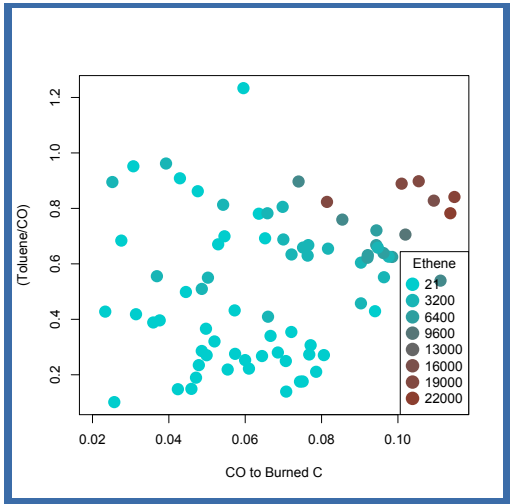

IMPROVED ESTIMATION OF AIR-QUALITY IMPACTS OF WILDFIRES

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Matthew Thomas,
Hanwant Singh and Laura Iraci
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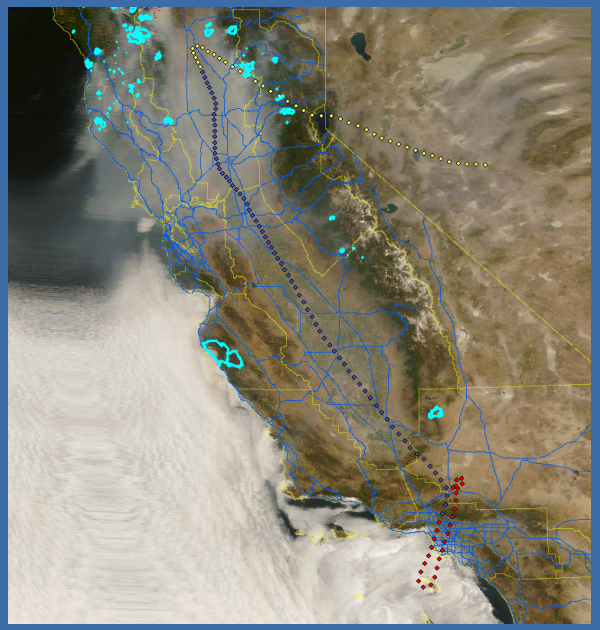
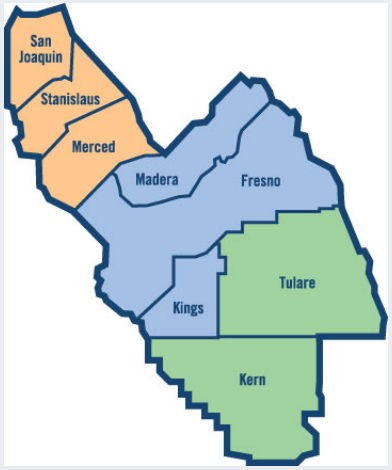
and Cal-ARB,
NRL, and Ames Partners

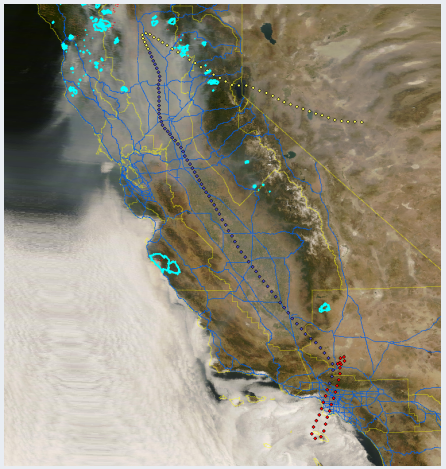


Which fire emissions contribute most radical production to ozone production?

Emissions Speciation

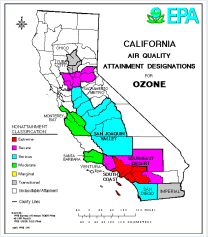
Improved Air Quality Simulations for San Joaquin Valley





- Significant challenges air pollution and health for "SJq." Air quality has resisted some improvements seen in LA and S. Coast
- Poor pulmonary health in the central cities (Fresno) is well known
- Out-of-compliance for both ozone and particles ($PM_{2.5}$)
- A very large amount of time, effort (and confusion) is taken in assessing "exceptional events," particularly with fires (these situations can combine some fire with other influences)

Our main cooperatinging client is California-Air Resources Board



Ajith Kaduwela
Manager Regional Air Quality Modeling Section
California Air Resources Board
Sacramento, CA

ARB Team
Ajith Kaduwela, lead modeler

Ames Team
... Robert Esswein, analyst/programmer
Hanwant Singh, analysis/emissions-composition
Vince Ambrosia, James Brass – fire behavior

Chenxia Cai*
principle CMAQ modeler
Sarika Kulkarni, developing WRF

Matthew Thomas – implement lofting
Robert Chatfield - "Lord High Everything Else"

Other advisors/providers:
Edward Hyer (Monterey NRL – emissions)
Christine Wiedenmyer, NCAR – FinnV1 emissions

Clearly, most collaboration is by video-con

Wild Fire Emissions

Focus of this presentation:

