Quantifying Molecular Hydrogen Emissions and an Industrial Leakage Rate for the South Coast Air Basin of California

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BACKGROUND

Why study atmospheric hydrogen?

Several factors:

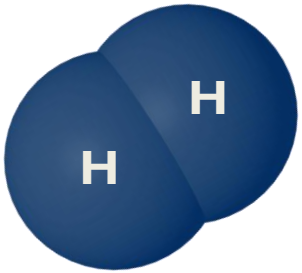
1. Atmospheric budget and distribution are poorly understood

2. An economy based on H_2 is a possibility in the near future

3. Increasing H_2 levels may harm global climate and stratospheric ozone

BACKGROUND

Basic information



Average mixing ratio: ~530 ppbv

Varies with season and latitude

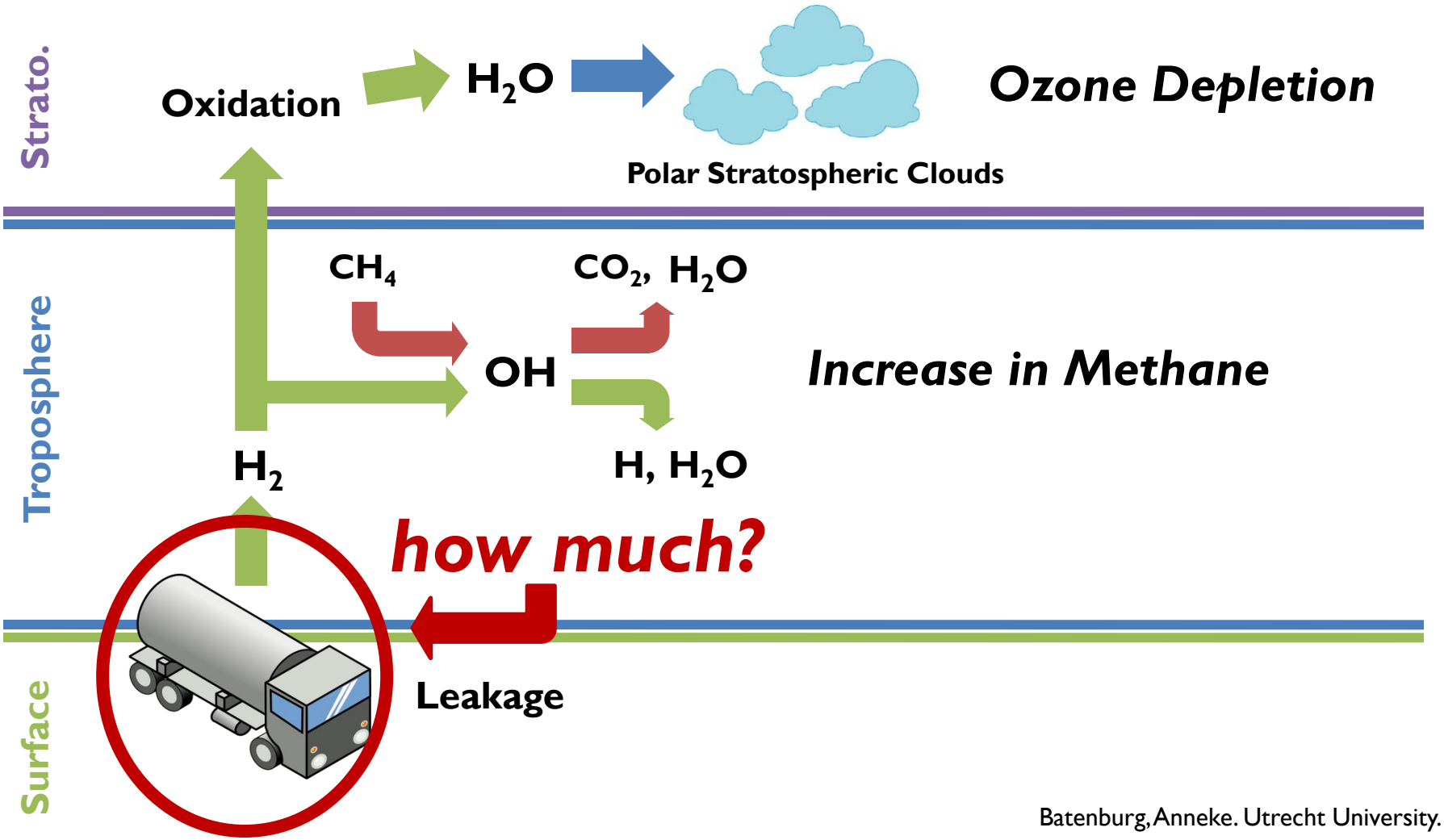
SOURCES (47 – 96 Tg yr^{-1})	
Anthropogenic (combustion and leakage)	21 – 23 %
Biomass/fuel burning	17 – 21%
Photochemical production	46 – 53%
N_2 fixation (biological)	6 – 12%

SINKS (70 – 107 Tg yr^{-1})	
Soil deposition	79 – 82%
Reaction with OH	18 – 21%

Novelli, P. C., Lang, P. M., Masarie, K. A., Hurst, D. F., Myers, R., and Elkins, J. W.: Molecular hydrogen in the troposphere: global distribution and budget, J. Geophys. Res., 104, 30427– 30444, 1999.

BACKGROUND

Hazardous impacts



Batenburg, Anneke. Utrecht University.

BACKGROUND

Debate on leakage

10-20%

Tromp et al. 2003, Science

0.1%

2-3%

Responses in *Science:*
Letters to the Editor

But to date, no top-down experimental estimates!

7%

Wuebbles 2005

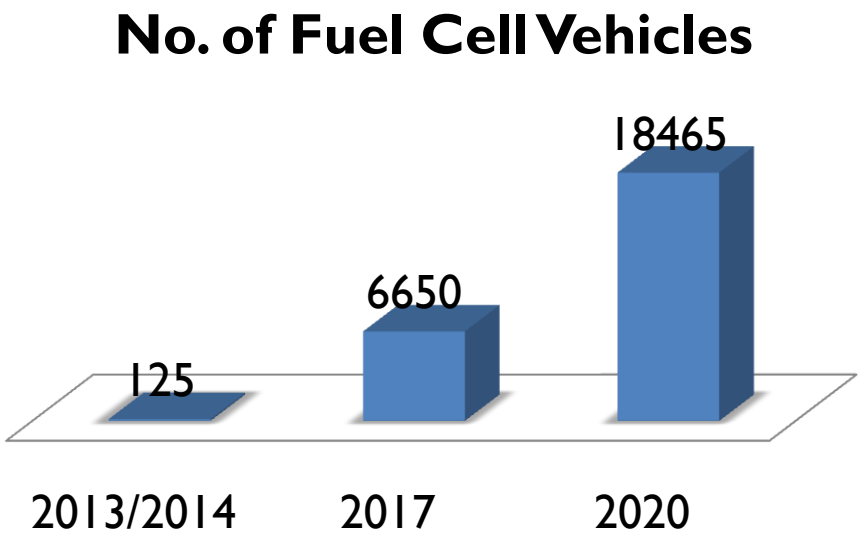
0.3-10%

B. Van Ruijven et al. 2011

BACKGROUND

Expansion of fuel cell industry

L.A. Hydrogen fueling stations[1]



Projected growth in No. of fuel cell electric vehicles in CA[2]

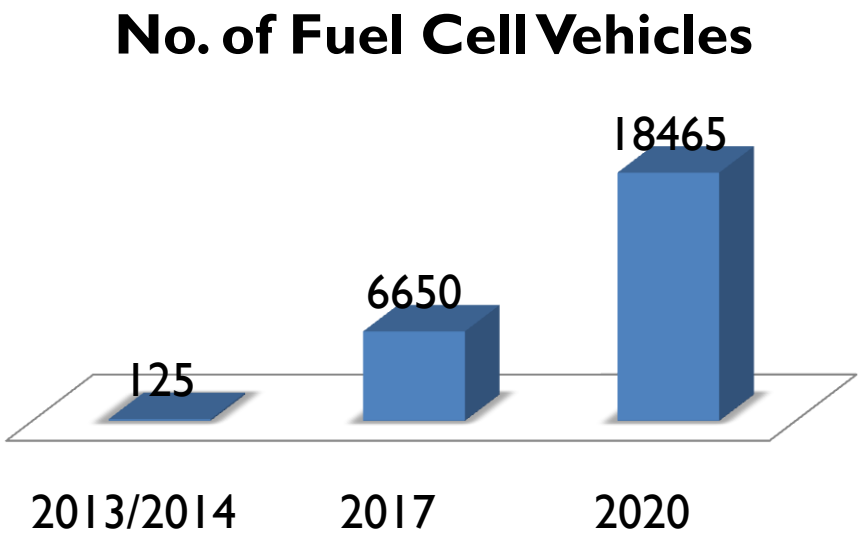
[1]California Fuell Cell Partnership.

