Observations of $^{14}CO_2$ at the Boulder Atmospheric Observatory (BAO)

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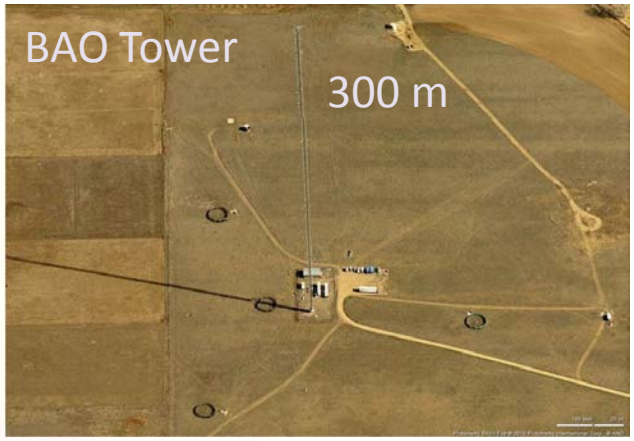


Whole air samples collected

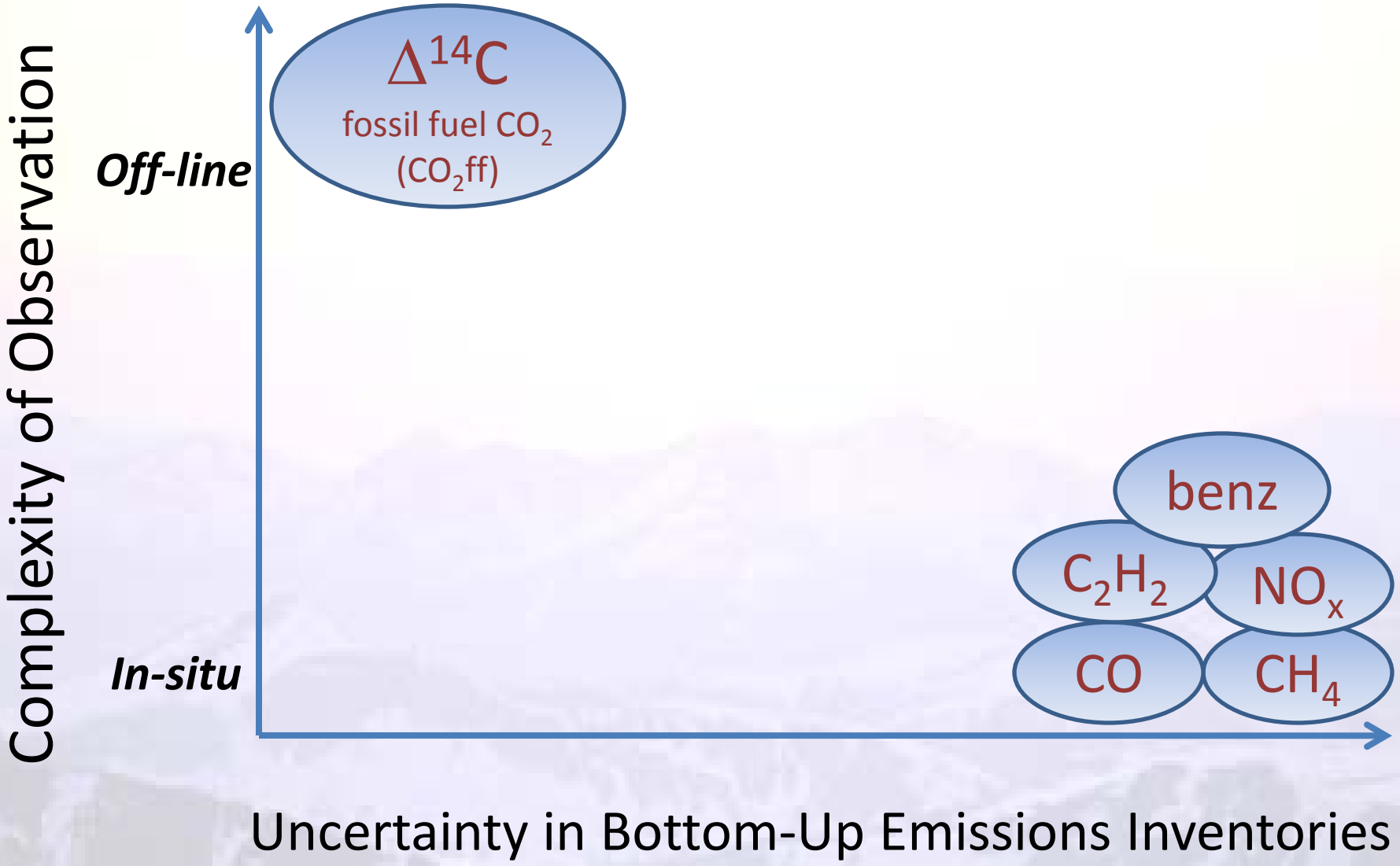
$$CO_2(g) + H_2(g) \xrightarrow[570\ ^oC]{Fe,\ Mg(ClO_4)_2} C(s) + H_2O\downarrow$$

