

Apportionment of fine particulate carbon to source types in the rural U.S.

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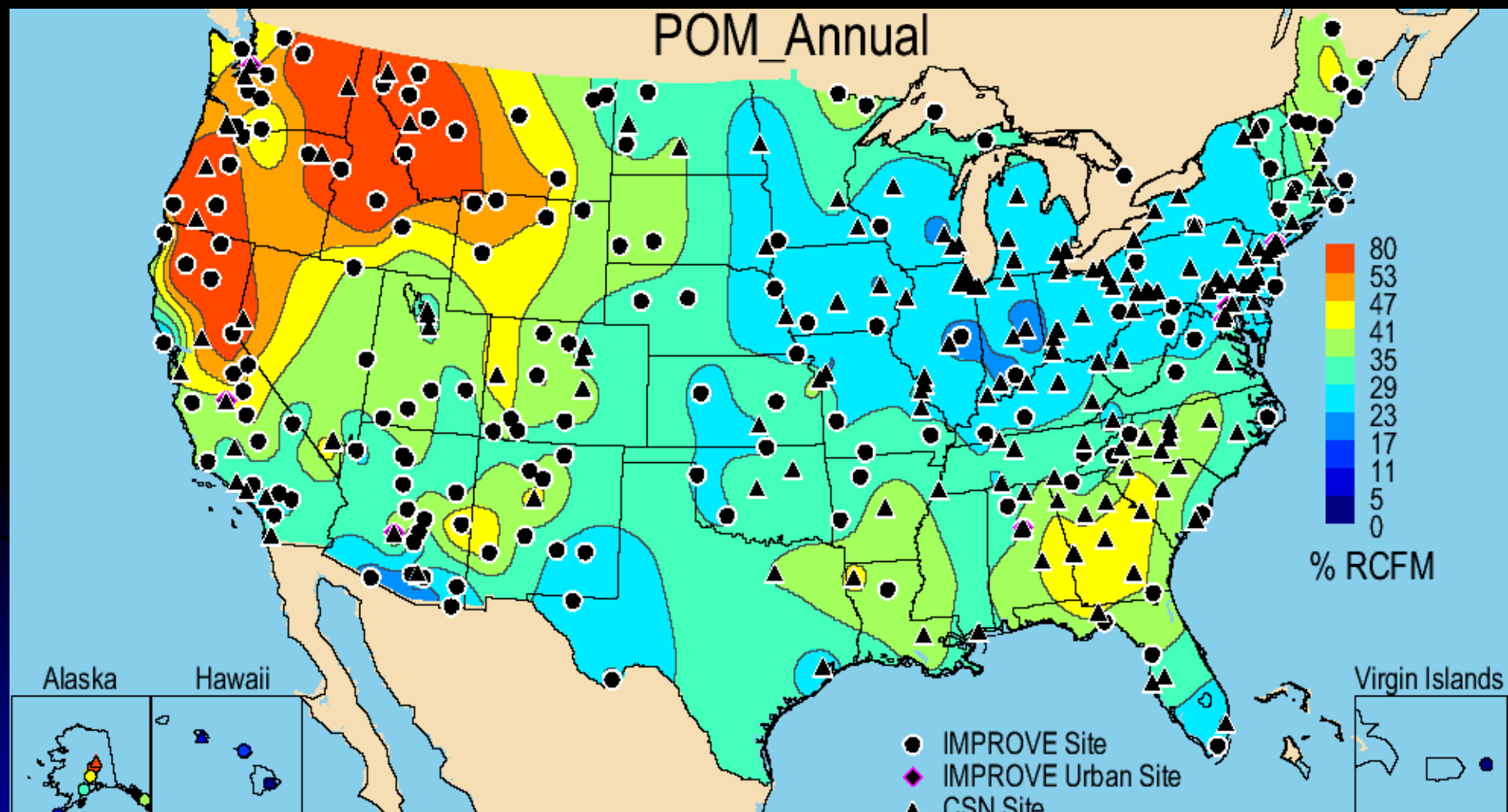
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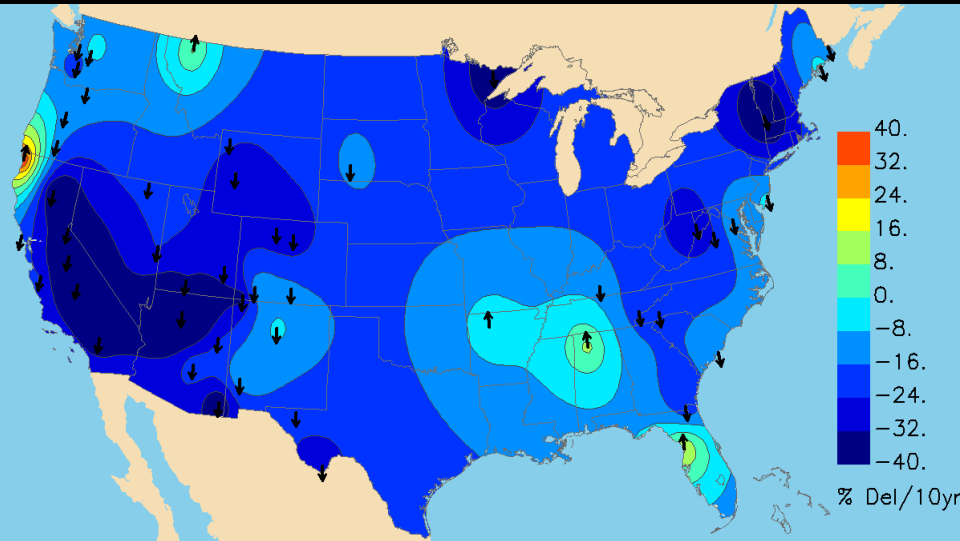
Funded by the National Park Service and Joint Fire Science Program (JFSP)

Fine Particulate Organic Matter (2005-08)

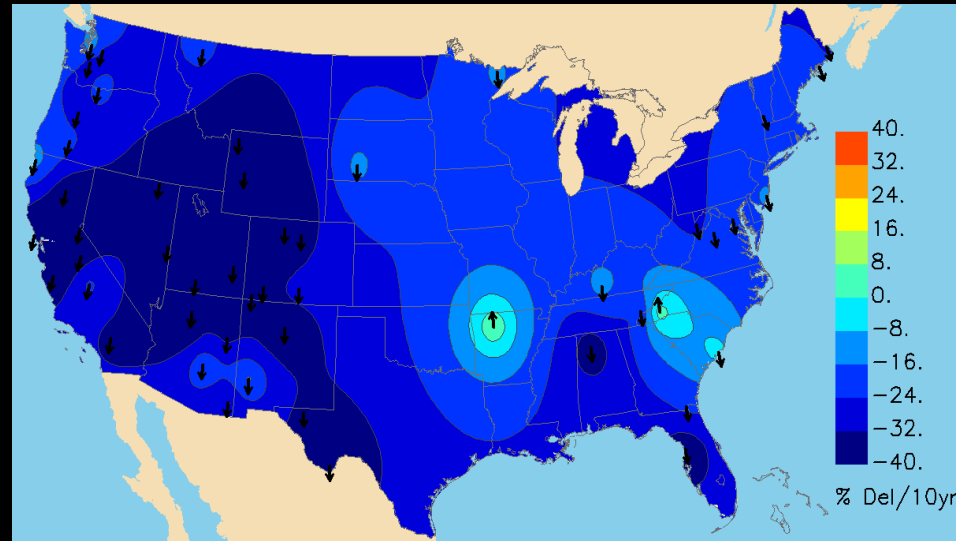


TC Seasonal Trends 1996-06

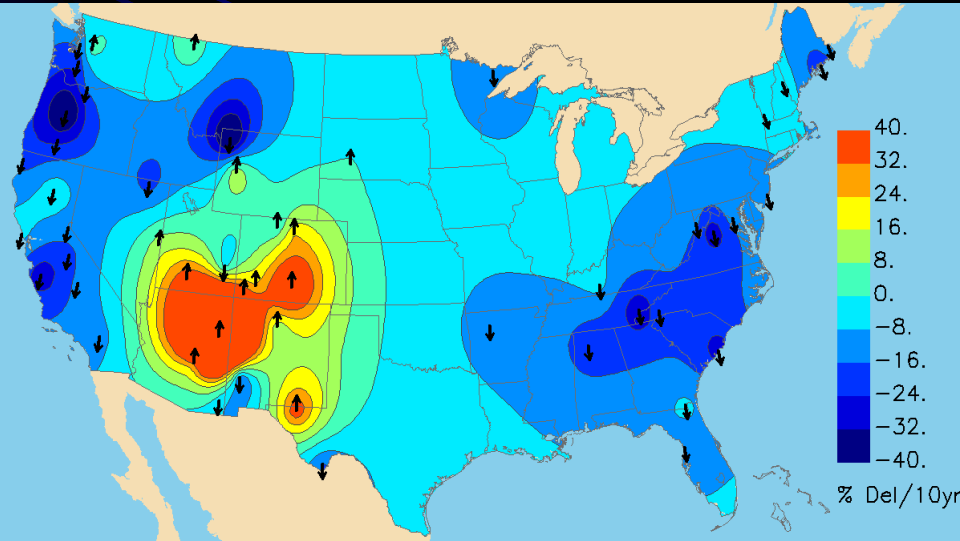
Winter



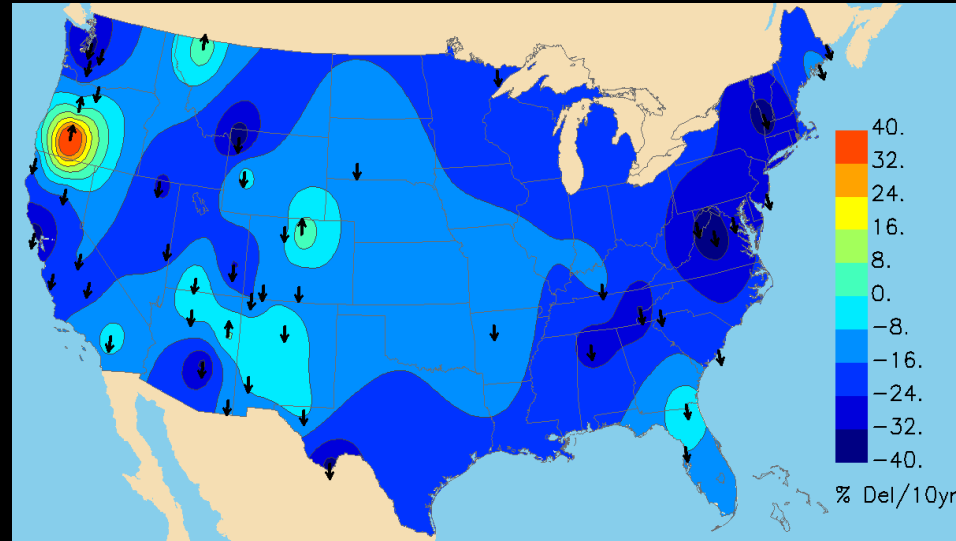
Spring



Summer

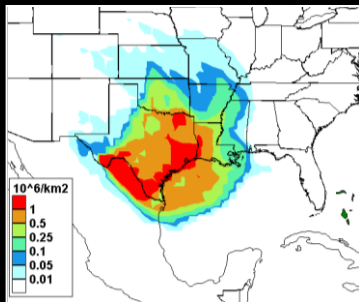


Fall

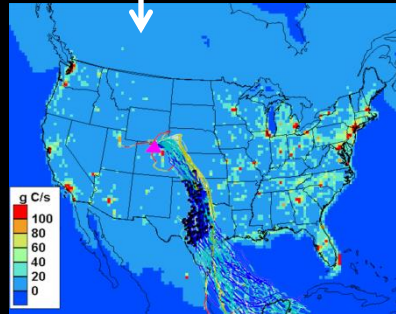


Semi-Quantitative TC Source Type Apportionment

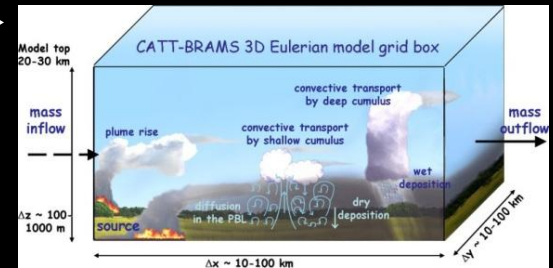
Qualitative Trajectory Analyses



Residence Time



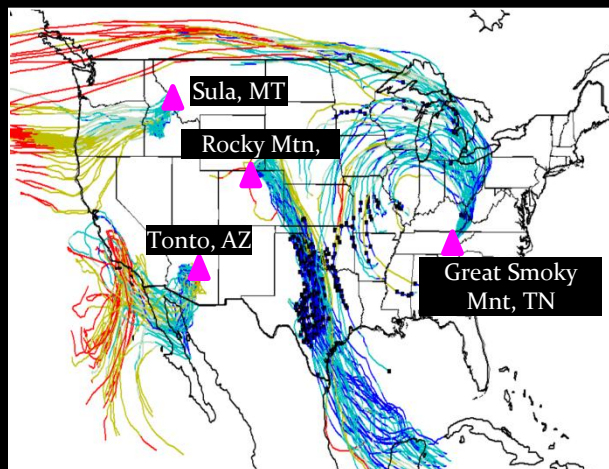
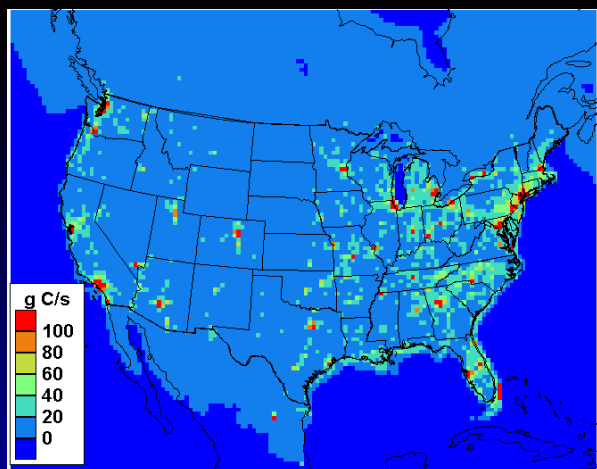
Quantitative Chemical Transport Models



- Bridge the gap between qualitative back trajectory analyses and quantitative chemical transport models
 - Incorporate emission fields and simple kinetics to separate contributions from different source types and regions to measured TC
 - Maintain the simplicity and efficiency of back trajectory methods
 - Incorporate known information and expert judgment
 - Diagnostic data interpretation tool

“Chemical” Transport Model to Apportion TC

- Simple chemical transport model using Capita Monte Carlo model particle dispersion model and back airmass histories
- Primary and secondary contributions from fire, mobile, vegetation, point, area and other sources simulated
- Model was fitted to TC from 162 IMPROVE sites in 2008



- Wet Removal
- Dry Removal
- First order SOA formation
- Optimized Rate Coeff.

- WRAP 2002 emission
- NCAR fire emissions

- Six-day air mass histories

- Kinetics

Conservation of mass along each particle trajectory

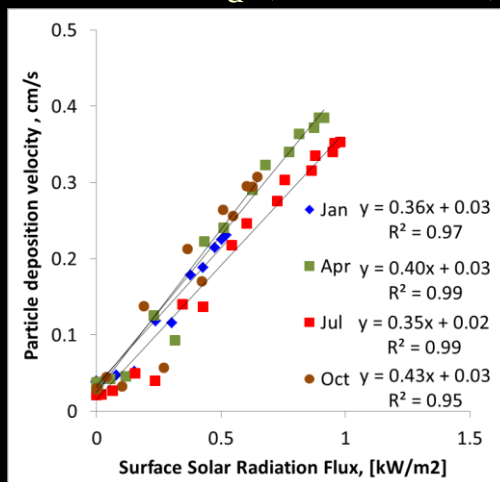
$$\frac{d}{dt} \left(\frac{C_i}{TC} \right) + \left(\frac{C_i}{TC} \right) \left(\frac{dTC}{dt} \right) = \left(\frac{C_i}{TC} \right) \left(\frac{dC_i}{C_i} - \frac{dTC}{TC} \right) + \left(\frac{C_i}{TC} \right) \left(\frac{dC_i}{C_i} - \frac{dTC}{TC} \right)$$

- TC is the particulate carbon mixing ratio
- VOC_i is an individual or class of VOC mixing ratio
- $k_{i,d}$, $k_{i,w}$, and $k_{i,t}$ are VOC gas to particulate carbon transformation, dry deposition, and wet deposition rate coefficients, respectively
- $k_{d,TC}$ and $k_{w,TC}$ are particulate carbon dry and wet deposition rate coefficients, respectively.

