

Pasadena
Ground Site



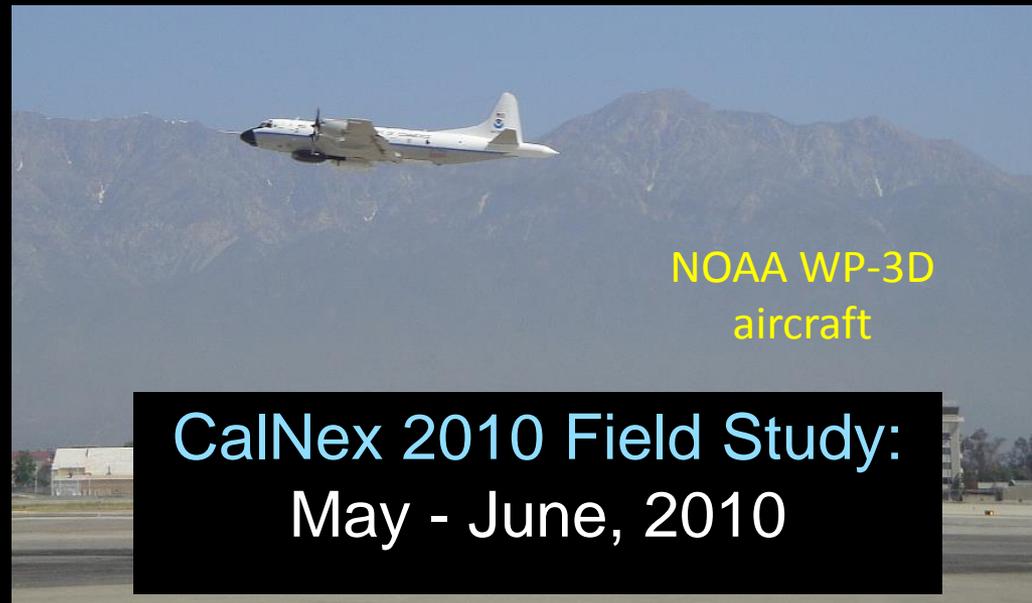
*1/2 time at CIRES
(Cooperative Institute for Research
in Environmental Sciences)
University of Colorado

Some Stories from CalNex 2010 Field Study

David Parrish*

Chemical Sciences Division
NOAA/ESRL
Boulder, Colorado USA

7 August 2014



NOAA WP-3D
aircraft

CalNex 2010 Field Study:
May - June, 2010

R/V Atlantis



Bakersfield
Ground Site



Twin Otter
Aircraft



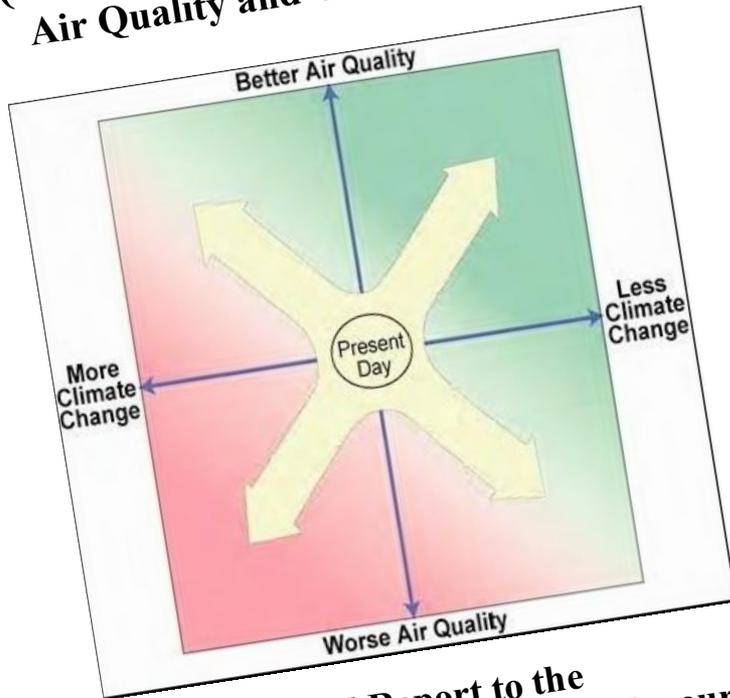
Some Stories from CalNex 2010 Field Study

1. Sources of methane (CH_4) emissions in California
2. Role of long-range pollutant transport in California
3. SJVAB vs. SoCAB Response to emission controls

Warning!!! Don't expect complete, final stories

CalNex Synthesis Completed

Synthesis of Policy Relevant Findings from the CalNex 2010 Field Study (California Research at the Nexus of Air Quality and Climate Change)



**Final Report to the
Research Division of the California Air Resources Board**

Prepared by **David D. Parrish**
Tropospheric Chemistry Group
NOAA/ESRL/Chemical Sciences Division
Day R/CSD7

Nearly everything
discussed today
is in here!

Available at:

<http://esrl.noaa.gov/csd/projects/calnex/synthesisreport.pdf>

CalNex Synthesis Completed

Synthesizes scientific results and implications of CalNex 2010 Field Study into clear language that policy-makers can use effectively

A substantial body of scientific publications have resulted from the study <http://tinyurl.com/CalNex-papers>

- 93 papers originally “promised”
- 106 papers published & in press (14 different journals)
- 6 other papers submitted

Special Section organized in *J. Geophys. Res.* –
Atmospheres

Synthesis organized around CalNex Science Questions

1. Sources of methane (CH₄) emissions in California

SoCAB – Landfills, dairies and natural gas

(Peischl, J., et al. (2013), Quantifying sources of methane using light alkanes in the Los Angeles basin, California, *J. Geophys. Res. Atmos.*, 118, 4974–4990, doi:10.1002/jgrd.50413.)

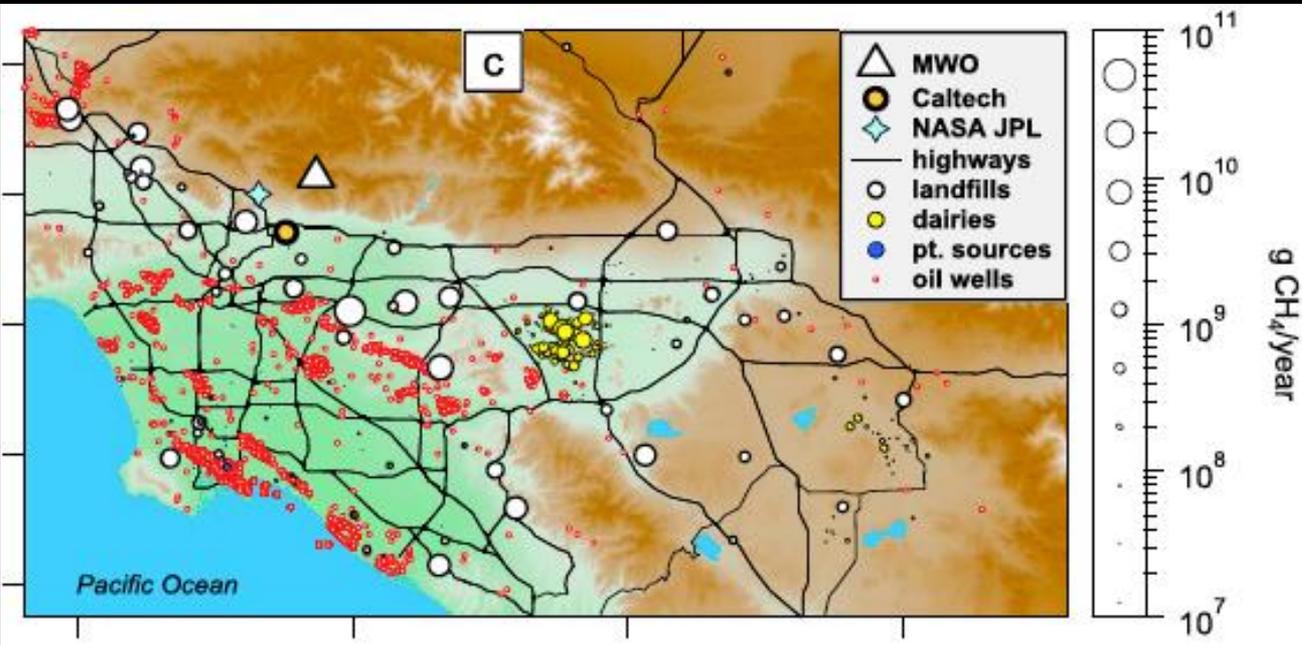
Sacramento Valley - Rice agriculture

(Peischl, J., et al. (2012), Airborne observations of methane emissions from rice cultivation in the Sacramento Valley of California, *J. Geophys. Res.*, 117, D00V25, doi:10.1029/2012JD017994.)

SJVAB – Petroleum operations and dairies

(Gentner, D.R., et al. (2014), Emissions of organic carbon and methane from petroleum and dairy operations in California's San Joaquin Valley, *Atmos. Chem. Phys.*, 14, 4955–4978, doi:10.5194/acp-14-4955-2014.)

1. Sources of methane (CH_4) emissions in California - SoCAB

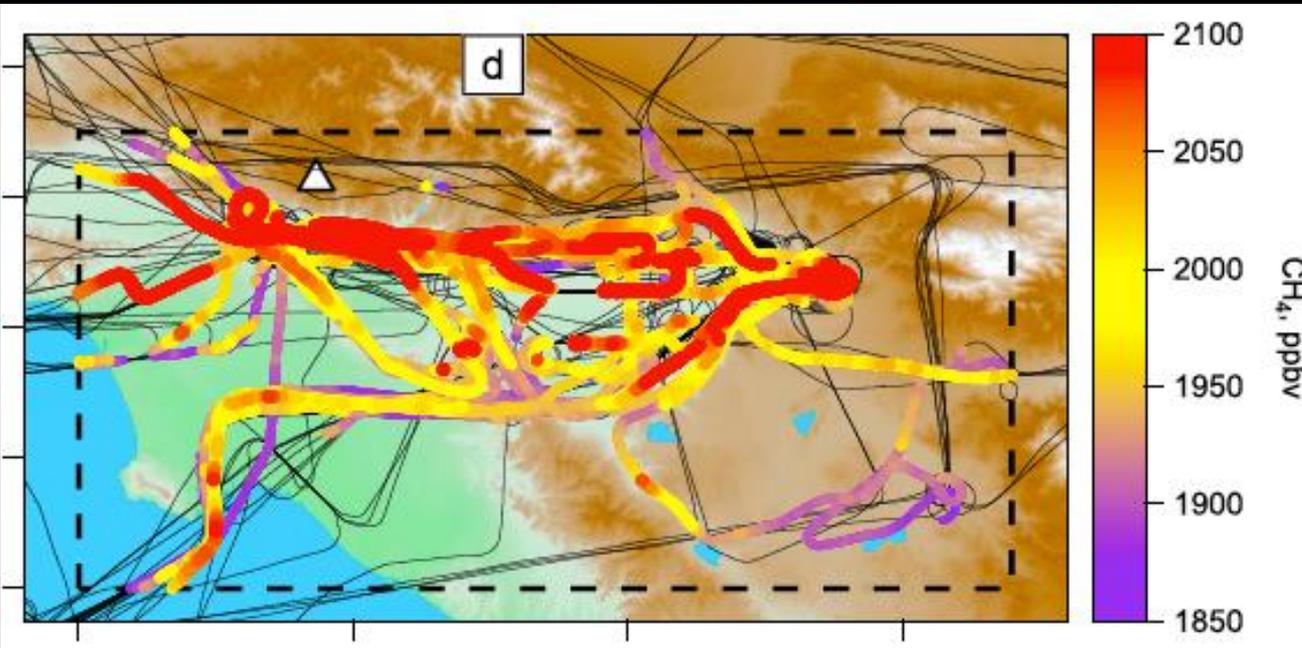


WMO = Mount Wilson Observatory (white triangle)

Complicated – many potential sources

- Natural gas – distribution system, local production, natural seeps.
- Landfills, dairies, mobile sources, waste water treatment.