Speciation of emissions

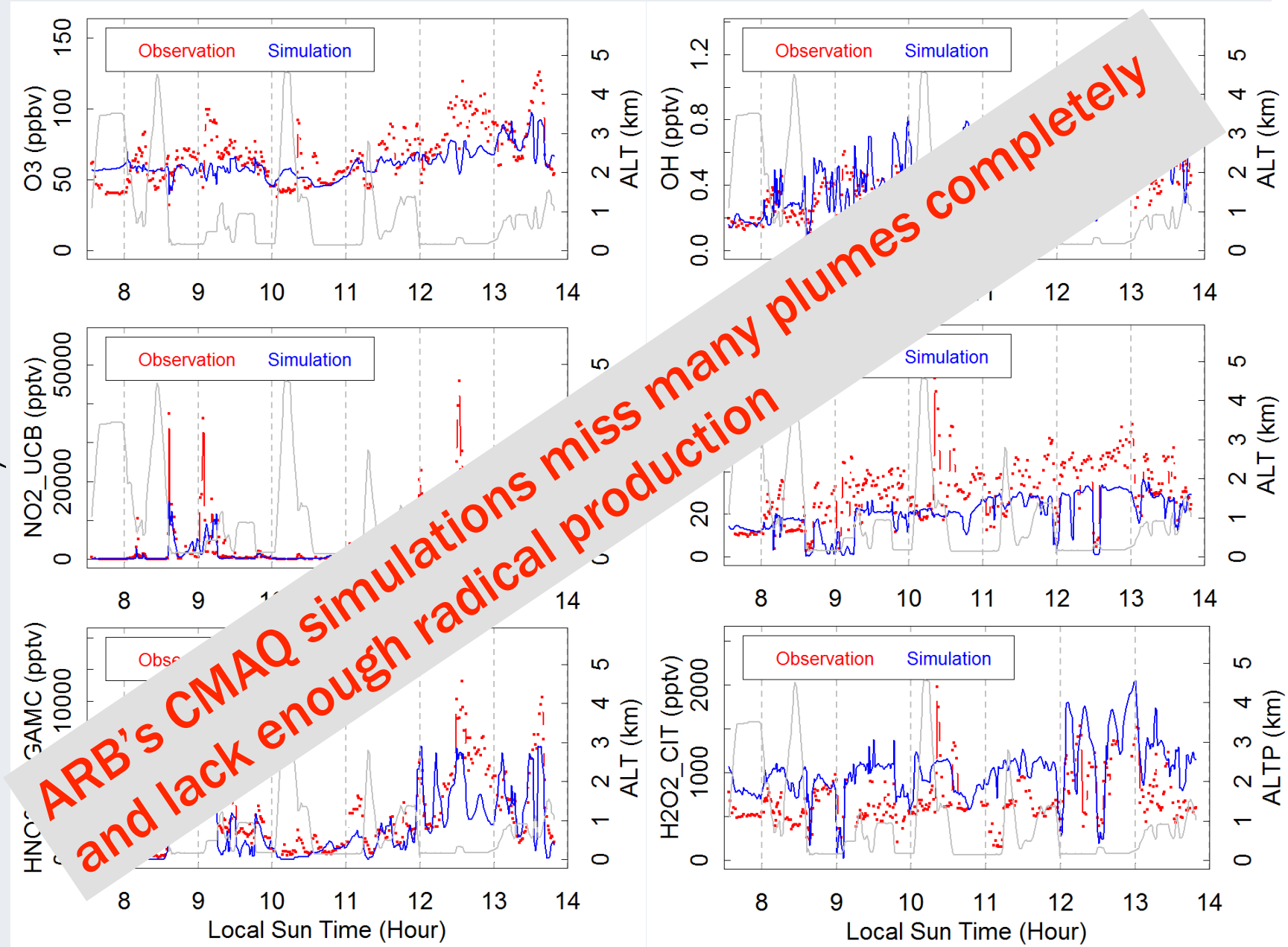
(back to, and from ARL 1)

Other work:

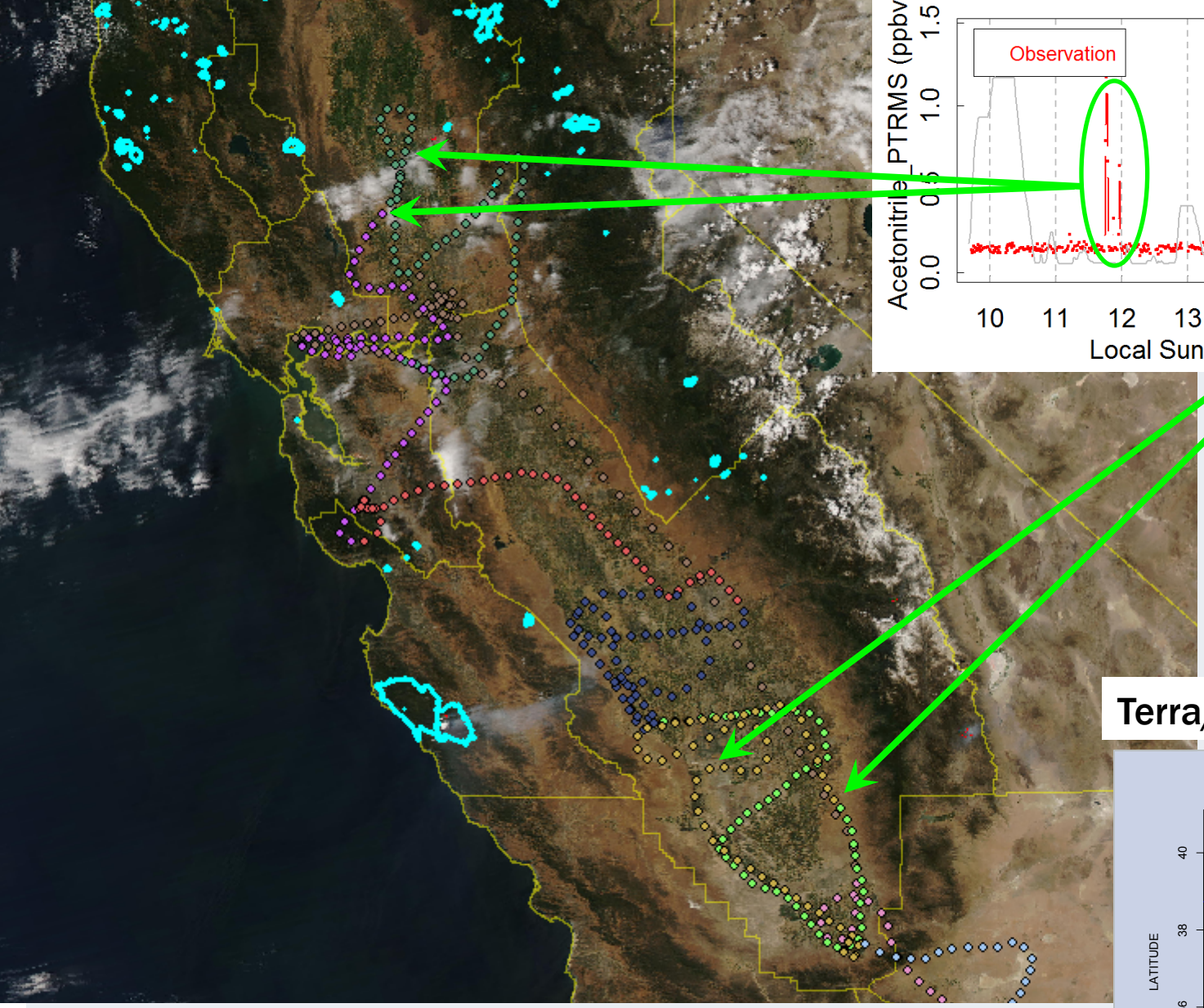
- Plume rise into CMAQ: ARL 2, pending ARB timing needs
- Emissions location and strength: ARL 3: specified
- 1 publication in revision, 1 in draft stage