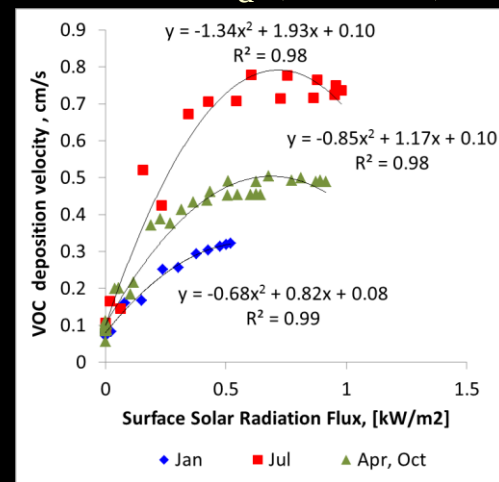
Rate Coefficients

- Particle and VOC dry V_d was parameterized by solar radiation flux
- Function form derived by regression analysis, scaled for best fit to measured TC

Particle V_d (CASTNet)



VOC V_d (CAMx)



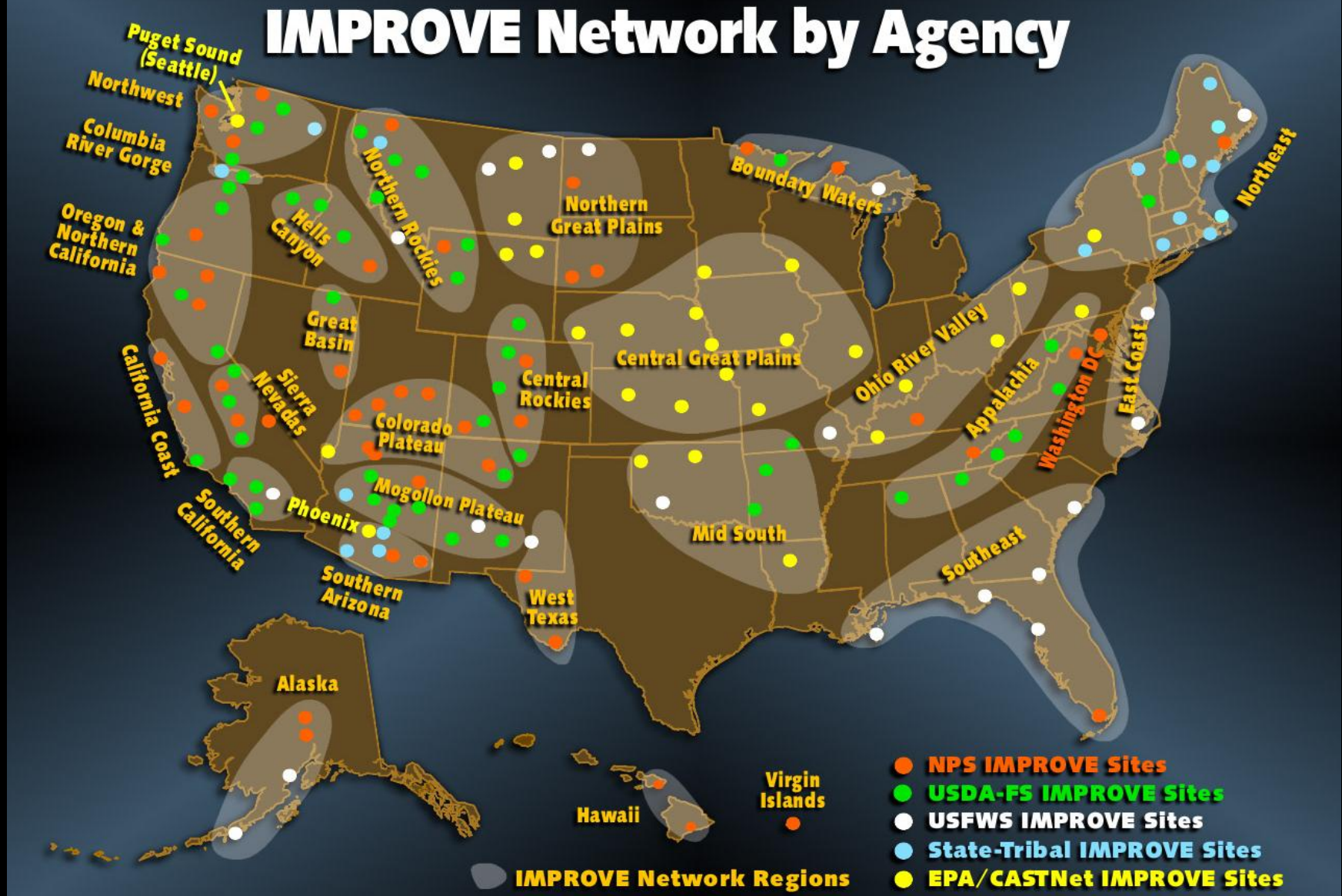
- Wet deposition

- Washout ratio (W) - The ratio of the concentration of the species in the precipitation to its concentration in the air
- Particle $W = 10^5$ (Bidleman, 1988)
- VOC $W = 3.5 \times 10^4$ (estimated from CAMx model simulation)

- SOA Formation

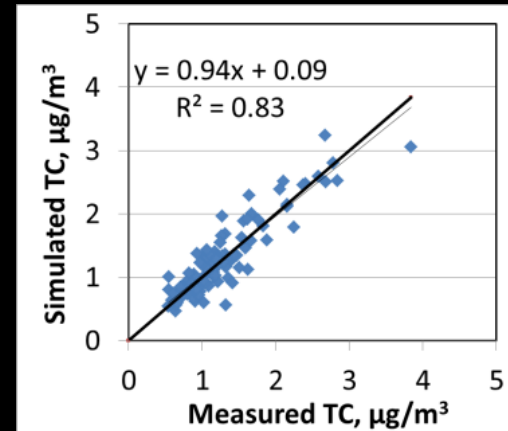
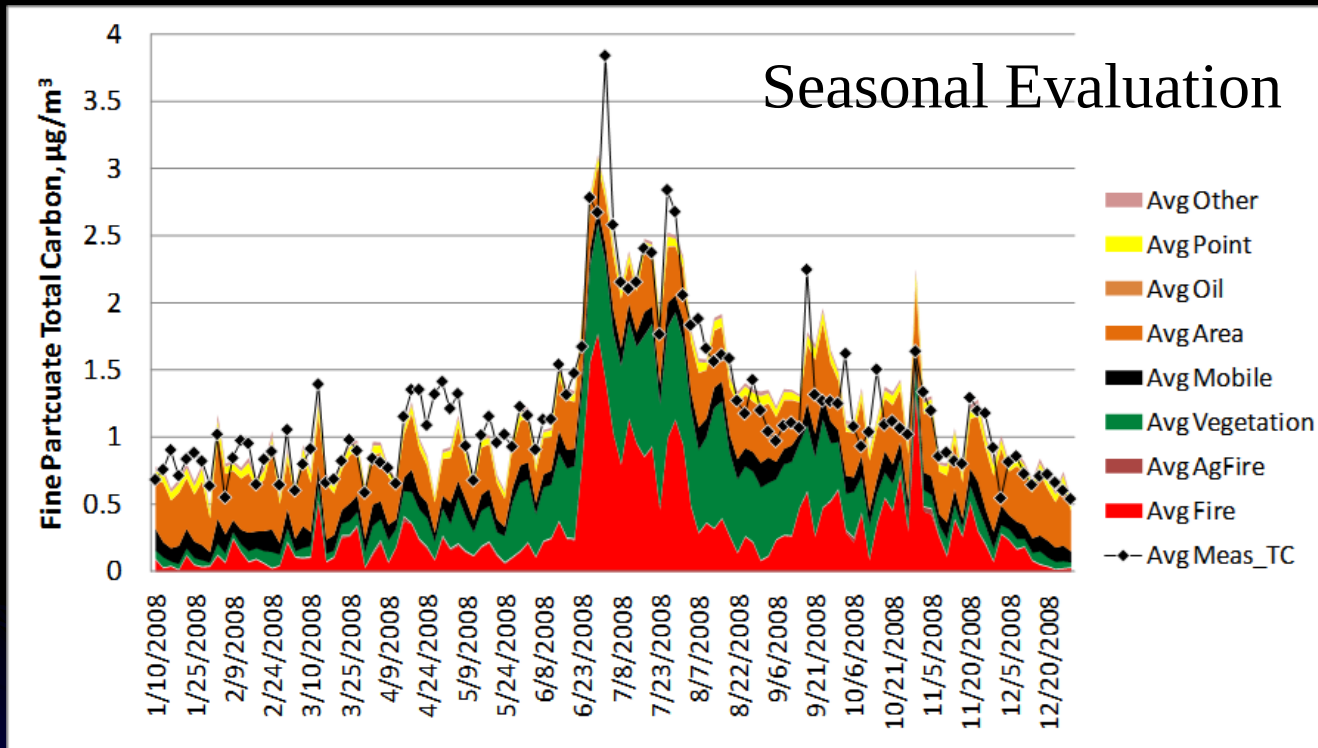
- Pseudo linear VOC transformation rate coefficients for high and less class of reactive VOC's and isoprene
- Rate coefficients were made a function of solar radiation and optimized by obtaining a best fit to 2008 IMPROVE TC concentration and measured SOA/ OC (Kleindienst et al., 2007; Lewandowski et al., 2008)

IMPROVE Network by Agency



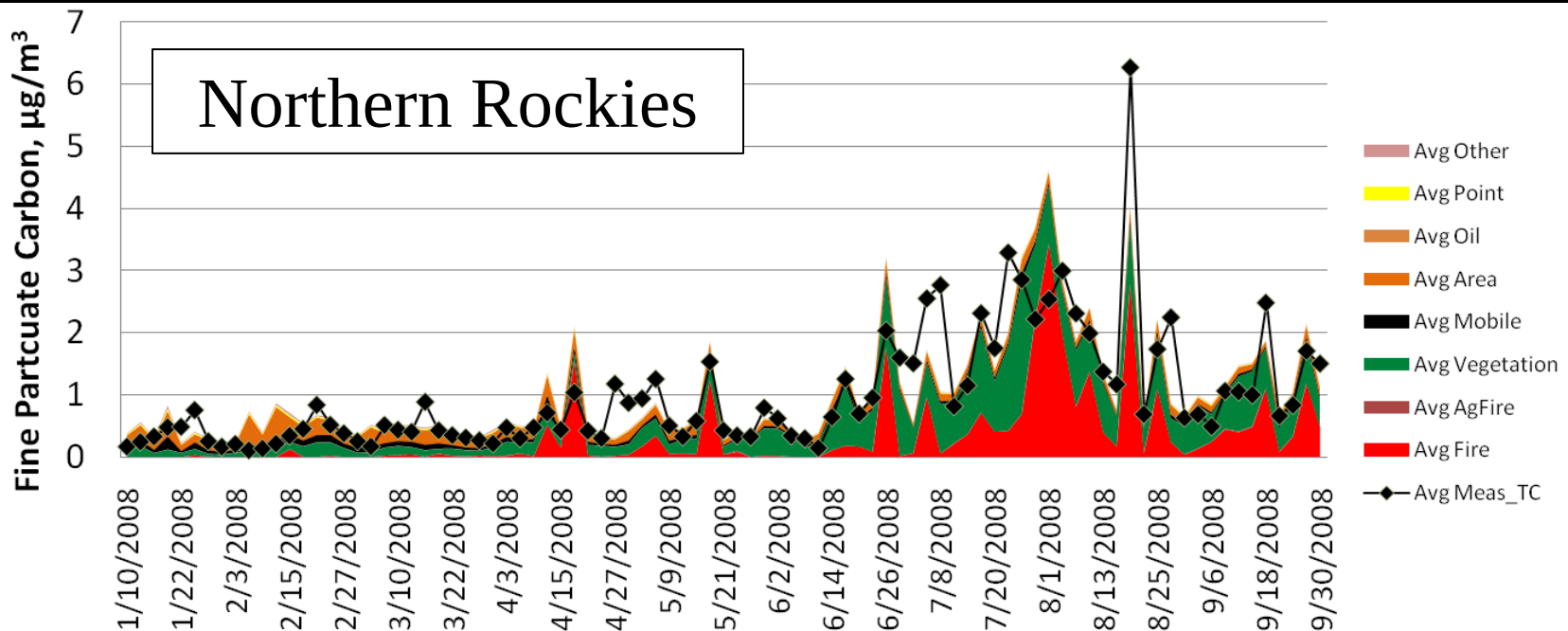
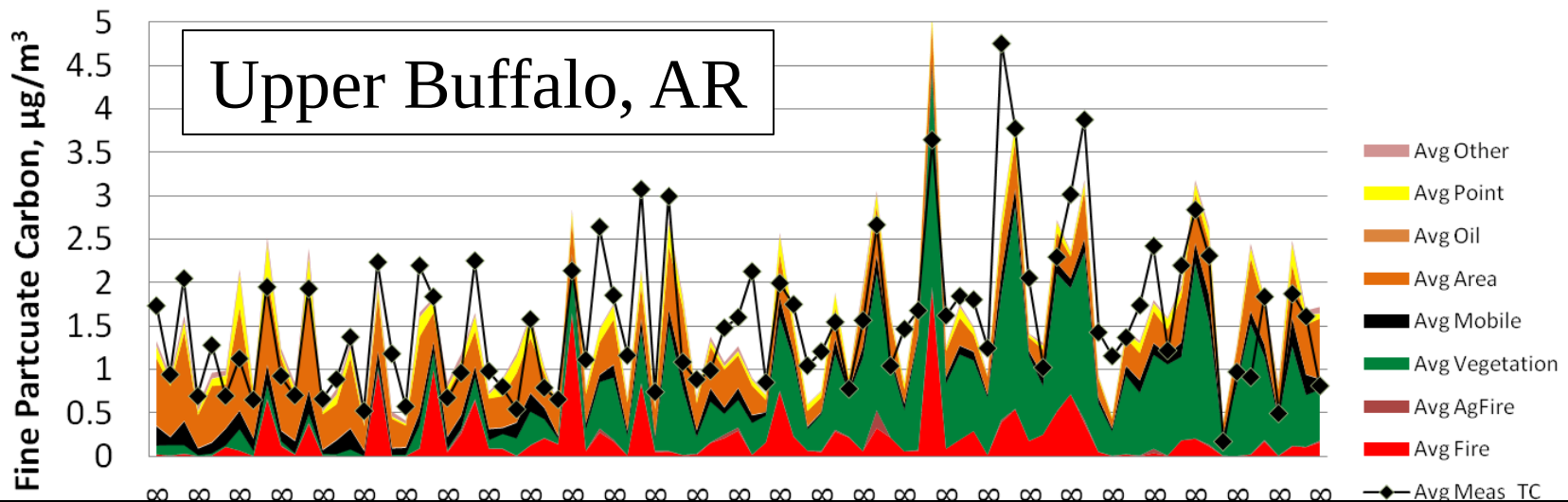
- Speciated PM_{2.5} and PM₁₀ mass monitoring network, > 160 sites
- Optimized model to 2008 TC data
- Applied model to 2006-2008 time period

Simulated vs. Measured TC, 2008



- Aggregated over all IMPROVE monitoring sites for each sample day from January – December 2008
- The model captures the temporal variability in the IMPROVE network
- Different TC source contributions are important in different seasons

Mcarlo Model Source Apportionment



Optimized Results

Spatial Evaluation

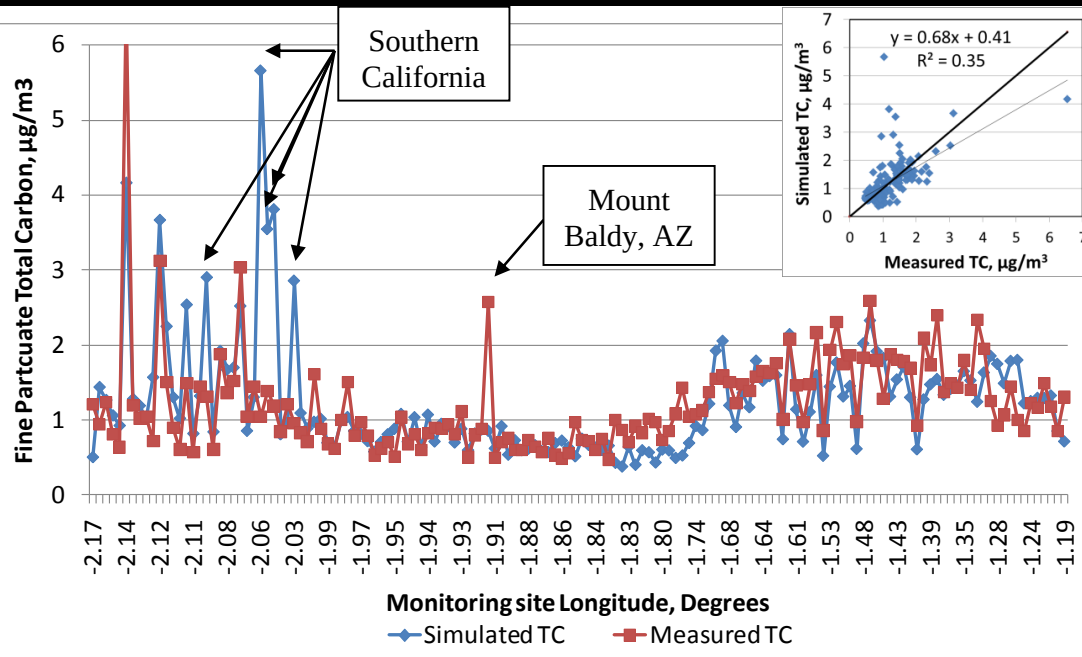


Figure 4. Comparison of the simulated and measured annual average TC concentrations at each IMPROVE monitoring site during 2008. In the line chart, the monitoring sites are sorted from west to east.

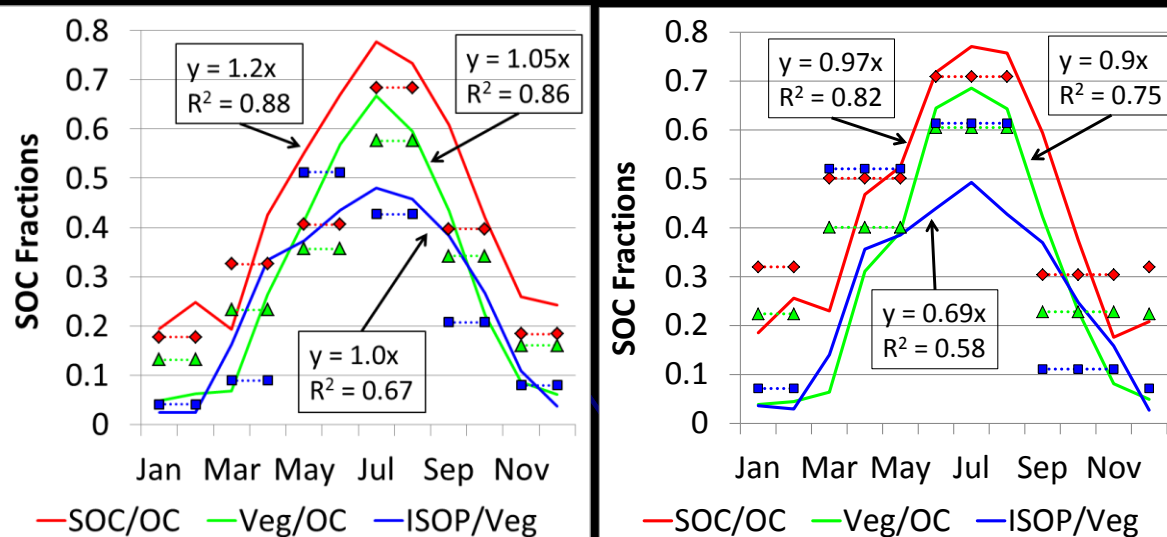
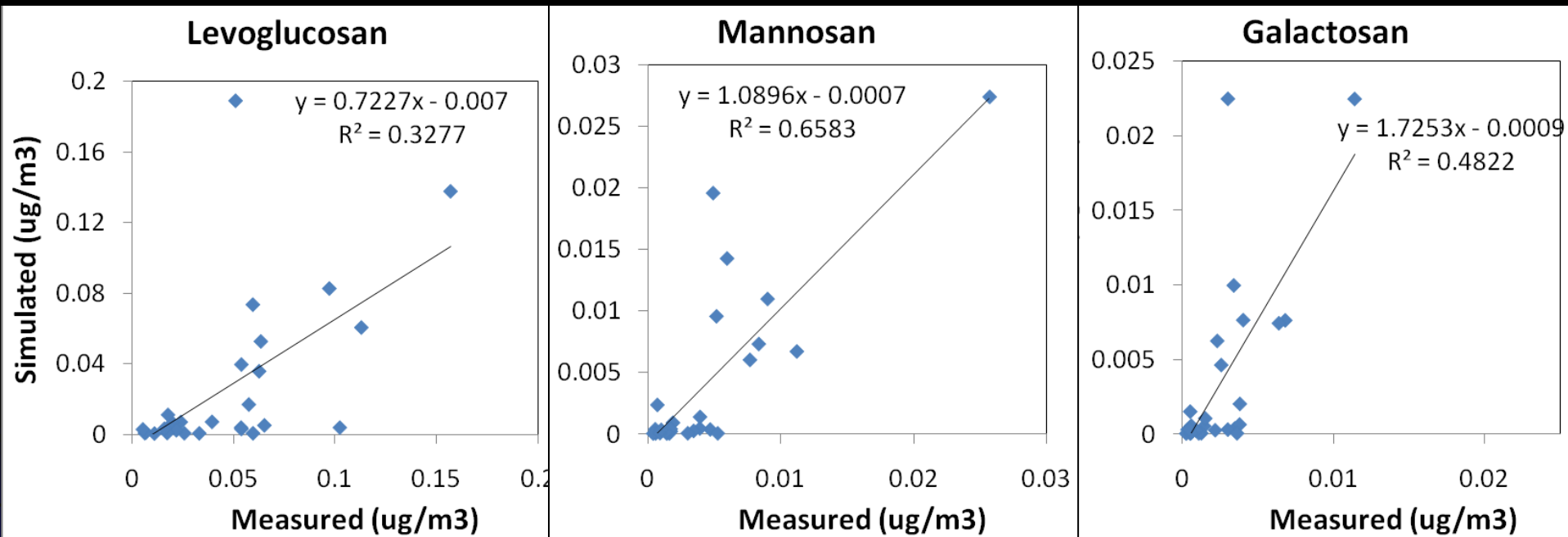


Figure 5. Simulated fractions of SOC from the CMC model and from the measured tracer concentrations at RTP, NC (left), and Bondville, IL (right). The solid lines are the CMC model simulations, and the symbols and dotted lines are from the tracer-derived results. Veg and ISOP are the SOC from vegetation and isoprene respectively. The November and December tracer-derived SOC data at RTP exclude one outlying sample. The regression line and r^2 for each comparison are also provided.

