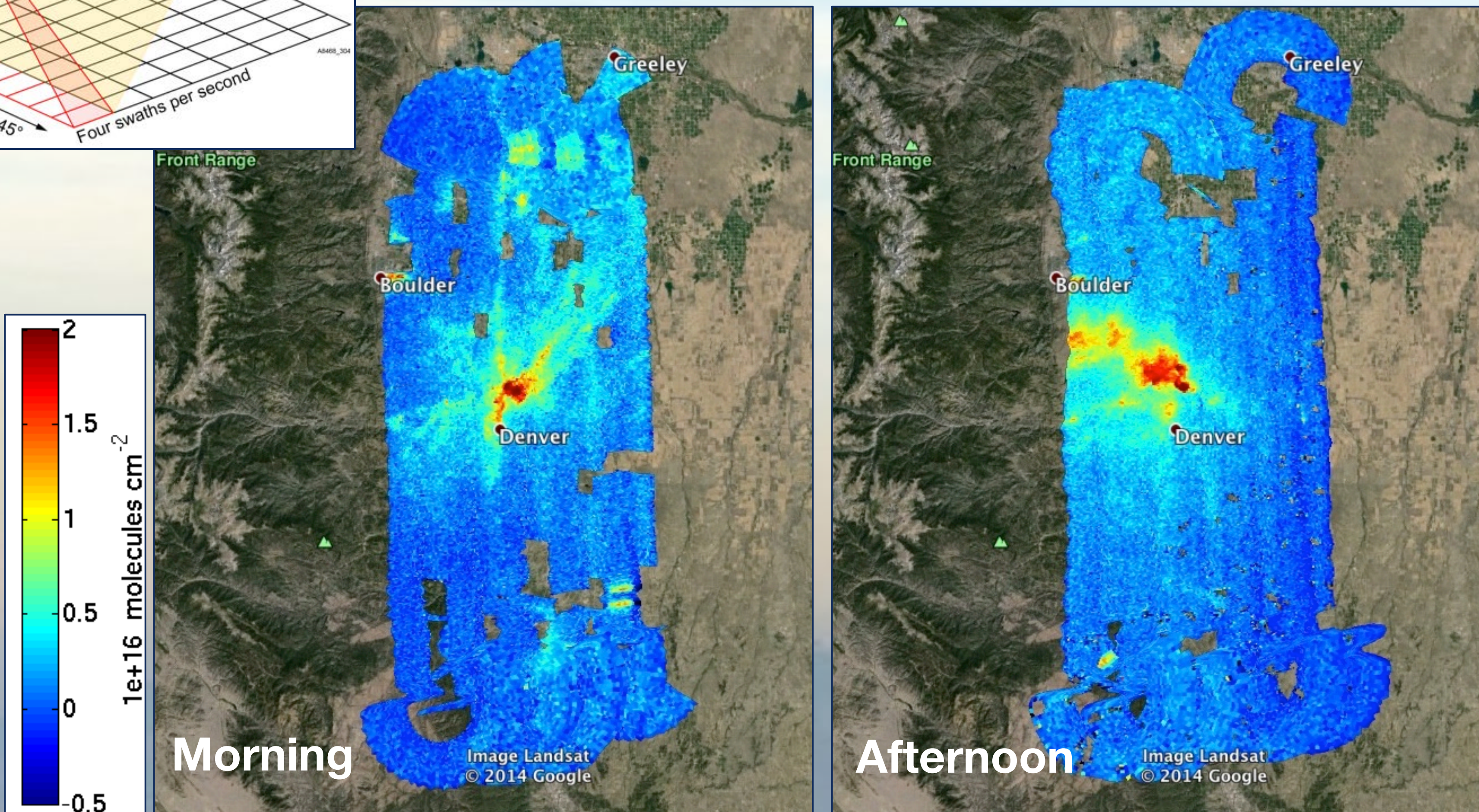
Highest NO_x in Denver urban area

12 August 2014

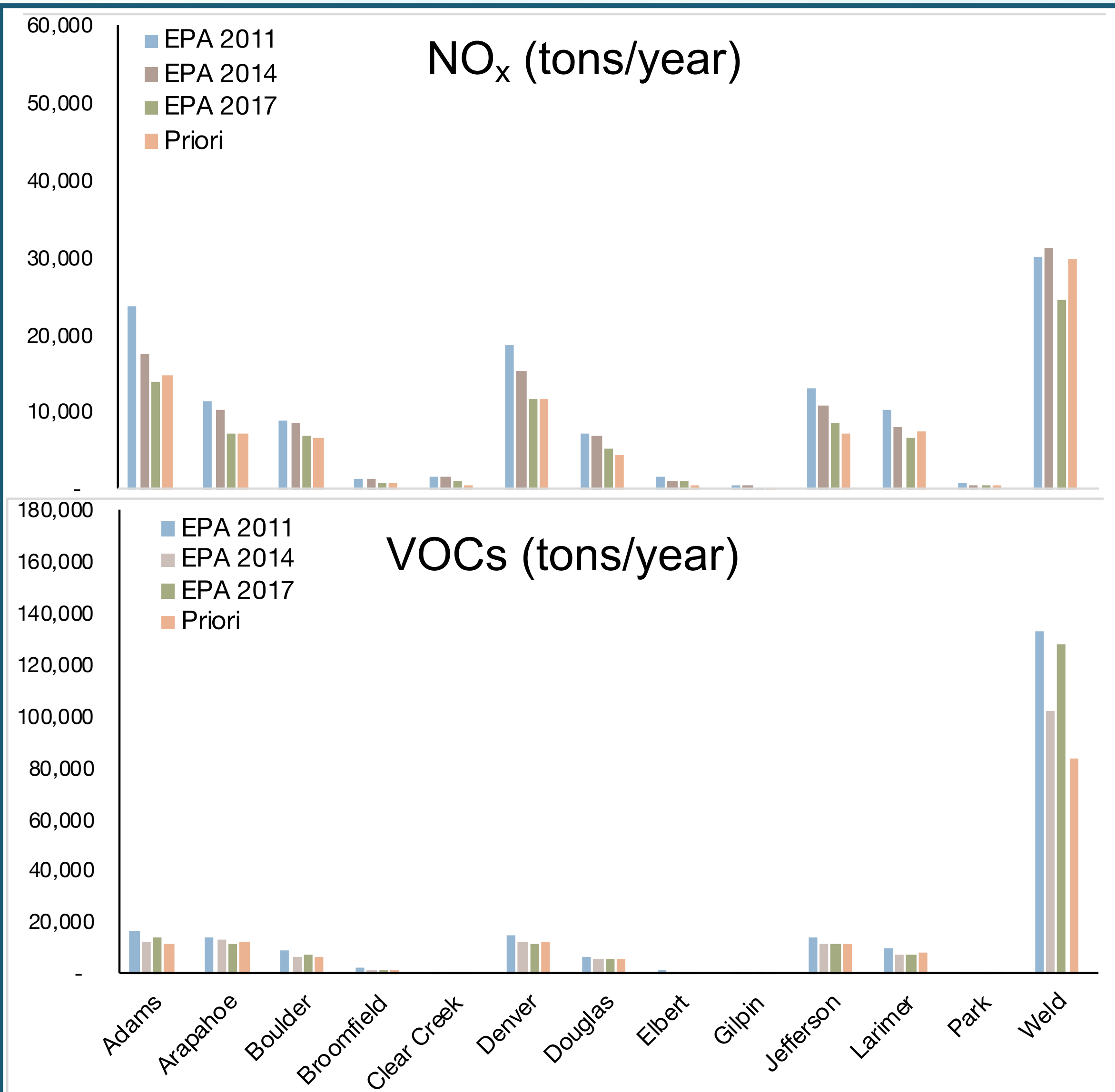
Emissions & Transport



NO_2 Slant Column, 02 August 2014



Emissions



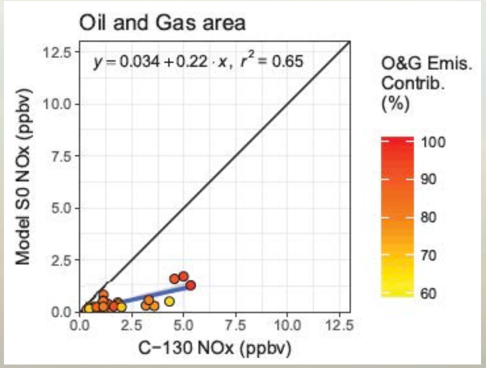
NEI 2011 provided by Stu McKeen (NOAA); NEI 2014 provided by U.S. EPA

EMISSION CONSTRAINTS

Run model with a priori emissions

Evaluate with aircraft data

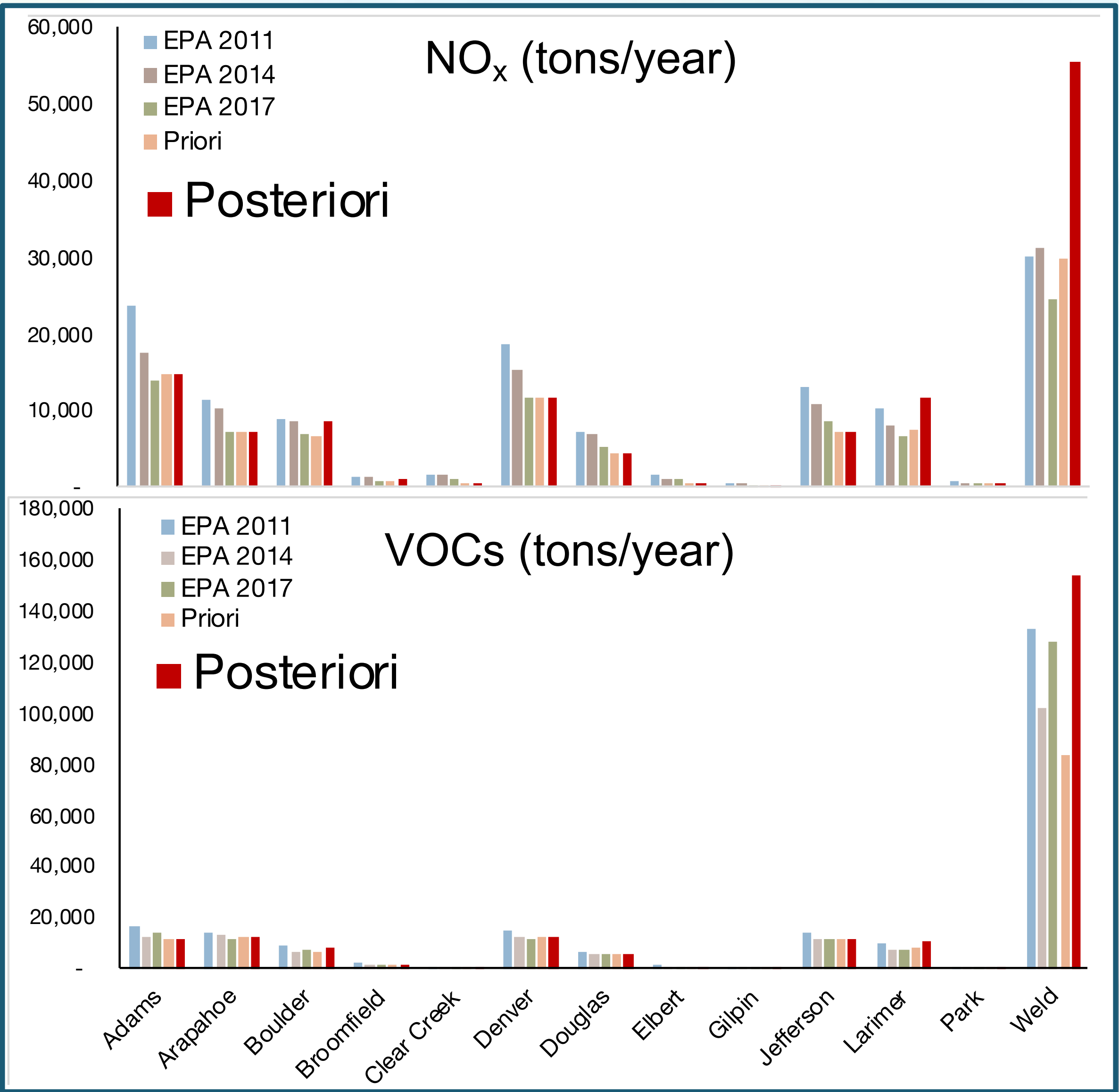
- Filter for data when modeled and observed winds from same sector
- Separate airmasses by chemical signatures (O&G, mobile)
- Evaluate absolute values & tracer ratios



