

# What drives high wintertime ozone in the oil and natural gas fields of the western U.S.?

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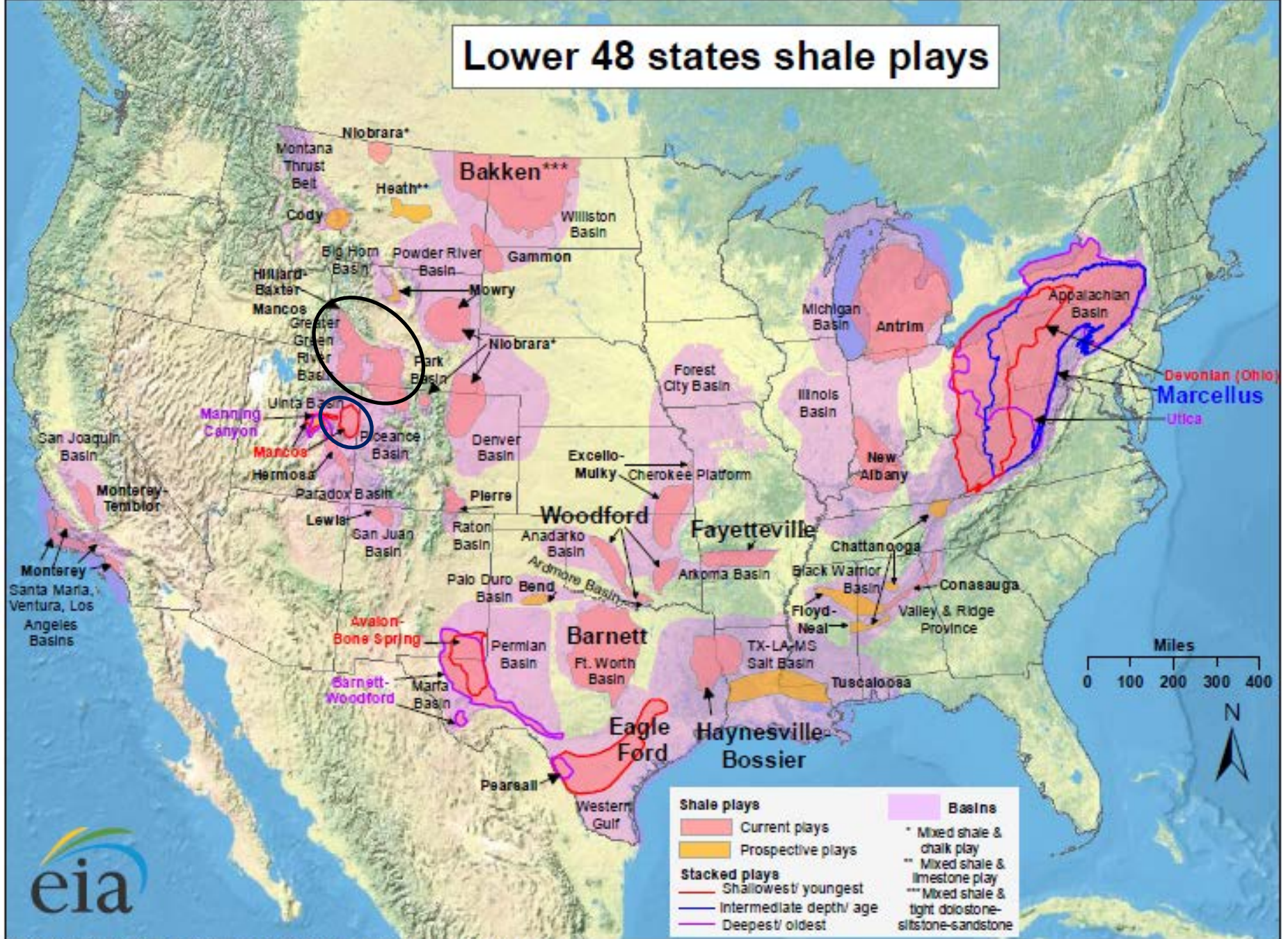
**S. McKeen<sup>1,2</sup>, M.Trainer<sup>2</sup>, G.J. Frost<sup>1,2</sup>, J.M. Roberts<sup>2</sup>, J. de Gouw<sup>1,2</sup>, C. Warneke<sup>1,2</sup>, J. Peischl<sup>1,2</sup>, J. Gilman<sup>1,2</sup>, Brown<sup>2</sup>, P.Edwards<sup>1,2</sup>, R.Wild<sup>1,2</sup>, Y. Pichugina<sup>1,2</sup>, A. Langford<sup>2</sup>, R. Banta<sup>1,2</sup>, A. Brewer<sup>1,2</sup>, C. Senff<sup>1,2</sup>, A. Karion<sup>1,2</sup>, C. Sweeney<sup>1,2</sup>, S. Oltmans<sup>1,2</sup>, G. Petron<sup>1,2</sup>, R. Schnell<sup>2</sup>, B. Johnson<sup>2</sup>, D. Helmig<sup>3</sup>**

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# Lower 48 states shale plays



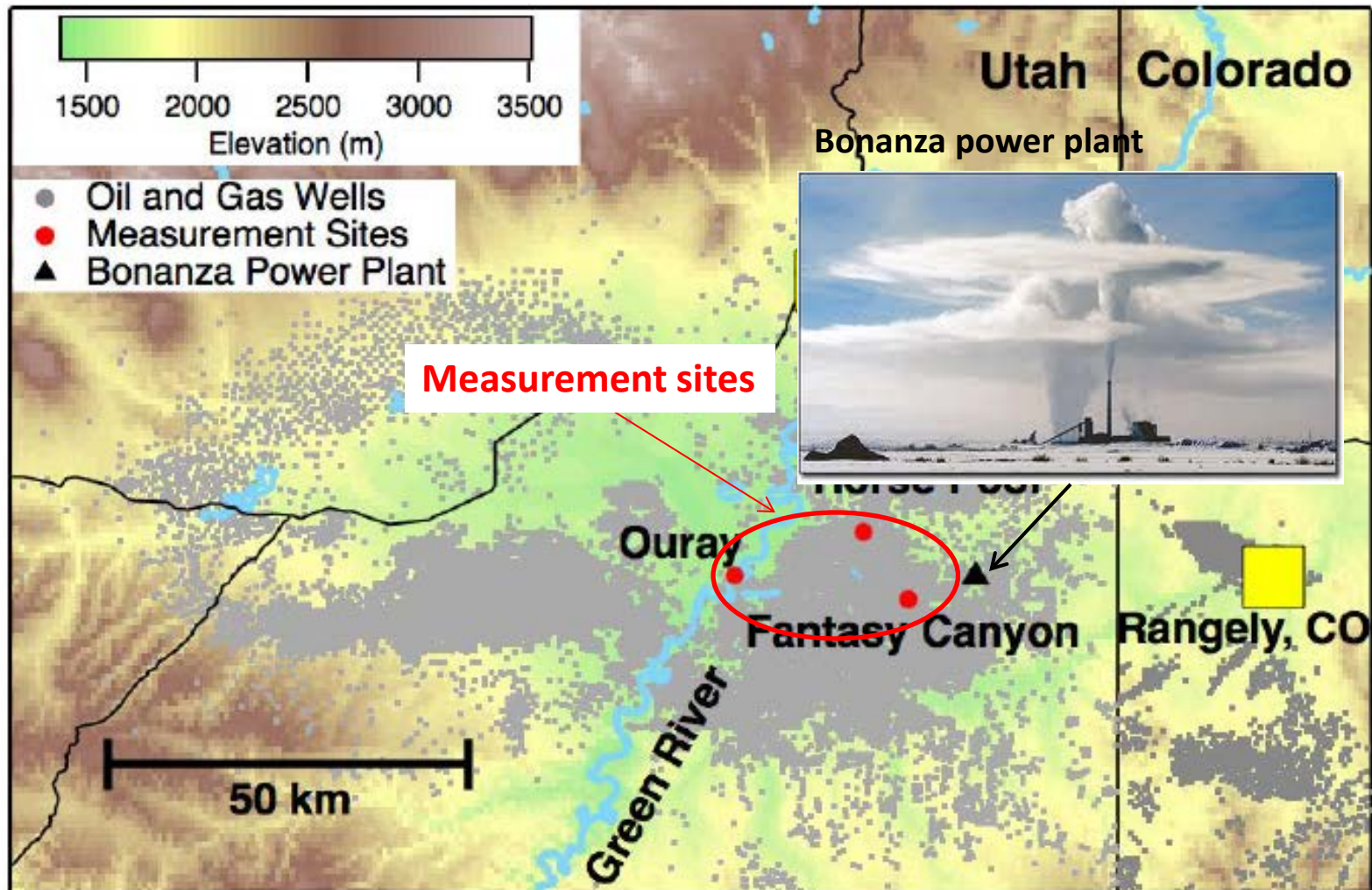
Source: Energy Information Administration based on data from various published studies.  
 Updated: May 9, 2011