Simulation of Smoke Marker Species



- 24-hour average concentrations at Upper Buffalo, AR in March and April 2008
- Smoke marker species emissions were simulated by scaling the OC biomass burning emission rate by the spatially variable smoke source profiles

Evaluation of Src Attribution Results

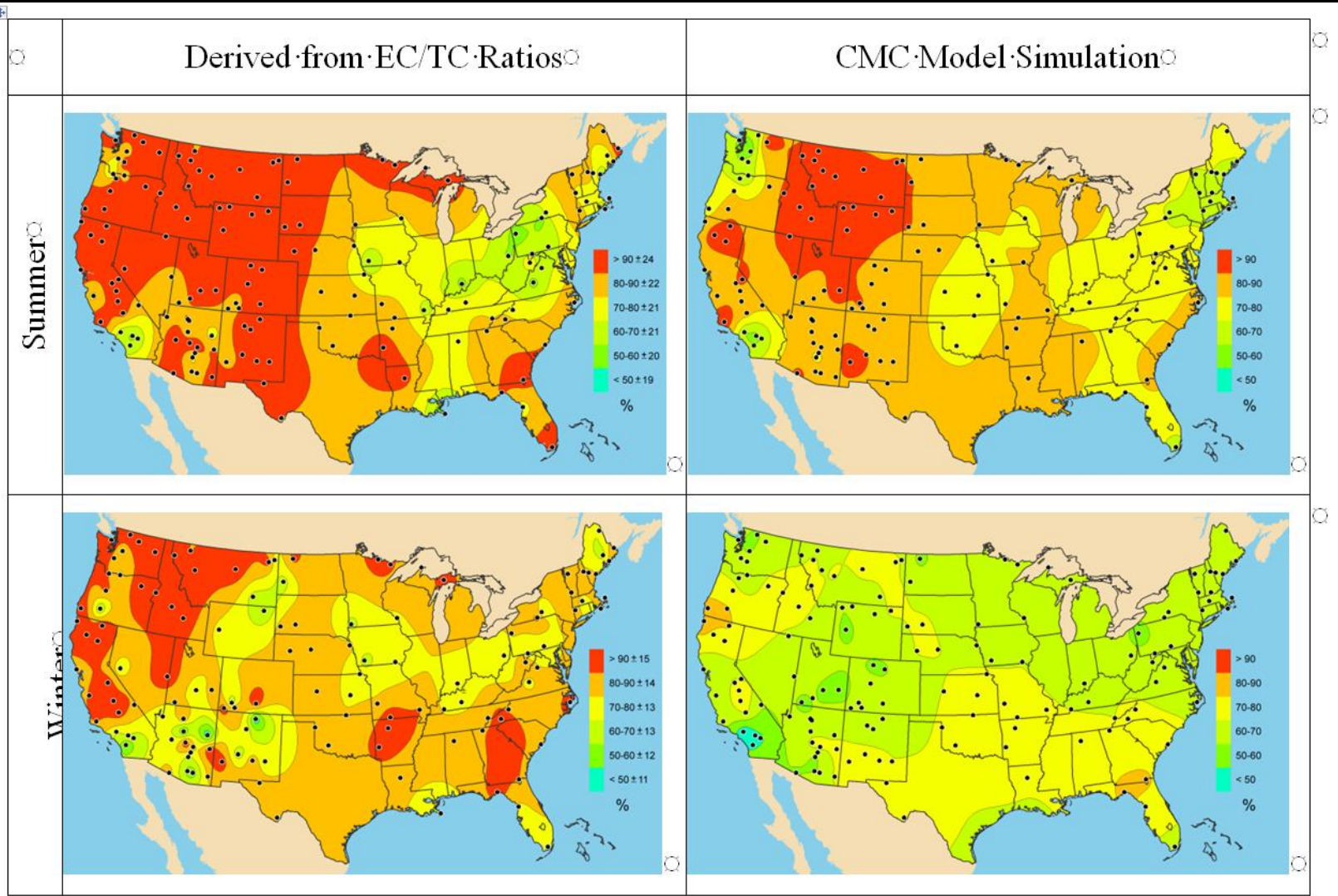
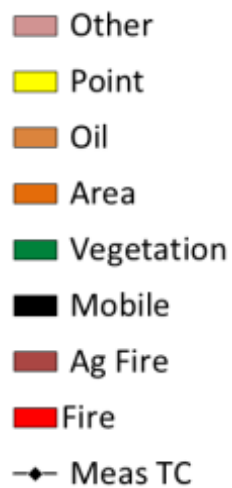
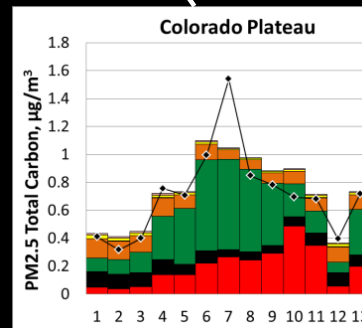
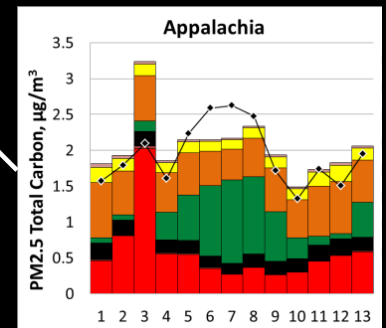
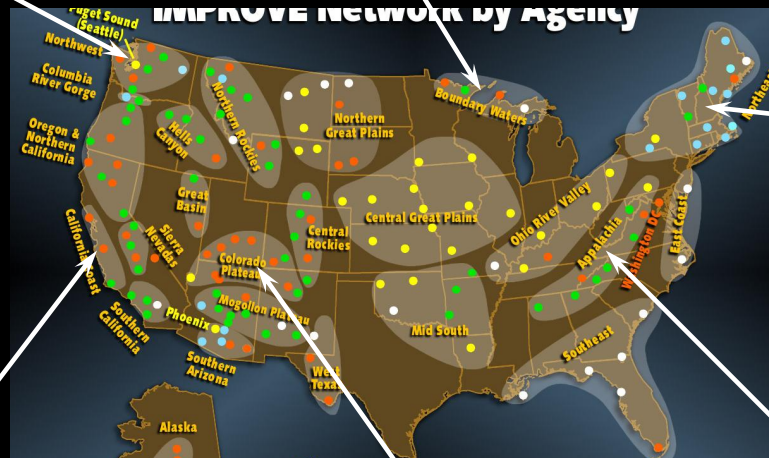
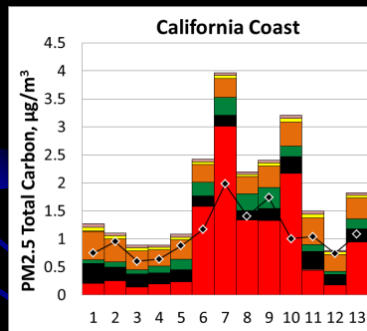
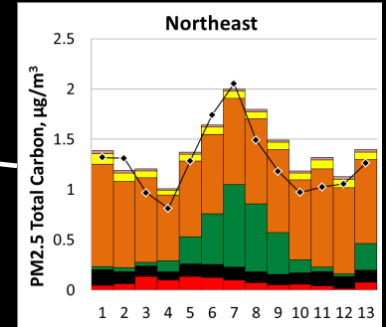
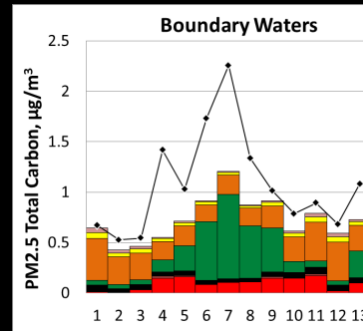
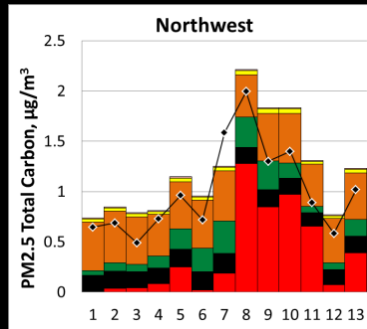


Figure 10. Comparison of the percent contribution of contemporary carbon to TC at rural IMPROVE sites for a summer and winter season, estimated from the 2004–2006 EC/TC ratios (Schichtel et al., 2008) and from the 2006–2008 CMC model simulation. ¶

Model 2006 – 08 Seasonal Source App



Refine Source Apportionment Results

Hybrid Receptor Modeling

Conservation of mass:

$$x_i = \sum_{k=1}^p g_{ik} + e_{ik}$$

x_i – i^{th} Total carbon concentration measurement

g_{ik} – Source contributions - the contribution of the k^{th} source factor to the receptor on the i^{th} measurement

e_{ij} - Residual for the j^{th} species on the i^{th} measurement

Model the error term as multiplicative bias m_k and additive distribution of residuals σ_k then:

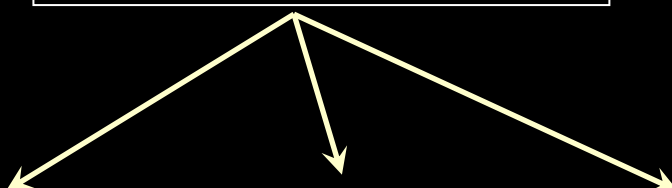
$$x_i = \sum_{k=1}^p g_{ik} a_k + \sigma_k$$

Where: $a_k = (1 + m_k)$

Solve for the scaling factors a

The measured TC concentrations and modeled source attribution are known. Invert the equation and solve for the terms a

Source Contributions



```
graph TD; A[Source Contributions] --> B["(Fire)"]; A --> C["(Veg)"]; A --> D["(Mobile)"];
```

$$\text{TC (Obs)}_i = a_1 * (\text{Fire})_i + a_2 * (\text{Veg})_i + a_3 * (\text{Mobile})_i \\ + a_4 * (\text{Area})_i + a_5 * (\text{Point})_i + \dots$$

Bayesian Least Squares – Reduce Instabilities

Incorporate prior estimates of the scaling coefficients and their variance.

$$J(\mathbf{a}) = \underbrace{\sum_{jk} (y_i - \sum G_{iu} a_u) X_{jk} (y_k - \sum G_{kv} a_v)}_{\text{Minimize square residuals}} + \underbrace{\sum (a_u - z_u) W_{uv} (a_v - z_v)}_{\text{Minimize squared difference between prior and post estimates}}$$

Minimize $J(\mathbf{a})$ to find the unknown biases $\mathbf{a}$

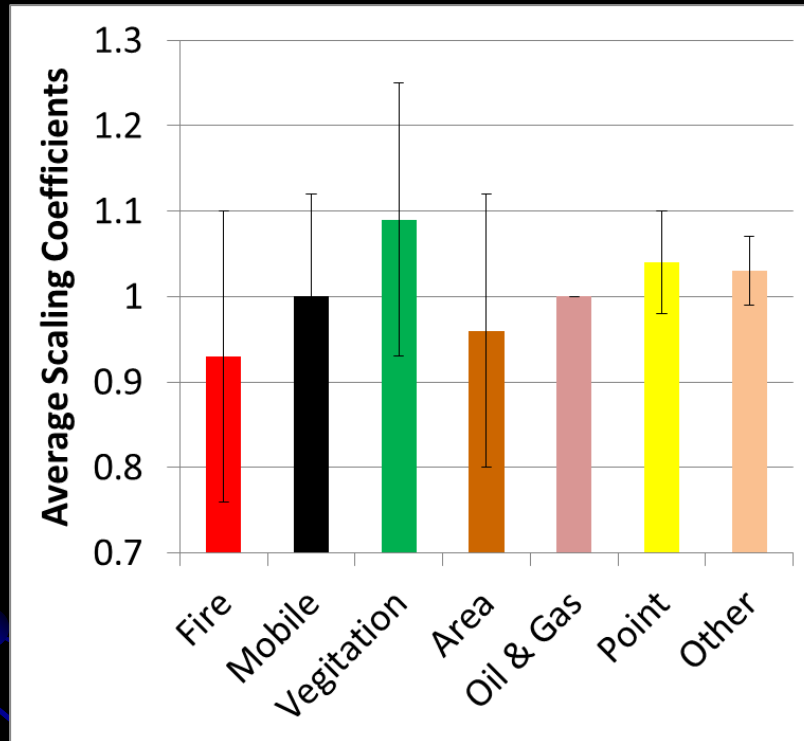
$\mathbf{z}$: prior estimates of the source attribution scaling coefficients
assumed $\mathbf{z} = 1$ (perfect model)

$\mathbf{W}$: diagonal matrix of the inverse variance of the prior estimates
(model error for monthly TC $\sim 72\%$) - $W_{uu} = 1/0.52$

Application of Inverse Method

- Data aggregated to monthly values
- All urban sites; 4 Southern CA and 2 Washington State sites with exceptionally poor model performance were filtered out
- Remove the potential biasing affects of large fire impacts on the regression analysis
 - All data with measured or simulated TC $> 8 \mu\text{g}/\text{m}^3$ was assumed to have large biomass burning impacts and filtered out of regression analysis
 - 99th TC percentile at Washington DC $\sim 8 \mu\text{g}/\text{m}^3$
 - In post analysis the Fire source contribution for these data points were adjusted to match the measured TC. This affected $\sim 1.8\%$ of data points
- Spatially and temporally varying α
 - Regression done for every site + 20 nearest neighbors for each quarter of each year.

Scaling Factors

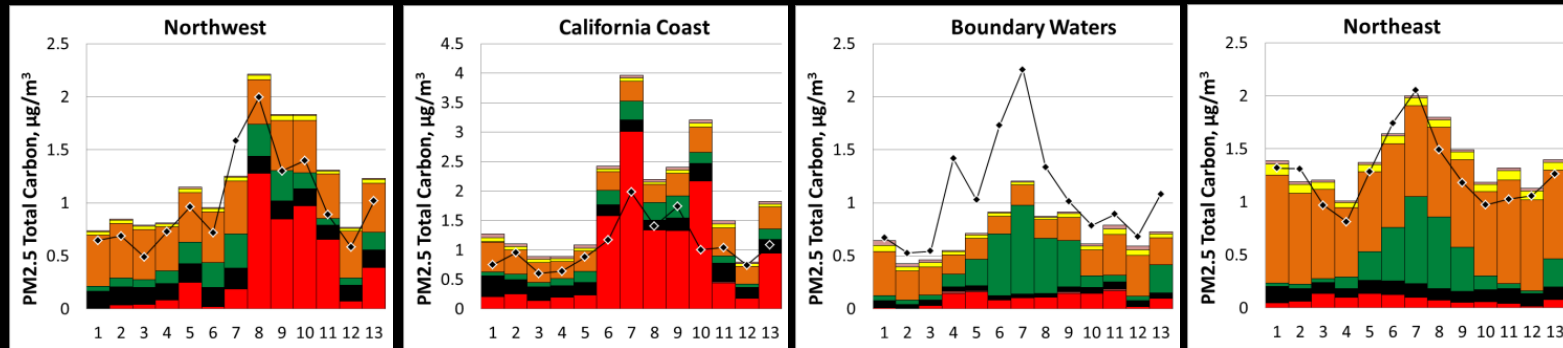


Mean and standard deviation of regression coefficients from all sites for each year and quarter

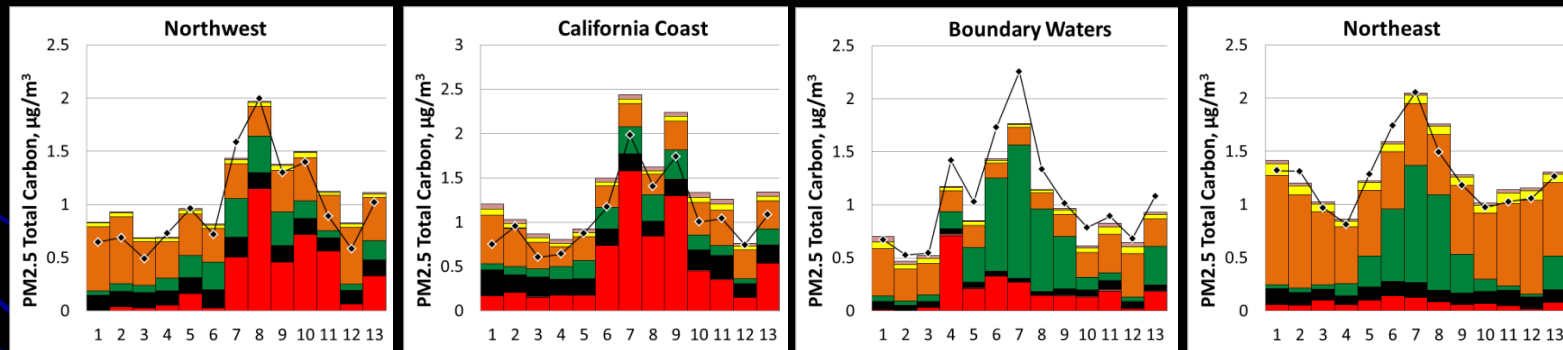
- Oil, Point and Other have little influence on the regressions
- The model appears to underestimate vegetation by 10% on average and 15-30% during summer months
- Area and Fire are overestimated up to 15% depending on the year and Qu