1. Sources of methane (CH_4) emissions in California - SoCAB



WMO = Mount Wilson Observatory (white triangle)

Data from 16 daytime NOAA P-3 aircraft flights plus canisters collected at WMO

1. Sources of methane (CH_4) emissions in California - SoCAB

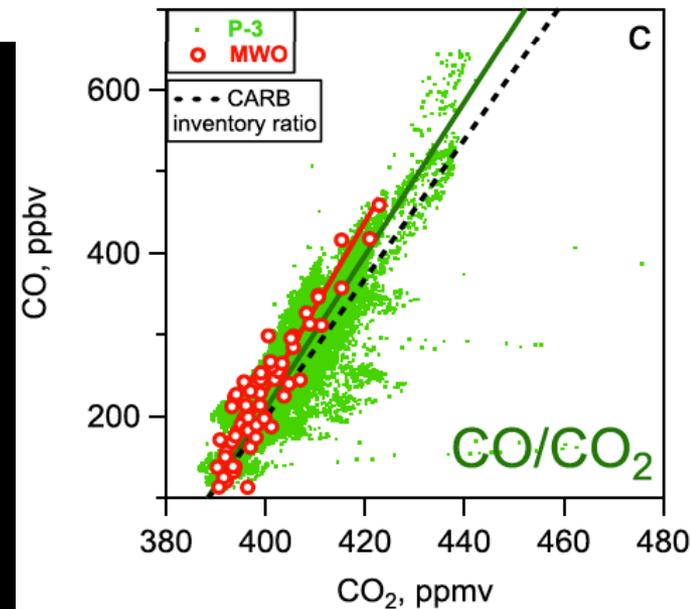
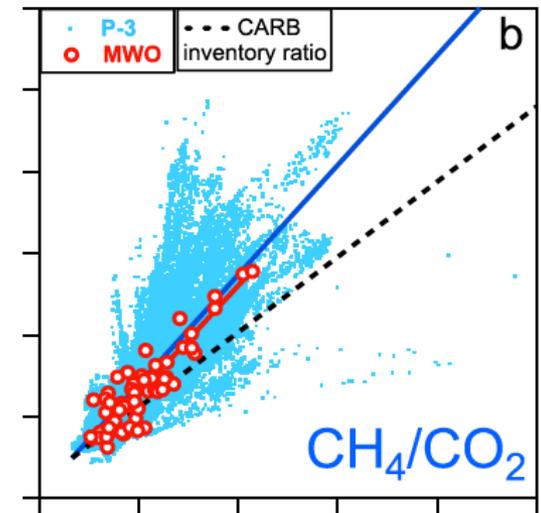
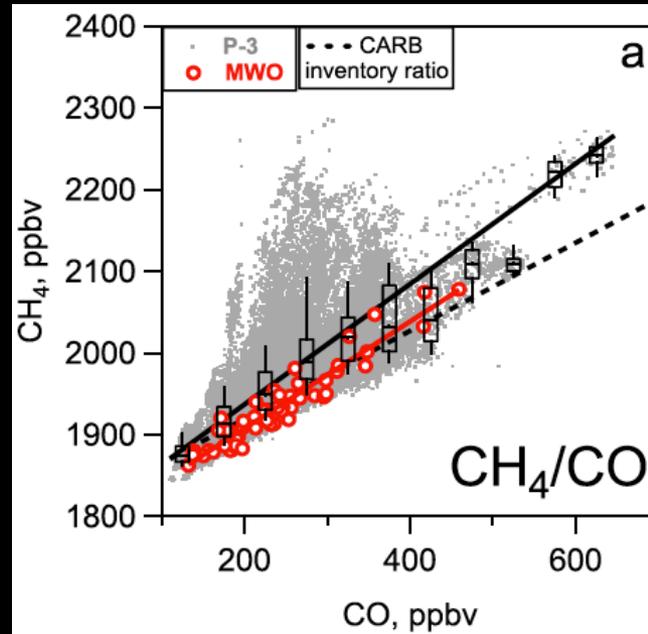
Correlation of CH_4 with CO and CO_2 , plus CO and CO_2 emission inventories allow total CH_4 emission estimate:

410 ± 40 Gg CH_4/yr
from SoCAB

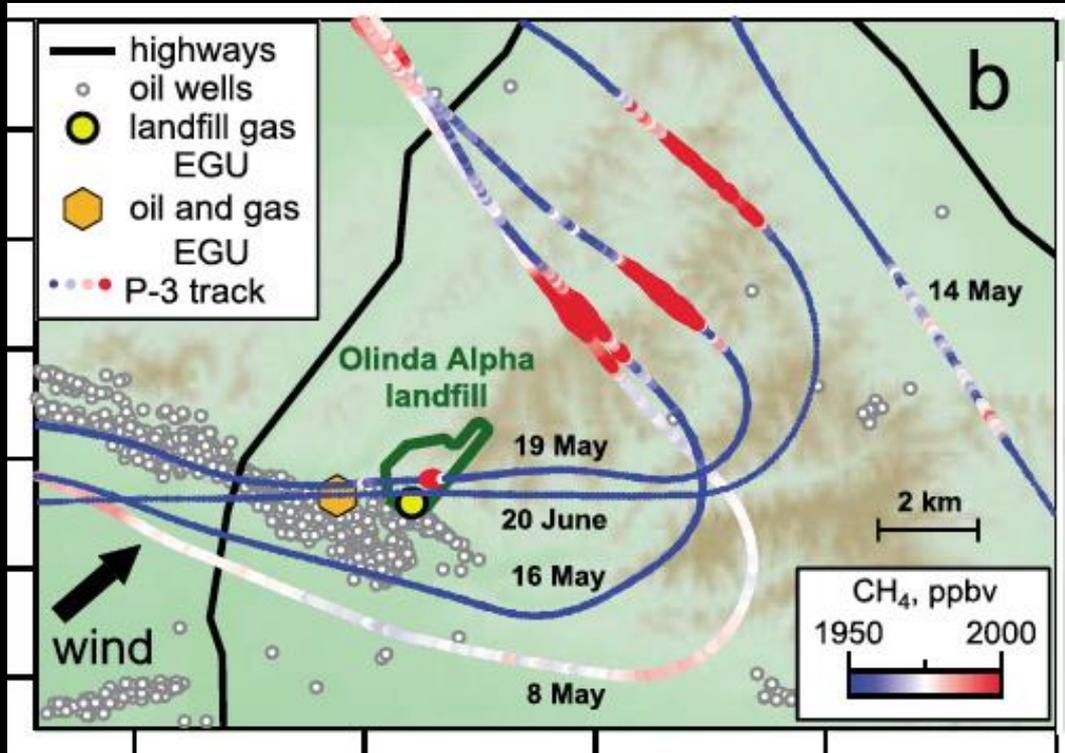
Significantly larger than 301 Gg CH_4/yr in
CARB 2009 GHG emission inventory

Consistent with *Wunch et al., 2009*; *Hsu et al., 2010* and *Wennberg et al., 2012*

What source is responsible for discrepancy?



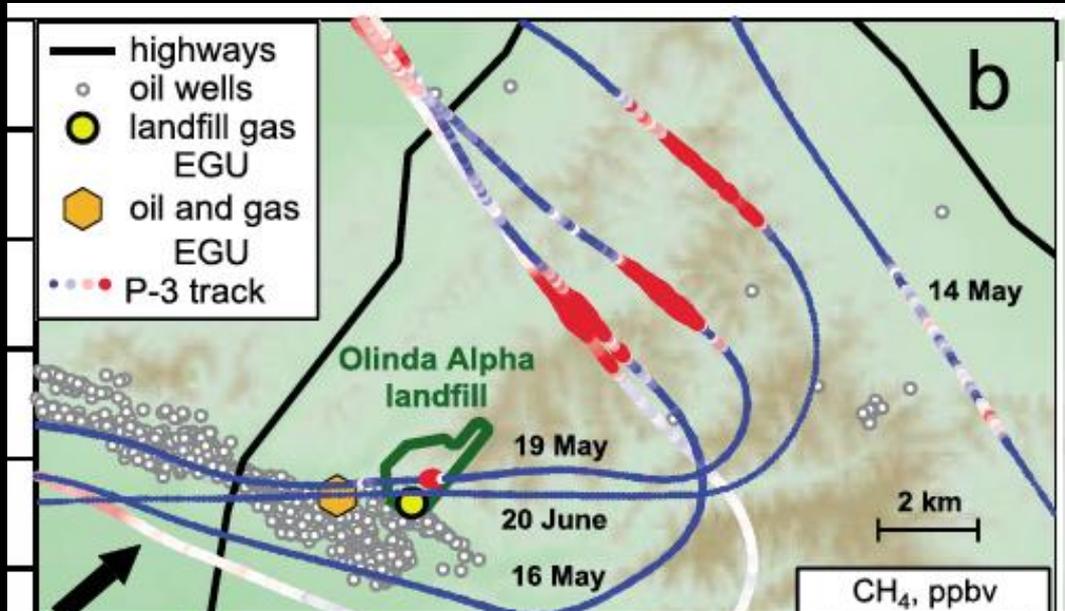
1. Sources of methane (CH₄) emissions in California - SoCAB



Fly through plumes downwind of landfills

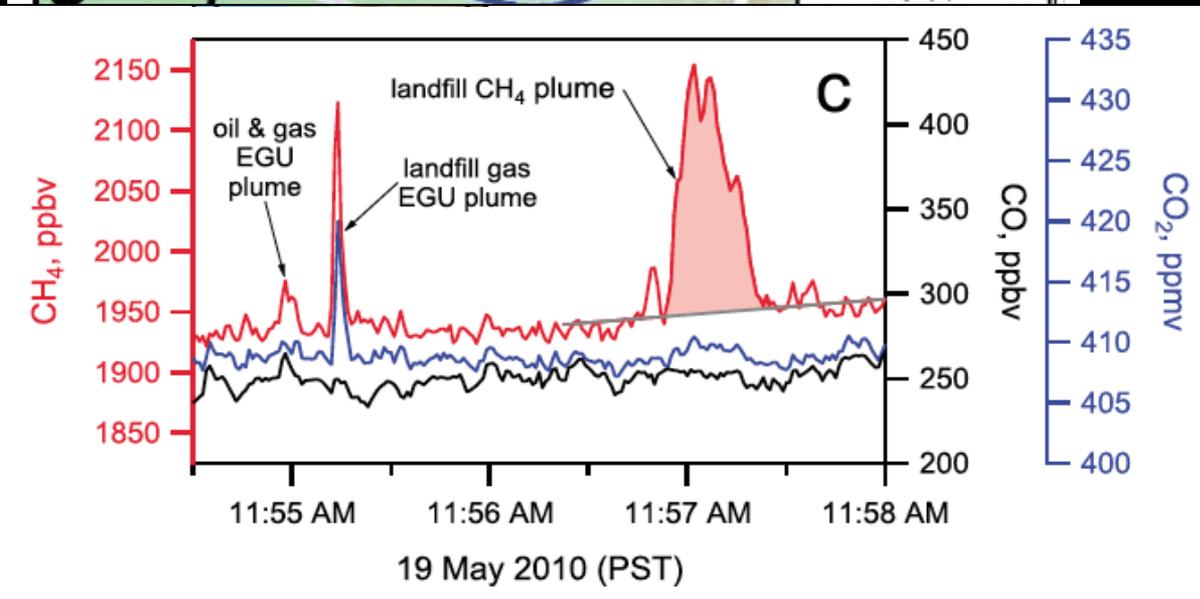
CH₄ data plus boundary layer height and wind speed and direction allows absolute flux to be calculated.

1. Sources of methane (CH₄) emissions in California - SoCAB



Fly through plumes downwind of landfills

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Co-measurement of CO₂ allows plume from landfill to be isolated from other sources.

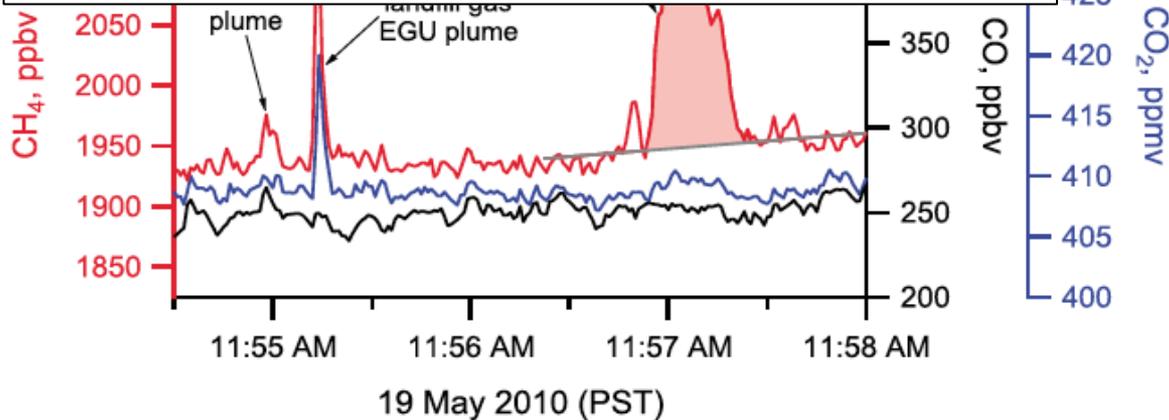
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Table 3. Landfill Emission Fluxes Determined Aboard the NOAA P-3 in 2010 From Downwind Plume Transects

Landfill	Transect Date	Flux (10 ²⁵ molecules/s)	Flux (Gg/yr)	2008 CARB GHG Inventory ^a (Gg/yr)
Olinda Alpha	8 May	1.13	9.5	11.0
	14 May	1.45	12.2	
	16 May	1.74	14.6	
	19 May	1.61	13.5	
	20 June	2.90	24.3	
	Average ^b	1.49 ± 0.35	12.5 ± 2.9	
Puente Hills	8 May	4.29	36.0	38.8
	19 May	3.62	30.4	
	20 June	4.48	37.6	
	Average ^b	4.06 ± 1.18	34.0 ± 9.9	

^adata from CARB (L. Hunsaker, personal communication, June 2011).

^bweighted average, assuming a 50% uncertainty in the individual flux determinations [Taylor, 1997].



Fly through plumes downwind of landfills

CH₄ data plus boundary layer height and wind speed and direction allows absolute flux to be calculated.

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Excellent agreement with CARB 2008 GHG emission inventory!

1. Sources of methane (CH₄) emissions in California - SoCAB

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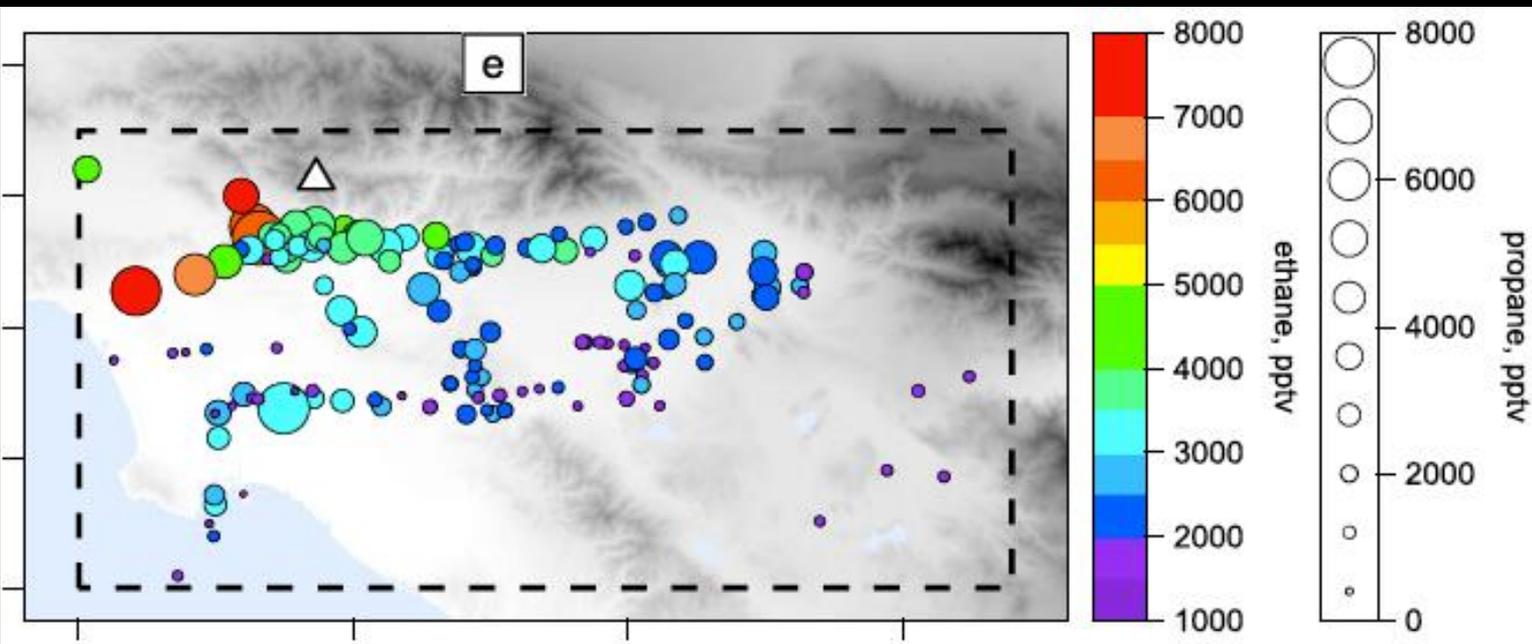
Dairies: Emissions/cow x population of cows, plus manure management considerations.