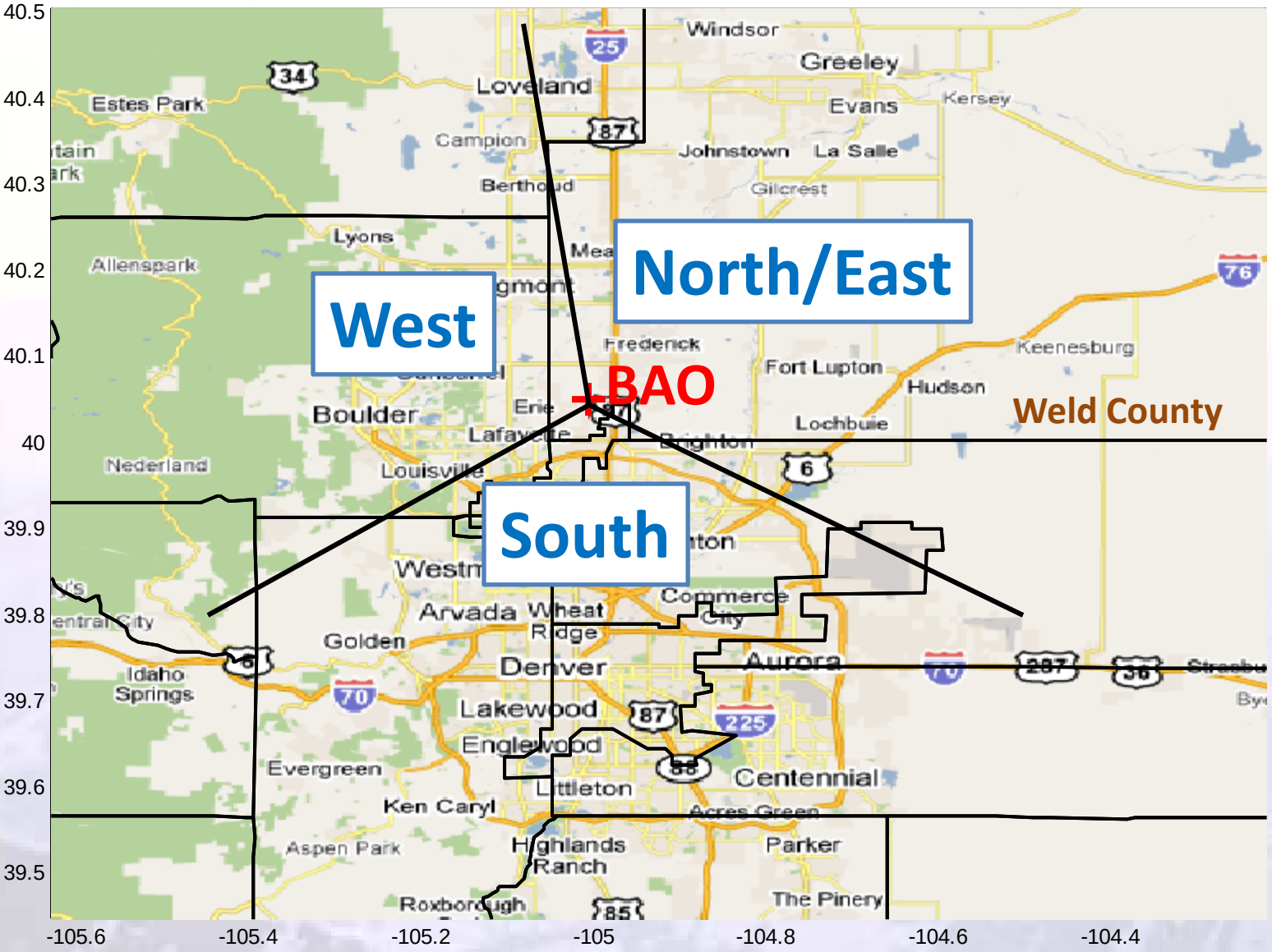
Programmable Flask Packages

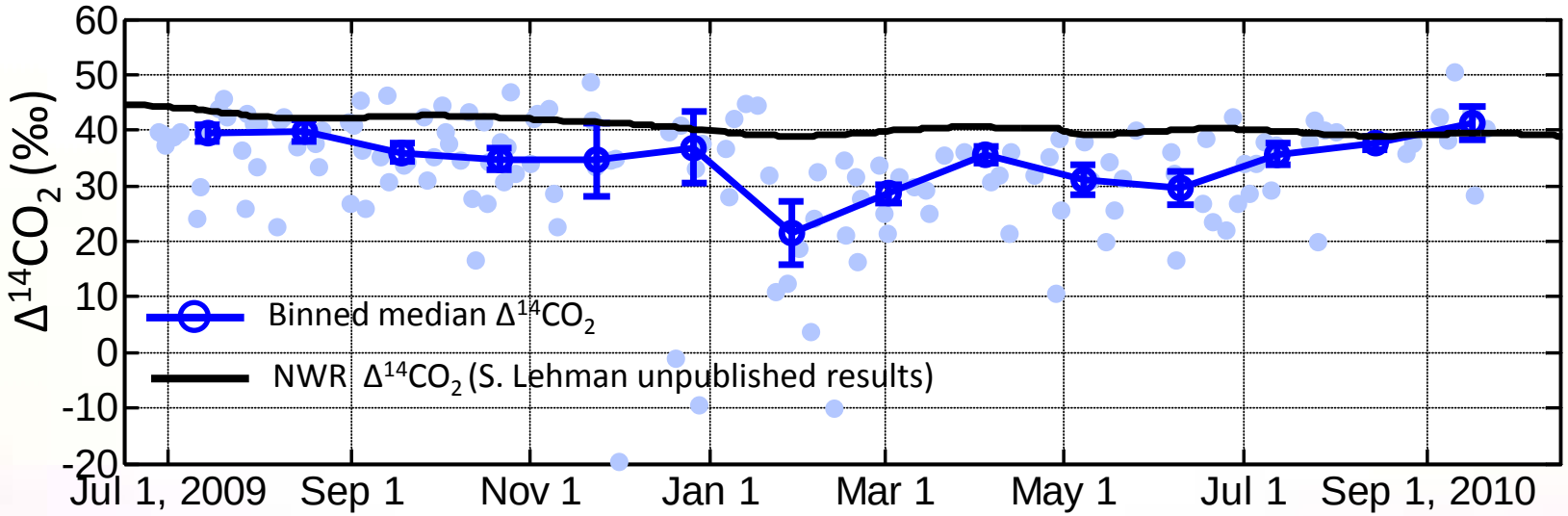
Cryogenic extraction

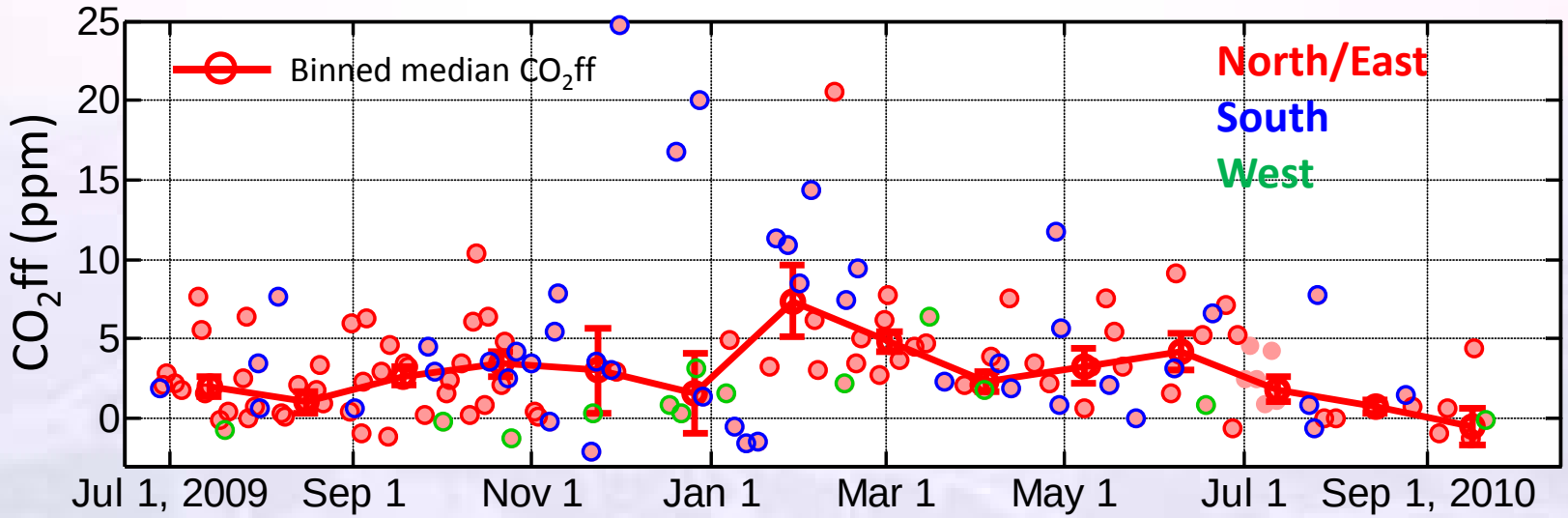
Purified CO_2

Motivation


Complexity of Observation
Off-line
In-situ
$\Delta^{14}C$
fossil fuel CO_2
(CO_2ff)
benz
C_2H_2
NO_x
CO
CH_4
Uncertainty in Bottom-Up Emissions Inventories