Final scaling of sectors/species after multiple iterations

Flocke, Pfister et al., JGR, 2020

Emissions



NEI 2011 provided by Stu McKeen (NOAA); NEI 2014 provided by U.S. EPA

EMISSION CONSTRAINTS

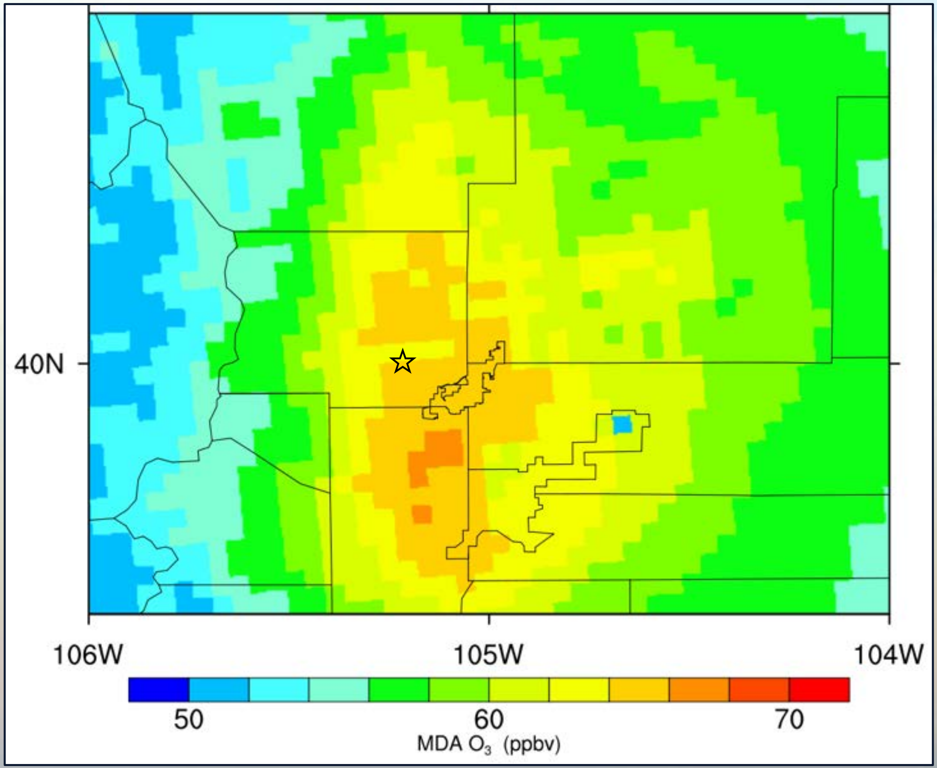
Results

- Doubling of all oil and gas emissions (except for ethane)
- Doubling of mobile emissions outside of Denver
- Doubling of (mobile) ethyne emissions

Flocke, Pfister et al., JGR, 2020

Source Contributions

Ozone MDA8



FRAPPÉ Average

What role do the different emission sectors play?

⇨ Zero-Out Scenarios

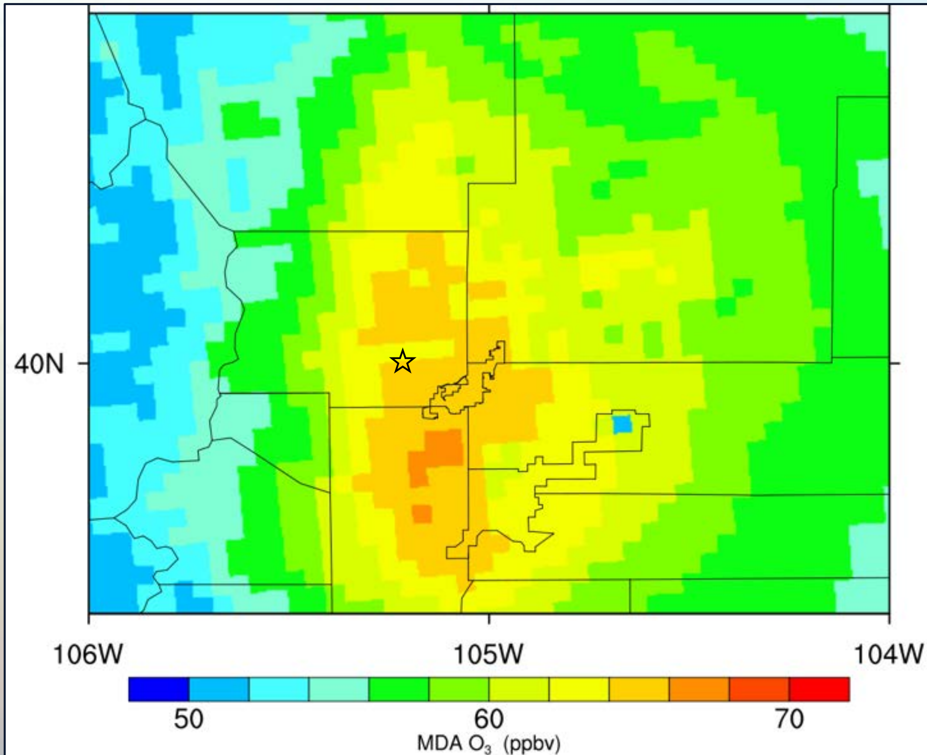
Model: WRF-CMAQ

MDA8 – Daily maximum 8-hour average

Pfister, Flocke et al., FRAPPÉ Final Report 2017
Flocke, Pfister et al., JGR, 2020

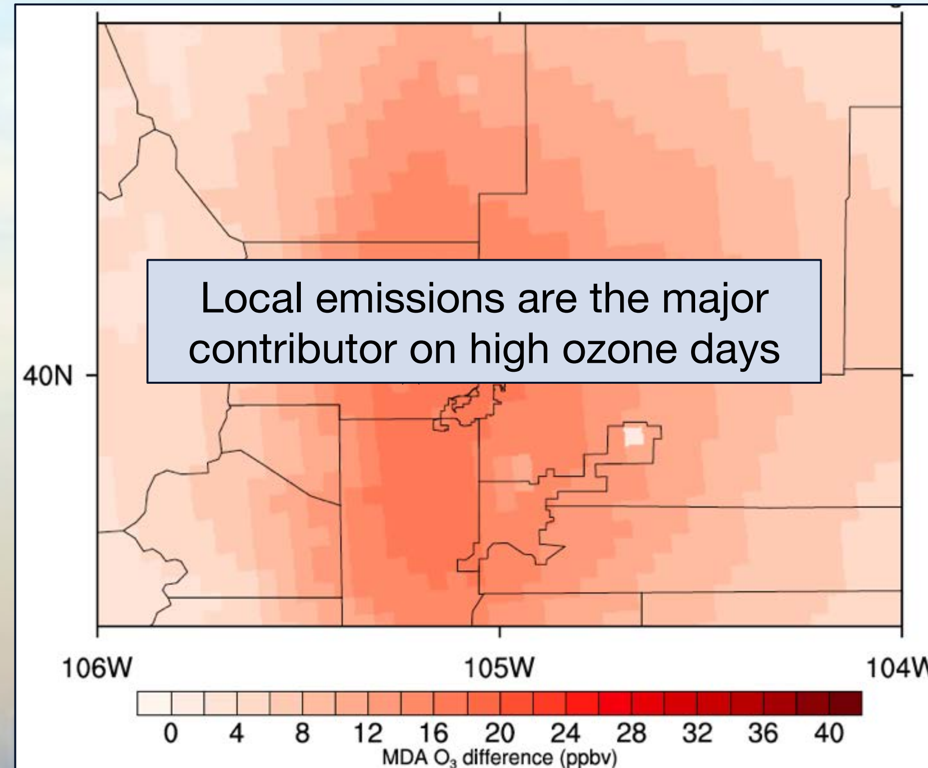
Source Contributions

Ozone MDA8



FRAPPÉ Average

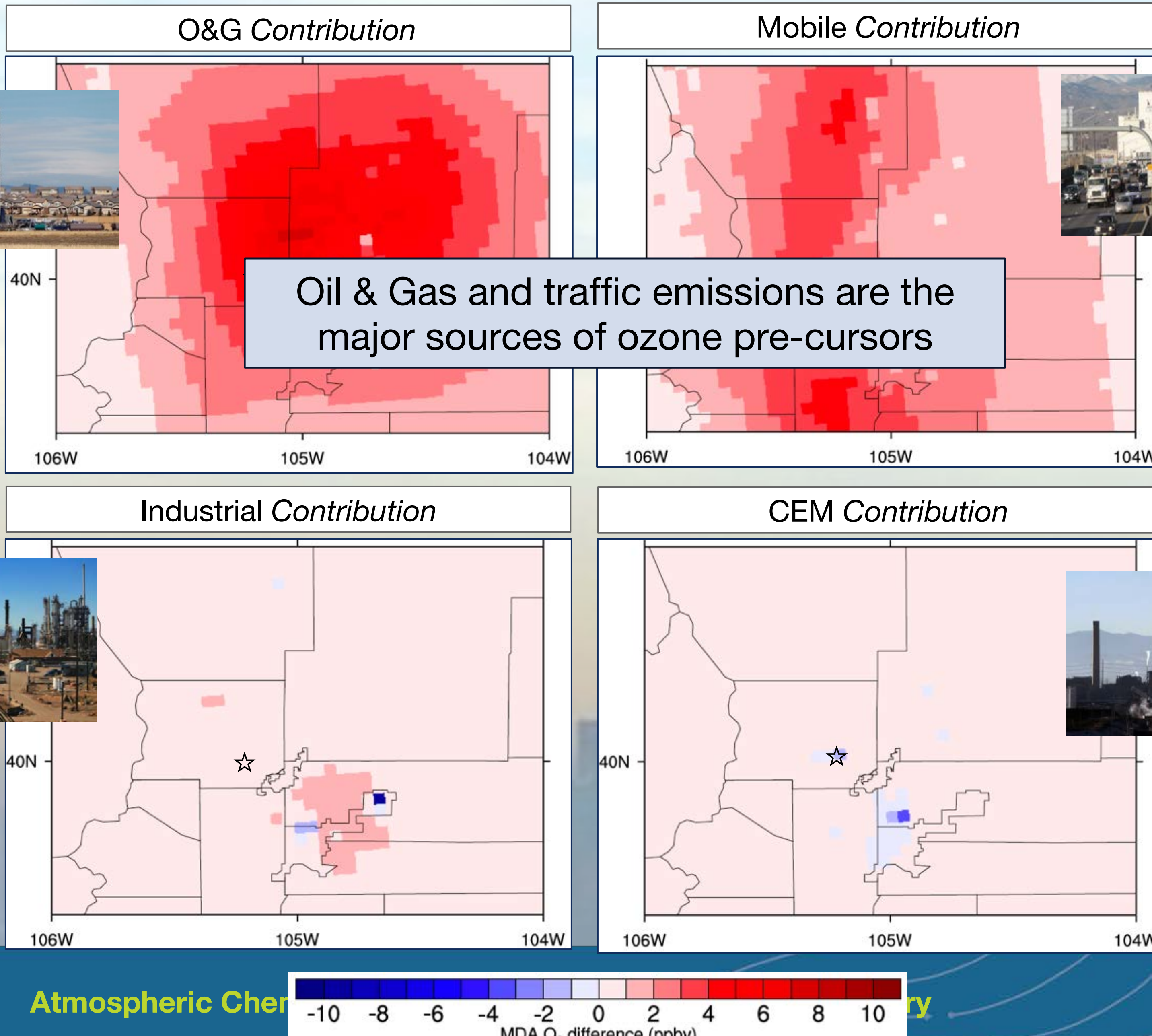
NFRMA Anthropogenic Emission *Contribution*

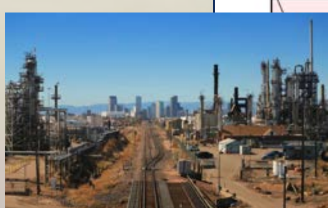


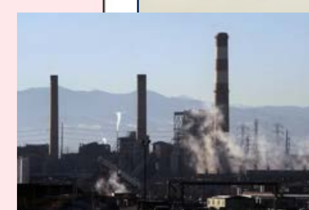
- Average 15-20ppb
- On high ozone days 20-30 ppb
- Maxima up to 40 ppb (28 July)