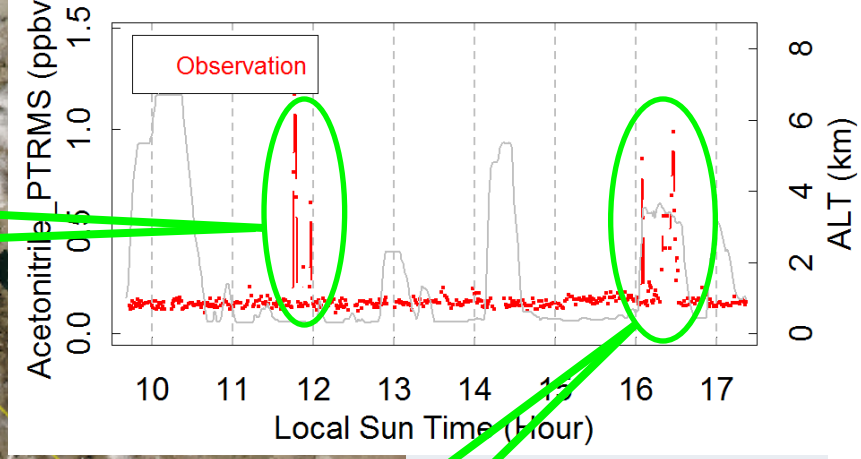
Precursor Limitations

June 18, 2008



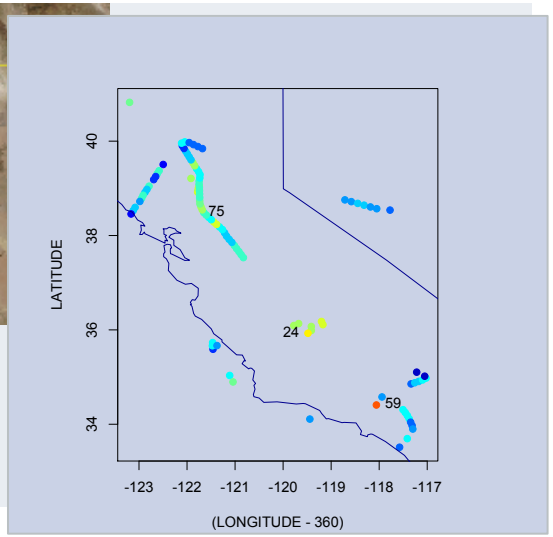
ARB's CMAQ simulations miss many plumes completely and lack enough radical production





June 20, 2008

Terra/MODIS 18:55 UTC



Ajith Kaduwela

Identified "clean: strong plumes

Good Emissions for Western Fires

(1) What do Western fire-modelers need?

It seems fairly dull: some long tables

Intermediate Combustion Efficiency:
High Aromatic / Alkene Emissions Group

Species or Parameter	R^2	Emission Factor molecule /atom C	*t*-value	Pr(>|*t*|)	Rel Var City / Burn	*N* of points
CH_3CN	0.84	0.16	14	2.2e-16	0	39
CO	0.5	58	5.3	6.4e-06	5.6	39
CH_4	0.74	16	10	1.4e-12	0	39
HCHO	0.71	2200	9.7	9.8e-12	0	39
Furan(+Isoprene)	0.92	170	19	2.2e-17	0	30
Benzene_PTRMS	0.67	170	8.9	1.1e-10	0	39
Toluene_PTRMS	0.64	75	8.3	5.1e-10	0	39
Methanol_PTRMS	0.89	2100	18	8.4e-20	0	39
ACETALDEHYDE_PTRMS	0.62	720	7.7	5.6e-09	0	37
Acetone_PTRMS	0.81	500	13	4.9e-15	0	39
MVK.MACR_PTRMS	0.67	84	6	2.2e-06	7	30
Isobutane_TOGA	0.74	9.6	9.6	8.5e-11	0	33
Butane_TOGA	0.82	34	12	2.5e-13	0	33
Isopentane_TOGA	0.45	14	5.3	1e-05	0	33
Pentane_TOGA	0.84	16	13	2.7e-14	0	33
Isoprene_TOGA	0.011	8.5	1.2	0.26	0	31
Benzene_TOGA	0.85	160	13	2.6e-14	0	33
Toluene_TOGA	0.85	89	14	1.1e-14	0	33
Ethylbenzene.m.p.xylene_T	0.87	16	15	2.1e-15	0	33
Methanol_TOGA	0.78	1400	11	5.2e-12	0	33
Ethanol_TOGA	0.56	99	6.5	3.4e-07	0	33
Acetaldehyde_TOGA	0.84	800	13	4.5e-14	0	33
Acetone_TOGA	0.79	390	11	2.1e-12	0	33
Propanal_TOGA	0.85	85	13	2.1e-14	0	33
MEK_TOGA	0.91	64	18	6.9e-18	0	33
Methacrolein_TOGA	0.2	25	3	0.0051	0	33
Methyl.Vinyl.Ketone_TOGA	0.076	15	1.9	0.066	0	33
butanal_TOGA	0.81	14	12	5.5e-13	0	33
mtbe_TOGA	0.089	0.11	2	0.051	0	33
Chloromethane_TOGA	0.075	4.3	1.9	0.067	0	33
Chloromethane_TOGA	0.075	4.3	1.9	0.067	0	33
Chloroform_TOGA	0.29	0.46	3.7	0.00078	0	33
Dichloromethane_TOGA	0.46	1	5.3	9.2e-06	0	33

Note:

Not fire emissions (this fire type)

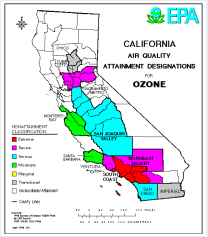
These do determine how fires may contribute to smog ozone,

... and how fire emissions interact with other emissions

High ozone may often be a combined natural & controllable phenomena

Good Emissions for Western Fires

(1) What do Western fire-modelers need?



Emissions estimates that match conditions of Western fires:

- **"Lab" or small-fire sampling: many advantages: great control of fire type.**

- **Emissions inferred from actual concentrated fire plumes**

— at an interval of ½ to 2 hours from emission

— match fuel types and conditions of "typical" fires, or even the fires used for SIP modeling and inference

— may well be more defensible in litigation (less extrapolation)

— interpretation of secondary products (aldehydes, organic nitrates) allows an accounting of "un-measurables" (A. Goldstein. Personal communication, submitted*)

Park., J-H., A.H. Goldstein, J. Timkovsky, S. Fares, R. Weber, J. Karlik, R. Holzinger, Active Atmosphere-Ecosystem Exchange of the Vast Majority of Detected Volatile Organic Compounds, *Science*, Vol. 341 no. 6146 pp. 643-647, doi: 10.1126/science.1235053, 2013.

Good Emissions for Western Fires

(2) Using actual plumes (sampled by aircraft) raises unsuspected problems

We must provide *"emissions factors"* (related directly to fuel burned) rather than uninterpreted *"emission ratios"*

(a) Very reactive emissions have reacted! Not so much a problem — remember, at a distance of ½ to 2 hours
But: this can be checked by looking for trends as plume intensity increases)
And: policy-relevant three-d models smooth out these details anyway, so is it best to provide "emissions factors" at the right scale.