Model 2006 – 08 Seasonal Source App

ORIGINAL model source attribution results

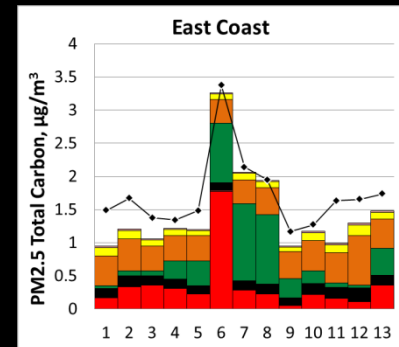
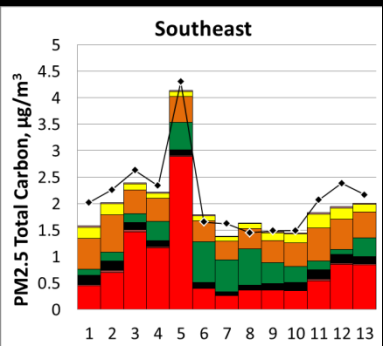
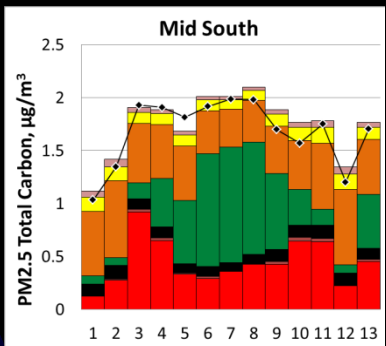
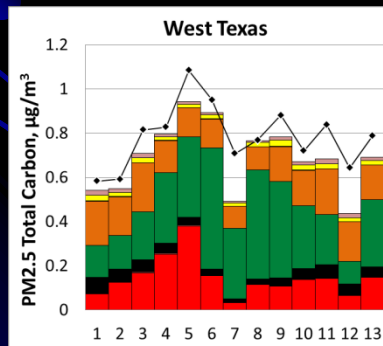
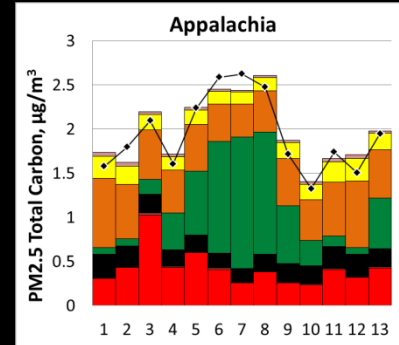
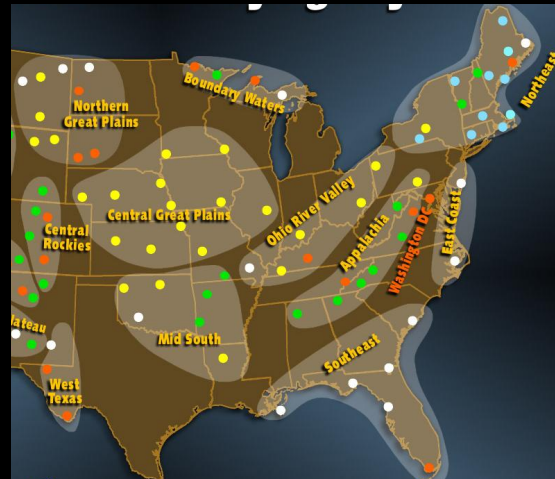
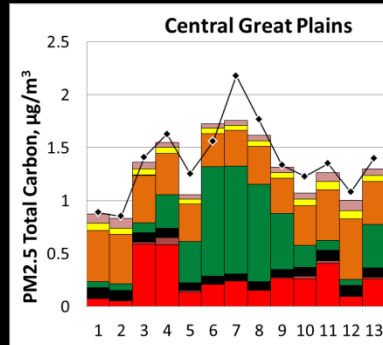
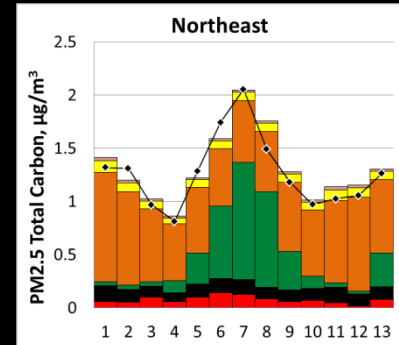
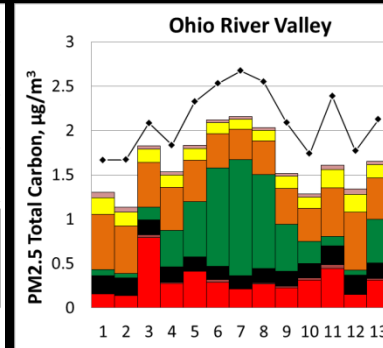
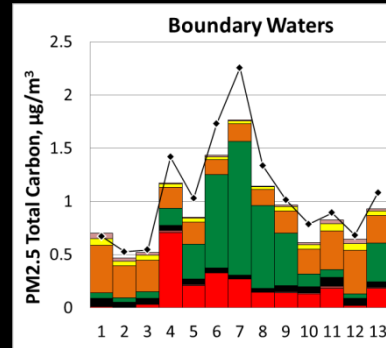
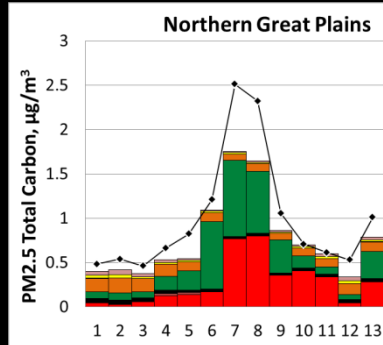
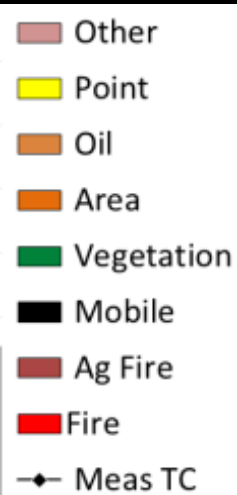


REFINED source attribution results

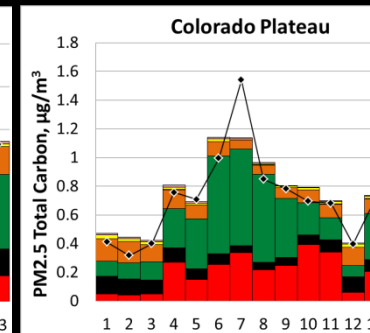
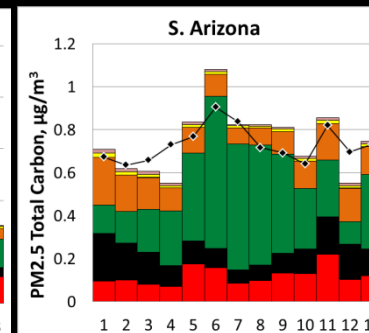
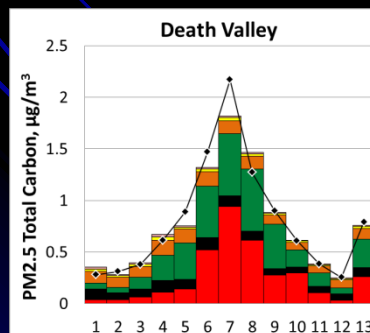
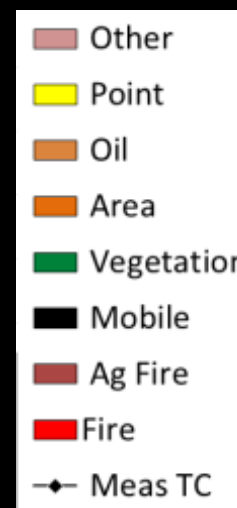
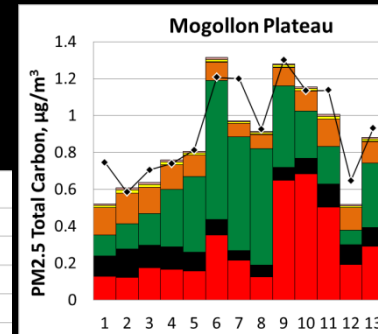
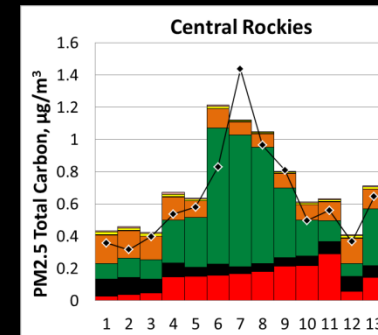
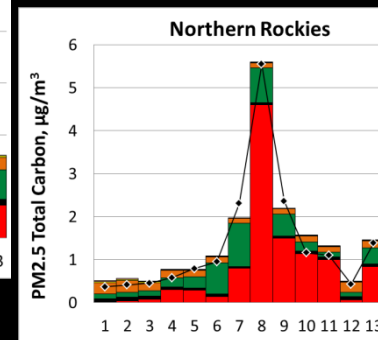
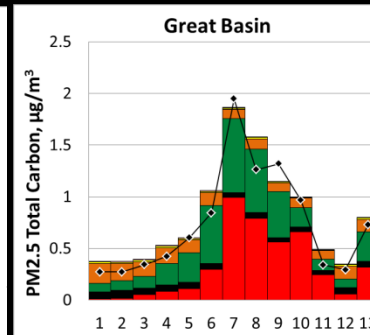
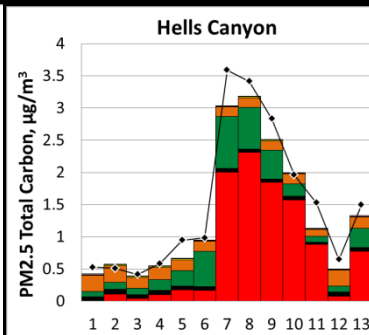
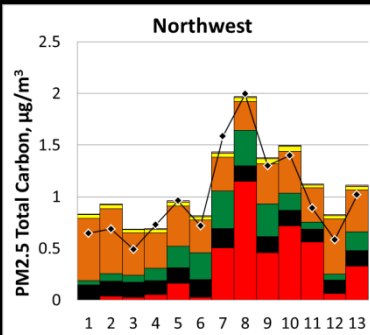
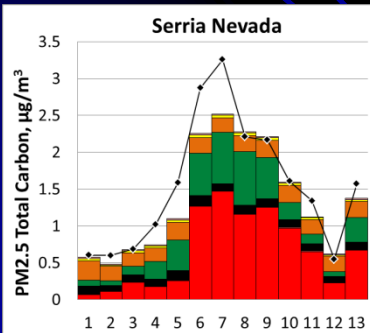
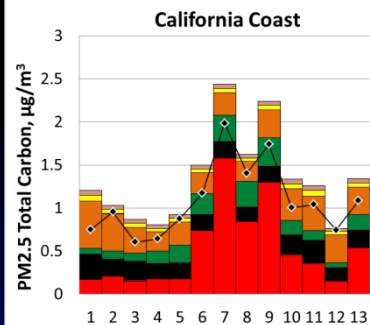
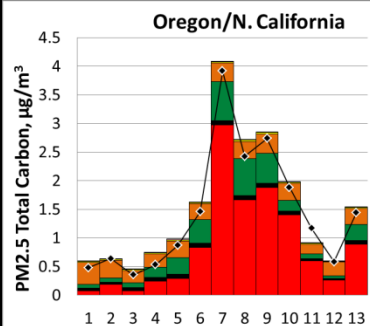
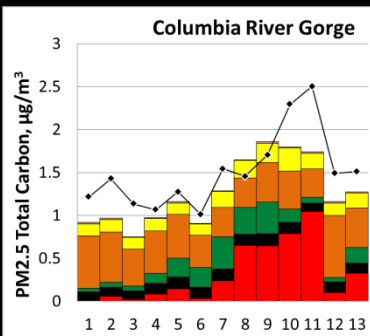


- The refined source attribution results:
 - maintains the good agreement in regions such as the Northeast
 - reduce biases e.g., by increasing vegetation contributions in boundary waters and decreasing fire along the California coast.