MDA8 – Daily maximum 8-hour average

Source Contributions

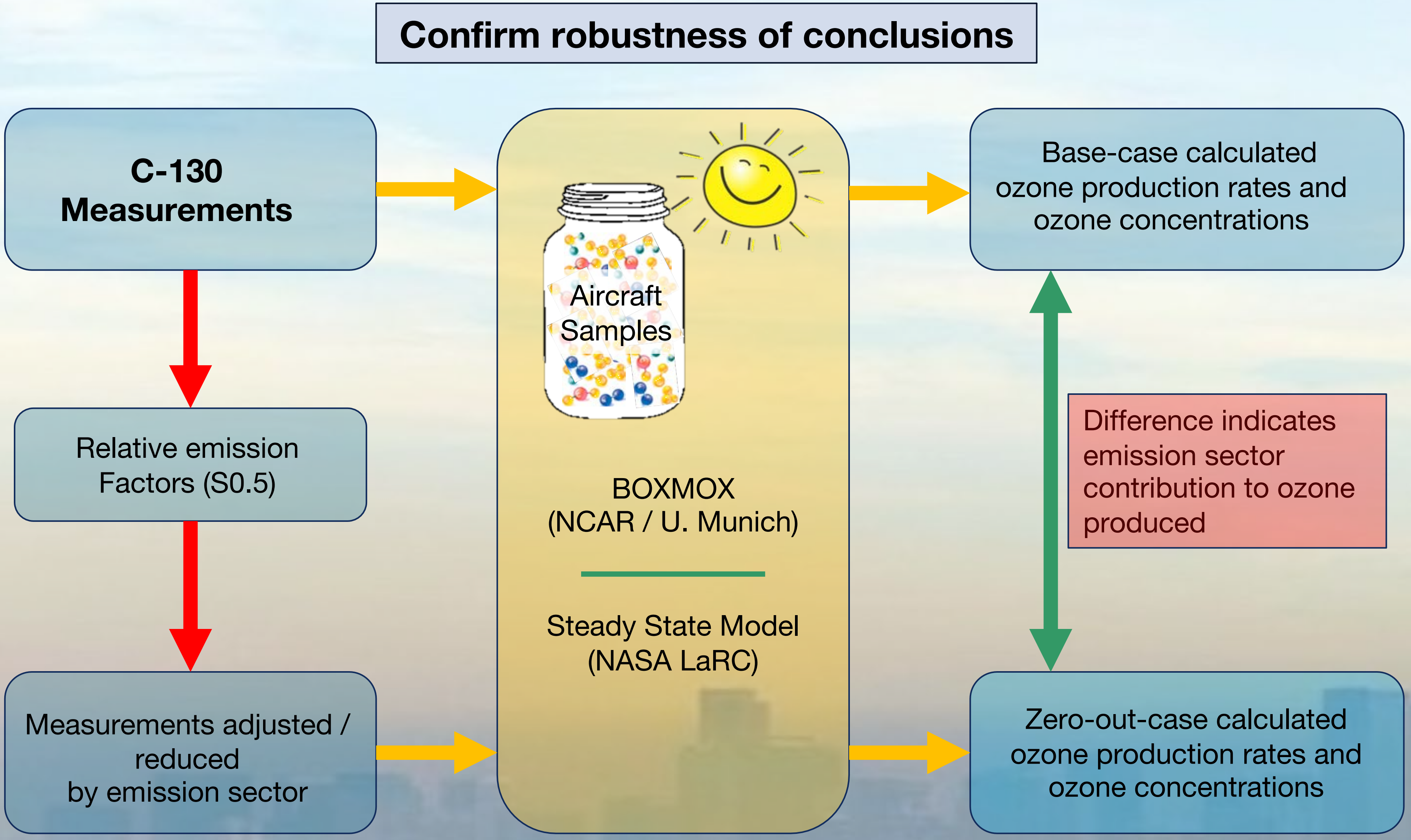






Oil & Gas and traffic emissions are the major sources of ozone pre-cursors

Source Contributions

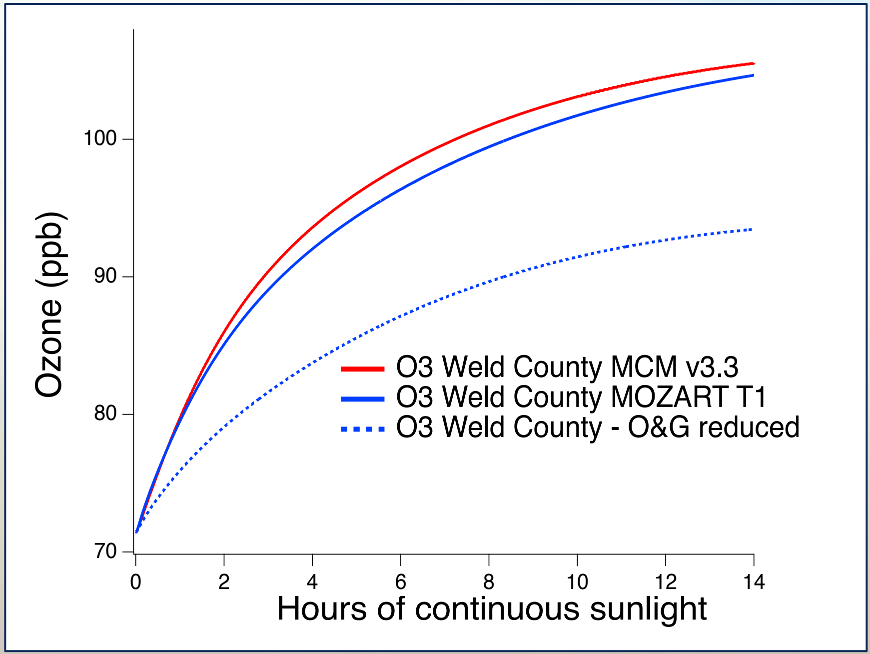


Pfister, Flocke et al., FRAPPÉ Final Report 2017; Flocke, Pfister et al., JGR, 2020

Source Contributions

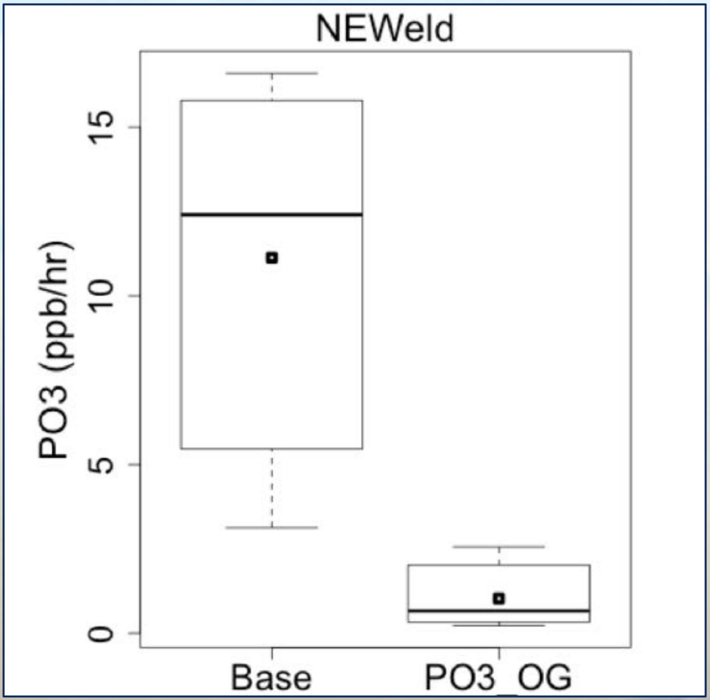
Confirm robustness of conclusions

Weld County: Oil and Gas emission dominated



BOXMOX

Steady State Model



Reduction of ~14 ppb of maximum ozone with O&G emissions removed

O&G accounts for over 80% of ozone production in Weld County

Pfister, Flocke et al., FRAPPÉ Final Report 2017; Flocke, Pfister et al., JGR, 2020

Ozone Chemistry & VOCs

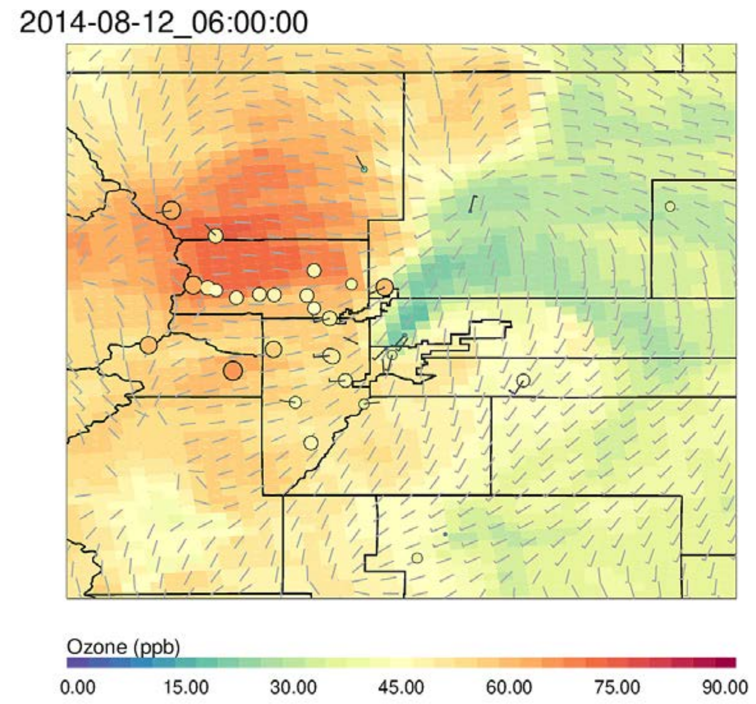
What is the relevance of individual VOC species to Ozone Production?

Study the role of different VOCs in ozone production
– Use of less reactive VOCs could provide cost-effective policies to reduce ozone

Model Diagnostics:

- **Integrated Reaction Rate Analysis (IRR)**: 3D output of individual gas phase reaction rates
- **Chemical Tendencies**: difference in concentrations before and after certain processes are called in model

WRF-Chem Simulations with different emission inventories and different physics settings