(b) We must use C as the conserved quantity that is related directly to the dry fuel biomass, C ~ 0.52 (Dry Biomass)
(CO is often used for emission ratios, but CO / C-burned is not constant!)

The requirement to relate to C introduces complexity

(3) How to relate C-burned to emission? First we must denigrate some reasonable approaches

The natural estimation is to use multiple regression for each target emission speces, regressions relating

C.burn.naive as "tracer"

(target emission – target_background)
~ *b* (*C.burn.naive* – *C.b_background*)

where *C.burn.naive* = CO_2 + CO as measured
good to within ≤1% as a description of the fate of actual burned fuel wood.

Regression relationships are not good: R^2 < 0.5 often
Why ?

The requirement to relate to C introduces complexity

Good Emissions for Western Fires

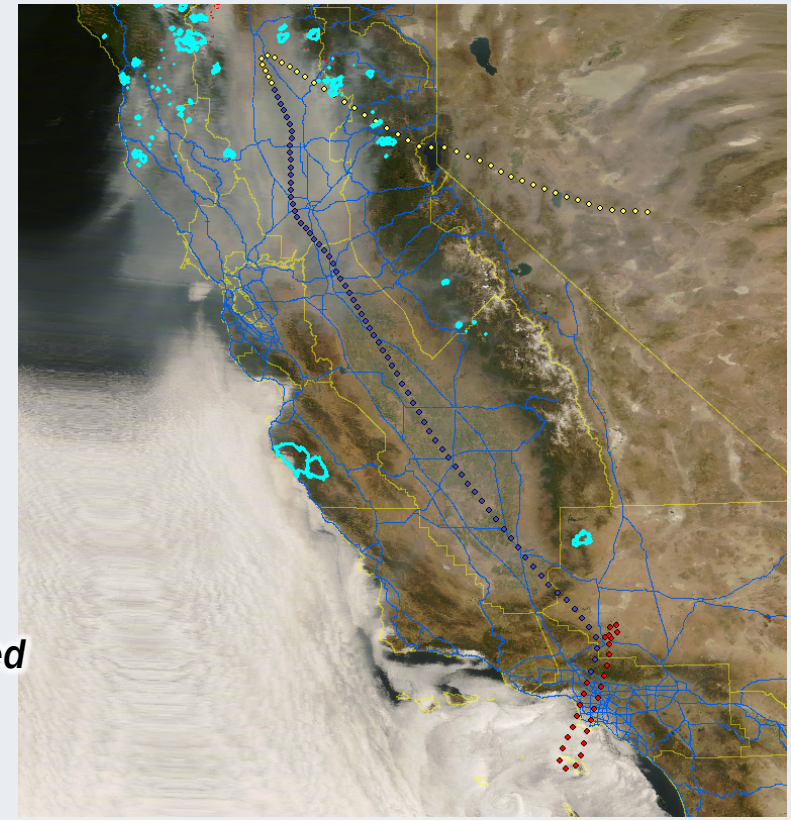
The requirement to relate to C introduces complexity!

Other reasons CO_2 + CO varies

High ***and*** ***Low*** ***CO_2 from inflowing air: West Coast air has very stratified filaments and often variable CO_2***

High CO_2 from industries

Base-inflow (boundary-layer) air and air entrained into rising and advecting plume have variable CO_2 due to all these reasons



High CO_2 from cities

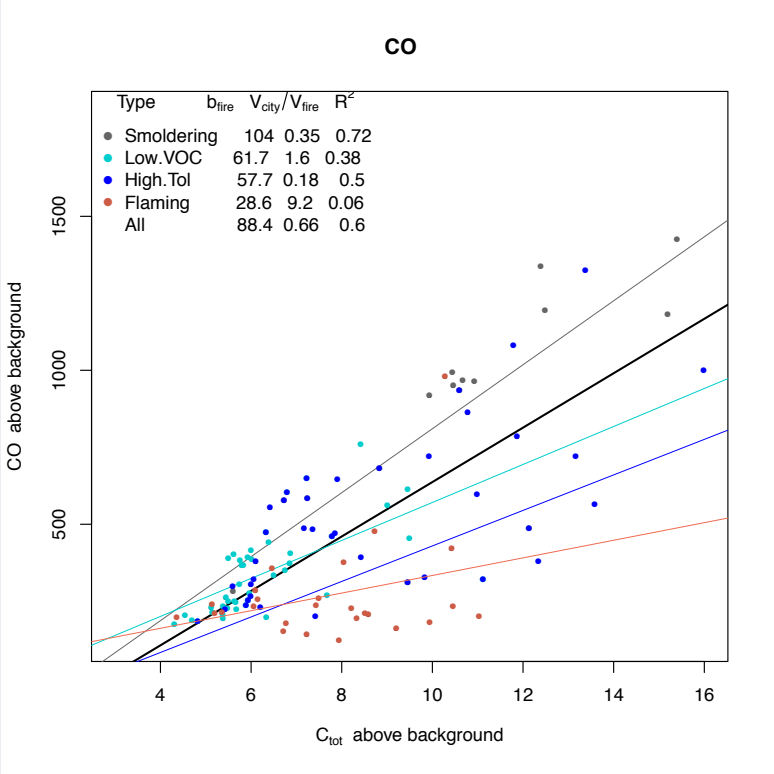
Low CO_2 from vegetation photosynthesis, and high CO_2 from respiration — large daily cycle

While fire plumes affect CO_2 quite clearly, these effects do also!

(3) How to relate C-burned to emission?
First … denigrate some reasonable approaches
CO is very popular

CO as "tracer"

Evidence from this analysis… consistent with small-fire studies



Low CO emissions from strong active flames

Smoldering

Intermediate Lo

Intermediate Hi

Flaming

(3) How to relate C-burned to emission? First we must destroy some poor, appealing appoaches that have been used …

Use another fire tracer like CO … very popular
but far too many other sources: autos, industries and … not emitted equally from all fires.

Low CO emissions from strong active flames

Much better relationships use target ~ CH_3CN (differences above background). Estimate of the background does not give much error.

Our early estimates, *delivered to ARB in May, 2013*, used CH_3CN, and then related CH_3CN to *C.burned.naive* and then to dry biomass.