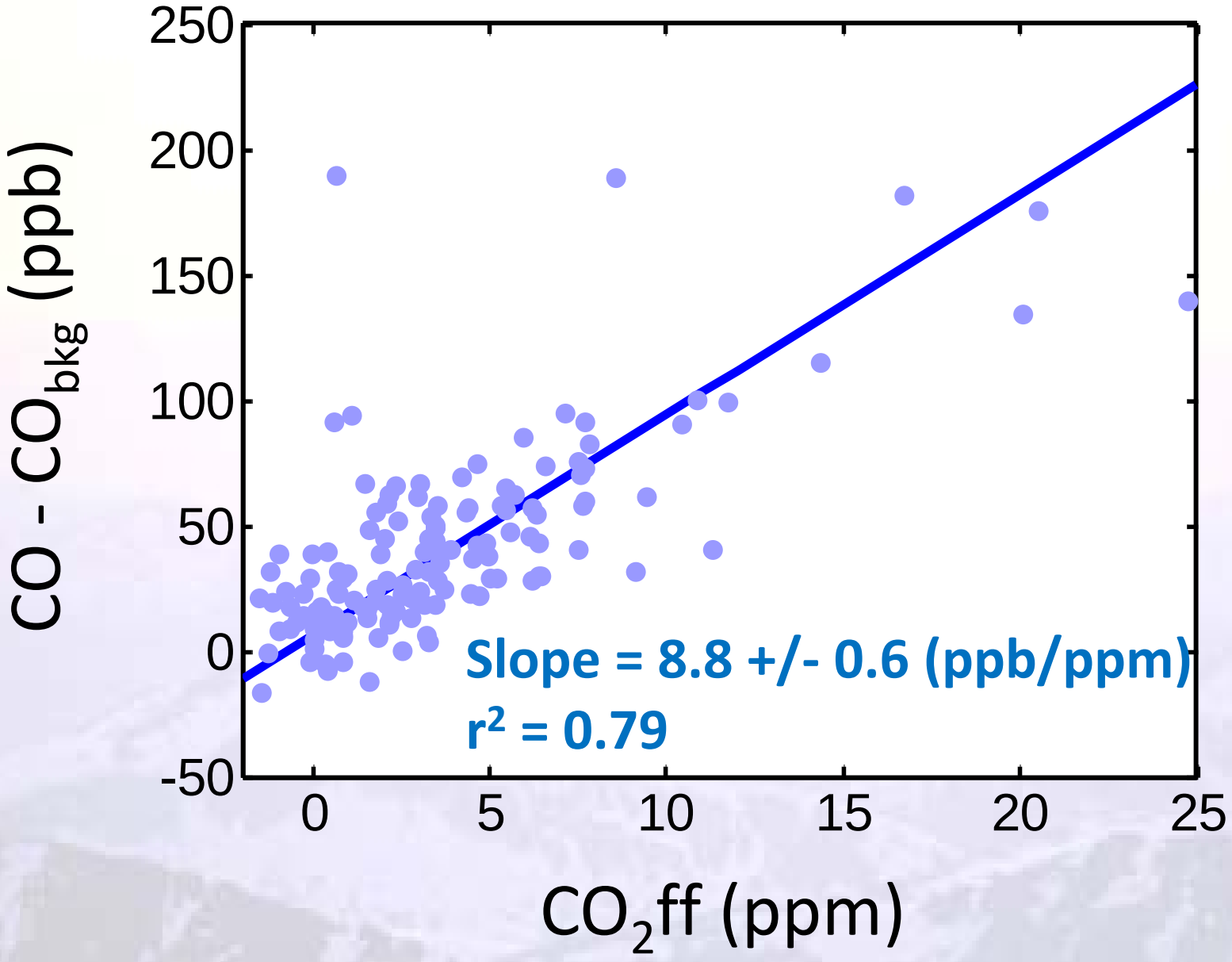

West
North/East
South
BAO
Weld County
Windsor
Greeley
Loveland
Evans
Kersey
Estes Park
Campion
Johnstown
La Salle
Berthoud
Gilcrest
Lyons
Allenspark
Mead
Frederick
Keenesburg
Fort Lupton
Hudson
Boulder
Erie
Lafayette
Lochbuie
Brighton
Nederland
Louisville
Westminster
Commerce City
Arvada
Wheat Ridge
Golden
Denver
Aurora
Idaho Springs
Lakewood
Englewood
Evergreen
Littleton
Centennial
Ken Caryl
Acres Green
Aspen Park
Highlands Ranch
Parker
Roxborough
The Pinery
40.5
40.4
40.3
40.2
40.1
40
39.9
39.8
39.7
39.6
39.5
-105.6
-105.4
-105.2
-105
-104.8
-104.6
-104.4



