

# Source Speciation of Central Valley non-CO<sub>2</sub> Greenhouse Gas Emissions using In-Situ Measurements of Volatile Organic Compounds at Walnut Grove tower

Allen Goldstein, Marc Fischer and Abhinav Guha  
University of California at Berkeley  
Lawrence Berkeley National Laboratory

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A. Andrews, J. Kofler, E. Dlugokencky (NOAA-ESRL),  
D. Bush (TBS Systems)



# Overview

- We investigated emission sources of CH<sub>4</sub> and N<sub>2</sub>O in California's Central Valley and their seasonal variability from summer 2012 through early fall 2013.
- Year-long measurements of GHGs, CO and a suite of VOCs at Walnut Grove tower were separated into seven seasonal periods and analyzed using two independent methods
  - Positive matrix factorization (PMF) of the full suite of tracers
  - Inverse modeling of the N<sub>2</sub>O and CH<sub>4</sub> observations

# Today's Presentation

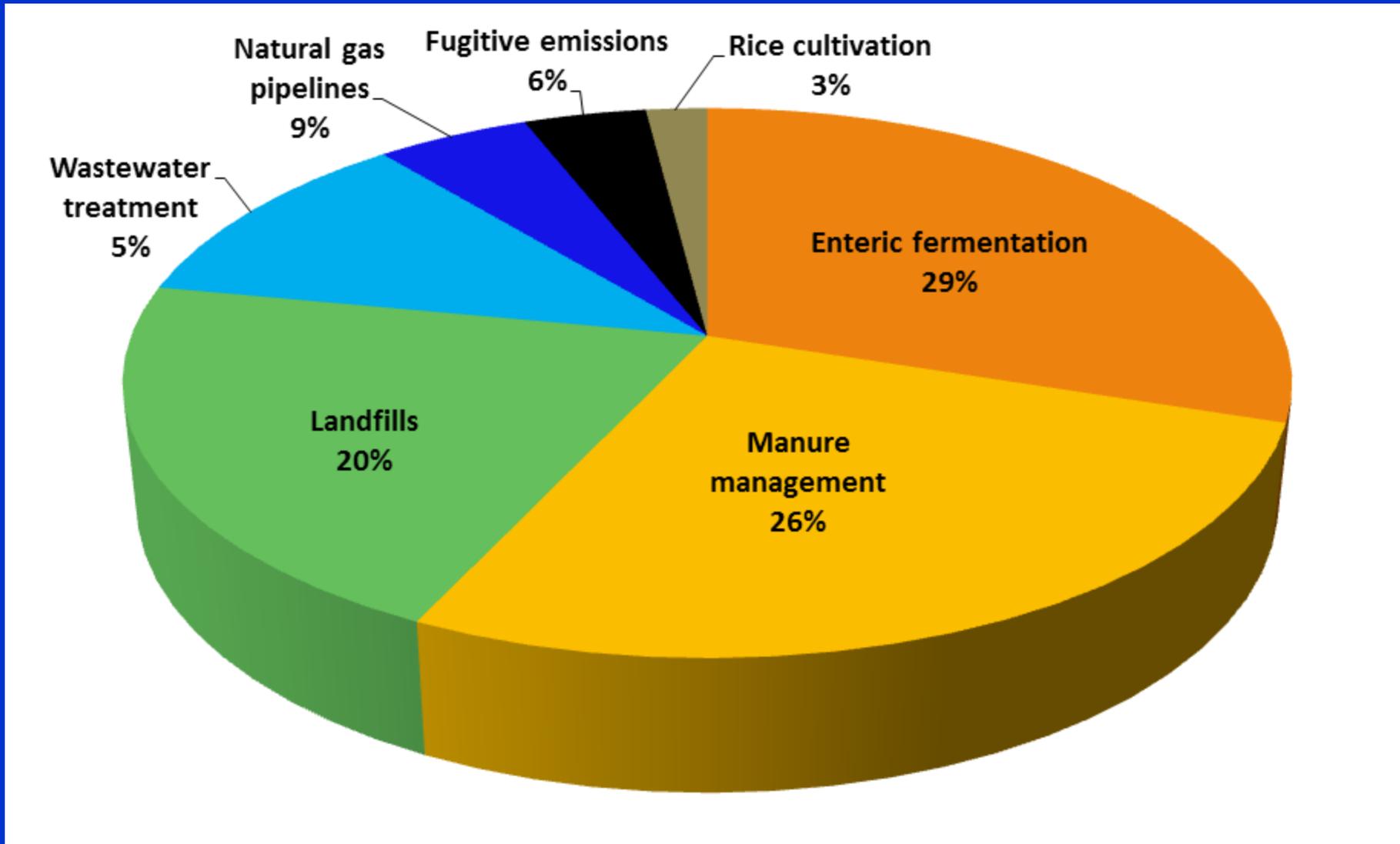
- 1) Overview, objectives, and approach – Allen Goldstein
- 2) Inverse modeling analysis and results – Marc Fischer
- 3) PMF analysis and comparison with inverse modeling and current inventories – Abhinav Guha
- 4) Conclusions – Allen Goldstein

# Overview

## California's Greenhouse Gases (GHGs)

- The California Global Warming Solutions Act 2006 (AB-32) aims to reduce GHGs to 1990 levels by the year 2020
- ARB developed California's state-wide GHG inventory using a combination of emission factors, activity data, and emissions modeling
- Current inventory has CH<sub>4</sub> as 9% and N<sub>2</sub>O as 3% of total GHG emissions in California
- N<sub>2</sub>O and CH<sub>4</sub> emissions are dominated by “area sources” that are biological in nature, display spatial heterogeneity and temporal variability and hence are difficult to measure
- Additional observational data and high resolution modeling estimates should be used to verify and validate the emission inventory from a top down perspective

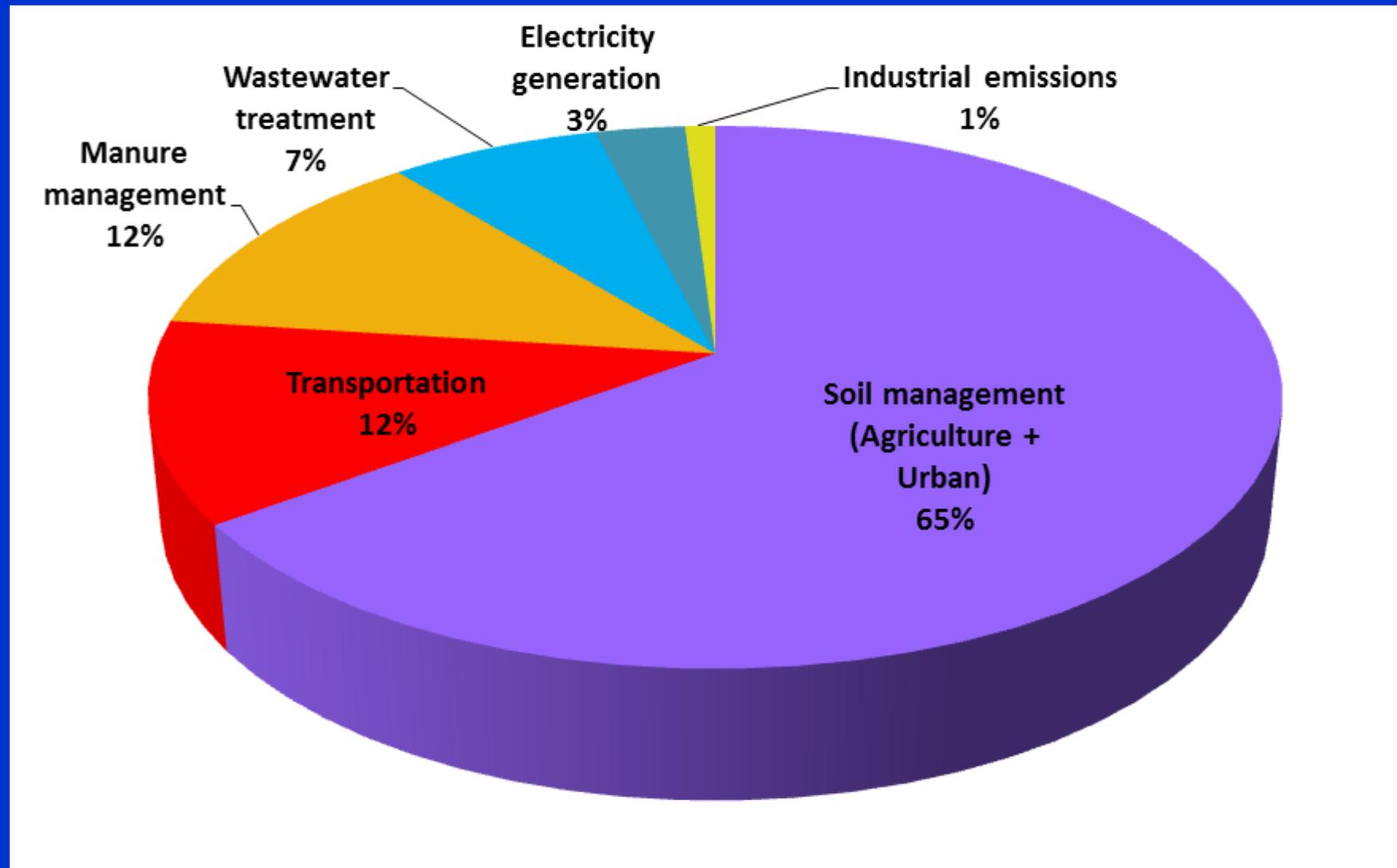
# California's CH<sub>4</sub> emissions inventory



2013 CH<sub>4</sub> emissions: 41.1 million tonnes CO<sub>2</sub>-eq @ GWP 25 (9% of total GHG emissions)

Source: CARB GHG Inventory Query Tool, Nov 2015

# California's N<sub>2</sub>O emissions inventory

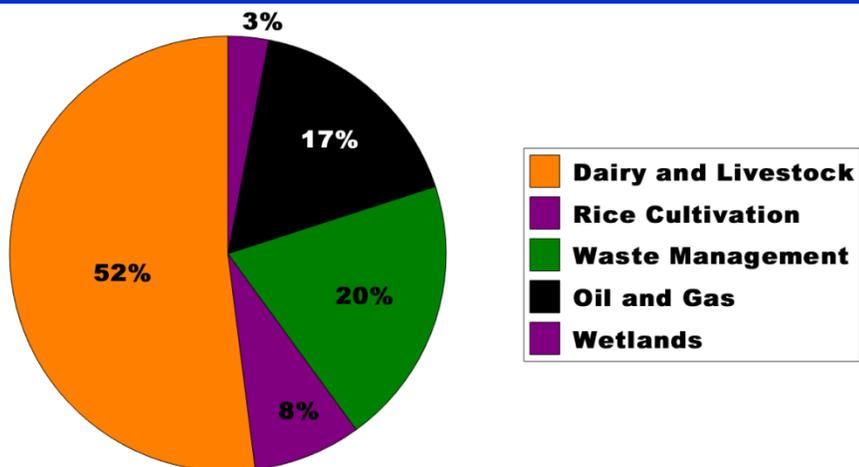


2013 N<sub>2</sub>O emissions: 13.1 million tonnes CO<sub>2</sub>-eq @ GWP 298 (3% of total GHG emissions)

Source: CARB GHG Inventory Query Tool, Nov 2015

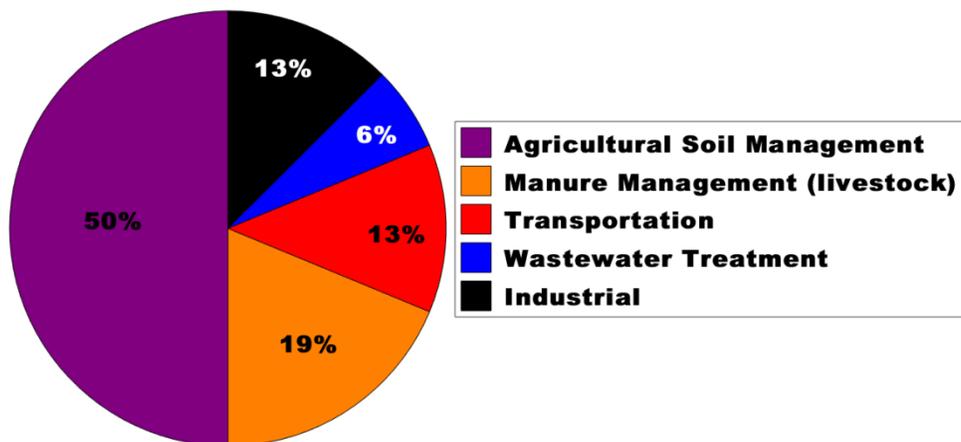
# We calculated annual inventory source distributions for Central Valley region surrounding study site (Regions 3, 7 and 8)

CH<sub>4</sub>



2008 CALGEM CH<sub>4</sub> Sources

N<sub>2</sub>O

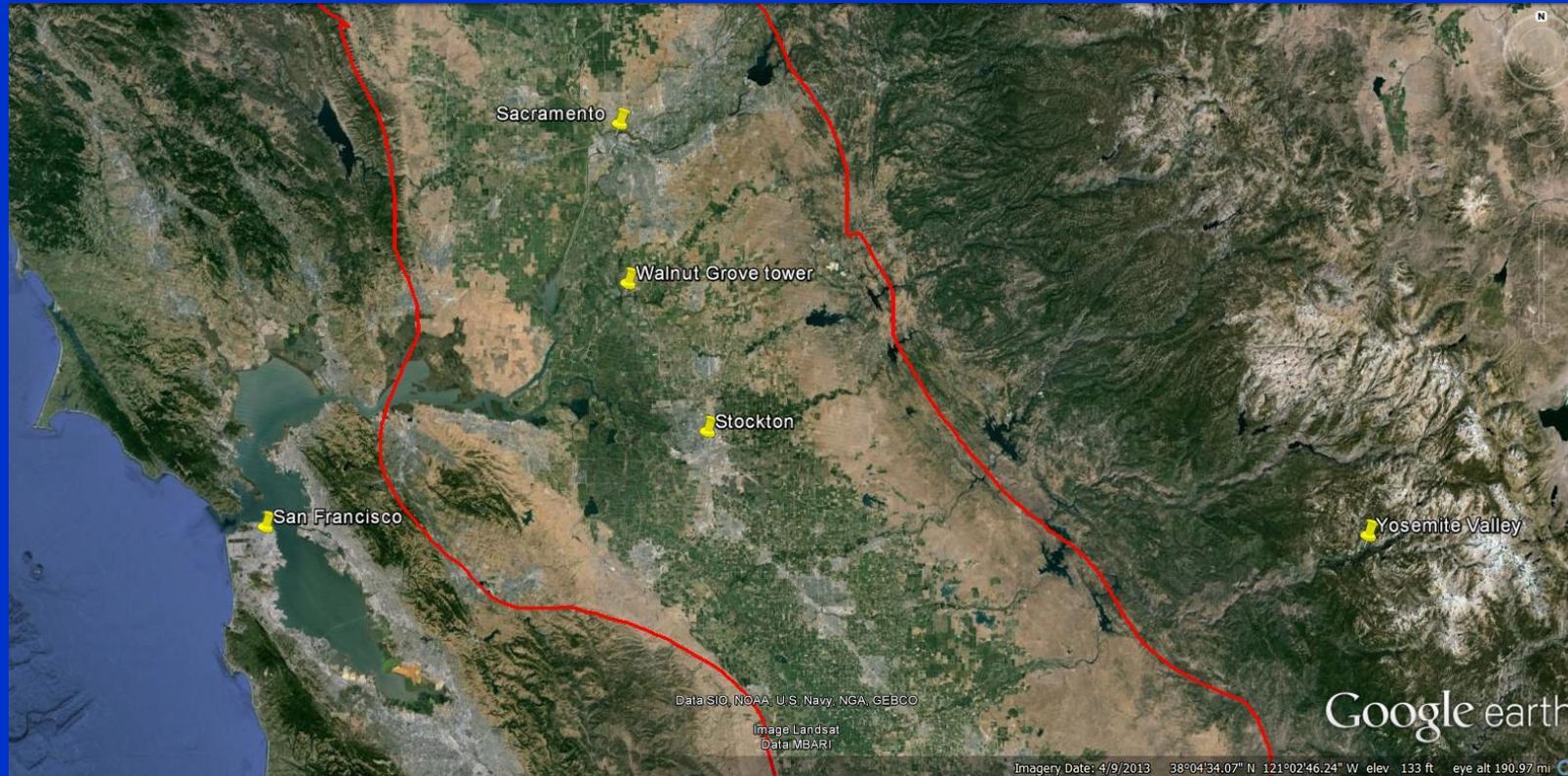


2008 EDGAR v4.2 N<sub>2</sub>O Sources

# Objectives and Approach

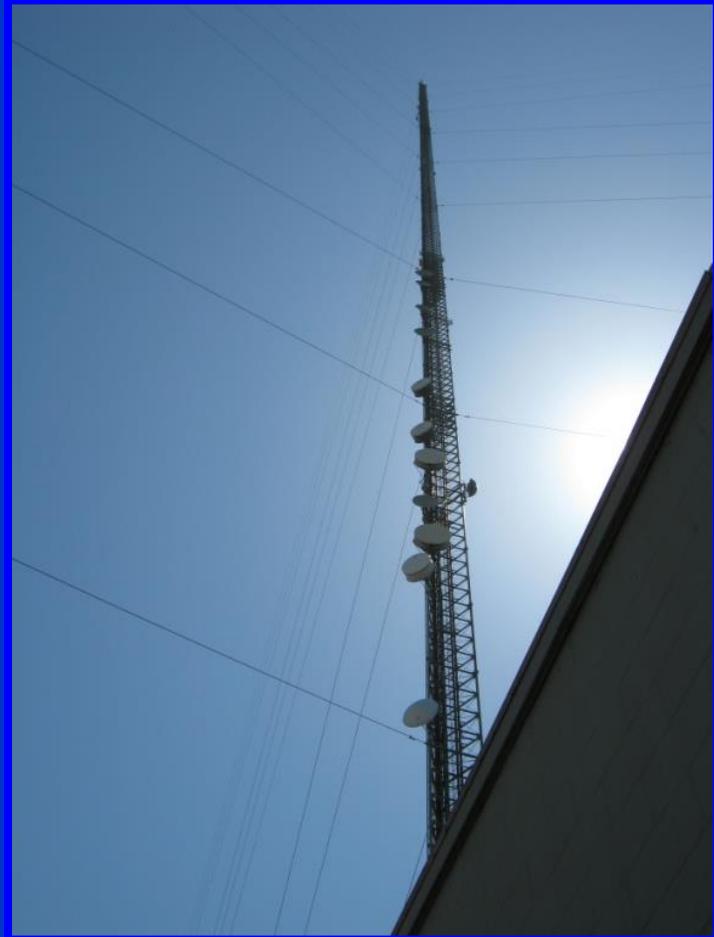
- Assess the seasonally changing apportionment of CH<sub>4</sub> & N<sub>2</sub>O sources in this region through observation of these gases, and gaseous tracers that can indicate their sources.
- Add continuous measurements of a suite of volatile organic compounds (VOCs) and N<sub>2</sub>O, coordinated with ongoing measurements of CO<sub>2</sub>, CH<sub>4</sub>, and combustion tracer CO over a complete annual cycle at the Walnut Grove tall tower site (WGC; Andrews et al., 2013) in California's Central Valley.
- Analyze the mixing ratio time series of GHGs and VOC tracers using a statistical source apportionment tool (Positive Matrix Factorization, "PMF"), in order to distinguish individual source category contributions to the regional CH<sub>4</sub> and N<sub>2</sub>O emissions.
- Perform inverse modeling of CH<sub>4</sub> and N<sub>2</sub>O to estimate seasonally changing source contributions.
- Compare the regionally averaged bottom up ARB emission inventory to the top down PMF and inverse modeling results.

# Walnut Grove Tower Study



30 miles south of Sacramento, at the western edge of Sacramento-San Joaquin river delta in the Central Valley of California, multi-level continuous measurements of GHGs, halocarbons, ozone and VOCs from a 525 m tall TV transmission tower

# Walnut Grove Tower Study

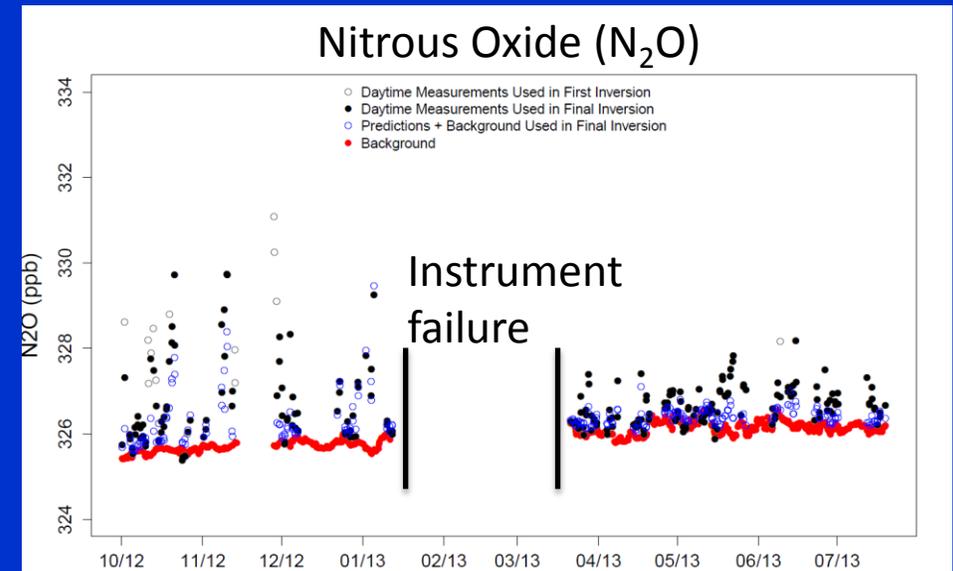
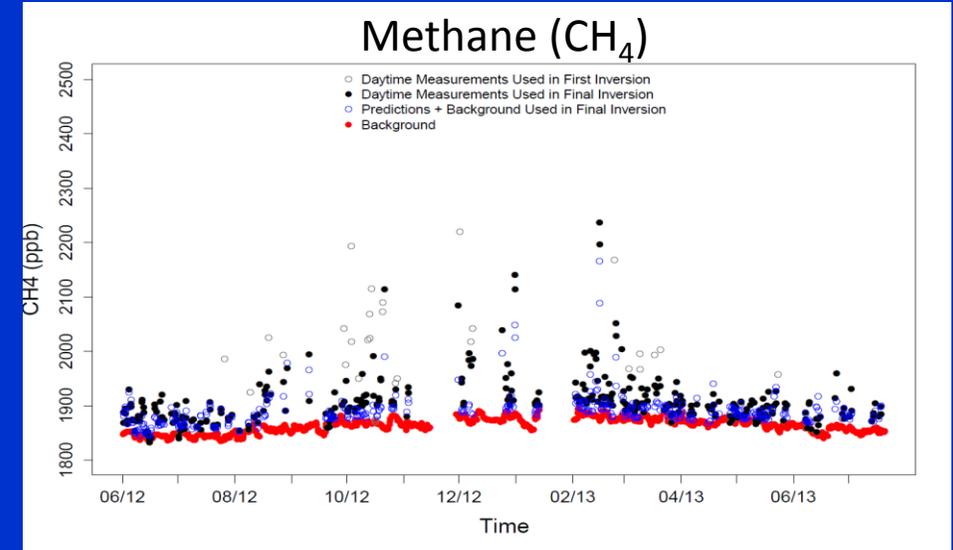
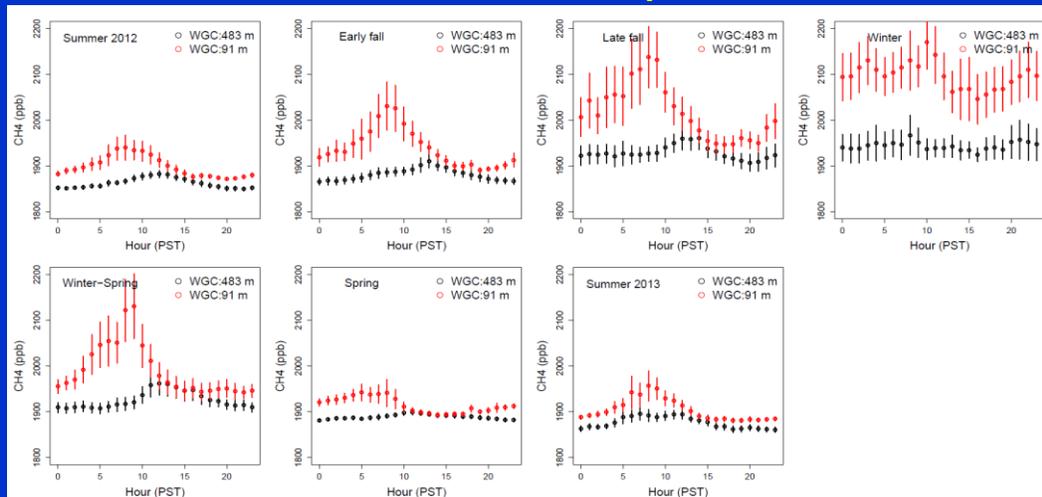


30 miles south of Sacramento, at the western edge of Sacramento-San Joaquin river delta in the Central Valley of California, multi-level continuous measurements of GHGs, halocarbons, ozone and VOCs from a 525 m tall TV transmission tower

# Measured GHG Mixing Ratios

- Measurement of methane and nitrous oxide at 91 and 483 m above ground
- Background inflow (red) subtracted to obtain local signals
- Seasonal variation in emissions and meteorology both affect signals