[2]California Air Resources Board.

BACKGROUND

Expansion of fuel cell industry

L.A. Hydrogen fueling stations[1]



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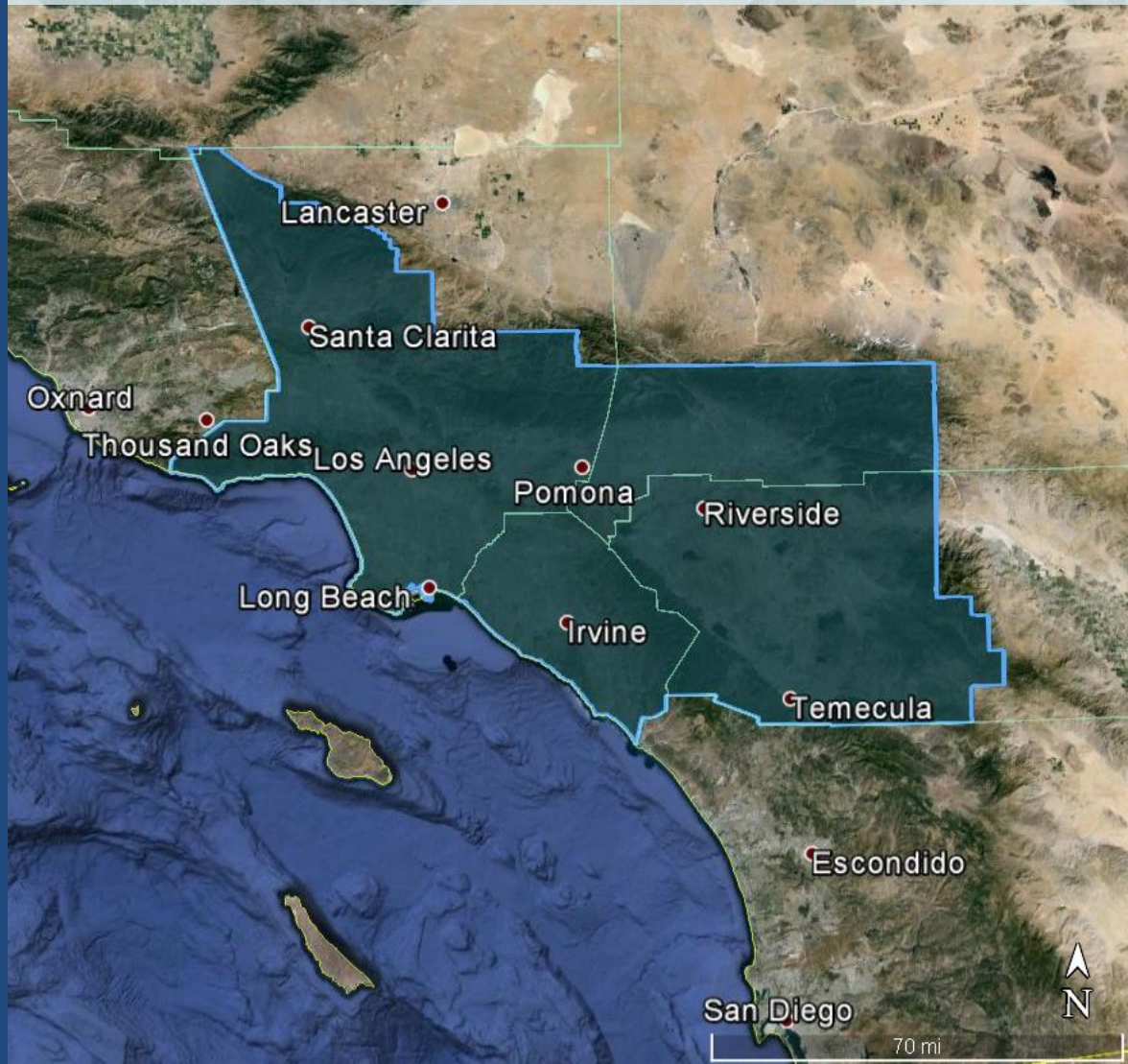
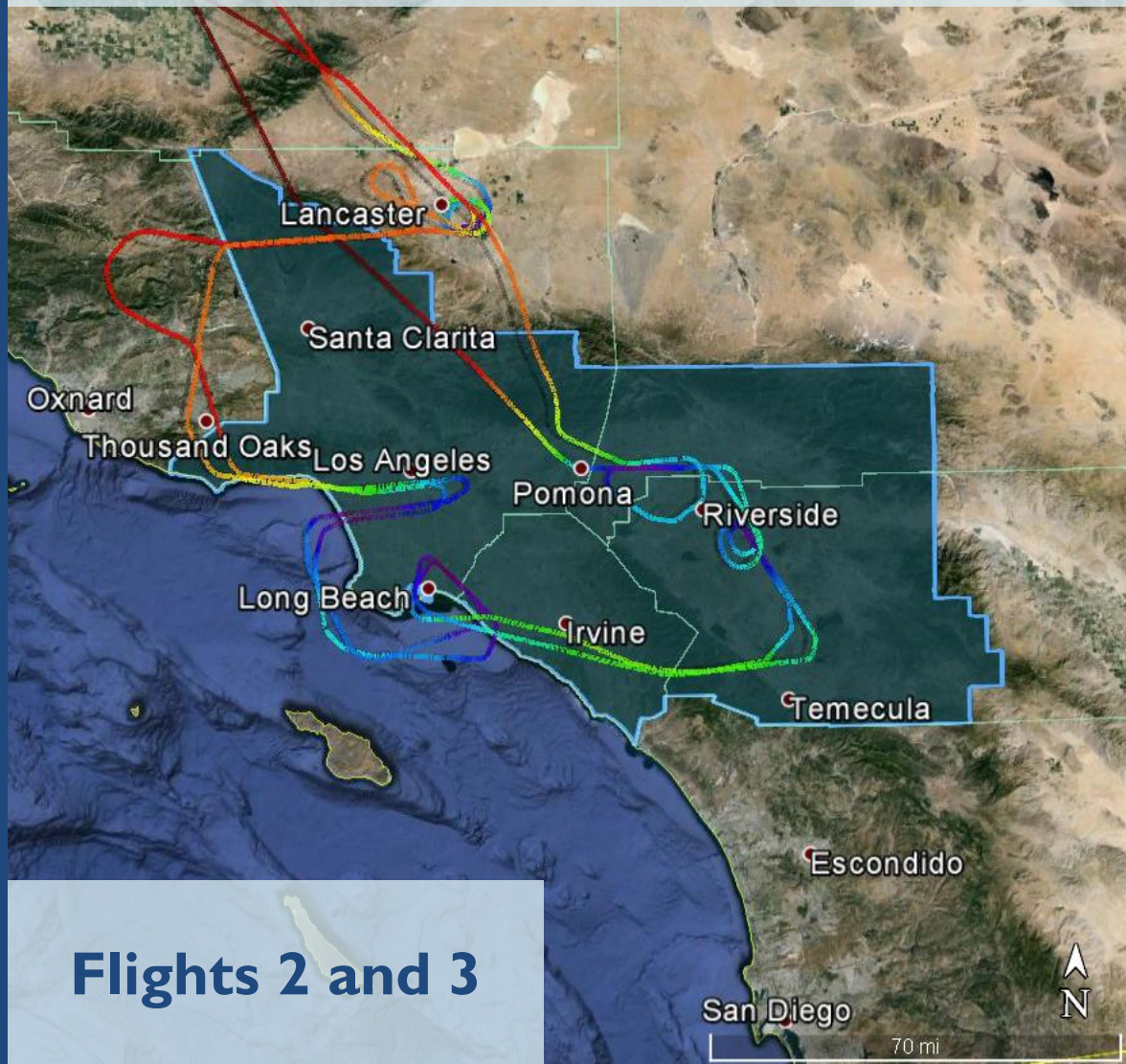
EMISSIONS ESTIMATION