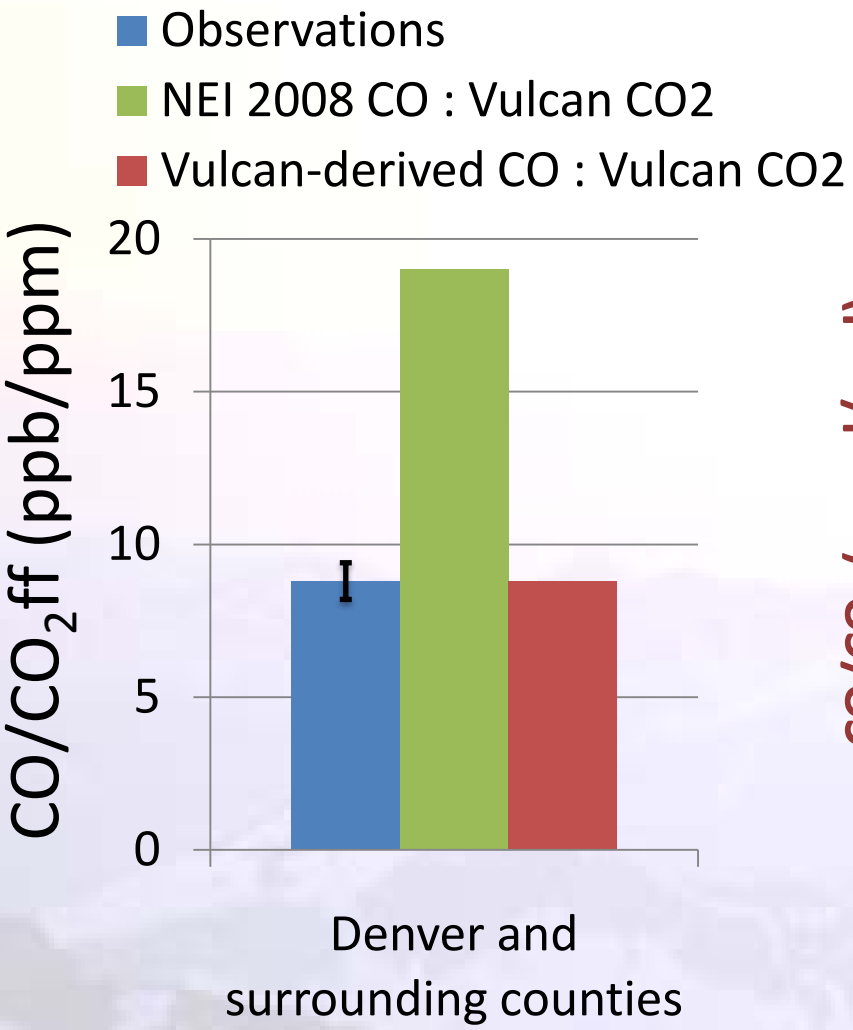


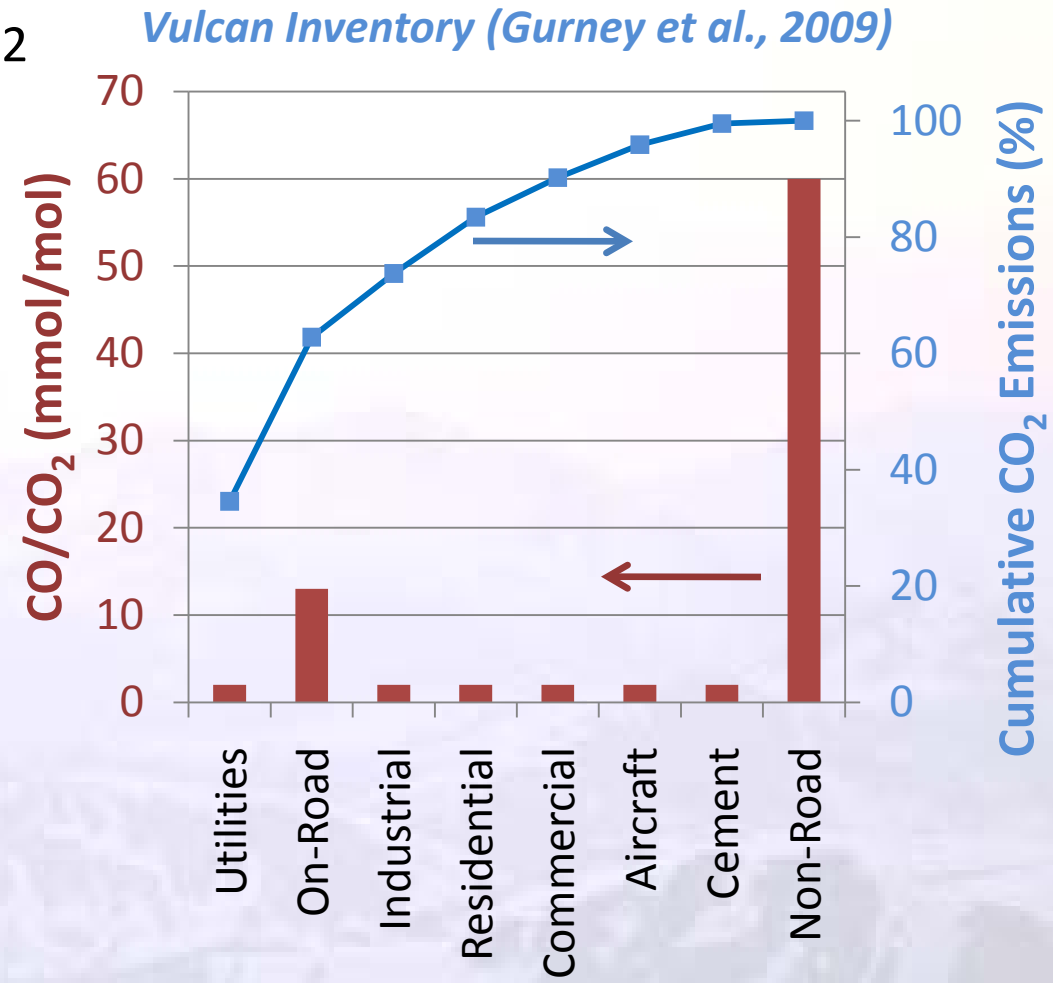
$$CO_2ff = \left(\frac{CO_2obs(\Delta^{14}_{obs} - \Delta^{14}_{bkg})}{(\Delta^{14}_{ff} - \Delta^{14}_{bkg})}\right) - \left(\frac{CO_2resp(\Delta^{14}_{resp} - \Delta^{14}_{bkg})}{(\Delta^{14}_{ff} - \Delta^{14}_{bkg})}\right)$$

Turnbull et al., 2006


250
200
150
100
50
0
-50
0
5
10
15
20
25
CO - CO$_{bkg}$ (ppb)
CO$_2$ff (ppm)
Slope = 8.8 +/- 0.6 (ppb/ppm)
r^2 = 0.79