Refined 2006 – 08 Seasonal Source App

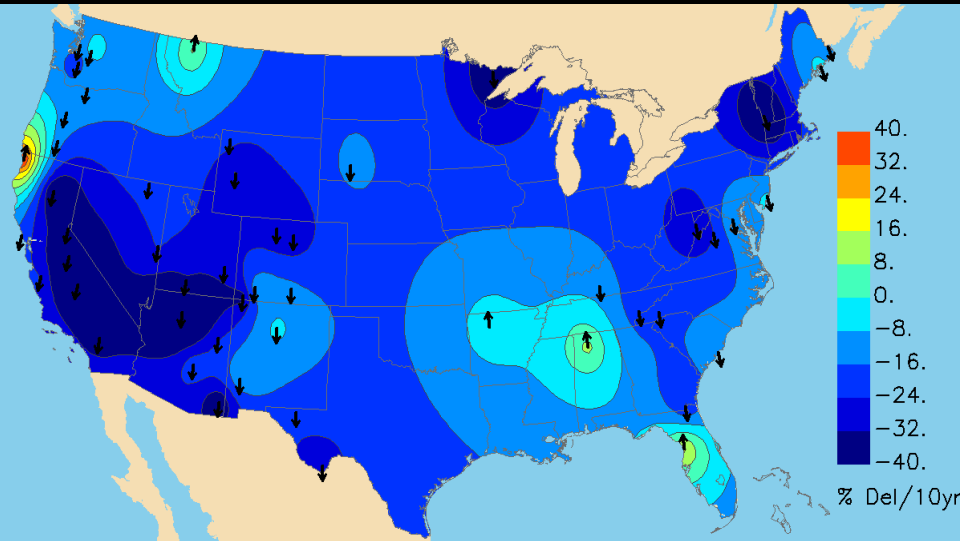


Refined 2006–08 Source App

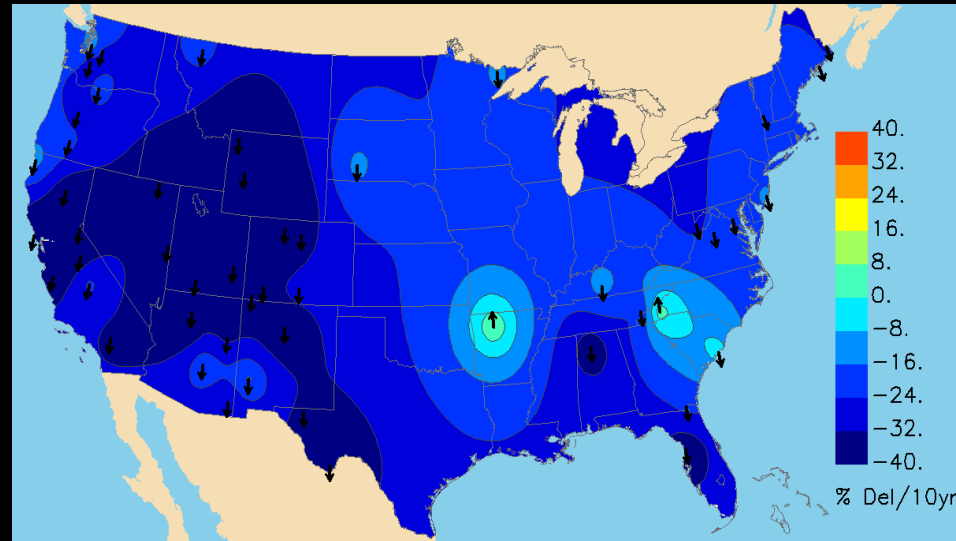


TC Seasonal Trends 1996-06

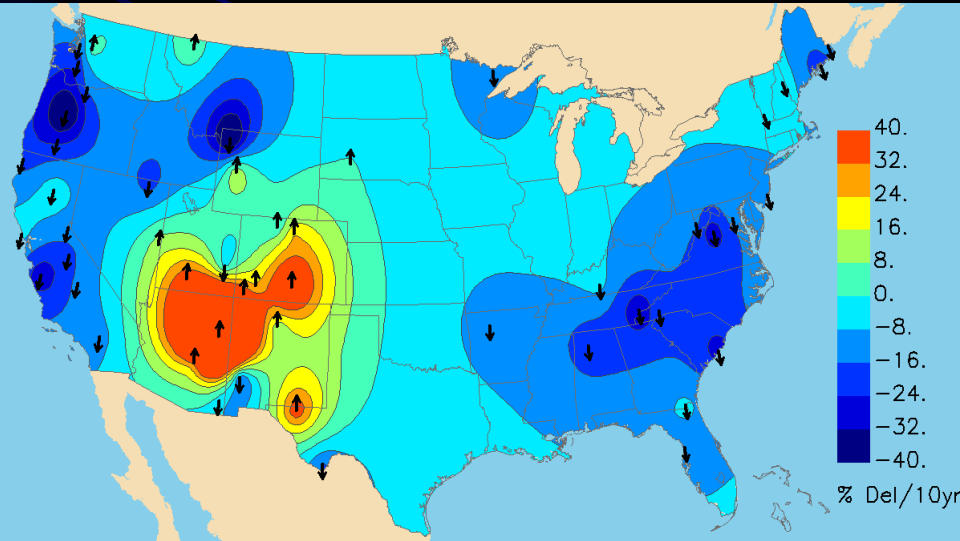
Winter



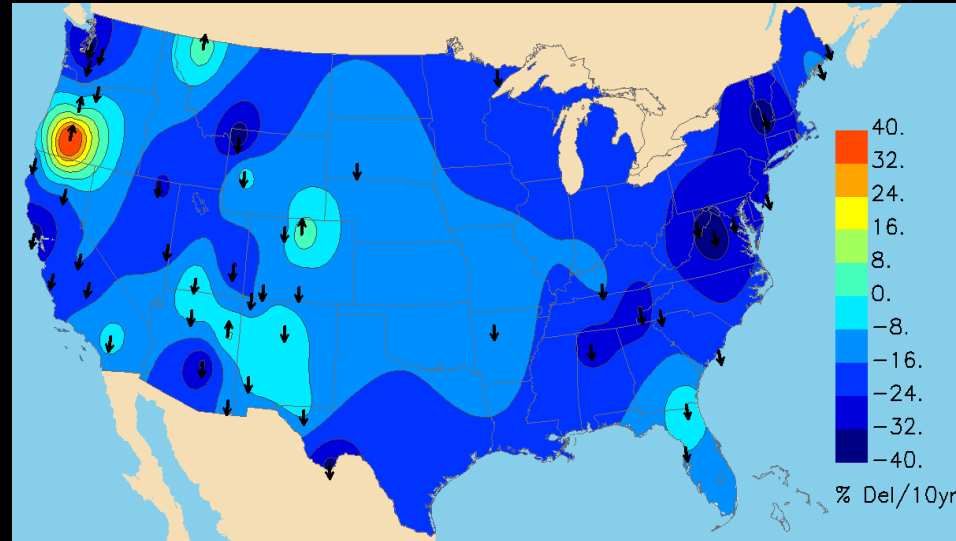
Spring



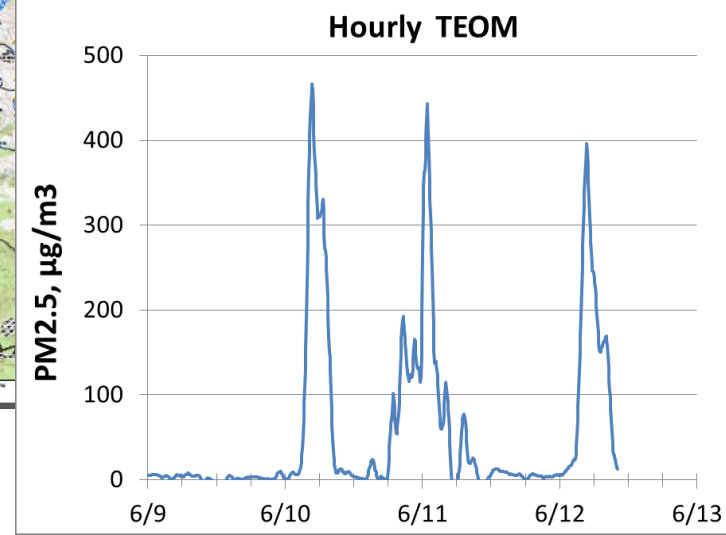
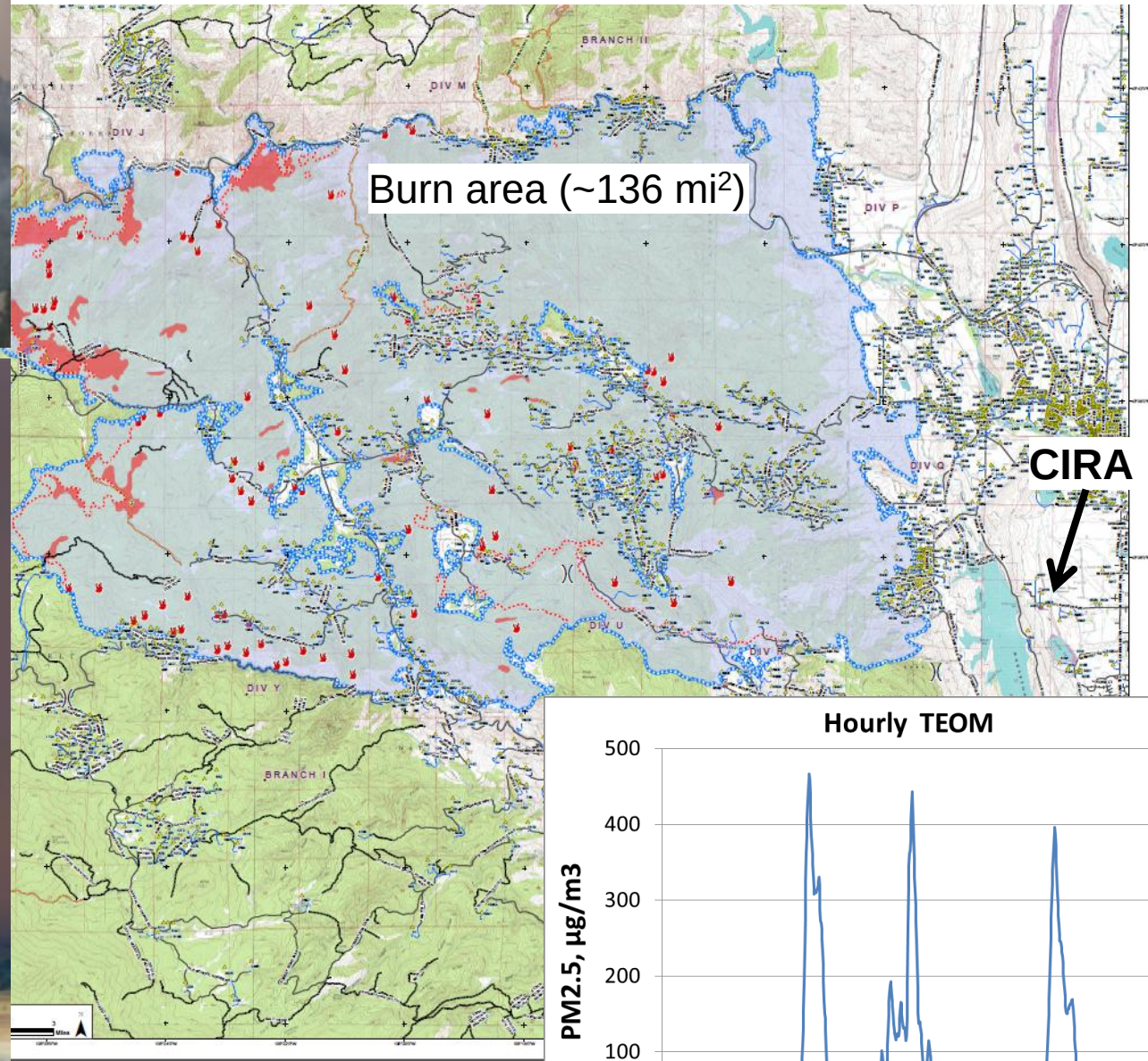
Summer



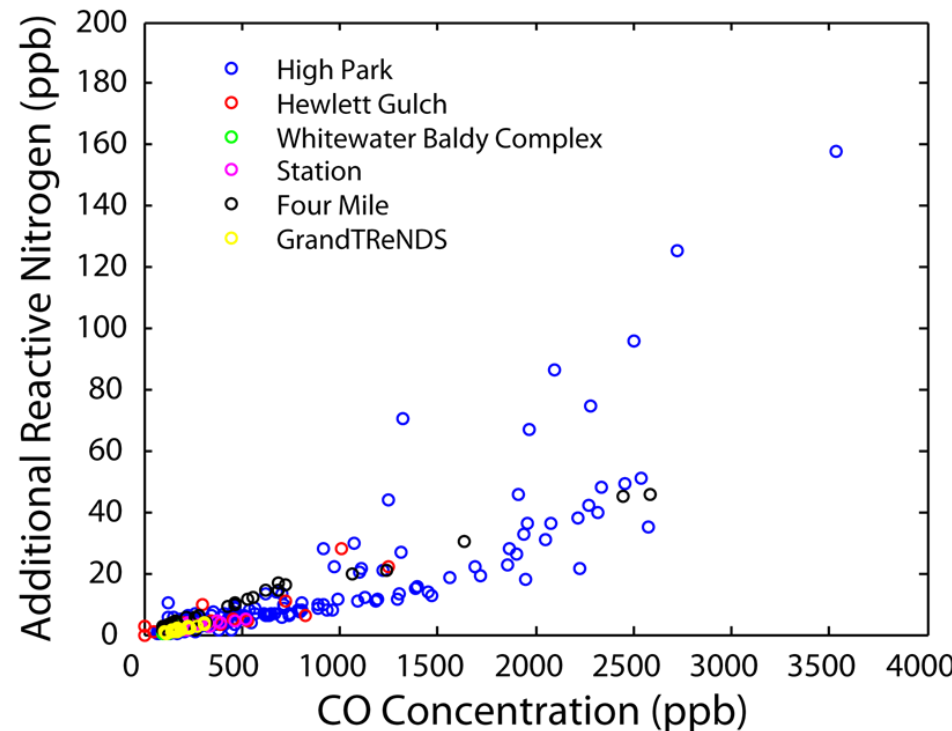
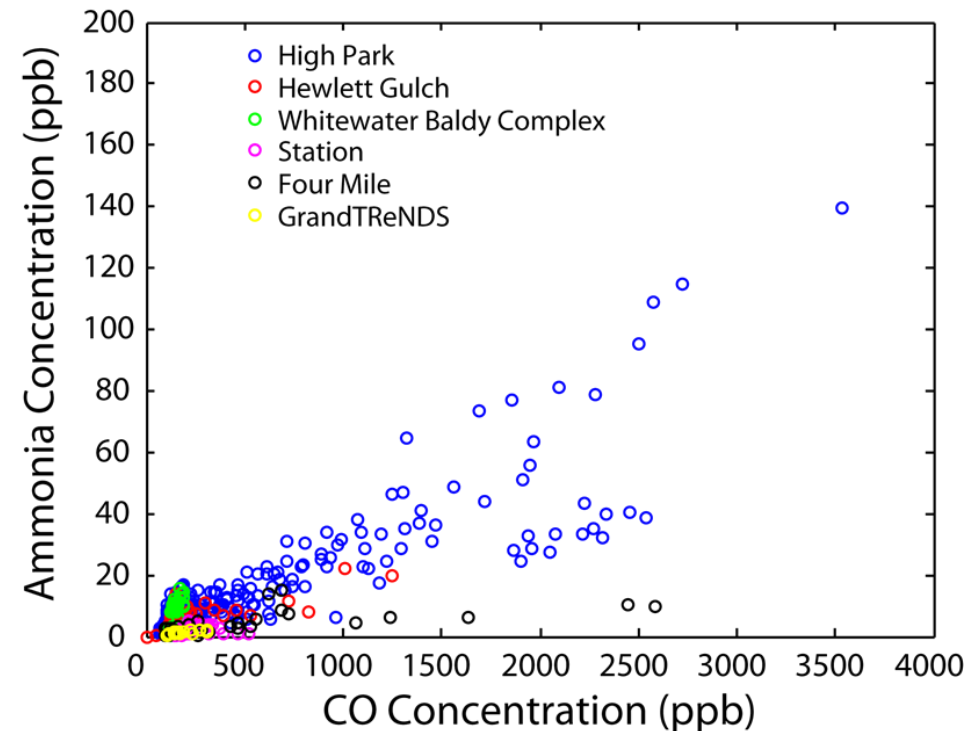
Fall



High Park Fire

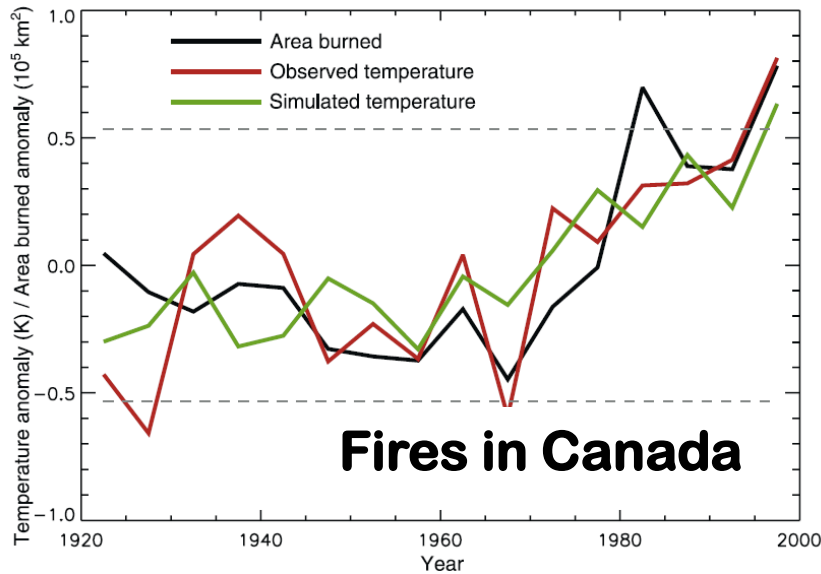


Reduced N in Fresh and Aged Biomass Burning Emissions (Preliminary Data)

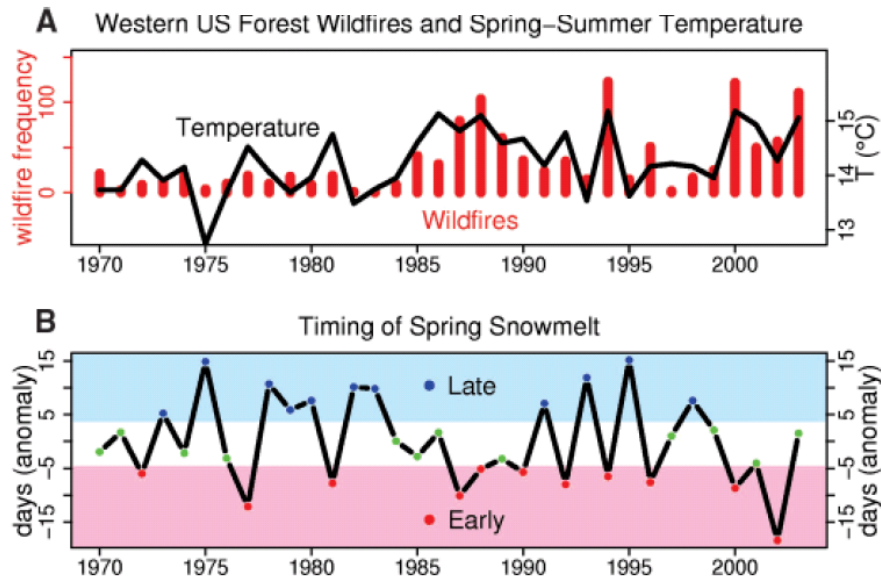


- Other measured N-species, e.g. NO_x and NO_y, also increase with CO/smoke.

Increasing Wildfire and Temperatures



Fires in western US



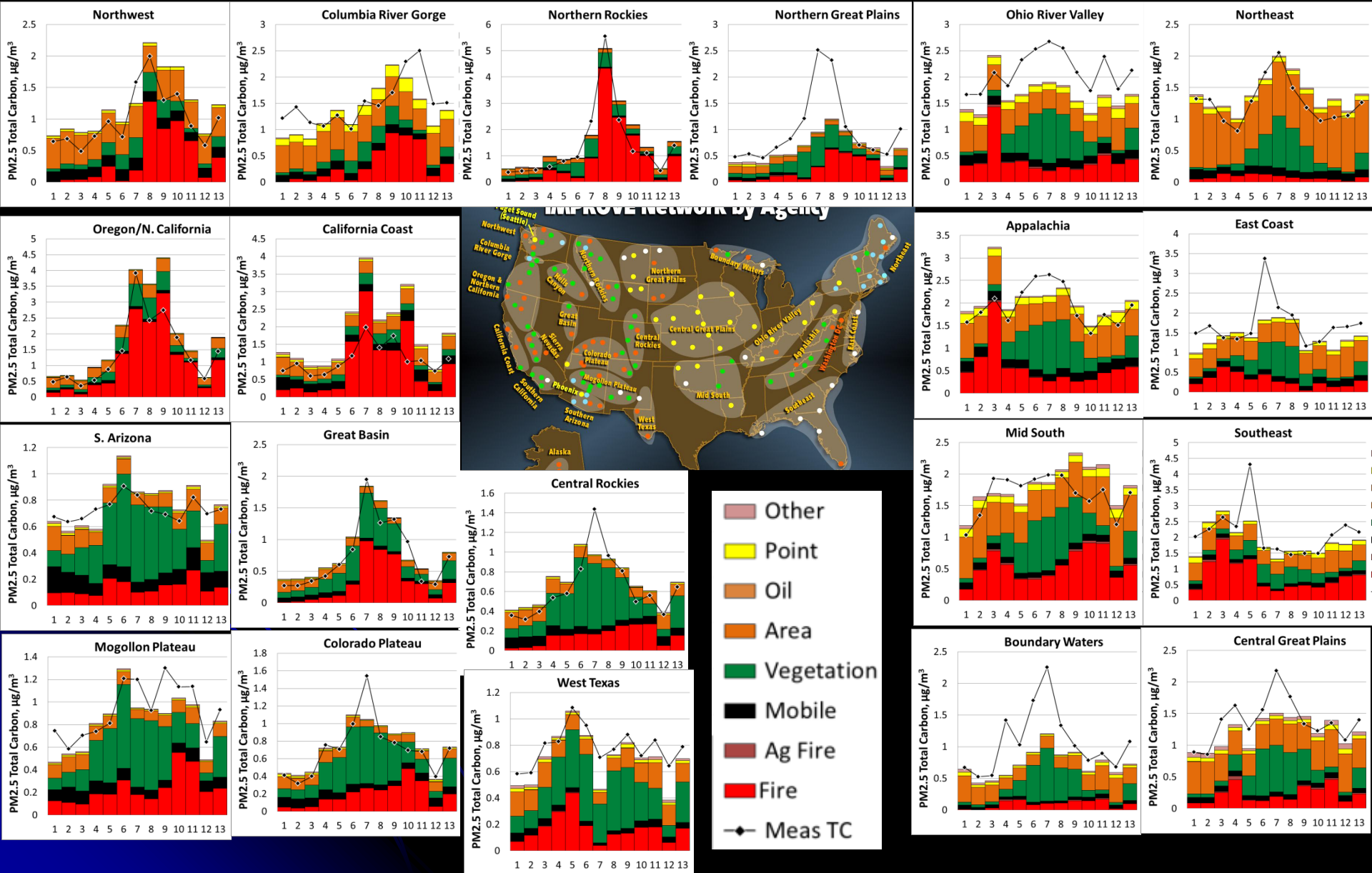
- Fire activity is correlated to temperature and snowmelt timing
- Climate change is projected to increase biomass burned in US by 50% in 2050

Westerling et al., 2007, Guillet et al, 2004, Spracklen et al, 2009 and Hudman et al, in prep

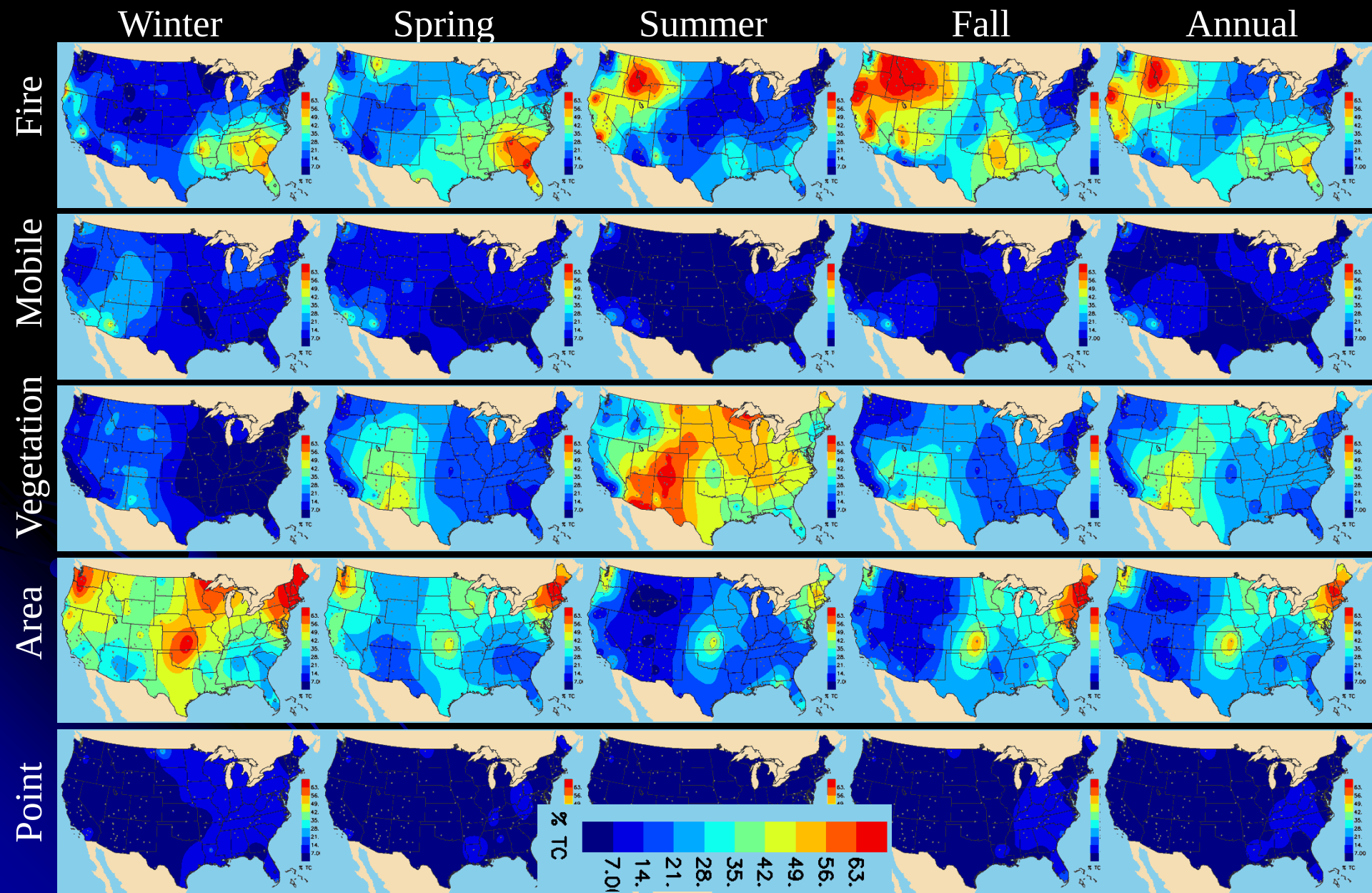
Questions?