# Background

- During some winters over rural areas with high oil and natural gas production in Wyoming and Utah high O<sub>3</sub> episodes were observed (*Schnell et al., 2009; Oltmans et al., 2014*).
- *Carter and Seinfeld (2012)* and *Edwards et al. (2014)* used detailed chemical mechanisms in box models to study high wintertime O<sub>3</sub> production observed in Wyoming and Utah, respectively. The authors stressed the need for full 3D air quality models to address the high wintertime O<sub>3</sub> episodes.
- NOAA/ESRL and other groups conducted two intensive field campaigns - Uinta Basin Winter Ozone Study (UBWOS) in January-February, **2012 (warmer, little or no snow conditions)** and **2013 (colder and snowy)** to study meteorology, oil/gas emissions and atmospheric chemistry in the Uinta Basin. **In 2013 the highest O<sub>3</sub> concentration in the U.S. was observed in the Uinta Basin during winter!**

# Topography of the Uinta Basin, Utah



The region is sparsely populated (~50,000 people). The urban VOC and NO<sub>x</sub> emissions are not high.

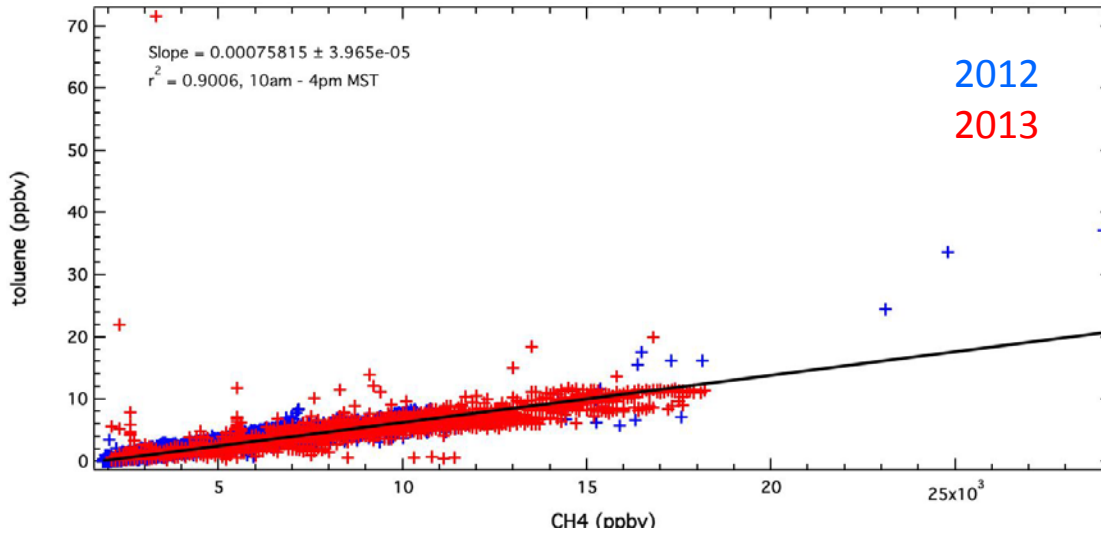
# Objectives of our modeling study

- Model the wintertime meteorological conditions in 2012 and 2013 over the Uinta Basin (UB), Utah; Focus on cold pool type stagnations during 2013;
- Estimate emissions of  $\text{NO}_x$  and VOCs for the oil/gas sector in the UB using the atmospheric measurements from the UBWOS field campaigns;
- Conduct air quality simulations using both bottom-up (EPA NEI-2011) and top-down emission scenarios;
- Investigate the major driving factors of high the wintertime ozone in the UB;

**A high resolution meteorology-chemistry modeling using WRF-Chem (with RACM gas chemistry) was conducted for January – February, 2012 and 2013.**

**The dry deposition and photolysis schemes in WRF-Chem were modified to take into account effect of snow cover.**

# Examples of CH<sub>4</sub> regressions, VOC/NO<sub>y</sub> measurements at the Horse Pool site – The basis of the Top-Down inventory

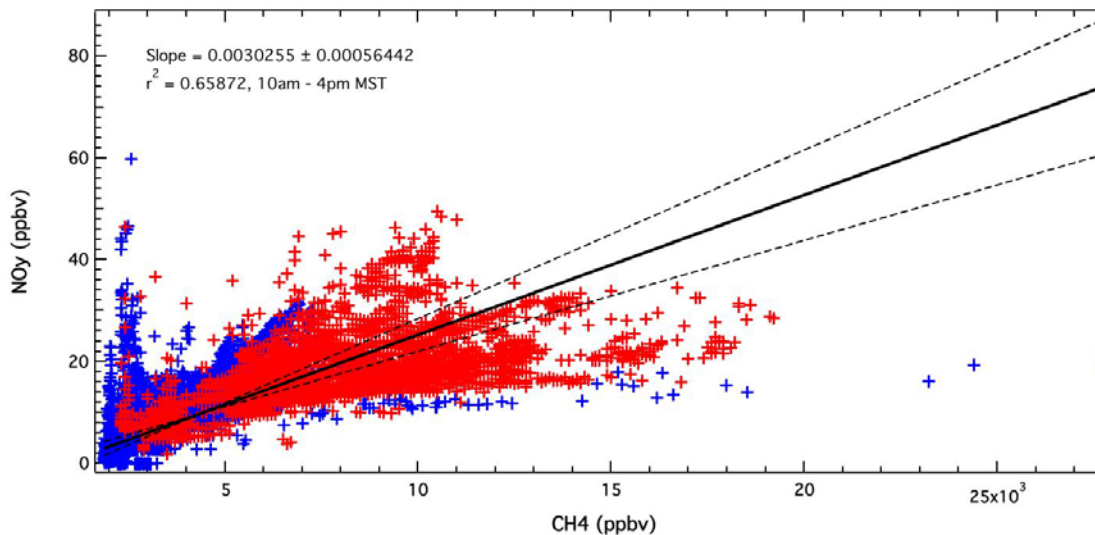


Daytime CH<sub>4</sub> regressions for:

- 49 Primary VOCs (GC and PTRMS)
- 10 Oxygenated VOCs
- NO<sub>y</sub>

Primary VOC regressions are:

- Very robust ( $0.85 < r^2 < 0.98$ )
- The same for 2012 and 2013



NO<sub>y</sub> – CH<sub>4</sub> regression:

- Combine 2012/2013 data
- r<sup>2</sup> = 0.66
- Slope used as “Best Guess” in the top-down inventory

## Anthropogenic emission scenarios used in the WRF-Chem model: Emission totals for the **oil and gas sector** in the Uinta Basin

Emission inventories	Inventory source	CH <sub>4</sub> (tons/year)	VOC (tons/year)	NO <sub>x</sub> (tons/year)
Bottom-up	EPA NEI-2011	110,539	111,536	18,131
Top-down	Regression analysis	531,457	203,389	4,583

Total CH<sub>4</sub> flux estimate is from *Karion et al., 2013*

Top-down: Using NO<sub>y</sub>/CH<sub>4</sub> and VOC/CH<sub>4</sub> ratios from surface observations during winters of 2012 and 2013

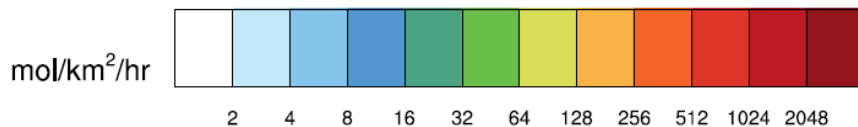
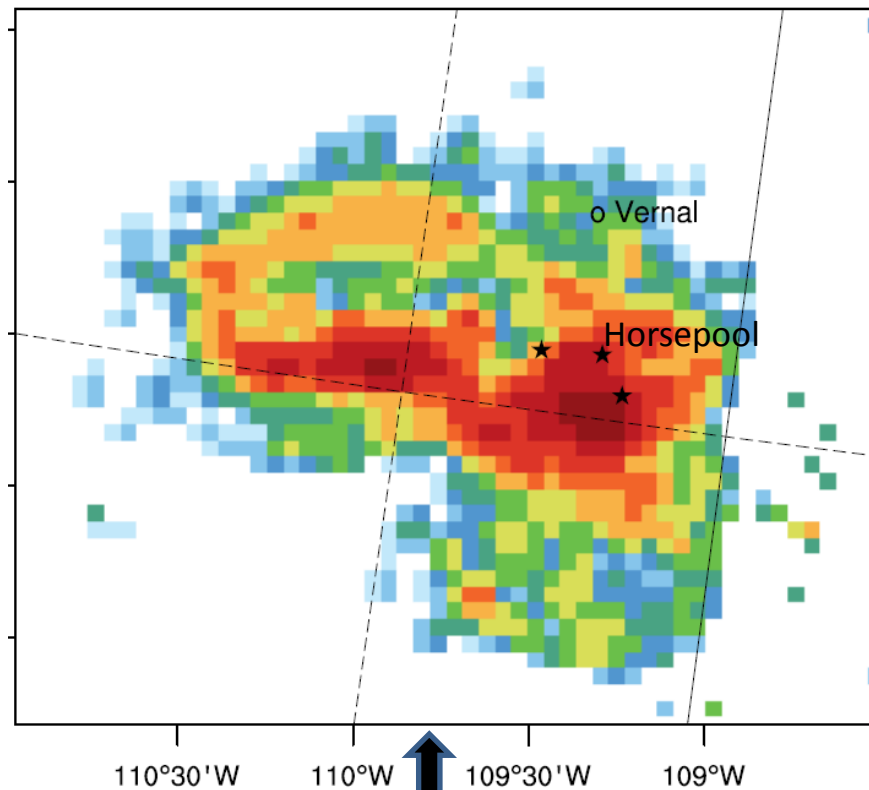
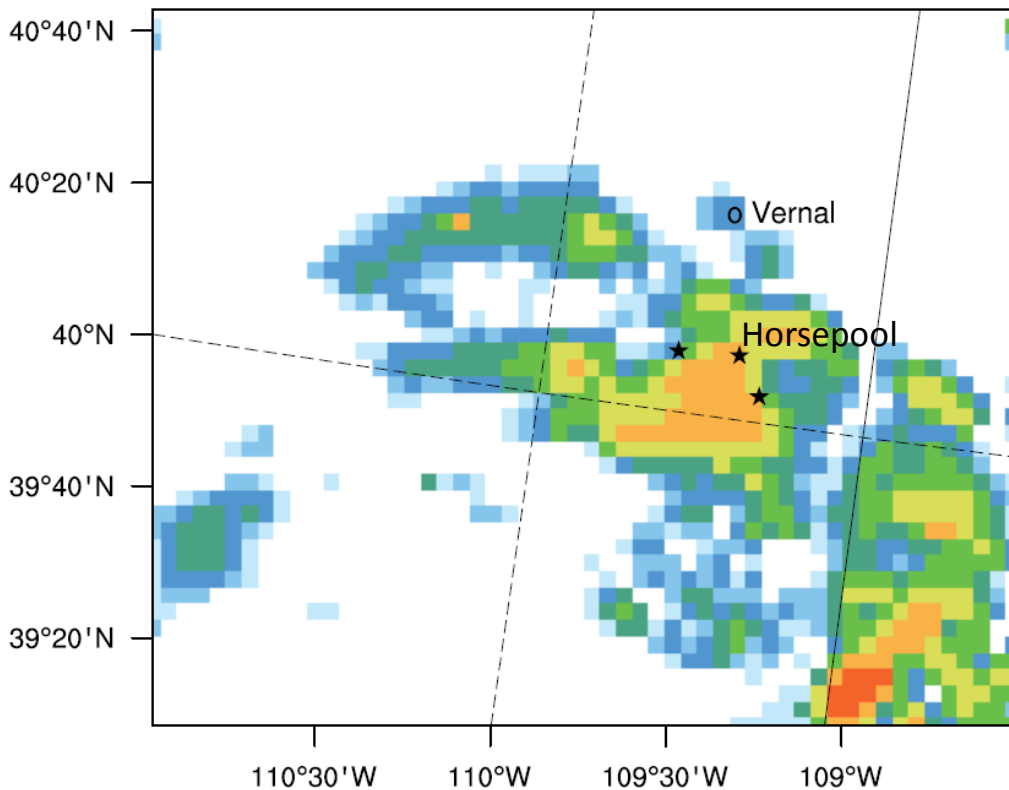
Total CH<sub>4</sub> and VOC emissions in NEI-2011 are lower by a factor of 4.8 and 1.8 than in the top-down estimates respectively!

Conversely, NO<sub>x</sub> emissions are 4.0 times higher in the NEI-2011 inventory!