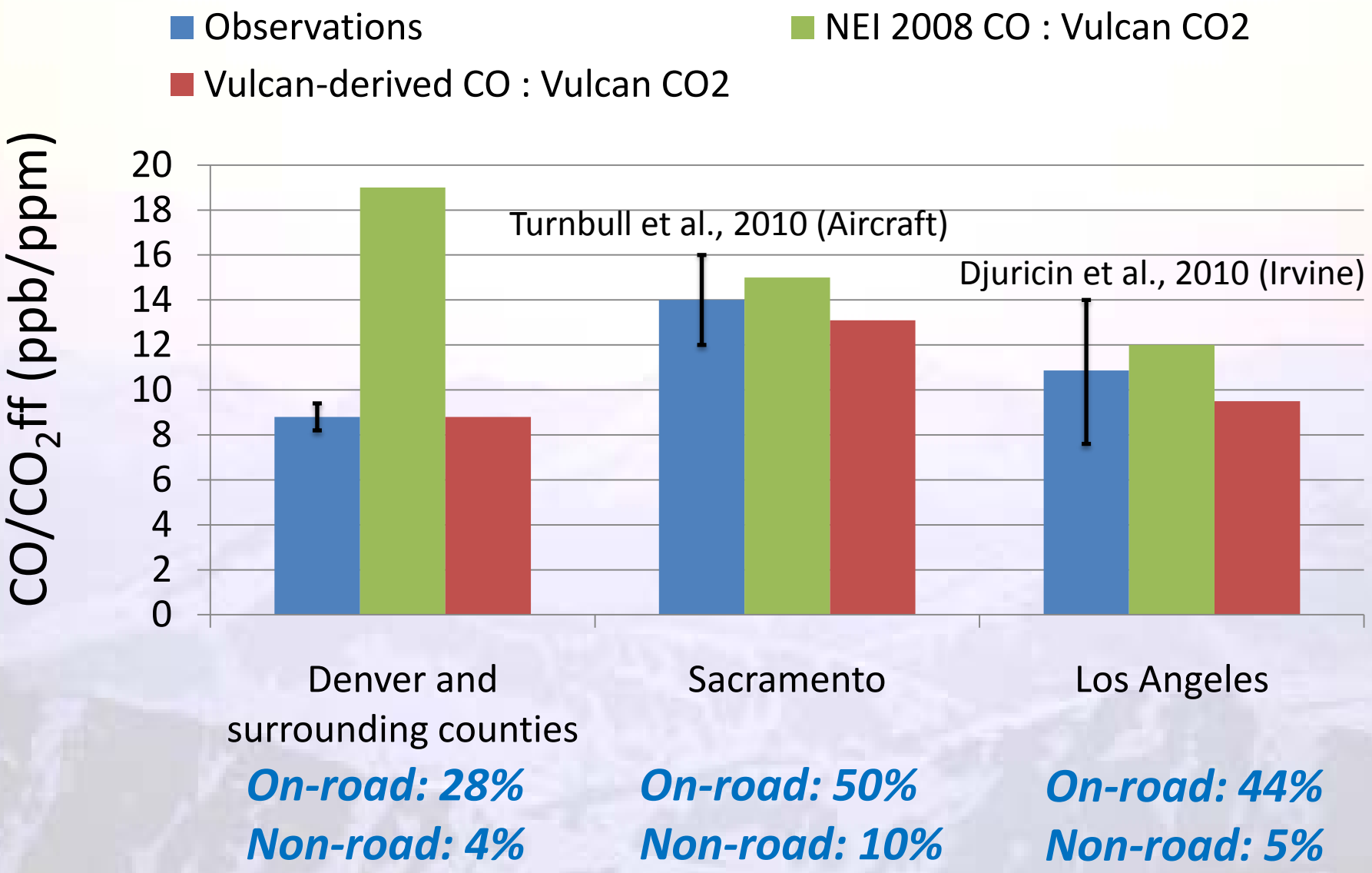
Reconciling Observations with Bottom-Up Inventories