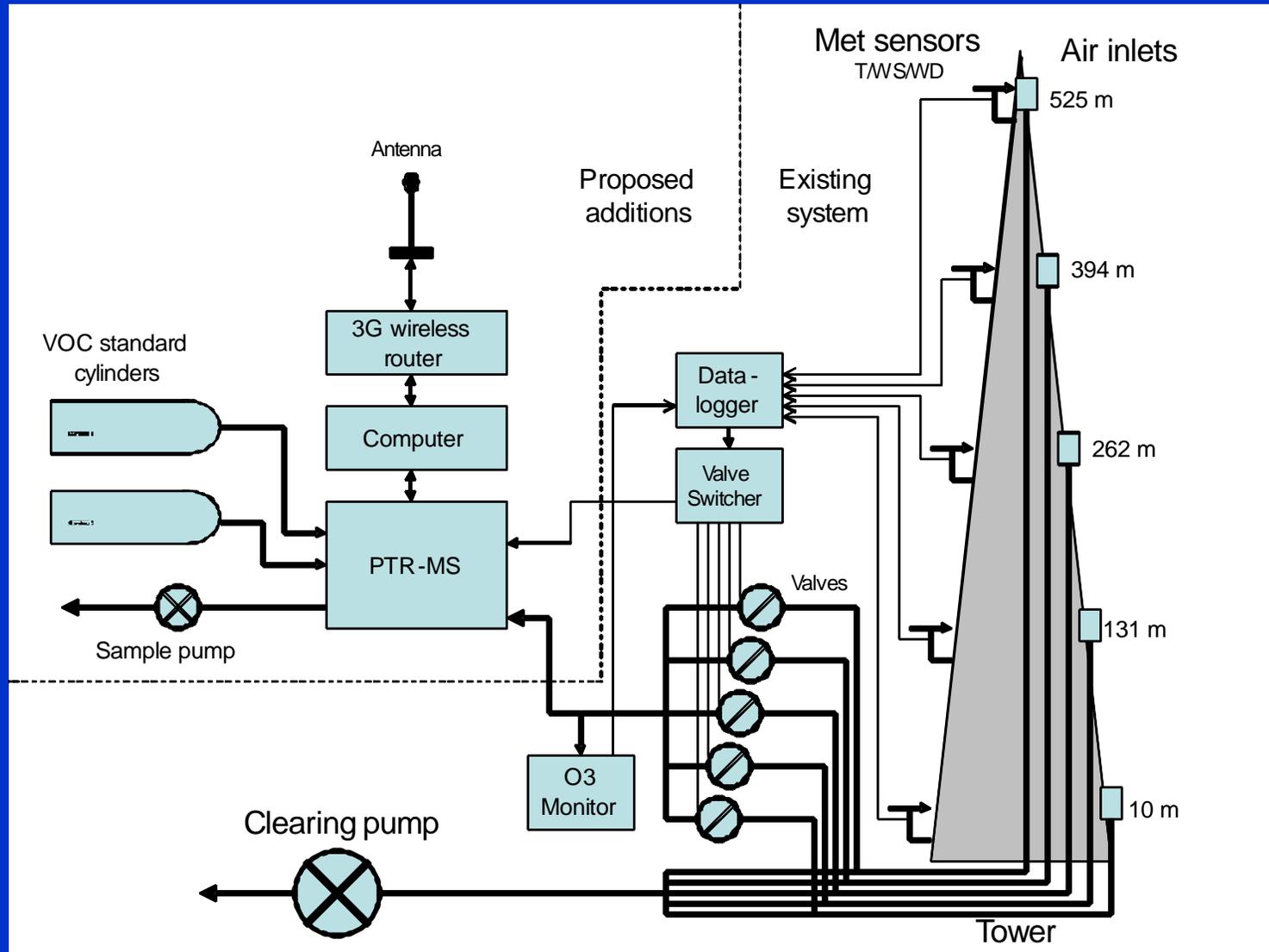
## Diurnal cycles of CH<sub>4</sub> by season



# VOC Measurement Setup

Pilot measurements June → Aug 2011

Continuous measurements summer 2012 → early fall 2013

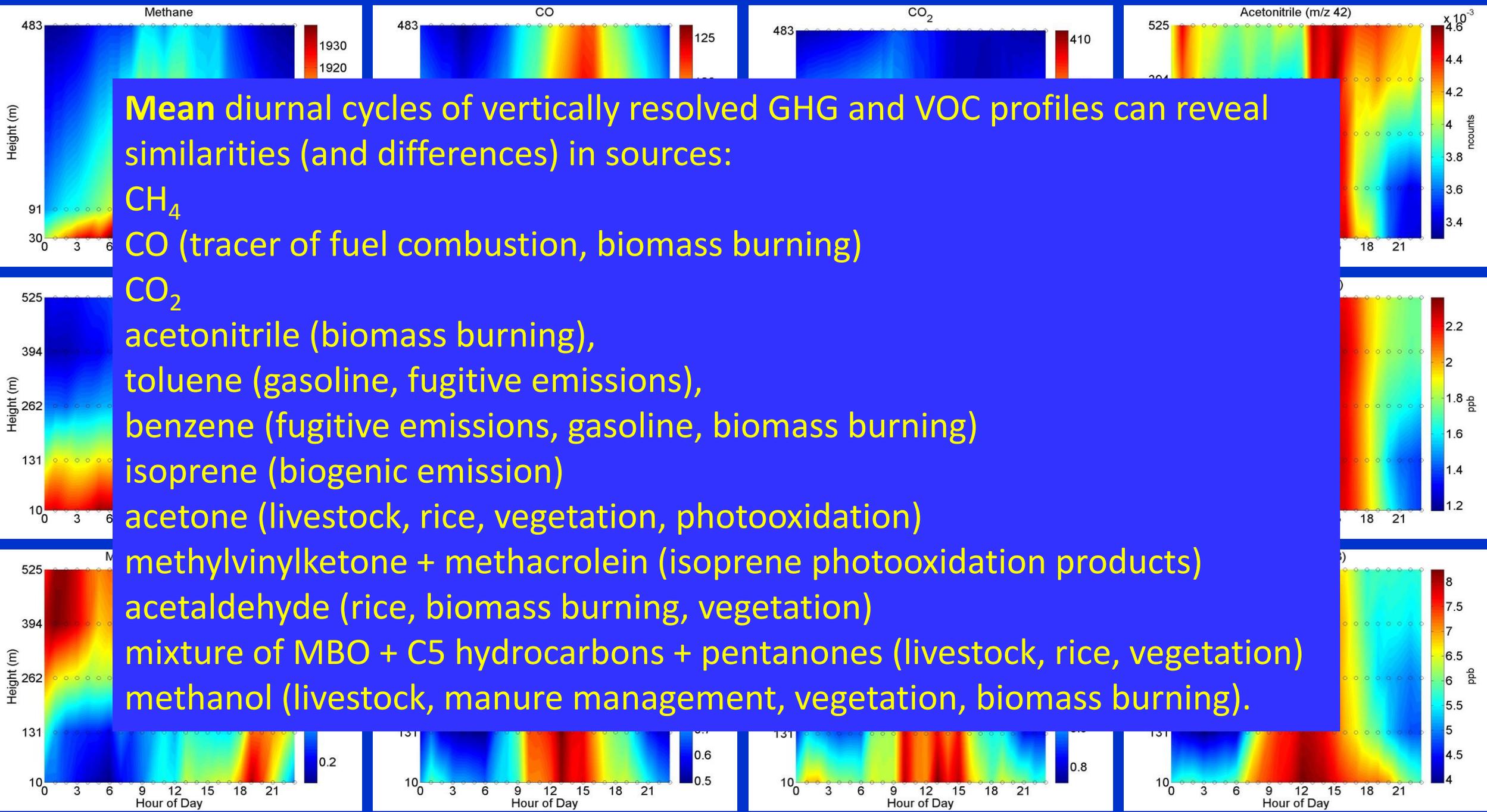


**VOC Measurements  
by PTR-MS  
5 inlet heights  
Vertical profile in 10 min  
(2 min/height)**

**(added to existing  
measurements of GHG's,  
CO, and O<sub>3</sub>).**

Protonated m/z	Name/Group of Compounds	Significant source(s)
33	Methanol	Livestock, Manure Management, Vegetation, Biomass Burning
35	Hydrogen sulfide	Landfills, Manure Management
42	Acetonitrile	Biomass burning
45	Acetaldehyde	Biomass Burning, Rice Cultivation, Vegetation, Photooxidation, Manure Management
47	Ethanol + Formic acid	Rice Cultivation, Livestock (fermenting feed), Gasoline
49	Methanethiol	Fugitive Emissions, Natural Gas Leakage
59	Acetone + Propanal	Livestock, Rice cultivation, Vegetation, Photooxidation
61	Acetic acid + Propanol	Rice Cultivation, Livestock
63	DMS + Ethanethiol	Landfills, Livestock, Rice cultivation, Fugitive Emissions
69	Isoprene, MBO	Vegetation (Mainly Oak trees-isoprene, Pine trees-MBO)
71	MVK+MACR	Isoprene Photooxidation Products
73	MEK	Manure Management, Landfills, Photooxidation of Anthropogenic VOCs
79	Benzene	Fugitive emissions, Gasoline, Biomass burning
81	Monoterpenes + Hexanals	Vegetation
83	C-6 wound compounds (hexanal)	Harvesting Tracer
87	MBO, C-5 hydrocarbons, Pentanones	Livestock, Rice cultivation, Vegetation
93	Toluene	Fugitive emissions, Gasoline
107	C8 aromatics, ethyl benzenes, xylenes	Fugitive emissions, Gasoline
109	Cresols	Livestock
113	Oxidation products	Isoprene and Terpene Photooxidation Product
121	C-9 aromatics, TMB	Fugitive emissions, Gasoline
137	Monoterpenes	Vegetation
143	Nonanal	Rice cultivation

**VOC's  
(tracers)  
measured  
by PTRMS  
and their  
sources**

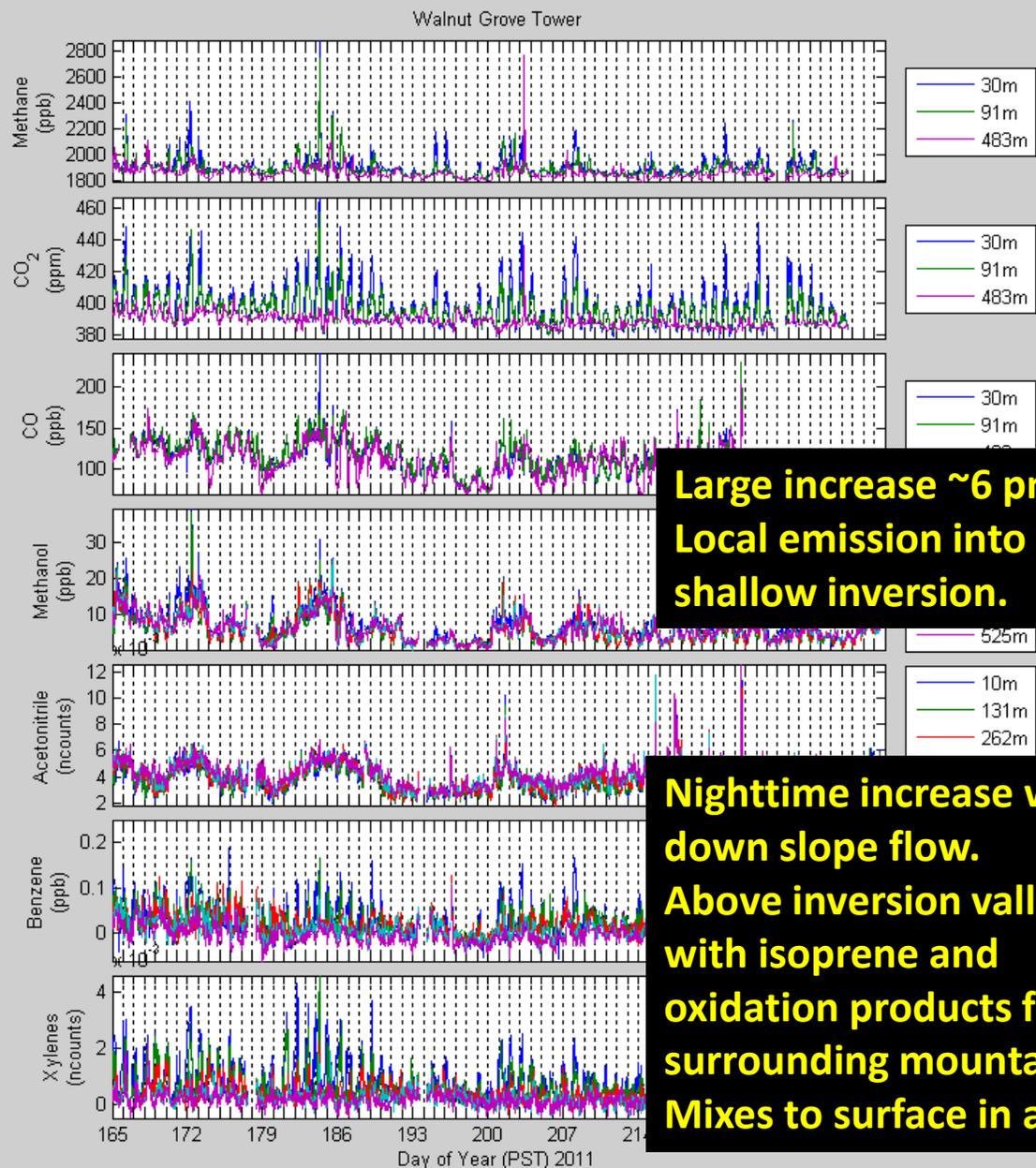


Mean diurnal cycles of vertically resolved GHG and VOC profiles can reveal similarities (and differences) in sources:

- CH<sub>4</sub>
- CO (tracer of fuel combustion, biomass burning)
- CO<sub>2</sub>
- acetonitrile (biomass burning),
- toluene (gasoline, fugitive emissions),
- benzene (fugitive emissions, gasoline, biomass burning)
- isoprene (biogenic emission)
- acetone (livestock, rice, vegetation, photooxidation)
- methylvinylketone + methacrolein (isoprene photooxidation products)
- acetaldehyde (rice, biomass burning, vegetation)
- mixture of MBO + C5 hydrocarbons + pentanones (livestock, rice, vegetation)
- methanol (livestock, manure management, vegetation, biomass burning).

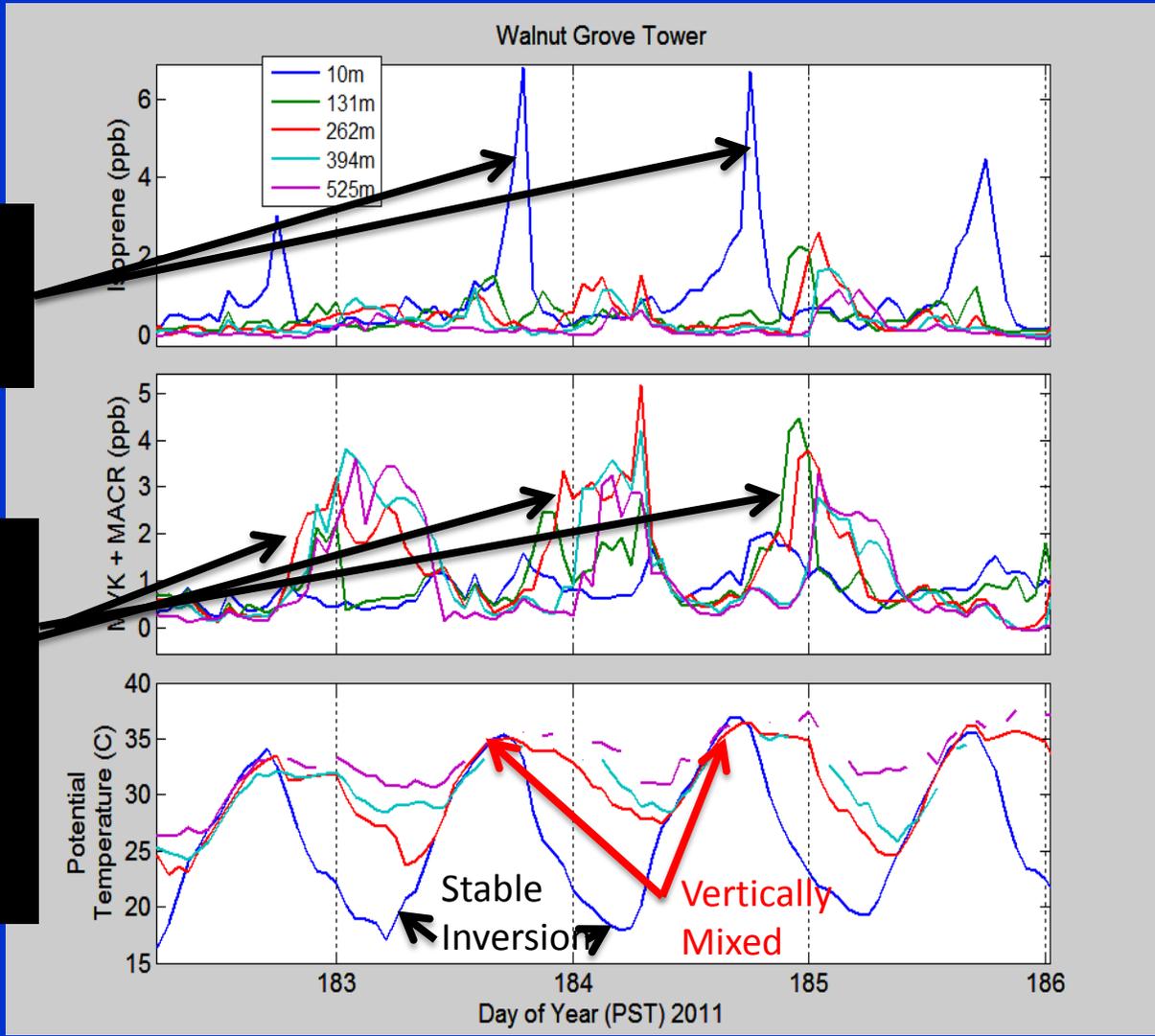
Time series GHG and PTR-MS VOC measurements at WGT (Jun 15-Aug 21, 2011).

Potential Temperature Gradient → Indicator of Mixing Separates Local Versus Transported BVOC

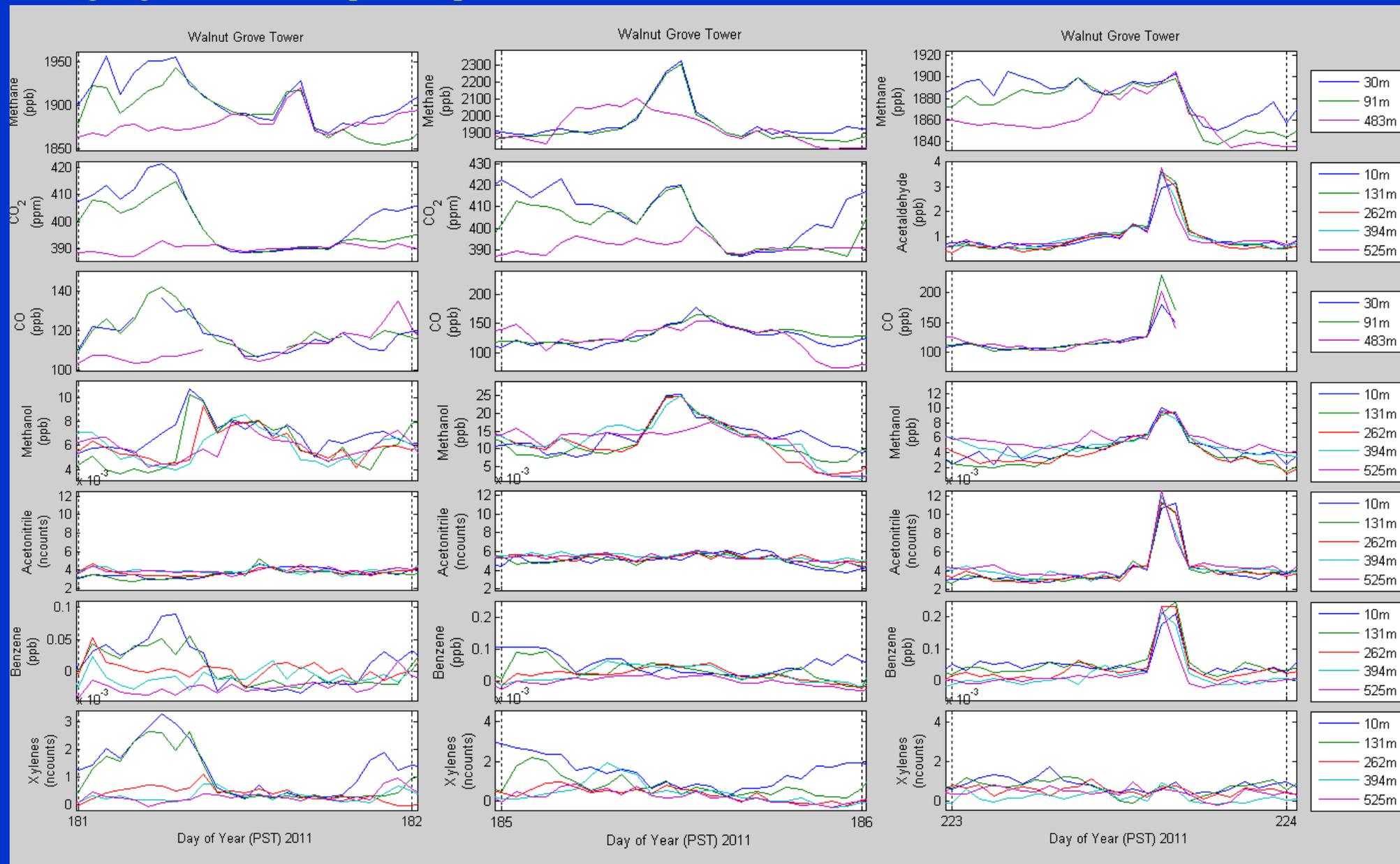


Large increase ~6 pm. Local emission into shallow inversion.

Nighttime increase with down slope flow. Above inversion valley fills with isoprene and oxidation products from surrounding mountains. Mixes to surface in a.m.



Example events highlight 3 different species specific GHG and VOC enhancements.

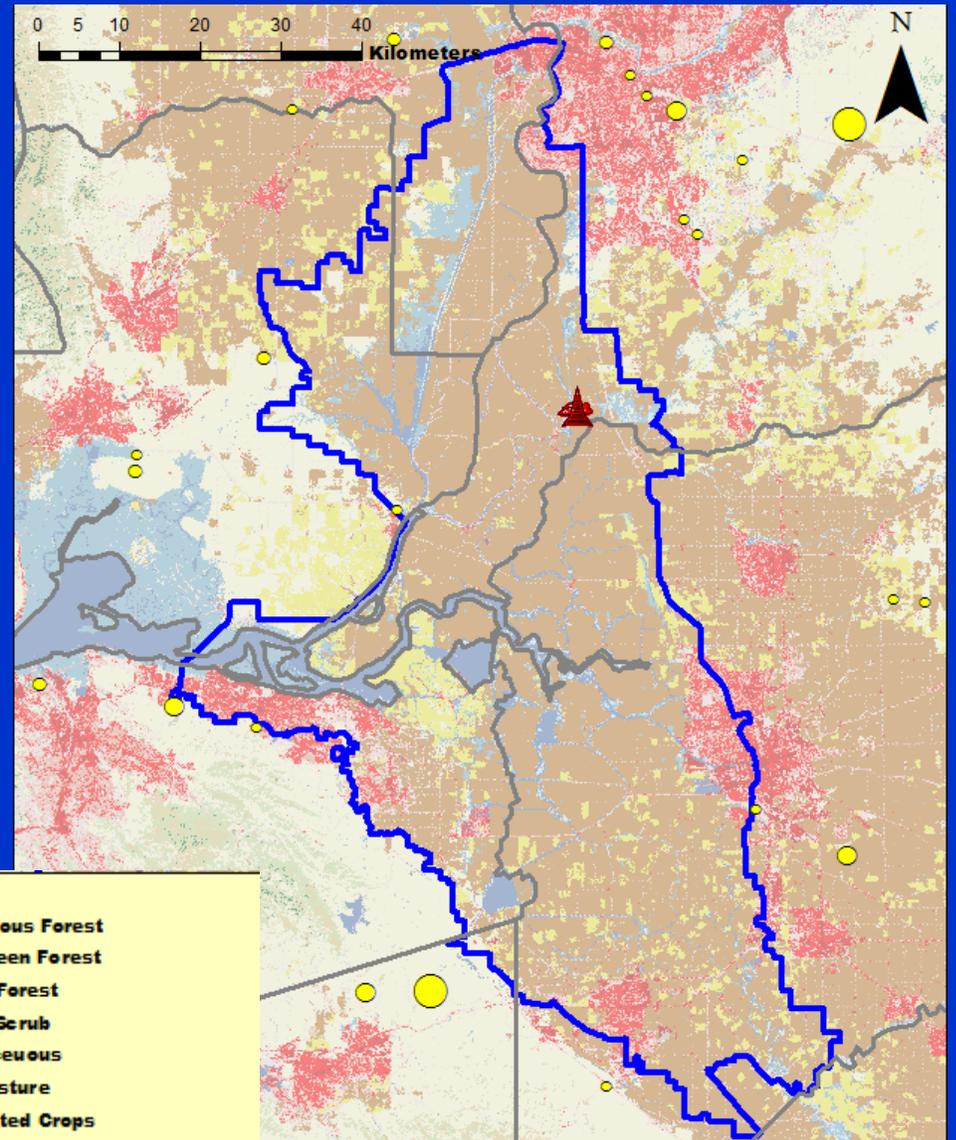
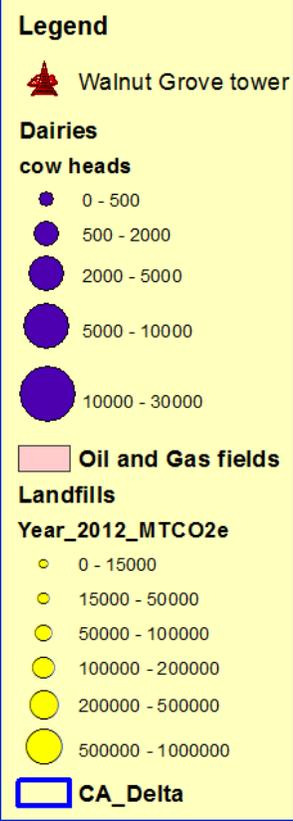
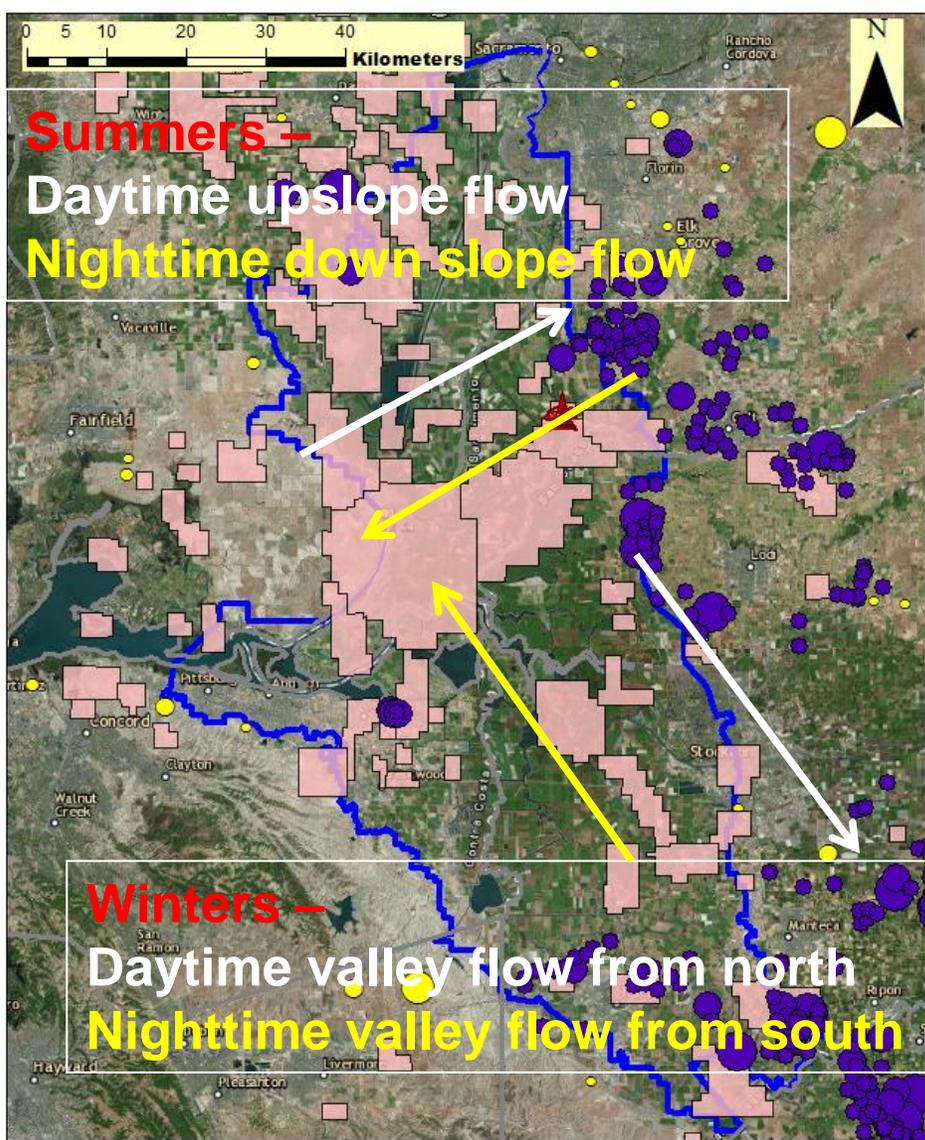