The South Coast Air Basin



EMISSIONS ESTIMATION

The South Coast Air Basin



Flights 2 and 3

EMISSIONS ESTIMATION

Tracer Ratio Method

- H_2 shares its main anthropogenic source, vehicular combustion, with carbon monoxide (CO)
- CO emissions inventory is well constrained
- Can use experimentally established molar ratio to calculate combustion-based H_2 emissions from CO emissions:

$$\frac{j_{H_2}^{emi,combust}}{j_{CO}^{emi}} \cong \frac{\Delta C_{H_2,combust}}{\Delta C_{CO}} = 0.48 \pm 0.07$$

Hammer, et al. 2009

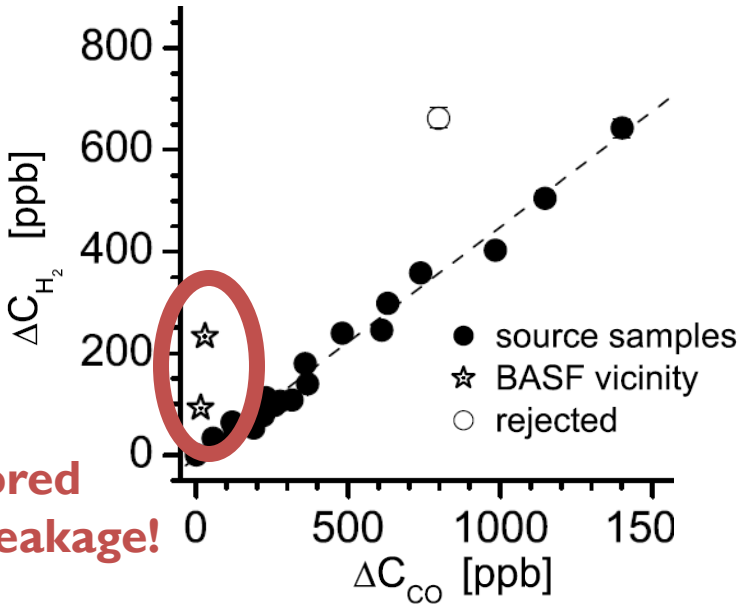
EMISSIONS ESTIMATION

Tracer Ratio Method

Combustion source emissions (previous work):

$$\frac{j_{H_2}^{emi,combust}}{j_{CO}^{emi}} \cong \frac{\Delta C_{H_2,combust}}{\Delta C_{CO}} = 0.48 \pm 0.07$$

Past work assumes that combustion alone comprises total anthropogenic H_2 emissions



Ignored H_2 leakage!

Hammer, et al. 2009

EMISSIONS ESTIMATION

Tracer Ratio Method

Combustion source emissions (previous work):

$$\frac{j_{H_2}^{emi,combust}}{j_{CO}^{emi}} \cong \frac{\Delta C_{H_2,combust}}{\Delta C_{CO}} = 0.48 \pm 0.07$$

Non-combustion source emissions (this project):

$$\frac{j_{H_2}^{emi,combust} + j_{H_2}^{emi,non-combust}}{j_{CO}^{emi}} \cong \frac{\Delta C_{H_2,combust} + \Delta C_{H_2,non-combust}}{\Delta C_{CO}}$$

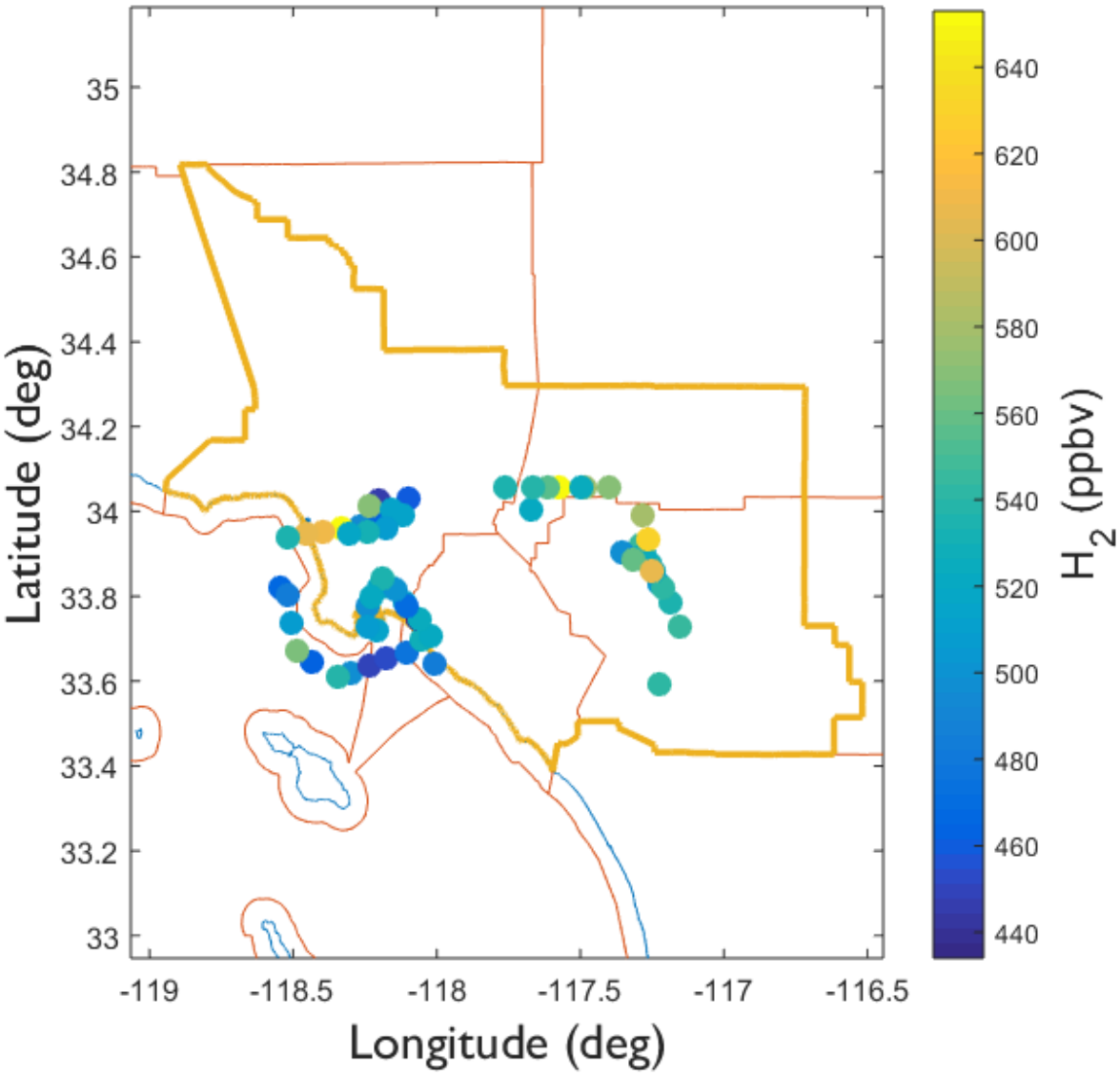
$$= 0.48 \pm 0.07 + \Delta C_{H_2,non-combust}$$