Landfills plus dairies = 182 ± 54 Gg CH₄/yr

Total from SoCAB = 410 ± 40 Gg CH₄/yr

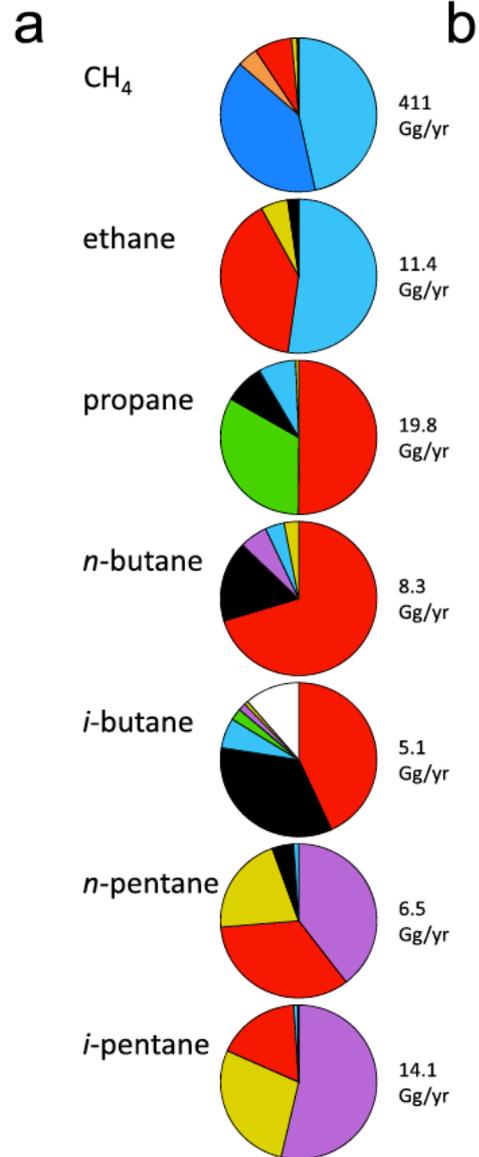
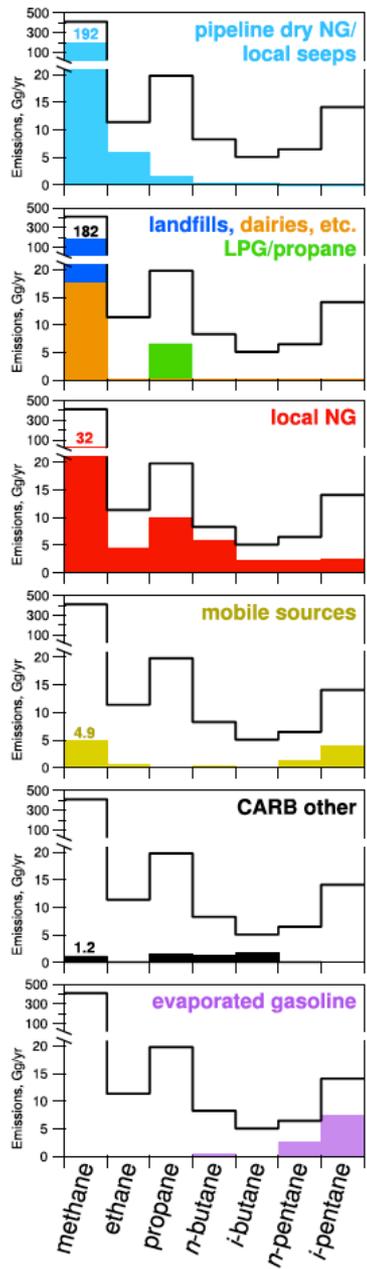
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1. Sources of methane (CH_4) emissions in California - SoCAB



Source apportionment based on light alkane measurements

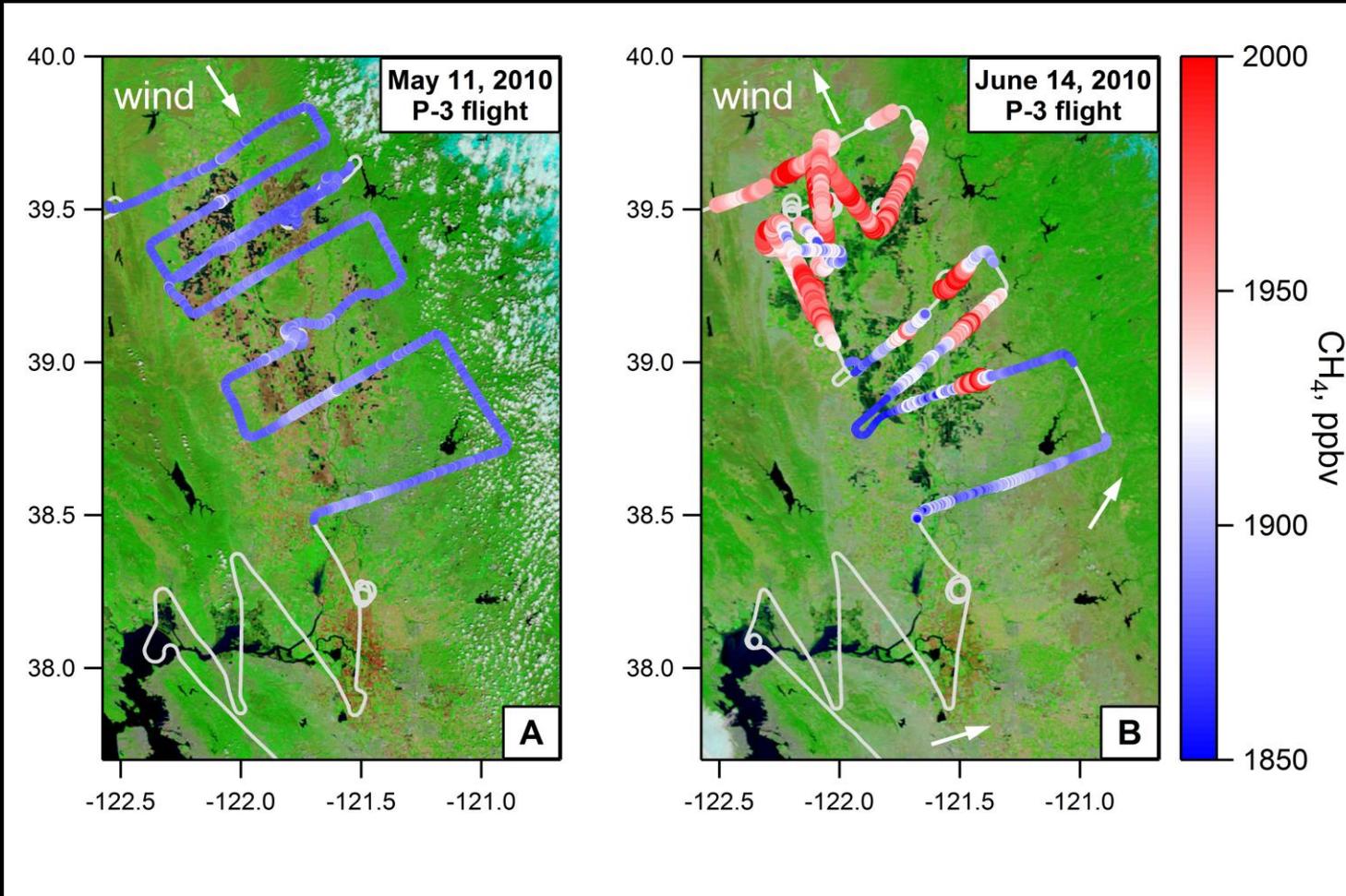
1. Sources of methane (CH₄) emissions in California - SoCAB



Source	Gg/yr in 2010
Natural gas distribution, Local seeps	192 ± 54
Landfills, Dairies, Wastewater	182 ± 54
Natural gas production	32 ± 7
Mobile sources	4.9 ± 1.3
CARB other	1.2 ± 0.3
Total	411 ± 77

Source apportionment based on light alkane measurements

1. Sources of methane (CH_4) emissions in California – Rice agriculture in Sacramento Valley



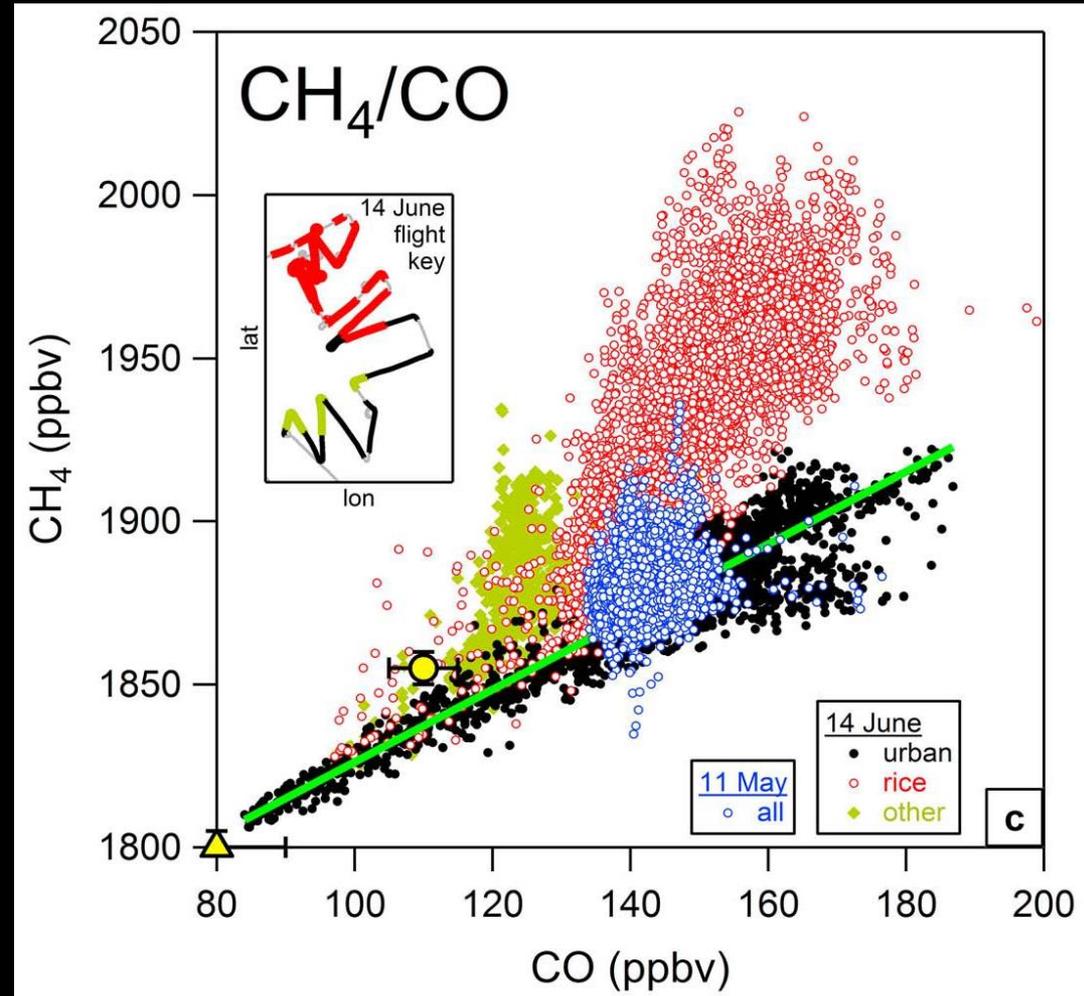
Two flights in Sacramento Valley:

- May 11 before rice fields flooded,
- June 14 after rice was growing

Peischl et al., *J. Geophys. Res.*, 2012

1. Sources of methane (CH₄) emissions in California – Rice agriculture in Sacramento Valley

Complex relationship between urban, biomass burning and agricultural emissions of CO, CO₂ and CH₄.