Fossil fuel: CH<sub>4</sub>, CO<sub>2</sub>, CO, benzene, xylenes

Likely dairy: CH<sub>4</sub>, CO<sub>2</sub>, methanol

Biomass burning: little CH<sub>4</sub>, acetaldehyde, CO, methanol, acetonitrile, benzene

# WGT potential GHG source maps



# Sampling periods for source apportionment analysis

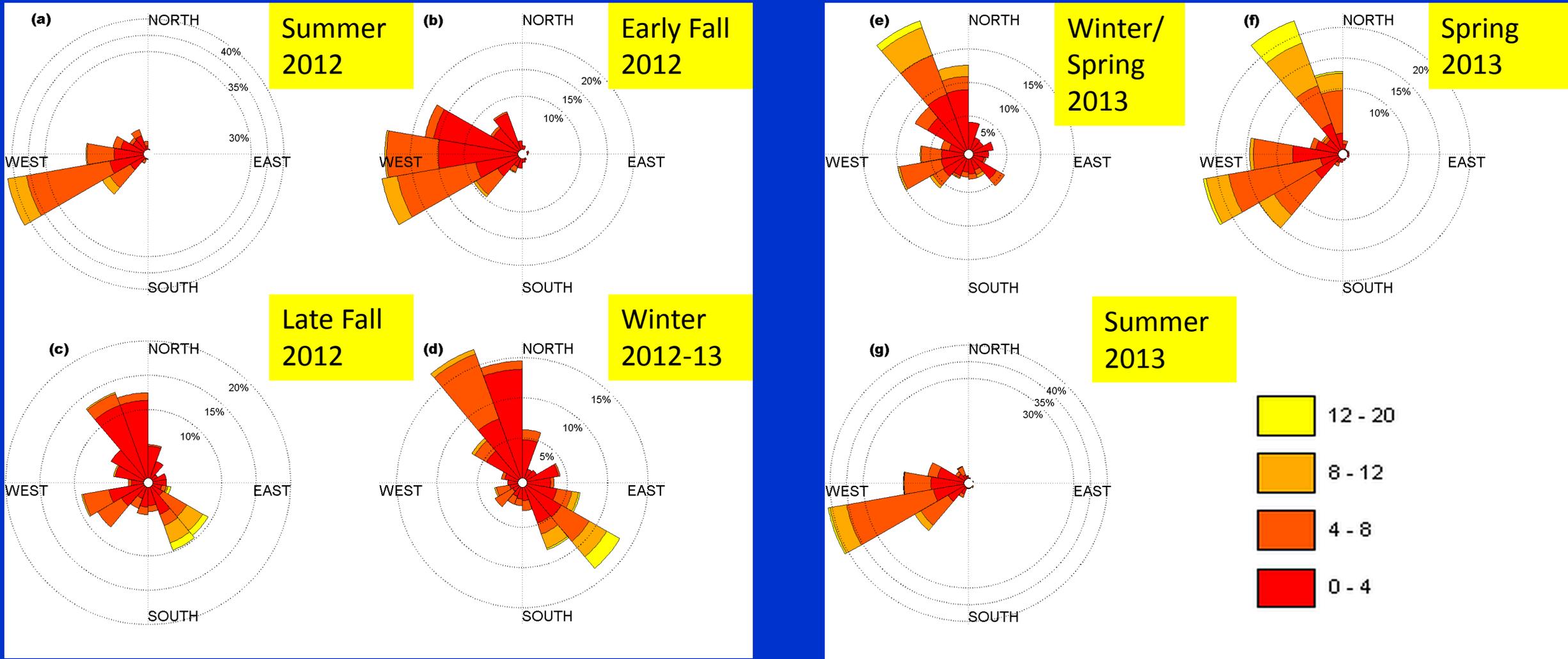
Season	Start/End date	Hourly average temperature range <sup>a</sup> (° C)	Species not measured <sup>b</sup>	Number of hourly samples <sup>c</sup>
Summer 2012	Jun 16 / Aug 31	14 - 30	N <sub>2</sub> O	1583
Early Fall 2012	Sep 1 / Oct 16	13 - 28	N <sub>2</sub> O	1061
Late Fall 2012	Oct 17 / Nov 30	9 - 20	N.A.	774
Winter / Wet season	Dec 1 / Jan 29	4 - 13	MeOH	744
Winter/ Spring 2013	Feb 16 / Apr 4	4 - 17	N <sub>2</sub> O , MeOH	1072
Spring 2013	Apr 6 / May 31	12 - 25	N.A.	1151
Summer 2013	Jun 1 / Aug 4	15 - 30	N.A.	1056

<sup>a</sup> range reflects average daily low and average daily high over the sampling period measured at 10 m a.g.l.

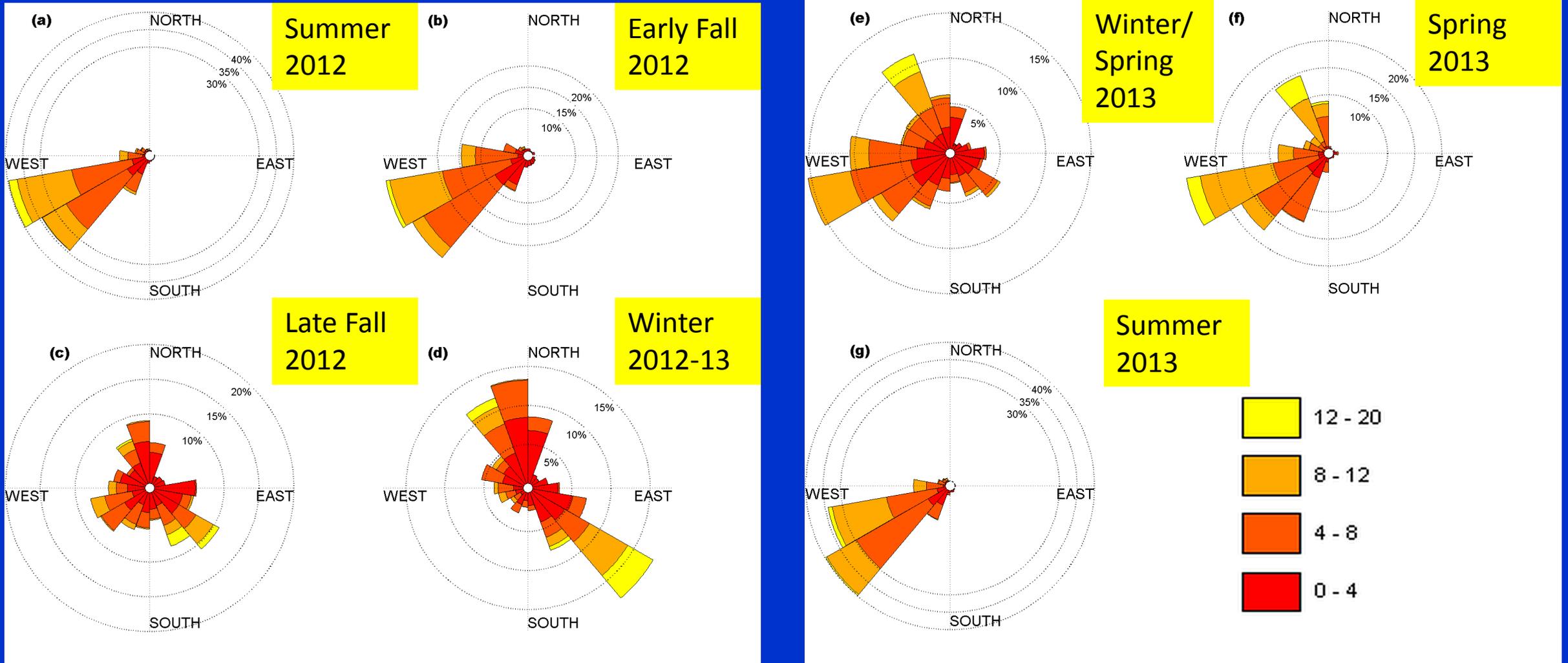
<sup>b</sup> N.A. - not applicable; all 13 tracers measured and included in PMF analysis; measured tracers include CH<sub>4</sub>, N<sub>2</sub>O, CO, benzene, toluene, acetonitrile, methanol, acetaldehyde, acetone, methyl ethyl ketone, methyl vinyl ketone + methacrolein, isoprene and monoterpenes.

<sup>c</sup> rows of data containing extended periods of missing VOCs removed all together.

# Daytime wind speed (m/s) and direction rose plots



# Nighttime wind speed (m/s) and direction rose plots



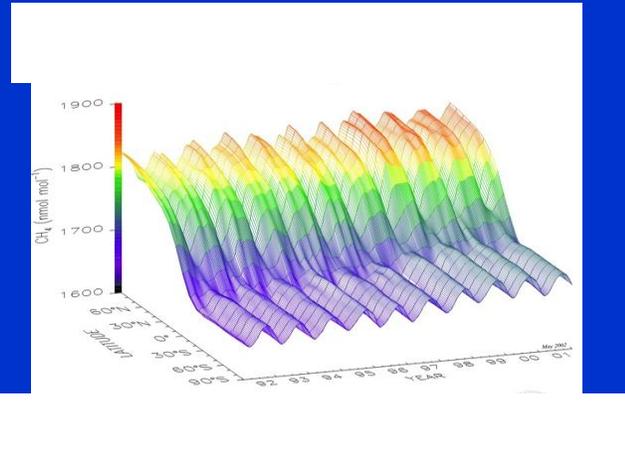
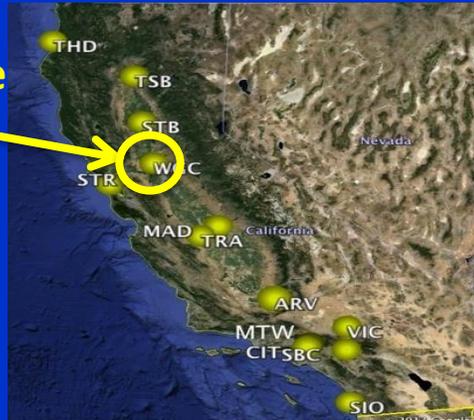
# Regional Inverse Emission Estimates

In-state Measurement

Inflow Background Measurement

*a priori* Emission Model with uncertainty

Walnut Grove (WGC)



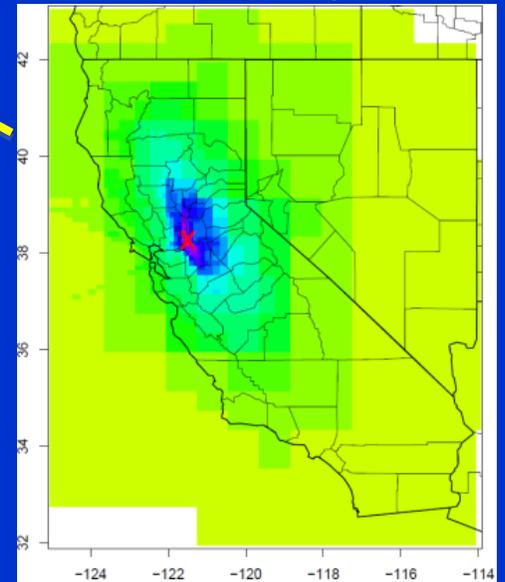
Measured Signals and uncertainties

Predicted Signal = *a priori* emissions \* footprint

Predicted Tower Footprint with uncertainty

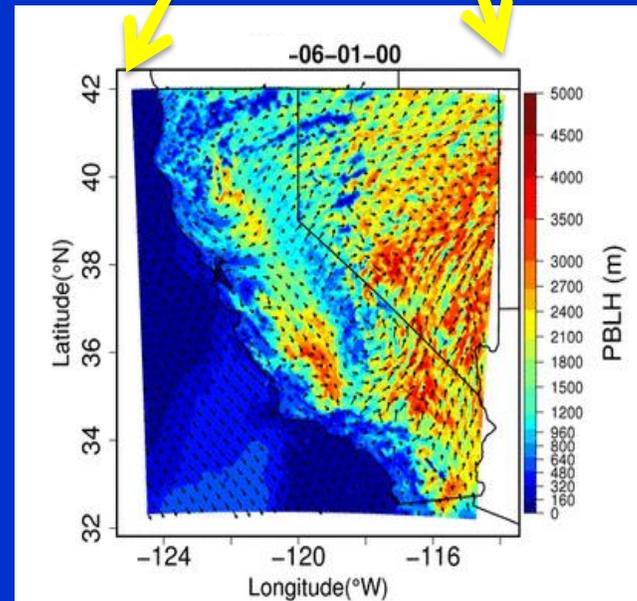
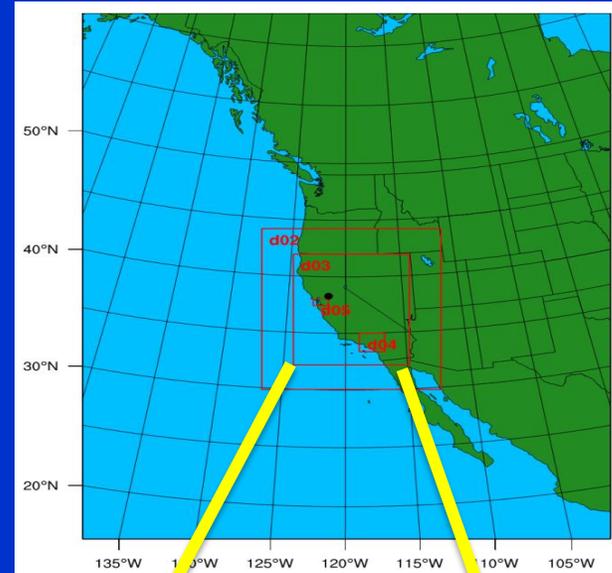
Bayesian Emission Estimate: Scale *a priori* emissions so predictions match measurements to within uncertainties

Posterior Emission Estimate w/ Uncertainties



# Meteorological Transport Model

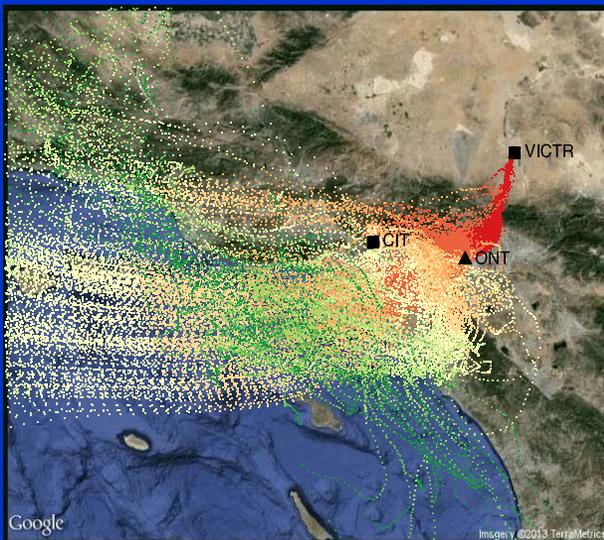
- NCAR Weather Research Forecast (WRF) model predicts winds and boundary layer depth in nested grids over western US
- Uncertainty in winds and boundary layer height (PBLH) measured at wind profilers near tower sites
- Footprints estimated from winds, turbulence, and boundary layer depths



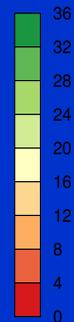
# Predicting Tower Footprints

- Sensitivity footprint links emissions from sources to mixing ratios at tower
- Weather model winds used to drive particle trajectory simulation
- Use transport model to estimate footprint for mid-day periods

2012x07x02x23x34.54Nx117.29Wx00090

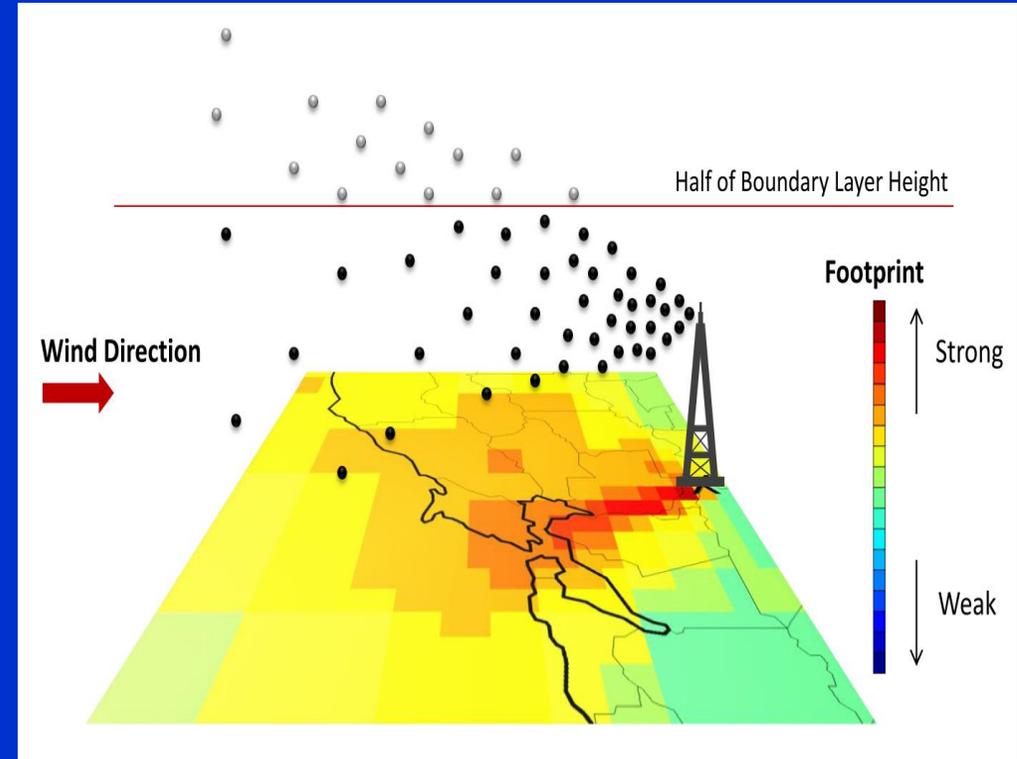


Hours back from receptor



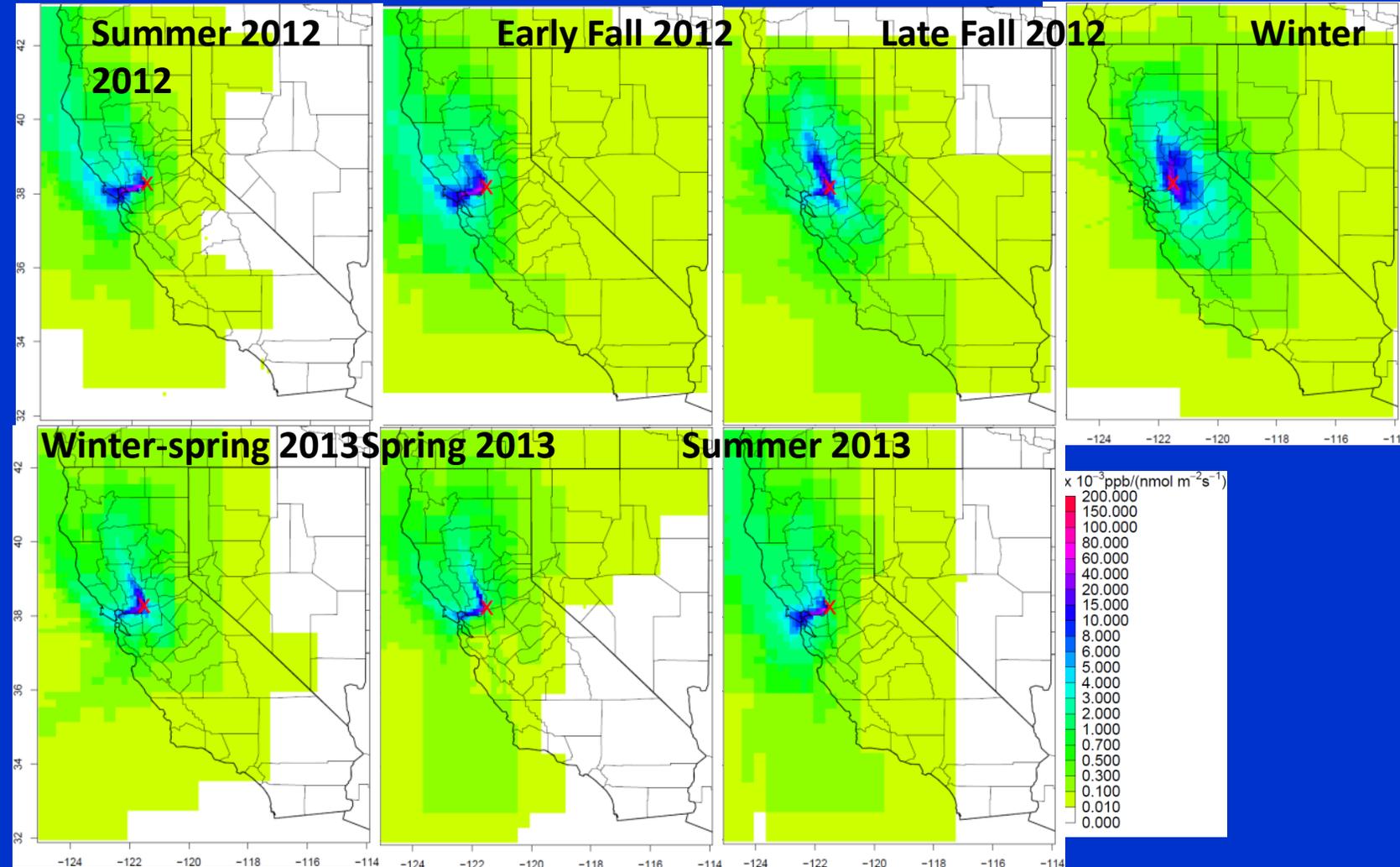
Example of particle trajectory simulations using STILT