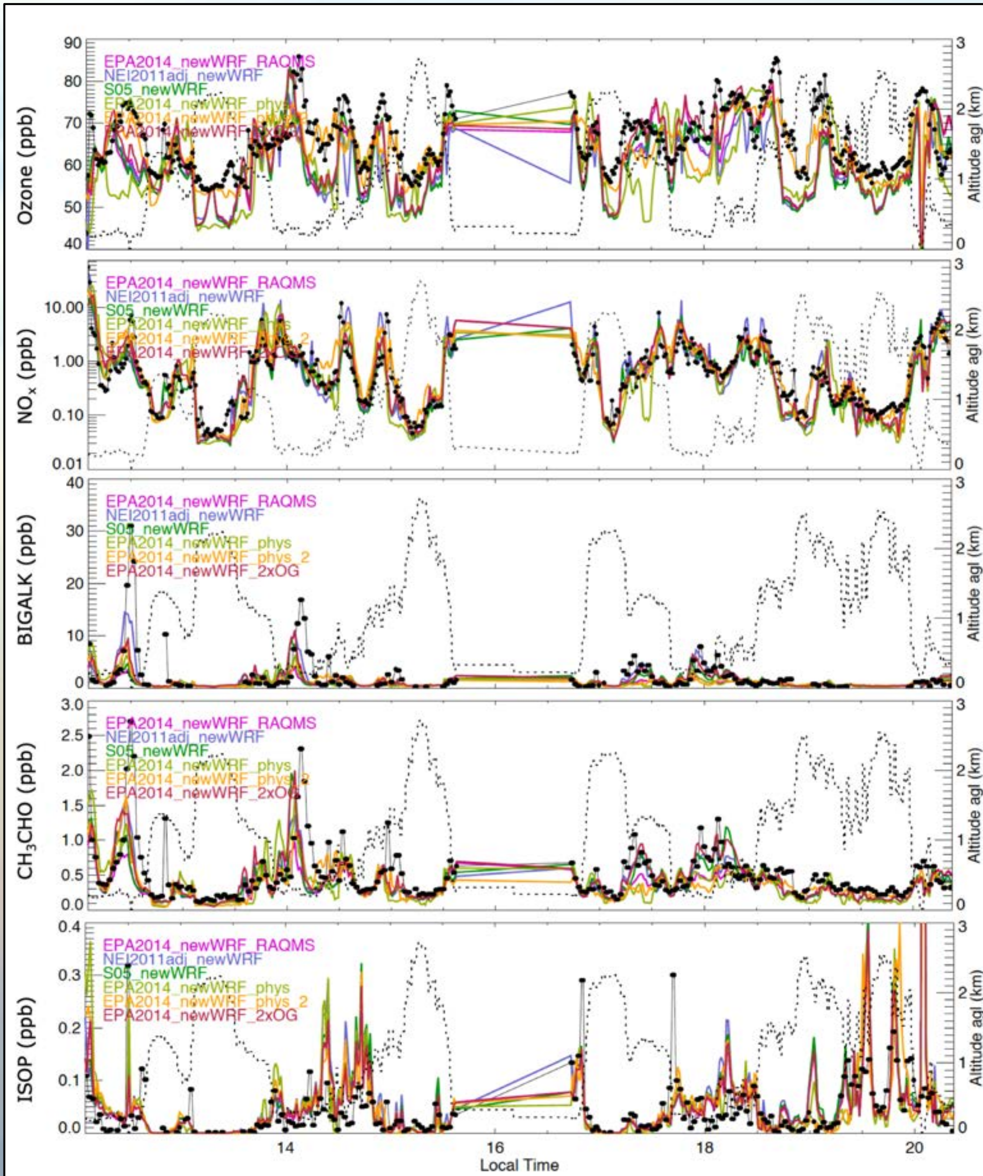


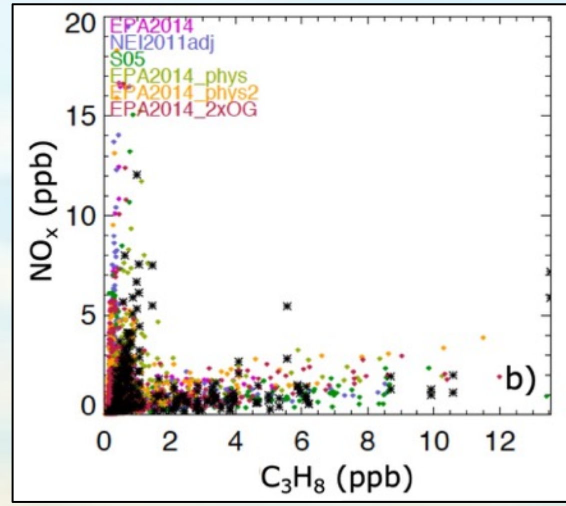
Case Study: 12 August 2014

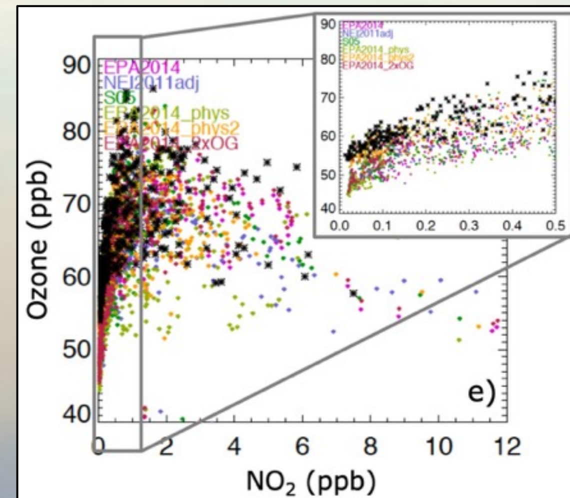
Pfister et al., JGR, 2019

Model Performance

12 August 2014 – C-130 Observations

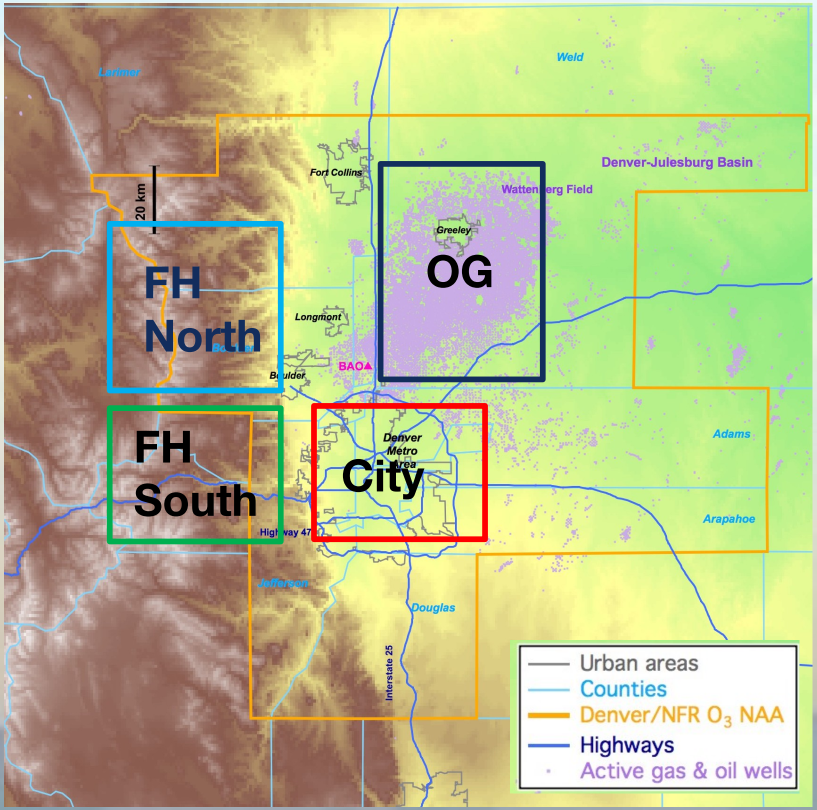






Evaluation for absolute values, ratios, chemical processes & meteorology

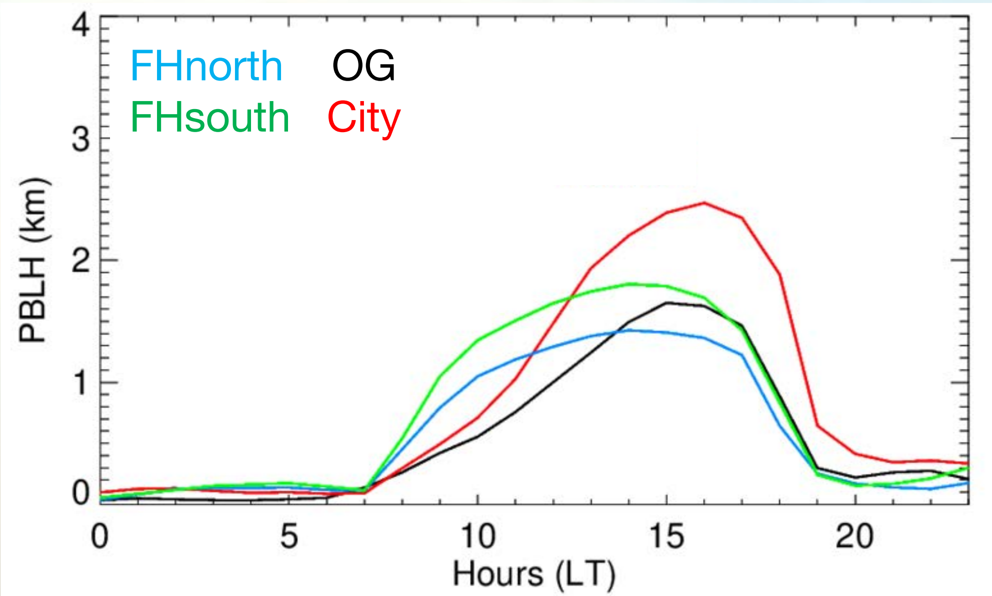
Chemical Analysis

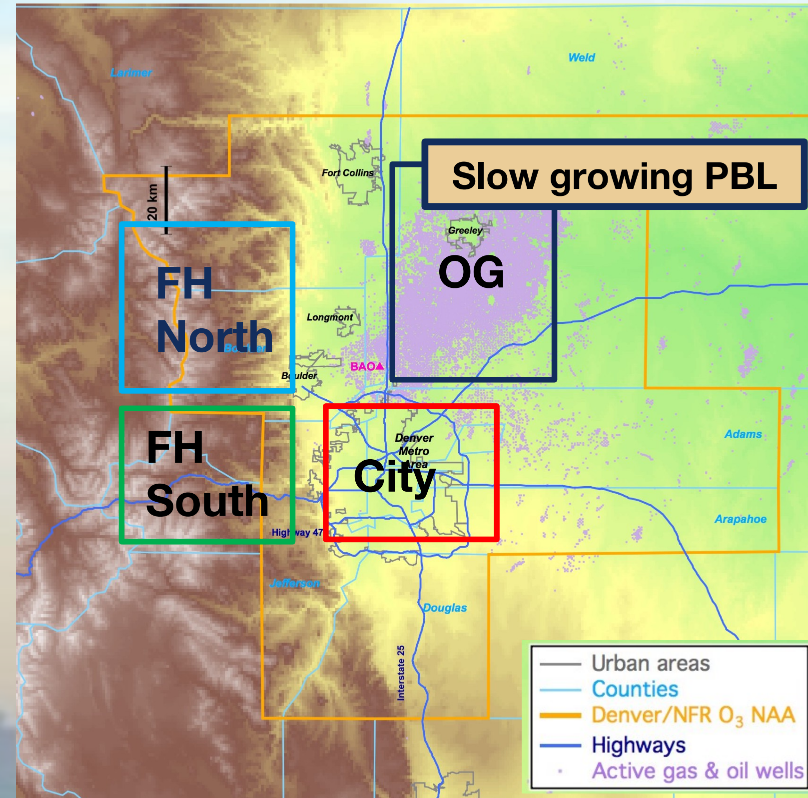


Pfister et al., JGR, 2019

Chemical Analysis

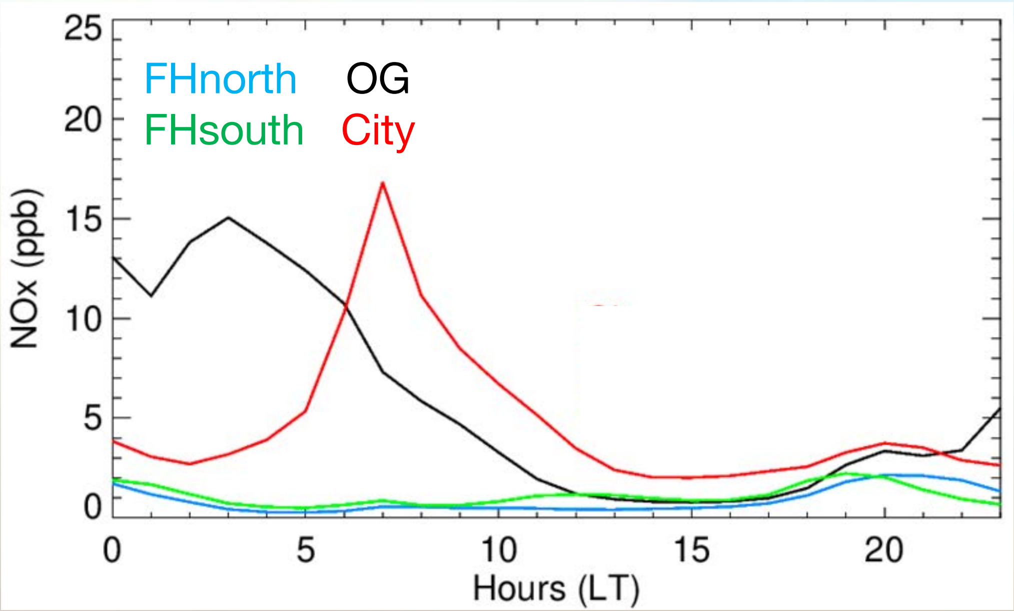
Boundary Layer Height (km)

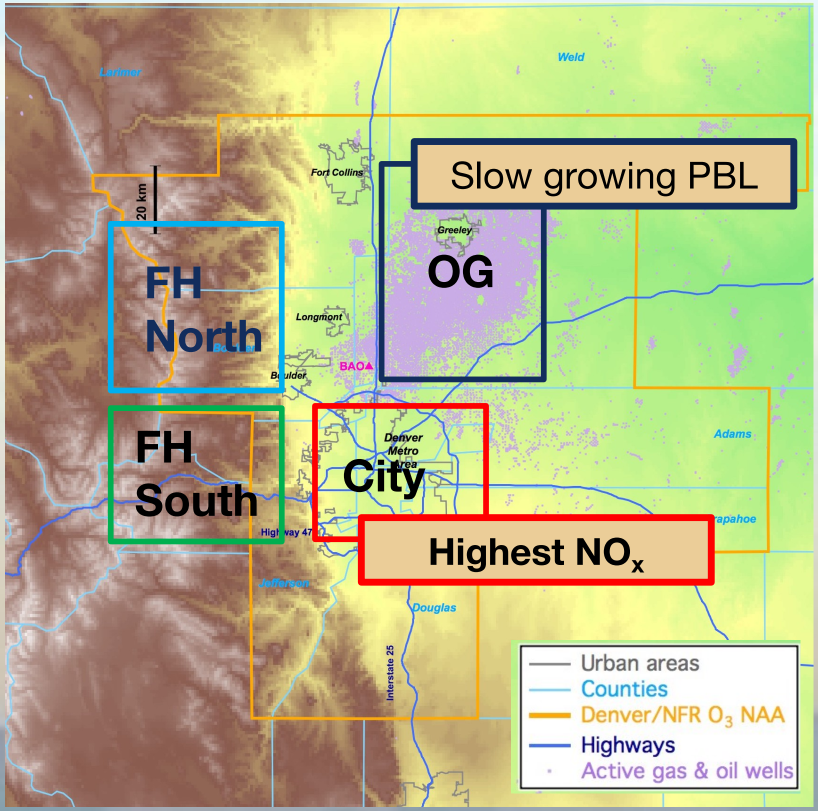




Pfister et al., JGR, 2019

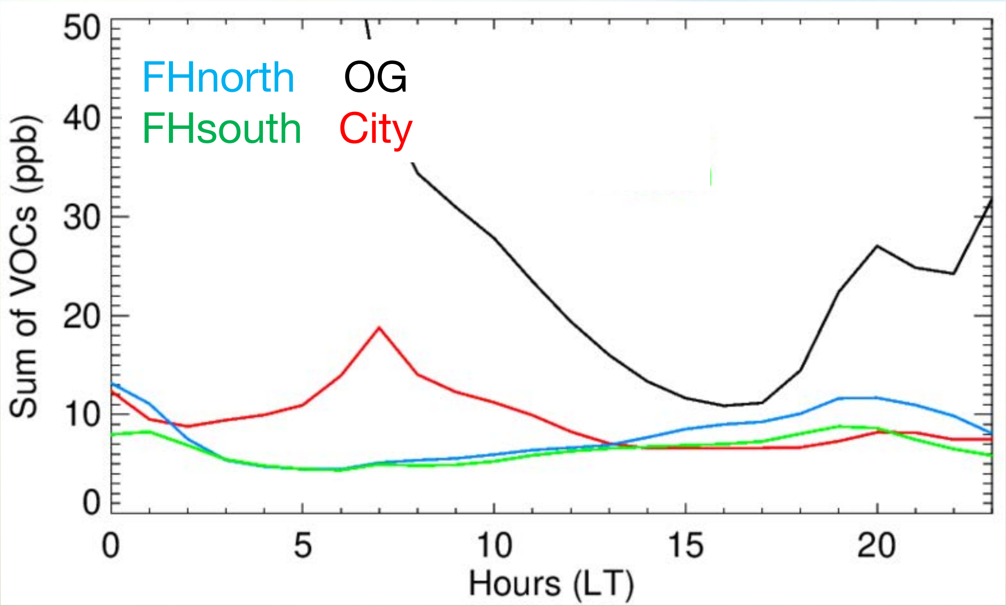
NO_x Mixing Ratios (ppb)

