Enhanced SOA formation from mixtures of biogenic and anthropogenic emissions during the CARES campaign.

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[2]EMSL
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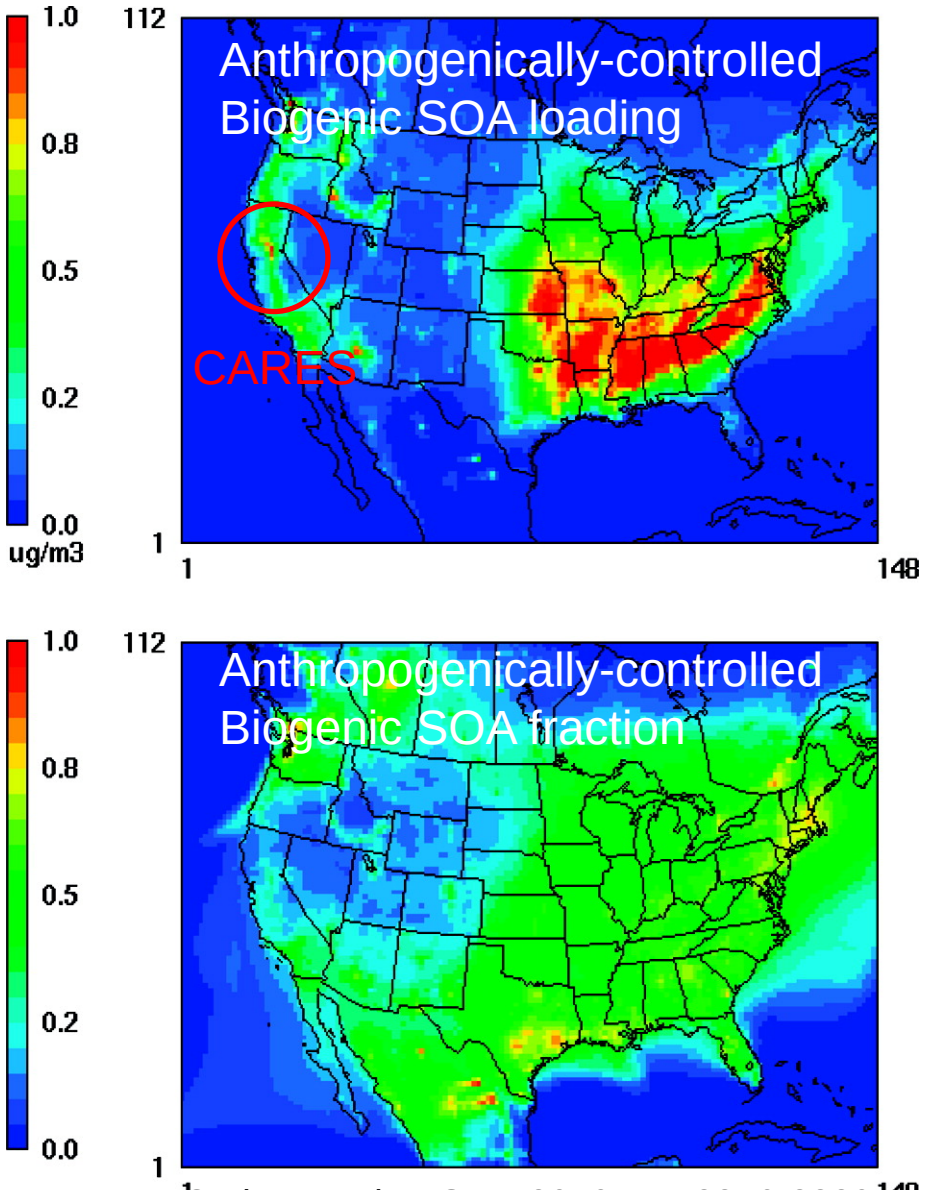
[4]BNL
[5]UC Davis

Anthropogenically Enhanced SOA Formation

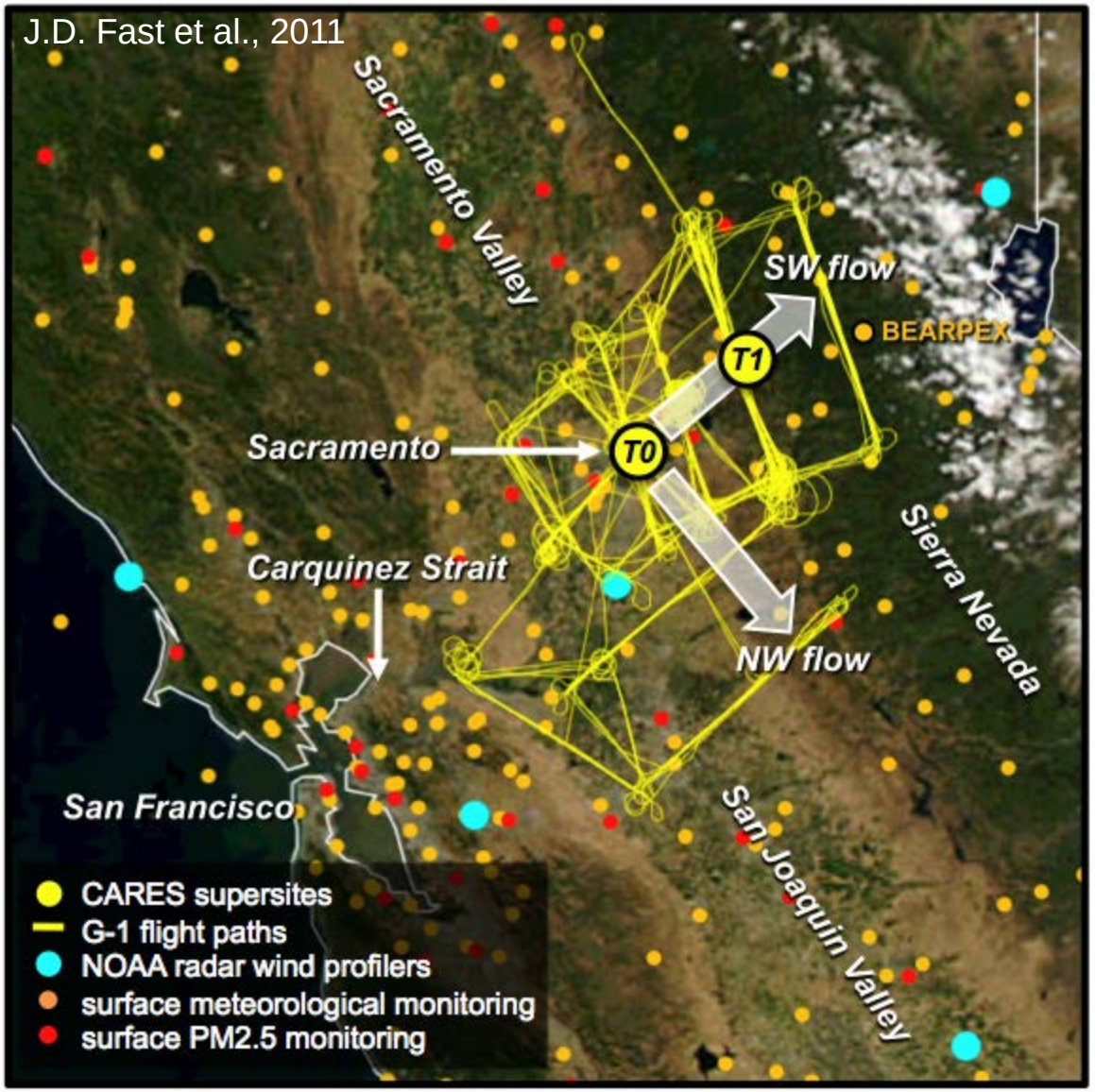
- SOA has correlates with anthropogenic tracers such as CO.
- ^{14}C studies indicate most (40-80%) of the aerosol carbon is modern.
- Observed SOA levels cannot be explained by known chemistry.
- Implies an enhancement of biogenic SOA by anthropogenic emissions.
- Affects aerosol loading and therefore aerosol direct and indirect effects.



Carlton et al., ES&T, 2010, 44, 3376-3380

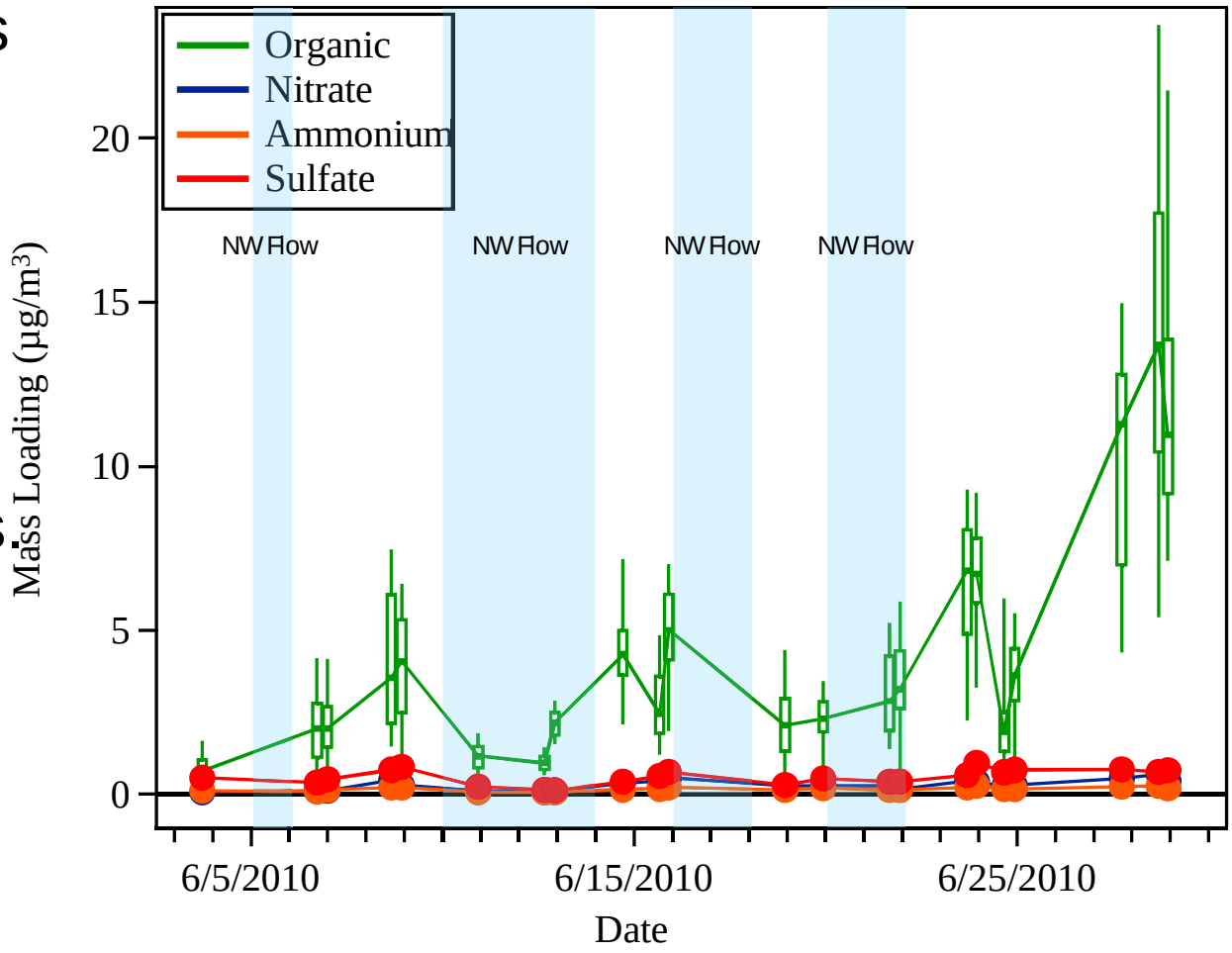
CARES Overview

- NW flow pattern transports the Sacramento plume into the valley and away from the biogenic sources in the foothills.
- SW flow pattern transports the plume into the foothills.
- Different meteorology allows us to investigate anthropogenic/biogenic interactions.
- G-1 flow 22 research flights to sample the plume



Overview of AMS particle measurements

- Fine particle mass is dominated by organics regardless of the meteorology.
- NW flow pattern generally produced low organic loadings.
- Extended periods of SW flow lead to elevated organic loadings.