# Anthropogenic methane emissions in the 4km resolution grid over the Uinta Basin (two inventories)

Bottom-up (NEI-2011)

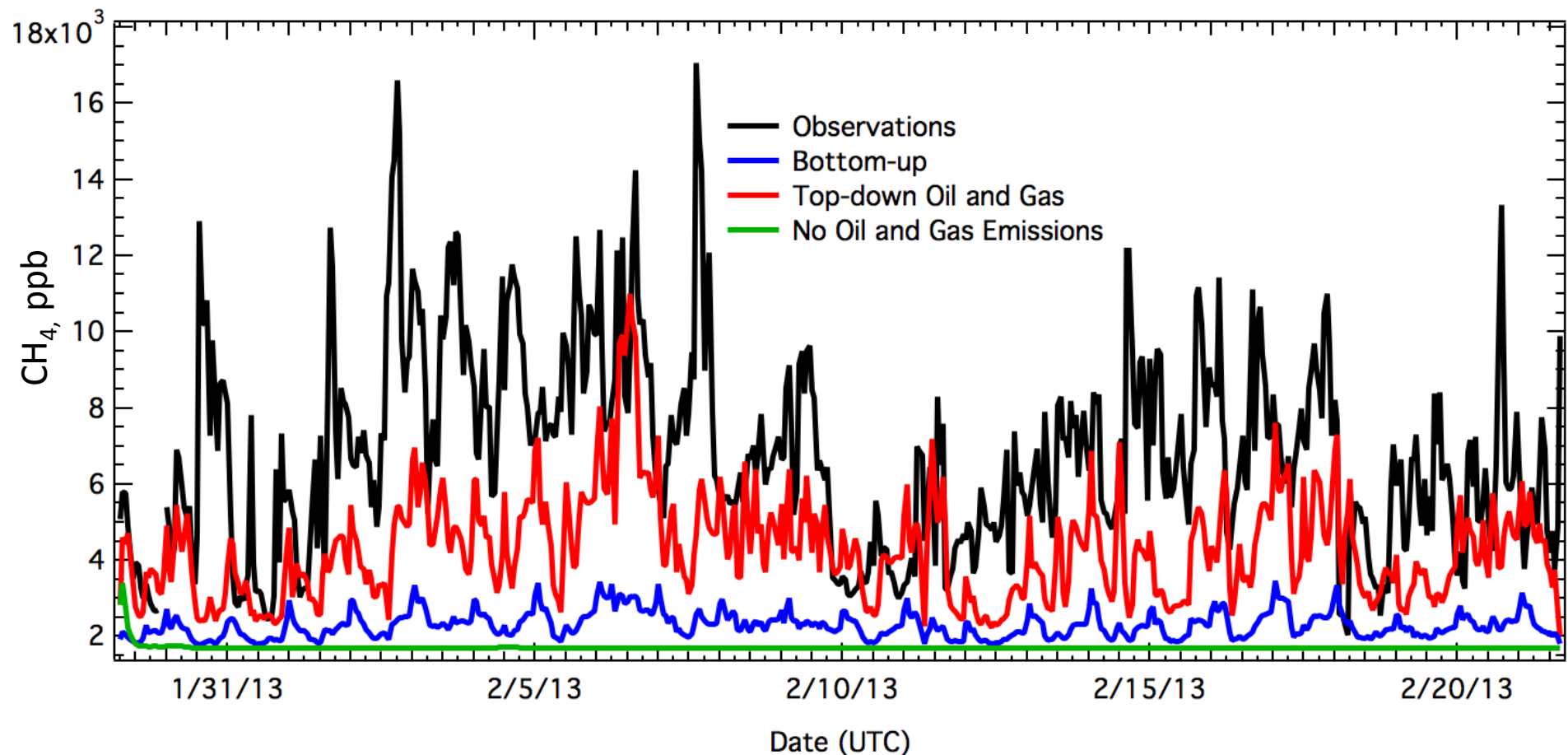
Top-down



Oil and gas well locations are from Utah Department of Environmental Quality



# Observed and modeled methane time series at the Horse Pool site in 2013

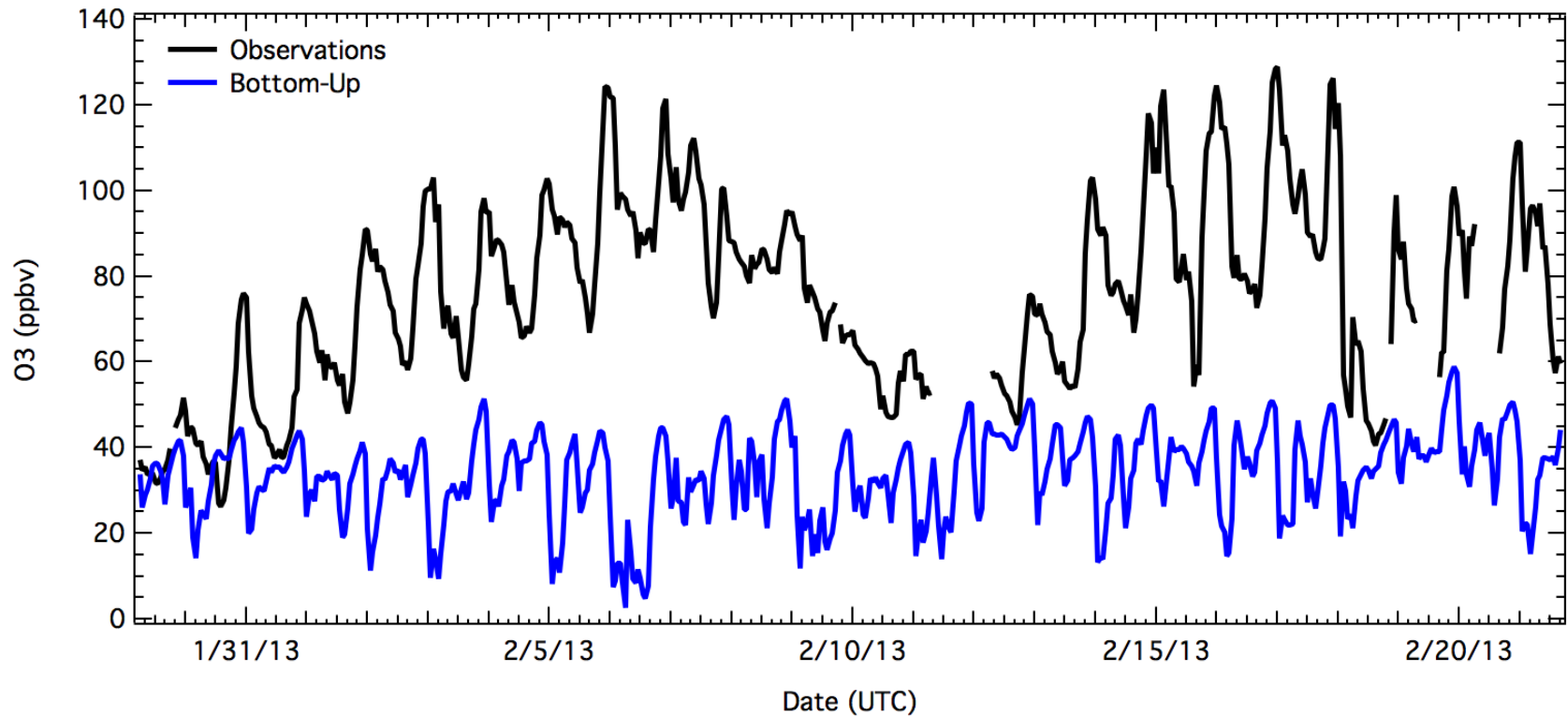


Daytime (9-17MST) statistics:

Bottom-up case:  $r = 0.29$ ,  $med. bias = -5.1 \text{ ppm}$ ,  $med. (mod./obs.) = 0.31$

Top-down case:  $r = 0.37$ ,  $med. bias = -2.9 \text{ ppm}$ ,  $med. (mod./obs.) = 0.61$