SAMPLE SELECTION & DISTRIBUTION

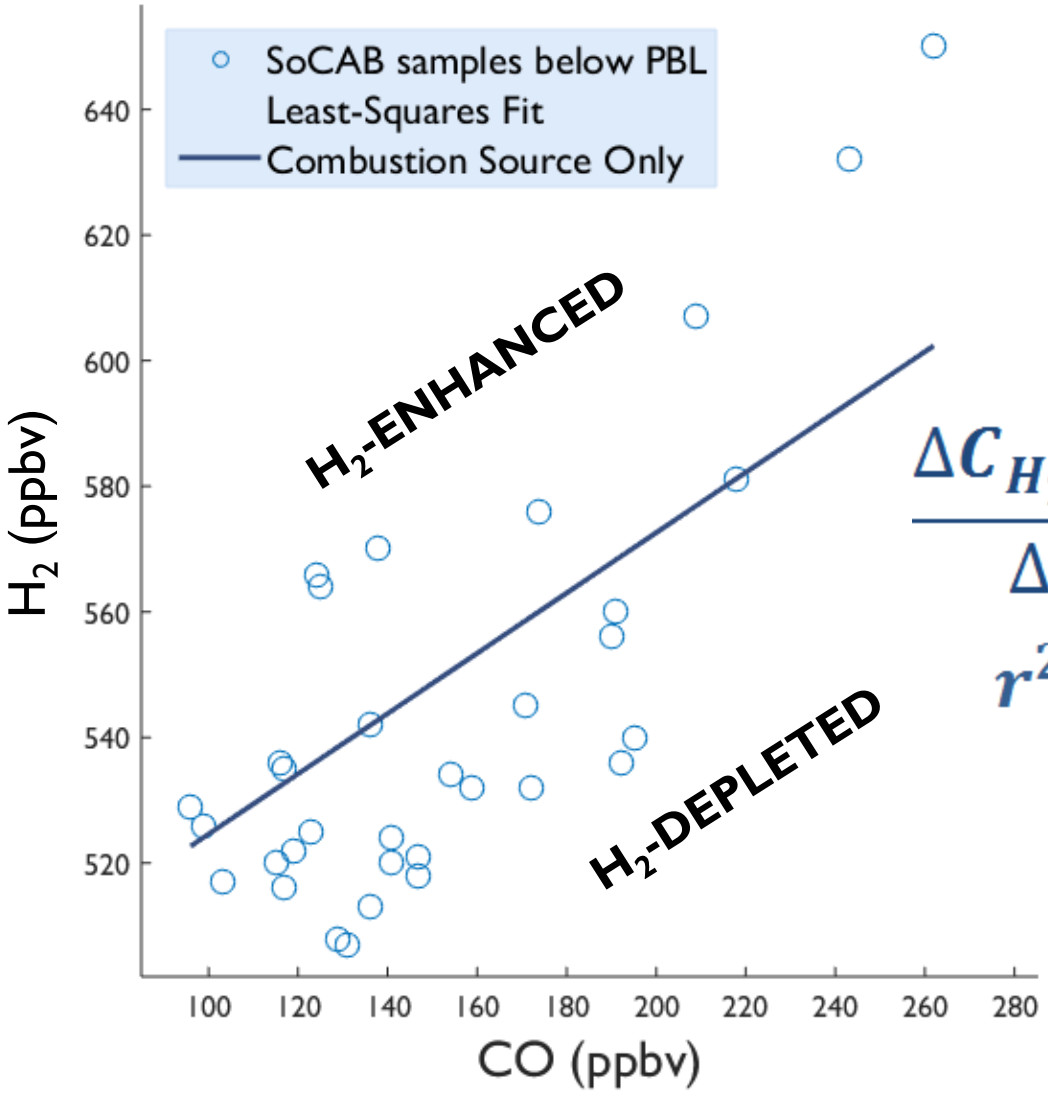
66 samples within 1000 m of boundary layer

10th percentile selected for background H_2 & CO mixing ratios

Only compared samples one std. deviation above background levels



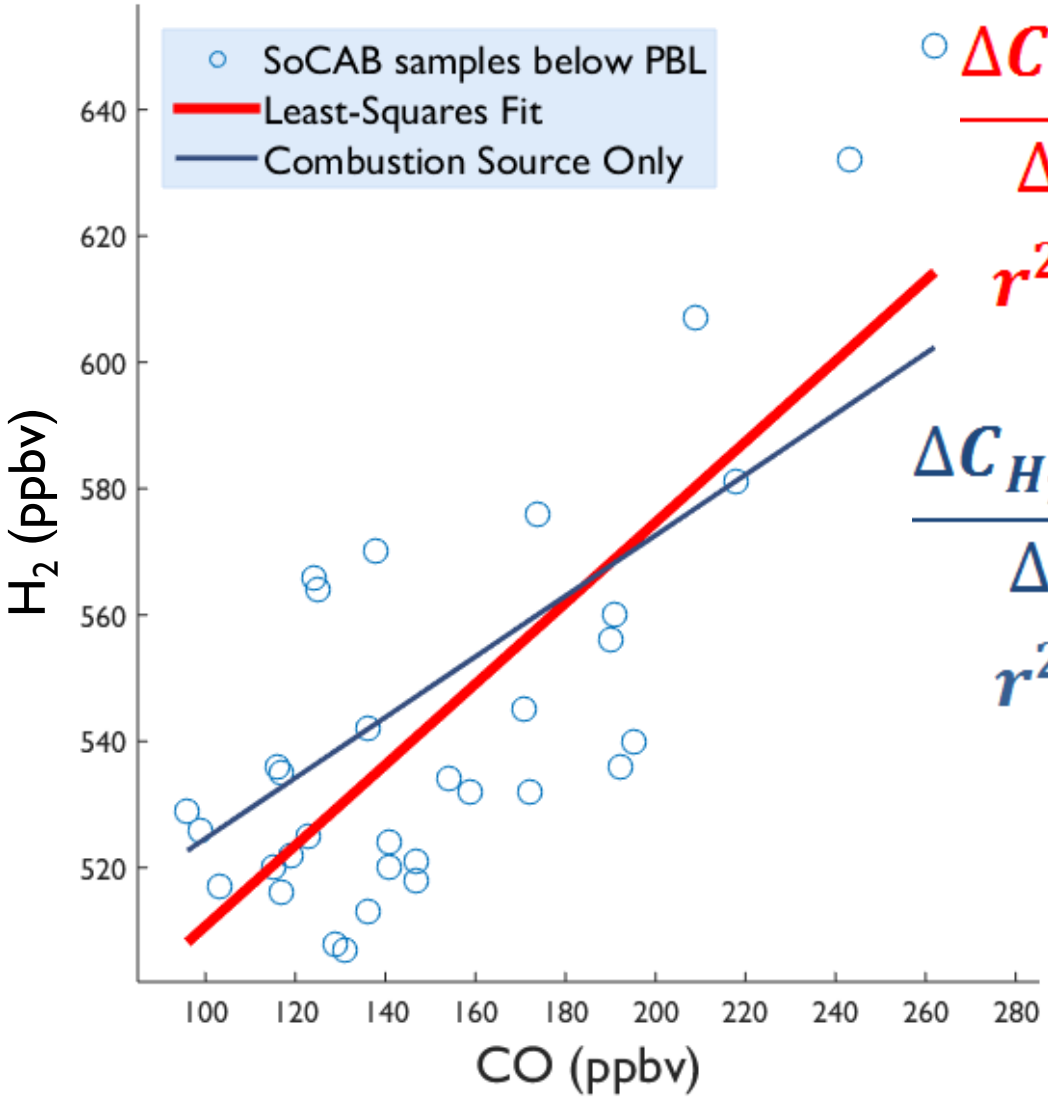
CALCULATING THE TRACER RATIO



$$\frac{\Delta C_{H_{2,combust}}}{\Delta C_{CO}} = 0.48 \pm 0.07$$

$$r^2 = 0.53$$

CALCULATING THE TRACER RATIO



$$\frac{\Delta C_{H_2,total}}{\Delta C_{CO}} = 0.64 \pm 0.09$$

$$r^2 = 0.60$$

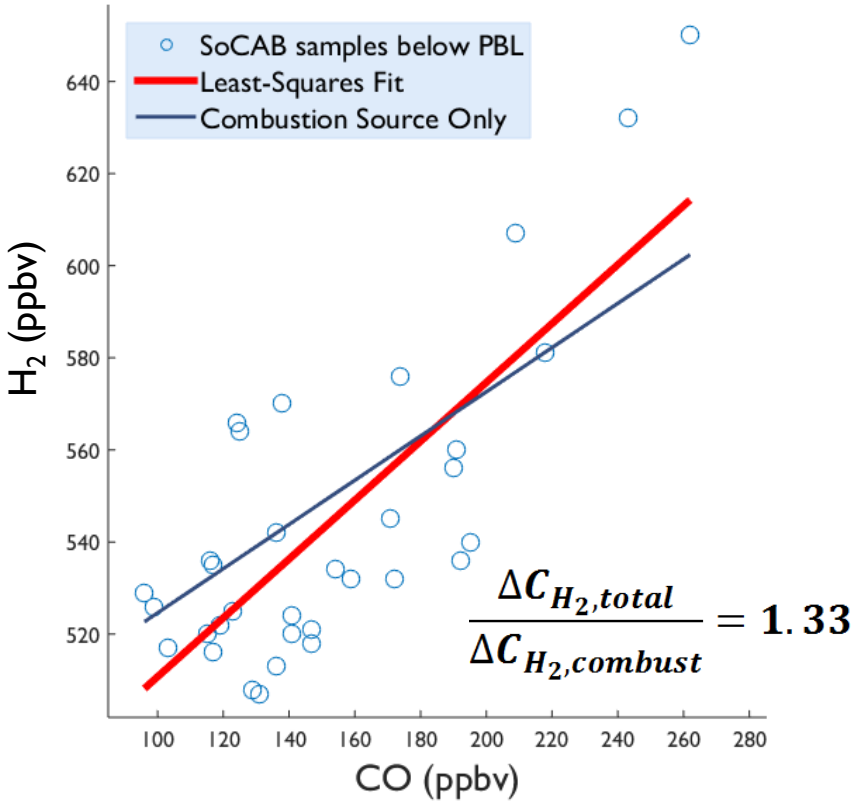
$$\frac{\Delta C_{H_2,combust}}{\Delta C_{CO}} = 0.48 \pm 0.07$$