Model 2006 – 08 Seasonal Source App



IMPROVE Seasonal 2006-08 TC Source Attribution (ratio of avgs)



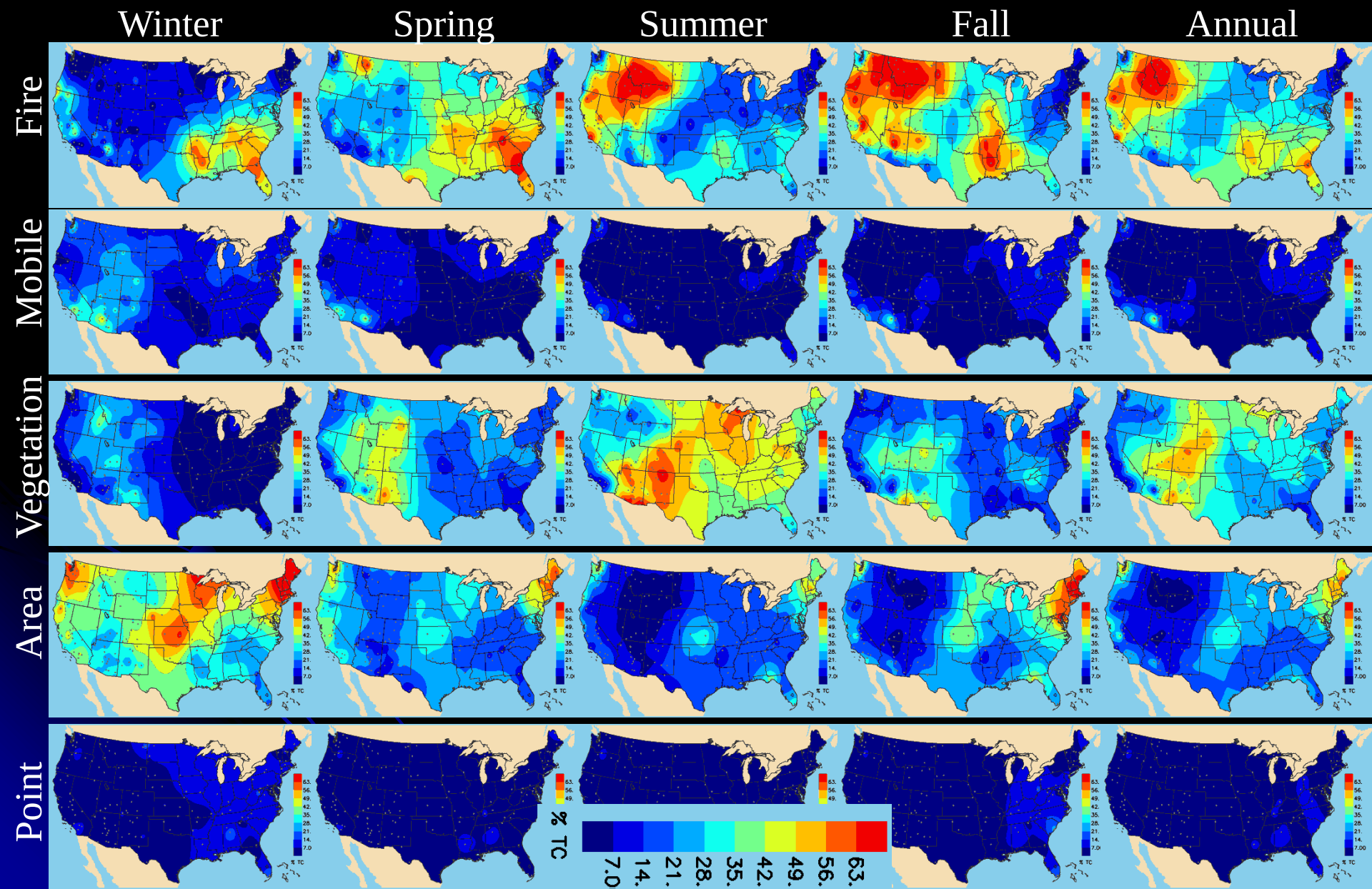
Scaling Factors

Mean and standard deviation of regression coefficients from all sites for each year and quarter

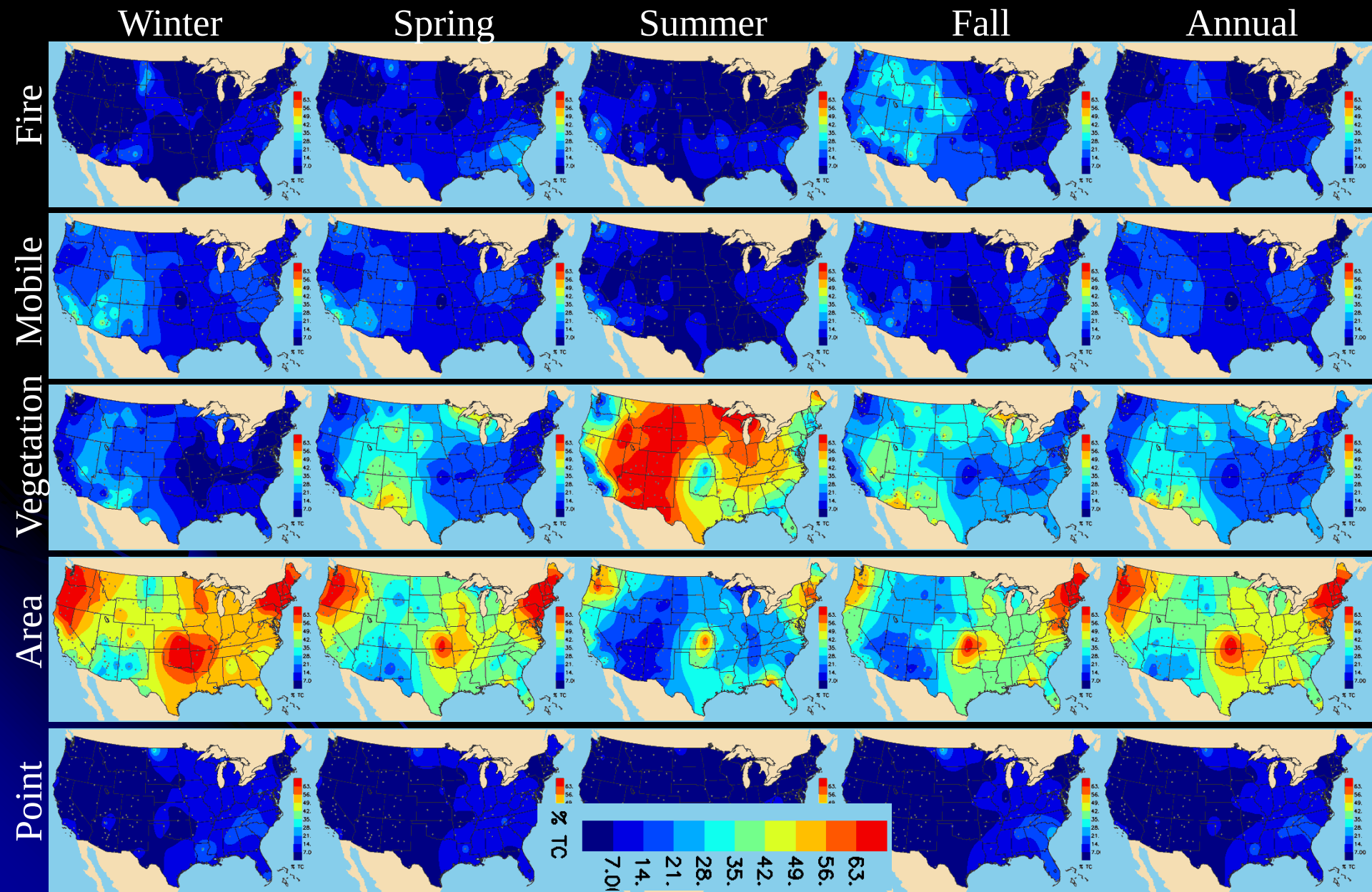
year	Qu	Sim TC	Mea TC	r	Fire	Mobile	Veg	Area	oil & gas	Pnt	Other
2006	1	0.85	0.92	0.40	0.89 ± 0.21	0.95 ± 0.14	0.97 ± 0.08	1.07 ± 0.14	1.00 ± 0.00	1.03 ± 0.08	1.02 ± 0.06
2006	2	0.98	1.02	0.58	0.73 ± 0.23	0.86 ± 0.13	0.79 ± 0.14	0.83 ± 0.18	1.00 ± 0.00	1.00 ± 0.05	1.00 ± 0.04
2006	3	1.54	1.67	0.59	1.02 ± 0.22	0.96 ± 0.11	1.17 ± 0.21	0.89 ± 0.12	1.00 ± 0.00	1.01 ± 0.03	1.01 ± 0.03
2006	4	1.12	1.18	0.63	0.88 ± 0.09	1.04 ± 0.11	1.15 ± 0.18	0.96 ± 0.12	1.00 ± 0.00	1.08 ± 0.10	1.03 ± 0.05
2007	1	0.82	0.88	0.45	0.94 ± 0.24	1.10 ± 0.15	1.12 ± 0.14	1.15 ± 0.15	1.00 ± 0.00	1.07 ± 0.06	1.06 ± 0.08
2007	2	0.99	1.04	0.71	0.90 ± 0.15	1.05 ± 0.06	1.21 ± 0.23	0.99 ± 0.15	1.00 ± 0.00	1.05 ± 0.04	1.02 ± 0.02
2007	3	1.51	1.61	0.54	0.94 ± 0.12	1.00 ± 0.11	1.26 ± 0.24	0.86 ± 0.18	1.00 ± 0.00	1.02 ± 0.04	1.02 ± 0.02
2007	4	1.14	1.18	0.68	0.85 ± 0.13	0.99 ± 0.13	1.04 ± 0.11	0.86 ± 0.17	1.00 ± 0.00	1.06 ± 0.08	1.01 ± 0.03
2008	1	0.74	0.77	0.47	0.91 ± 0.11	1.05 ± 0.17	1.01 ± 0.10	1.03 ± 0.11	1.00 ± 0.00	1.08 ± 0.09	1.06 ± 0.08
2008	2	0.88	0.96	0.58	1.08 ± 0.13	1.06 ± 0.09	1.28 ± 0.10	1.10 ± 0.17	1.00 ± 0.00	1.06 ± 0.04	1.04 ± 0.04
2008	3	1.50	1.58	0.69	0.97 ± 0.17	0.96 ± 0.09	1.27 ± 0.22	0.85 ± 0.19	1.00 ± 0.00	1.01 ± 0.03	1.00 ± 0.03
2008	4	1.04	1.10	0.61	1.01 ± 0.19	1.03 ± 0.12	0.86 ± 0.15	0.94 ± 0.18	1.00 ± 0.00	1.07 ± 0.07	1.04 ± 0.05
mean		1.09	1.16	0.58	0.93±0.17	1.00±0.12	1.09±0.16	0.96±0.16	1.00±0.00	1.04±0.06	1.03±0.04

- Oil, Point and Other have little influence on the regressions
- The model appears to underestimate vegetation by 10% on average and 15-30% during summer months
- Area and Fire are overestimated up to 15% depending on the year and Qu

IMPROVE Seasonal 90th %-ile TC Source Attribution (Avg of Ratios)



IMPROVE Seasonal 10th %-ile TC Source Attribution (Avg of Ratios)



IMPROVE Average Seasonal TC Source Attribution (Avg of Ratios)