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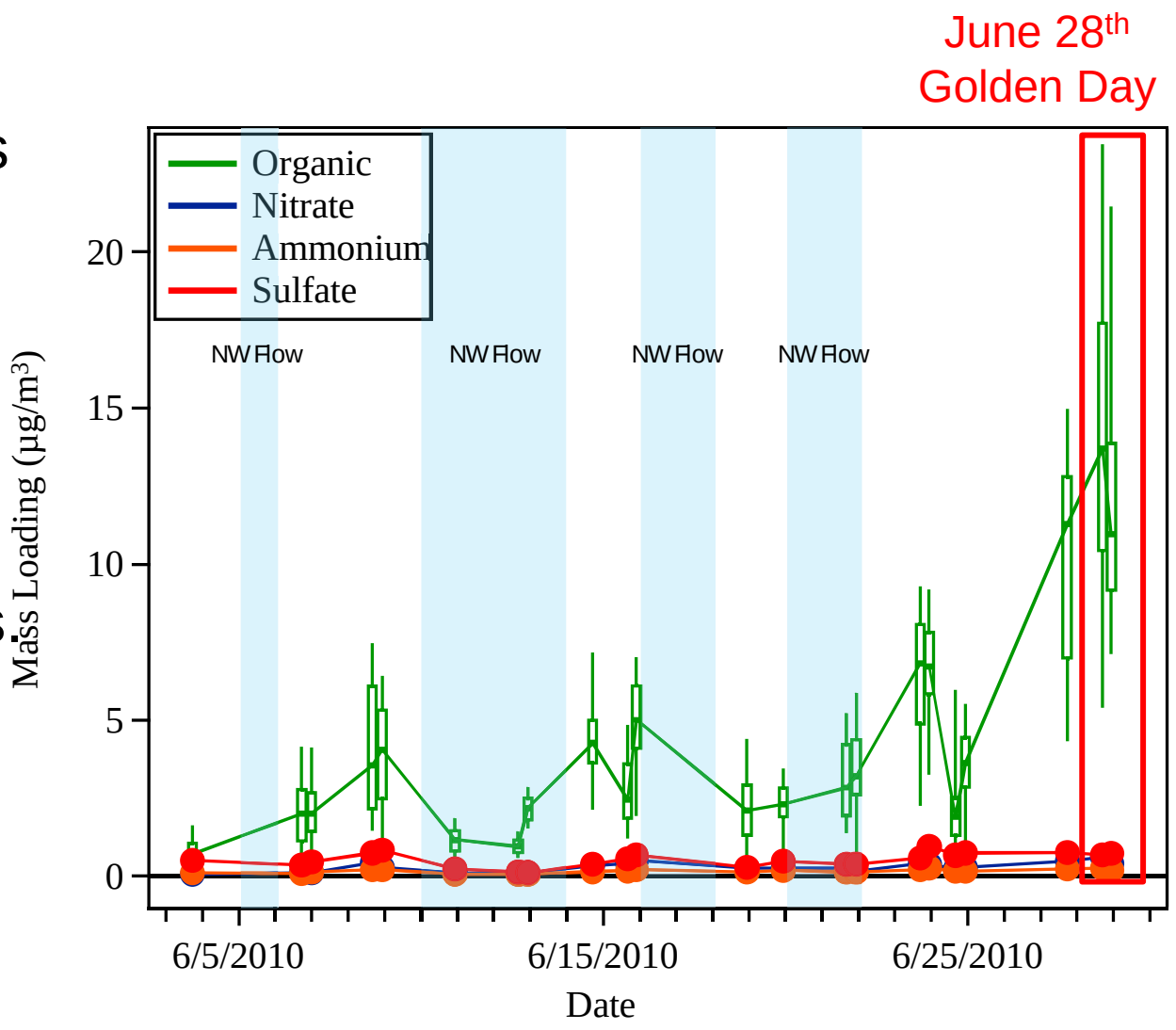
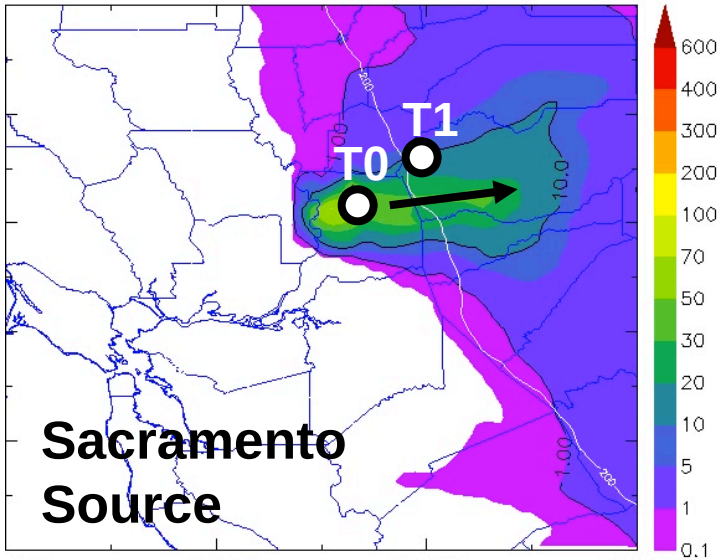
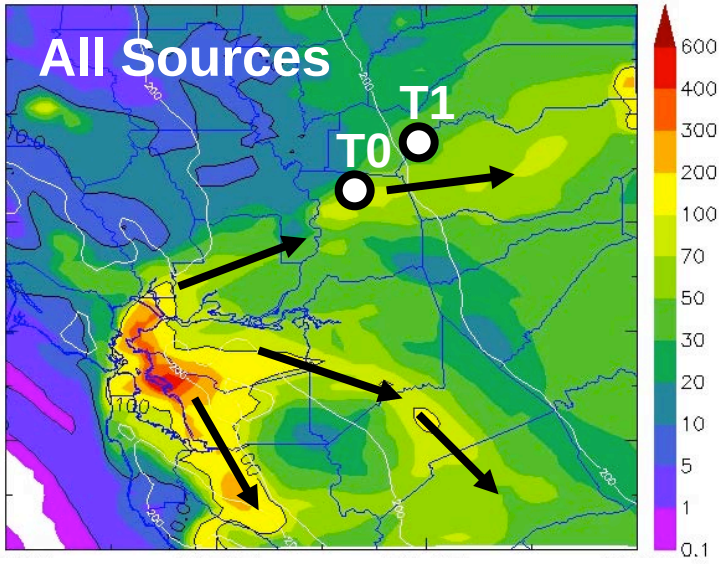


Case 1: SW flow pattern on June 28th: interaction of anthropogenics and biogenics.

- Sacramento plume transported to T1 in early afternoon.



- Bay area plume predominantly transported to the south.



For more information see J.D. Fast et al., ACP, 2012.

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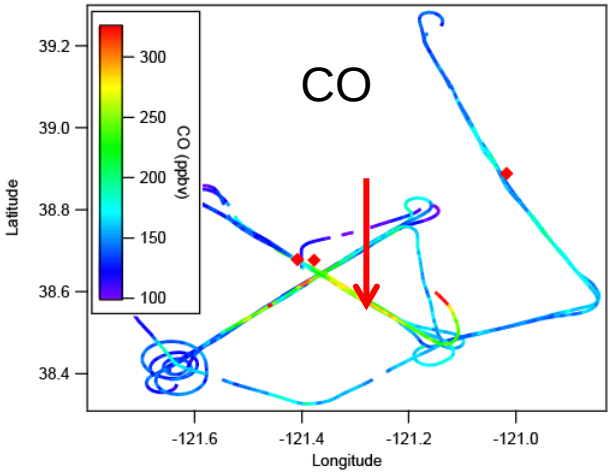
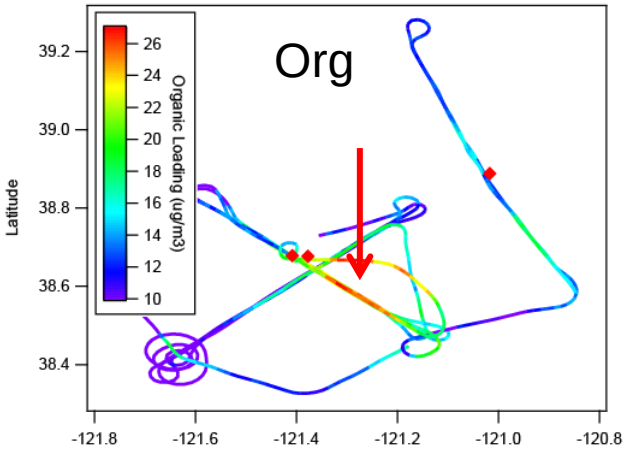
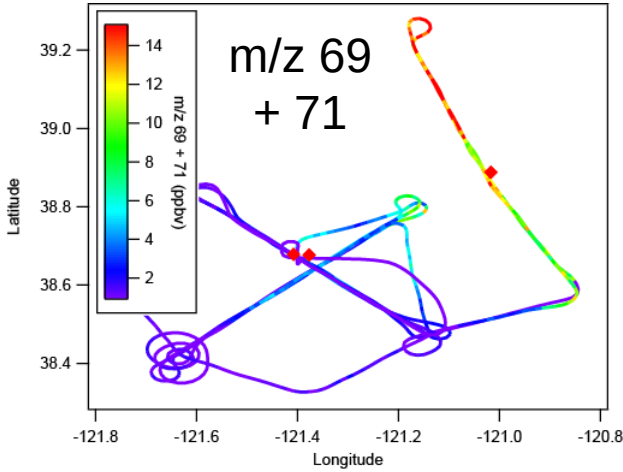
G-1 observations of urban plume evolution on June 28th.

- Urban plume transported to the foothills in the afternoon.