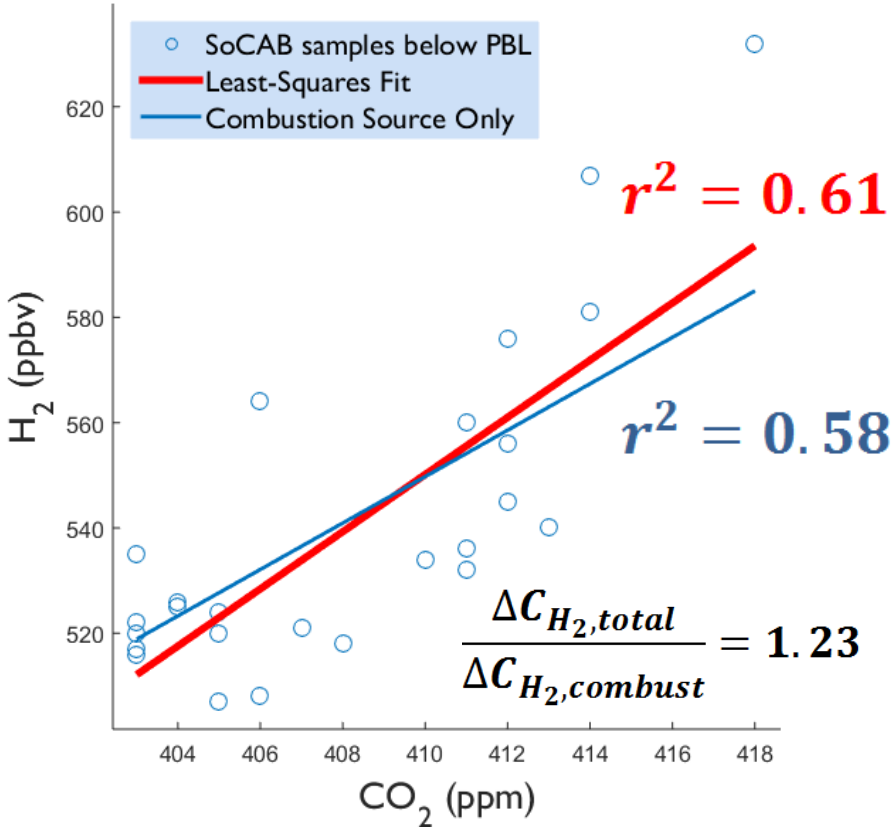
$$r^2 = 0.53$$

$$\frac{\Delta C_{H_2,total}}{\Delta C_{H_2,combust}} = 1.33$$

CALCULATING THE TRACER RATIO

Comparing with known CO_2 ratio:





$\frac{\Delta C_{H_2,total}}{\Delta C_{H_2,combust}}$ **are within 8% of one another.**

EMISSIONS ESTIMATION

Calculating estimates

$$\frac{j_{H_2}^{emi,combust}}{j_{CO}^{emi}} \cong \frac{\Delta C_{H_2,combust}}{\Delta C_{CO}} = 0.48 \pm 0.07$$

Inventory

$$j_{H_2}^{emi,combust} =$$

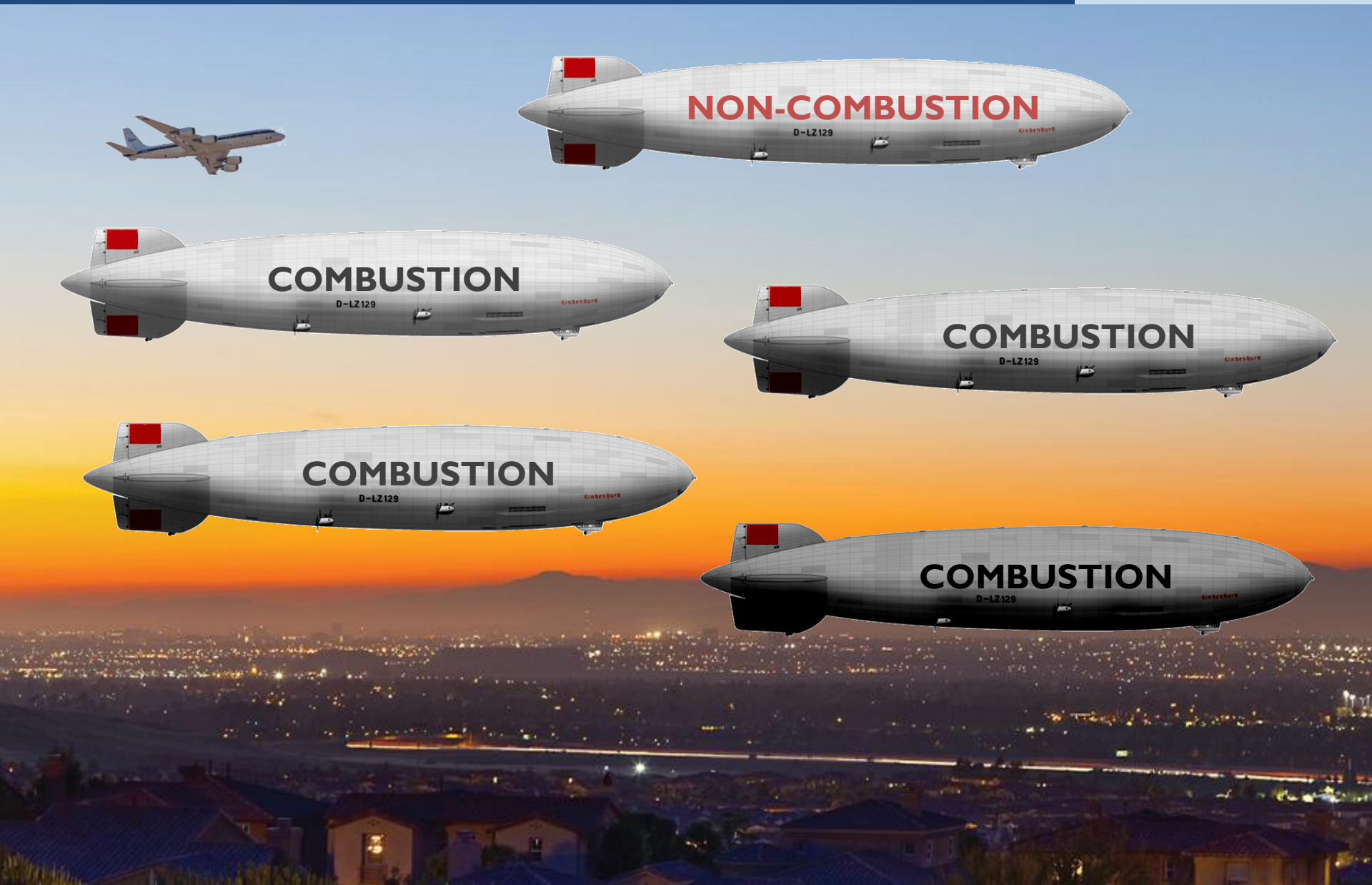
24.8 ± 3.6 Gg yr^{-1}
or 68.1 ± 9.9 tons day^{-1}