Two flights in Sacramento Valley:

- May 11 before rice fields flooded,
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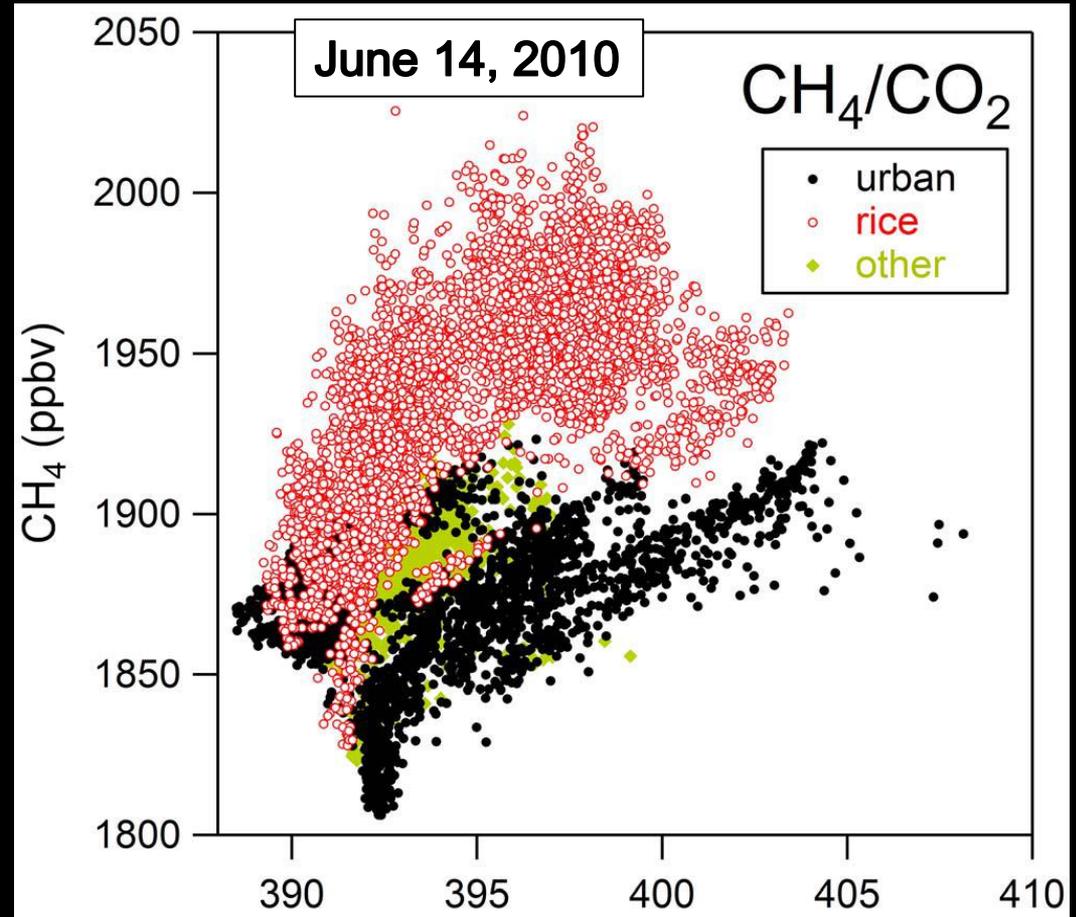
1. Sources of methane (CH₄) emissions in California – Rice agriculture in Sacramento Valley

Complex relationship between urban, biomass burning and agricultural emissions of CO, CO₂ and CH₄.

~ 0.6% of CO₂ uptake by photosynthesis was released as CH₄.

Findings of *McMillan et al.* [2007] are representative of the Sacramento Valley rice growing region.

Emissions approximately 3 times the CARB GHG inventory rate of 122 kg/ha.

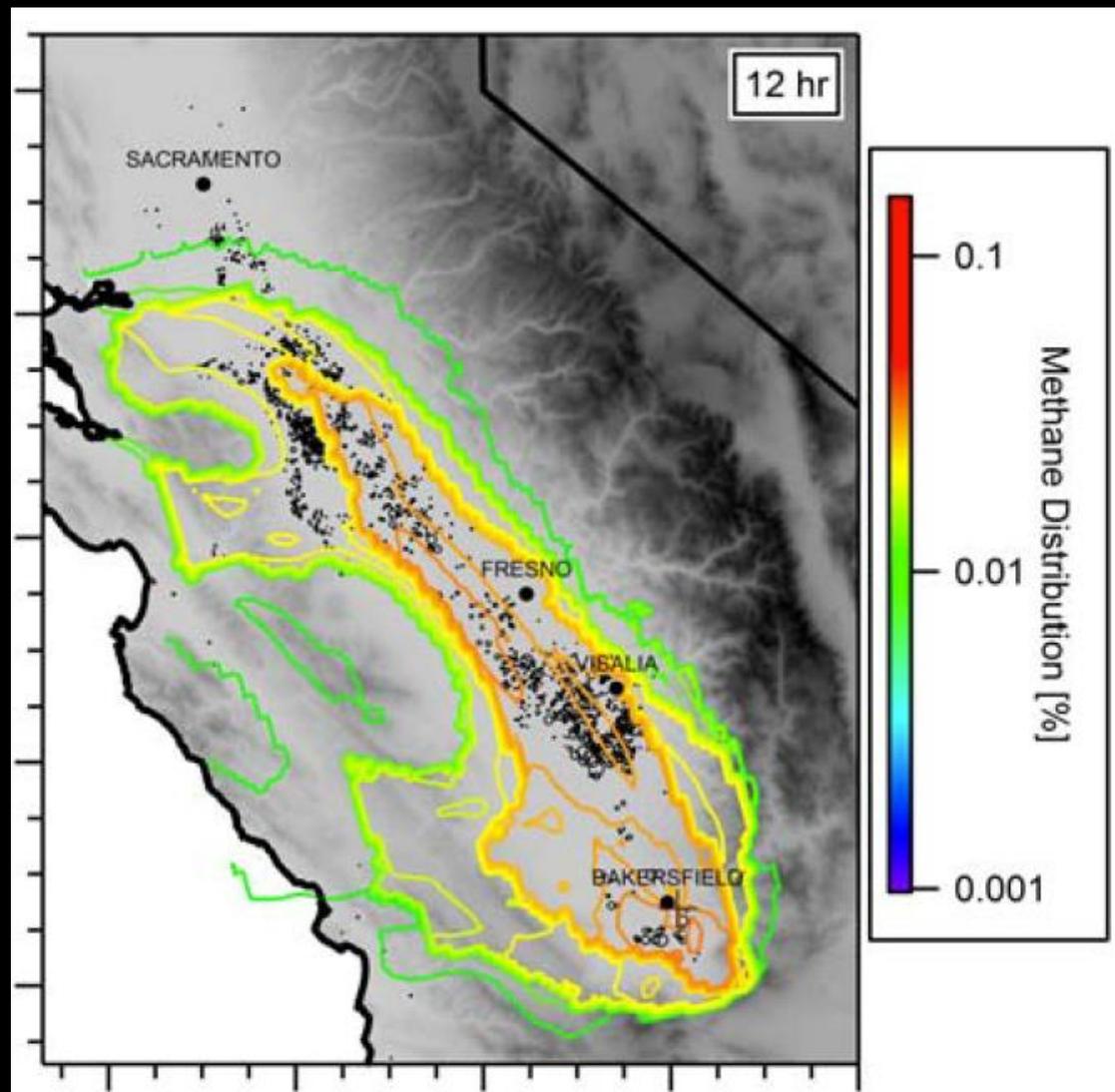


Difference attributed to mandated decrease of crop residue burning – Win for air quality - Lose for climate change.

1. Sources of methane (CH_4) emissions in California - **SJVAB**

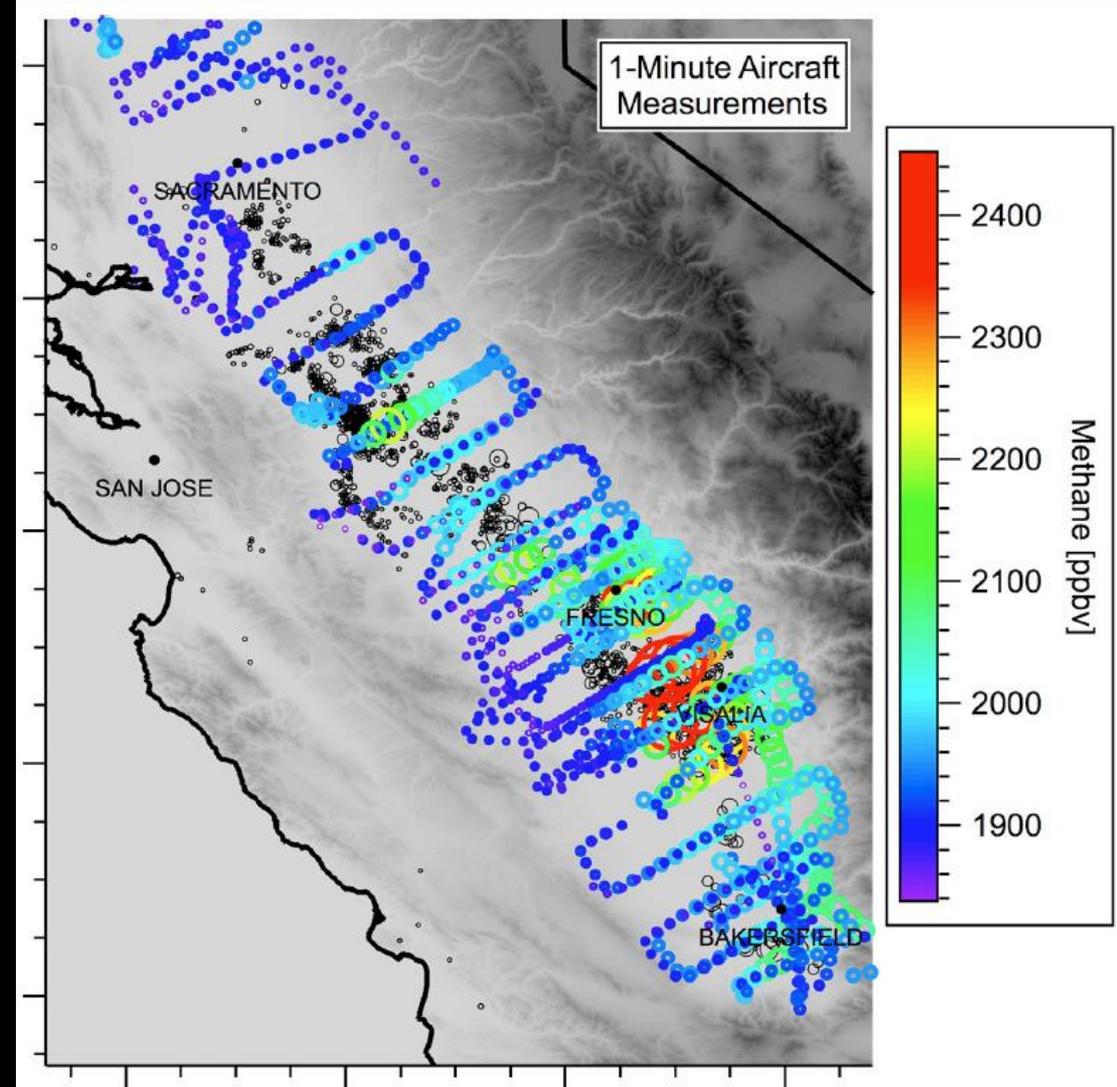
Back trajectory tracer model derives “foot print” of methane emissions – points to dairies rather than oil and gas activities as major methane source

Large sources of paraffinic hydrocarbons from petroleum, but CH_4 not included. Fugitive emissions of condensate (residual natural gas after methane and ethane removed).



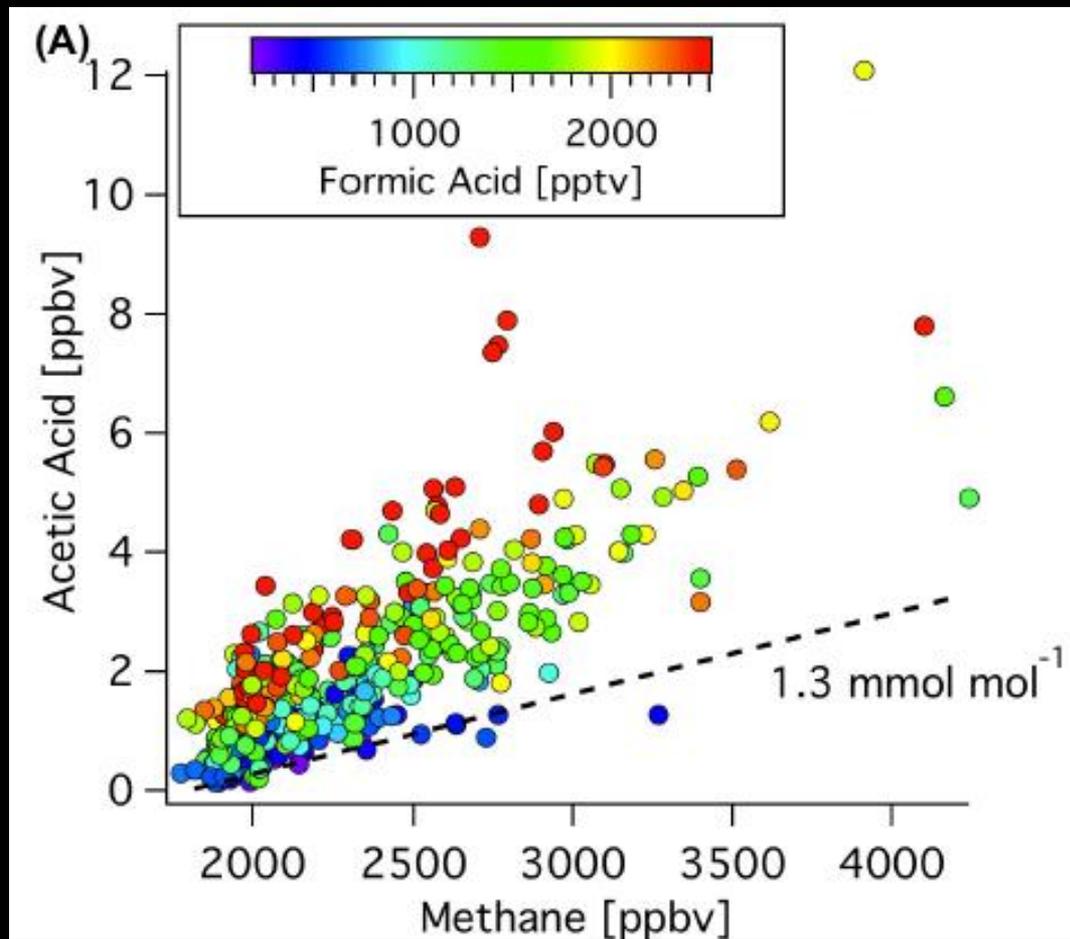
1. Sources of methane (CH_4) emissions in California - **SJVAB**

Aircraft measurements also find elevated CH_4 concentrations primarily over dairies.