Fire
Mobile
Vegetation
Area
Point

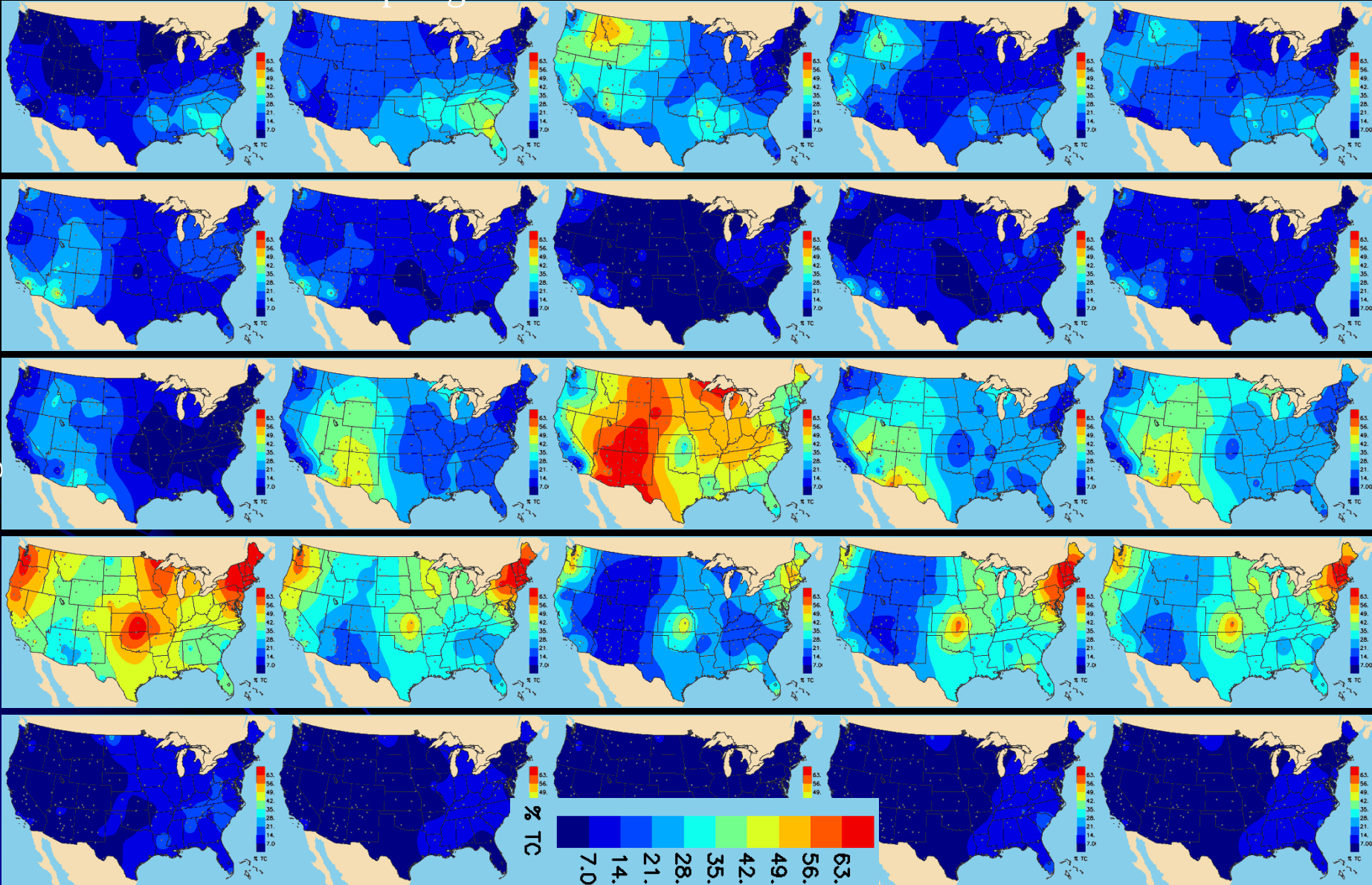
Winter

Spring

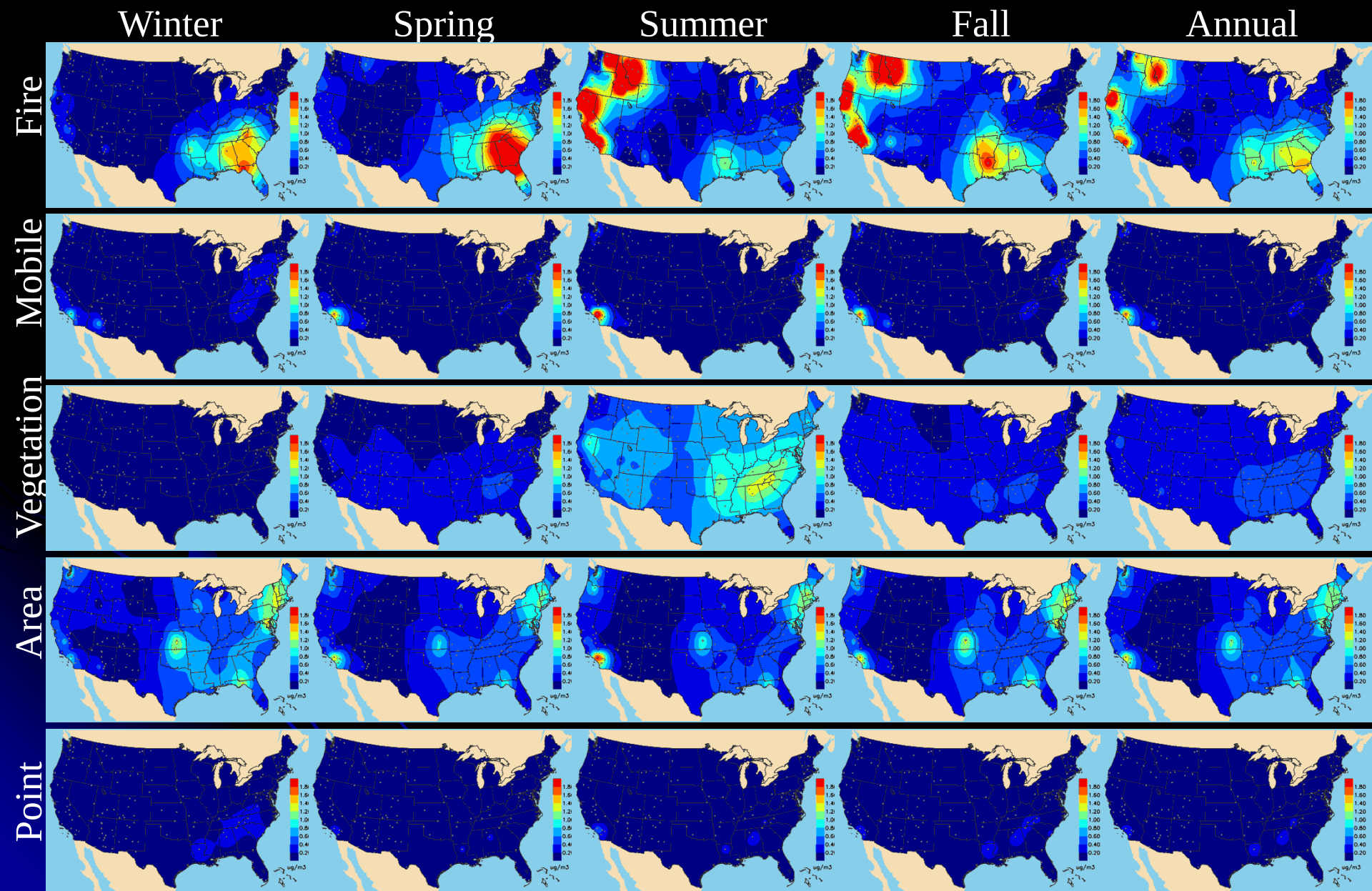
Summer

Fall

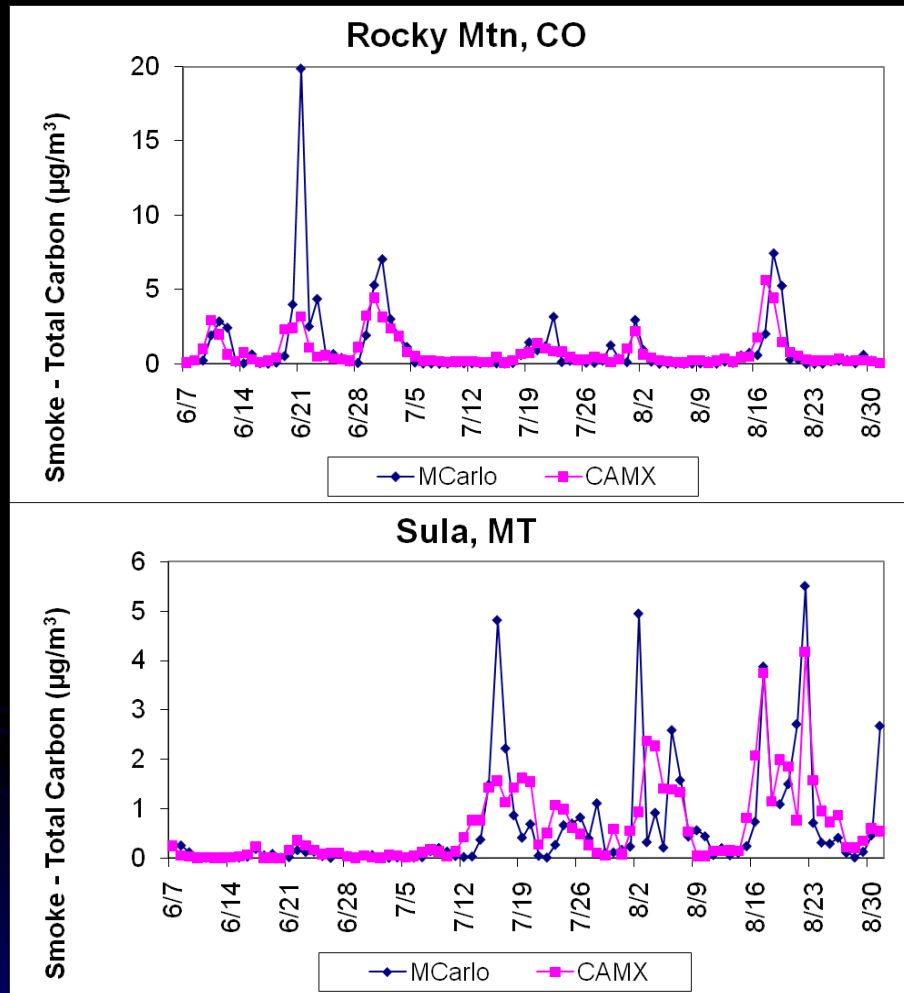
Annual



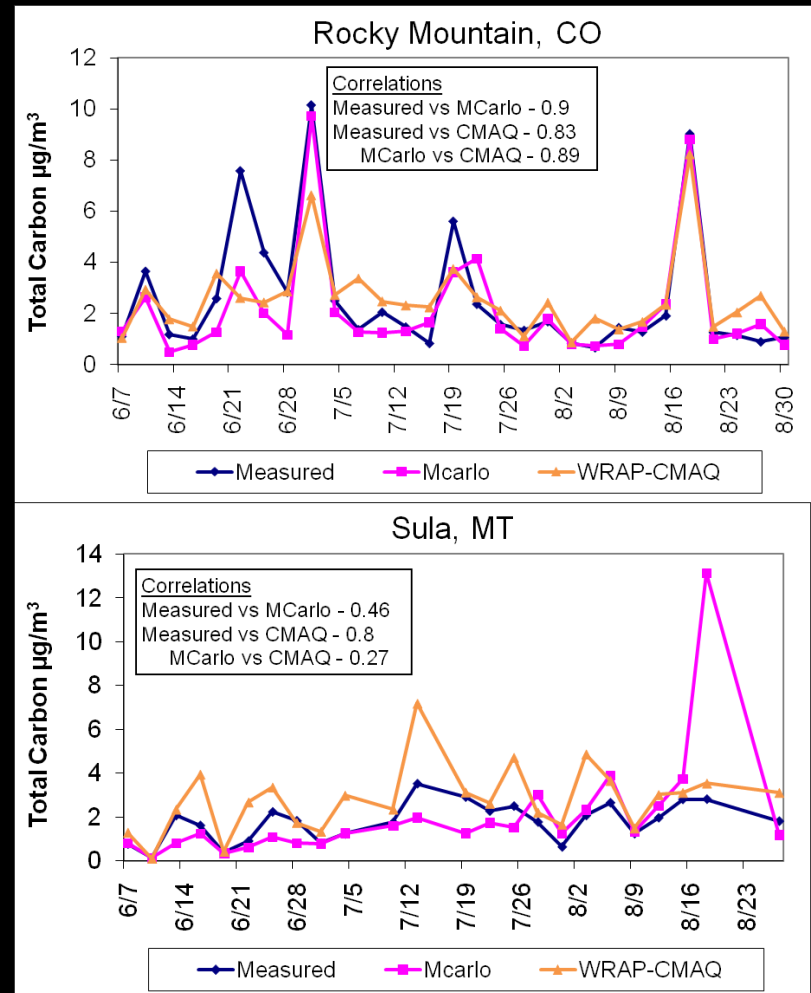
IMPROVE Average Seasonal TC Source Attribution ($\mu\text{g}/\text{m}^3$)



Mcarlo vs. CMAQ Smoke TC

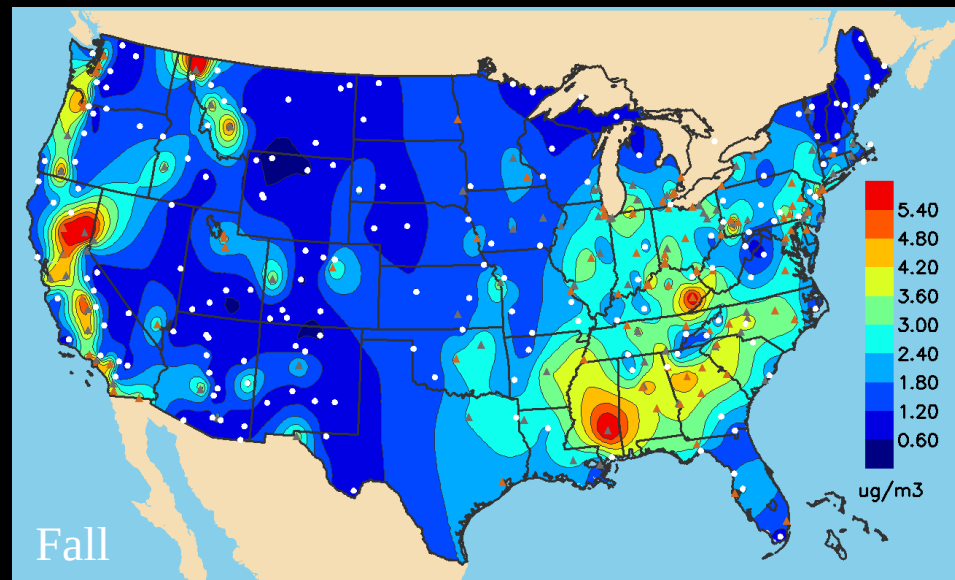
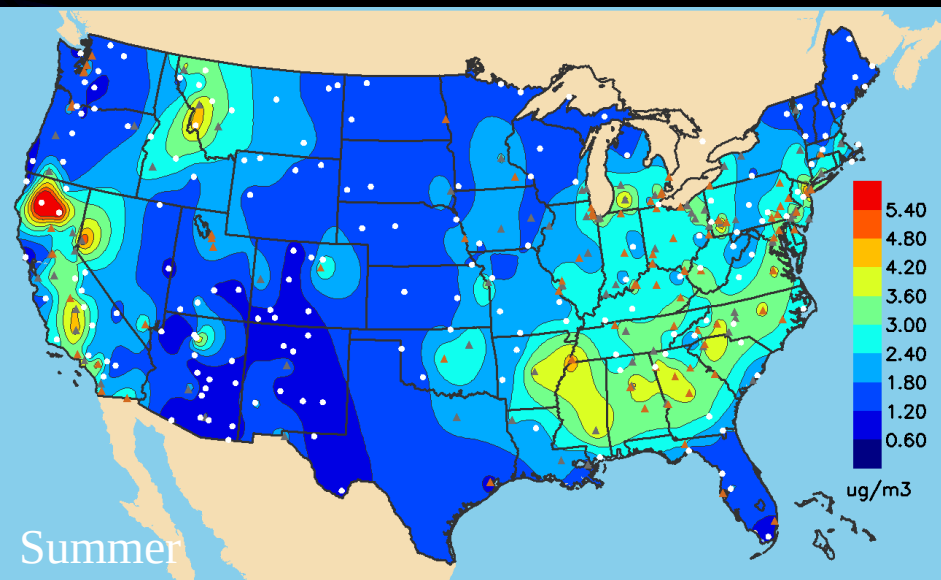
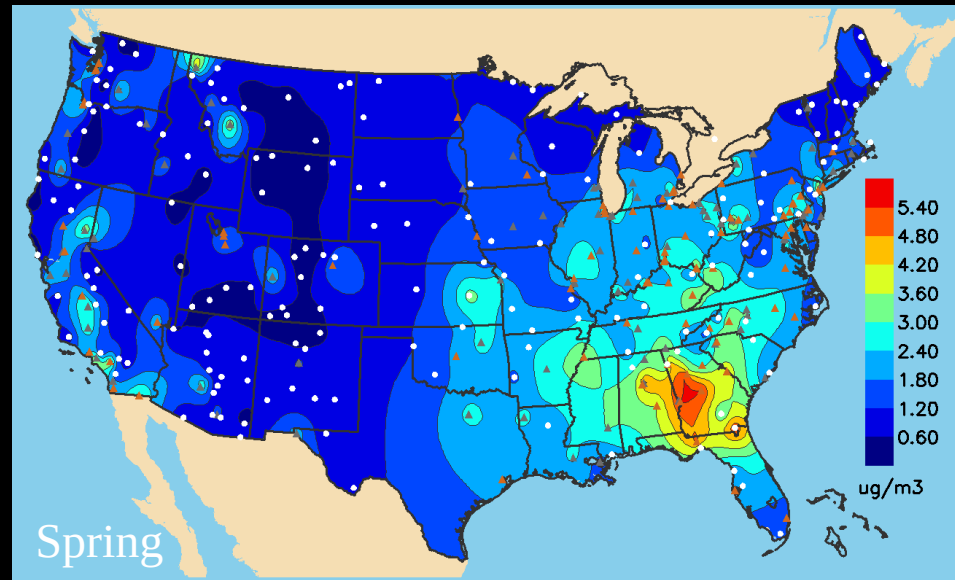
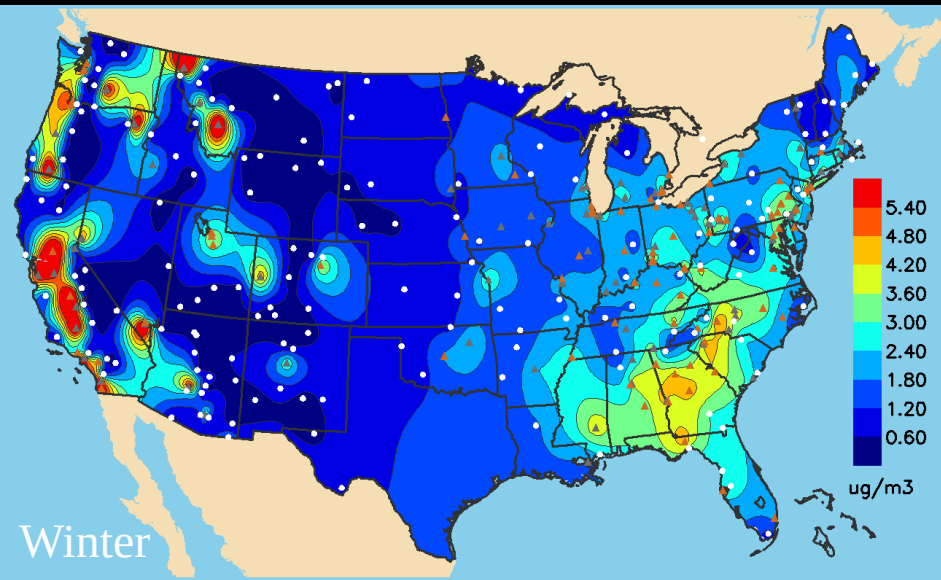


Simulated vs. Measured TC



- Models use same emission inventory but different meteorological fields, dispersion and removal and production mechanisms
- In general the two model have similar timing and magnitudes for smoke impacts and similar performance for TC

Seasonal TC Concentrations



Performance Stats

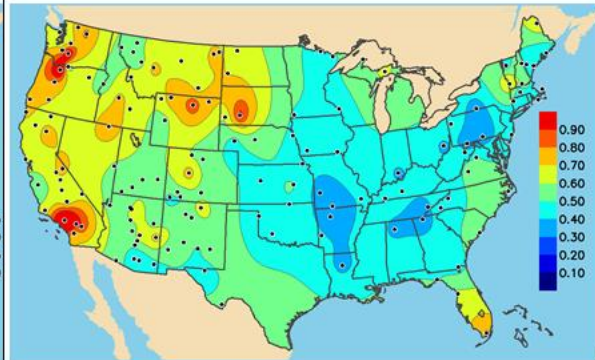
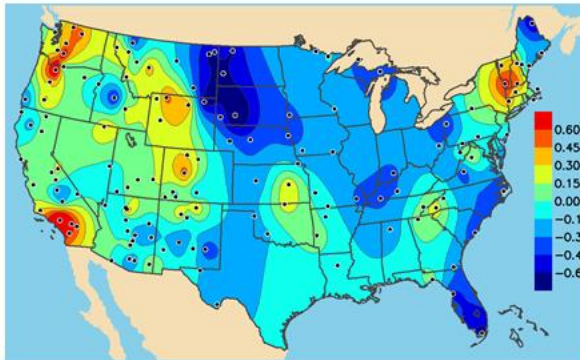
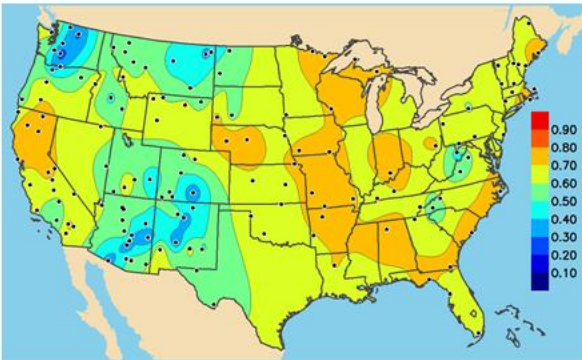
□

Person Correlation Coefficient□

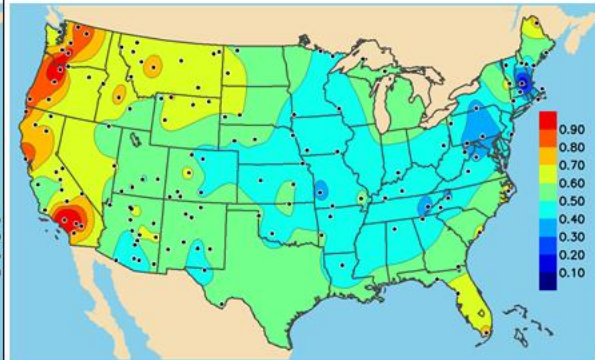
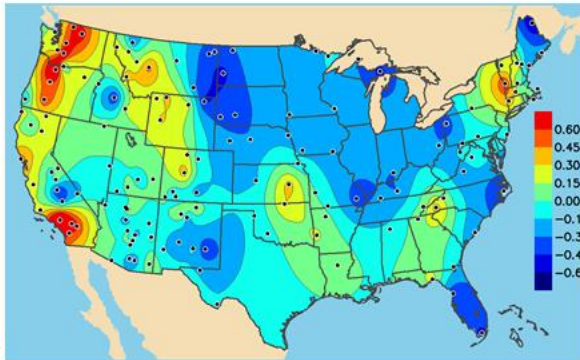
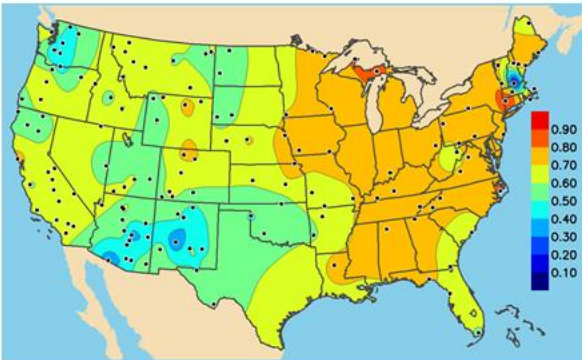
Fractional Bias□

Fractional Error□

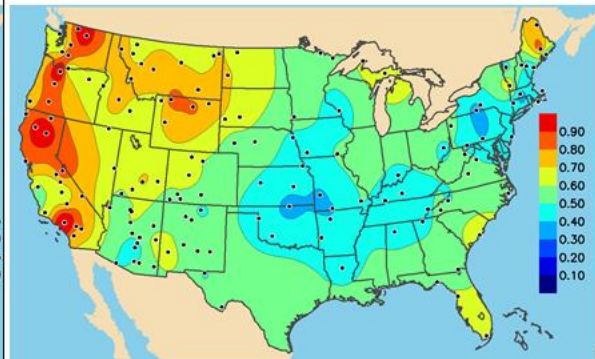
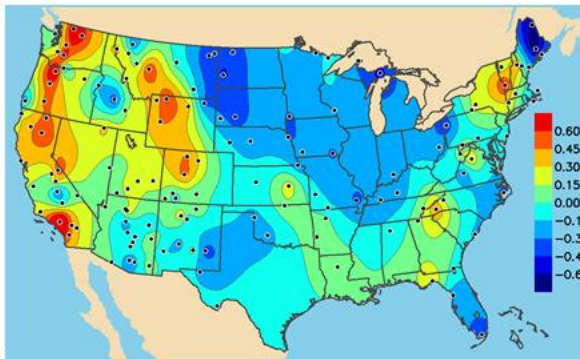
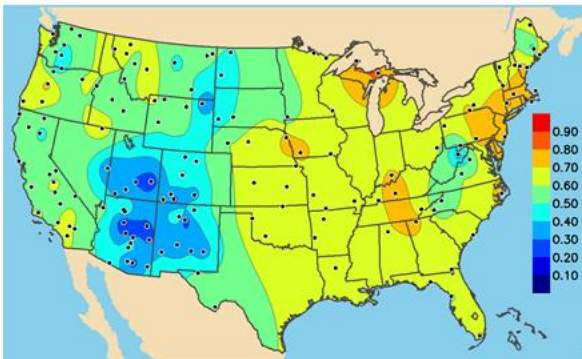
2008□