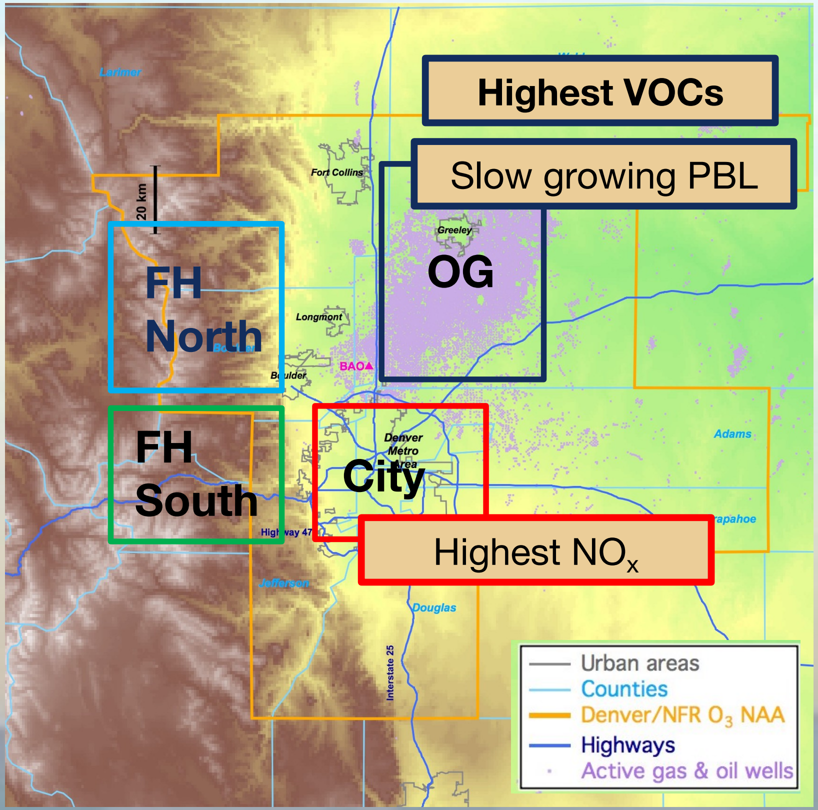




Pfister et al., JGR, 2019

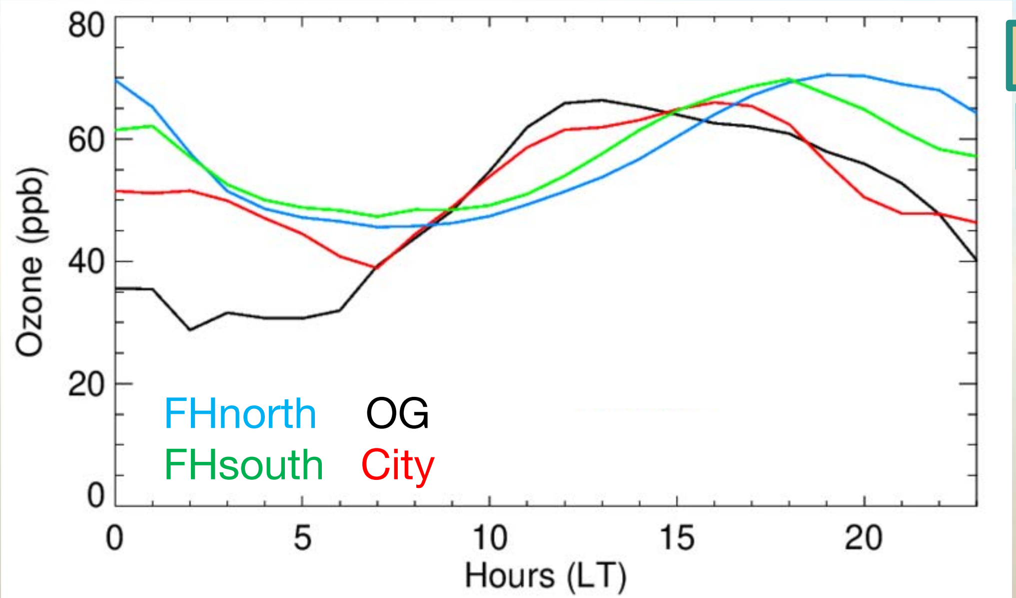
VOC Mixing Ratios (ppb)

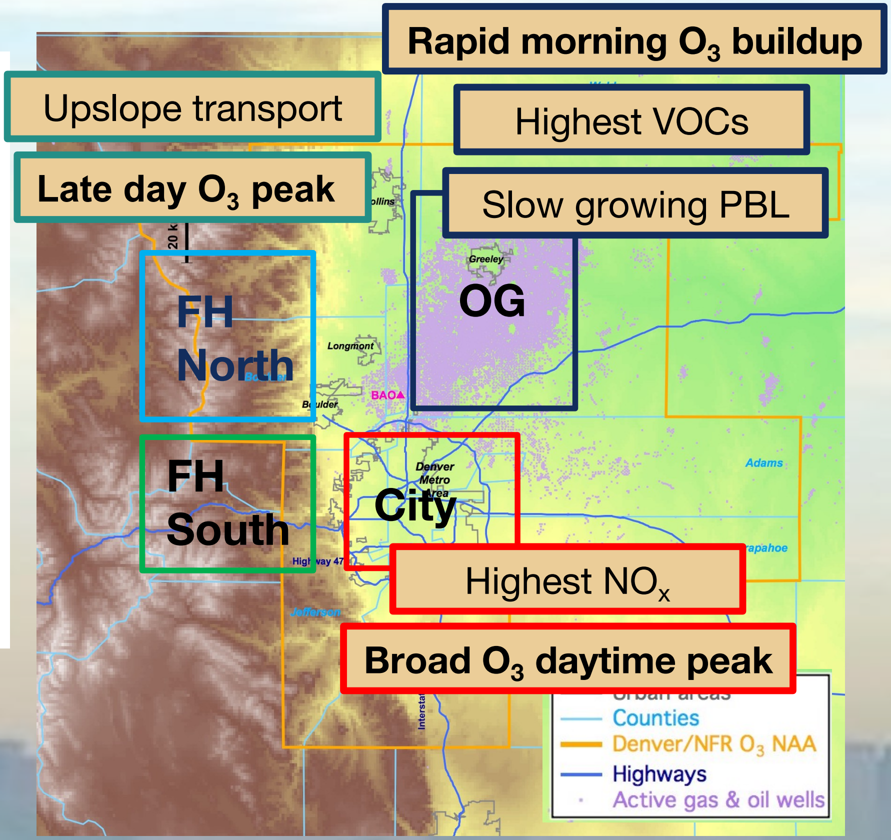




Pfister et al., JGR, 2019

Ozone Mixing Ratios (ppb)

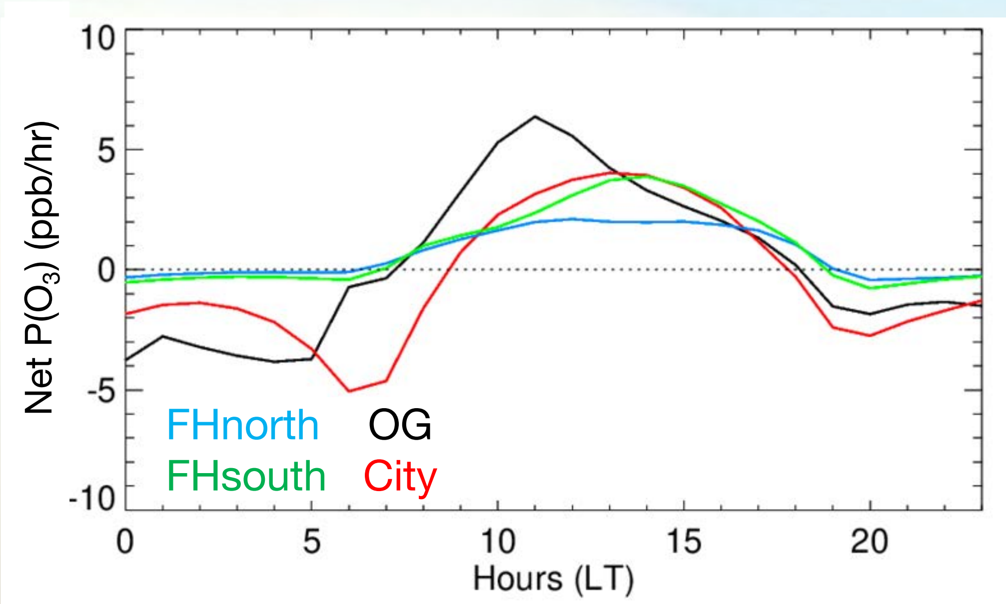


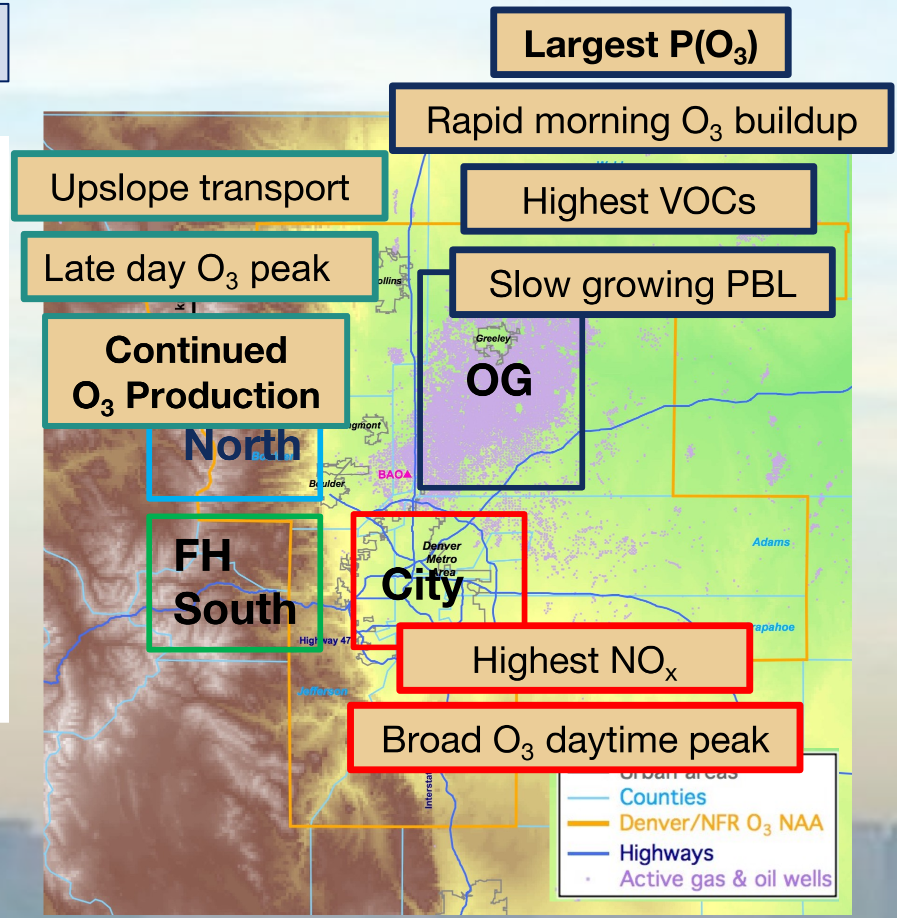


Pfister et al., JGR, 2019

Chemical Analysis

Net Chemical Ozone Production (ppb/hr)