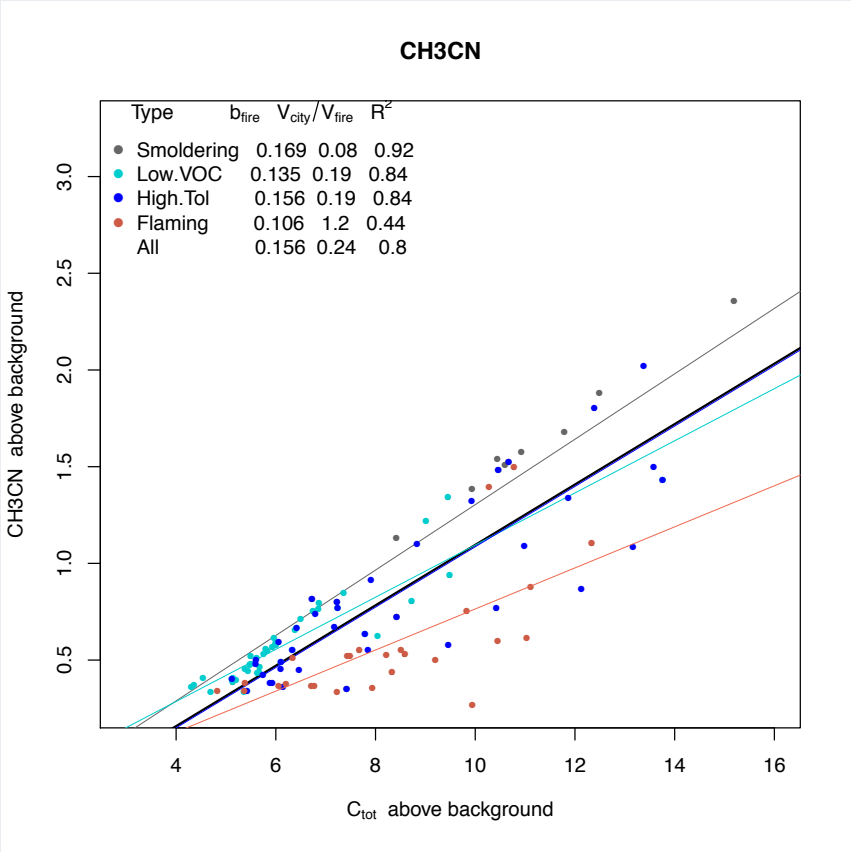
Lower CH_3CN emissions from wood than leaves, variable N

CH_3CN as "tracer"

(3) How to relate C-burned to emission?
First … denigrate some reasonable approaches
Acetonitrile, CH_3CN appears good

CH_3CN as "tracer"

Evidence from our results … consistent with small-fire studies



Smoldering

Intermediate Hi

Intermediate Lo

Flaming

More consistent emissions from all combustion conditions 1.5 (+.2, –.5)

However, CH_3CN should depend on N content of fuels:
Do Western Forest Fires have Variable N? Chapparel ??

(3) How to relate C-burned to emission? A proxy created from CO_2+CO

"

So we create a proxy CO_2 + CO that represent sources we can identify including some urban/industrial, and create a C-burned proxy excluding them but including emissions indicators: smoke properties enhance CH_3CN

Certain CO_2 variations cannot be assessed easily: e.g., diurnal photosynthesis & respiration

CO_2 + CO multiple regression as a function of these variables

```
Coefficients:
                                Estimate Std. Error  t value Pr(>|t|)
(Intercept)                     381.7861     0.7469   511.18  < 2e-16 ***
CH3CN                             4.9407     0.3211    15.39  < 2e-16 ***
CCl4                              0.2749     0.0860     3.20   0.0018 **
CH2Cl2                            0.0316     0.0216     1.46   0.1459
Absorption/Scattering (1-SSA) 60.8265     8.3991     7.24  6.2e-11 ***
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
Multiple R-squared: 0.776
```

F.Fires

Urb./Ind.

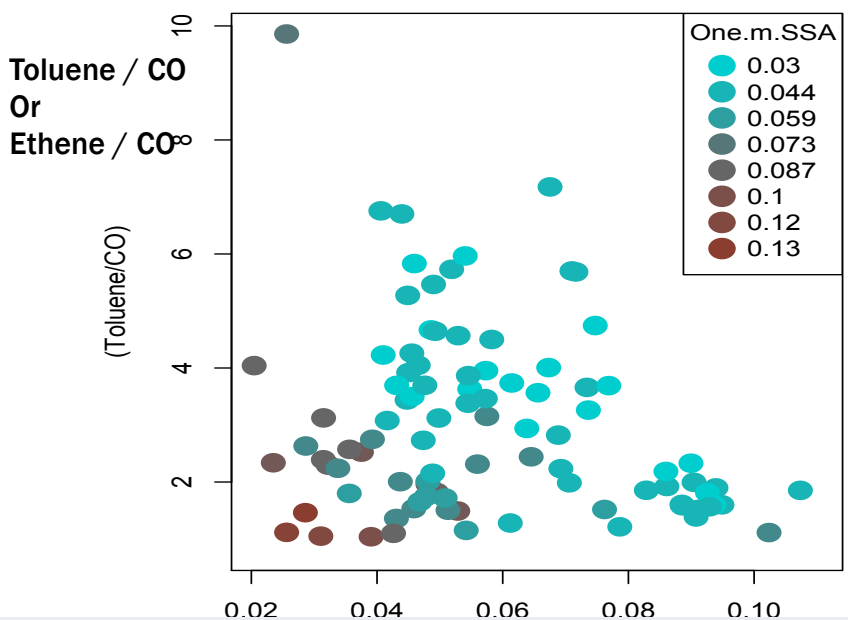
F.Fires

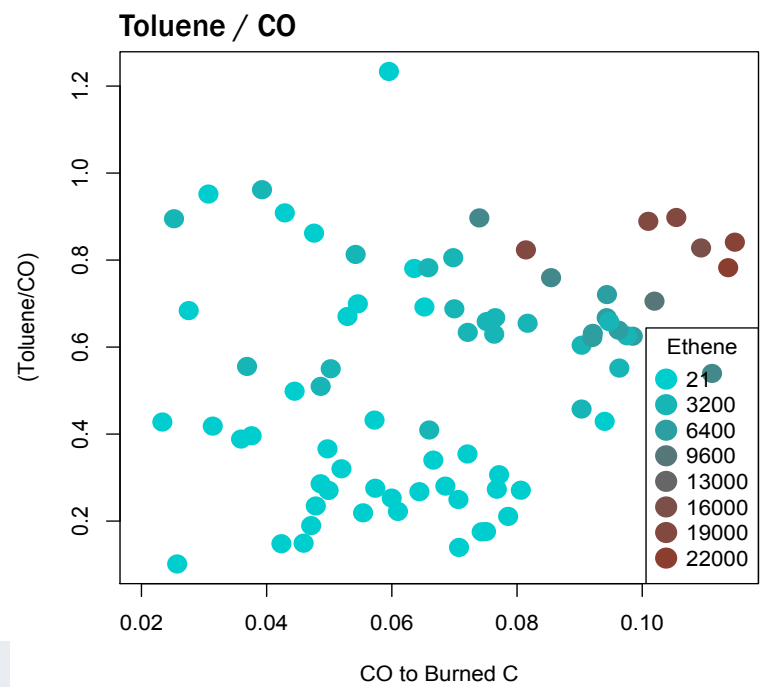
Perfect reproduction of dependent variable (R^2 = 1.0) not desired!