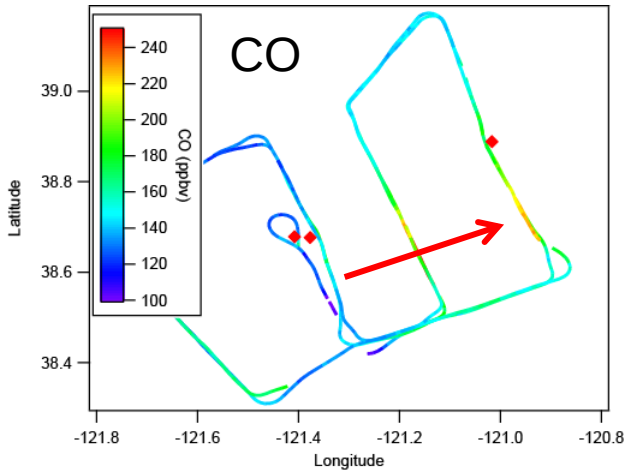
Morning

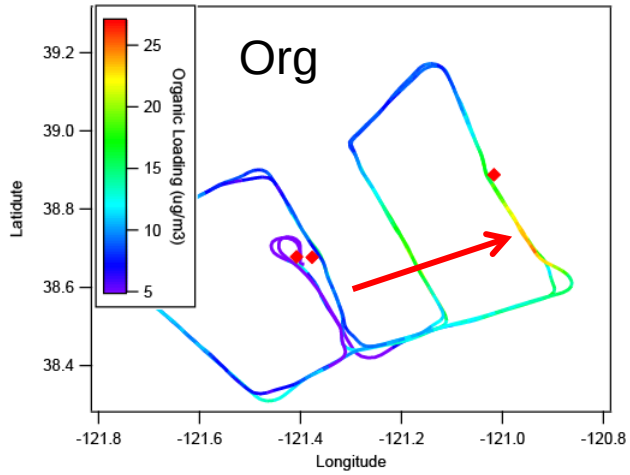


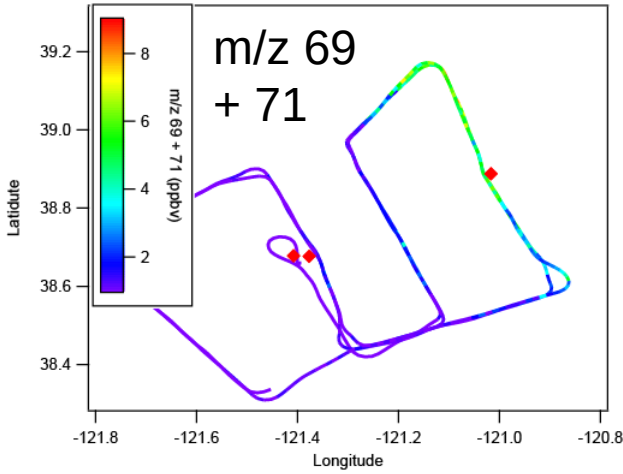




Afternoon

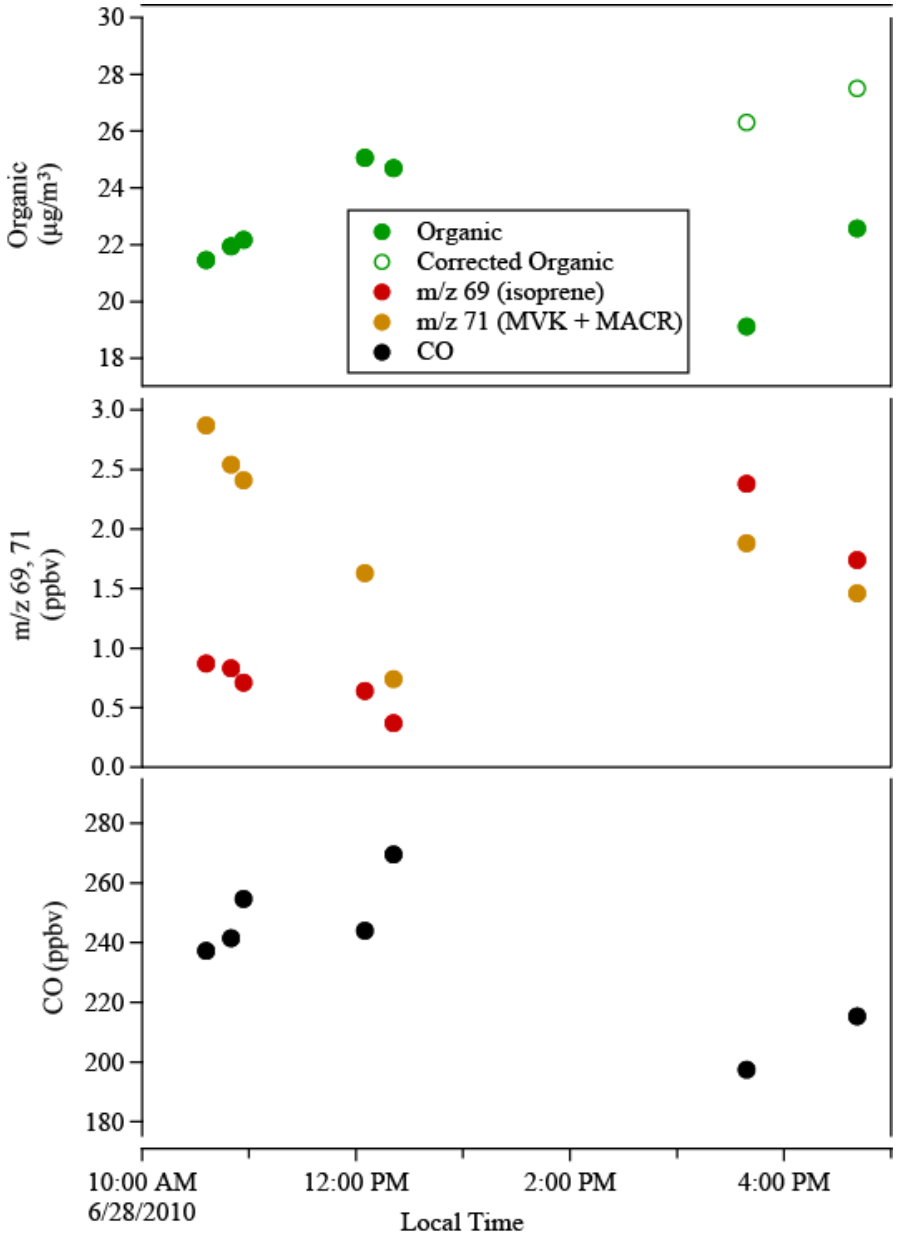






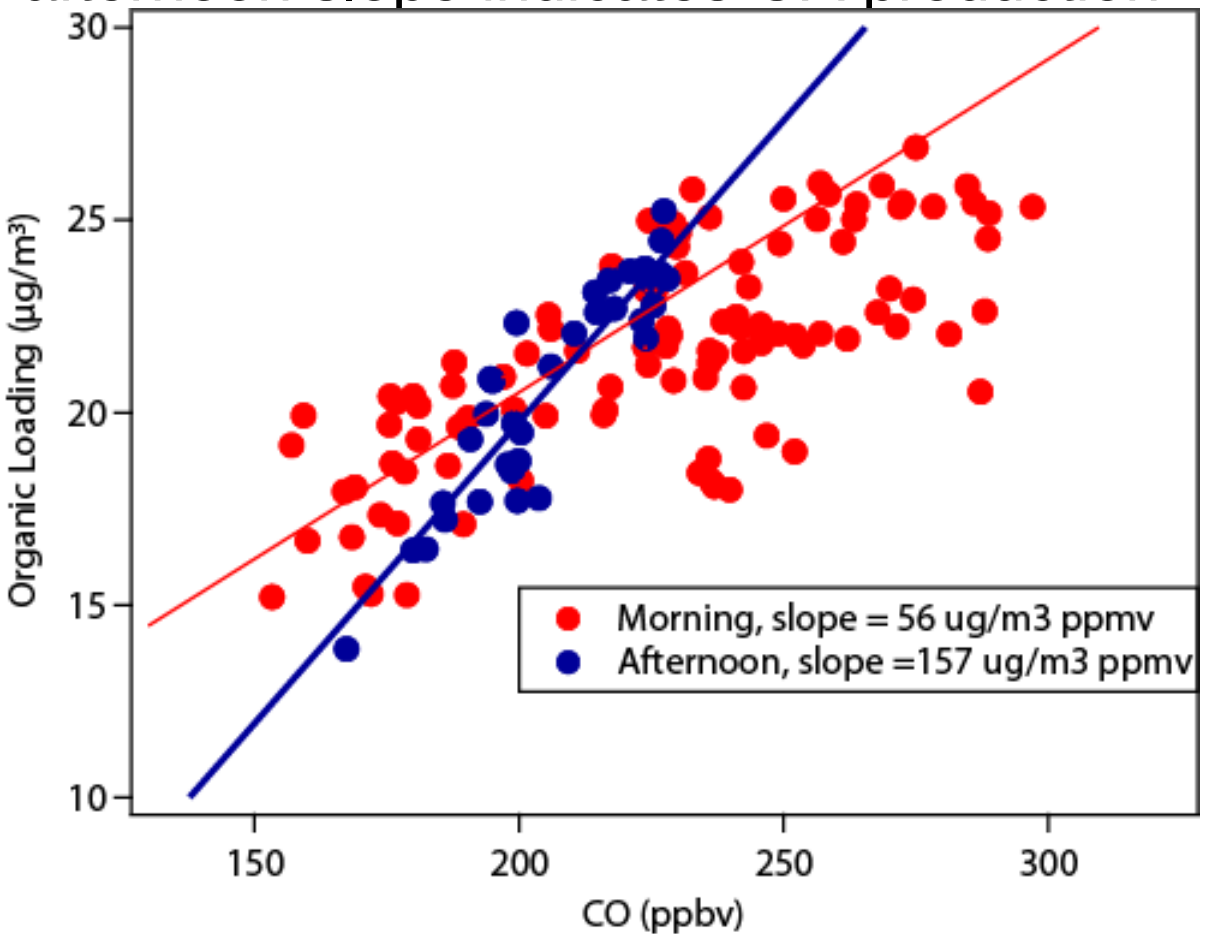
June 28th OA Formation in Mixed Plume

- Increase in organic mass correlates with loss of isoprene and its oxidation products.
- During the morning flight, organic mass increased 4 μg/m³ in1.5 hours.
- Organic loading is reduced in afternoon relative to morning due to dilution.
  - Correcting for dilution suggests organic mass increased 6 μg/m³ over 6 hours (additional 2 μg/m³ from morning).



Plot of Organic loading vs CO supports additional OA productions in the afternoon.

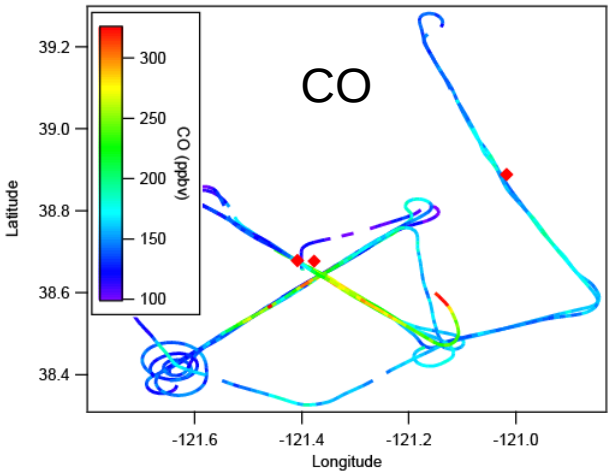
- Morning is complicated due to simultaneous production and emissions
- Higher afternoon slope indicates OA production.

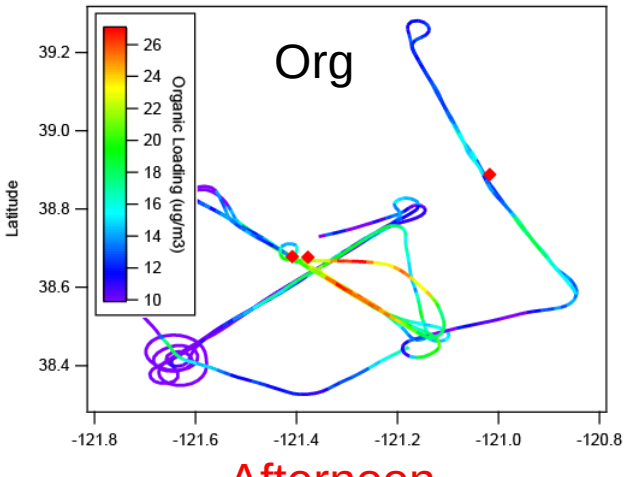


Case 2: Airmass impacted primarily by biogenic emissions on June 28th

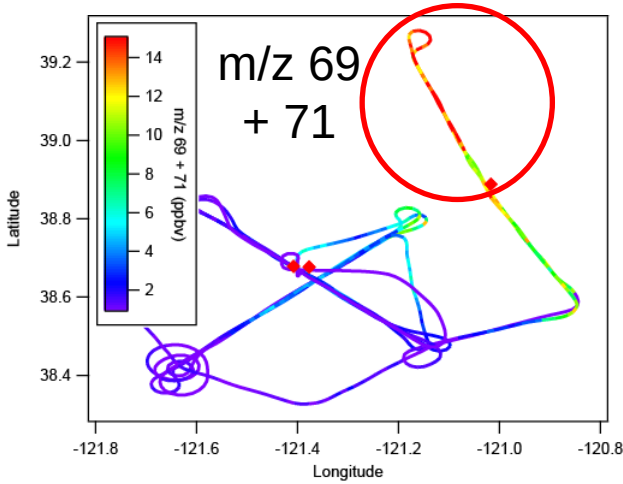
- Urban plume remains in southern foothills.