# Observed and modeled ozone time series at the Horsepool site

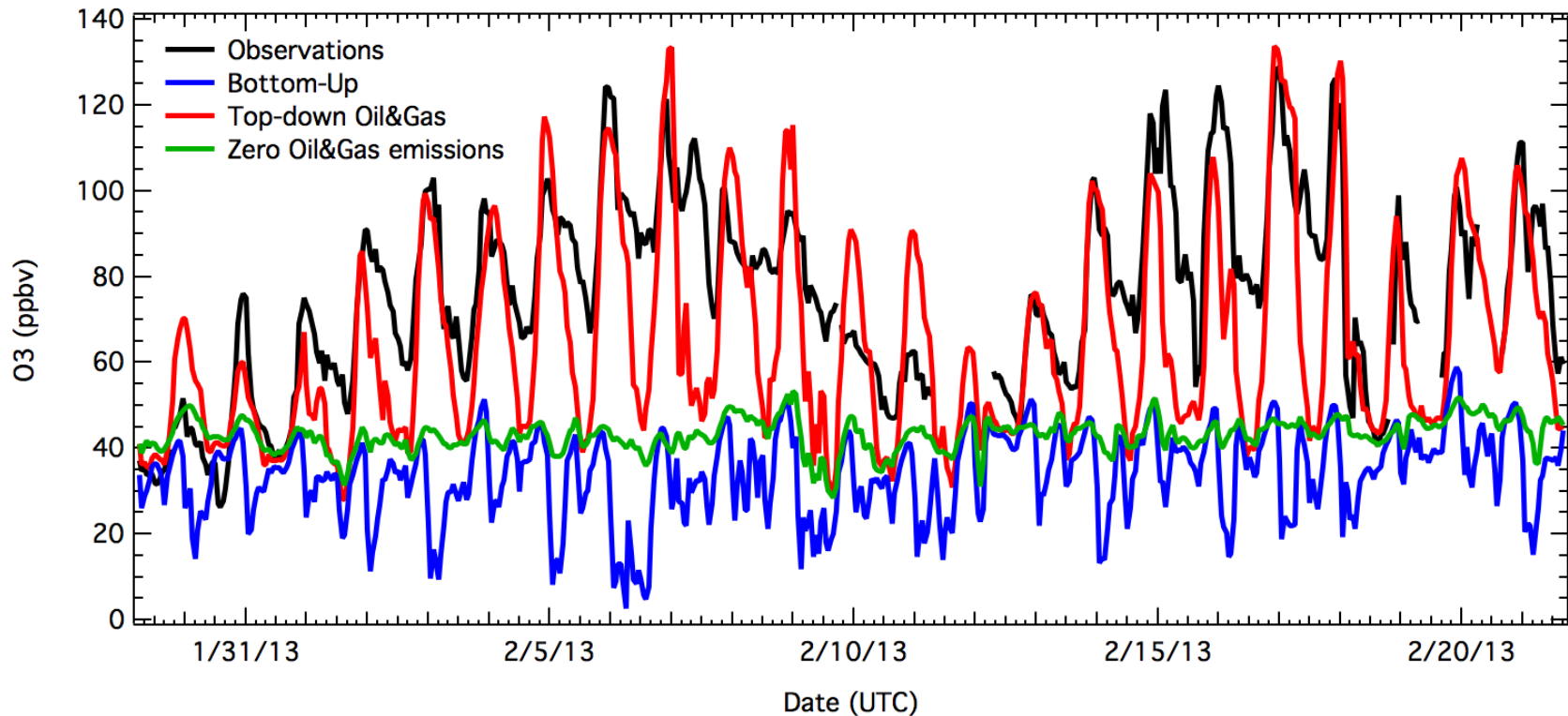


# Observed and modeled **ozone** time series at the Horsepool site, 2013

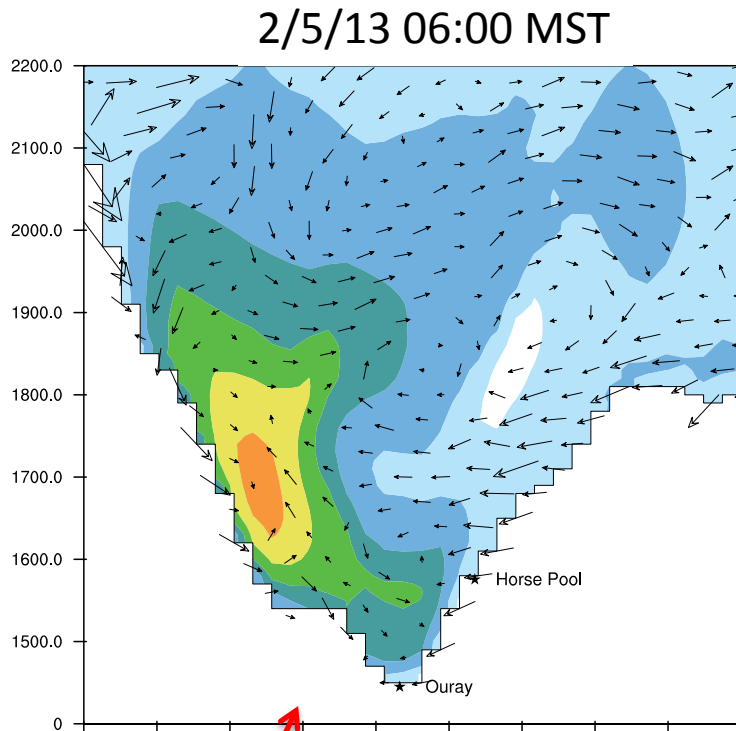
Daytime (9-17MST) statistics:

Bottom-up case:  $r = 0.33$ , *med. bias* = -39.8 ppb, *med. (mod./obs.)* = 0.51

Top-down case:  $r = 0.85$ , *med. bias* = -5.3 ppb, *med. (mod./obs.)* = 0.93

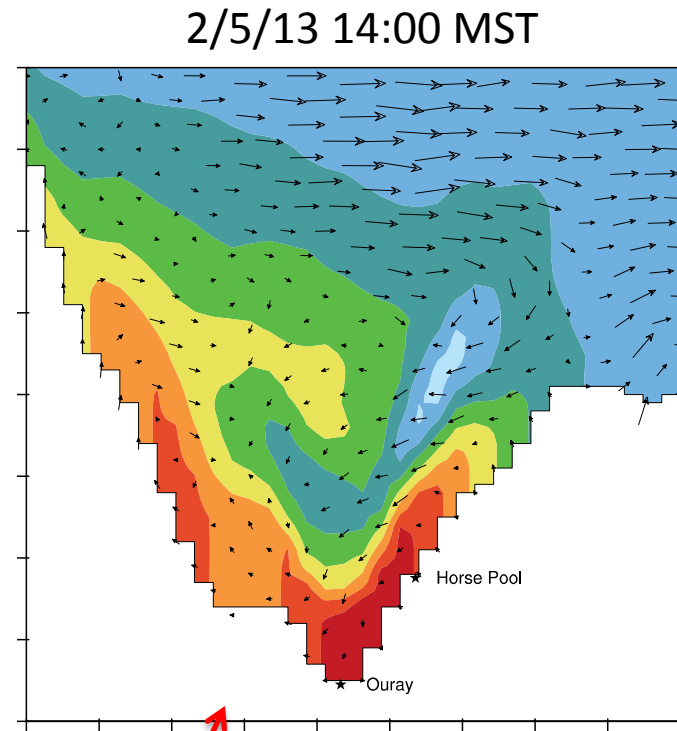
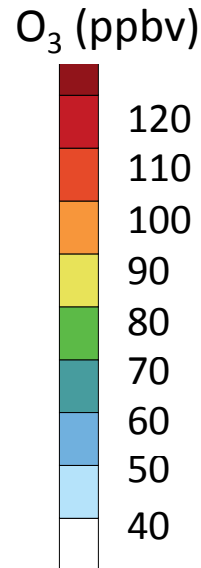