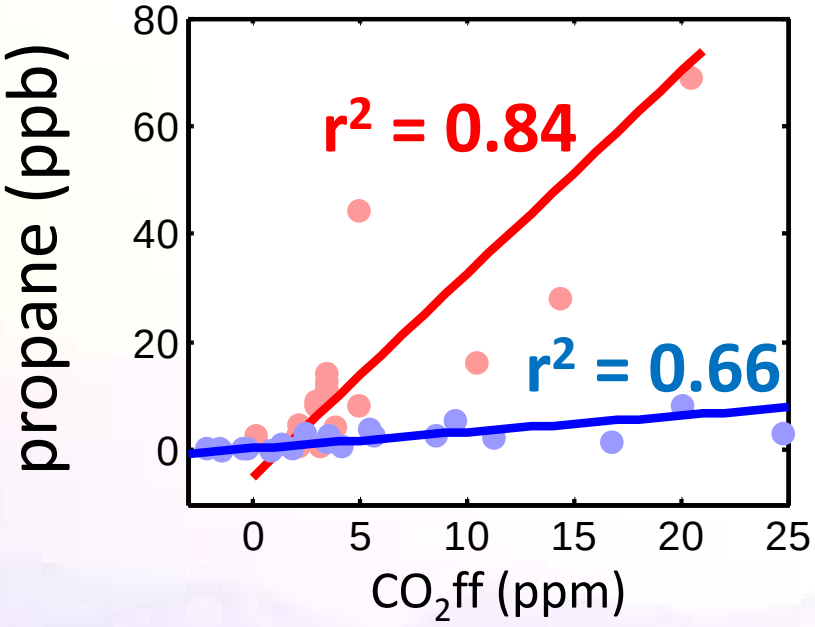


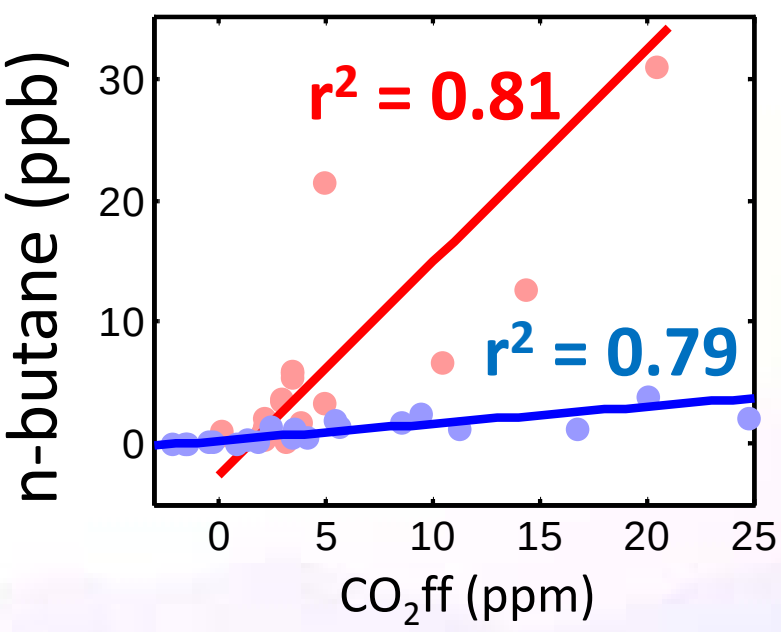
On-road CO/CO_2 ratio from Bishop and Stedman, 2008
Other sectors "hand-tuned" to fit observations

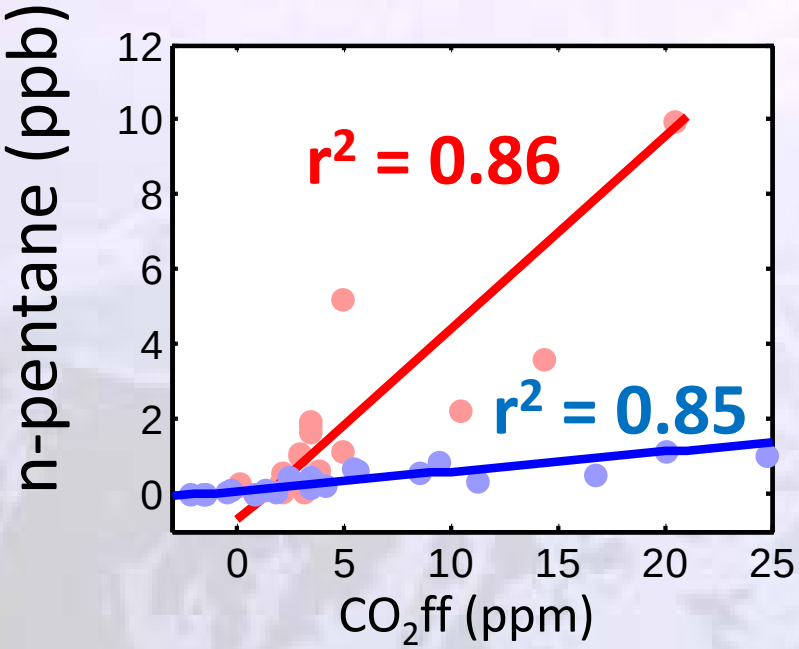
Reconciling Observations with Bottom-Up Inventories