Morning

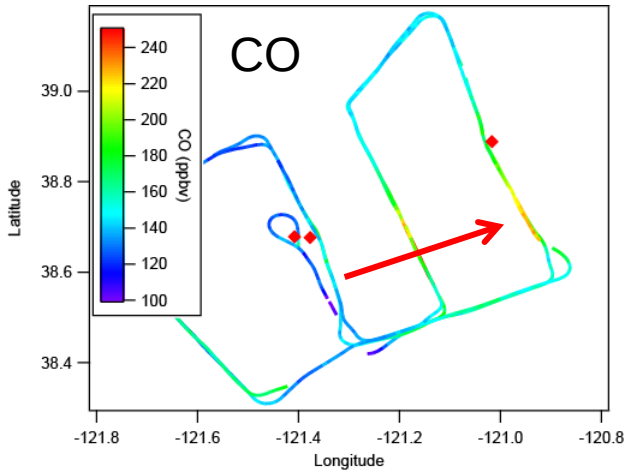


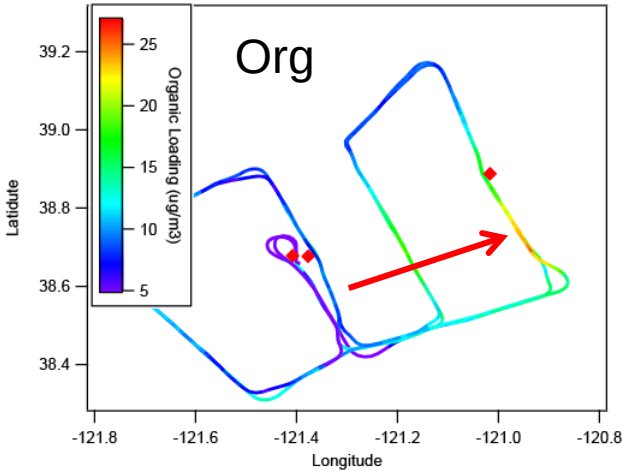


biogenics

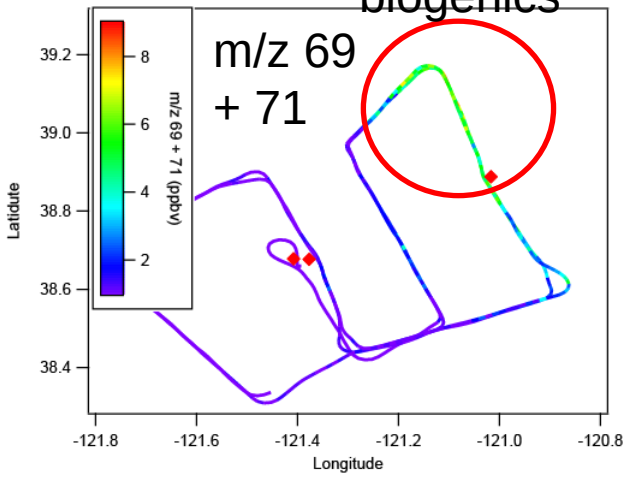


Afternoon



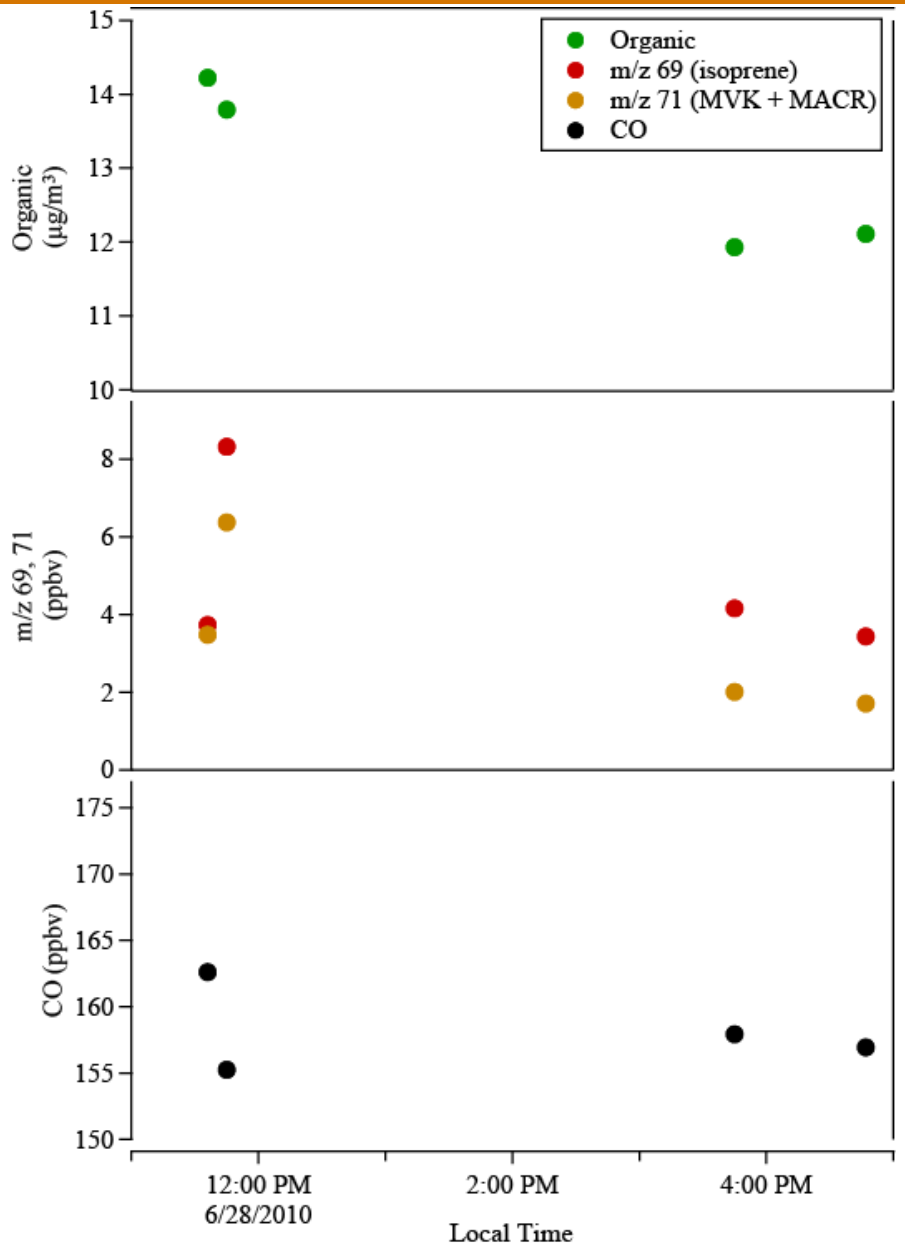


biogenics



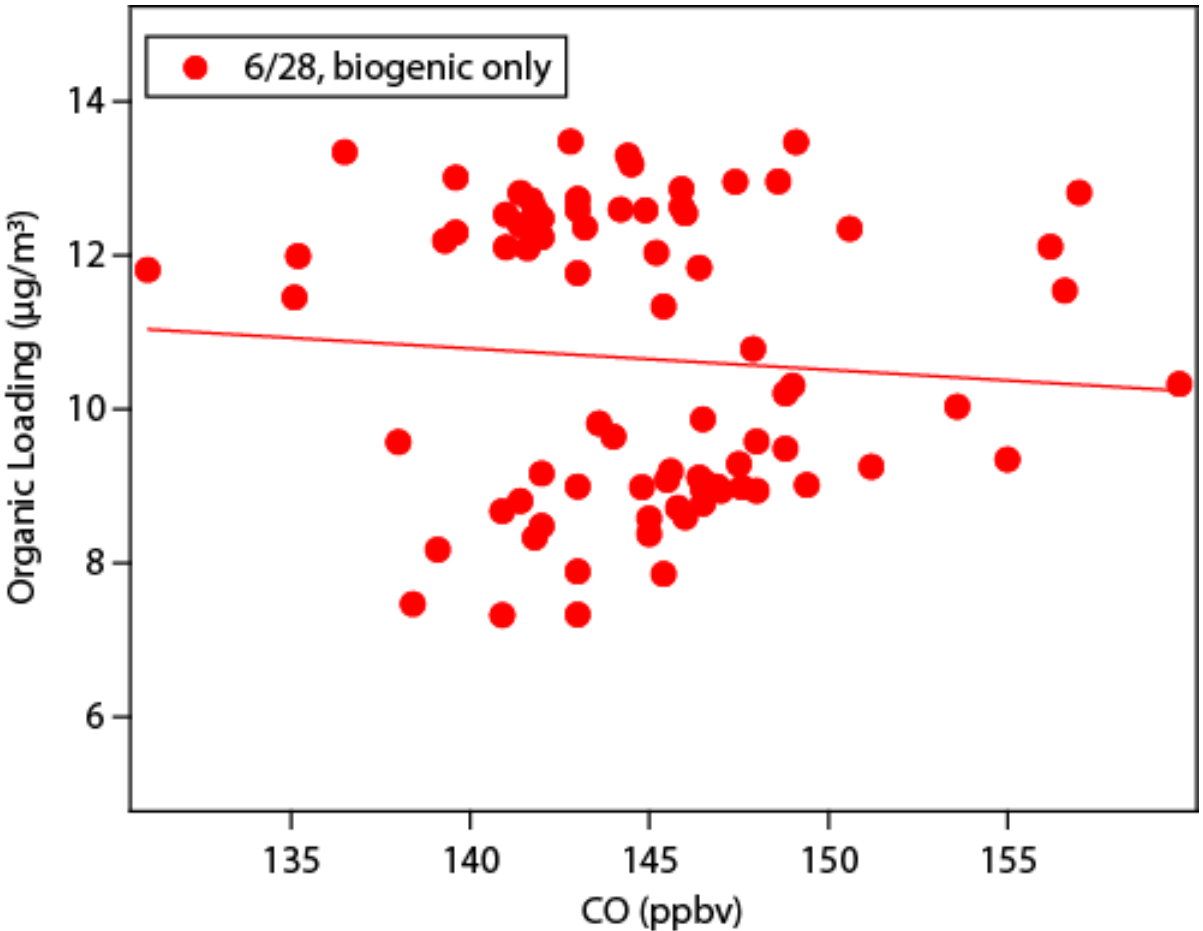
June 28th: OA formation in Biogenic Airmass

- Though OA levels are significant, no net OA production was observed.
- Large concentrations of isoprene and its oxidation products are present.
- Significant ozone (60 - 80 ppbv) is present.
  - Sufficient OH should be available to oxidize VOCs.



OA vs CO in biogenic airmass on June 28th

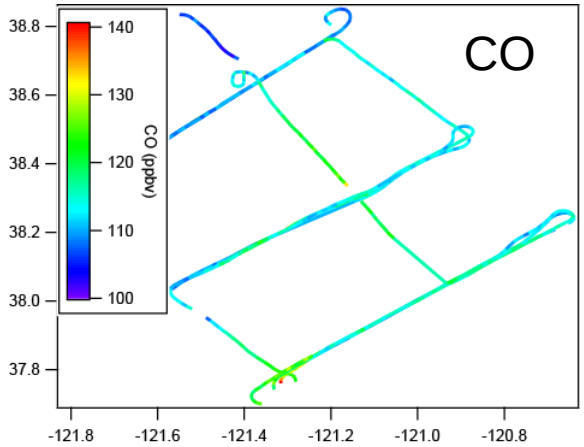
- ΔOA/ΔCO is zero, but there is little dynamic range in the measurement
  - OA and CO are near the background for the day.

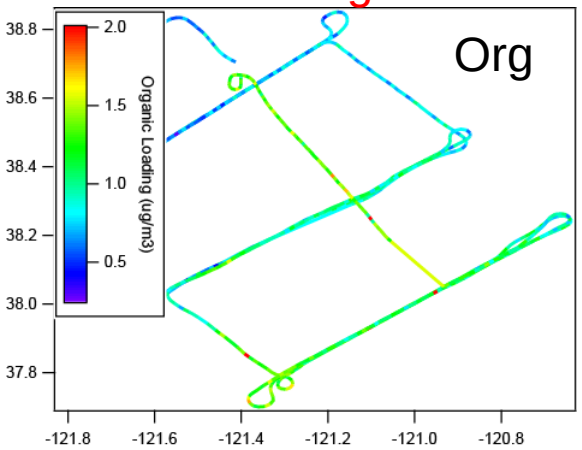


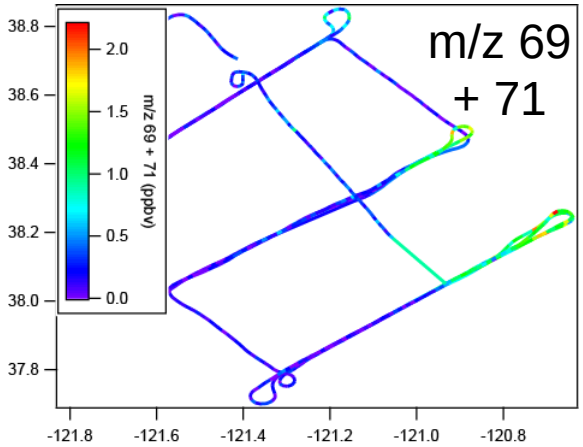
Case 3: Airmass impacted primarily by anthropogenic emissions: June 12th

- Sacramento plume transported to the south through regions with little biogenic emissions.