$$\frac{\Delta C_{H_2,total}}{\Delta C_{H_2,combust}} = 1.33$$

$$j_{H_2}^{emi,non-combust} =$$

8.2 ± 3.6 Gg yr^{-1}
or 22.6 ± 1.3 tons day^{-1}

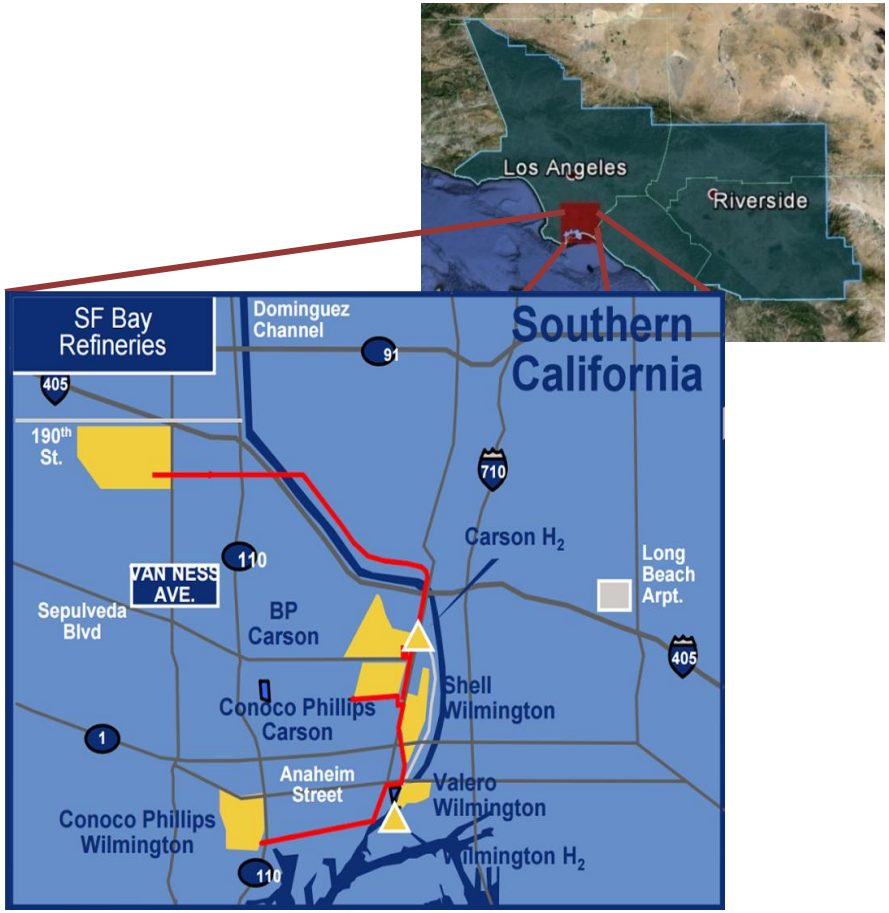
Daily H_2 emissions from the SoCAB…



H_2 LEAKAGE RATE

Total Commercial Production

Source	Daily Output Mt H_2/day
Carson Air Products Hydrogen Plant	227
Wilmington Air Products Hydrogen Plant	196
Hydrolytic production at H_2 fueling stations	2
DAILY OUTPUT:	**425**

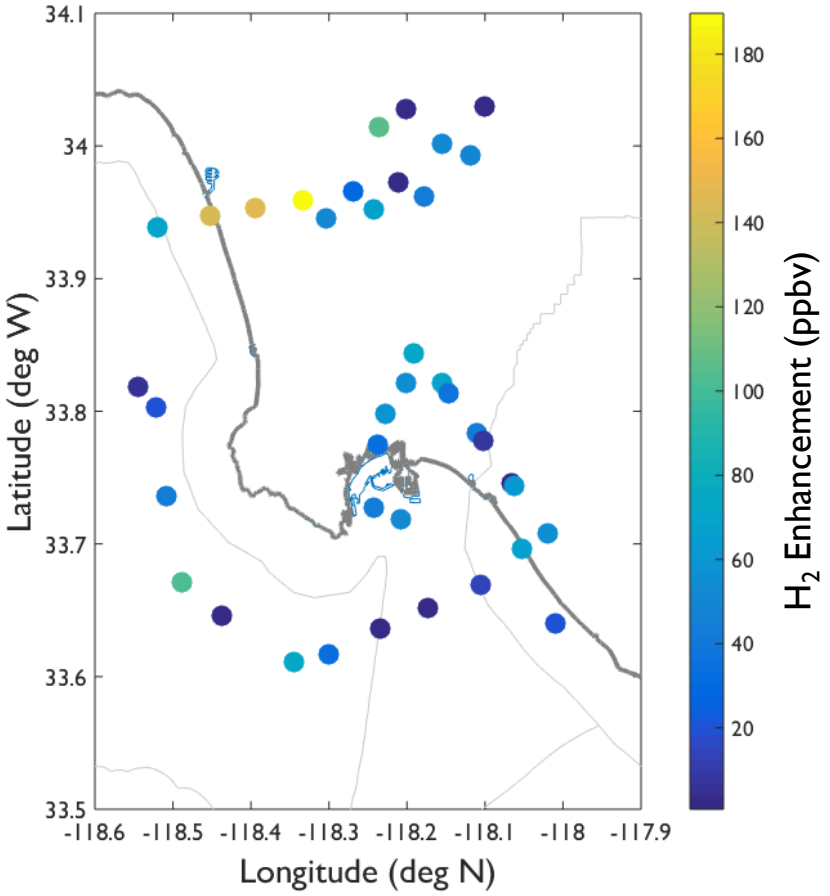


Air Products and Chemicals, Inc.
Abele, Andris R.