1. Sources of methane (CH_4) emissions in California - **SJVAB**

Bakersfield measurements:
Elevated CH_4 correlates
with oxygenated VOCs
(species emitted from
dairies) rather than
alkanes from oil and gas
production.



Dairy operations are responsible for the vast majority of CH_4 emissions in the SJVAB.

2. Role of long-range pollutant transport in California

Layers of enhanced O₃ aloft are common

(Neuman, J. A., et al. (2012), Observations of ozone transport from the free troposphere to the Los Angeles basin, *J. Geophys. Res.*, 117, D00V09, doi:10.1029/2011JD016919.)

Mixing of stratospheric O₃ to surface has significant impact

(Langford, A. O., et al. (2012), Stratospheric influence on surface ozone in the Los Angeles area during late spring and early summer of 2010, *J. Geophys. Res.*, 117, D00V06, doi:10.1029/2011JD016766.)

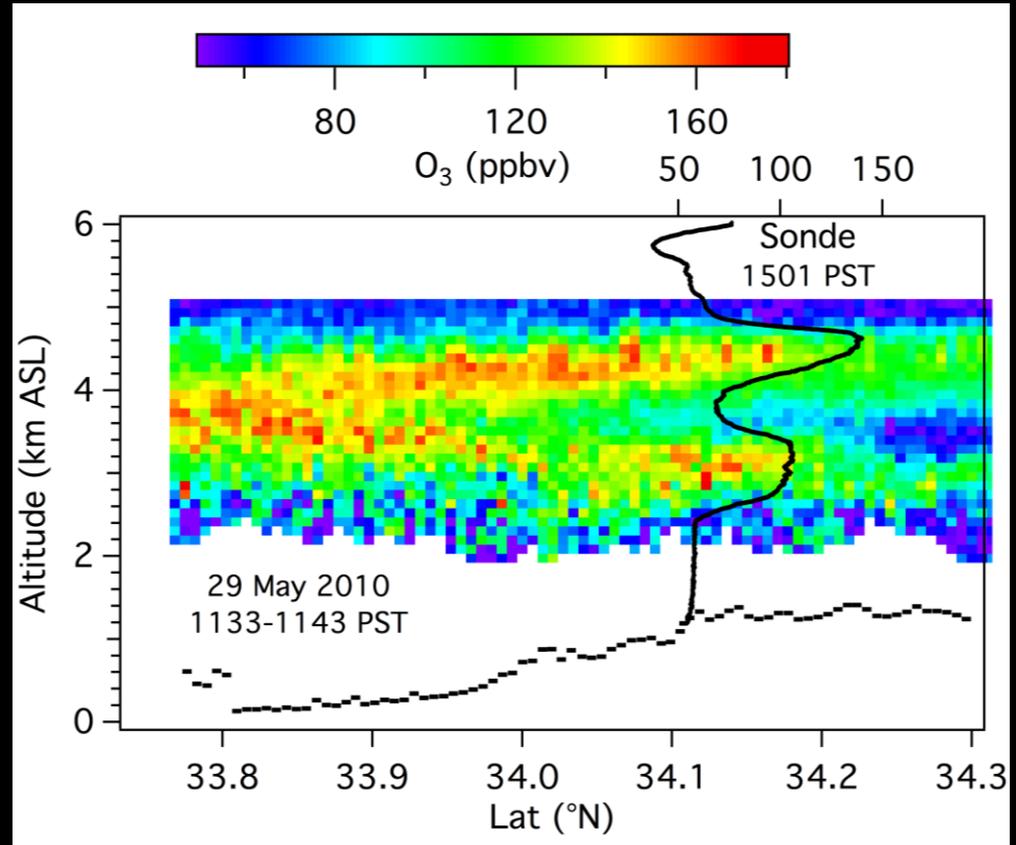
(Lin, M., et al. (2012), Springtime high surface ozone events over the western United States: Quantifying the role of stratospheric intrusions, *J. Geophys. Res.*, 117, D00V22, doi:10.1029/2012JD018151.)

California is also a source of transport to downwind areas.

(Langford, A. O., et al. (2010), Long-range transport of ozone from the Los Angeles Basin: A case study, *Geophys. Res. Lett.*, 37, L06807, doi:10.1029/2010GL042507)

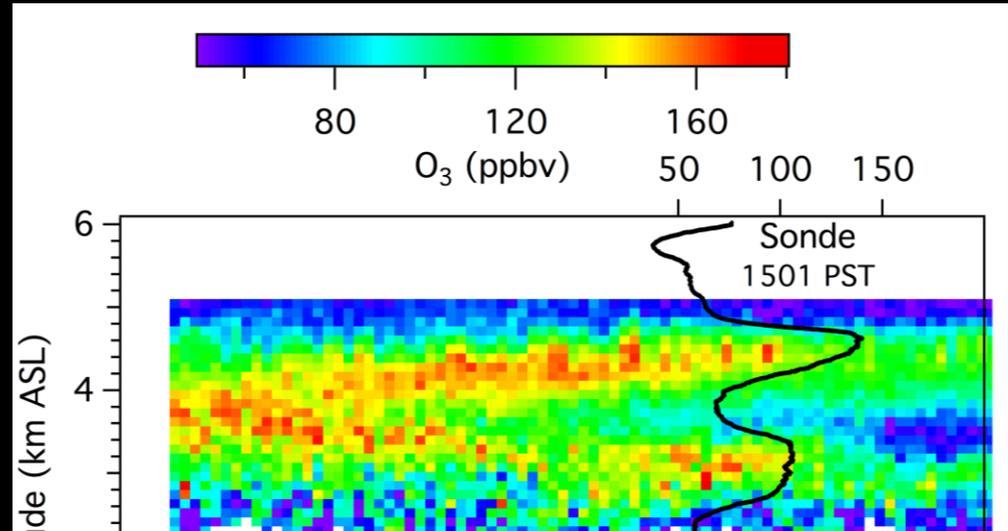
2. Role of long-range pollutant transport in California – Layers of enhanced O_3 aloft are common

Layers from stratospheric O_3 descent, long-range transport of anthropogenic emissions (e.g., from Asia), and lofted aged regional pollution (e.g., from California urban areas).

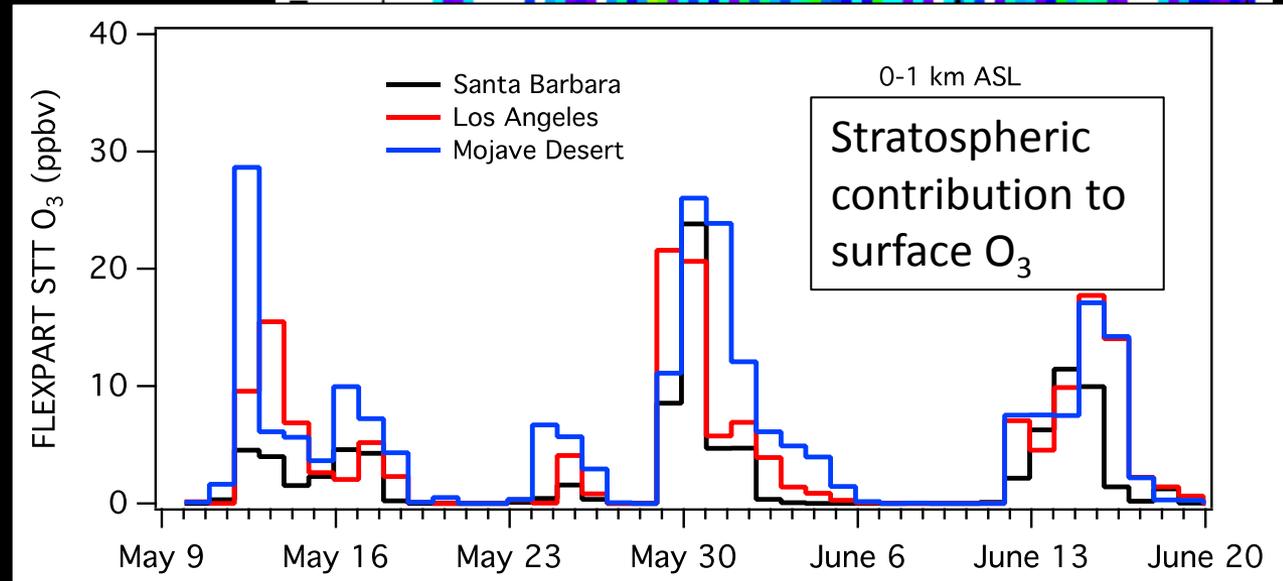


2. Role of long-range pollutant transport in California – **Mixing of stratospheric O₃ to surface has significant impact**

These layers are entrained into the convective boundary layer throughout California, thereby enhancing surface level ozone concentrations.



FLEXPART results (a Lagrangian particle dispersion model)

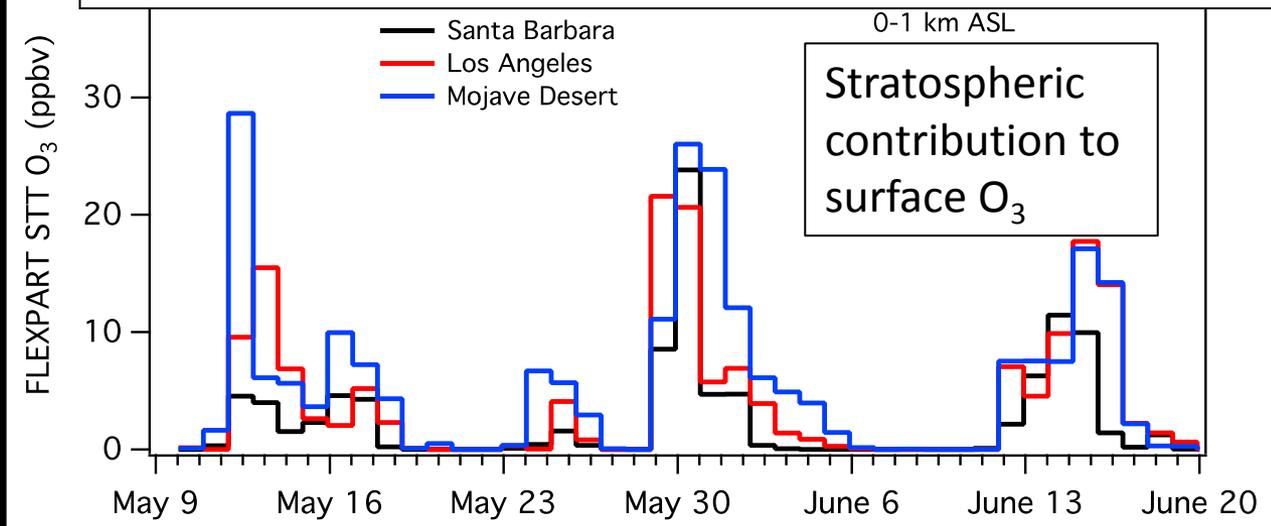
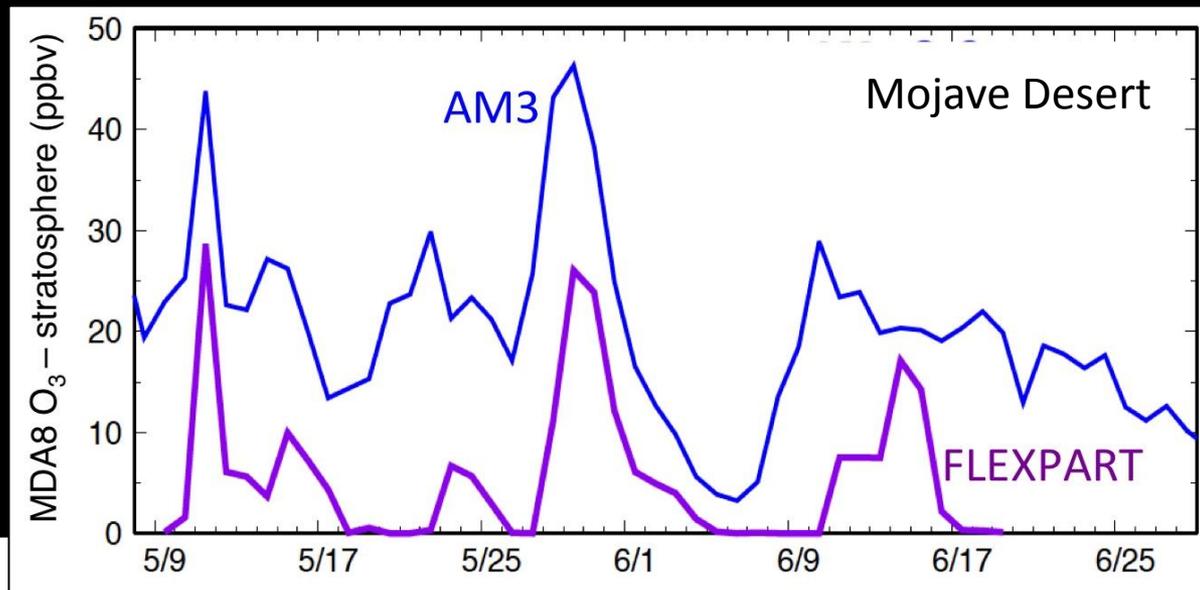


2. Role of long-range pollutant transport in California – **Mixing of stratospheric O₃ to surface has significant impact**

Chemistry-transport model suggests that FLEXPART underestimates total stratospheric contribution.