## Particle trajectories sensitivity footprint



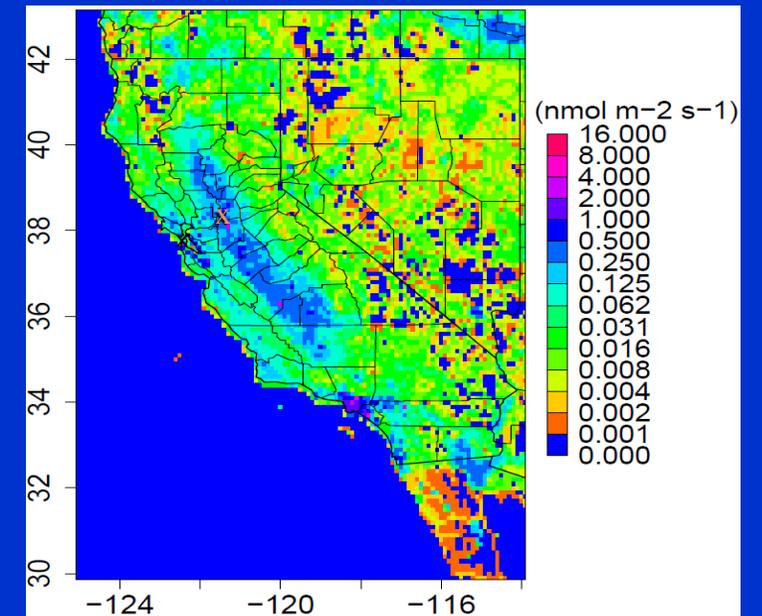
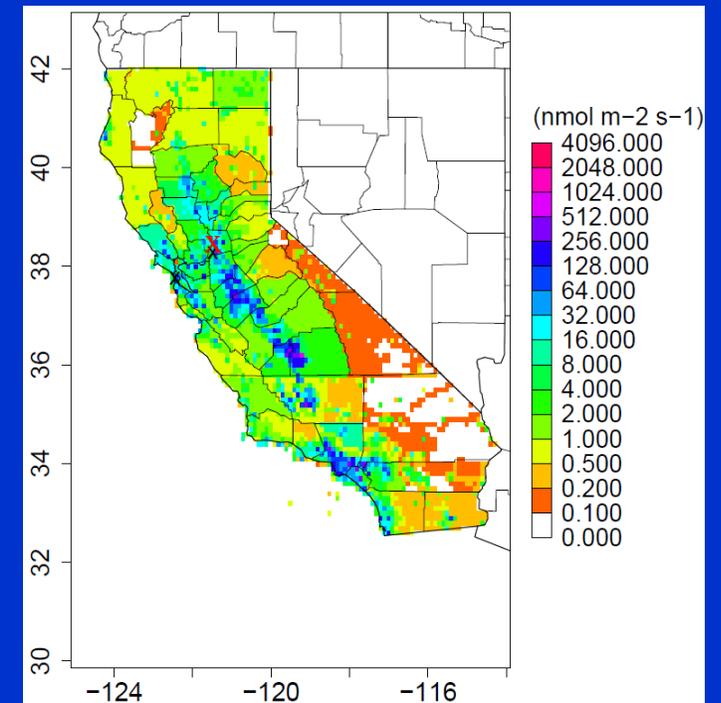
# Seasonality of Tower Footprints

- Summer sun causes upwelling boundary layers in valley that draws air from SFBay
- Weak winter sun gives shallow boundary concentrated in central valley
- Spring & fall are transition seasons
- Uncertainty in footprint strength  $\sim 30\text{-}50\%$  (Jeong et al., 2013)



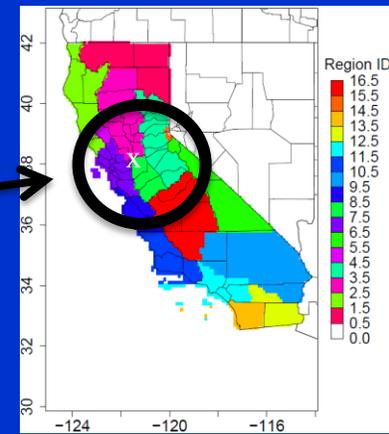
# *a priori* Emission Maps

- California-specific CH<sub>4</sub> and global “EDGAR” N<sub>2</sub>O emission maps
- 0.1 degree (~ 10km) resolution w/ multiple source sub-sectors
- Calibrated to CARB inventory by sector
- Assume *a priori* emissions by sector and region are uncertain at 70% level (1  $\sigma$ )



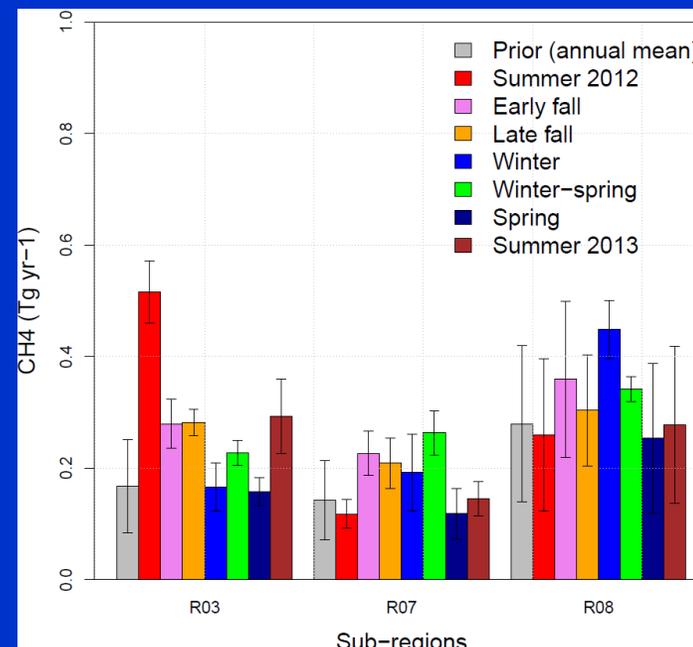
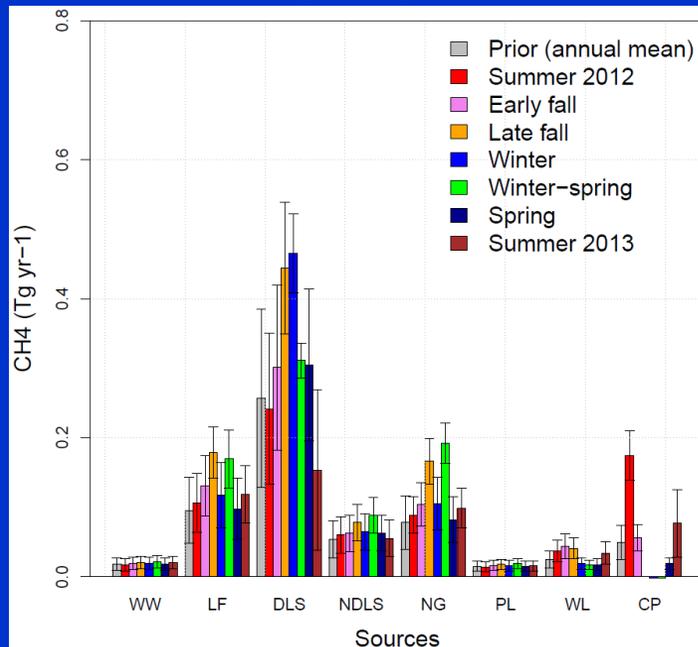
# Posterior CH<sub>4</sub> Emission Estimates

- Majority of emissions observed at Walnut Grove tower likely from Central Valley region
- Posterior annual average emissions slightly higher (1.1 – 1.5 times) prior model
- Note: contribution from specific source sectors can not be uniquely determined without VOC tracers



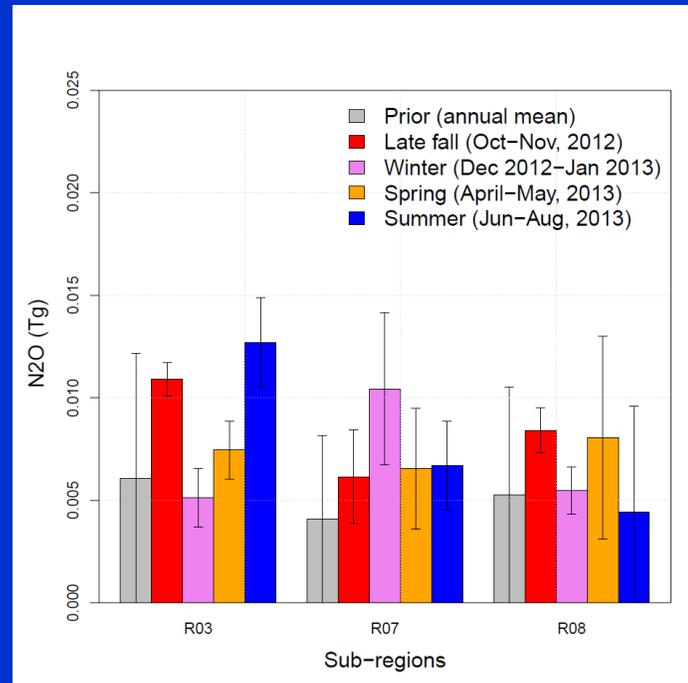
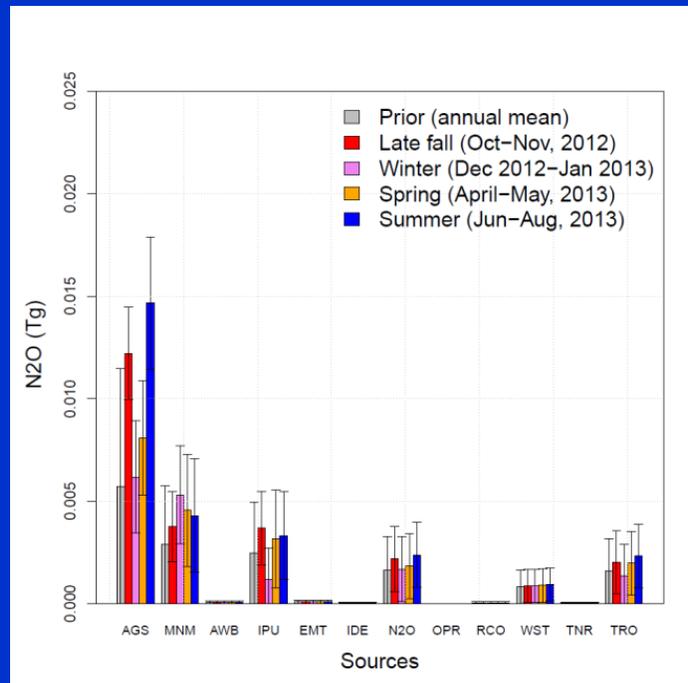
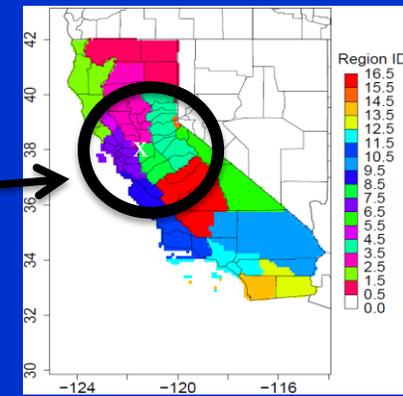
CH<sub>4</sub> Emissions ((Tg CH<sub>4</sub> yr<sup>-1</sup>))

Source	Prior	Posterior
Crop (CP)	0.05	0.05 ± 0.02
Dairy (DLS)	0.26	0.32 ± 0.09
Landfill (LF)	0.10	0.13 ± 0.04
Other livestock (NDLS)	0.05	0.07 ± 0.03
NatGas (NG)	0.08	0.12 ± 0.03
Petroleum(PL)	0.01	0.02 ± 0.01
Wetland (WL)	0.02	0.03 ± 0.01
Wastewater (WW)	0.02	0.02 ± 0.01
<b>Total</b>	<b>0.59</b>	<b>0.76 ± 0.11</b>



# Posterior N<sub>2</sub>O Emission Estimates

- Majority of emissions observed at Walnut Grove tower likely from Central Valley region
- Posterior annual average emissions somewhat higher than (1.2 – 1.9 times) prior model
- As with CH<sub>4</sub>, source sectors can not be uniquely separated without VOC tracers



## N<sub>2</sub>O Emissions (Tg N<sub>2</sub>O yr<sup>-1</sup>)

Source Sectors	Prior	Posterior
AGS ( Ag Soil)	0.006	0.01±0.003
AWB (Ag Waste burning)	0	0±0
EMT (electric power)	0	0±0
IDE (indirect)	0	0±0
IPU (industrial)	0.002	0.003±0.002
MNM (manure)	0.003	0.004±0.002
N2O (indirect ag)	0.002	0.002±0.002
OPR (patroleum)	0	0±0
RCO (residential)	0	0±0
TNR (mon-road)	0	0±0
TRO (on-road)	0.002	0.002±0.002
WST (waste)	0.001	0.001±0.001
<b>Total</b>	<b>0.015</b>	<b>0.023±0.005</b>

# POSITIVE MATRIX FACTORIZATION (PMF)

- ✓ Number of sources impacting a receptor site unknown
- ✓ Chemical composition of individual source profiles unknown or cannot be assumed
- ✓ Concentration time series of large number of coincidentally measured tracers and their uncertainty ranges are known
- PMF is a receptor-only un-mixing model which breaks down a measured data set containing time series of a number of measured GHGs and VOCs into a mass balance of an arbitrary number of constant source profiles contributing varying concentrations over the timeline of the data set
- **PMF Input:** 2-D  $m \times n$  matrix  $\mathbf{X}$  with  $i$  rows containing mixing ratios at sampling time  $t_i$  and  $j$  columns containing time series of each sampled tracer  $x_j$
- **PMF Input:** Corresponding uncertainty matrix  $(\sigma_{ij})$  representing weight or experimental uncertainty for each input measurement

# POSITIVE MATRIX FACTORIZATION (PMF)

- **PMF Output:**  $X_{ij} = \sum_p g_{ip} f_{pj} + e_{ij}$

**g** – time series of each factor (**Source Contribution**)    **f** – chemical profile of factor  
(**Source Profile**)

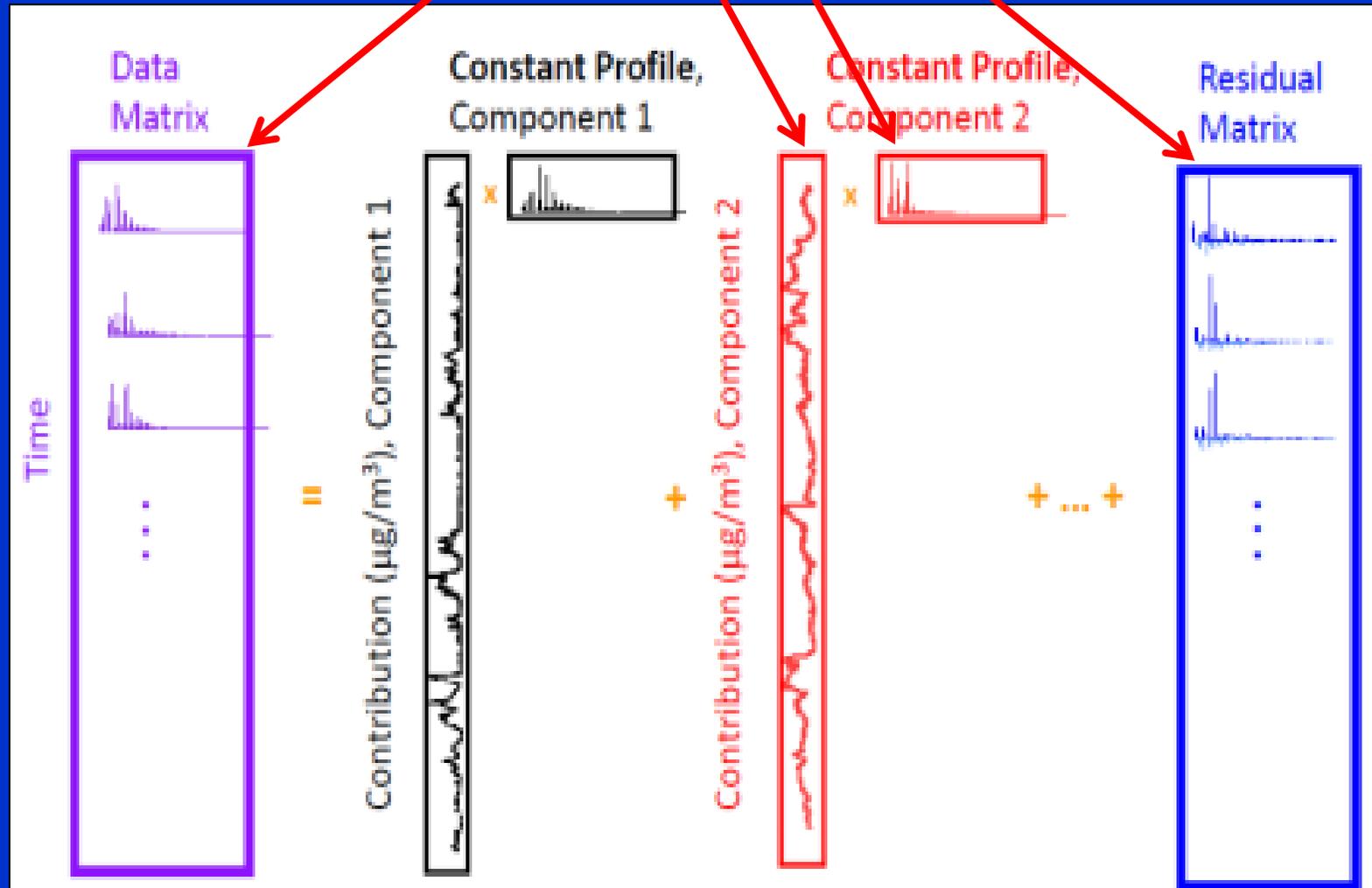
**p** – no. of factors / sources

**e<sub>ij</sub>** - residual matrix

- PMF uses the covariance (or lack thereof) of enhancements of different tracers to predict the composition of each factor
- PMF uses a least-squares algorithm to iteratively fit the values of G and F by minimizing a “quality of fit” parameter Q that minimizes the sum of squares of error-weighted model-measurement deviations  
$$Q = \sum_{i=1}^m \sum_{j=1}^n \left( \frac{e_{ij}}{\sigma_{ij}} \right)^2 \text{ while } Q_{exp} = (i \times j) - p \times (i+j)$$
- No. of factors chosen based on minimum value of  $Q/Q_{exp}$  that characterize the quality of reconstruction and physical plausibility of factor (**based on Paatero et al. 1997; Ulbrich et al. 2009; Williams et al. 2010; Bon et al. 2011**)

# POSITIVE MATRIX FACTORIZATION (PMF)

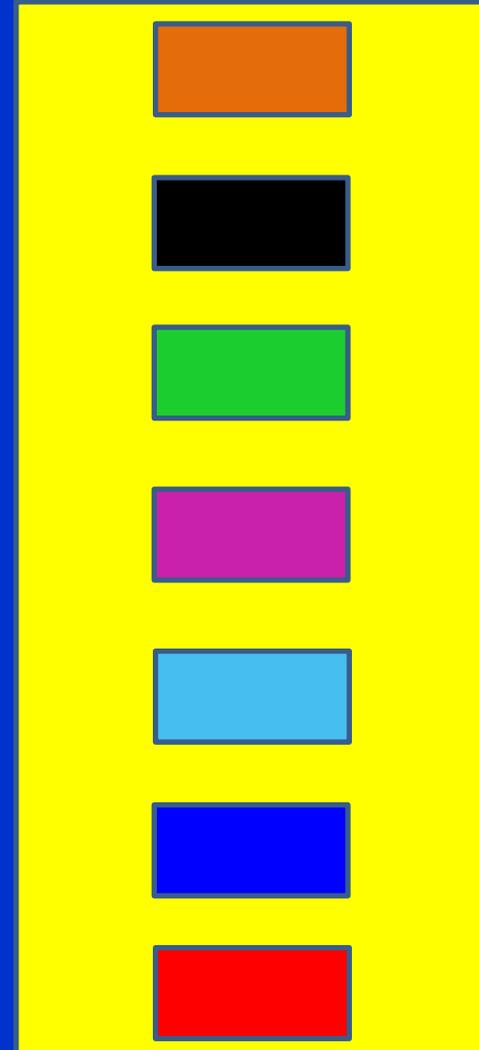
$$X_{ij} = \sum_p g_{ip} f_{pj} + e_{ij}$$



# PMF RESULTS

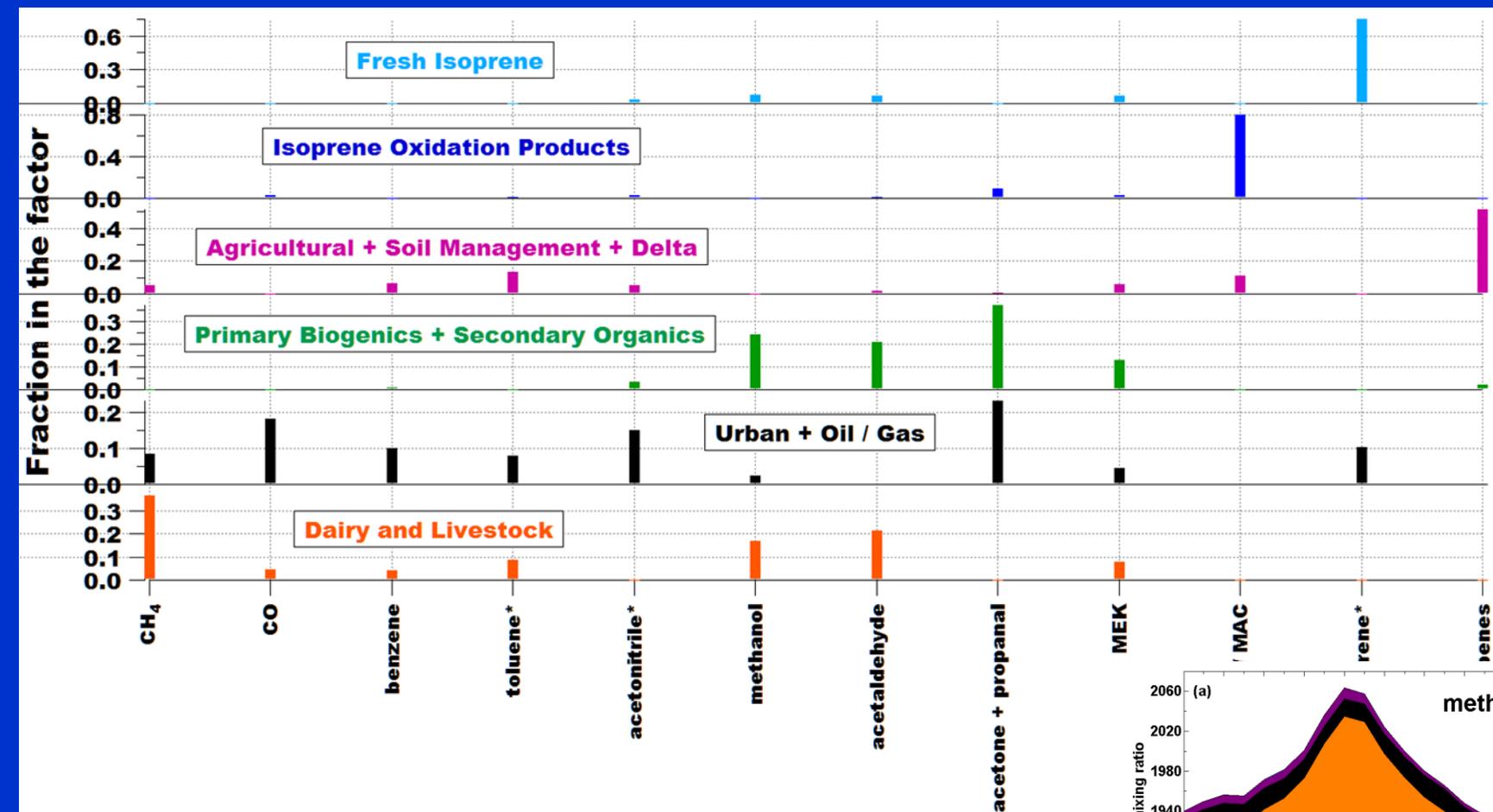
## Description of Source Factors

- Dairy and Livestock
- Urban + Oil and Gas
- Primary Biogenics and Secondary Organics
- Agriculture + Soil Management + Delta
- Fresh Isoprene emissions
- Isoprene Oxidation products
- Forest Fires



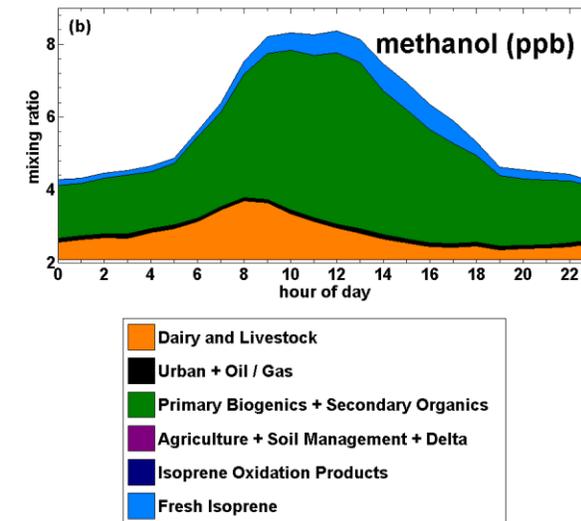
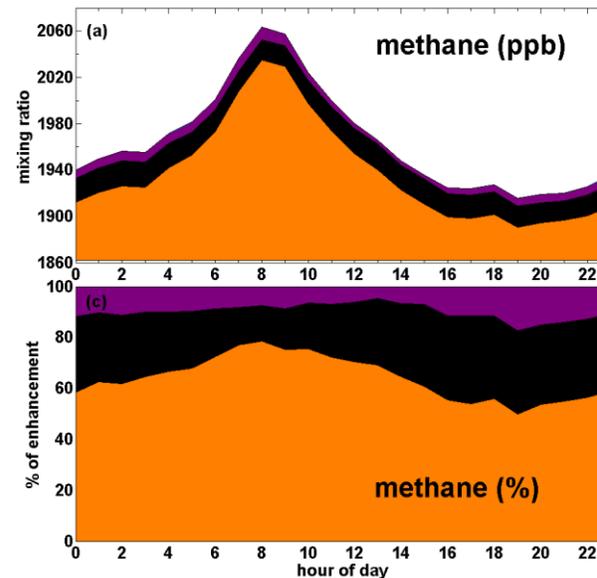
**Early Fall 2012 (Sep 1 – Oct 15)**

PMF source-apportioned diurnal distribution plots



**6-factor profile solution**

- All six PMF source factors detected
- Source factors contributions vary based on time of day (and wind direction)
- Black source factor has non-biological origins
- Orange source factor has dairy-like origins



# Dairy and Livestock

- Significant source of  $\text{CH}_4$  and  $\text{N}_2\text{O}$
- VOCs like methanol (MeOH), acetaldehyde, acetone + propanal and methyl ethyl ketone (MEK) also reported in several dairy studies (Filipy et al., 2006; Shaw et al., 2007; Ngwabie et al., 2008; Chung et al., 2010)
- Presence of MeOH indicates biological origin and not combustion / fossil-fugitive
- $\text{MeOH} / \text{CH}_4$  ( $\text{mmol mol}^{-1}$ ) conform with cow chamber studies (Shaw et al., 2007), dairy plumes measured by aircraft (Gentner et al., 2014a; Guha et al., 2014).
- $\text{N}_2\text{O} / \text{CH}_4$  ( $\text{mmol mol}^{-1}$ ) similar to that of the dairy and livestock factor in the PMF analysis at Bakersfield of (Chapter 2; Guha et al., 2014).