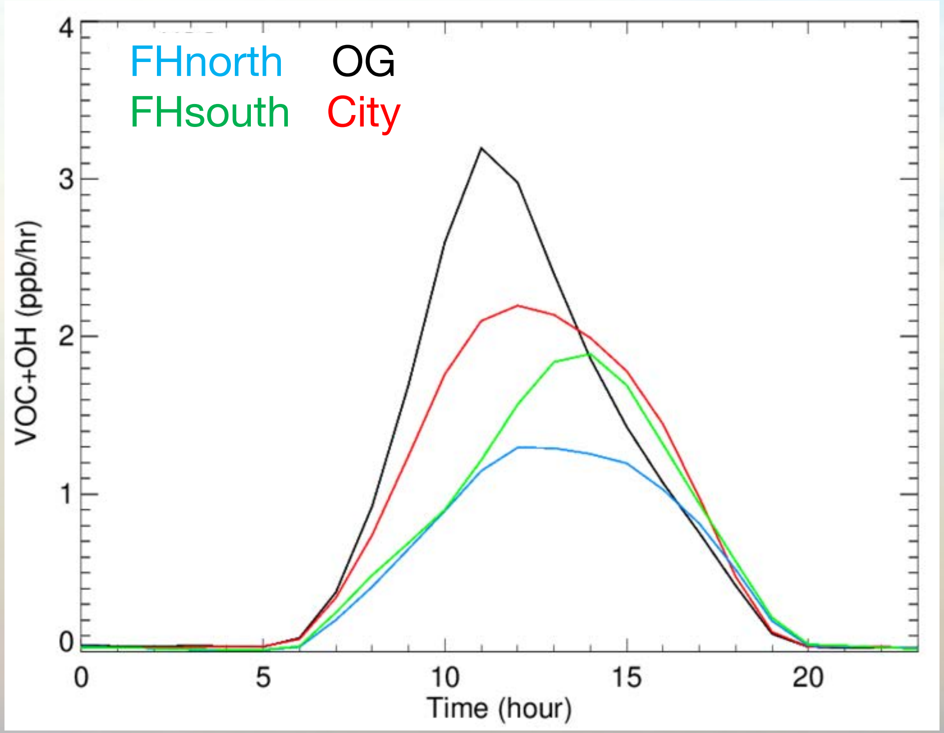
Daytime Net $P(O_3)$

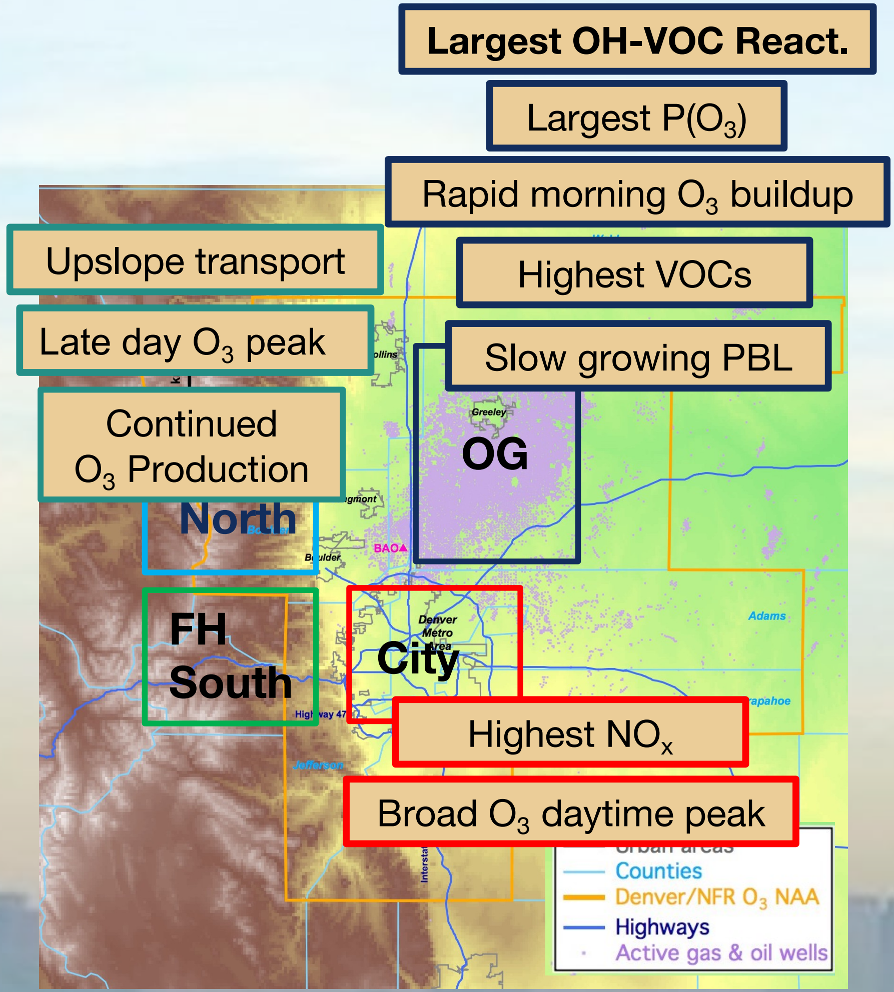
15-20 ppb	30-40 ppb
20-25 ppb	15-30 ppb

Pfister et al., JGR, 2019

Chemical Analysis

OH+VOC Reactivity (ppb/hr)



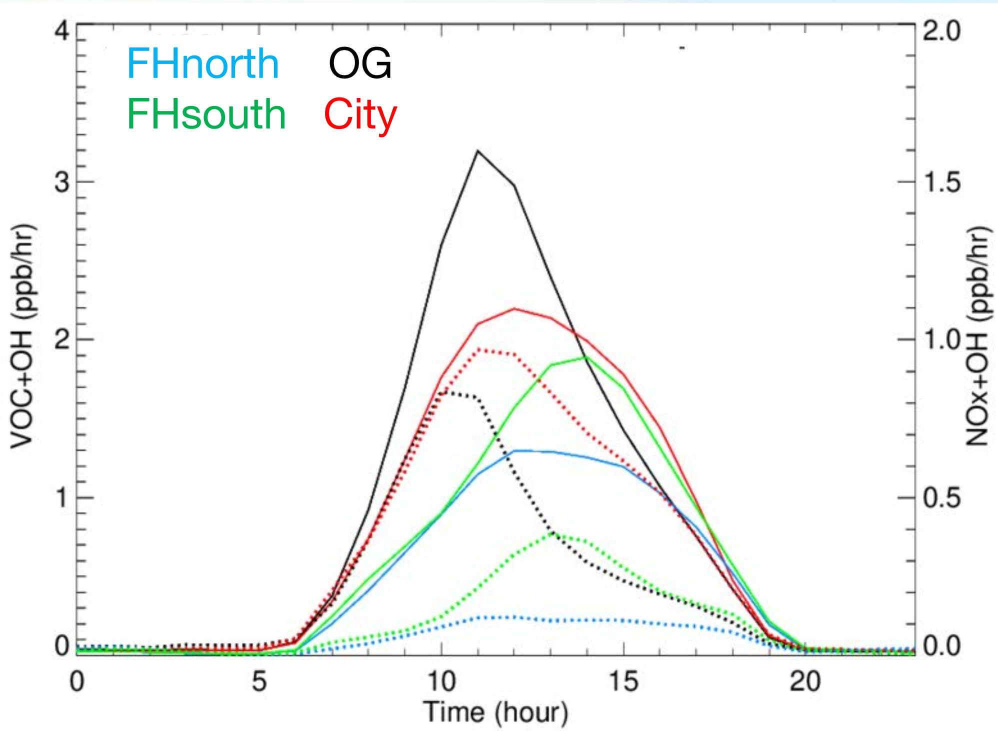


Pfister et al., JGR, 2019

Chemical Analysis

OH+NO_x Reactivity (ppb/hr)

OH+VOC Reactivity (ppb/hr)



Largest OH-VOC React.

Largest P(O_3)

Rapid morning O_3 buildup

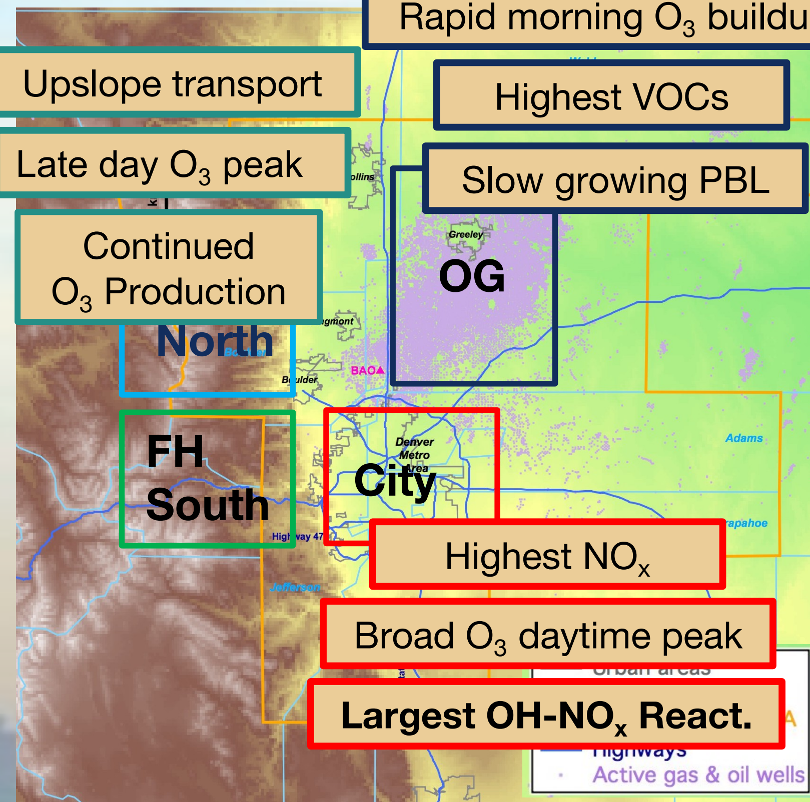
Upslope transport

Highest VOCs

Late day O_3 peak

Slow growing PBL

Continued
O_3 Production



Highest NO_x

Broad O_3 daytime peak

Largest OH-NO_x React.

OH + VOC React. / OH + NO_x React.	~5-10	~5
	~5-10	~2

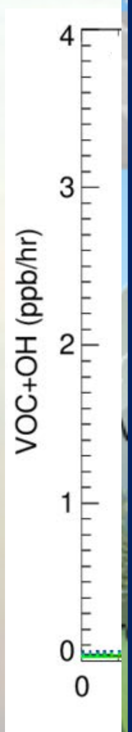
HIGH: Per

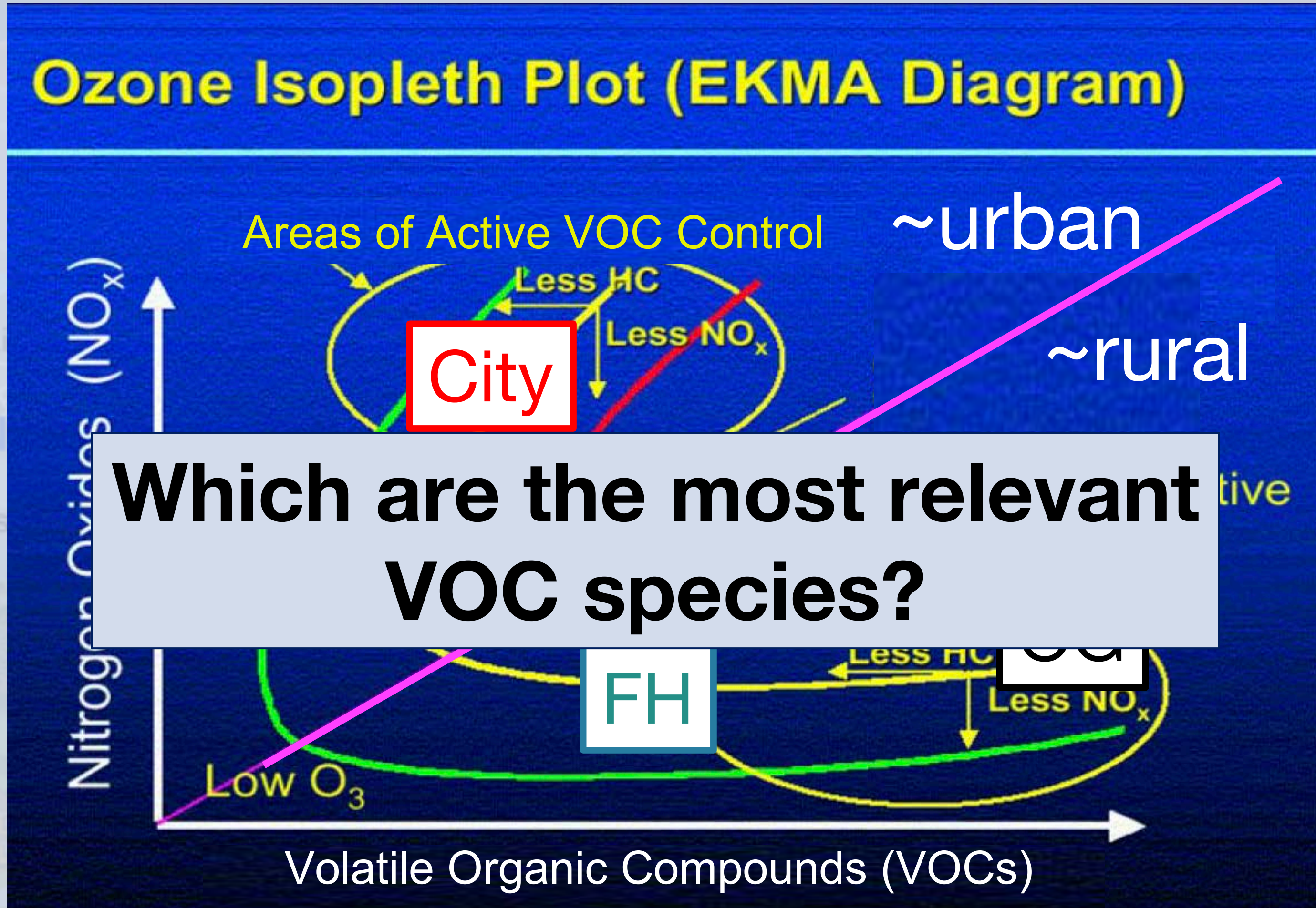
LOW: NO_2+OH

City closer to VOC limited
Other regions NO_x limited

OH+NO_x Reactivity (ppb/hr)

Largest OH-VOC React.