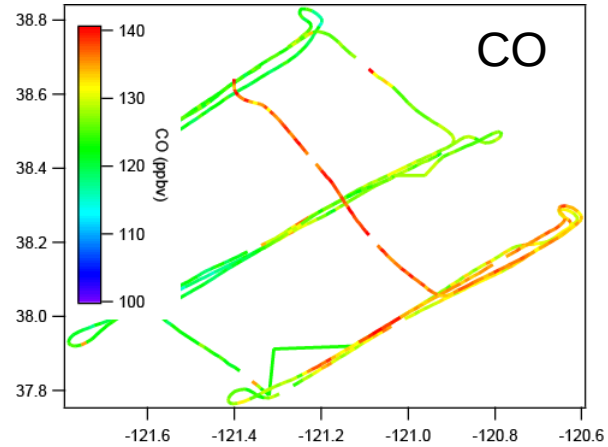
Morning

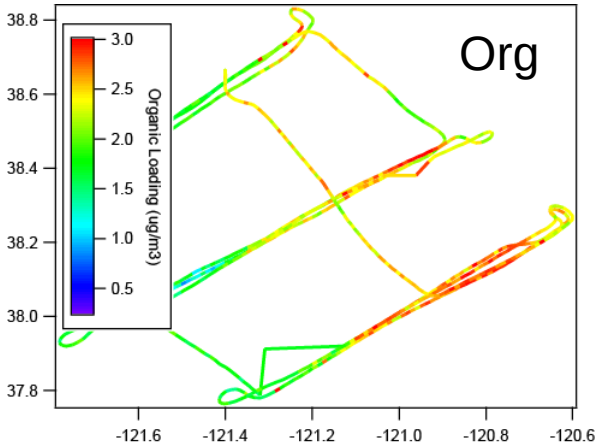






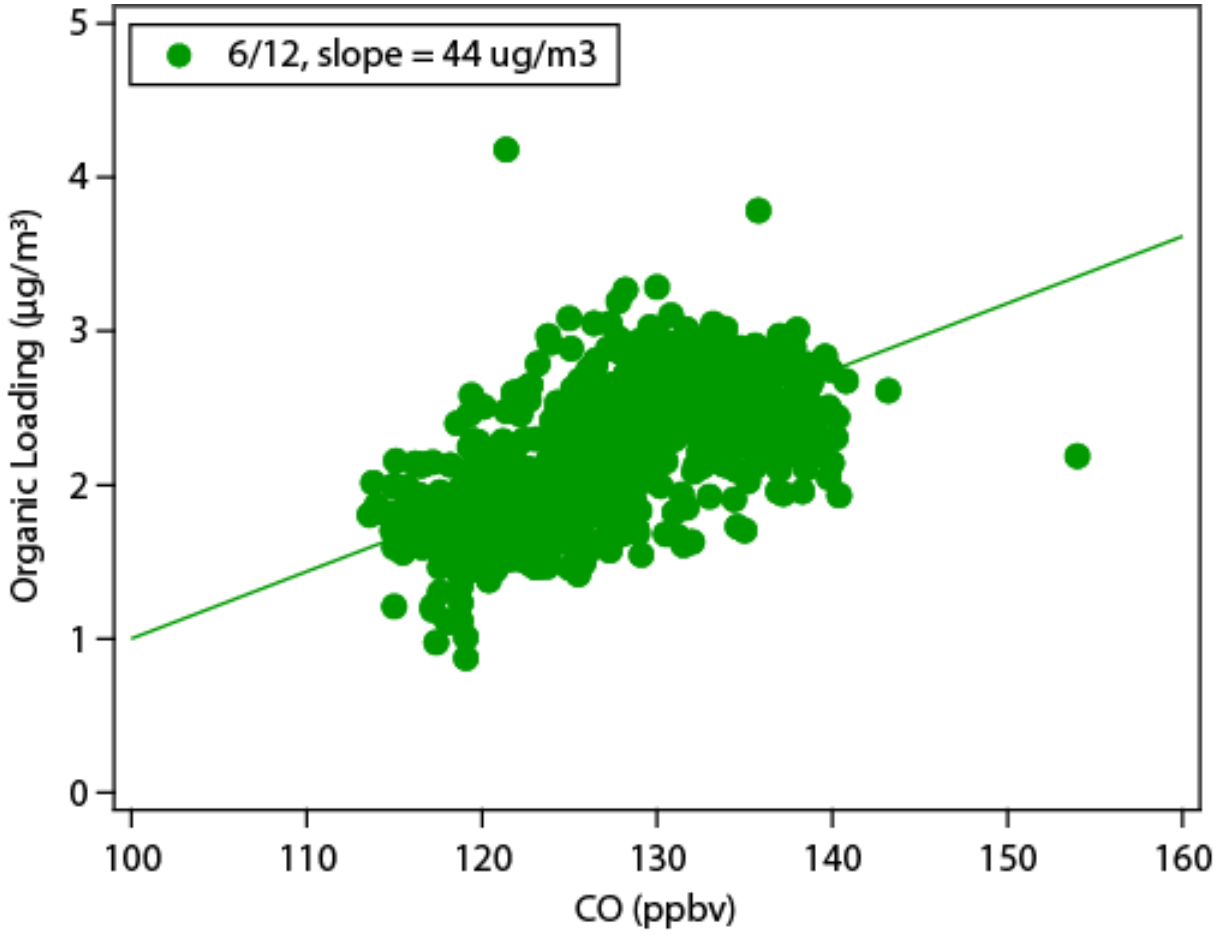
Afternoon





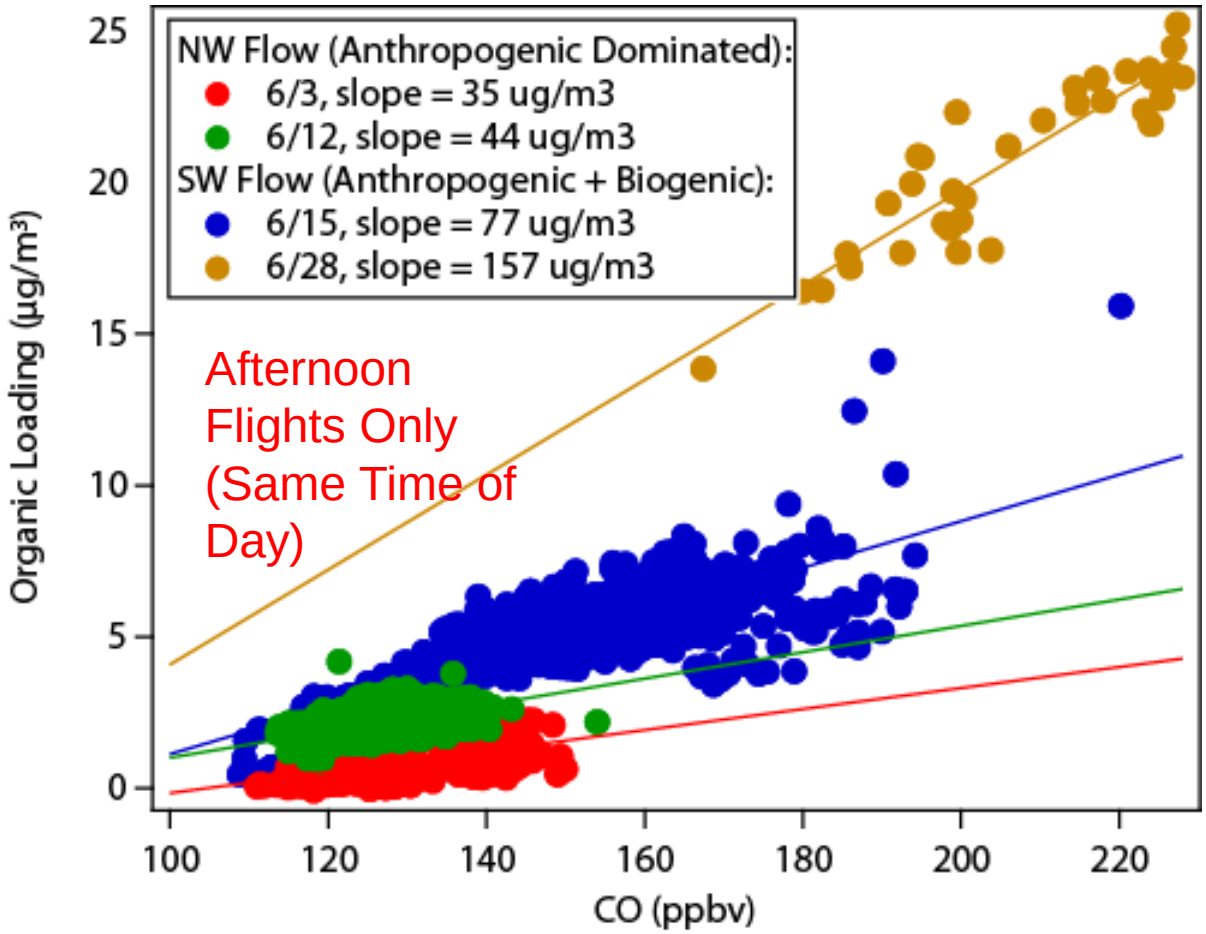
OA production in anthropogenically dominated airmass

- Airmasses influenced primarily by anthropogenic emissions showed lower OA production.



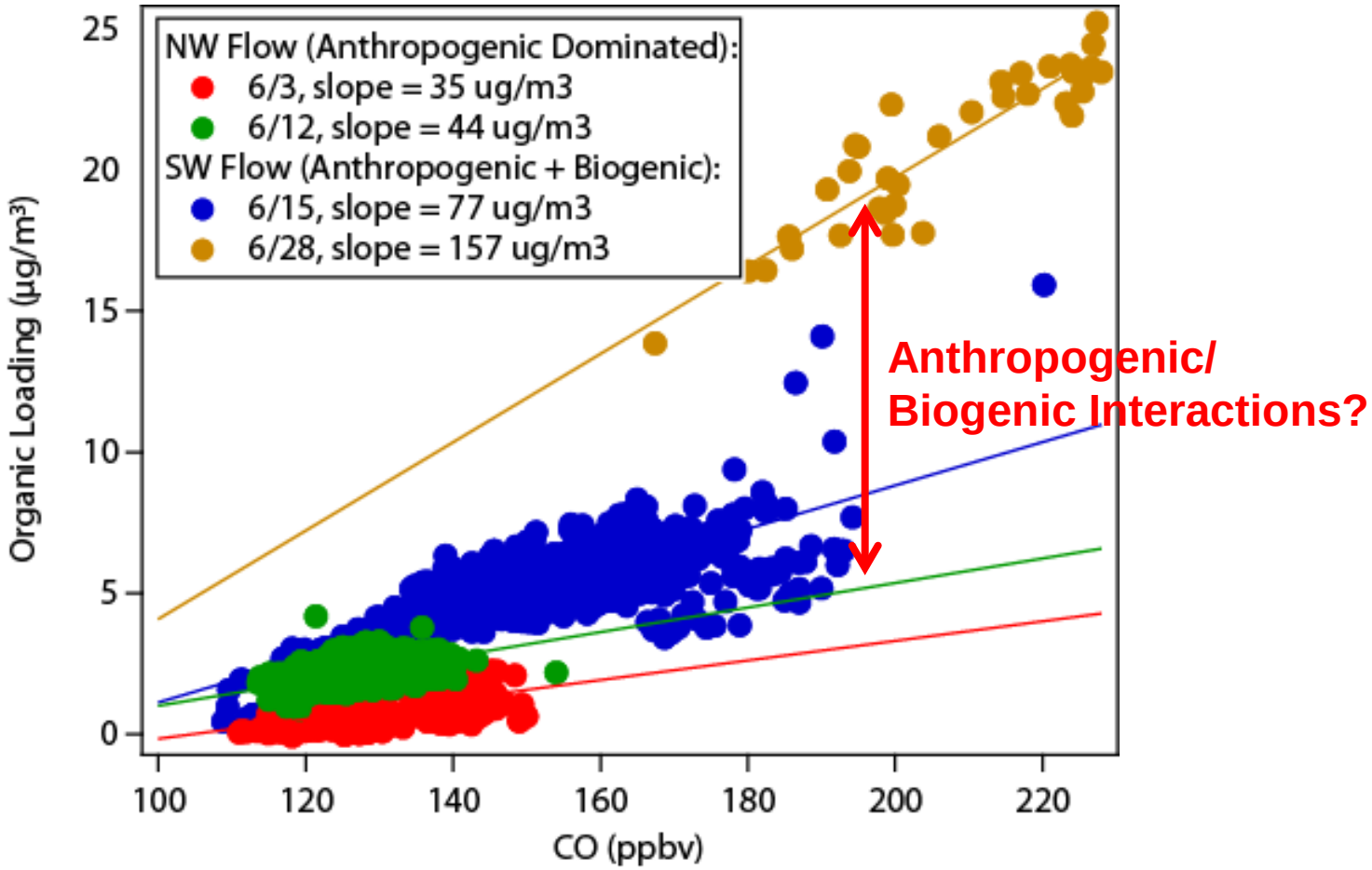
Summary of OA vs. CO plots as a function of meteorology

- SW flow pattern (biogenic/anthropogenic mix) produced more OA than NW flow pattern (anthropogeic).