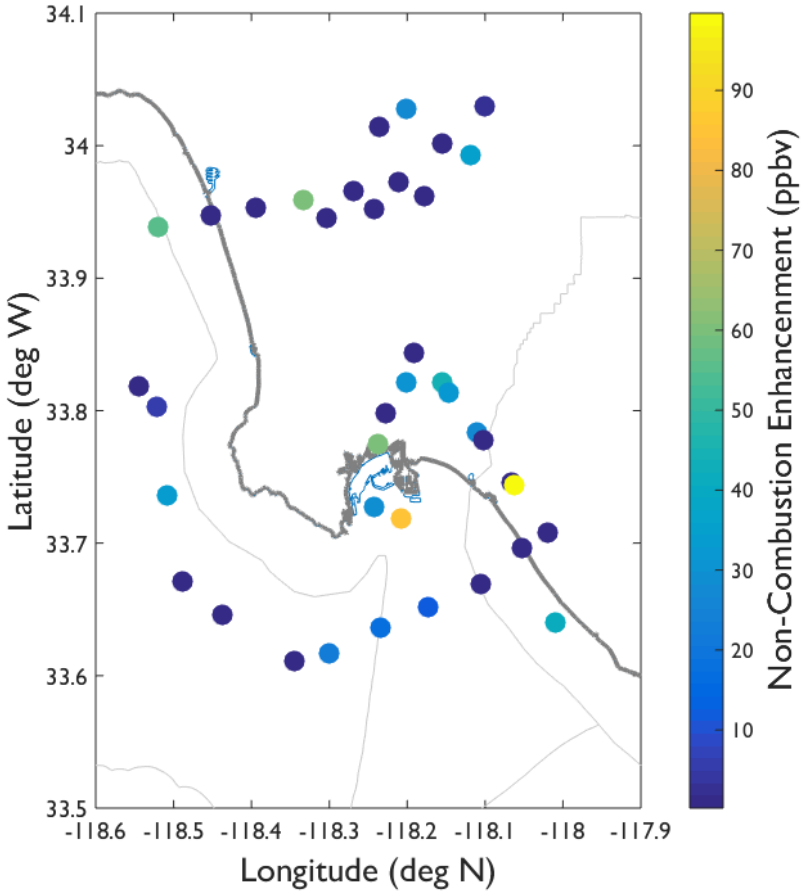
H_2 LEAKAGE RATE

Locating Leakage

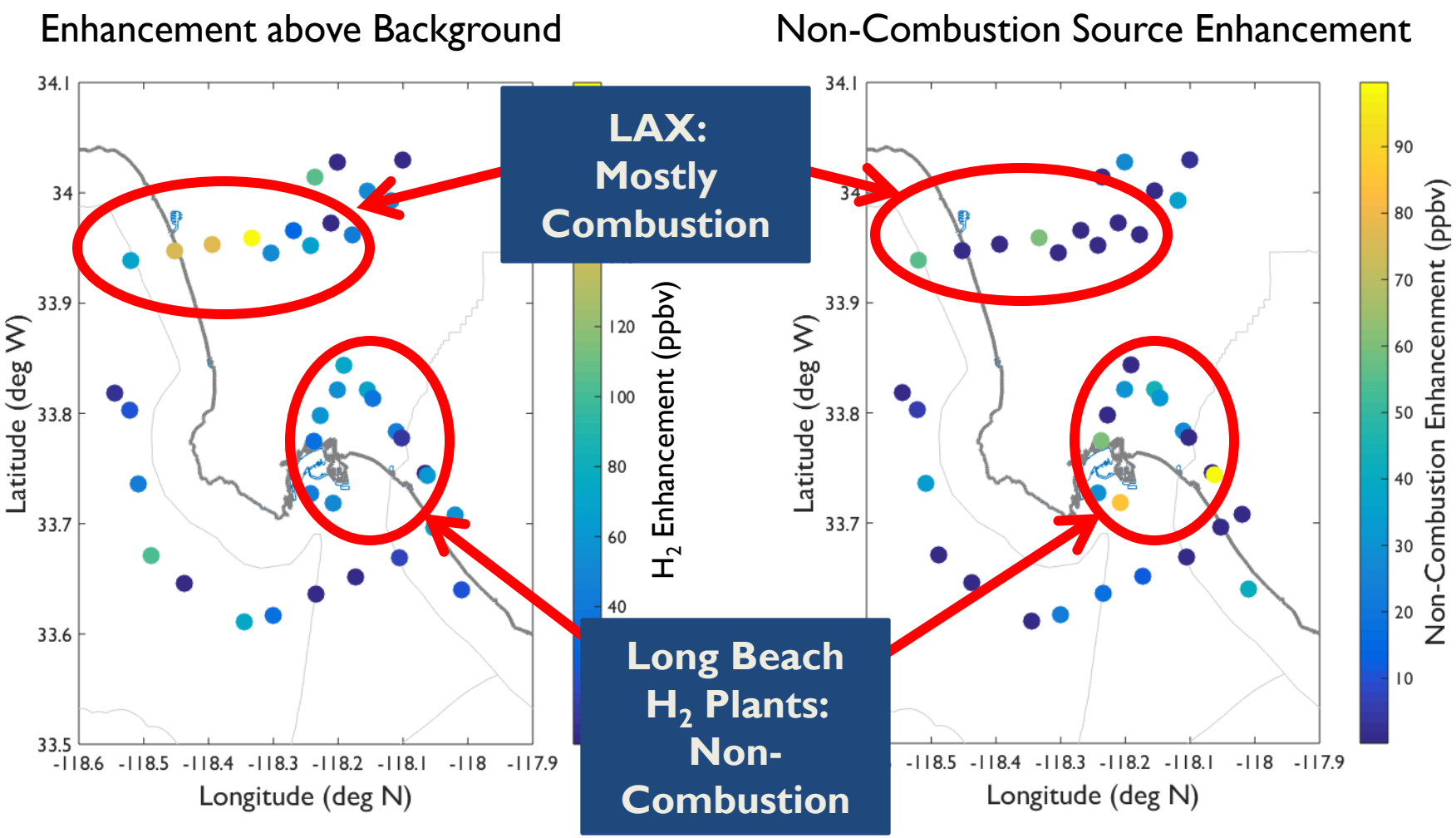
Enhancement above Background



Non-Combustion Source Enhancement



Locating Leakage



H_2 LEAKAGE RATE

A new estimate

10-20%

Tromp et al. 2003, Science

0.1%

2-3%

Responses in *Science*: *Letters to the Editor*

~~**But to date, no top-down experimental estimates!**~~

7%

Wuebbles 2005

< 5%

Matt

0.3-10%

B. Van Ruijven et al. 2011

CONCLUSIONS

Summary of Findings

- H2 emissions totals for SoCAB were derived through a top-down approach
  - Contributions from industry separated from traffic sources for the first time
- Upper limit leakage rate was calculated for H_2 infrastructure
  - Infrastructure not yet well developed—should be used as baseline for future studies
- Much more work needed
  - D/H isotope studies
  - direct source observations at production plants, fuel pumps, etc.

CONCLUSIONS

Acknowledgements

- Dr. Jason Schroeder
- Snake 'n' Blake team
- Prof. Don Blake
- Blake Lab
- Dr. Emily Schaller
- Nick Heath
- SARP 2015 participants
- Mom

Thanks! Questions?

CONCLUSIONS

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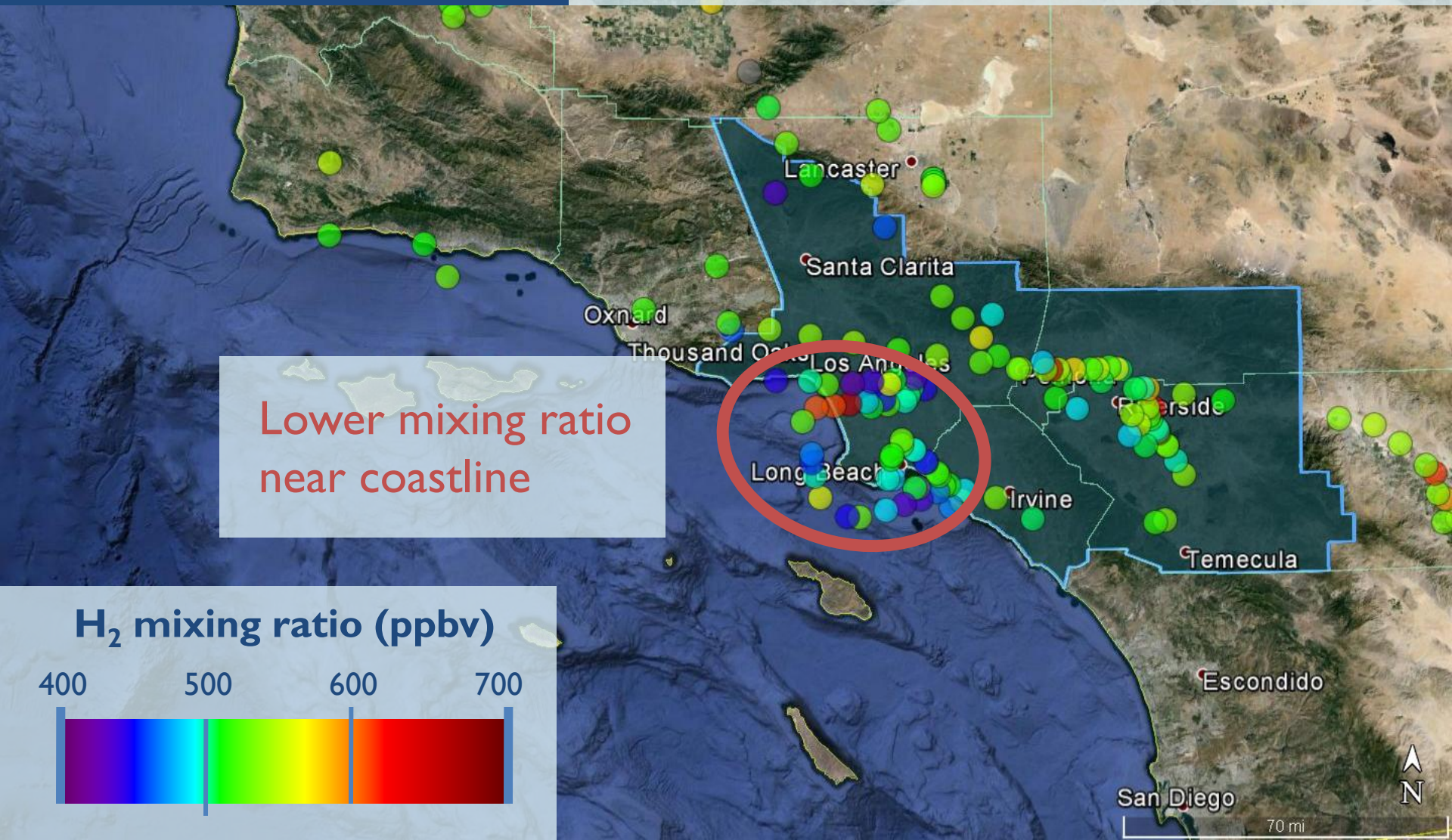
Reasons NOT to worry about H_2 emissions

- Total H2 emissions would likely decrease as HFCEVs replace combustion vehicles
- Pre-catalytic converter era already saw extreme anthropogenic emissions of H2
- Soil sink (75% of sink for molecular hydrogen) has been shown to increase as soil becomes drier, so frequent droughts will sequester H2!