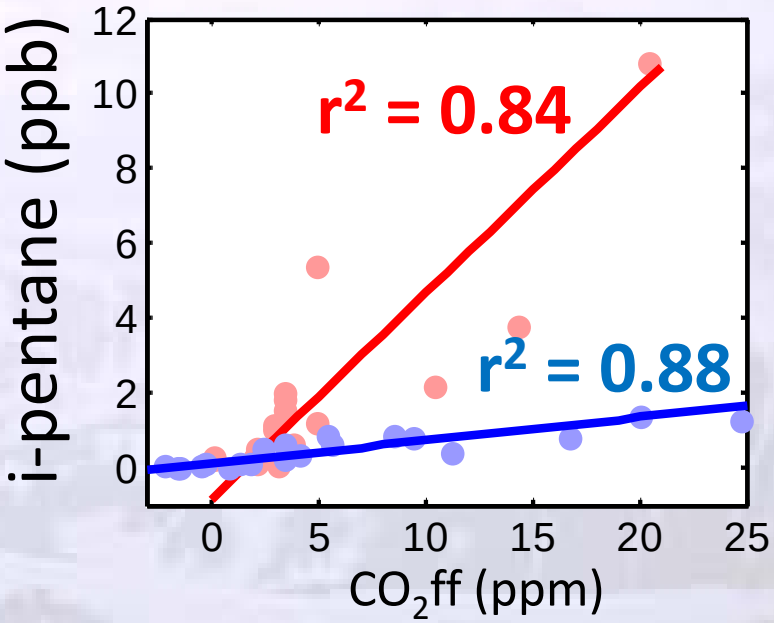


North/East vs South Wind Sectors

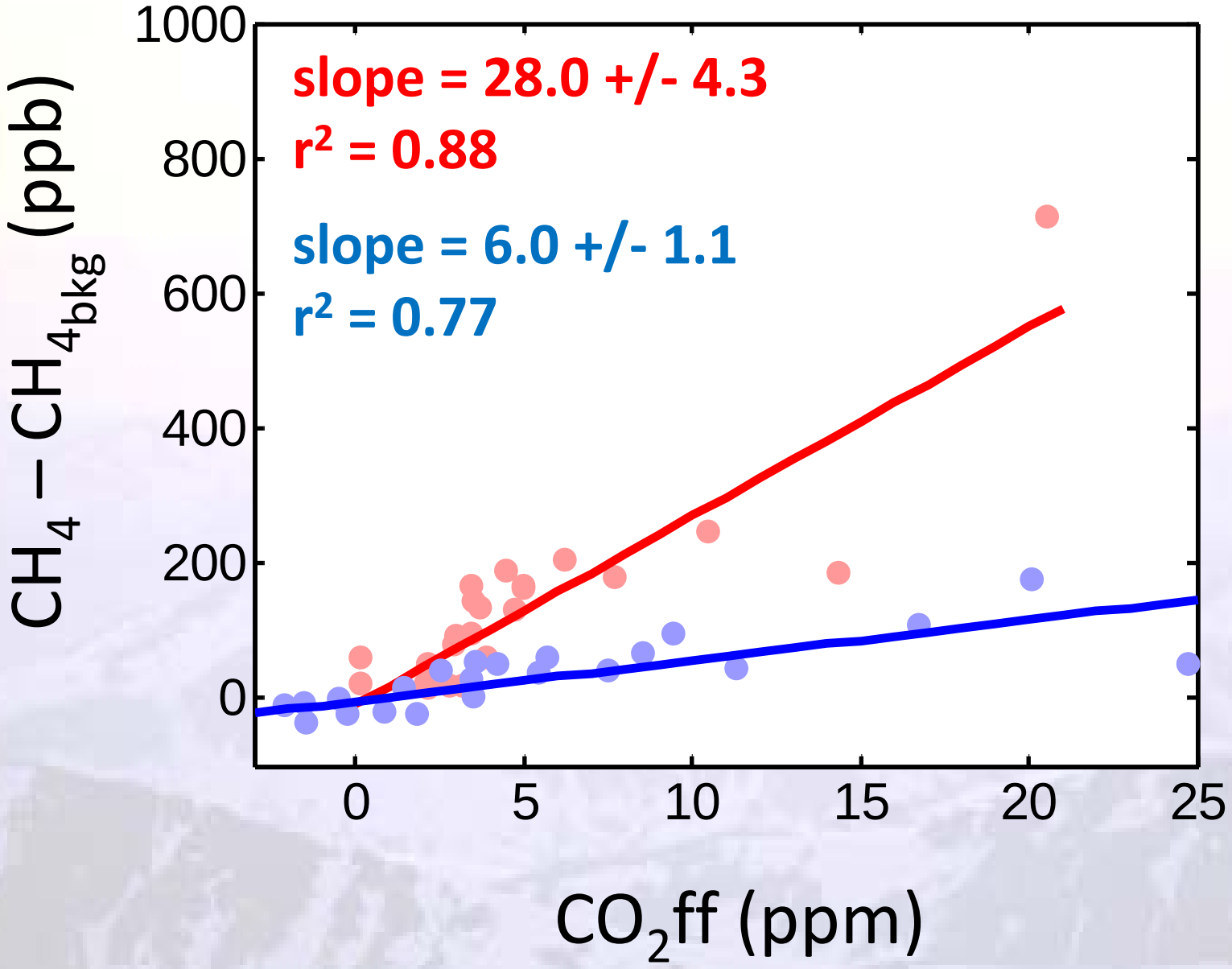




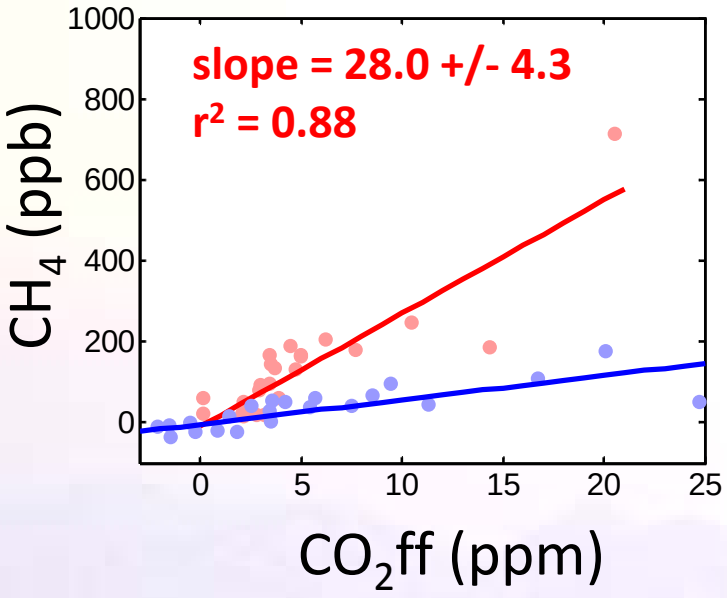




Methane vs CO_2ff



Estimating CH_4 Emissions



$$E_{CH4} = E_{CO2} \times [CH_4]/[CO_2]$$

$$E_{CH4} = (1.93 \text{ Tg C yr}^{-1}) \times (0.028)$$

Vulcan estimate for Weld Co.

CH_4 emissions from Weld County:

- 94 (51-178) Gg/year (Petron et al., in prep)
- 72 +/- 11 Gg/year (this work)

Summary

- ***Fraction of fossil emissions from on-road vehicles drives the CO/CO_2ff ratio***
  - NEI 2008 2x too high in Colorado; CA appears OK

- ***Wind direction greatly influences tracer mixing ratios observed at BAO relative to CO_2ff***

- ***CO_2ff observations, in combination with Vulcan, provide a constraint on CH_4 emissions from oil and gas operations to the north and east of BAO***