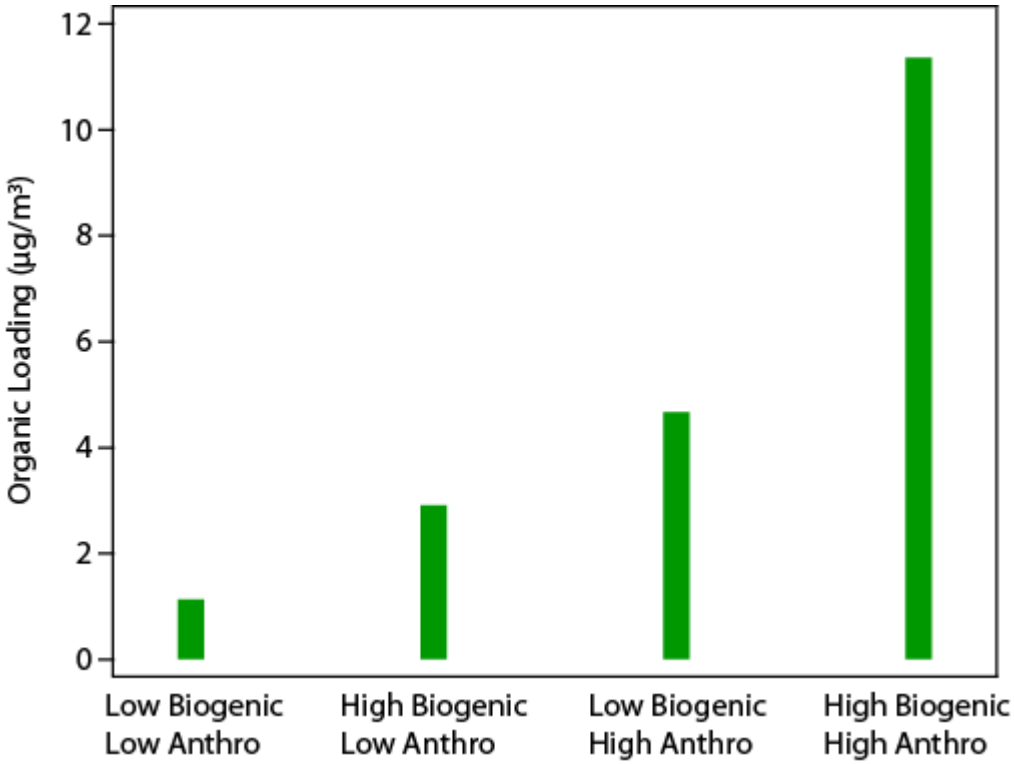
Summary of OA vs. CO plots as a function of meteorology

- More OA is produced when anthropogenic and biogenic emissions mix.



Tracer binning of organic loading

- Tracer species percentiles are calculated and organic loading is binned based on levels of biogenic (m/z 69 + 71) and anthropogenic (CO) tracers.
  - Upper and lower quartiles define high and low, respectively.
- OA loading largest when both anthropogenic and biogenic tracers are elevated.



Conclusions

- Highest organic loadings were observed when both biogenic and anthropogenic tracers were elevated.
- Production of OA was enhanced by an **unknown mechanism** when biogenic and anthropogenic emissions mixed.
- Controlled laboratory studies will be key in determining the mechanism for the enhancement.
- Models must account for this process to constrain aerosol forcing and aerosol-cloud interactions.
  - Anthropogenic and biogenic emissions are in close proximity over wide regions of the world.

Acknowledgements

- Funding: The US DOE's ARM Climate Research Facility and Atmospheric System Research Program.
- G1 pilots: B. Hannigan, B. Svancara, M Hubbell, D. Hone.
- G1 mechanics: G. Dukes, B. Svancara.
- ACRF operations team: B. Schmid, J. Hubbe, C. Kluzek, J. Comstock, J. Tomlinson.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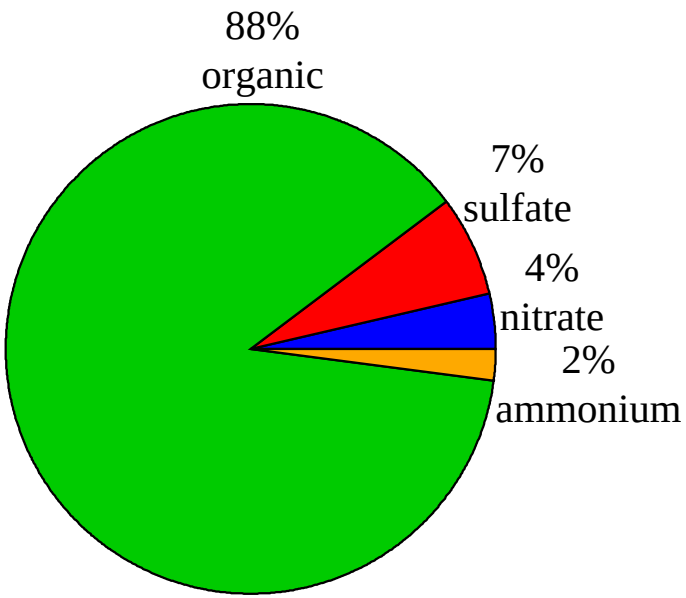
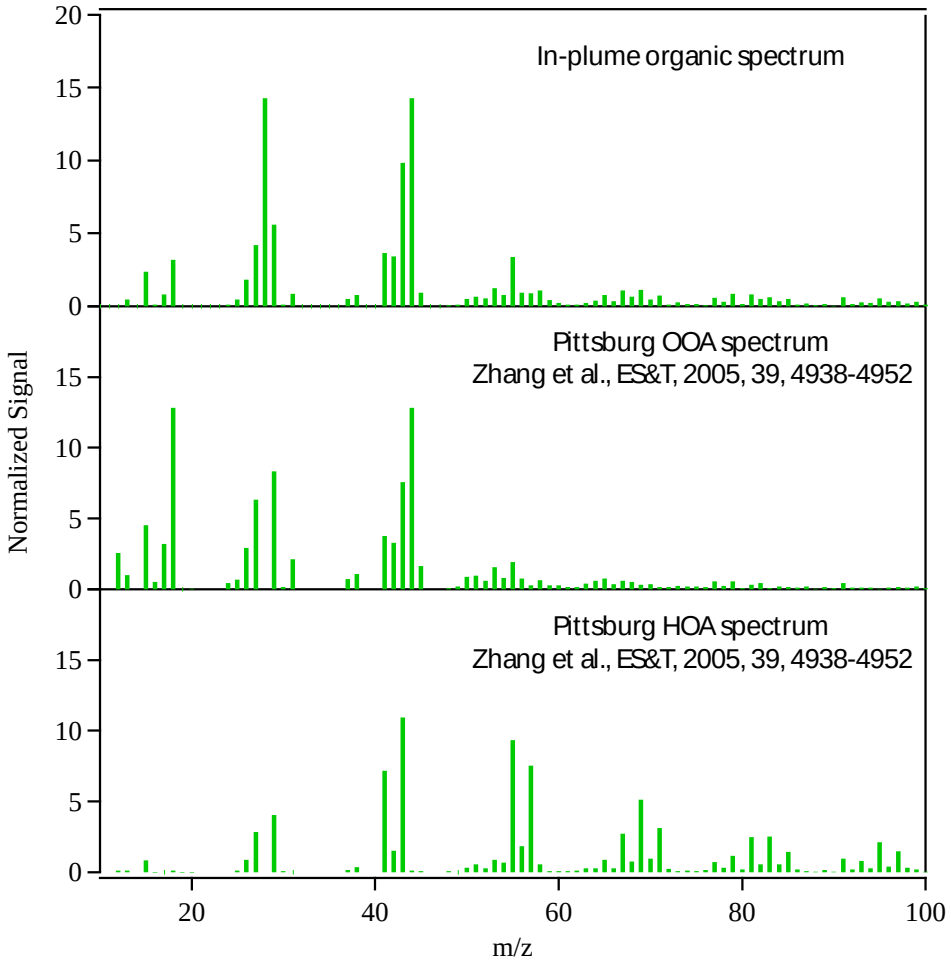
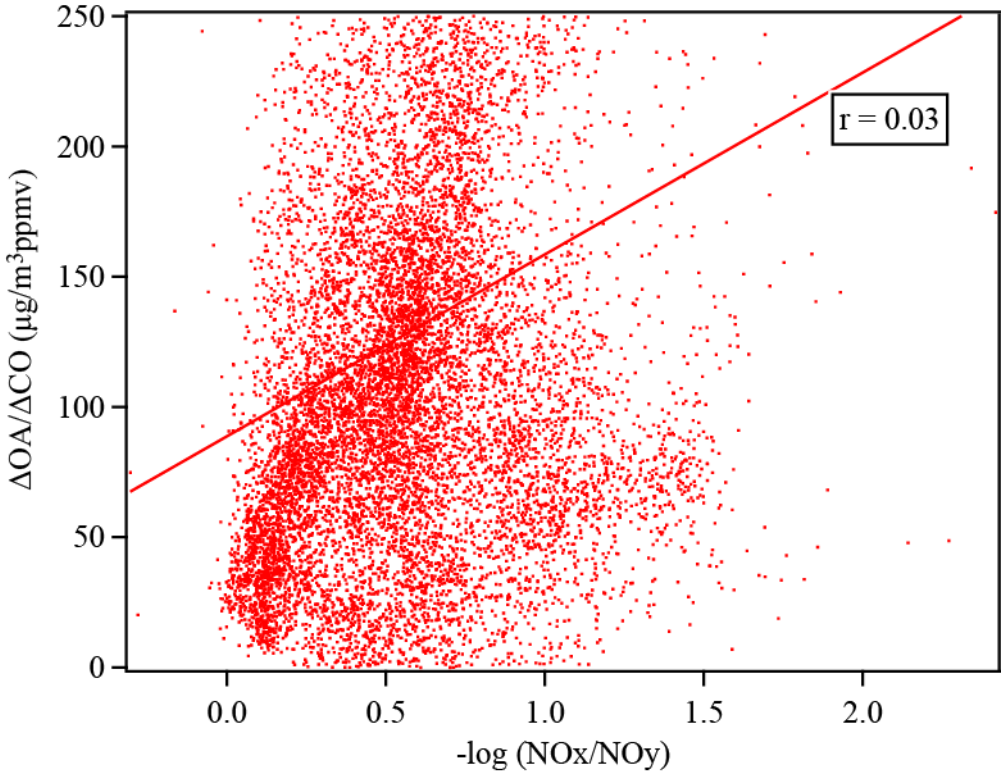
Chemical composition of the plume