# West-East Cross-section through the Uinta Basin



## Nighttime and Early Morning

- Strong drainage flow
- Complicated circulation within Basin
- O<sub>3</sub> from previous day trapped

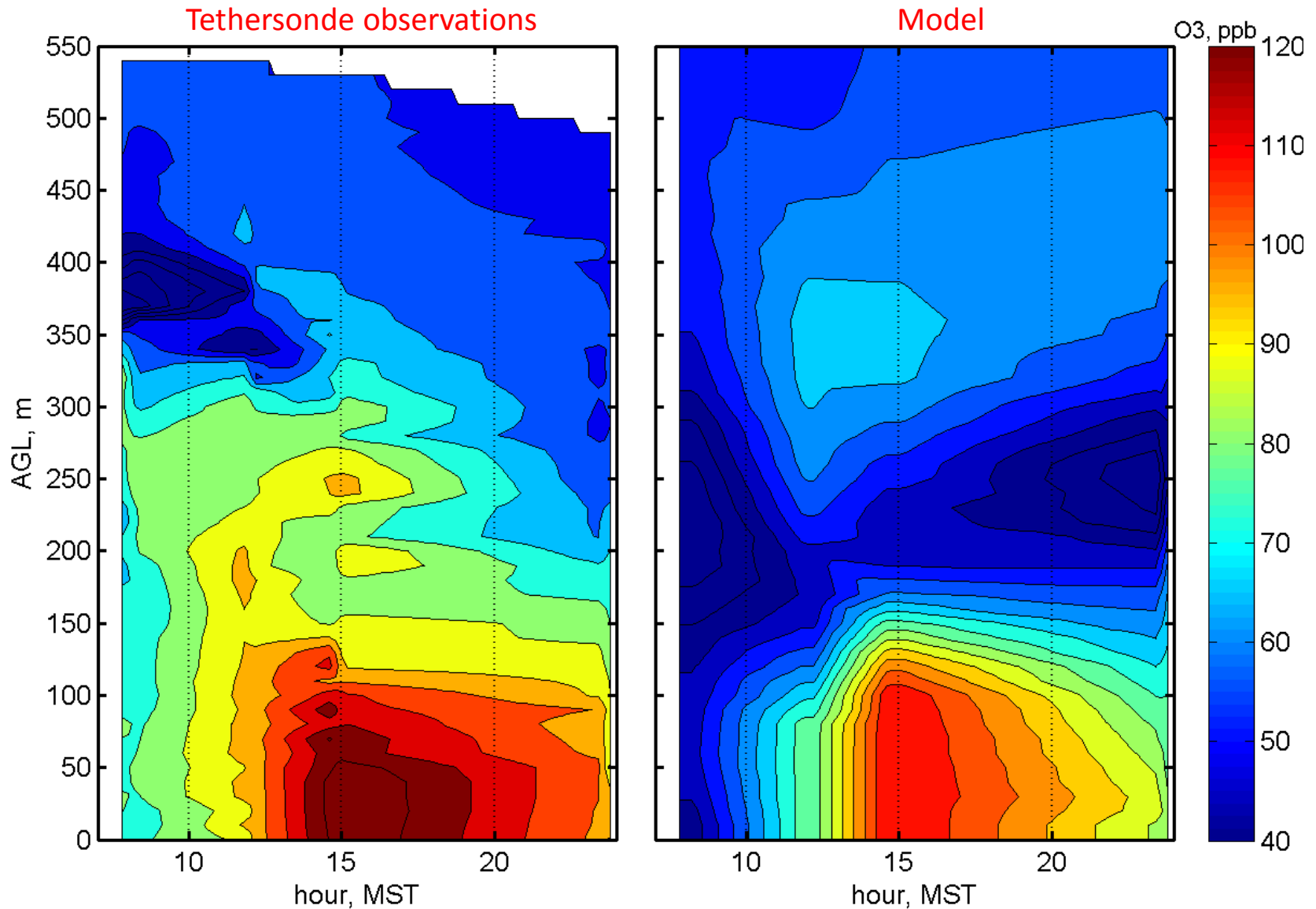


## Daytime

- Light winds within Basin
- Low Mixing Heights
- Significant O<sub>3</sub> buildup in shallow layers



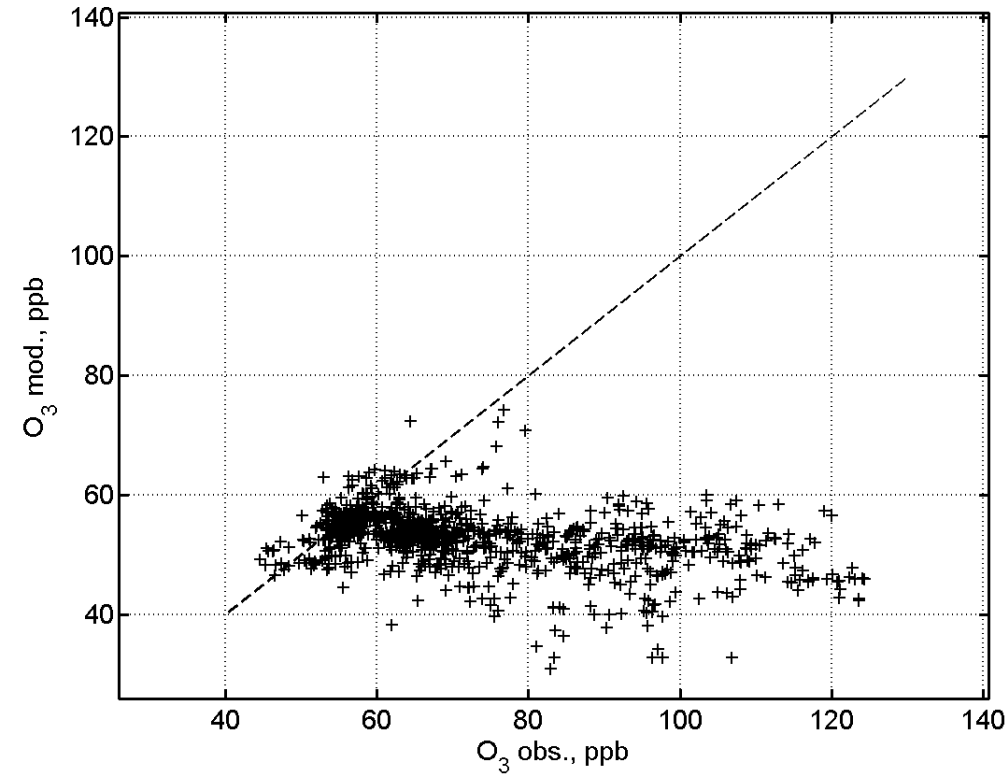
# O<sub>3</sub> distribution over Horse Pool on February 5th, 2013