## Urban + Oil and Gas

- Significant source of CO, benzene and toluene; also contains acetaldehyde and acetone
- Toluene to benzene molar ratios depleted as compared to fresh urban plumes. This indicates likely influence of transported combustion emissions from the urban corridor at the mouth of the Delta
- Lack of any N<sub>2</sub>O in the presence of CH<sub>4</sub> points to fugitive O&G source. No methanol is apportioned to this factor in any seasonal PMF analysis.
- Lower toluene / benzene ratios more typical of plumes from natural gas leakage. A large CH<sub>4</sub> enhancement (~120 ppb) was observed while flying over the Rio Vista gas field to the west during the CABERNET campaign in 2011

## Urban + Oil and Gas

- Secondary production of acetaldehyde from photo-oxidation of light alkanes largest global source (Millet et al., 2009); and minor source of acetone (Goldstein and Schade, 2000; Schade and Goldstein, 2006; Hu et al., 2013)
- In winters, some anthropogenic contributions on  $m/z$  69 (typically isoprene in summers) from pentadienes and cyclopentenes which are by-products in petroleum industry plumes.
- Some contributions to  $m/z$  42 are potentially alkanes.  $m/z$  137 contribution during winters is from known anthropogenic monoterpenes while  $m/z$  71 potentially contains contributions from refinery by-products like pentenes and 2-methyl-2-butene

# Primary Biogenics + Secondary Organics

- One of three source factors present in each seasonal PMF solution. Dominant source of oxygenated VOCs with primary biogenic and secondary photochemical sources. No CH<sub>4</sub> or N<sub>2</sub>O.
- Diurnal and vertical profiles indicate local ground-based sources with emissions peaking during daytime.
- No noticeable contribution of CO, aromatics and acetonitrile
- Daily rise and decline of oxygenated VOCs occur at slightly different times which are well corroborated by differences in biogenic release mechanisms and source types, light and temperature-driven and photochemical production pathways
- Even during winters, agricultural residues in the post-harvested fields, and potential double cropping may result in some biogenic emissions

# Agriculture + Soil Management + Delta

- Major contributor to  $\text{N}_2\text{O}$  enhancements and most of monoterpene ( $m/z$  137) which is majorly emitted from crops. Contribution of this source factor to  $\text{CH}_4$  and  $\text{N}_2\text{O}$  is highly seasonal and coincides with the growing / agriculture season.
- Difference in diurnal profiles and emission pathways leads to some OVOCs getting apportioned to the 'green' factor
- Summertime biological toluene ( $m/z$  93) along with methanol and monoterpenes most likely originating from corn and managed grassland harvesting (White et al., 2008; Ruuskanen et al., 2011; Graus et al., 2013)
- Small mass fraction of  $\text{CH}_4$  apportioned to this factor likely originating from upwind periodically flooded and drained peatland pastures, natural and restored wetlands, and rice agriculture which is coterminous with agricultural farm lands,

## **Fresh Isoprene emissions**

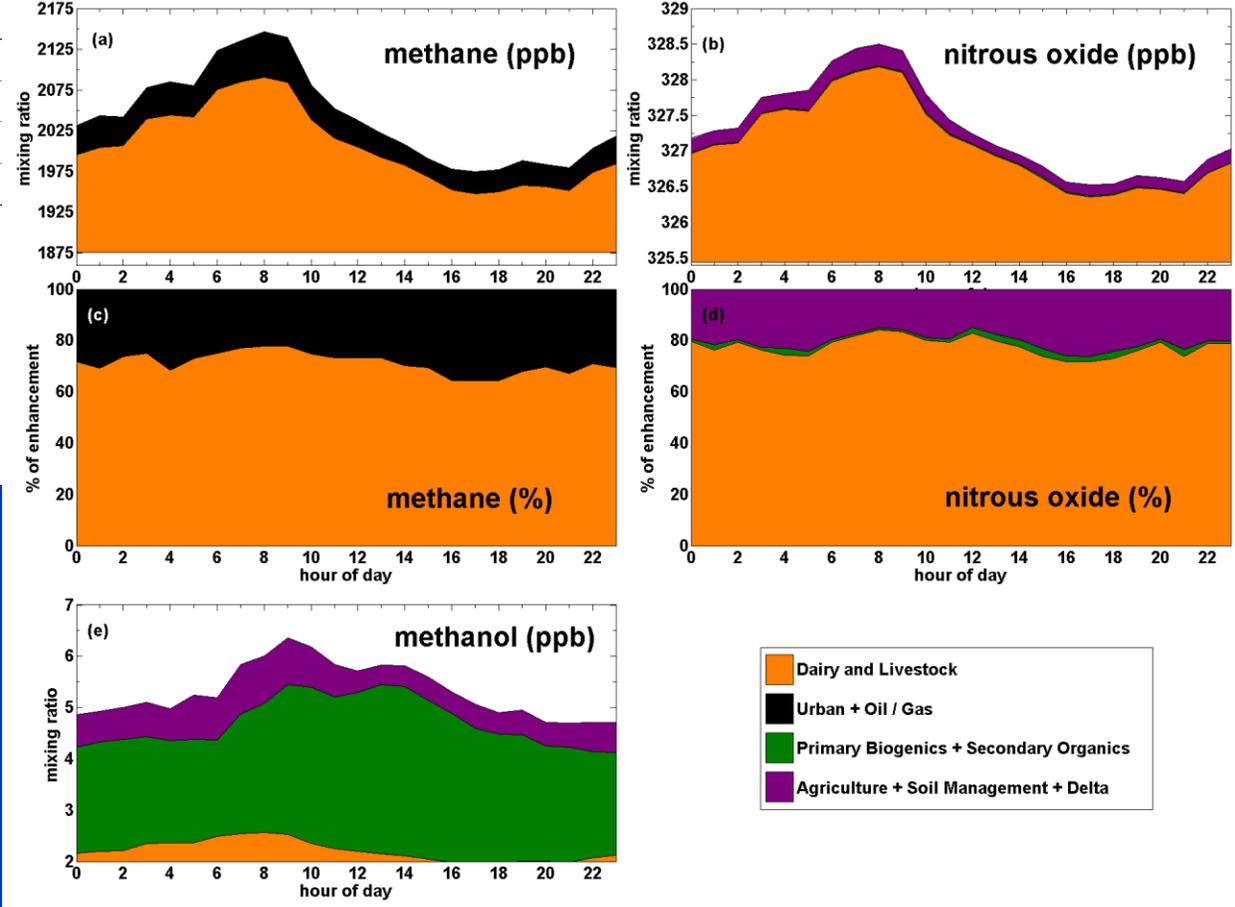
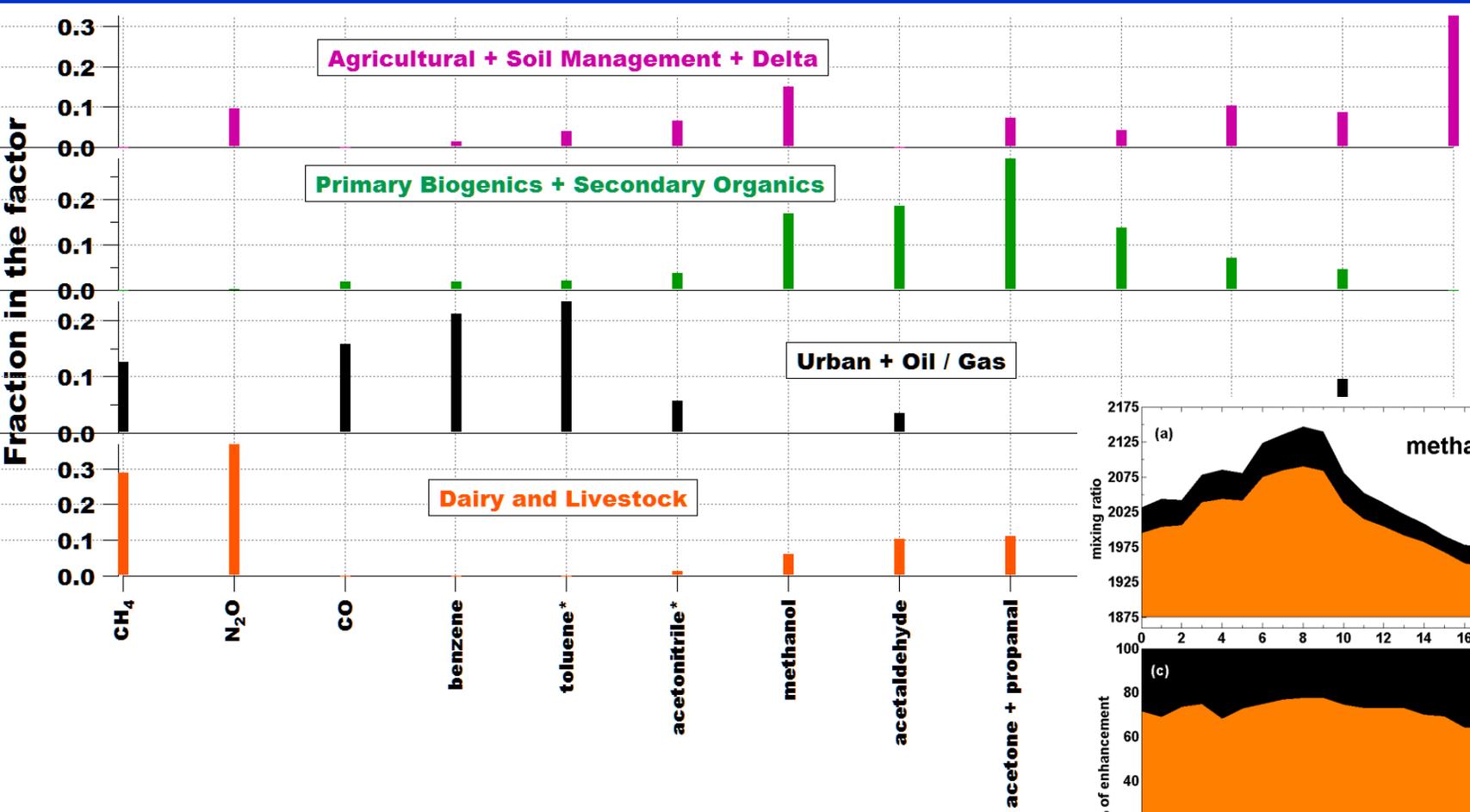
- Highly seasonal factor peaking sharply during the day and in summer, and negligible in the nighttime and winter due to light and temperature dependence
- Isoprene has very short lifetime ( ~ 1 h) and the emission mechanism and loss processes results in a unique diurnal profile unlike other species and hence apportioned into an exclusive PMF factor

## **Isoprene Oxidation Products**

- Contains principally methyl vinyl ketone (MVK) and methacrolein (MAC) and diurnal profile coincides with but lags behind isoprene emissions
- MVK and MAC measured at the top heights are mostly result of entrainment of advected and oxidized biogenic plumes in the easterly downslope winds

**Late Fall 2012 (Oct 16 – Nov 30)**

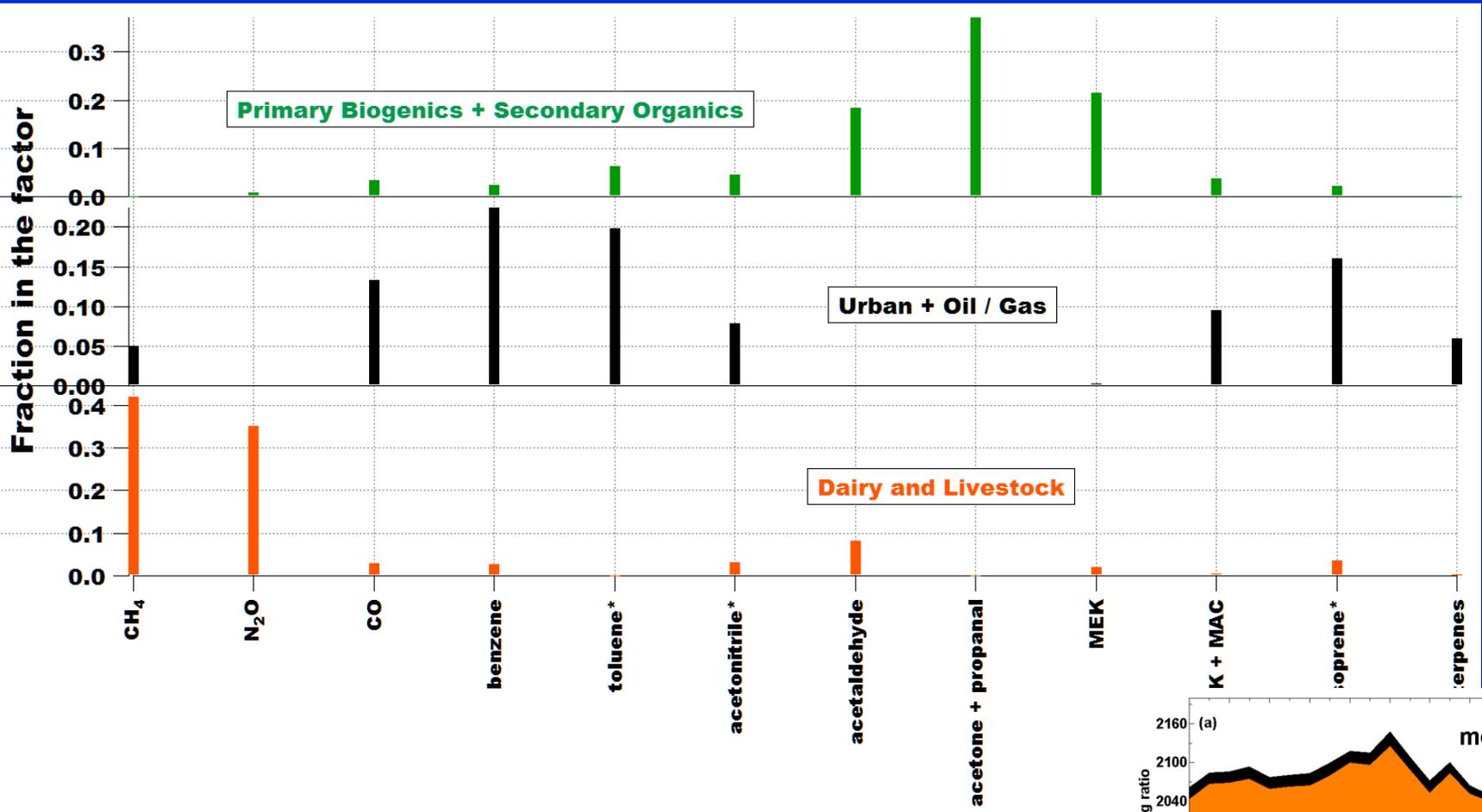
PMF source-apportioned diurnal distribution plots



4-factor profile solution

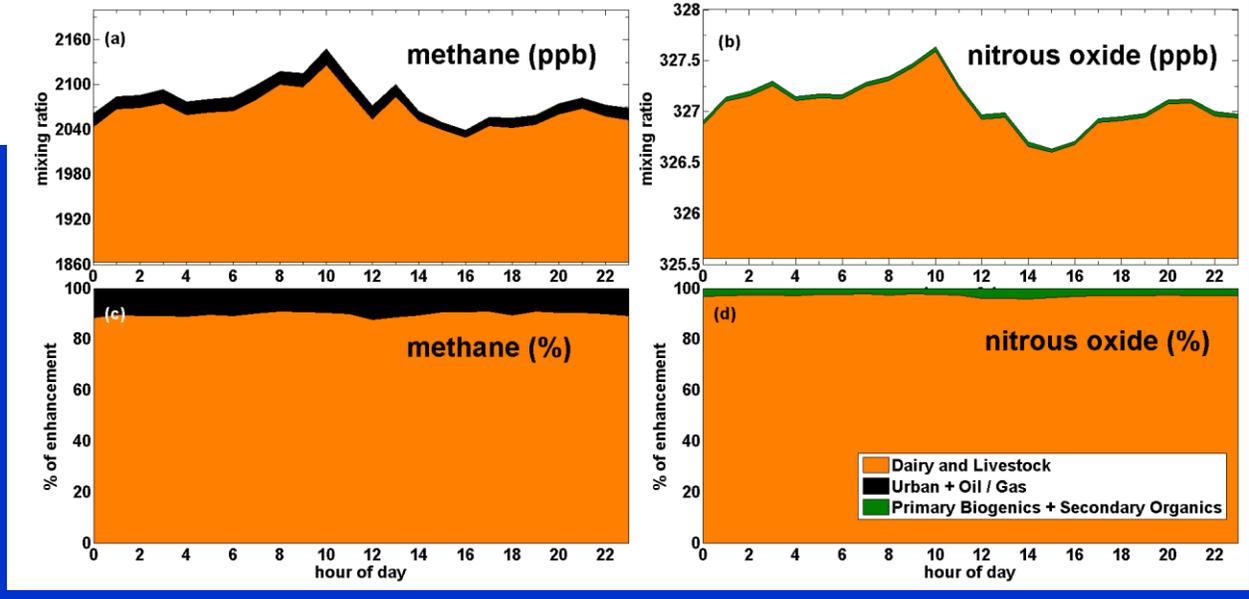
- Lower temperatures; no isoprene related source factors detected
- CH<sub>4</sub> still primarily split between two sources
- N<sub>2</sub>O primarily apportioned to dairy factor

**Winter / Wet season (Dec 1, 2012 – Jan 29, 2013)**



**PMF source-apportioned diurnal distribution plots**

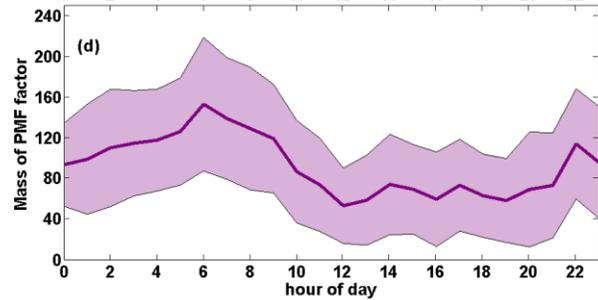
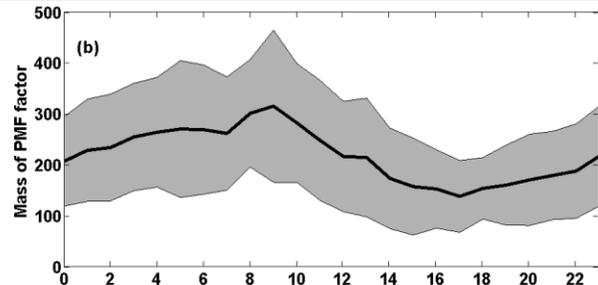
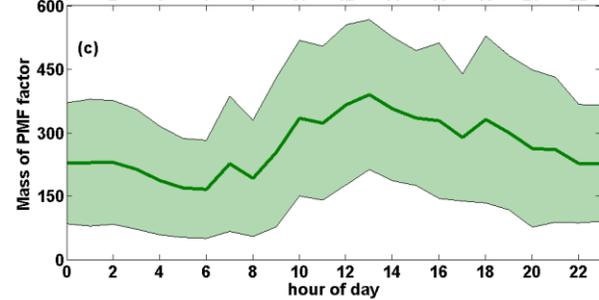
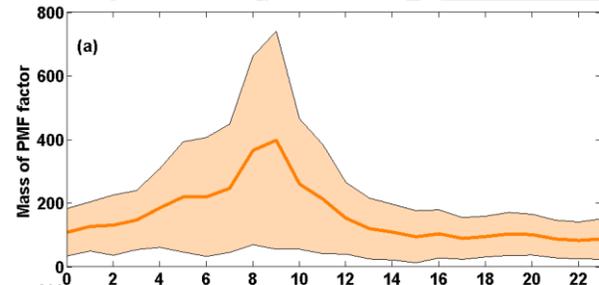
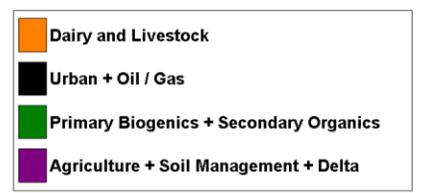
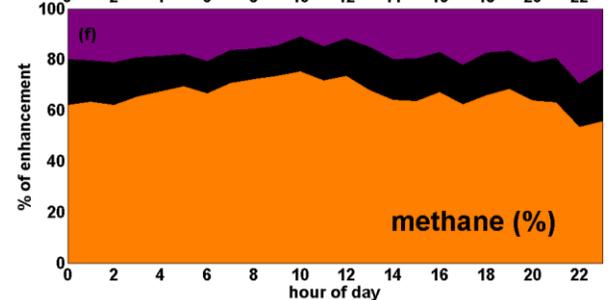
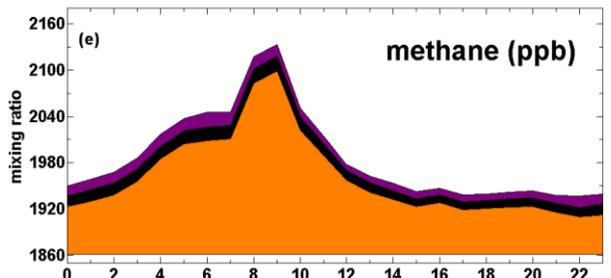
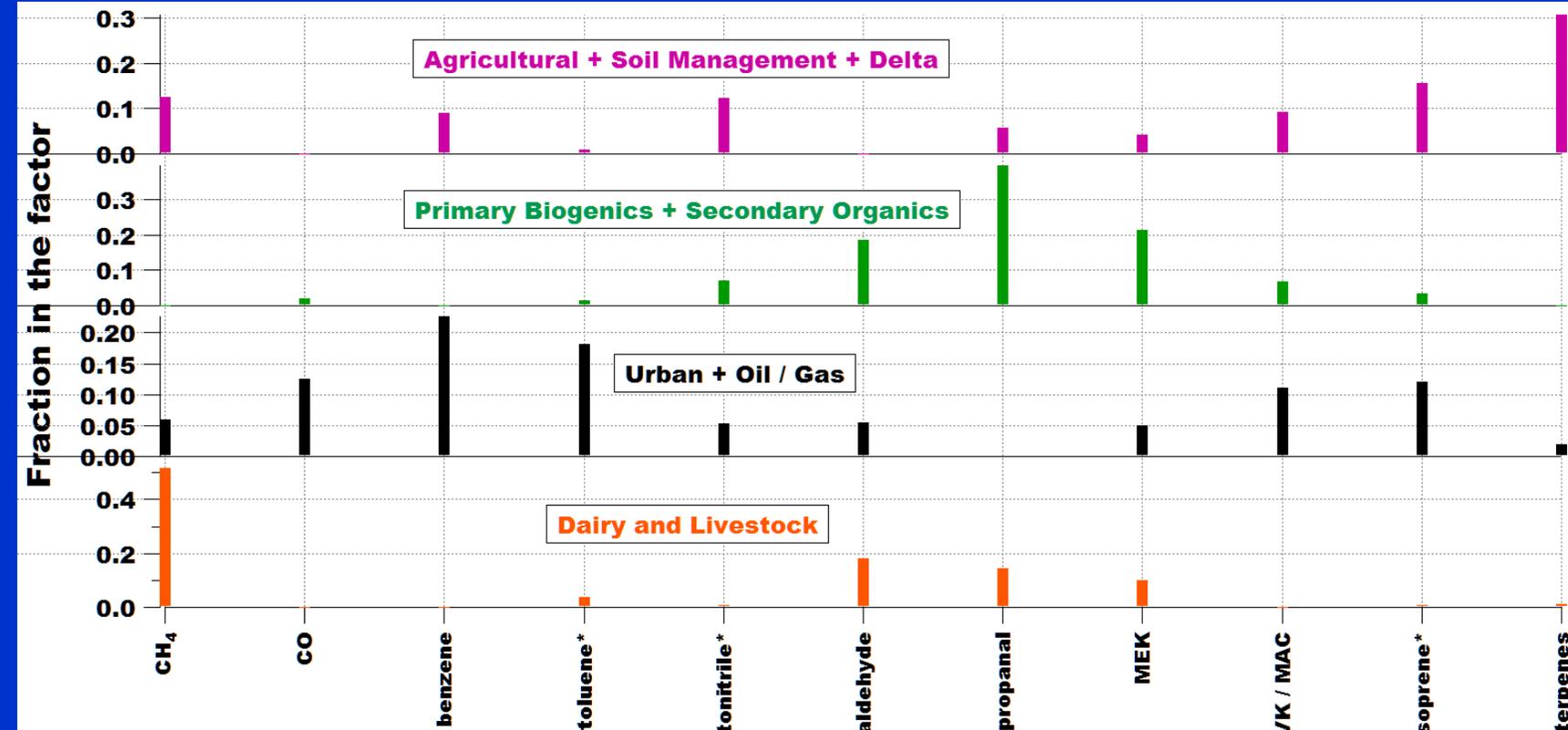
- 3-factor profile solution**
- Post-harvesting season; no agriculture related factor; biogenic factor contribution tiny
  - CH<sub>4</sub> mostly from dairy factor although urban factor is detected in minor proportion
  - No N<sub>2</sub>O in the urban factor