EMISSIONS ESTIMATION

Preliminary analysis



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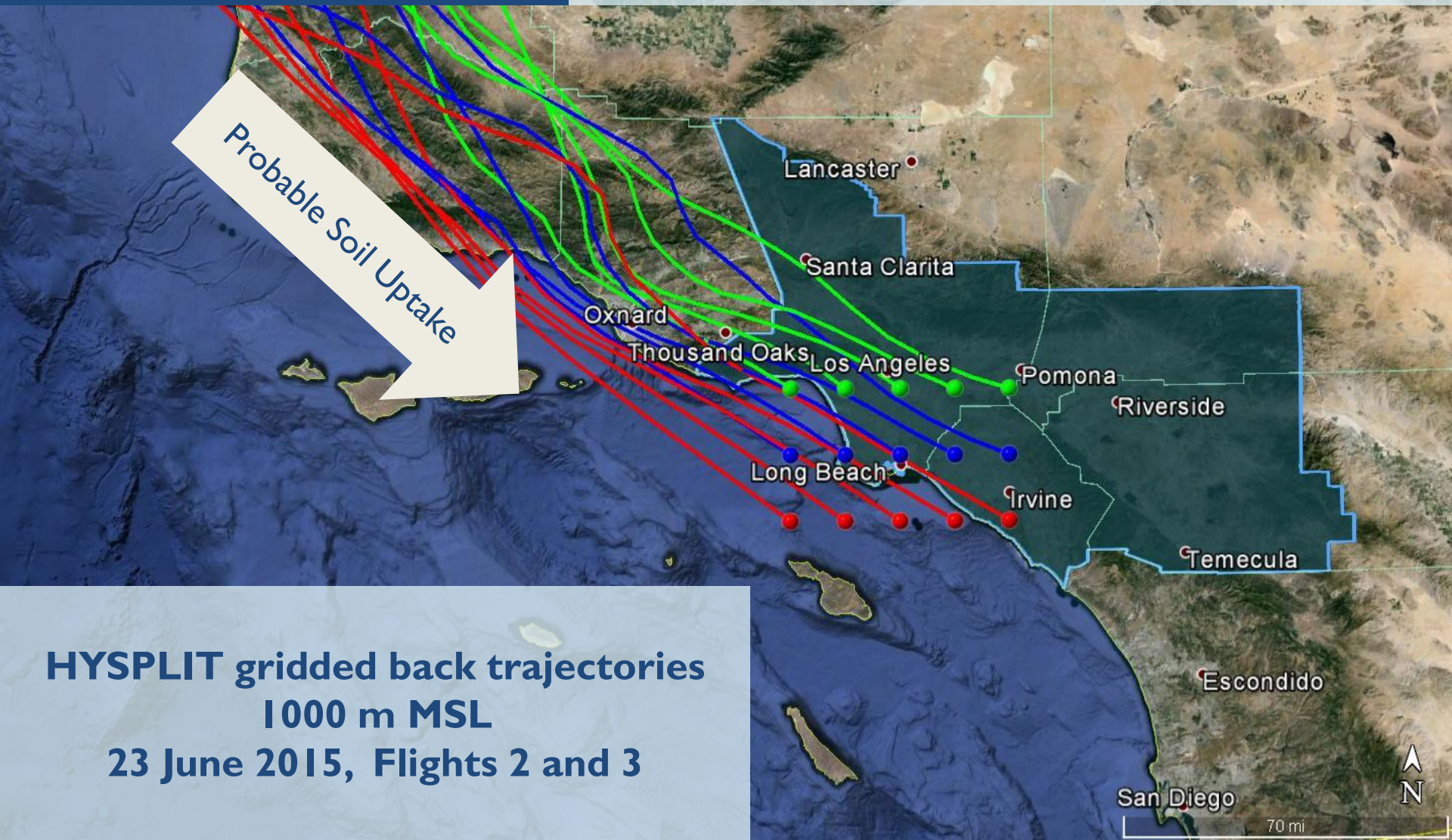

HYSPLIT gridded back trajectories
1000 m MSL
23 June 2015, Flights 2 and 3

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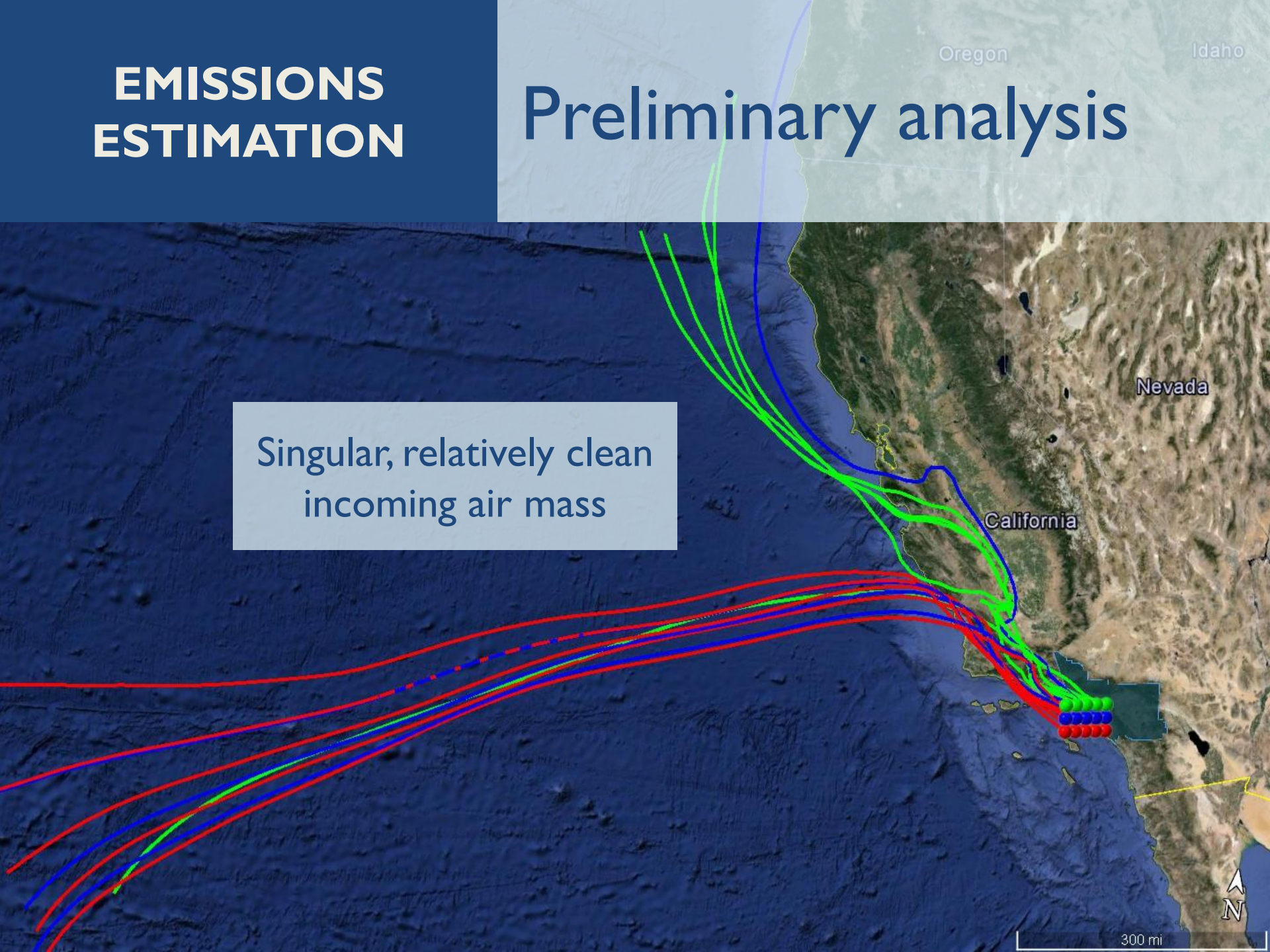

Singular, relatively clean incoming air mass

CARSON AIR PRODUCTS HYDROGEN PLANT