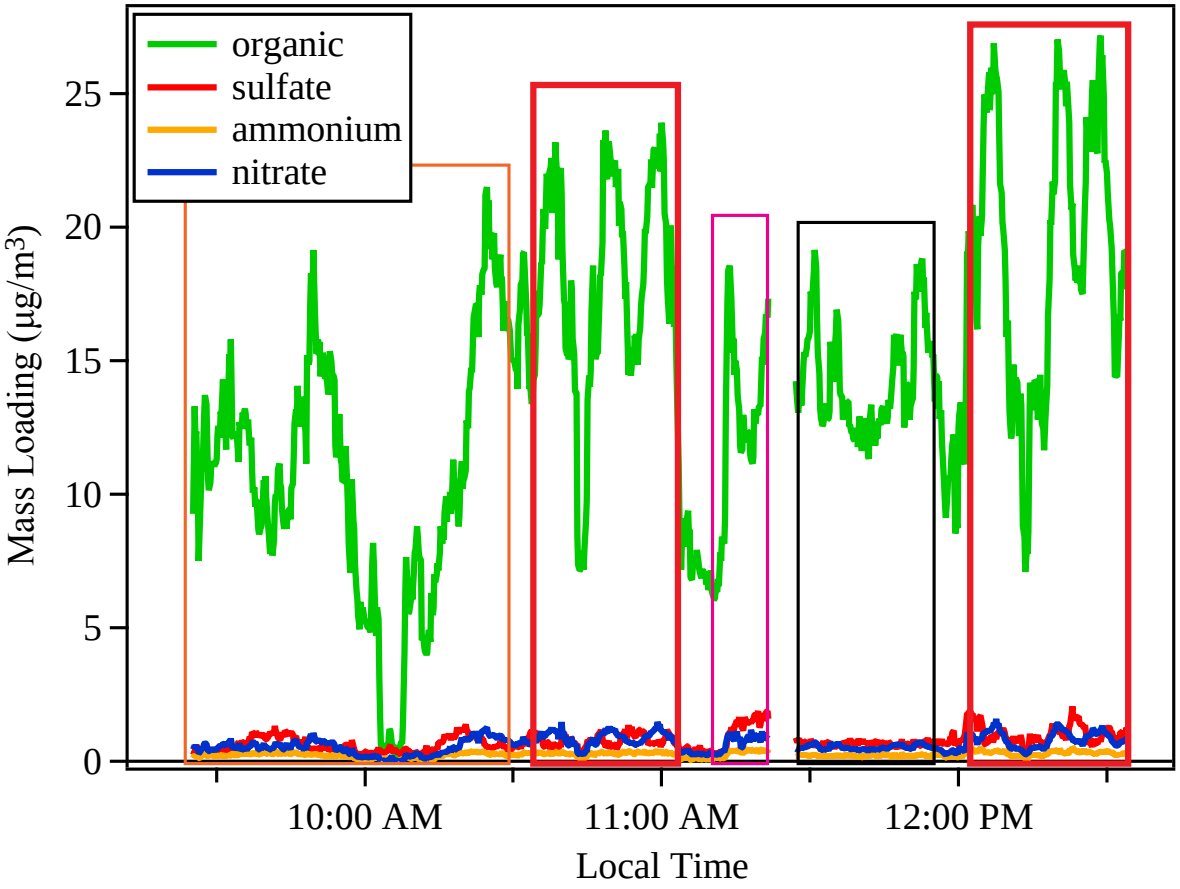
- Comparison to literature spectra suggest organics are dominated by OOA (SOA).

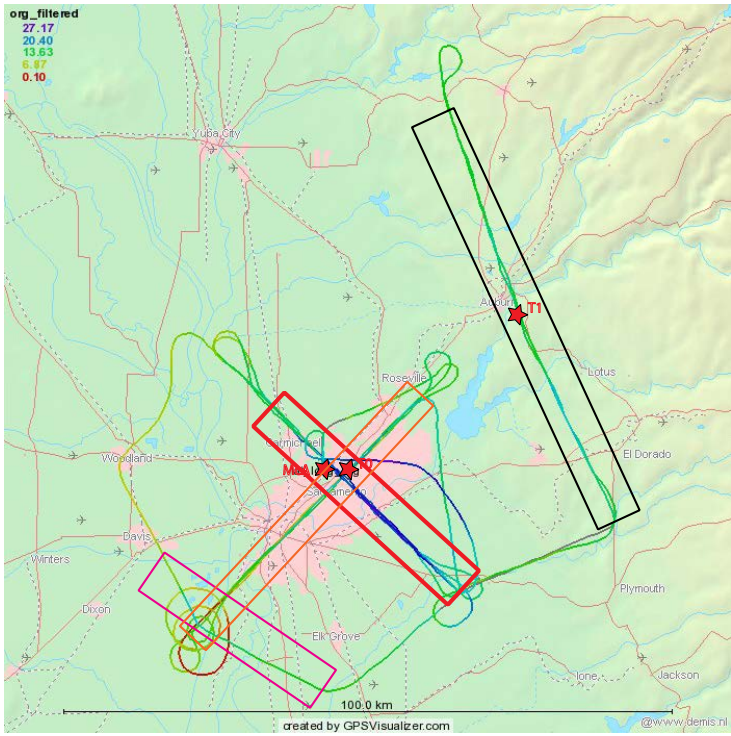
Effect of Aging on OA Production



- No correlation between ΔOA/Δ CO and aging of airmass on the timescale of the NO_x clock.

June 28th Morning Organics





- Intense plume dominated by organics is observed SE of city in morning.
- Evidence of fast growth ~ 5 µg/m^3 mass added in 1.5 hr.

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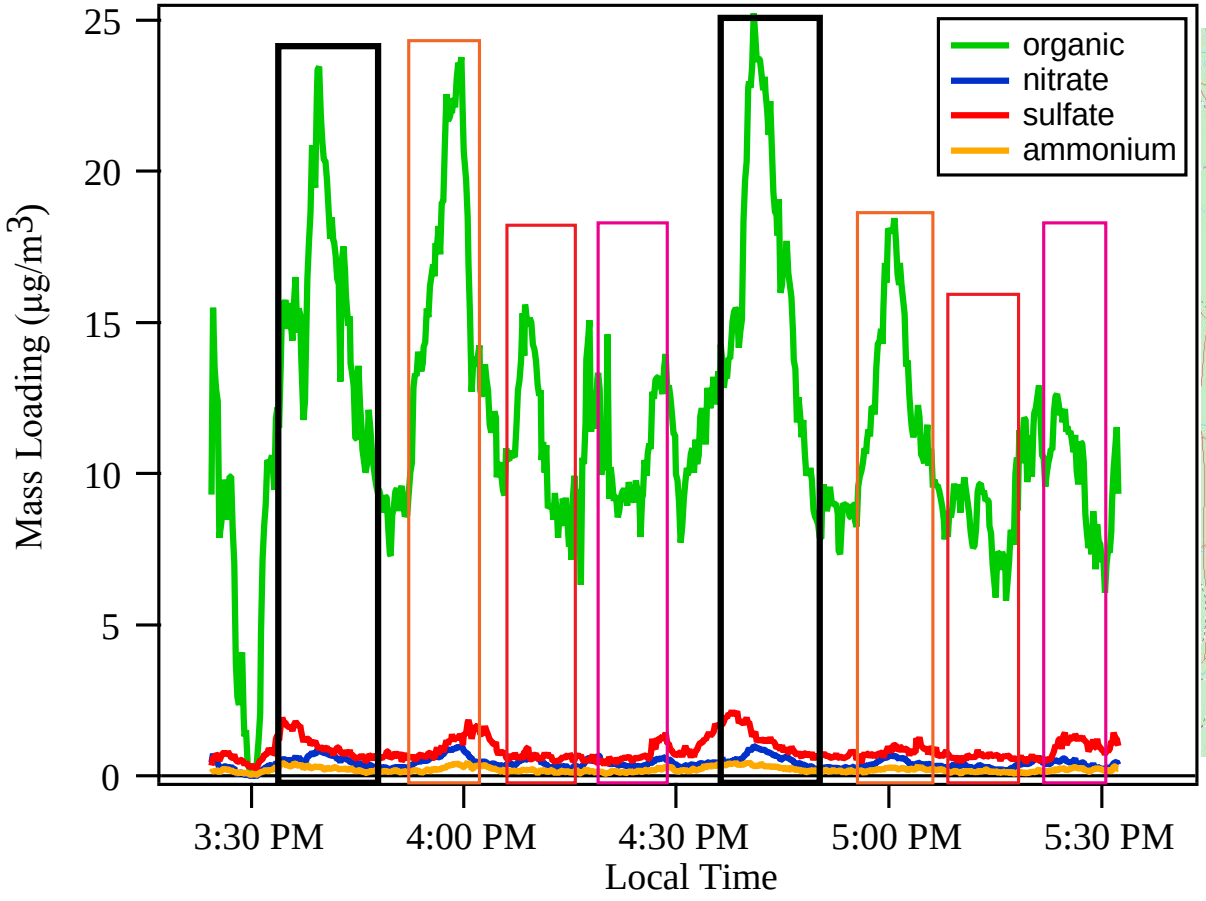
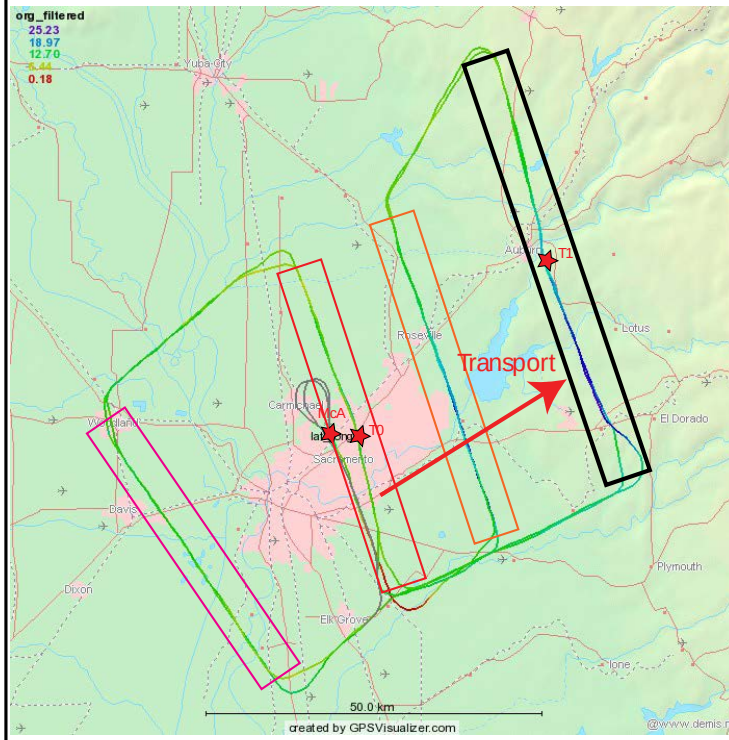
June 28th Afternoon Organics





- Plume transported to the NE toward T1 in agreement with WRF predictions.
- Plume evolution can be investigated.