# Late Winter / Early Spring season 2013 (Feb 15 – Apr 5)

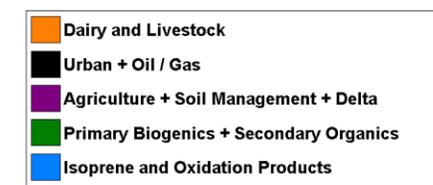
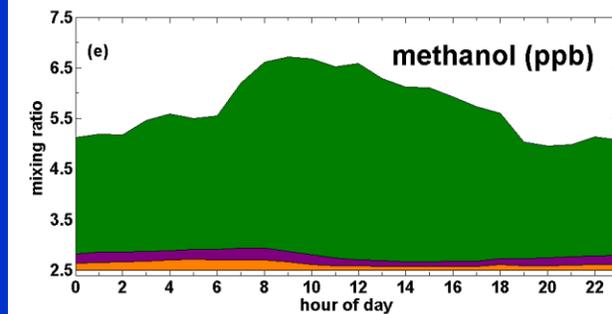
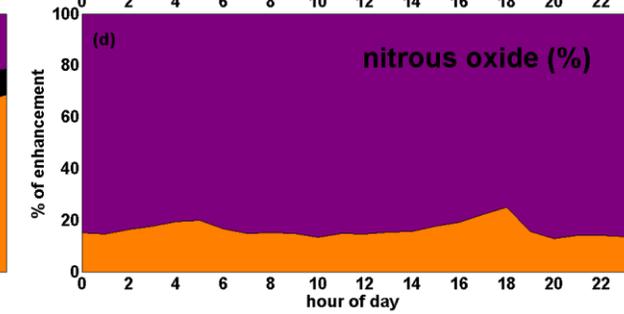
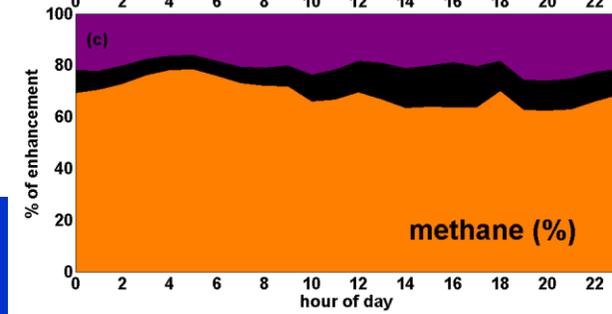
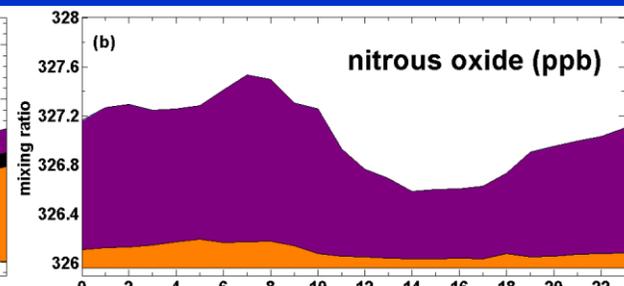
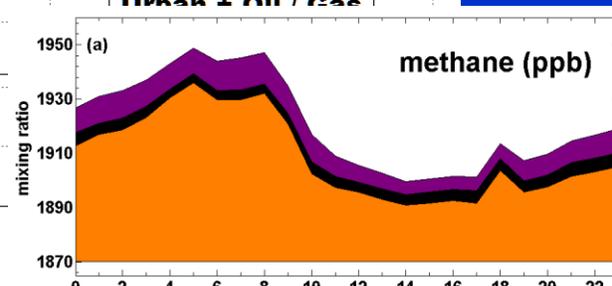
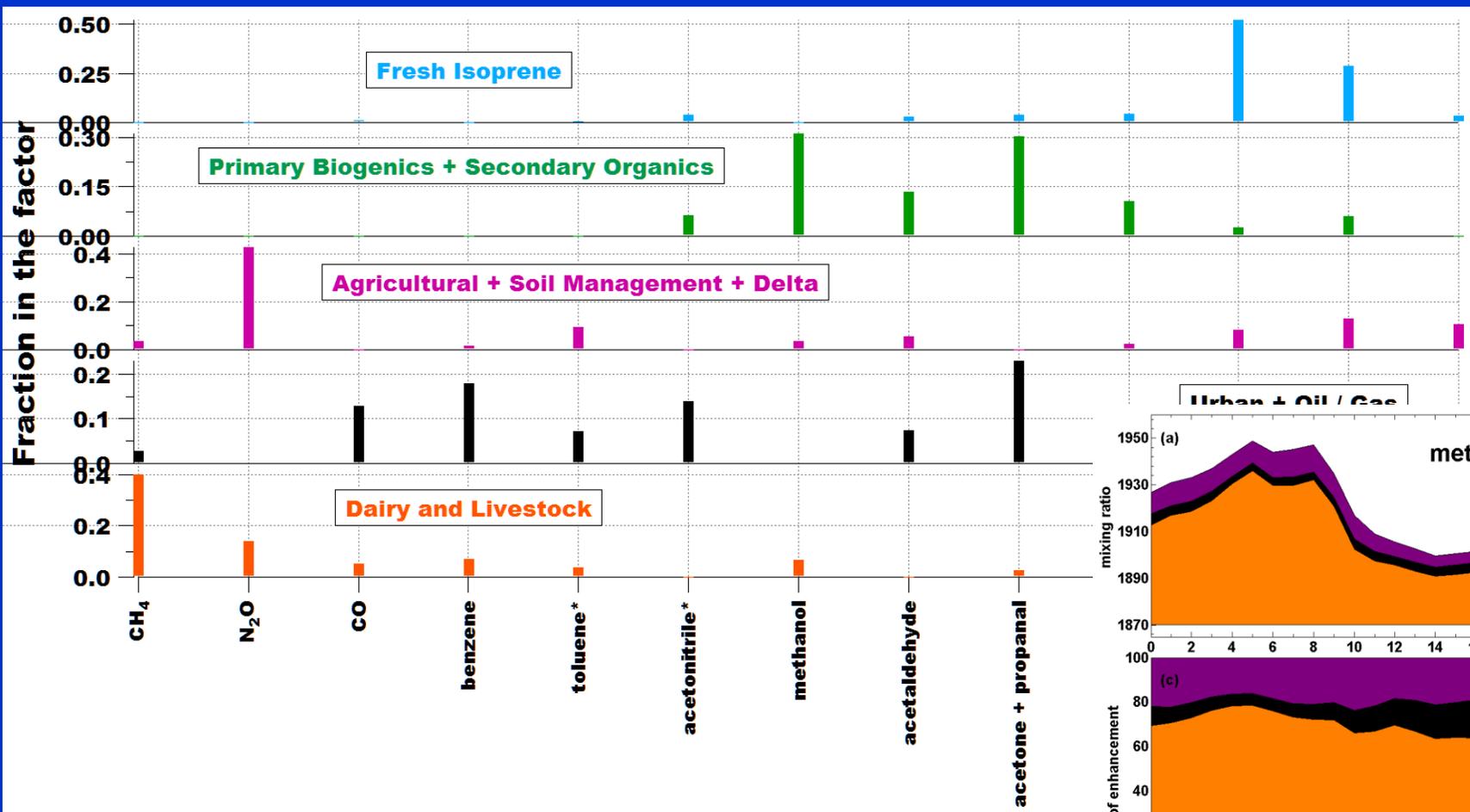
- Early planting season; ag factor detected with CH<sub>4</sub> present; no N<sub>2</sub>O measured
- Source mass diurnal profiles reveal interesting trends

## PMF source-apportioned diurnal distribution plots



**Spring 2013 (Apr 6 – May 31)**

PMF source-apportioned diurnal distribution plots

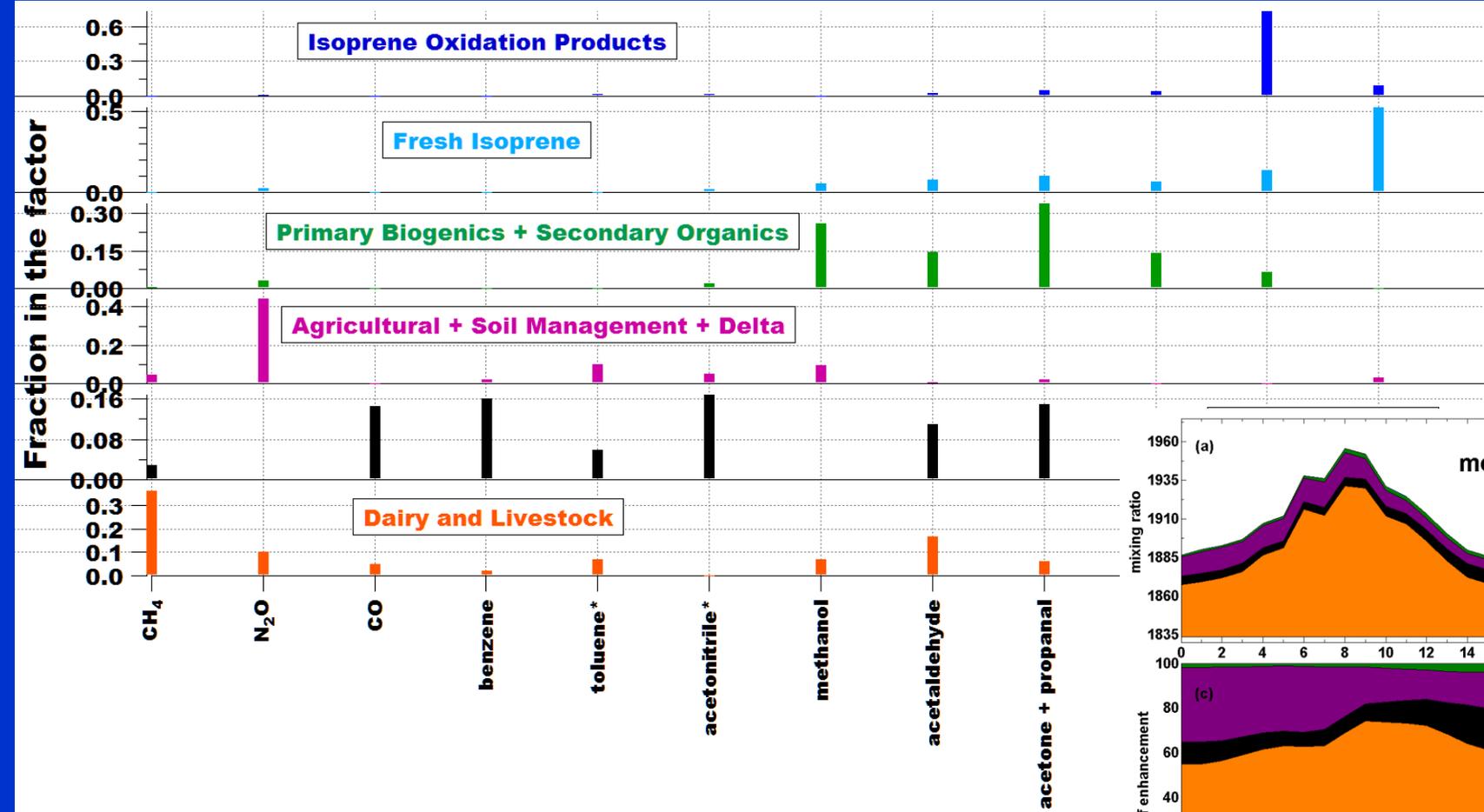


**5-factor profile solution**

- Most of N<sub>2</sub>O detected from agriculture related factor; CH<sub>4</sub> contribution consistent
- Biogenic MeOH overwhelms other source contributions
- Daytime CH<sub>4</sub> from urban/O&G source

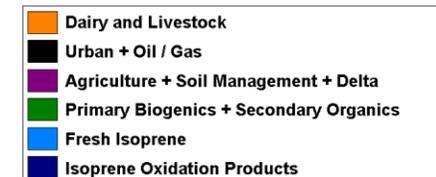
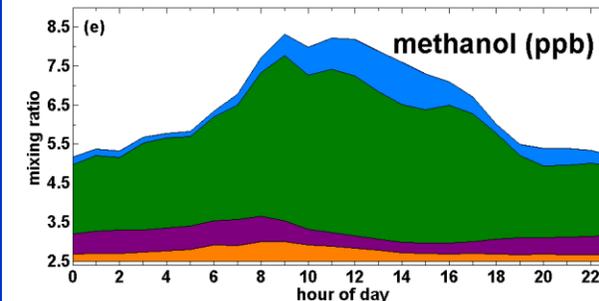
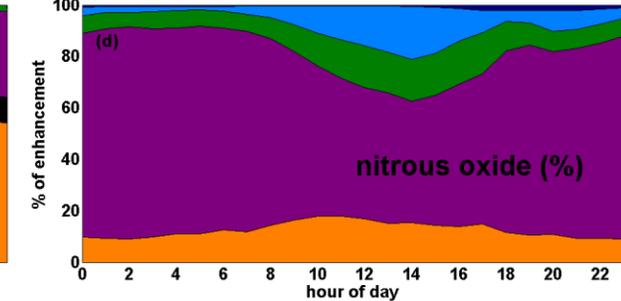
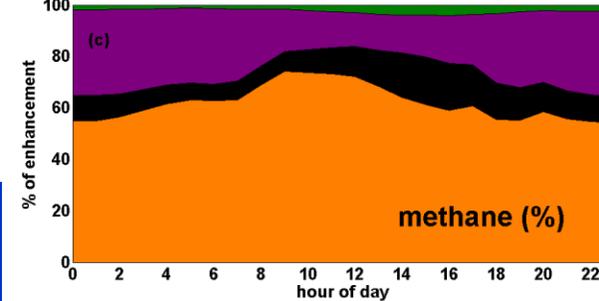
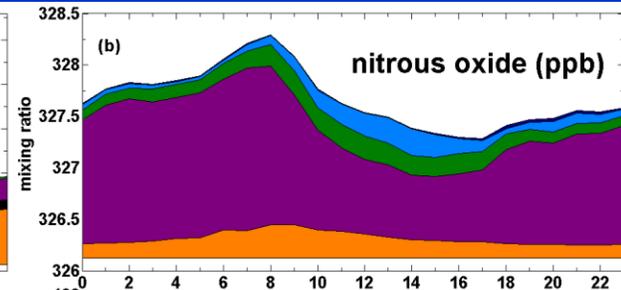
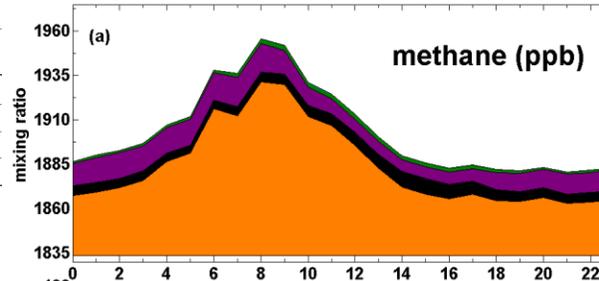
Summer 2013 (Jun 1 – Aug 4)

PMF source-apportioned diurnal distribution plots

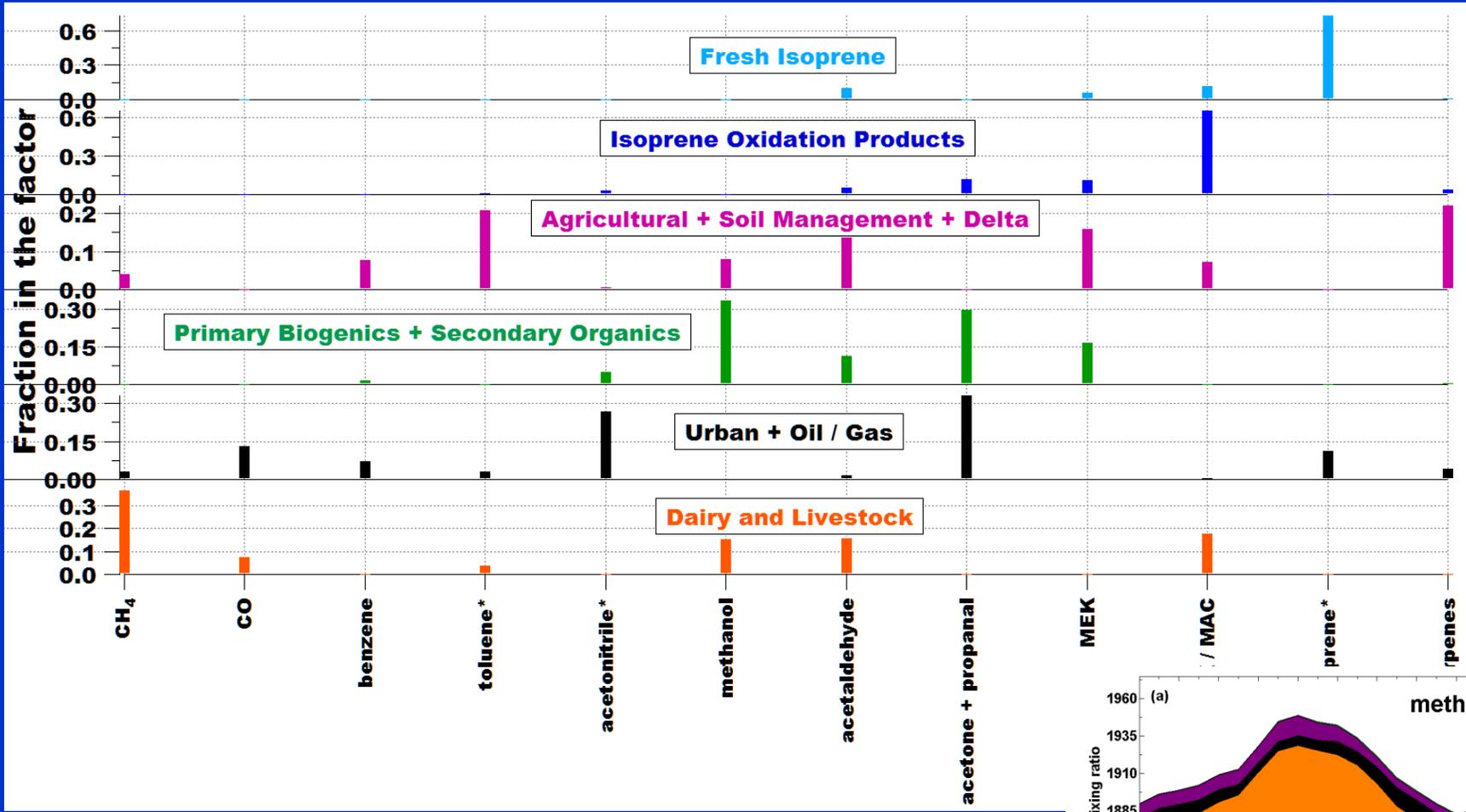


6-factor profile solution

- Urban / O&G source contributions to CH<sub>4</sub> increases; N<sub>2</sub>O apportionment consistent
- Contributions from biogenic / photochemical sources stronger
- Splitting of contributions to collocated sources

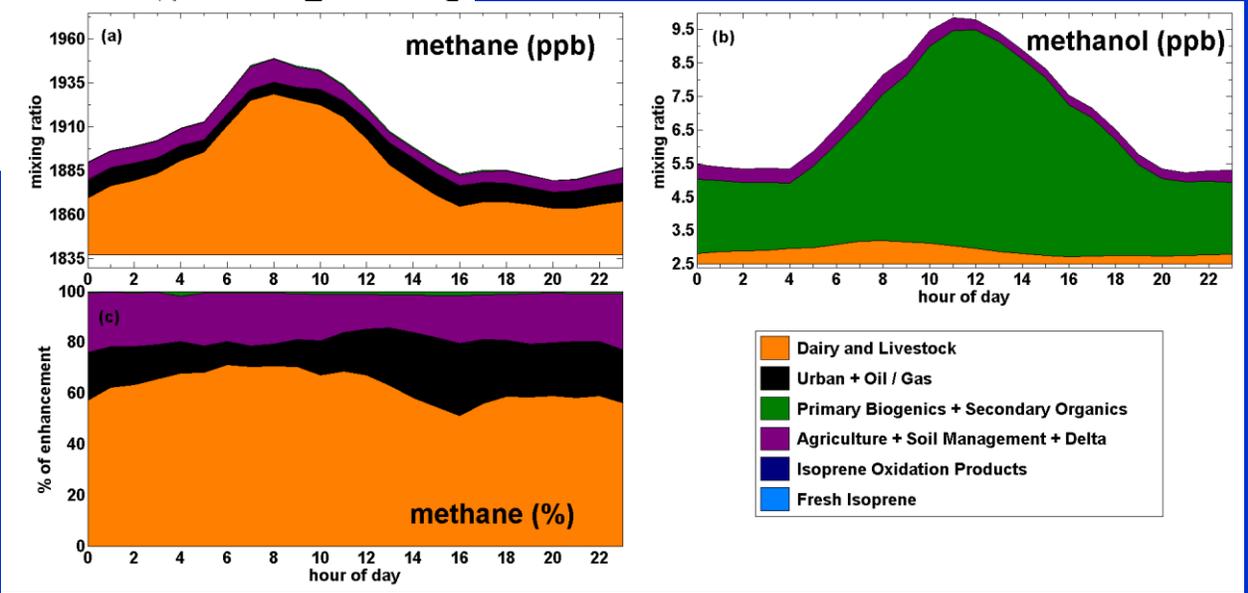


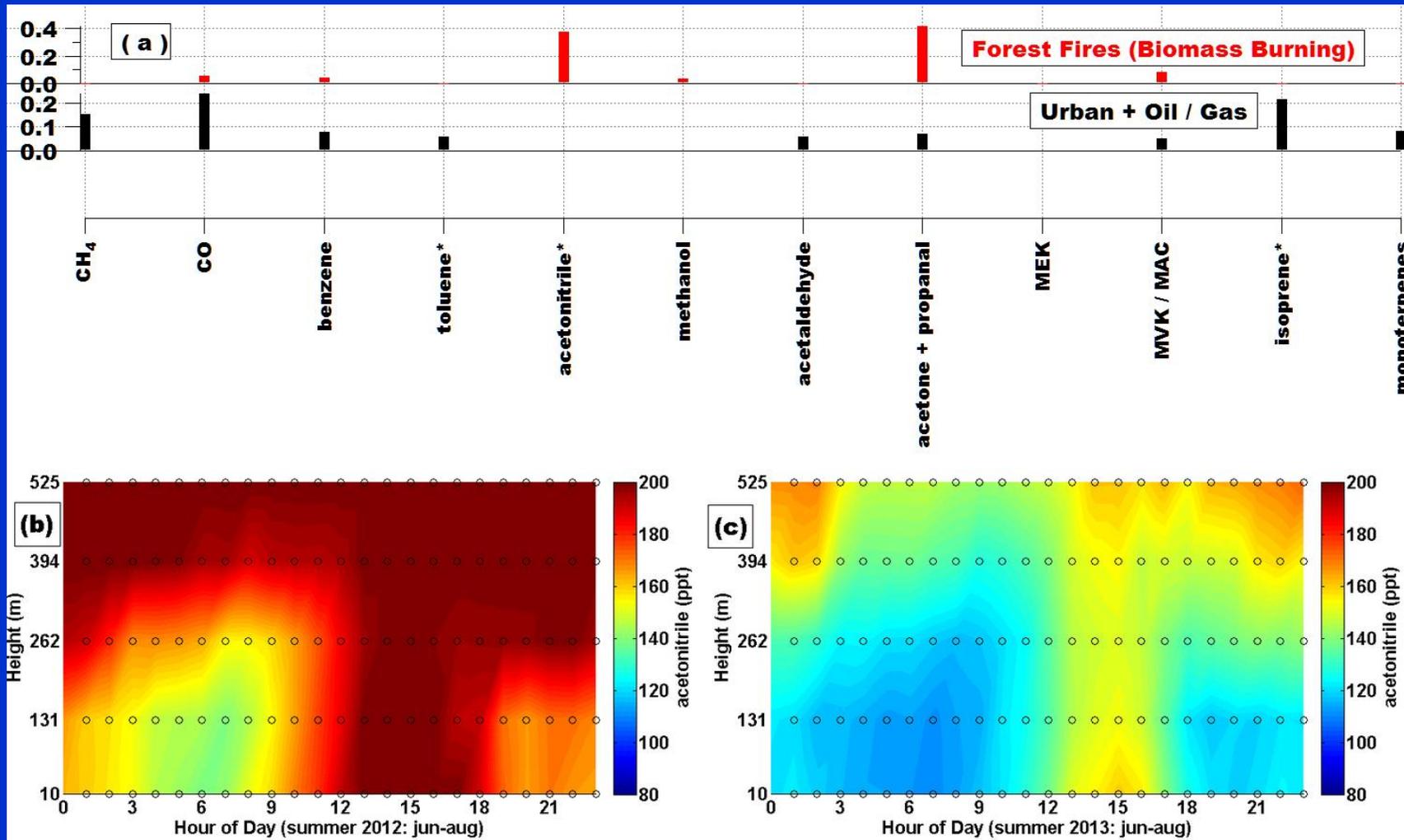
# Summer 2012 (Jun 15 – Aug 31)