Stratospheric O₃ is a major fraction of “background” O₃ coming into any urban or rural area

FLEXPART results (a Lagrangian particle dispersion model)



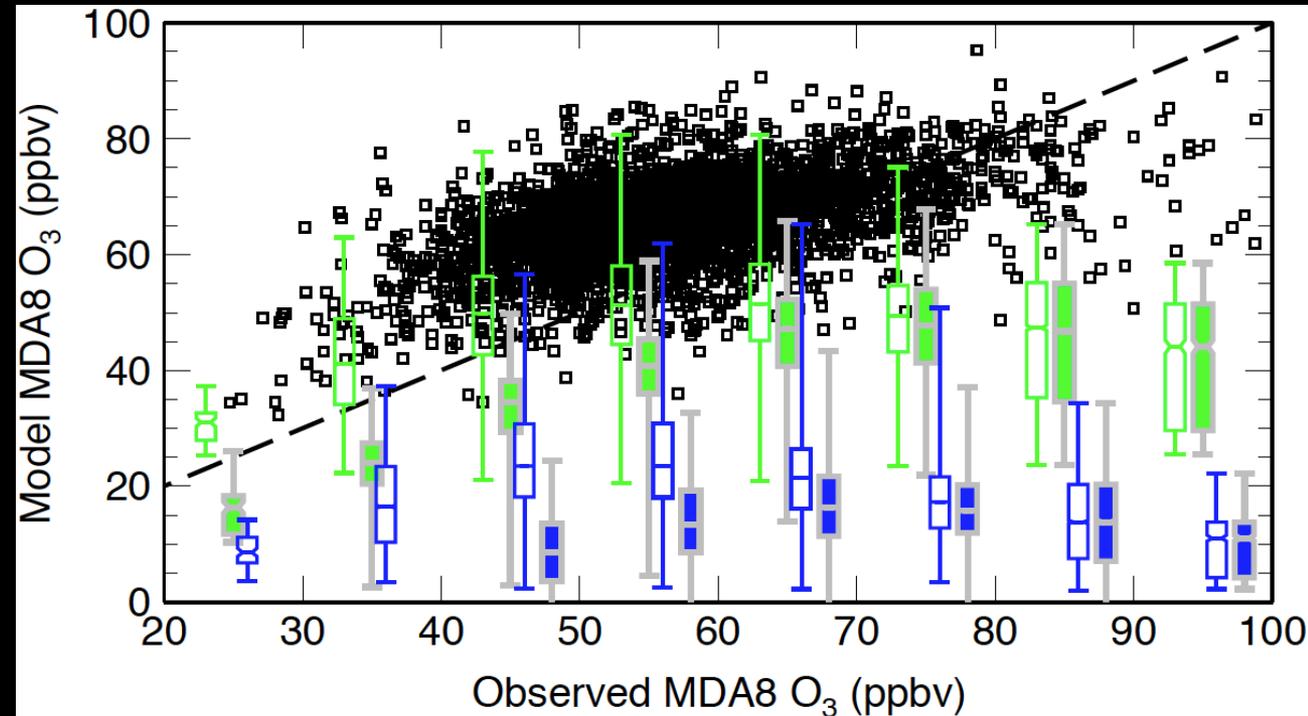
2. Role of long-range pollutant transport in California –
Transport of baseline O_3 accounts for a majority of surface O_3 concentrations in California at urban as well as rural locations, both on average and during many exceedance events.

Chemistry-transport model results.
(Filled boxes are bias corrected.)

PRB O_3 is green.

Stratospheric O_3 contribution is blue

During CalNex, contribution from Asian transport was small.



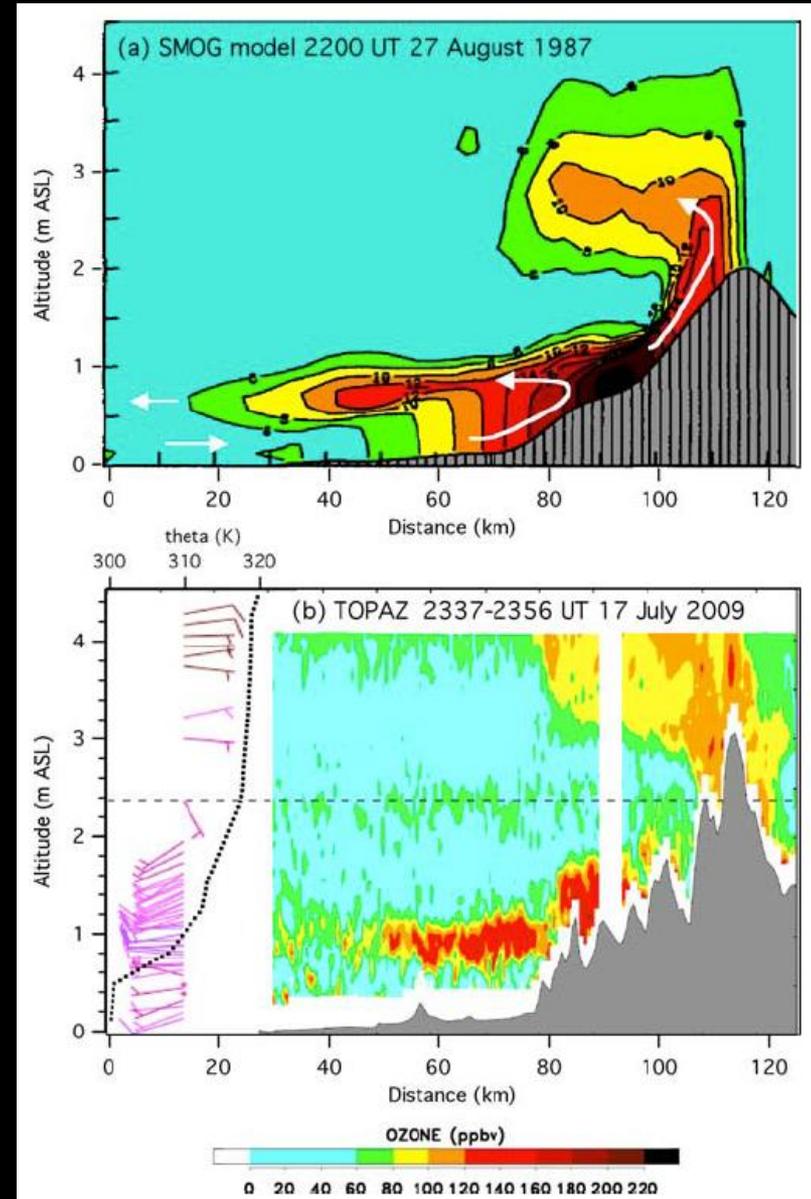
MDA8 surface O_3 for April–June 2010 at polluted sites in the densely populated regions of the Central Valley, Southern California, and Las Vegas, Nevada. The box-and-whisker plots give minimum, 25th, 50th, 75th percentiles, and maximum.

2. Role of long-range pollutant transport in California – California is also a source of transport to downwind areas

Orographic lifting of O₃ from the surface to the free troposphere by the San Gabriel Mountains.

Lidar observations from 17 July 2009 (bottom) very similar to model calculations [Lu and Turco, 1996] for 27 August 1987 (top).

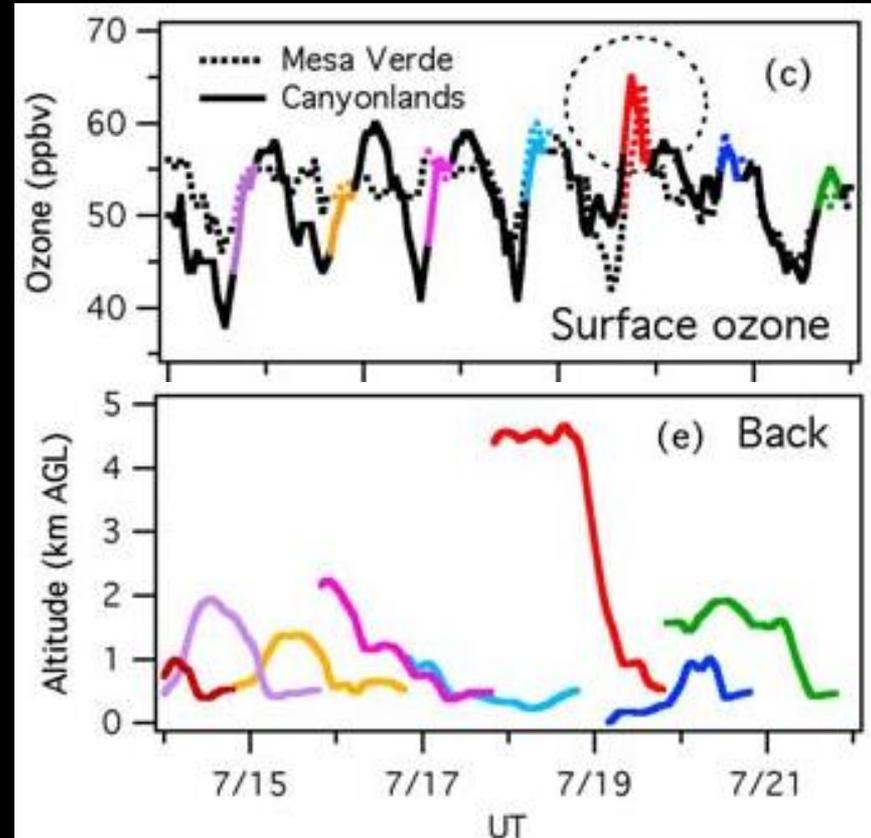
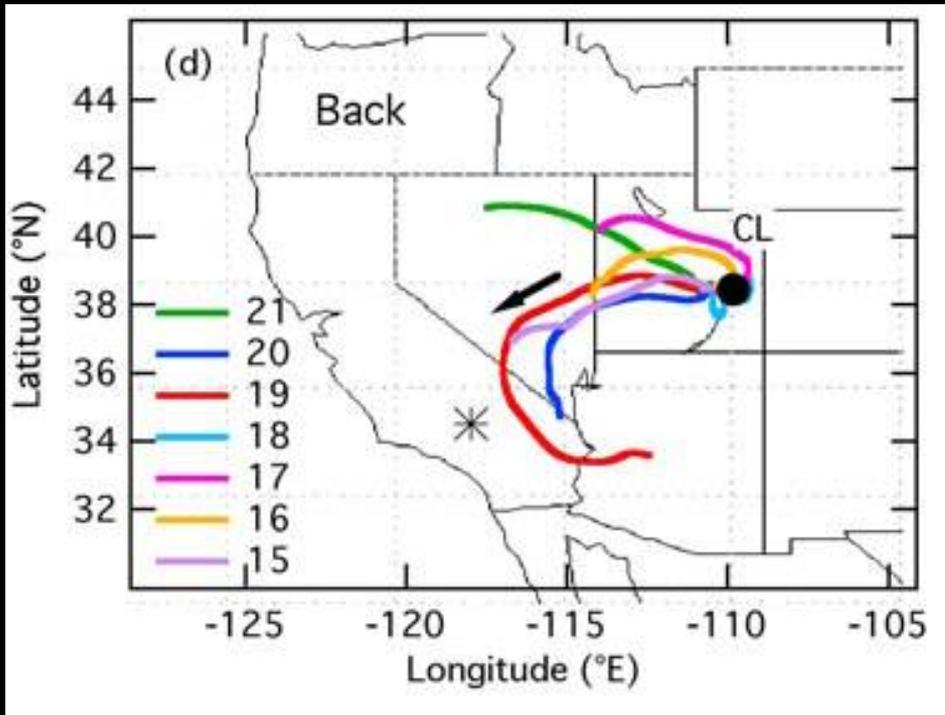
Subject to efficient transport in free troposphere.



2. Role of long-range pollutant transport in California – California is also a source of transport to downwind areas

Generally lofted O_3 would contribute to northern mid-latitude baseline O_3 that circulates zonally – layer of enhanced O_3 over downwind neighbor.

Trajectory calculations can plausibly argue that O_3 lofted from Los Angeles on 17 July 2009 affected Mesa Verde and Canyonlands NPs 2 days later.



3. SJVAB vs. SoCAB Response to emission controls

Different gasoline and diesel mix give different VOC/NO_x ratio evolution between basins

(McDonald, B.C., et al., (2012), Long-term trends in nitrogen oxide emissions from motor vehicles at national, state, and air basin scales, *J. Geophys. Res.*, 117, D00V18, doi:10.1029/2012JD018304.)