Certain basic fire types appear when we plot up ratios of "defining" emissions

(1) Simple "inefficiency" of burn has long been used $CO / (CO_2 + CO)$, often communicated as Modified Carbon Effiency = MCE = $1 - CO / (CO_2 + CO)$

(2) We found a useful grouping using the ratio Toluene / CO or Ethene / CO
Each ratio also extended to describe particle properties, e.g. "dark smoke" or 1 – SSA



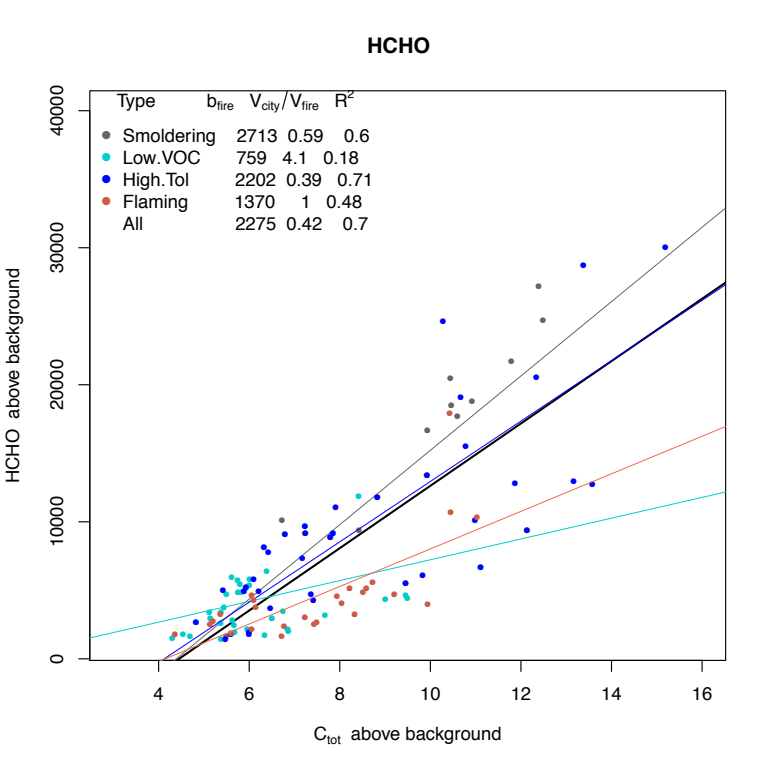


Fire Regimes Vary Widely

Thanks, Amber Soja !

Significance for future SIP photochemical modeling

The second Toluene / CO classification distinguishes the highly reactive alkene and aromatic emissions from less reactive emissions like alkanes, acetone.
Burning chemistry => controls => subsequent photochemistry



Smoldering

Intermediate Hi

Flaming

Intermediate Lo

Many non-flaming emissions are low radical-generators!

Our particular dataset suggests that HCHO, a strong signal of radical-producing photochemistry of VOC's is higher when fire conditions produce Toluene-rich emissions:

What burns does matter.

Photos: Stocks and Soja

Science and Applications Directions

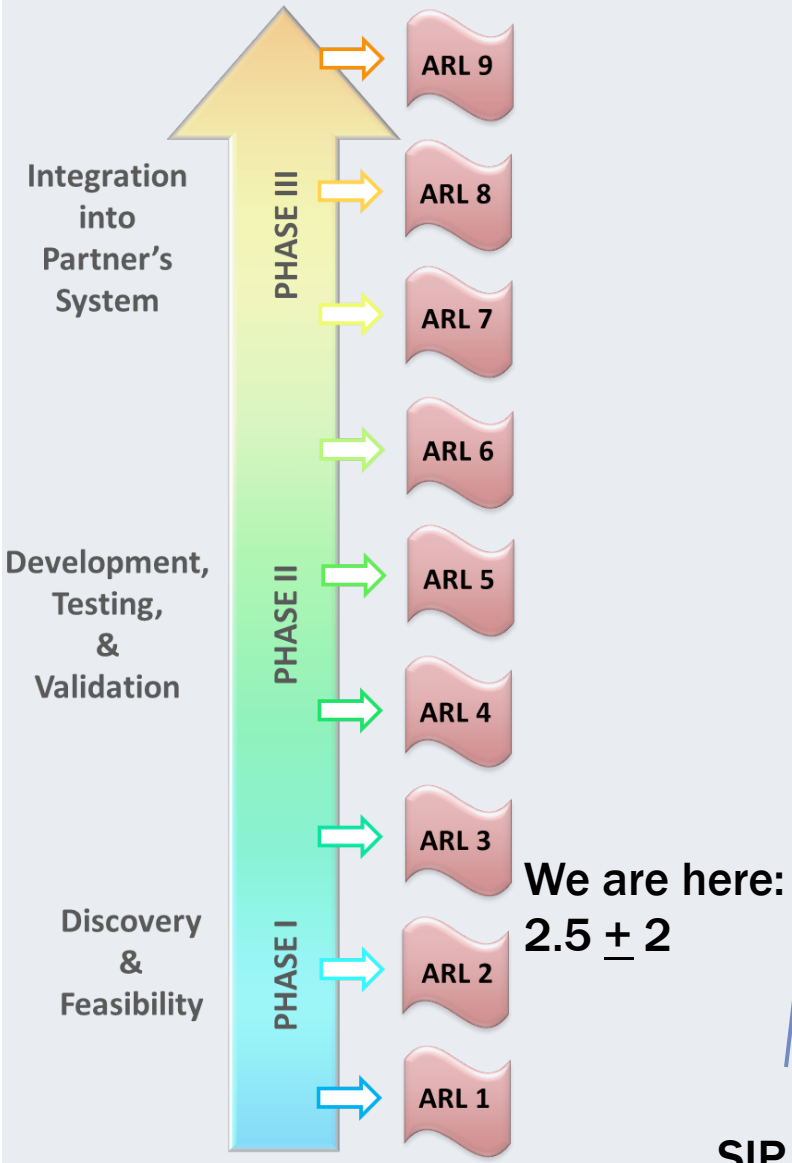
The science direction:
These observations agree well with lab-fire and local-fire descriptions of combustion types and burning chemistry
(e.g., Yokelson papers, esp. 1999, 2003, Isobel, 2011, Akagi, 2011, and others)
However: Need checks against other fire regions, other fires in the far West and Intermountain regions, especially chaparal … then eastward ?