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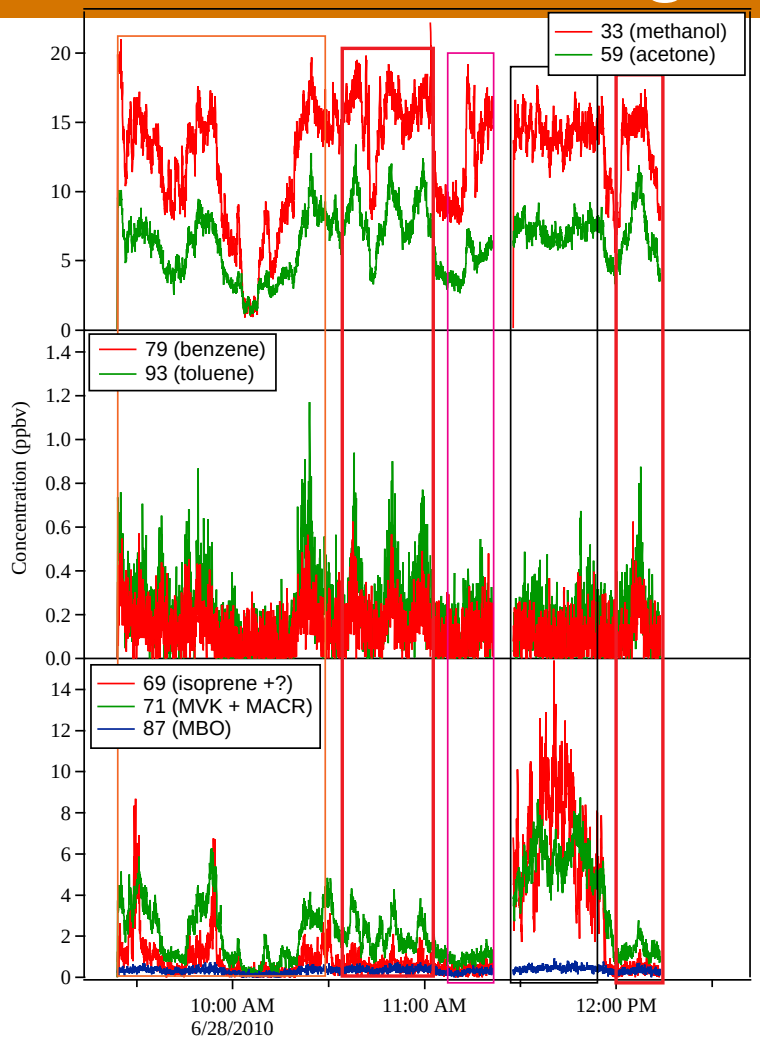
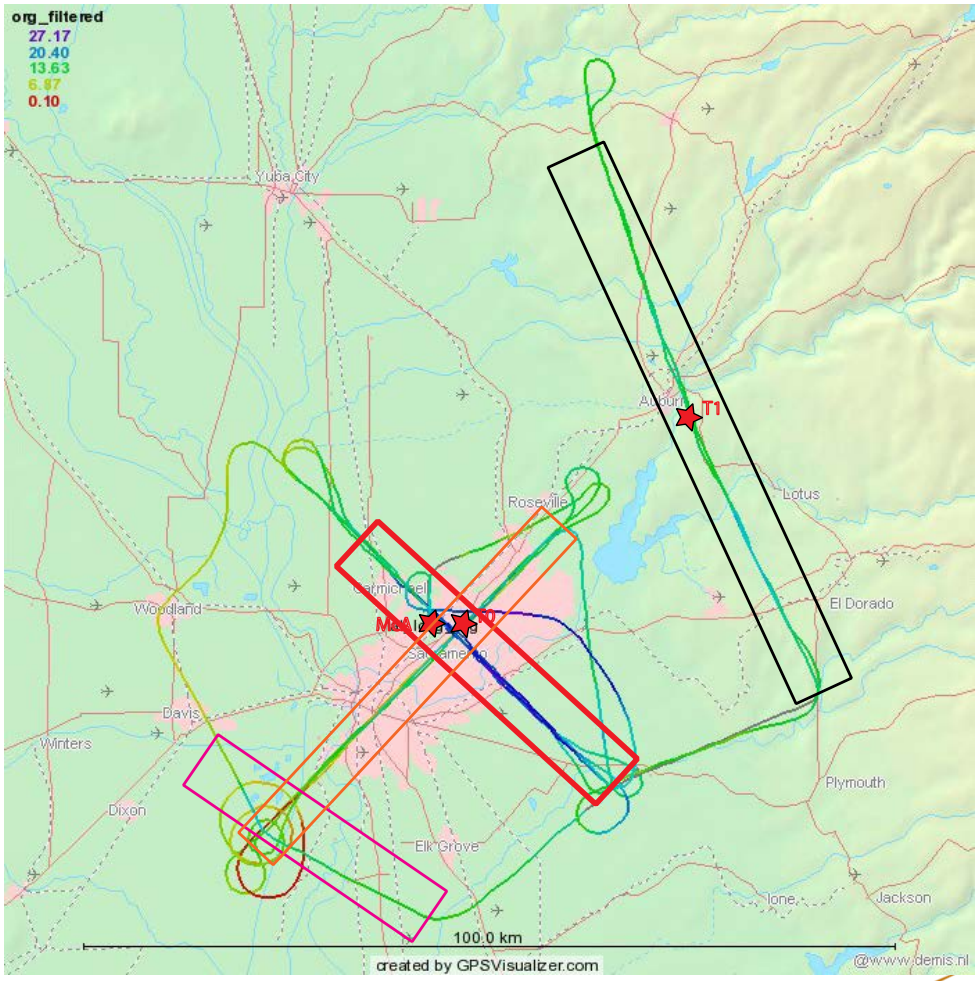
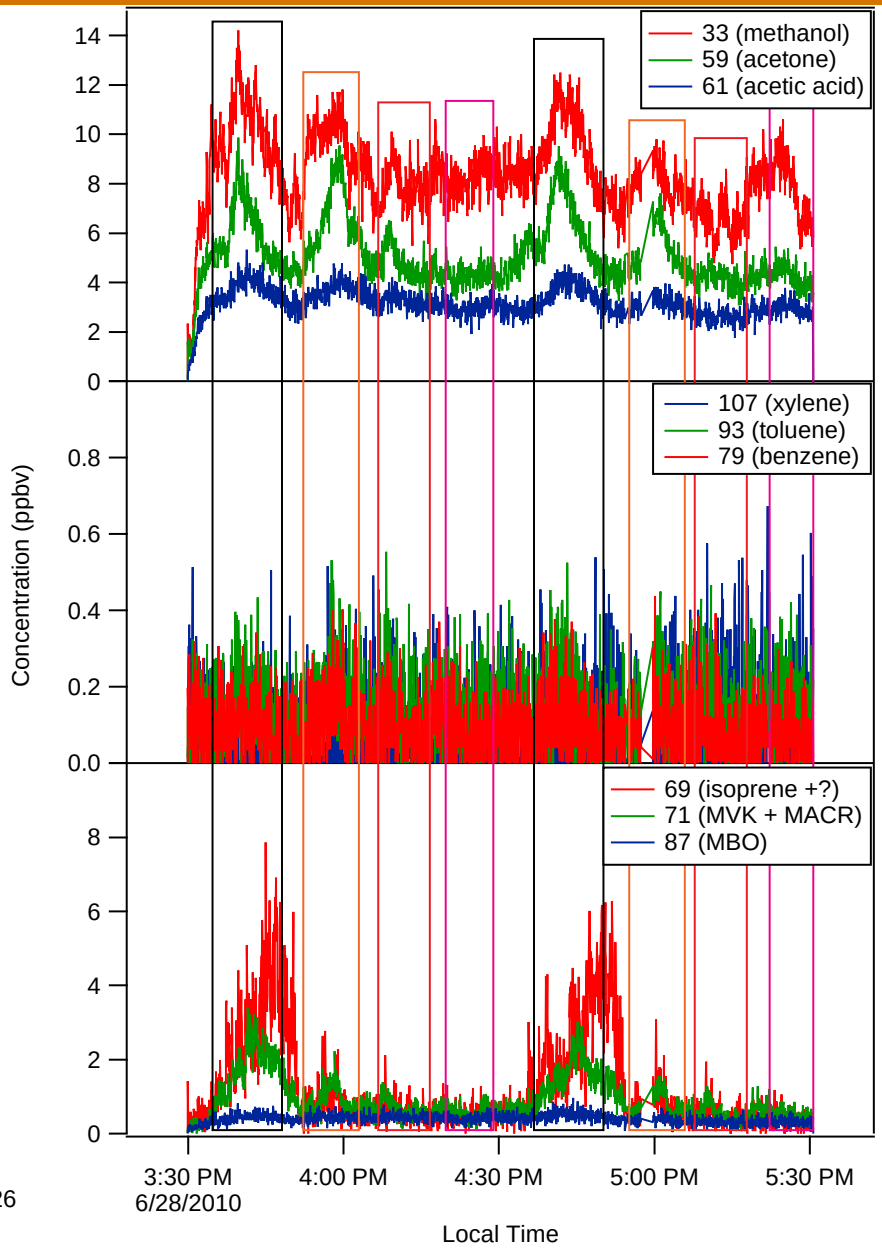
June 28th Morning PTRMS

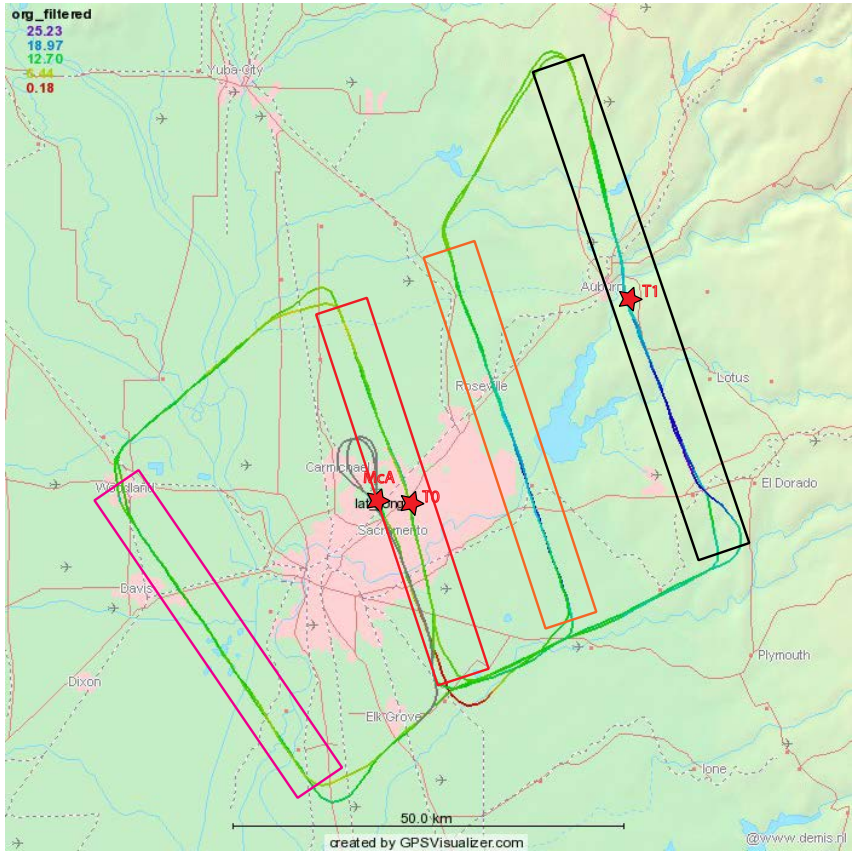




- Significant MVK/MACR and isoprene in plume
- Benzene/Toluene clock suggests plume age is 9 hours.

June 28th Afternoon PTR-MS





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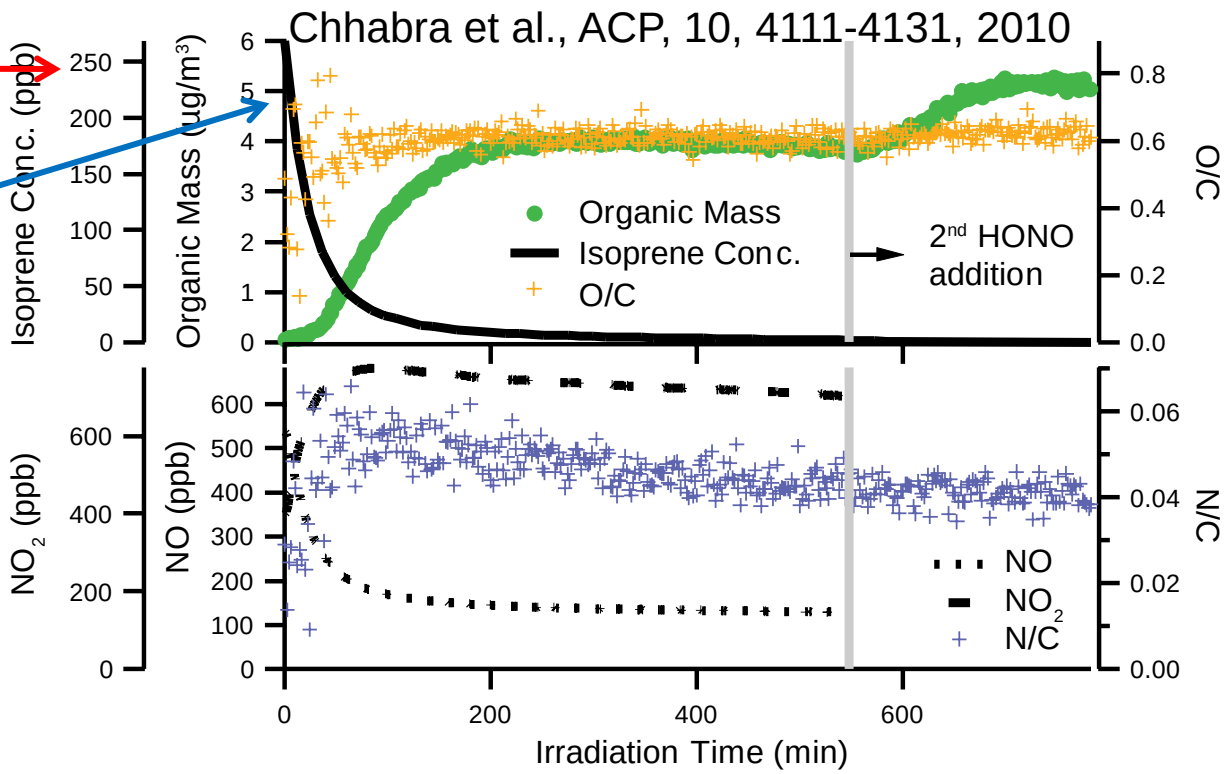
Isoprene Chamber Data

Δisoprene = 267 ppbv

ΔSOA = 5 μg/m³



- Our observations of the plume temporal evolution are consistent with chamber observations of SOA formation from isoprene.
- O:C and H:C ratios and evolution are consistent.
- Yields are not consistent.

Plot of Organic loading vs CO supports additional OA productions in the afternoon.

- Higher afternoon slope, suggests OA production.
- Slope of morning points flattens as m/z 69, 71 deplete and CO emissions continue.