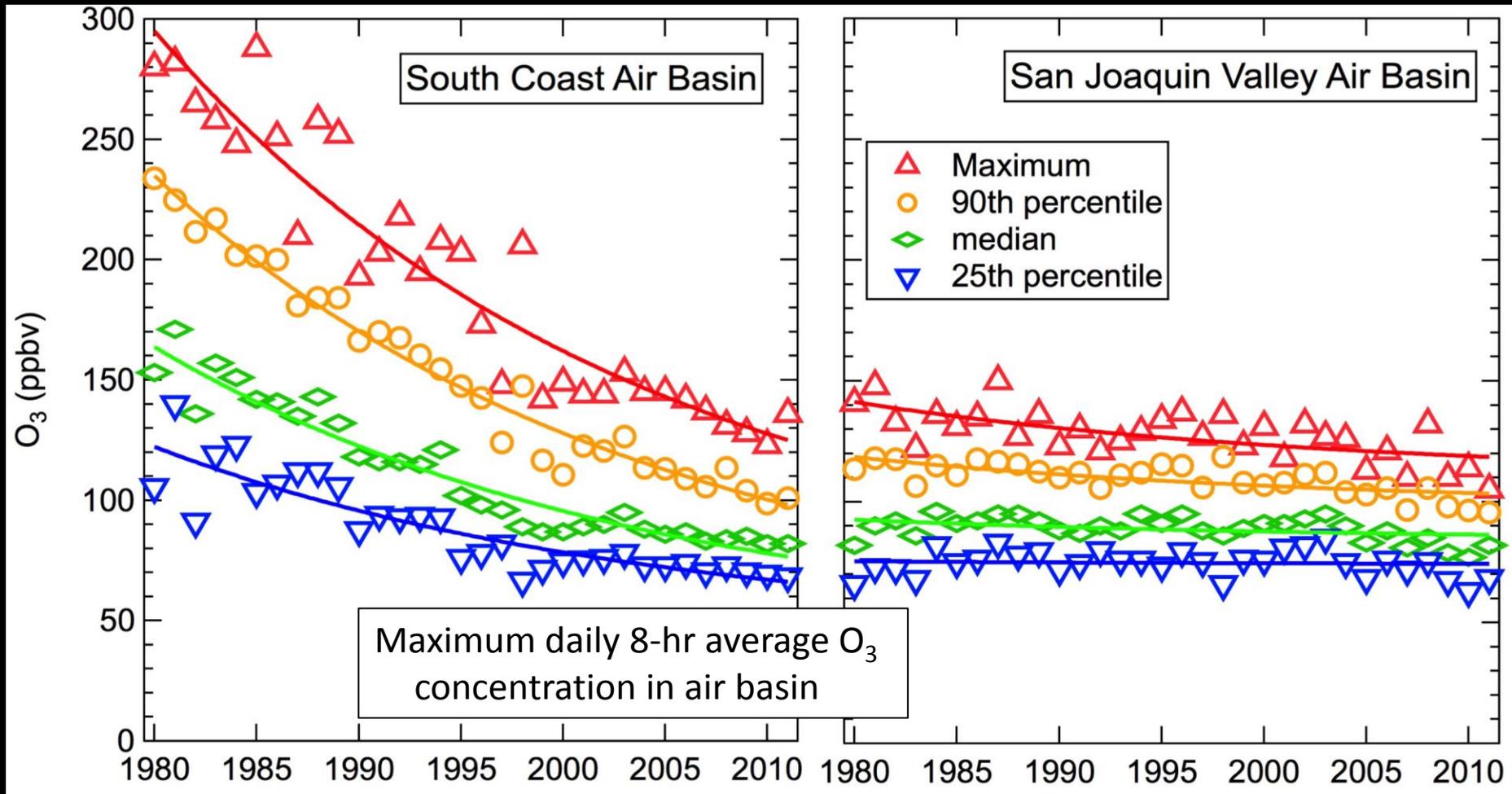
Unknown VOC source in SJVAB

(Pusede, S.E., et al., (2014), On the temperature dependence of organic reactivity, nitrogen oxides, ozone production, and the impact of emission controls in San Joaquin Valley, California, *Atmos. Chem. Phys.*, 14, 3373–3395, 2014, doi:10.5194/acp-14-3373-2014.)

Long-range transport may affect air basins differently

(Parrish, D.D., et al., (2014), work in preparation.)

3. SJVAB vs. SoCAB Response to emission controls



Very large differences !

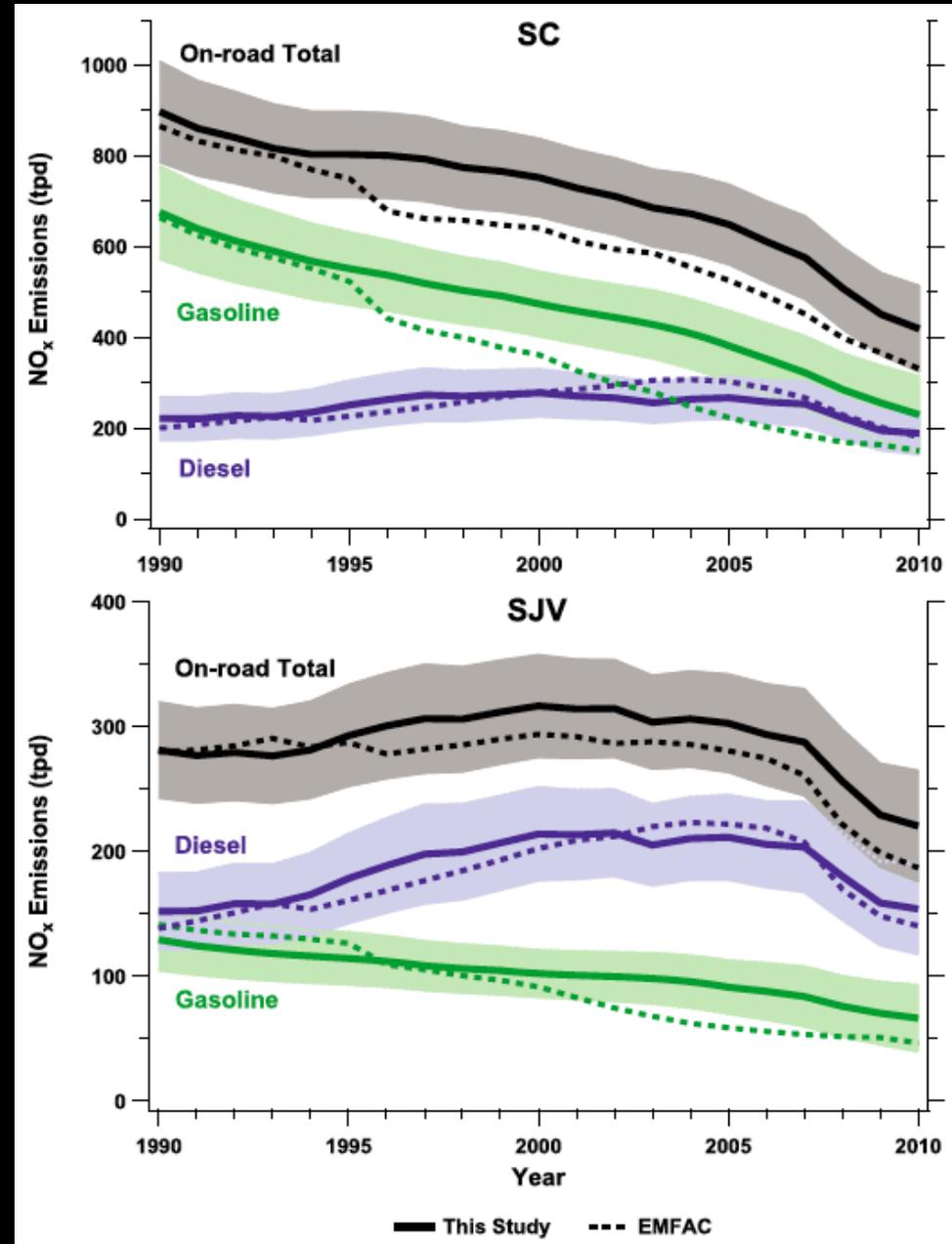
3. SJVAB vs. SoCAB Response to emission controls - **Different gasoline and diesel mix**

Fuel-based approach to estimating vehicle NO_x emissions; some differences from EMFAC.

Very different gasoline and Diesel mix between the two air basins. Diesel dominates in SJVAB, gasoline in SoCAB.

From 1990-2000 vehicle NO_x emissions increased in SJVAB, but decreased in SoCAB. Therefore very different VOC/NO_x ratio evolution.

Is this relevant to discussion of efficacy of NO_x vs. VOC emission controls?



3. SJVAB vs. SoCAB Response to emission controls - Unknown VOC source in SJVAB

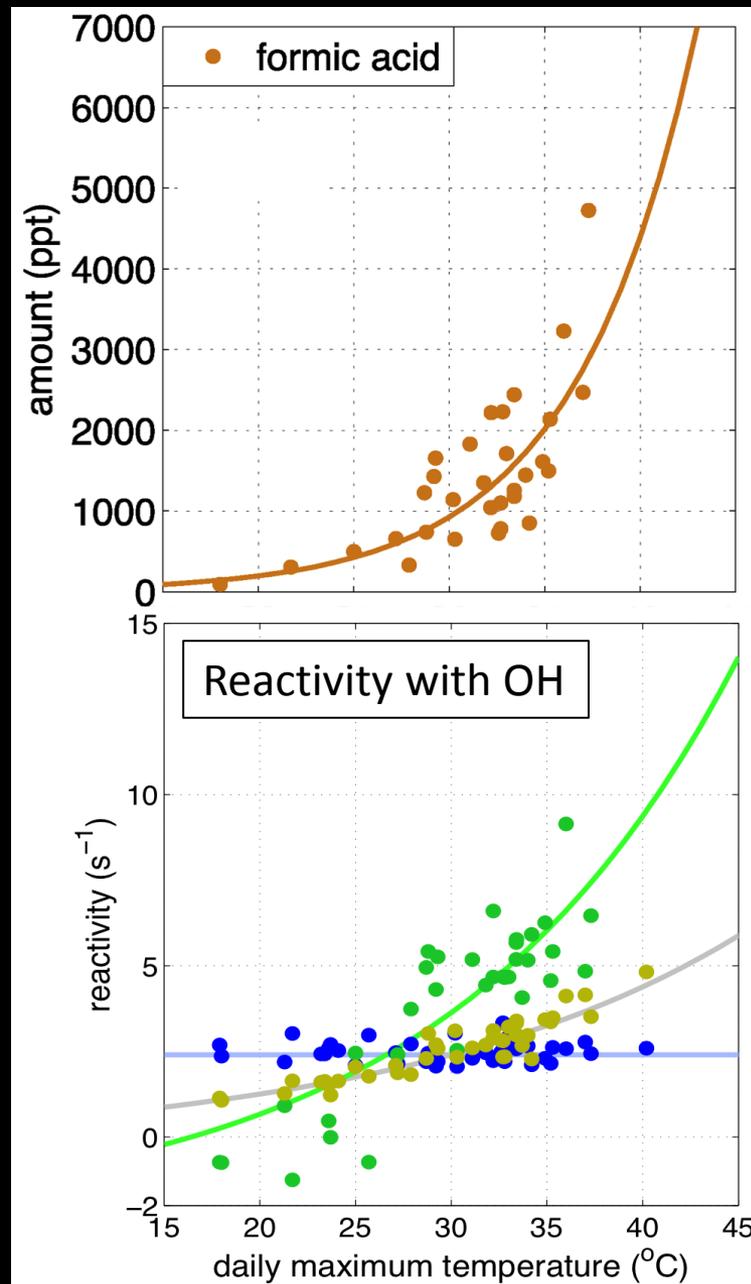
Temperature-independent reactivity associated with motor vehicles dominates on cool days (blue data).

At high temperatures, characteristic of days with high ozone, the largest portion of the total organic reactivity increases exponentially with temperature.

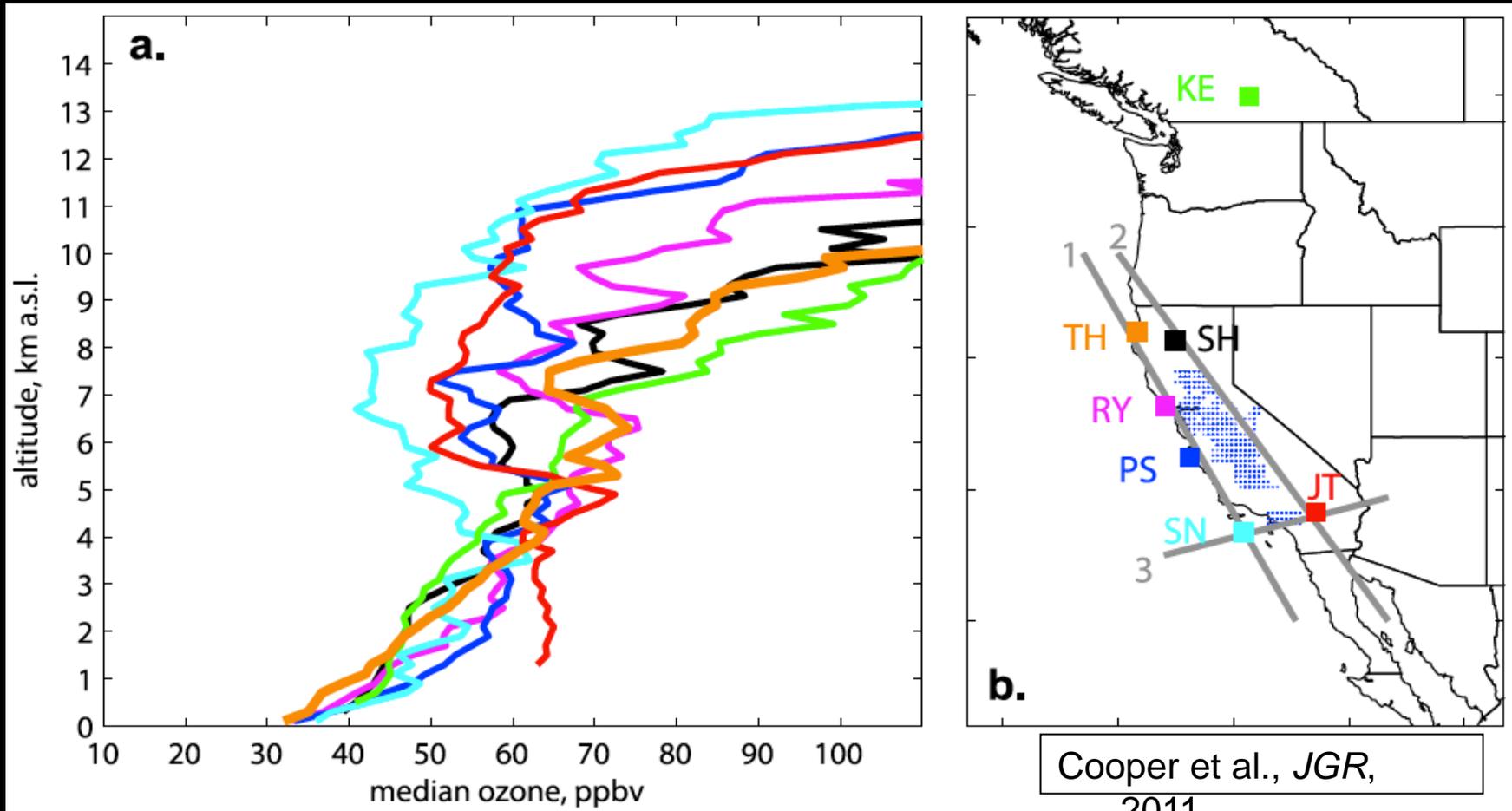
Temperature dependent reactivity (green data) is dominated by small, oxygenated organics (yellow data) and unidentified species.