## PMF source-apportioned diurnal distribution plots

6-factor profile solution



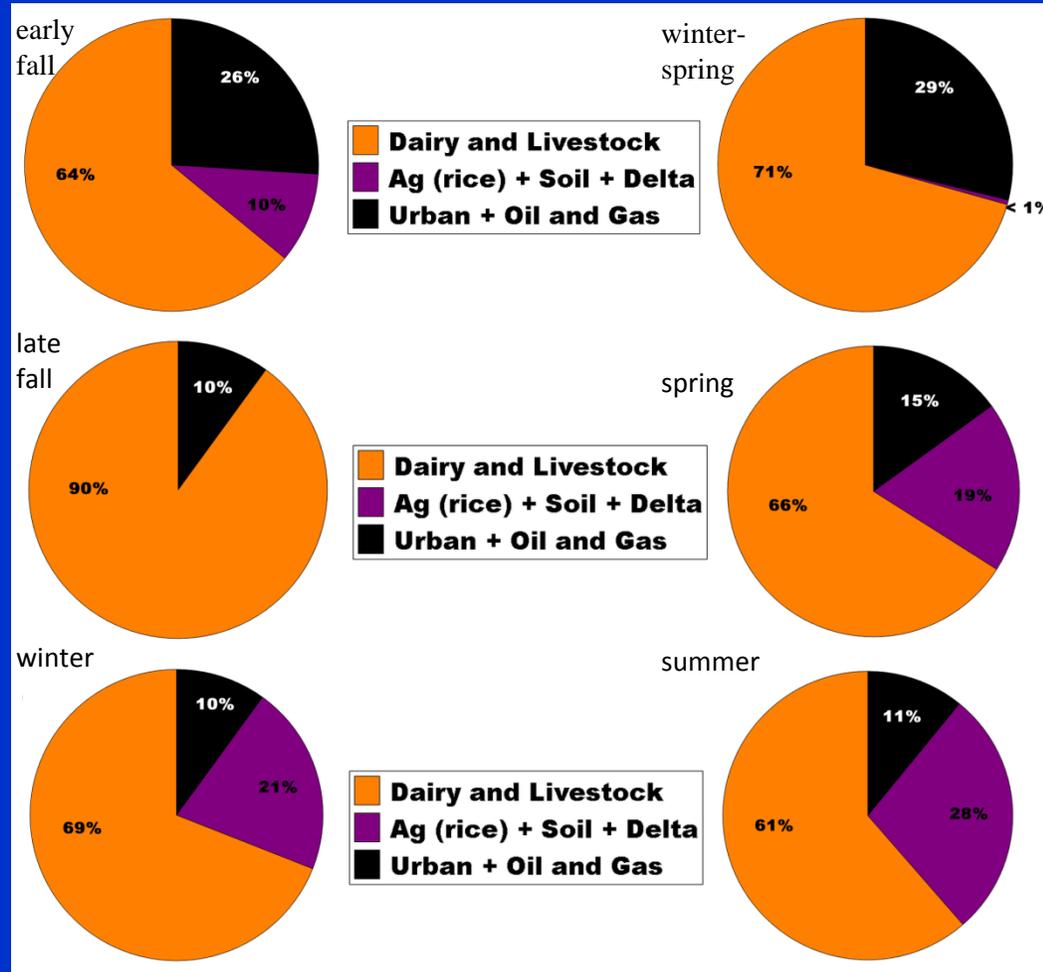


**PMF apportions and produces a Forest Fire factor in an extended 7-factor solution in summer 2012**

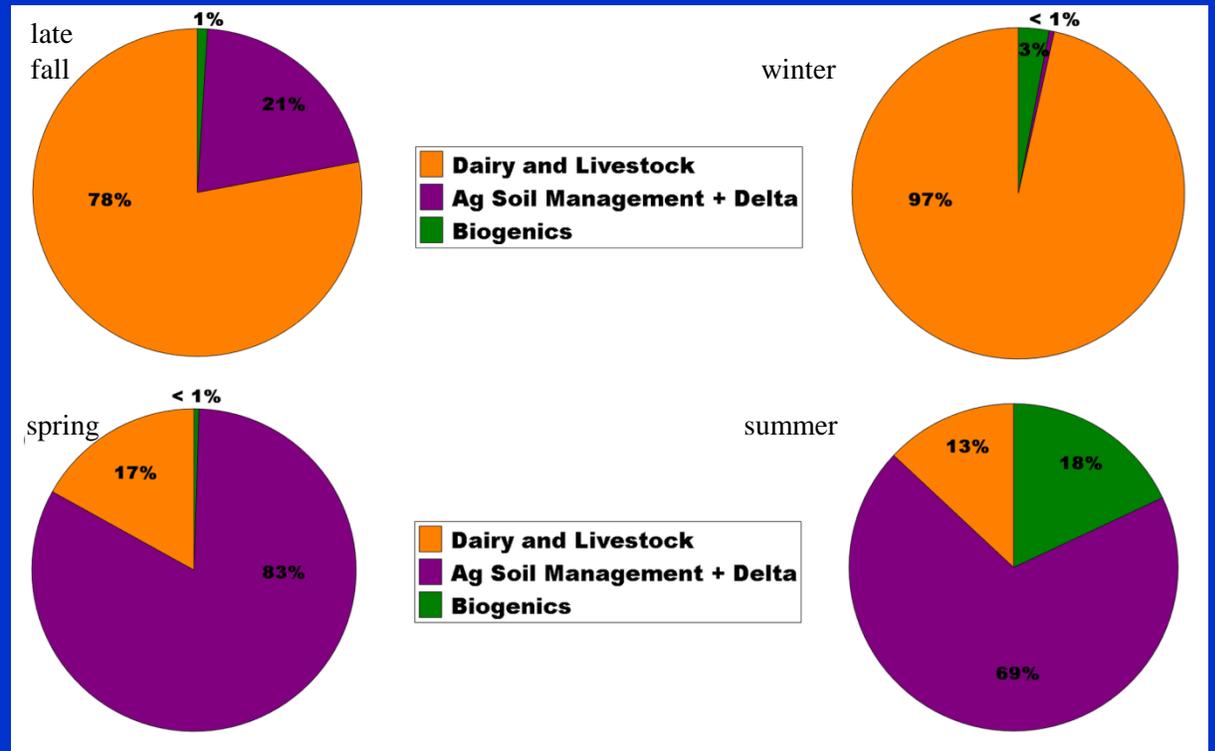
# PMF RESULTS

## Seasonal distributions of GHG sources

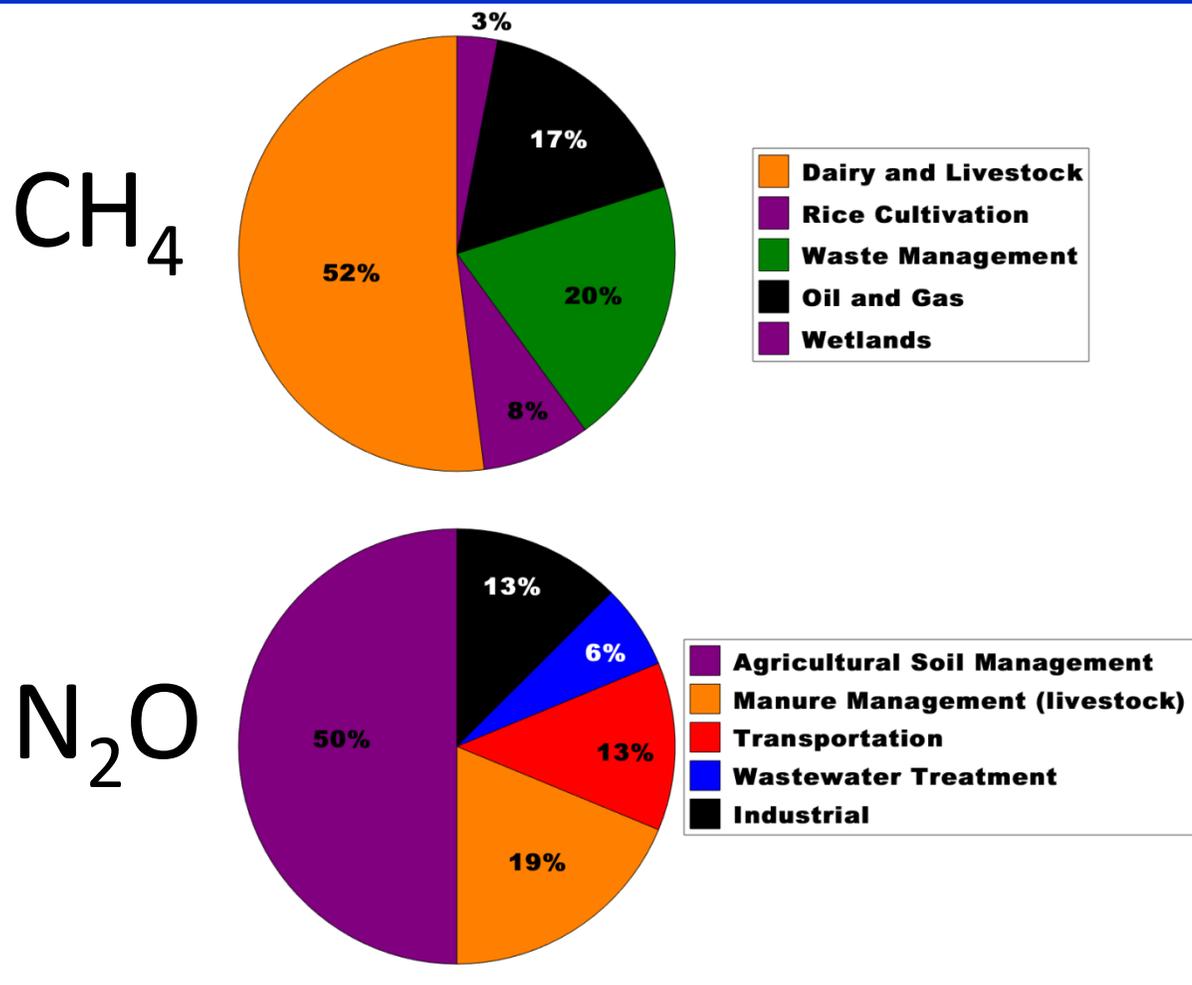
**PMF-based CH<sub>4</sub> enhancement % distribution in different seasons**



**PMF-based N<sub>2</sub>O enhancement % distribution in different seasons**



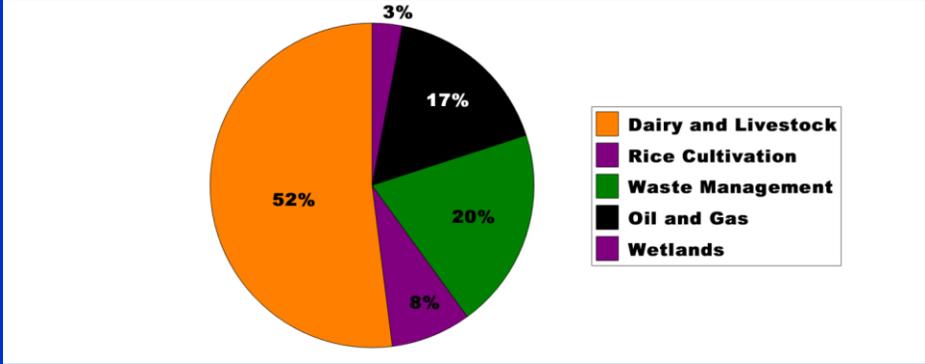
# Annual inventory source distributions specifically for regions 3, 7 and 8, to compare with PMF and inversion based source apportionment at WGC



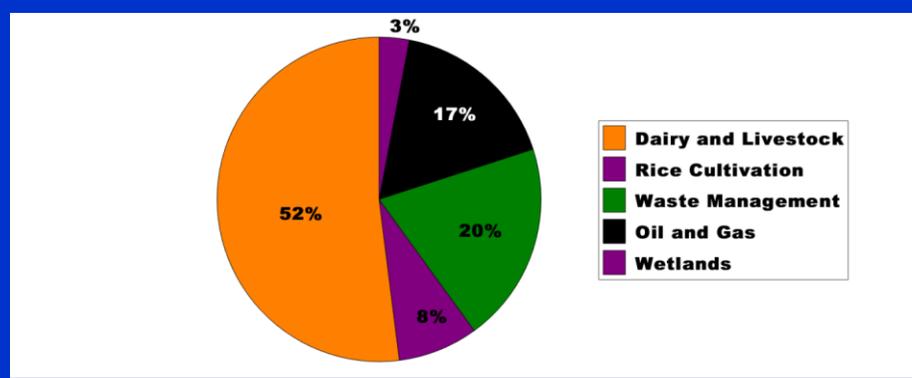
2008 CALGEM CH<sub>4</sub> Sources

2008 EDGAR v4.2 N<sub>2</sub>O Sources

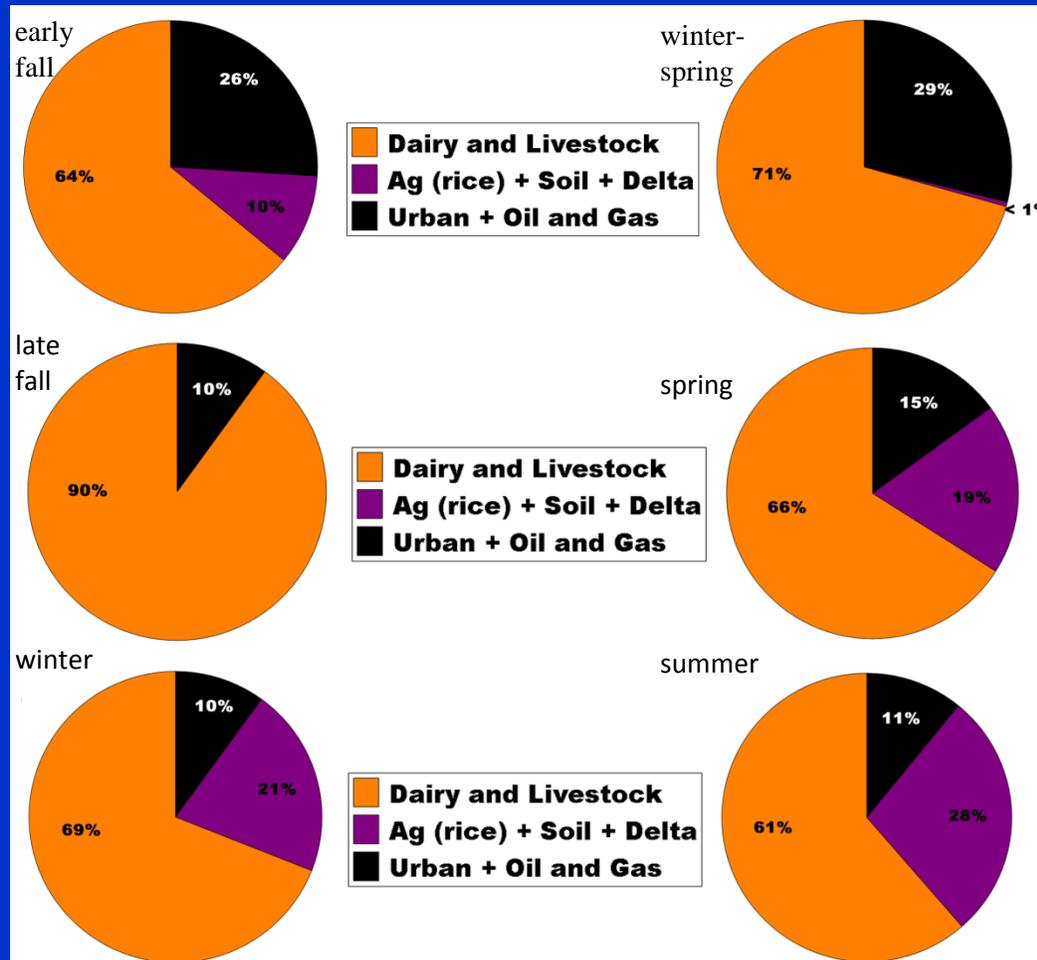
Annual 2008 CALGEM CH<sub>4</sub> Sources



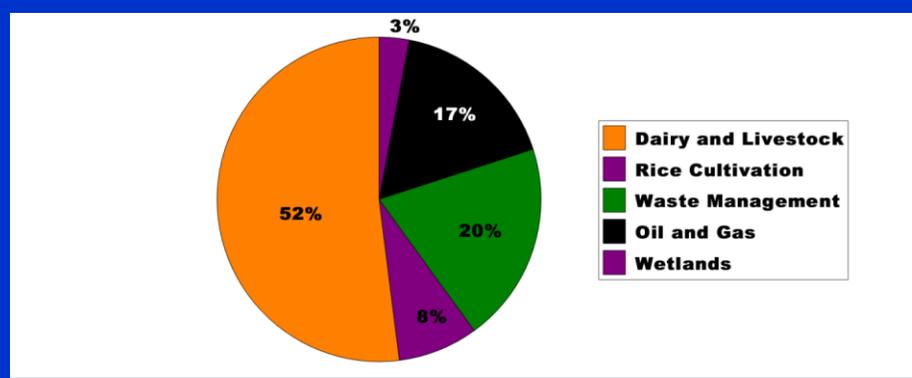
# Annual 2008 CALGEM CH<sub>4</sub> Sources



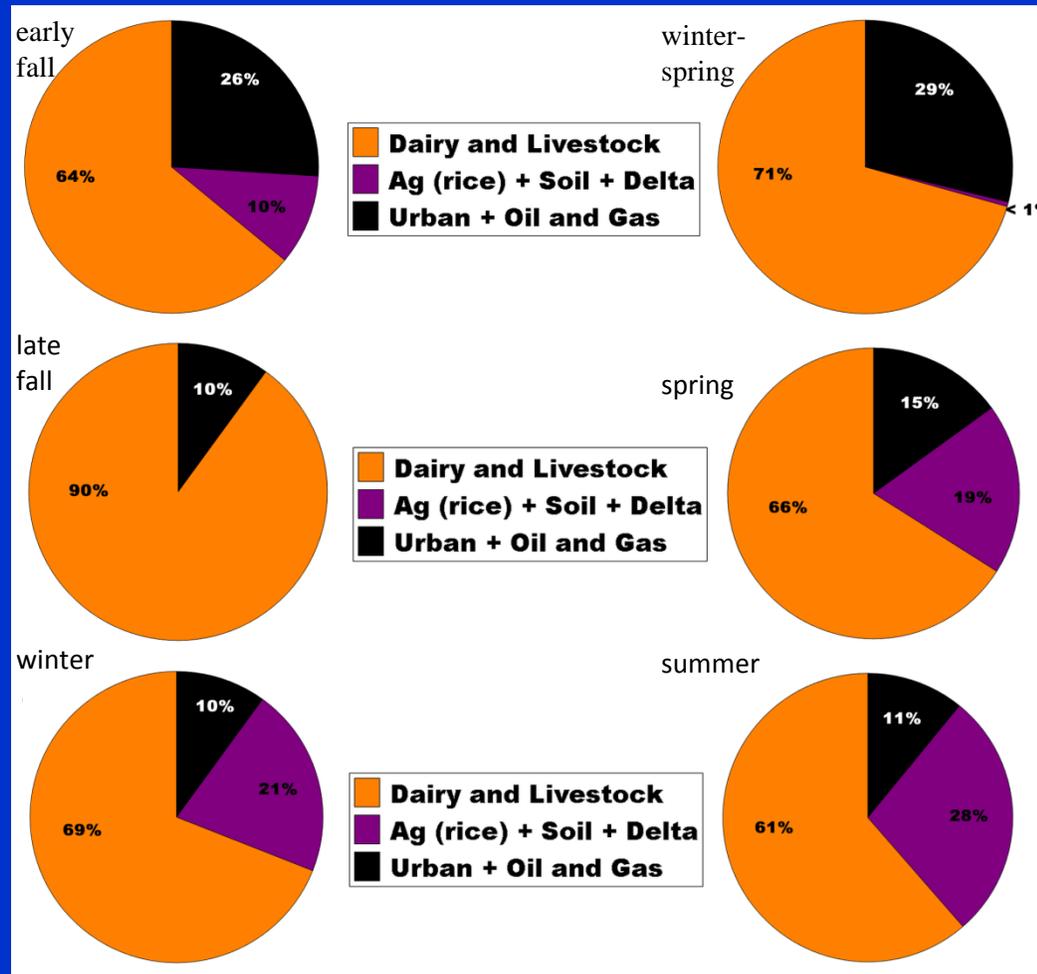
## PMF-derived CH<sub>4</sub> emissions by season



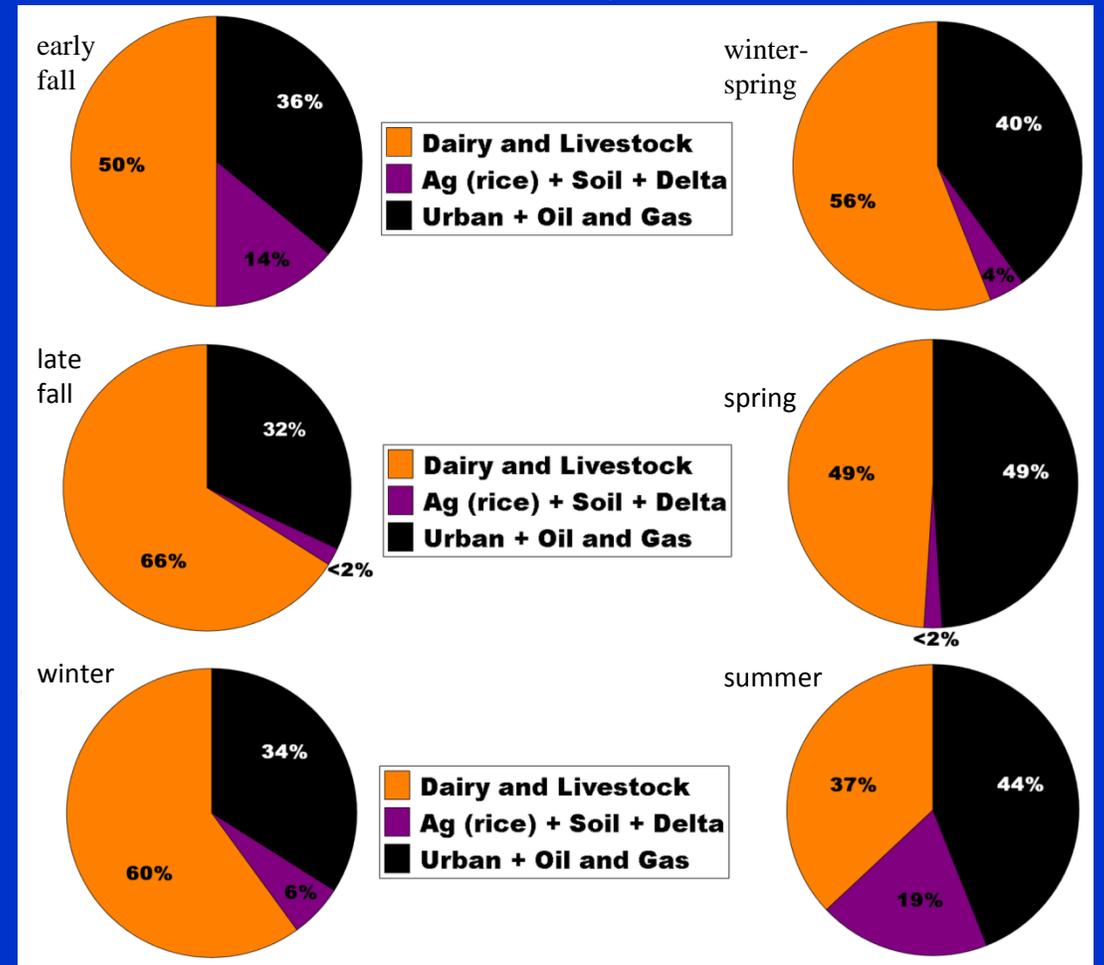
# Annual 2008 CALGEM CH<sub>4</sub> Sources



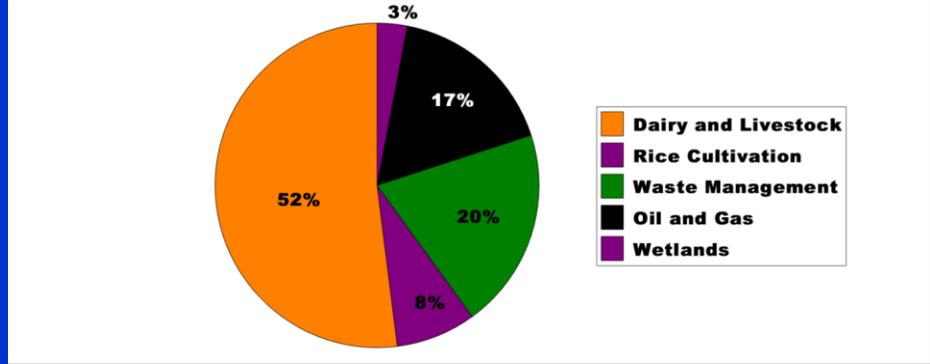
## PMF-derived CH<sub>4</sub> emissions by season