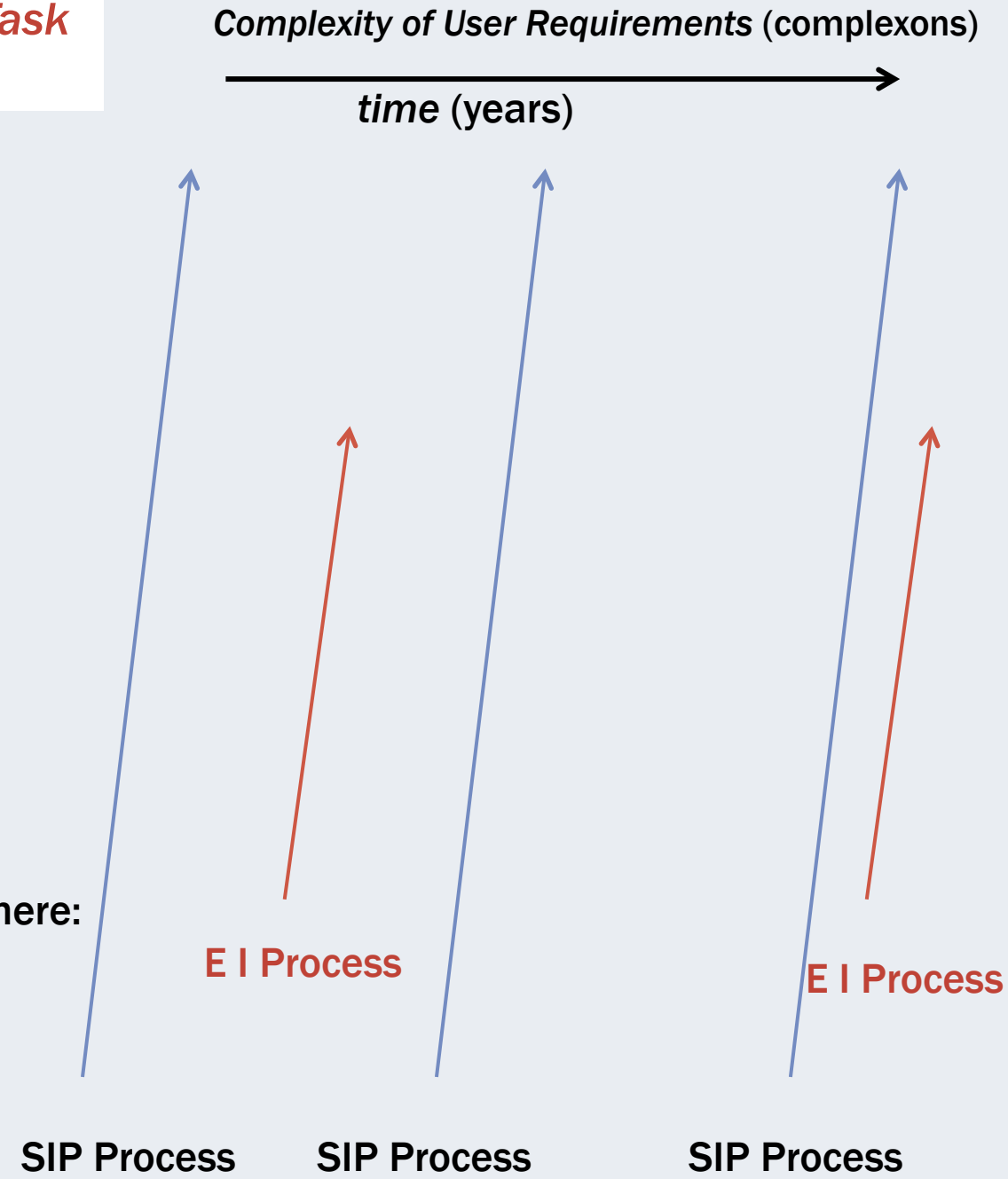
The SIP/customer direction:
Publication must precede fullest adoption (SIP modeling-based rationale)
— we are in draft-publication stage

We should move over model-development / SIP cycles to identify rules for prescribing emissions categories and fractions

flaming … low-reactive… high-reactive … smoldering (most reactive) — fire type
(dark smoke) (lighter smoke) (white-smoke) — SSA remote sensing?
(crown fire) (cooler "distillation" "aromatization") (residual) — FRP / fire reports

Conclusion: The Sysiphian Task of pushing up ARL's



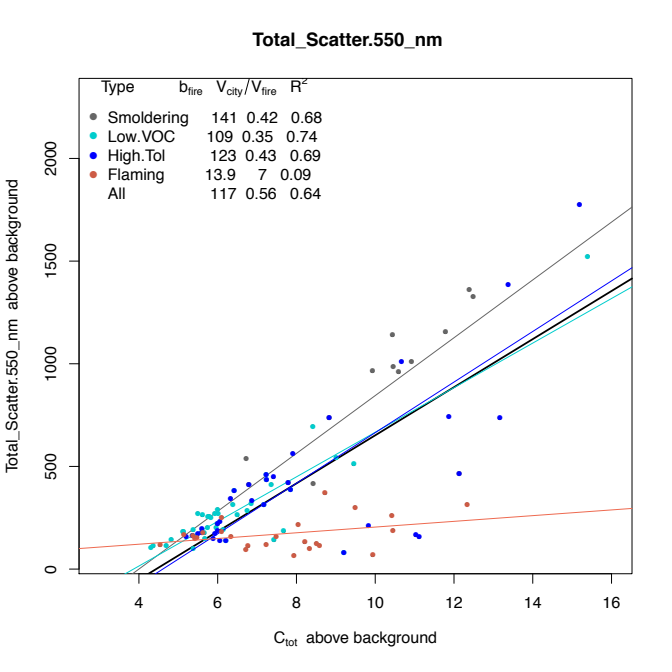


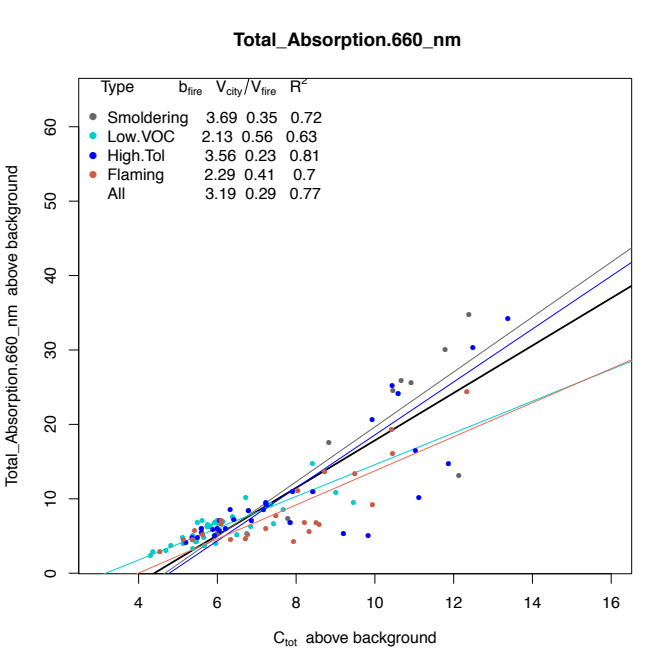
(THE END)