NO_x reductions are the most effective control option for reducing the frequency of O₃ violations in the southern SJV.

Pusede et al., *Atmos. Chem. Phys.*, 2014



3. SJVAB vs. SoCAB Response to emission controls - Long-range transport may affect air basins differently

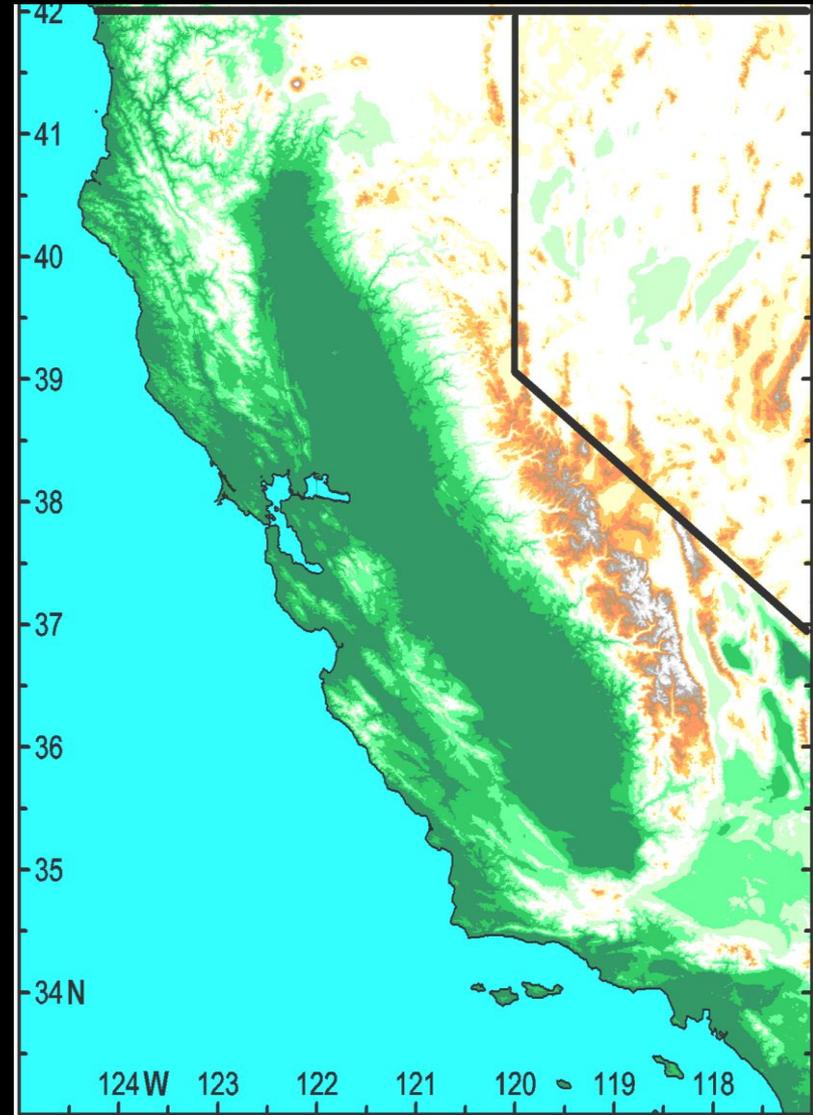


O₃ concentrations coming ashore to California increase with altitude in lower few kilometers.

3. SJVAB vs. SoCAB Response to emission controls - Long-range transport may affect air basins differently

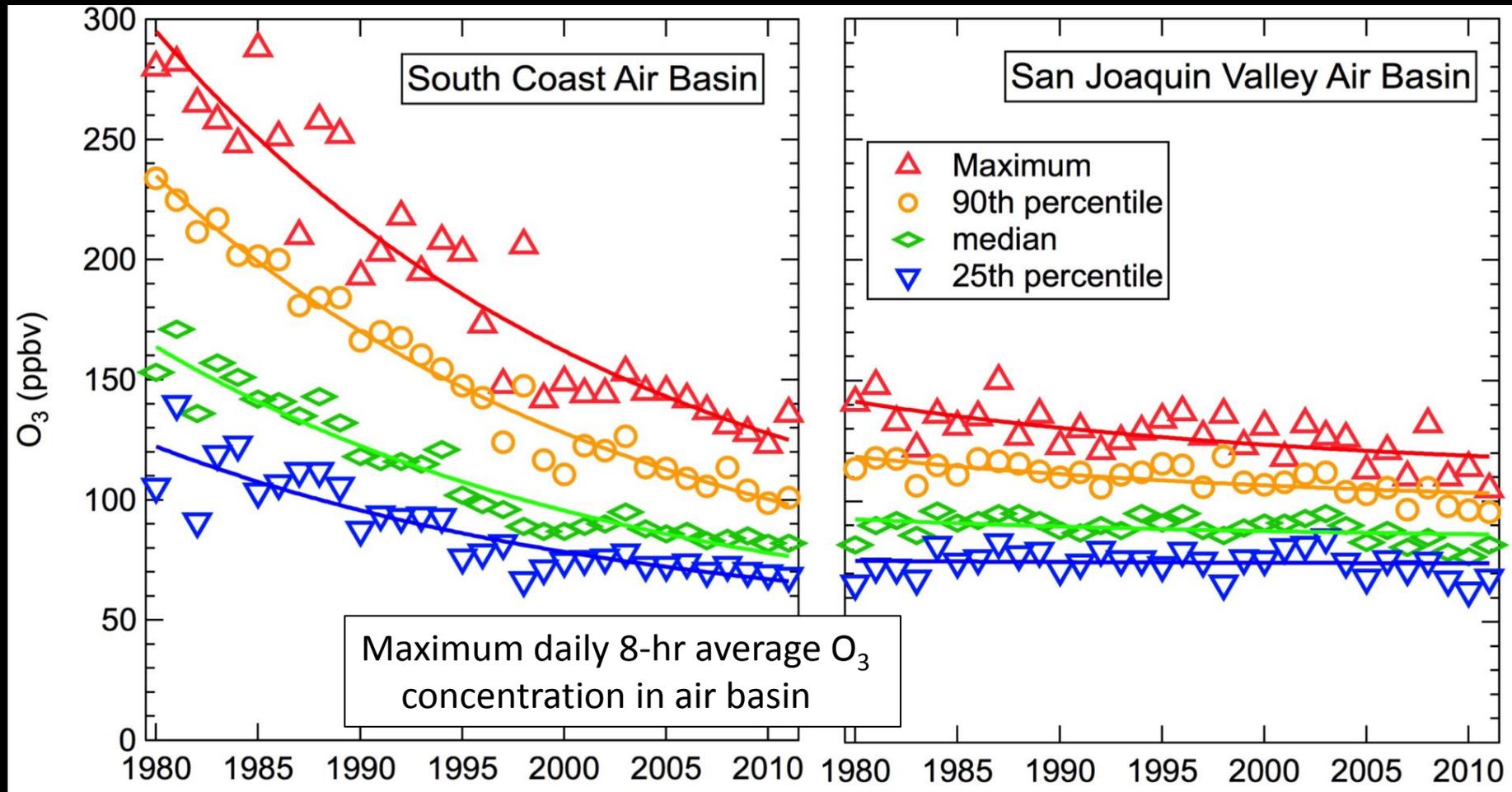
Coastal air basins receive inflow from the Pacific marine boundary layer:
~ 30 ppbv in summer.

Central Valley air basins are partially isolated from the Pacific marine boundary layer – may receive higher O₃ concentrations from aloft.



Parrish et al., *in preparation*, 2014

3. SJVAB vs. SoCAB Response to emission controls - Long-range transport may affect air basins differently



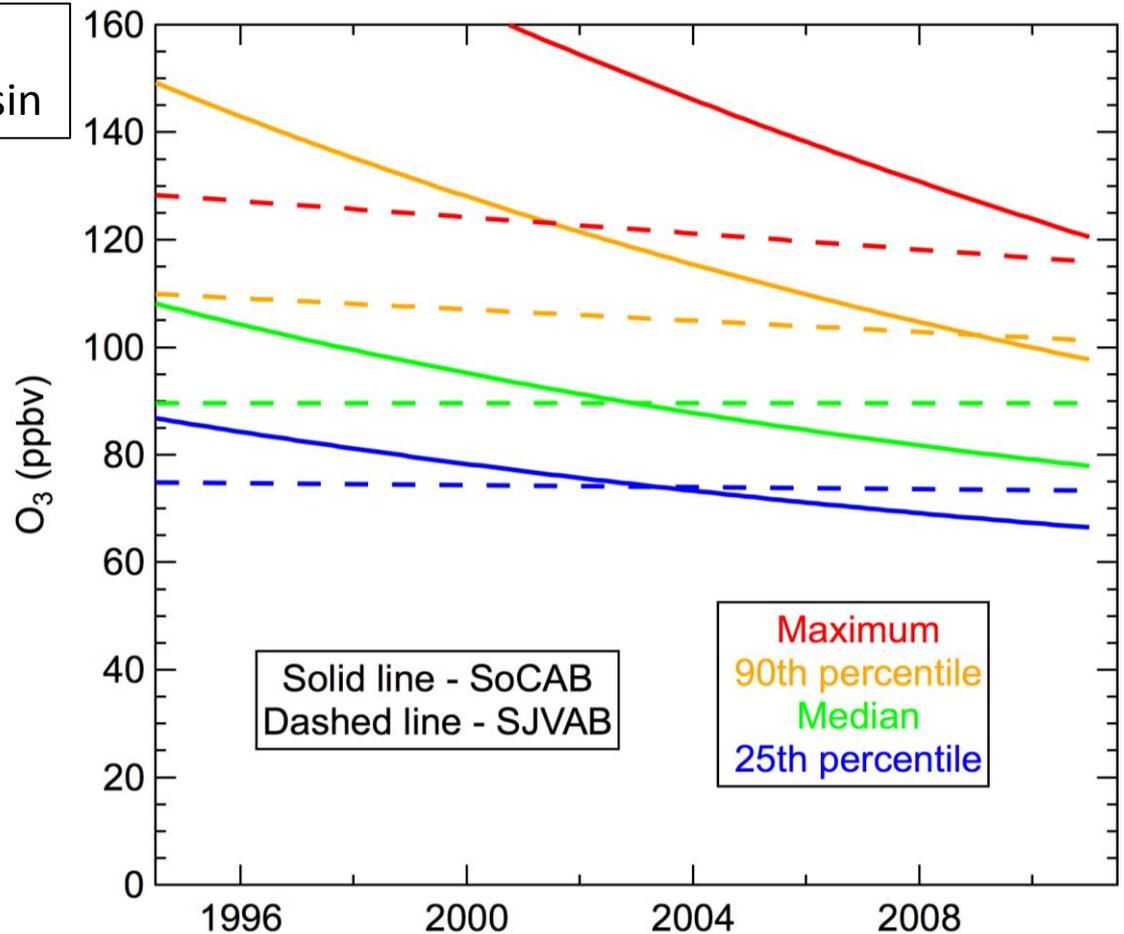
Very large differences !

3. SJVAB vs. SoCAB Response to emission controls - Long-range transport may affect air basins differently

Maximum daily 8-hr average
O₃ concentration in air basin

By 2011, 25th, 50th, and 90th
percentiles of MDA8 are
lower in SoCAB than
SJVAB!

MDA8 in SoCAB and
SJVAB seem to be
converging to different
lower limits. Higher
background O₃, due to
inflow from higher altitude
on average?



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(McDonald, B.C., et al., (2012), Long-term trends in nitrogen oxide emissions from motor vehicles at national, state, and air basin scales *J. Geophys. Res.*, 117, D00V18, doi:10.1029/2012

These plus other differences may all contribute!

Unknown VOC source in SJVAB

(Pusede, S.E., et al., (2014), On the temperature dependence of organic reactivity, nitrogen oxides, ozone production, and the impact of emission controls in San Joaquin Valley, California, *Atmos. Chem. Phys.*, 14, 3373–3395, 2014, doi:10.5194/acp-14-3373-2014.)

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NOAA WP-3D
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Thank you for your attention!



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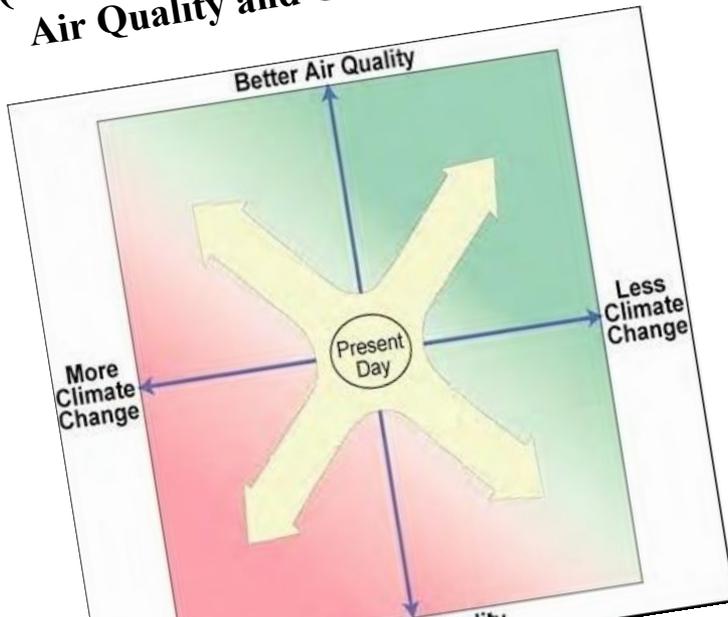
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**Synthesis of Policy Relevant Findings
from the CalNex 2010 Field Study
(California Research at the Nexus of
Air Quality and Climate Change)**



Many more stories!

**They all rely on the work
of the authors of the
112 CalNex papers!**

Bakersfield
Ground Site