Which are the most relevant VOC species?

$\frac{\text{OH}}{\text{OH + NO}_x\text{ React.}}$

~5-10	~2

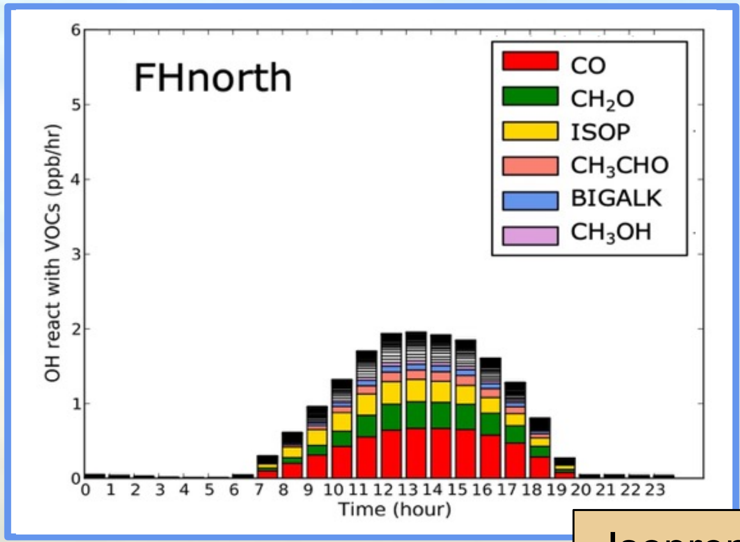
Other regions NO_x limited

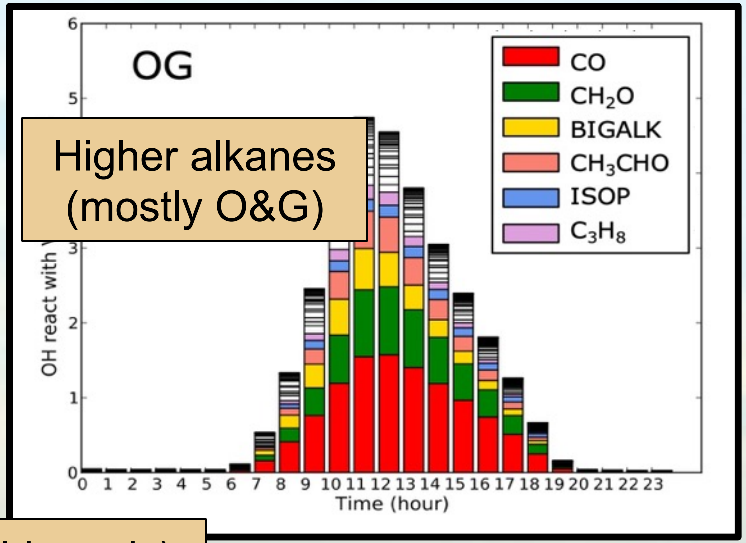
Chemical Analysis

OH+VOC Reactivity (ppb/hr)

⇒ CO and Formaldehyde largest contributors

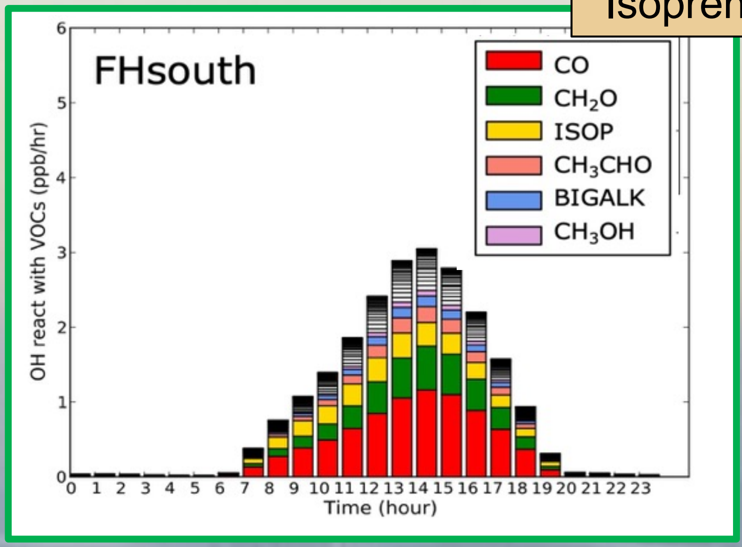
& acetaldehyde (mobile & photochemical prod.)

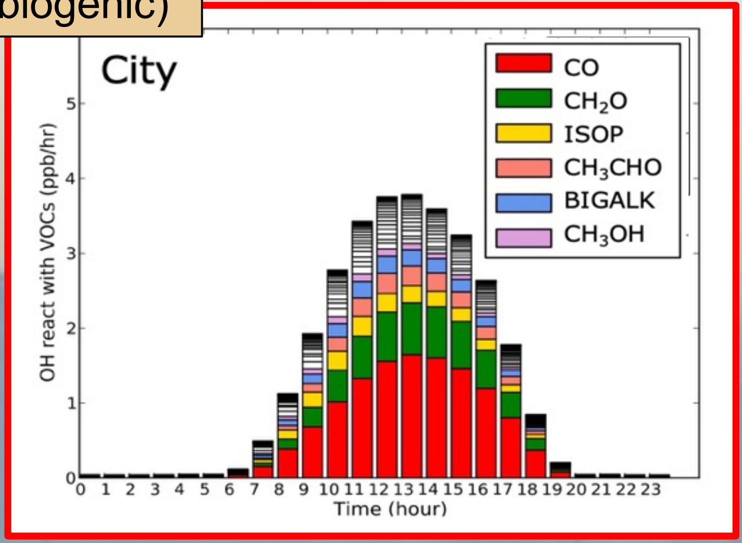




Higher alkanes (mostly O&G)

Isoprene (mostly biogenic)

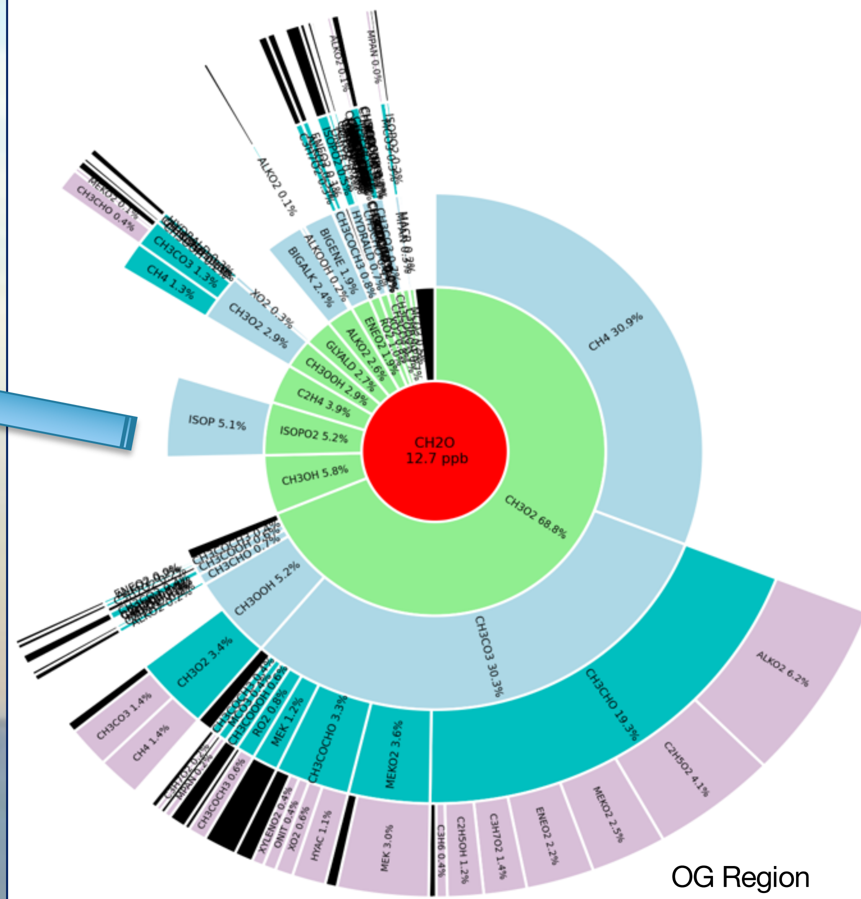




Formaldehyde – Emissions or Chemistry?

	OG	City	FHnorth	FHsouth
CH4	**29.4%**	**26.7%**	**27.1%**	**25.6%**
CH3OH	5.7%	4.4%	5.3%	5.2%
C2H4	3.8%	3.5%	2.7%	2.8%
C2H6	3.2%	0.3%	0.7%	0.0%
C2H5OH	1.2%	1.8%	1.3%	1.5%
C3H6	**7.9%**	**11.0%**	4.5%	4.7%
C3H8	2.4%	0.1%	0.1%	0.0%
BIGALK	**16.8%**	9.6%	**8.4%**	**8.2%**
BIGENE	4.1%	5.4%	3.2%	2.7%
ISOP	**7.9%**	**13.4%**	**26.2%**	**24.4%**
XYLENES	0.4%	1.5%	0.0%	0.0%
TOLUENE	0.0%	0.5%	0.0%	0.0%
TERP	0.4%	1.6%	6.2%	5.2%
TOTAL	***83.2%***	***79.8%***	***85.9%***	***80.4%***

Pre-cursor emissions for CH_2O



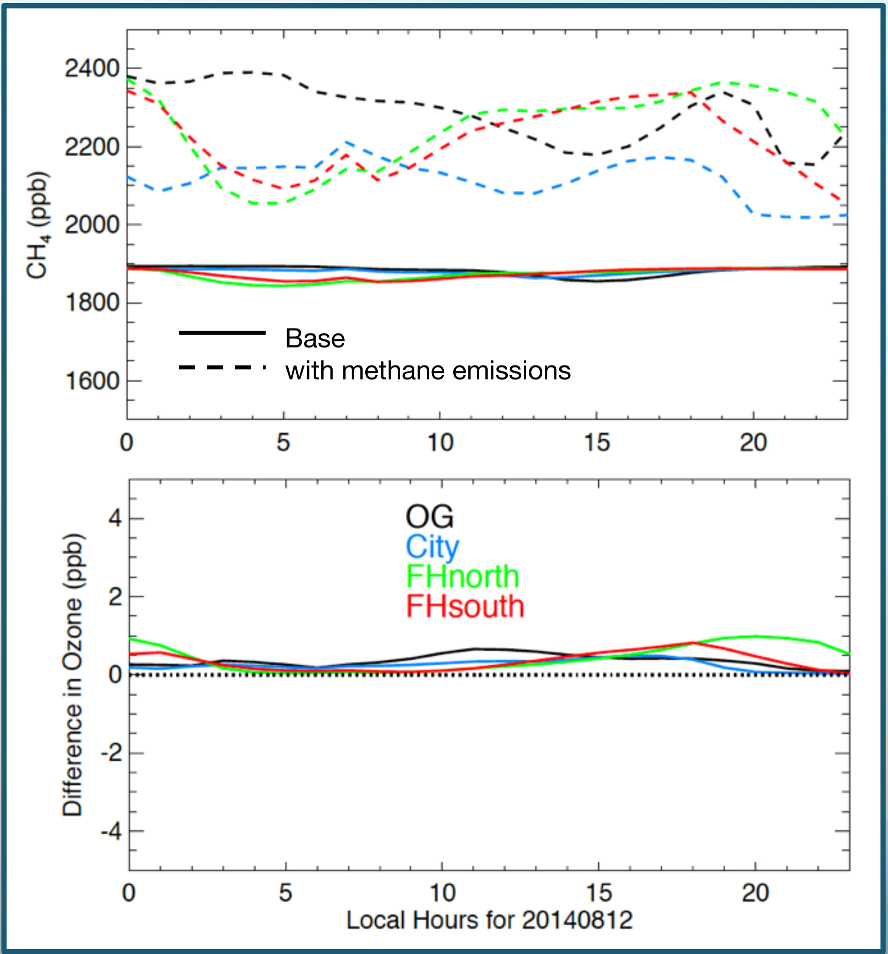
Most of formaldehyde from secondary formation and traced back to emissions of methane, higher alkanes, propene, and isoprene.