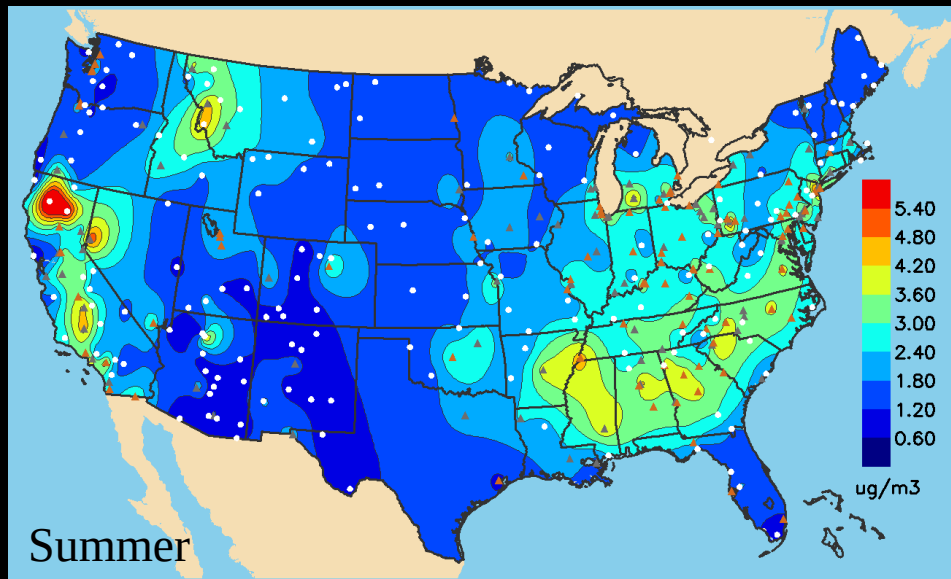
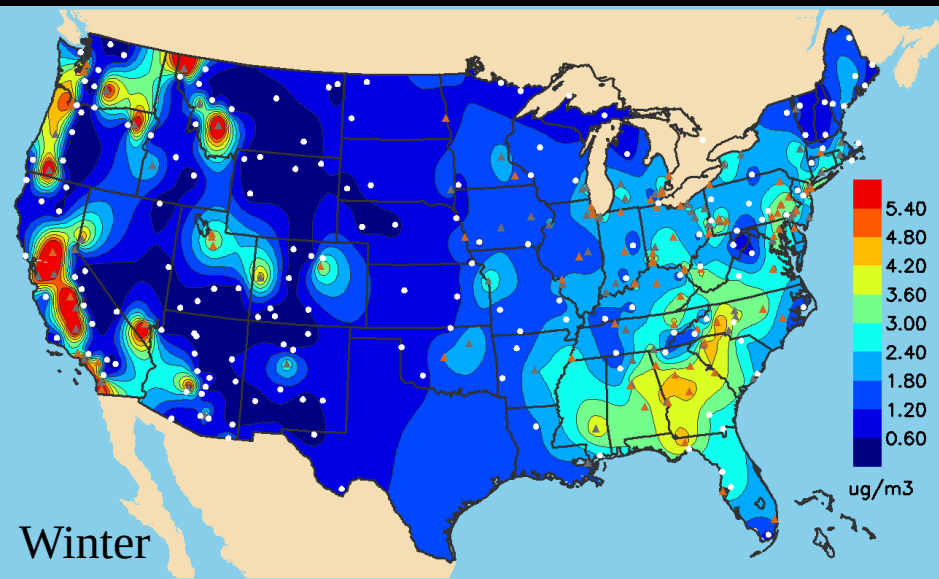
2007□



2006□



Seasonal TC Concentrations (2007-09)



- Interagency Monitoring of Protected Visual Environments (IMPROVE)
 - Rural sites
- U.S. EPA Chemical Speciation Trend Network (CS)
 - Urban sites
- Thermal optical reflectance measurement on 24-hr samples collected on quartz fiber filters

CMC vs CMAQ

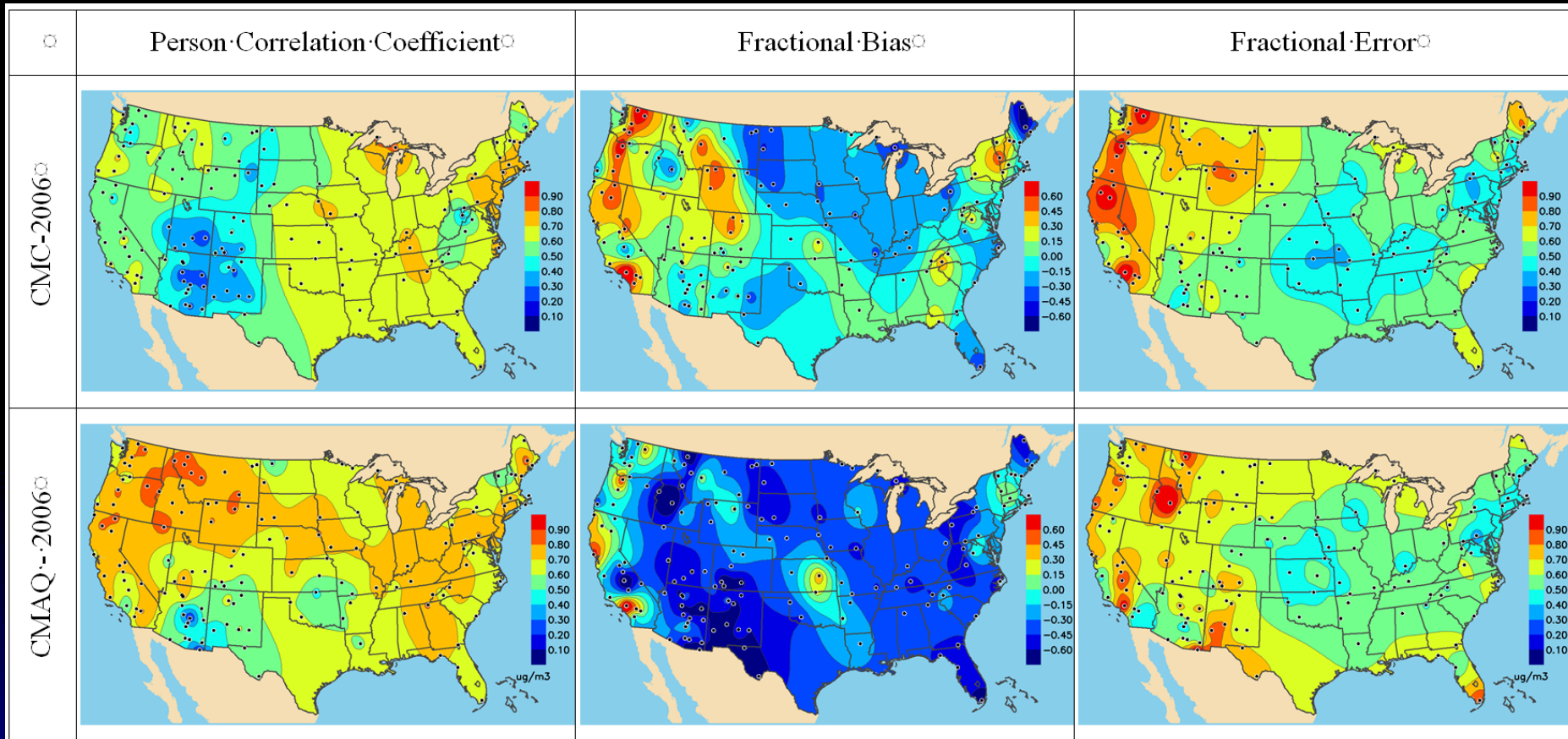


Figure 6. Model performance statistics from the comparison of simulated to measured TC at rural IMPROVE monitoring sites. The top row is for the CMC 2006 model simulation period and the bottom is from the U.S. EPA CMAQ simulation. The maps were created by first calculating the model performance at each rural IMPROVE site (black dots) then spatially interpolating these data using a Kriging algorithm.

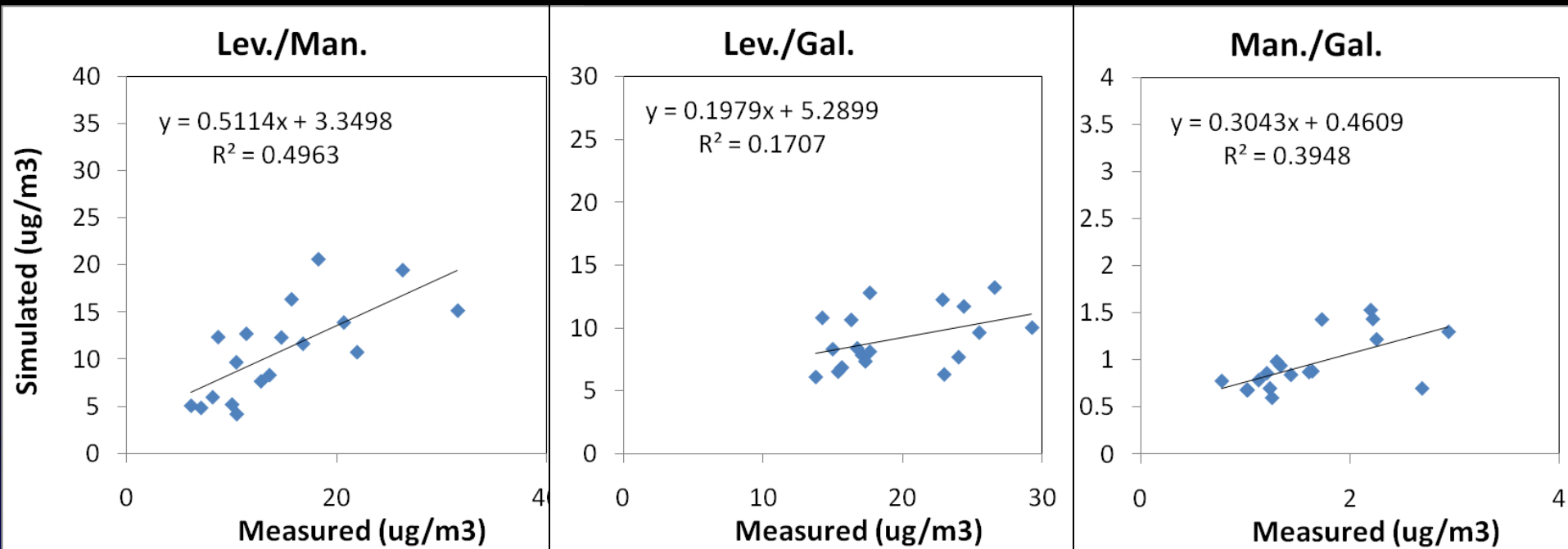
Model Performance Stats

Model performance statistics for TC concentration simulations at 145 rural IMPROVE monitoring sites using the CMC model for 2006–2008 and the CMAQ model for 2006¶

	2008	2007	2006	CMAQ- 2006
Average measured TC, $\mu\text{g}/\text{m}^3$	1.04 (0.70, 1.73)	1.10 (0.77, 2.01)	1.14 (0.75, 1.91)	1.14 (0.74, 1.93)
Average simulated TC, $\mu\text{g}/\text{m}^3$	1.01 (0.63, 1.71)	1.17 (0.70, 2.04)	1.32 (0.75, 1.95)	1.07 (0.50, 1.74)
Correlation coefficient	0.59 (0.46, 0.71)	0.57 (0.38, 0.72)	0.48 (0.34, 0.64)	0.58 (0.41, 0.73)
Bias of annual means (%)	-2 (-29, 31)	-4 (-25, 33)	6 (-21, 46)	-24 (-42, 19)
Fraction bias	-0.05 (-0.33, 0.30)	-0.08 (-0.32, 0.24)	0.02 (-0.30, 0.35)	-0.36 (-0.59, 0.03)
Fractional error	0.55 (0.42, 0.73)	0.53 (0.44, 0.69)	0.58 (0.44, 0.76)	0.61 (0.48, 0.78)
Relative root mean square error (%)	82 (54, 138)	92 (61, 191)	93 (64, 193)	80 (59, 216)
Median of the absolute relative error (%)	45 (33, 60)	45 (34, 57)	48 (36, 70)	46 (39, 57)

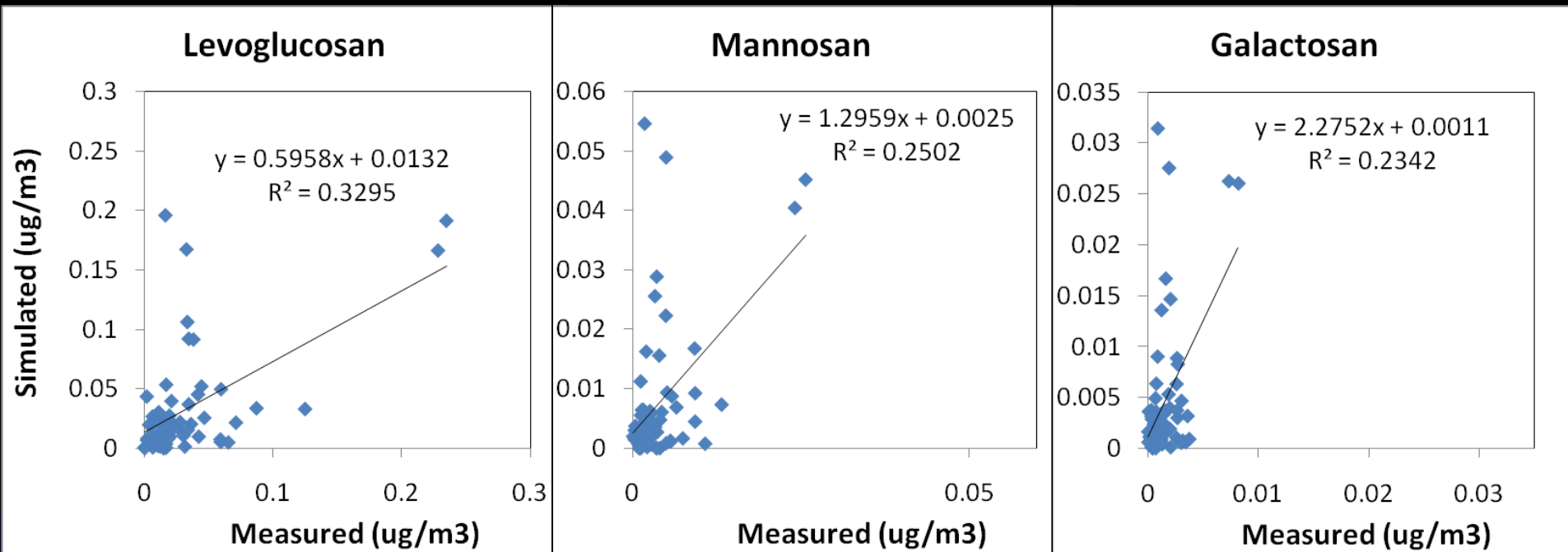
For each model performance statistic, the median value across all monitoring sites is presented. The parenthetical values are the 16th and 84th percentiles across the monitoring sites.¶

Simulation of Ratios of Smoke Marker Species



- 24-hour average concentrations at Upper Buffalo, AR in March and April 2008

Simulation of Smoke Marker Species



- 24-hour average concentrations at Monture, MT in July – September 2008

Could add a slide on problems with ctm and receptor models alone

- A) Start with regulatory needs
- B) The CMB model has been increasingly used for apportioning primary smoke using organic marker species such as Lev
 - Issues with using CMB model
 - 1) measured data availability
 - 2) can't apportion secondary material
 - 3) source profiles are variable
 - 4) can't distinguish between similar source types
 - We propose a method to address the second two issues
- C) show the framework – Concept for hybrid smoke apportionment
- D) Move to source profiles
 - Show variability in profiles – amy's work
 - Show spatial source profiles – leighs work
- E) show mcarlo model
- F) show value of integration model for source profiles variability at IMPROVE sites
- G) show actual data
- Show concept of merging back trajectories, fire emissions and source profiles
- Show how we do it with weidenmyers emissions, mcarlo, and simply kinetics. (show simple example of success of model) seasonal variability in continental tc simulation and fire impacts.
- Show special study
 - Show correlation of smoke marker species

thoughts

- This work supports the notion of biogenic carbon dominating the rural pm.

- Area sources are a major component and need to better understand these and separate them in future emission inventories. IN the paper give a table on relative contribution of major area source types.

- Jointly sponsored by the Department of Chemistry and Biochemistry, CIRES, and the Environmental Program

- **Known and Unexplored Organic Constituents in the Earth's Atmosphere: Instrument Development to Enhance Exploration**

- Allen Goldstein

- Professor, Department of Environmental Science, Policy, and Management and

- Department of Civil and Environmental Engineering, University of California at Berkeley, USA

- **Abstract**

- A substantial fraction of the atmospheric organic chemicals in both gas and particle phases have not been, or have very rarely been, directly measured. Even though our knowledge of them is limited, these compounds clearly influence the reactive chemistry of the atmosphere and the secondary formation, transformation, and likely the climate impact of aerosols. A continuing challenge in the coming decade of atmospheric chemistry and aerosol research will be to elucidate the sources, structure, chemistry, and fate of these clearly ubiquitous yet poorly constrained organic atmospheric constituents. Critical questions include: *What atmospheric organic compounds do we know about and understand? What organic compounds are present as gases and in aerosols? What evidence exists for additional organic compounds in the atmosphere? How well do we understand the transformations and fate of atmospheric organics?*

The complex chemical composition of atmospheric aerosols, particularly the organic carbon portion, presents unique measurement challenges. We developed the Thermal Desorption Aerosol Gas chromatograph (TAG) system for hourly in-situ speciation of a wide range of primary and secondary organic compounds in aerosols. This instrument combines a particle collector with thermal desorption followed by gas chromatography and mass spectrometric detection to provide separation, identification, and quantification of organic constituents at the molecular level. Observed compounds include alkanes, aldehydes, ketones, PAHs, monocarboxylic acids, and many more. The hourly time resolution measurements provided by TAG capture dynamic and frequent changes in aerosol composition. We have incorporated a two-dimensional chromatography (GC×GC) capability into TAG with a time of flight (TOF) MS detector. Two-dimensional chromatography provides two types of compound separation, most typically by volatility and polarity using two columns with different stationary phases connected in series separated by a modulator. The modulator periodically traps analytes eluting from the first column, and injects fractions of this effluent onto the second column in the form of narrow pulses providing additional separation for co-eluting peaks. The approach is especially useful for distinguishing polar compounds that would otherwise be buried in the unresolved complex mixture (UCM). We are developing a semivolatile collection system that allows simultaneous measurement of chemically specific semivolatile organics in the gas and particle phases, enabling in-situ analysis of speciated organic partitioning in the real atmosphere. We have also developed and deployed a combined TAG-AMS (Aerosol Mass Spectrometer) instrument for simultaneous measurements of the total and speciated aerosol composition. This talk will review our recent developments (TAG, 2DTAG, SVTAG, TAG-AMS), and present new observations of speciated semi-volatile separations between the gas and particle phases, 2DTAG and TAG-AMS observations in ambient air and controlled chamber source oxidation studies. New experiments using soft ionization techniques to more fully separate the UCM and to identify more of the organic species in aerosols will also be presented.