# Model O<sub>3</sub> comparisons against the aircraft measurements (Feb. 5, 2013)

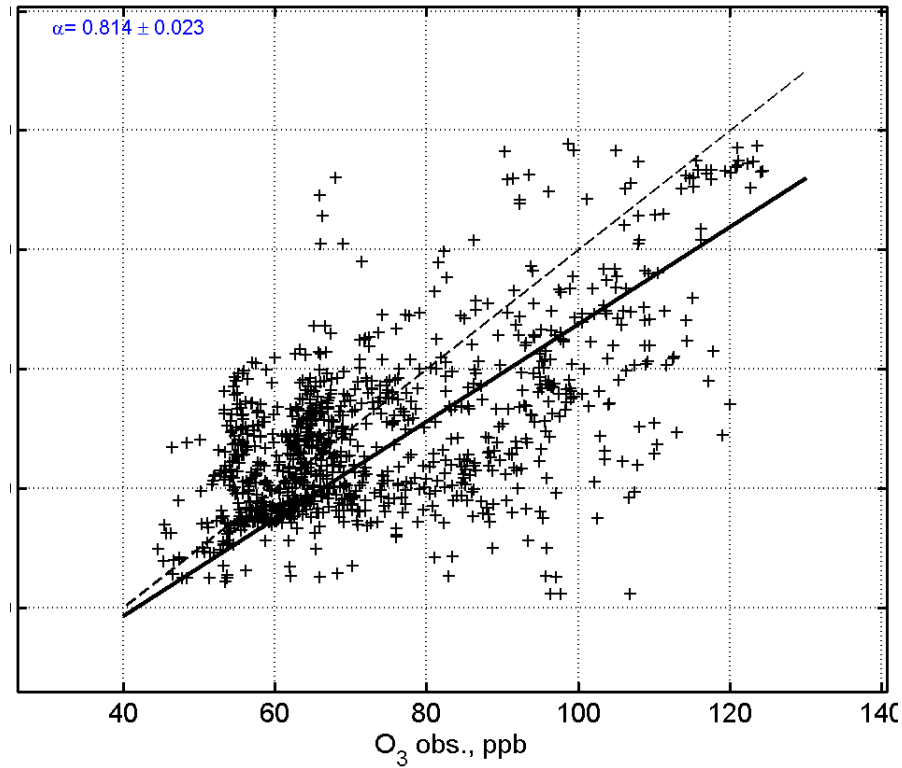
## Bottom-up (NEI2011)

20130205, 9-17LT, 25-500m AGL



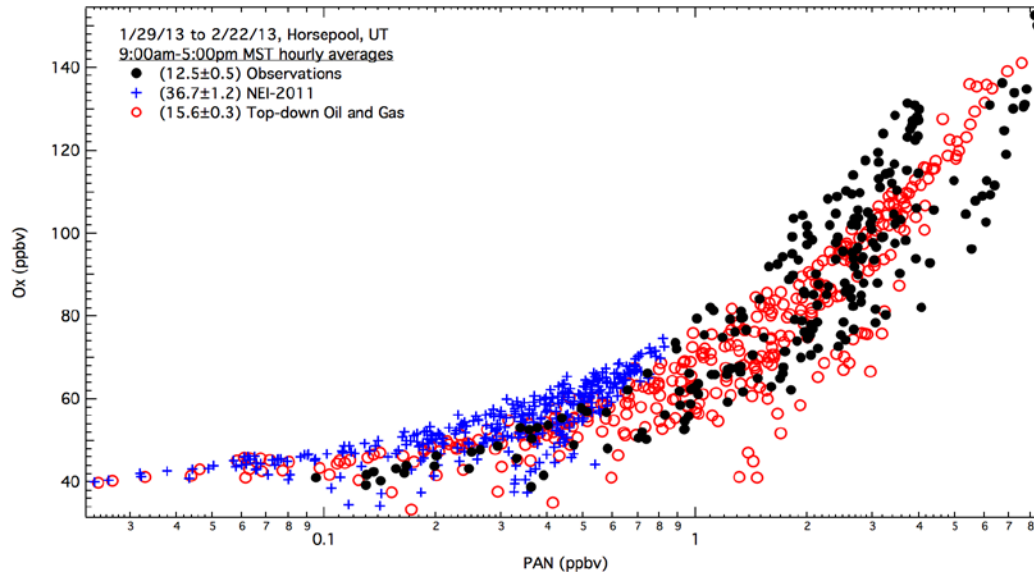
## Top-down

20130205, 9-17LT, 25-500m AGL



# Horse Pool measurements used for model/inventory verification

## O<sub>x</sub> versus PAN at the Horsepool site, 2013



O<sub>x</sub> – PAN relationship  
Depends on:  
VOC/NO<sub>x</sub> ratios  
Photochemical mechanism

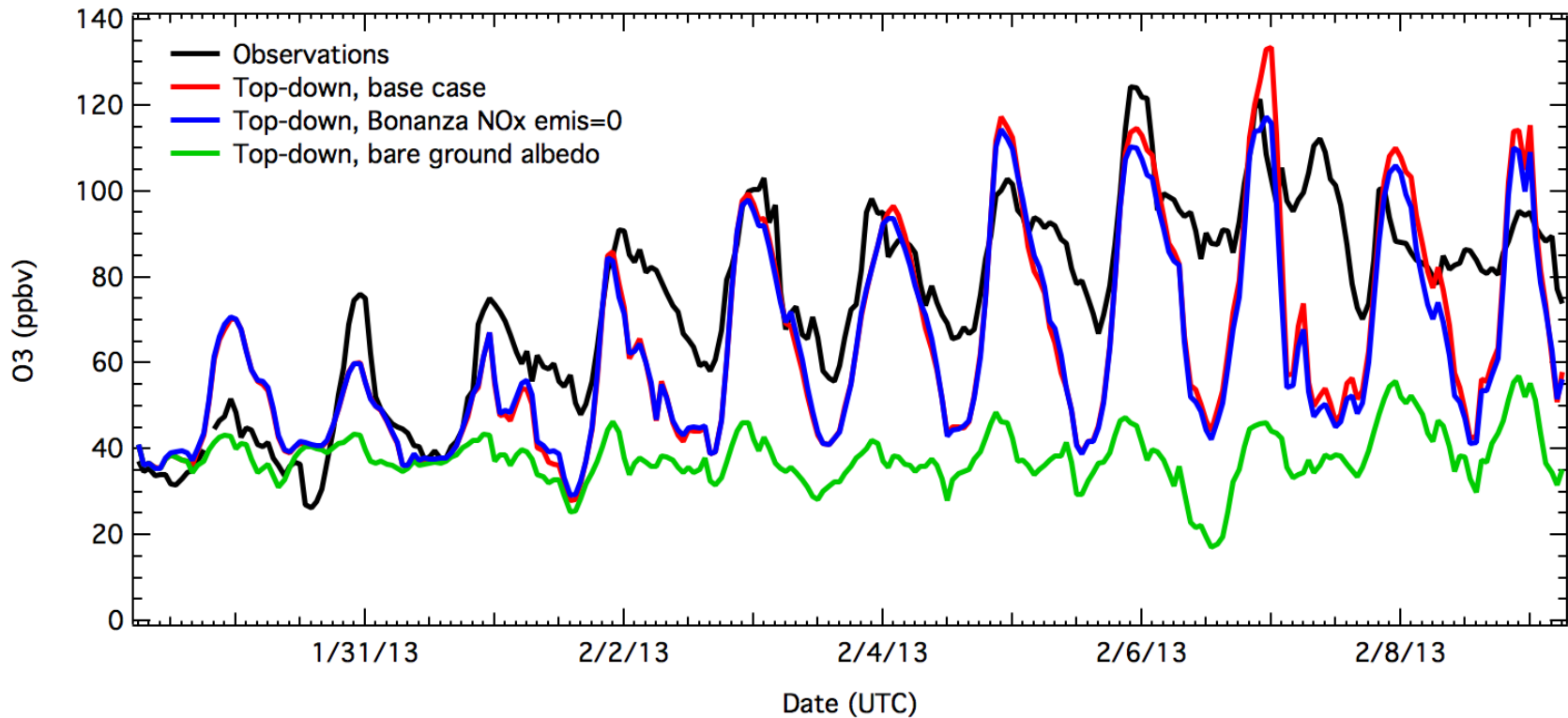
## NO<sub>x</sub> emission inventory assessment