Pfister et al., JGR, 2019

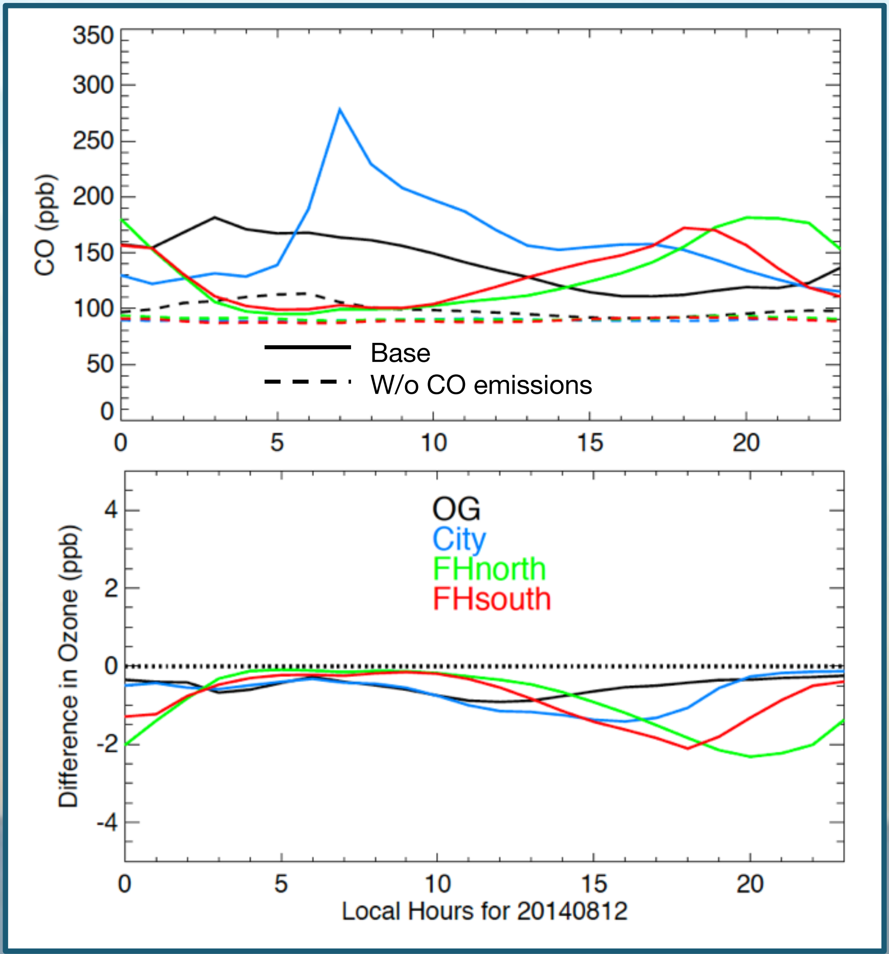
Chemical Analysis

Role of Methane and CO

With local methane emissions



Without local CO emissions



Methane not only relevant on climate scales, should also be considered in air quality

Local CO emissions are not negligible

Pfister et al., JGR, 2019

FRAPPÉ - Summary

- What and where are the relevant sources?

Local emissions, largest impact from OG and mobile sources

- How do these emissions get transported?

Upslope flows dominate on high ozone days –> pollution impacts pristine areas

- How do they get chemically processed?

Highly reactive VOC mix and abundance of NO_x

- How much pollution comes into Colorado?

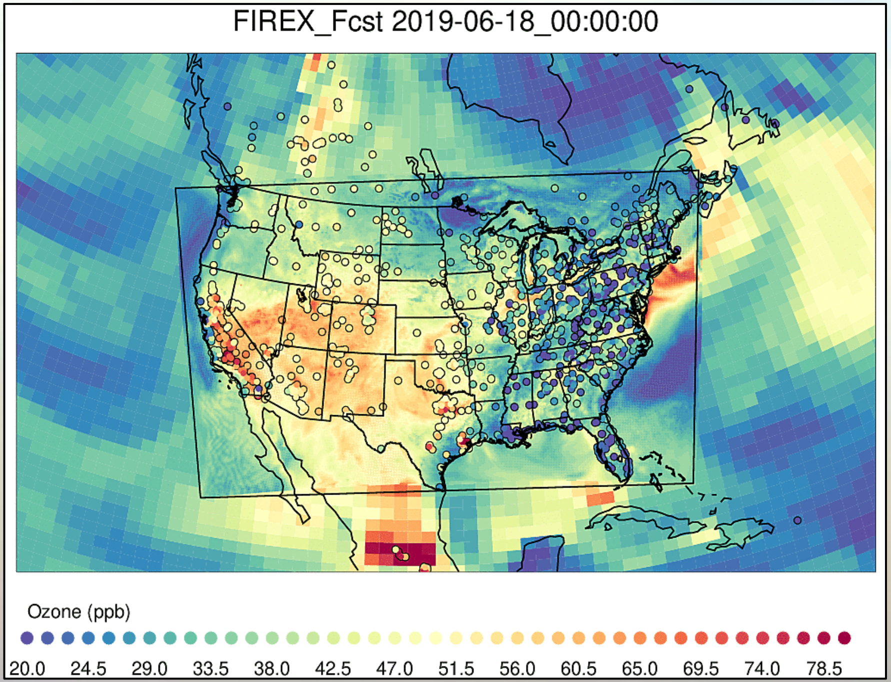
Most of excess ozone is due to local production

- Which are the best ways to improve air quality?

Reduction in O&G and mobile sources. Focus on pre-cursor species to Formaldehyde. Some benefits from methane and CO reductions.

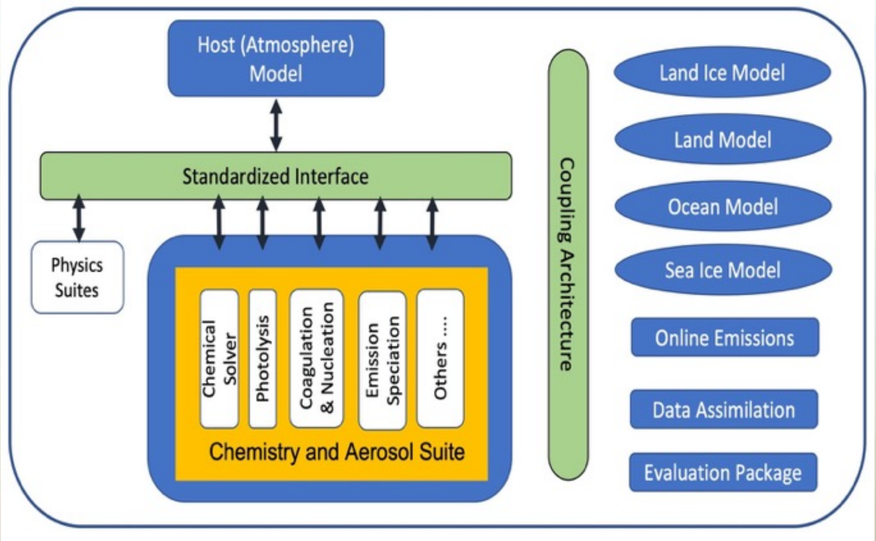
Past/Current AQ Studies

Future AQ Studies



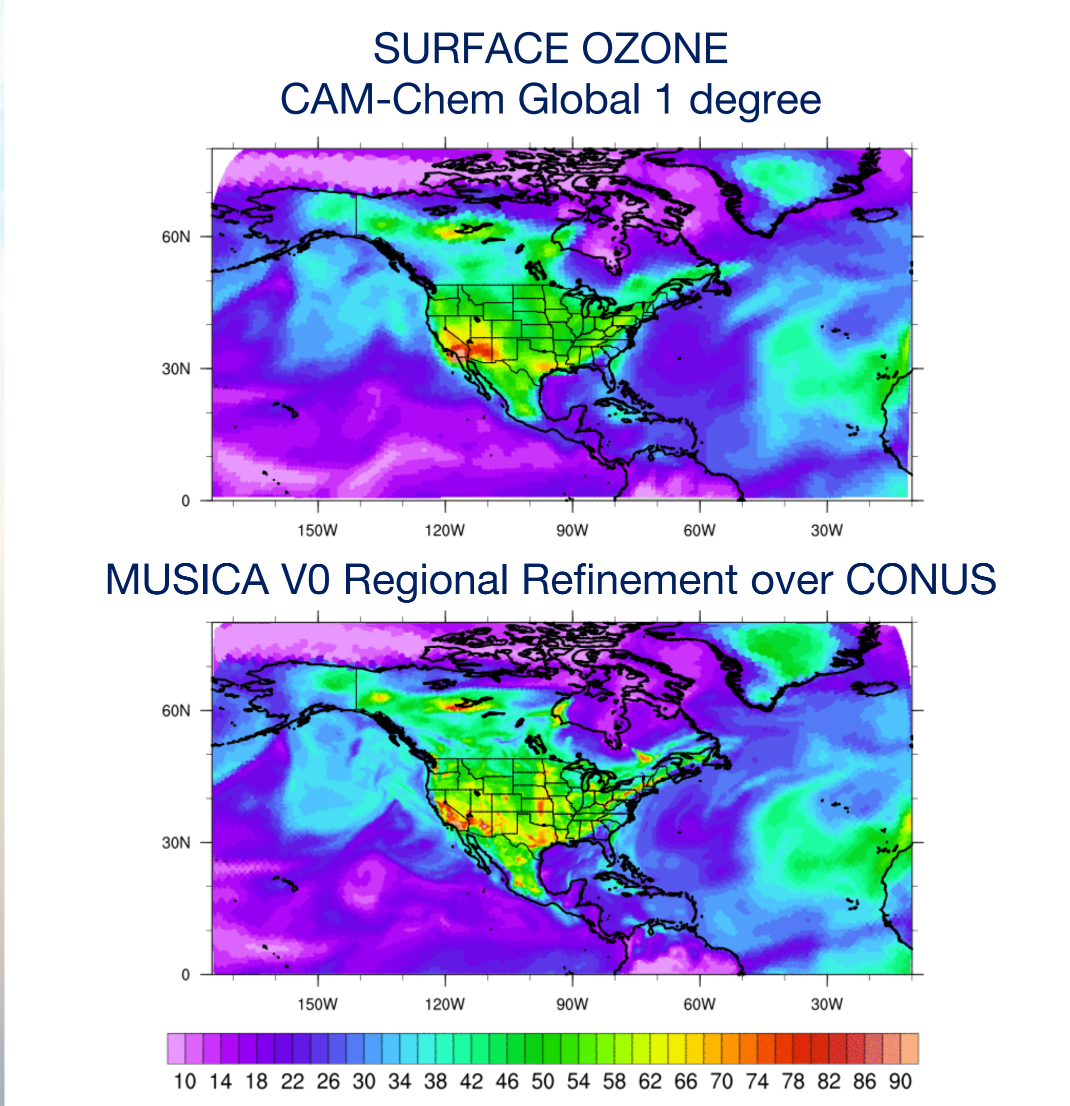
MUSICA

Multiscale Infrastructure for Chemistry and Aerosols



Unified and modular community infrastructure for studying atmospheric composition across all relevant scales in the Earth System.

Pfister et al., 2020, under revision for BAMS



MUSICA

Multiscale Infrastructure for Chemistry and Aerosols

VERSION 0

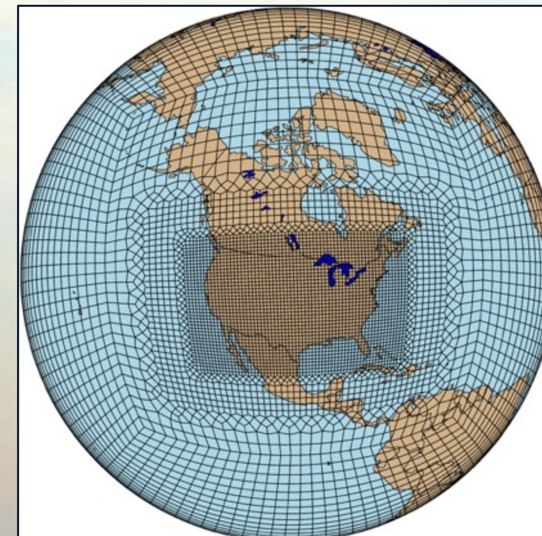


Figure Credits: Rebecca Schwantes and Forrest Lacey

https://www2.acom.ucar.edu/sections/multi-scale-chemistry-modeling-musica

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