## Bayesian inverse analysis CH<sub>4</sub> emissions by season

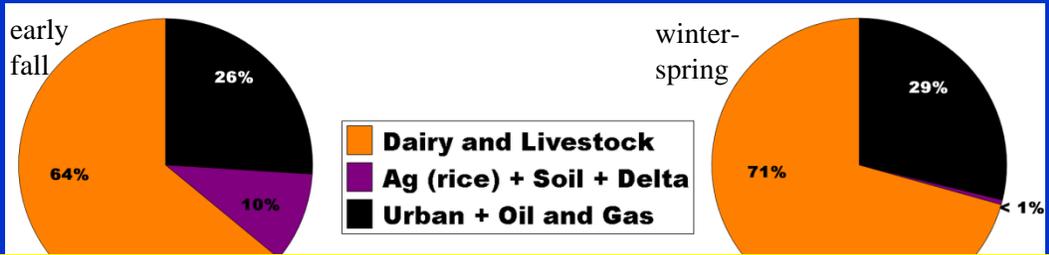


# Annual 2008 CALGEM CH<sub>4</sub> Sources



**Black factor in inverse analysis includes landfills, POTWs, oil and natural gas contributions**

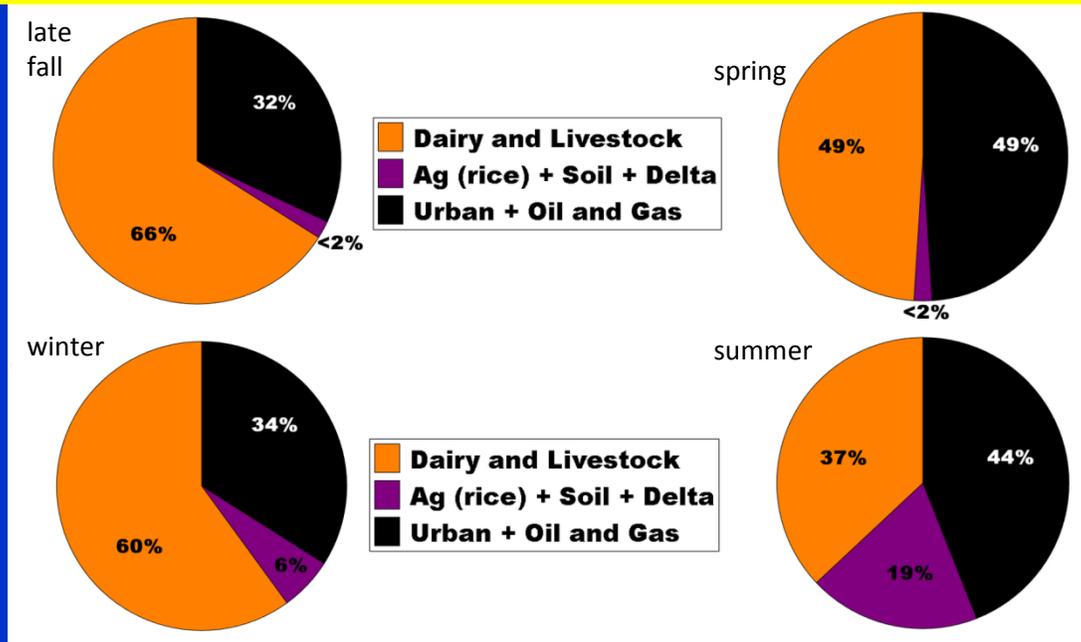
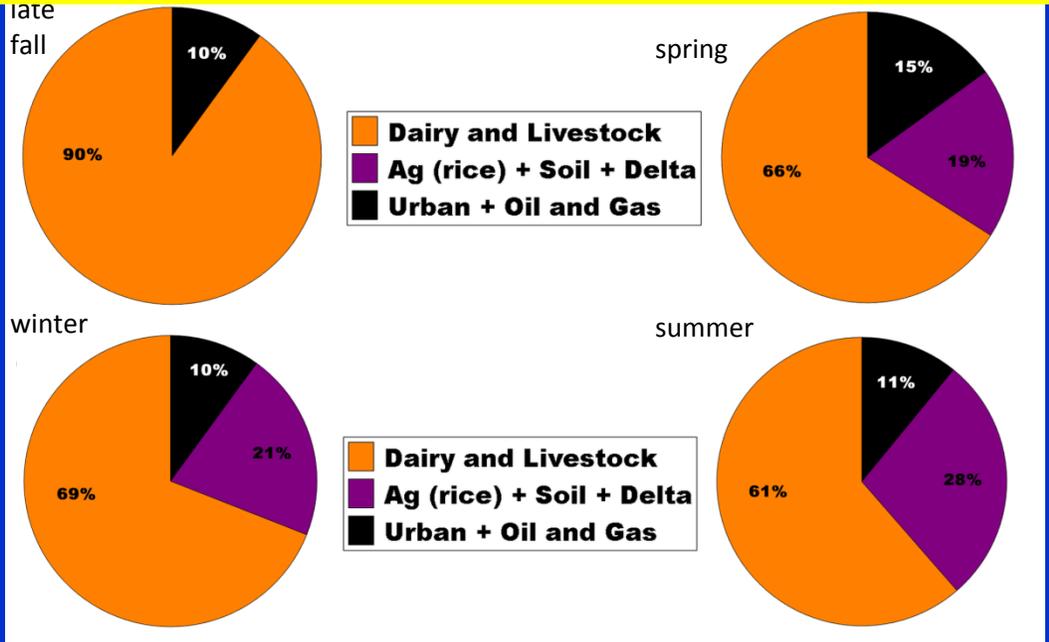
## PMF-derived CH<sub>4</sub> emissions by season



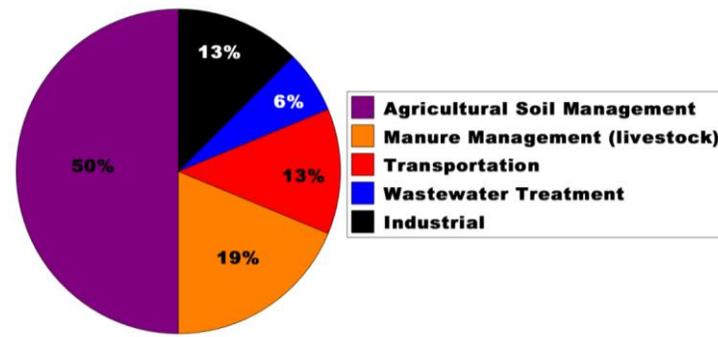
## Bayesian inverse analysis CH<sub>4</sub> emissions by season



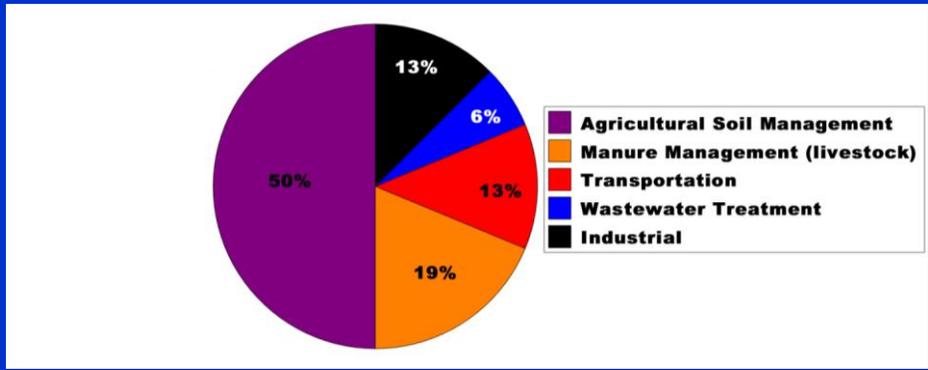
**Differences indicate higher influence of local and near-source emissions in PMF results**



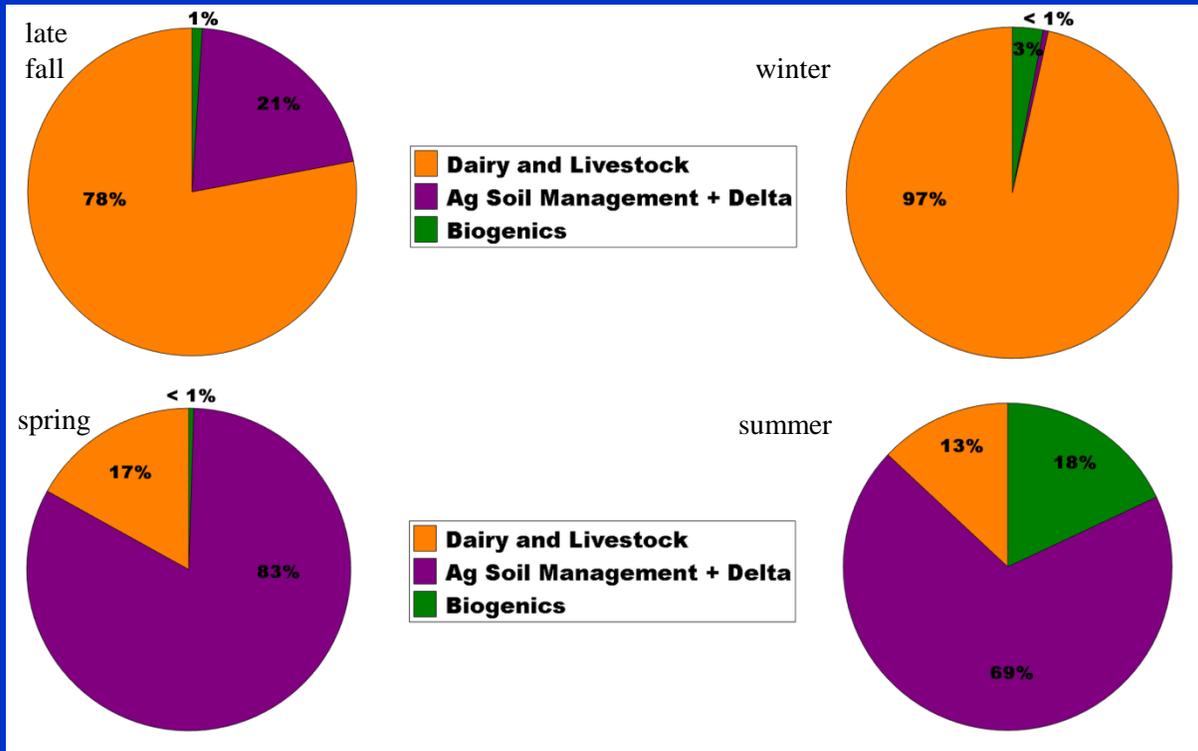
## Annual 2008 EDGAR v4.2 N<sub>2</sub>O Sources



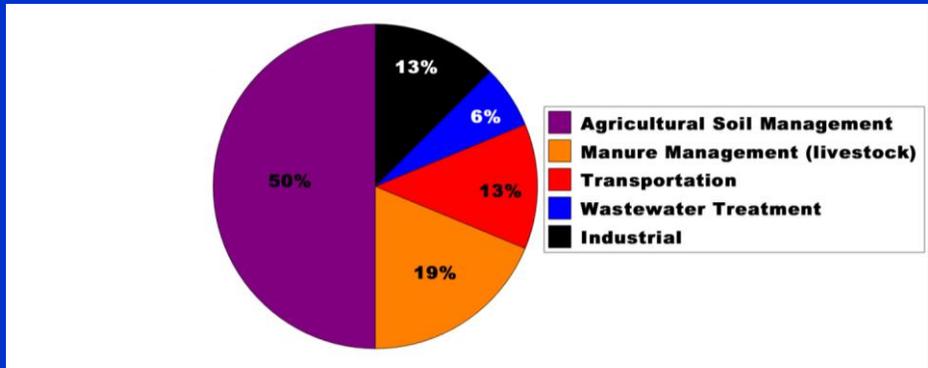
# Annual 2008 EDGAR v4.2 N<sub>2</sub>O Sources



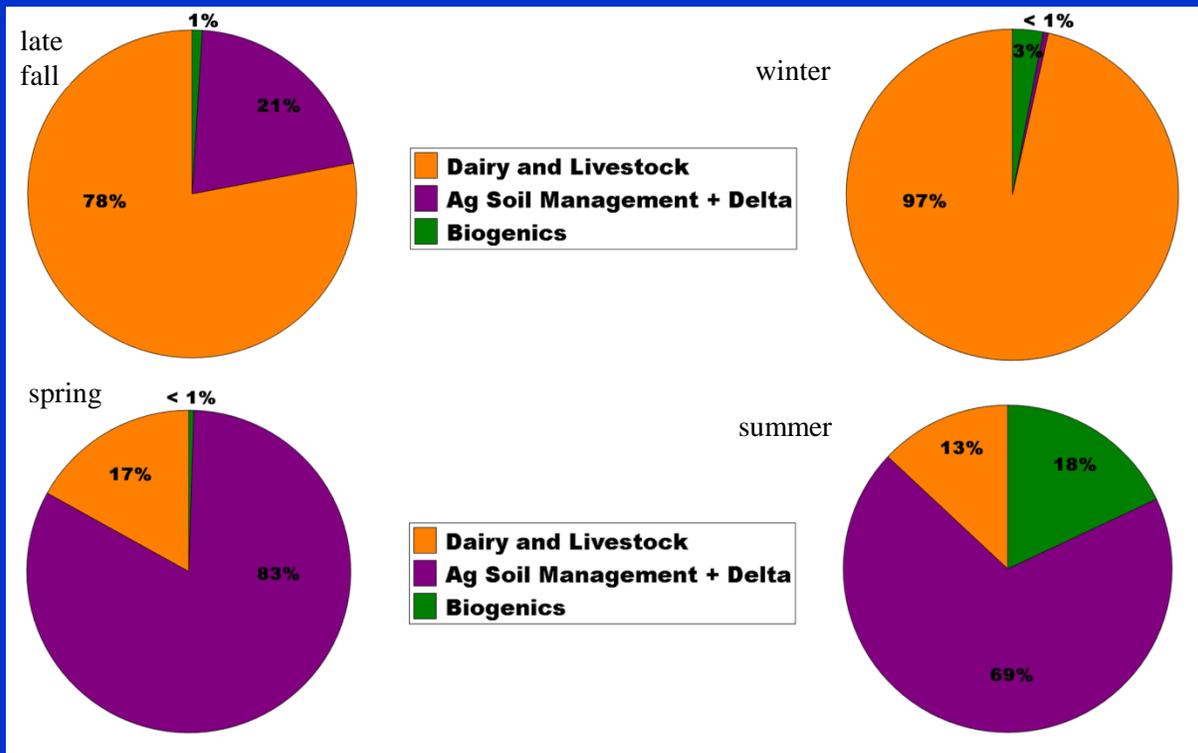
## PMF-derived N<sub>2</sub>O emissions by season



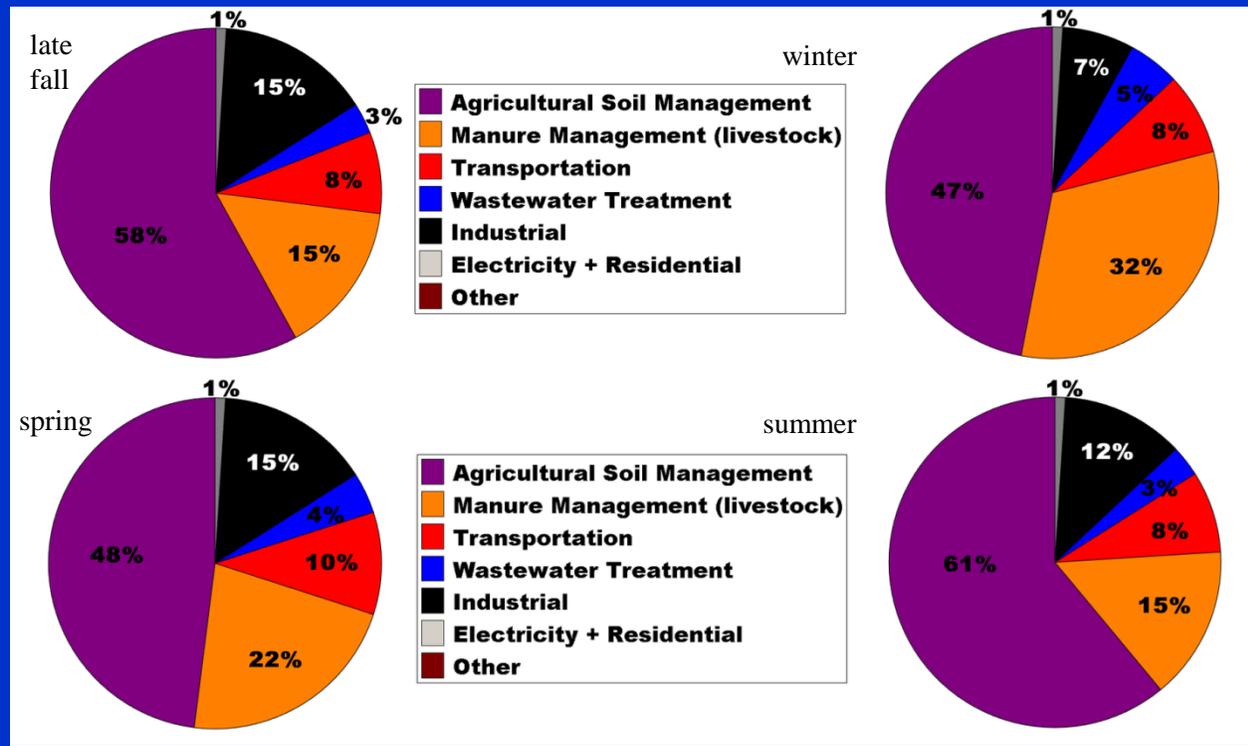
# Annual 2008 EDGAR v4.2 N<sub>2</sub>O Sources



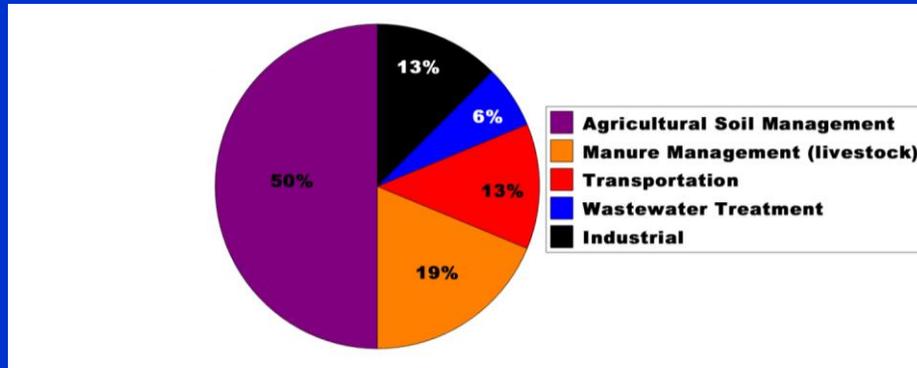
## PMF-derived N<sub>2</sub>O emissions by season



## Bayesian inverse analysis N<sub>2</sub>O emissions by season



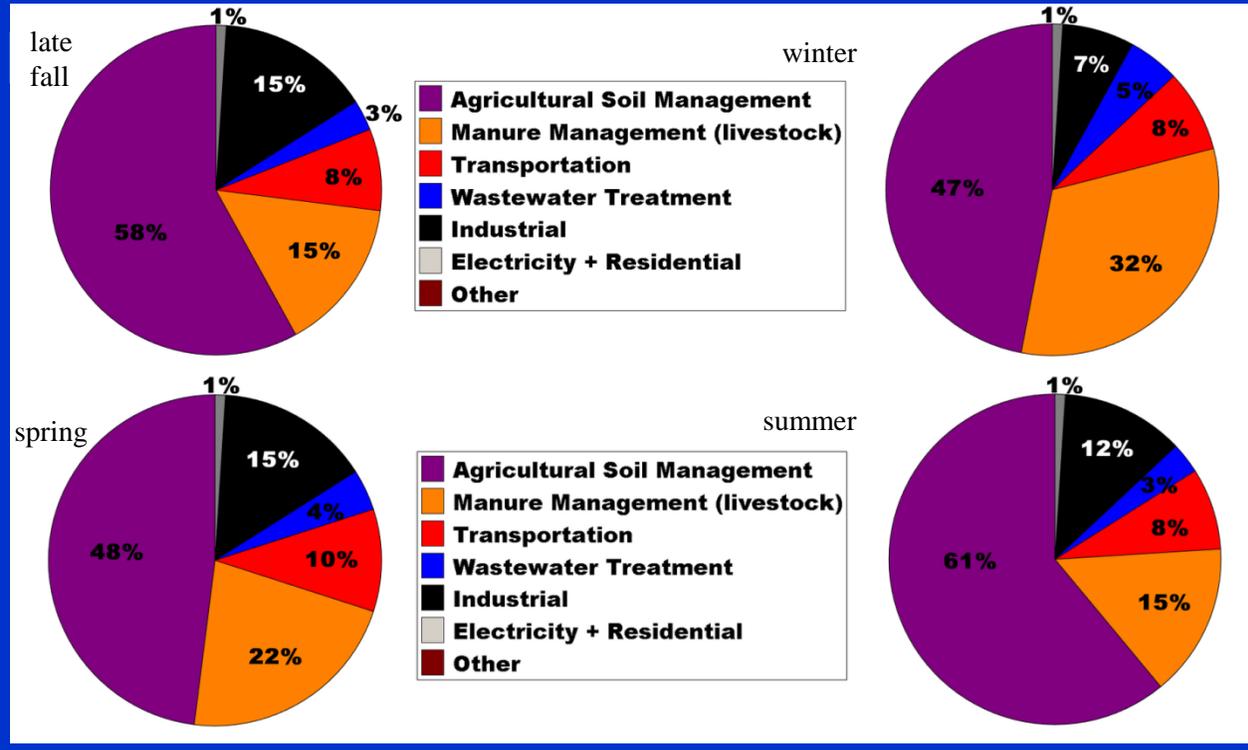
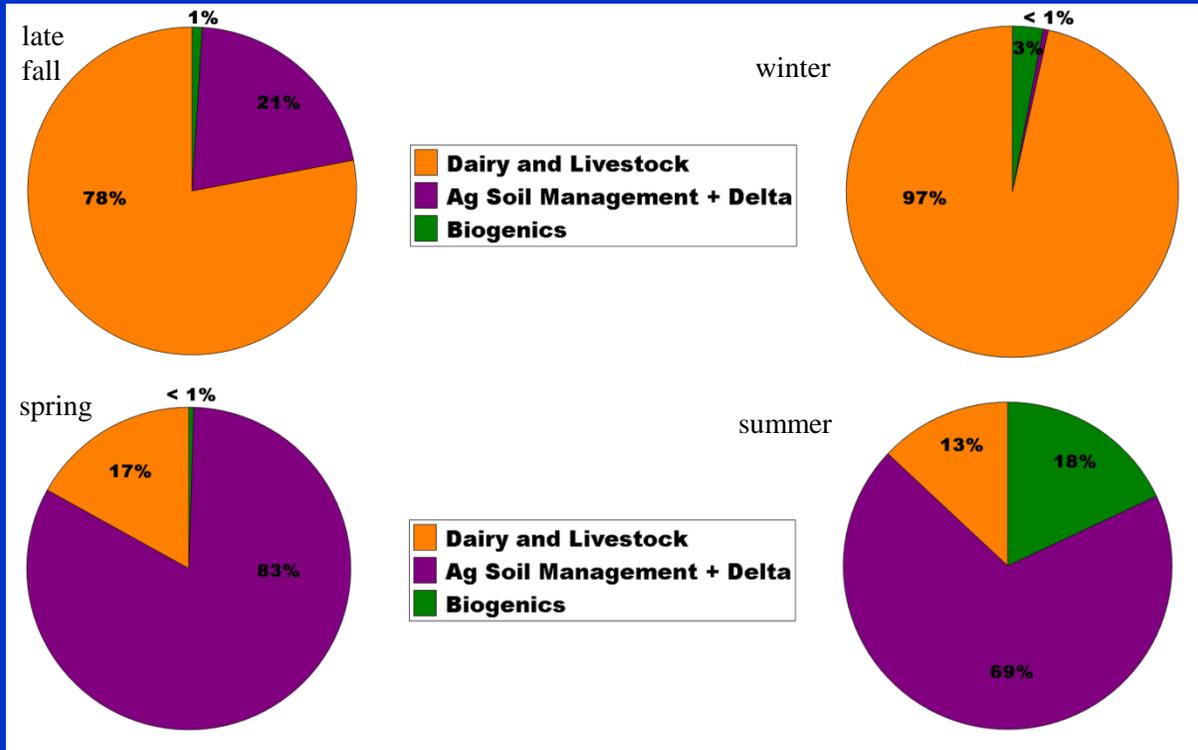
# Annual 2008 EDGAR v4.2 N<sub>2</sub>O Sources



**Differences indicate higher influence of local and near-source emissions in PMF results**

### PMF-derived N<sub>2</sub>O emissions by season

### Bayesian inverse analysis N<sub>2</sub>O emissions by season



# Conclusions

Livestock are the largest regional source of  $\text{CH}_4$  (max % contribution in late fall/winter when other sources are smaller).

A second highly seasonal source of  $\text{CH}_4$  is microbially-mediated with temperature-dependent emissions from 'agriculture + soil management + delta' wetland ecosystems.

A third 'urban and oil / gas source', containing  $\text{CH}_4$  but no  $\text{N}_2\text{O}$ , is from an aggregation of upwind sources in the SF Bay Area and the Rio Vista natural gas fields.

Only two significant source categories of  $\text{N}_2\text{O}$  are discerned from the PMF analysis – an 'agriculture + soil management + delta' source containing microbe-driven soil emissions of  $\text{N}_2\text{O}$  resulting from fertilizer application (dominant in spring and summer) and a dairy / livestock manure-management source (dominant in late fall and winter).

Seasonality has a strong influence on  $\text{CH}_4$  and  $\text{N}_2\text{O}$  biological emissions and this phenomenon is clearly observed using top-down measurement and inversion modeling approaches.

# Recommendations for future research

Two conclusions from this work suggest the need for further research to improve the CARB GHG emission inventory

1) The seasonality of major sources of CH<sub>4</sub> and N<sub>2</sub>O from the agricultural sector:

The seasonal variation of emissions observed for CH<sub>4</sub> and N<sub>2</sub>O from biologically mediated sources has implications for how data from short-term studies should be used for inventory verification.

A network of long-term ground based measurements of concentrations and fluxes, combined with modeling, should be developed to quantify CH<sub>4</sub> and N<sub>2</sub>O seasonality from specific source categories. Projects funded by CARB that share these goals are already underway.

2) The magnitude of N<sub>2</sub>O from the transportation sector:

There was a lack of N<sub>2</sub>O associated with the “urban” source factor in all seasonal PMF analyses. This is inconsistent with the current inventory and should be investigated further. Again, this is a topic that CARB is already working on.

Finally, our work has developed a baseline understanding of how to use VOC's as GHG source tracers in top down PMF analysis, and we recommend that ARB invest in further application and development of this approach. A critical next step would be to include more VOC tracers that could serve as source markers, specifically adding a suite of alkanes as tracers of fossil fuel derived sources.

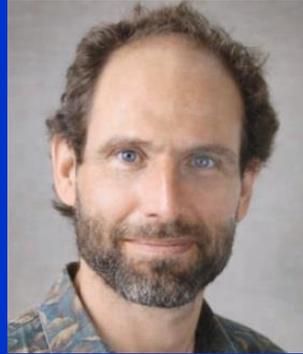
# Our Team



**Allen  
Goldstein**  
*UC  
Berkeley*



**Abhinav  
Guha**  
*UC  
Berkeley*



**Marc  
Fischer**  
*LBNL  
Berkeley*



**Seongeun  
Jeong**  
*LBNL  
Berkeley*



**Pawel  
Misztal**  
*UC  
Berkeley*



**Robin  
Weber**  
*UC  
Berkeley*

**NOAA  
researchers  
(Andrews et al.)**

**Special  
thanks to  
Dave  
Bush**