	NO <sub>x</sub>	Top-Down		Bottom-up (NEI-2011)	
	Observed Median (ppbv)	Median Mod/Obs Ratio	r coefficient	Median Mod/Obs Ratio	r coefficient
2012	4.81	0.70	0.64	1.55	0.67
2013	17.16	0.75	0.46	1.86	0.35

# Is O<sub>3</sub> photochemistry sensitive to Bonanza power plant emissions and snow albedo?

Bonanza power plant: **No**

Snow albedo: **Yes**





# Highlights of perturbation/sensitivity analysis

Physical Processes - Perturbation Case	Impact on model O <sub>3</sub> from oil/gas
Bare ground surface albedo (no snow)	104%
Bare ground O <sub>3</sub> surface deposition	48%

Snow is essential for high O<sub>3</sub>

NO <sub>x</sub> Emission Perturbation Case	Impact
Top-Down Oil&Gas NOx Emission Reduced 30%	1%
Top-Down Oil&Gas NOx Emission Reduced 67%	14%
Top-Down Oil&Gas NOx Emission Reduced 100%	45%

High O<sub>3</sub> events are insensitive to NO<sub>x</sub> reductions

VOC Emission Perturbation Case	Impact
Top-Down Oil&Gas VOC emis. Reduced 30%	33%
>C-2 Alkane VOC emis. set to zero	44%
Aromatic VOC emis. set to zero	37%

O<sub>3</sub> is VOC limited

Aromatics have a disproportionate influence

Top-down Aromatic/(>C-2 alkane) flux ratio = 0.10

# Model O<sub>3</sub> sensitivity to emissions of radical precursors

(Horse Pool site, Jan 29 to Feb 9, 2013, daytime)

## Base Case NO<sub>x</sub> emissions:

NO: 90%

NO<sub>2</sub>: 8%

HONO: 2%

**The model can predict high O<sub>3</sub> concentrations without primary HONO emissions!**

	Impact Percentage
All NO <sub>x</sub> emissions were included as NO	5%

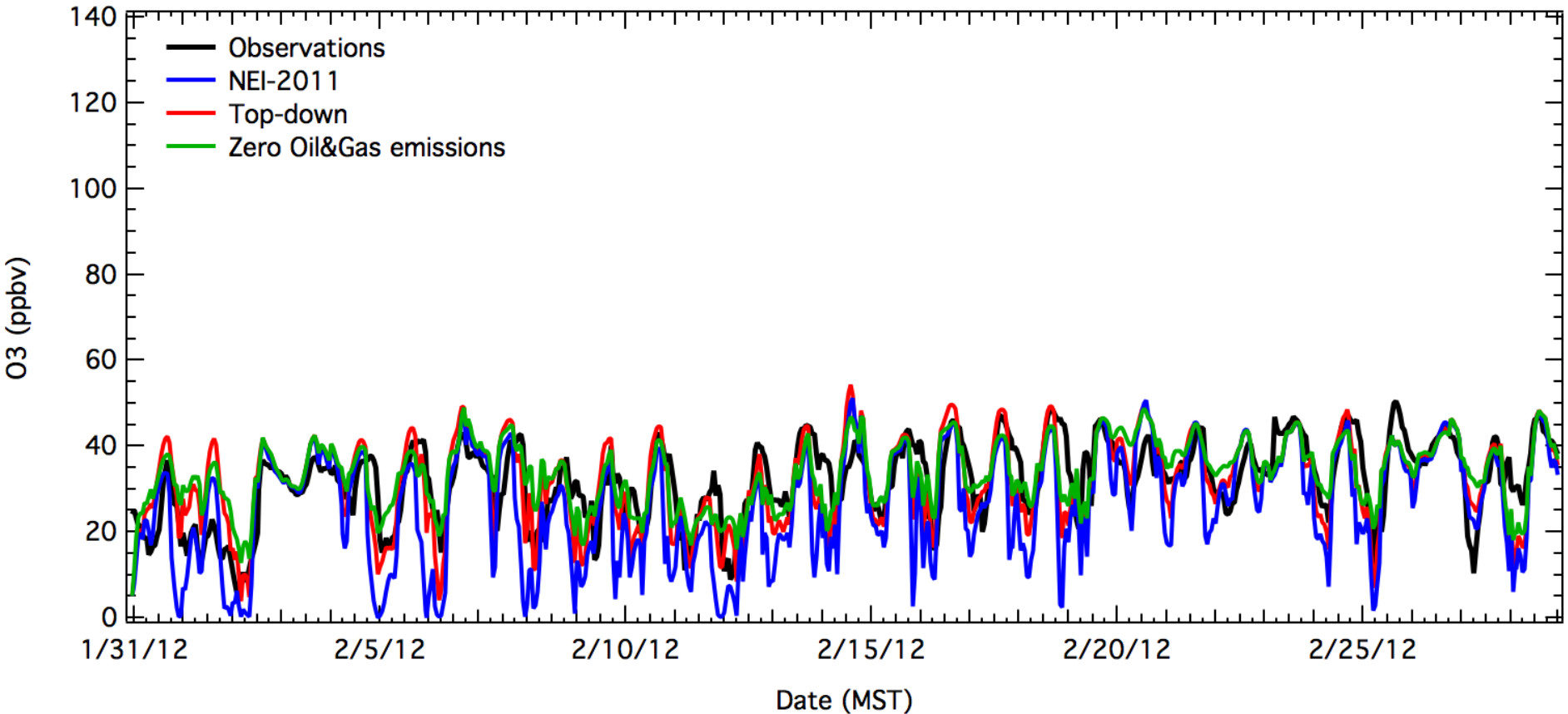
CH<sub>2</sub>O Statistics: Median Model/Observed Ratio = 0.53

	Impact Percentage
CH <sub>2</sub> O primary emissions set to zero	18%

CH<sub>2</sub>O Median Model/Observed Ratio = 0.36 after emissions removal

**The primary formaldehyde emissions need to be considered!**

# Observed and modeled **ozone** time series at the Horsepool site, 2012



**The same model settings and emissions for the 2012 and 2013 cases were used!**

# Summary

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- The emission inventories ( $\text{CH}_4$ , VOCs,  $\text{NO}_x$ ) for the oil/gas sector can be significantly improved by using the top-down emission estimates.
- The model is able to simulate high  $\text{O}_3$  episodes in winter of 2013 using the top-down inventory, but not the bottom-up (NEI-2011) inventory.
- The sensitivity simulations show reducing the VOC emissions would be an efficient way to mitigate wintertime  $\text{O}_3$  problem in the Uinta Basin.
- High ozone in the Uinta Basin are primarily caused by the very high VOC versus  $\text{NO}_x$  emissions from the oil/gas sector, persistent stagnation episodes and high surface albedo and reduced deposition effect due to snow cover.



Thank you for your attention!



*Uintah Basin, 2013  
Photo by S.Sandberg*