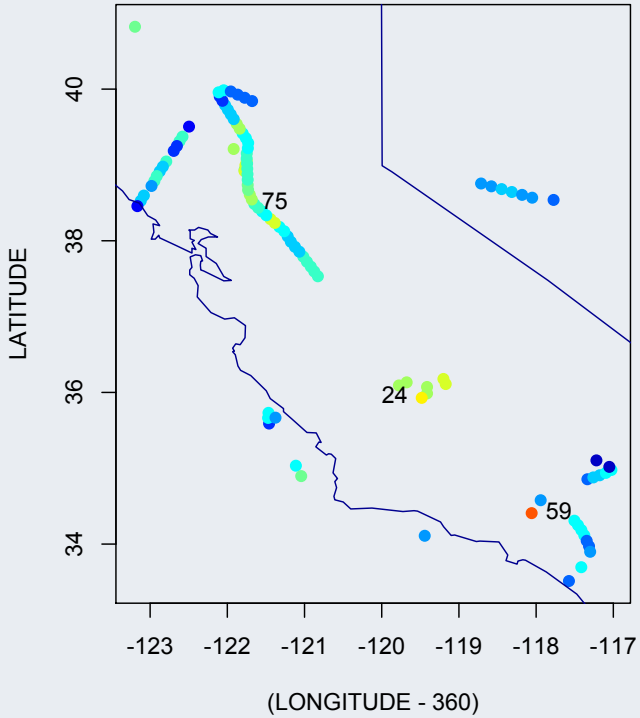
Extra slides

Is dark smoke so polluting for chemistry or climate?

- **Flaming fires produce less smoke (scattering) and similar absorption: this causes the differences in SSA (darkness)**





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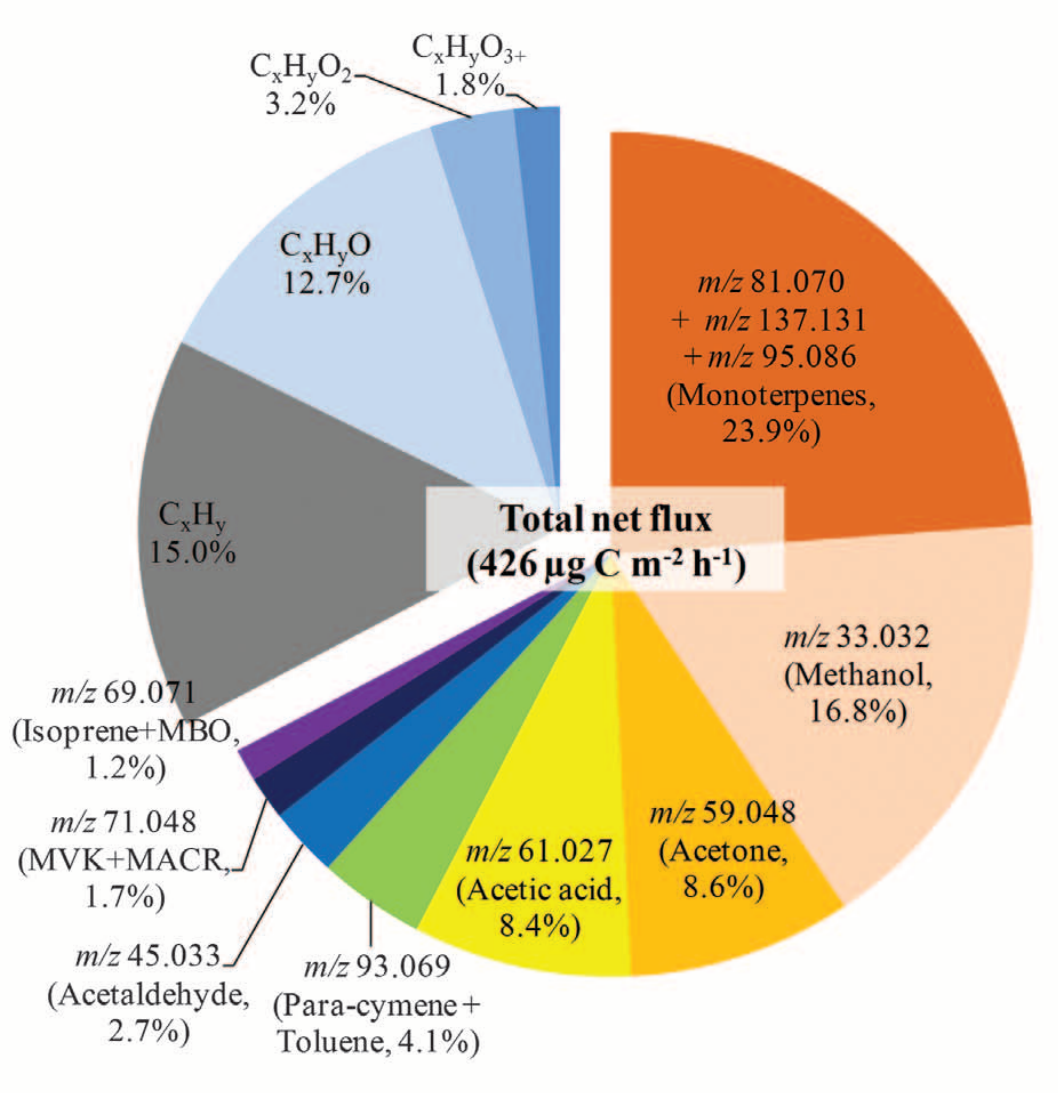
$C_xH_yO_2$
3.2%
$C_xH_yO_{3+}$
1.8%
C_xH_yO
12.7%
C_xH_y
15.0%
m/z 81.070
+ *m/z* 137.131
+ *m/z* 95.086
(Monoterpenes,
23.9%)
Total net flux
(426 µg C m^{-2} h^{-1})
m/z 33.032
(Methanol,
16.8%)
m/z 69.071
(Isoprene+MBO,
1.2%)
m/z 71.048
(MVK+MACR,
1.7%)
m/z 59.048
(Acetone,
8.6%)
m/z 61.027
(Acetic acid,
8.4%)
m/z 45.033
(Acetaldehyde,
2.7%)
m/z 93.069
(Para-cymene +
Toluene, 4.1%)