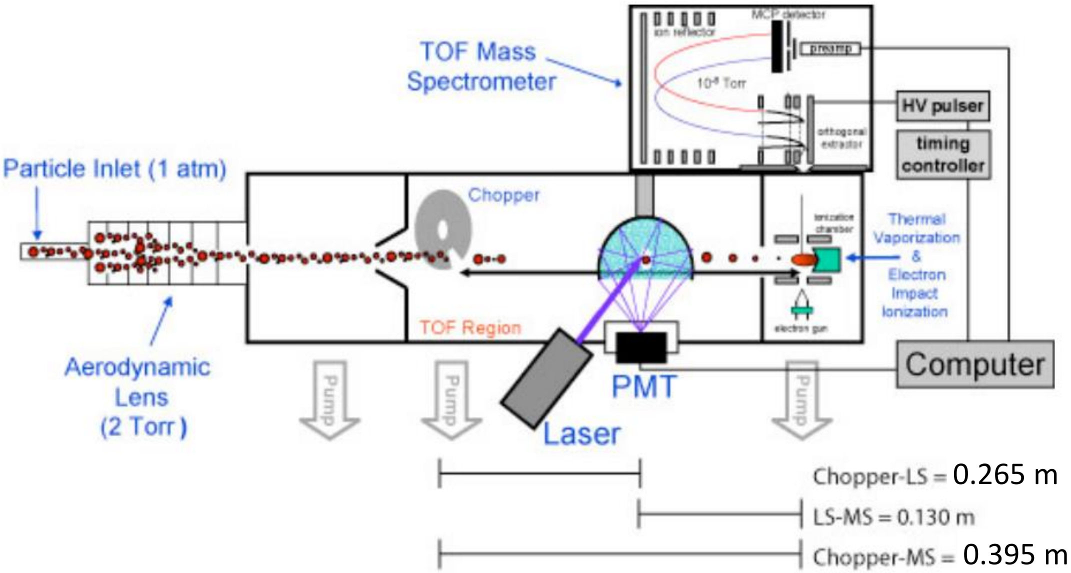
Aerosol Chemical Composition and Formation Processes from SENEX

Middlebrook, Liao, Welti, Angevine, Brioude, Brock, Graus, Hanisco, Holloway, Horowitz, Kaiser, Keutsch, Lee, Lopez-Hilfiker, Mao, Murphy, Neuman, Nowak, Thornton, Trainer, Warneke, Wolfe, and de Gouw

SAS Data Workshop, March 31-April 2, 2014

WORK IN PROGRESS!

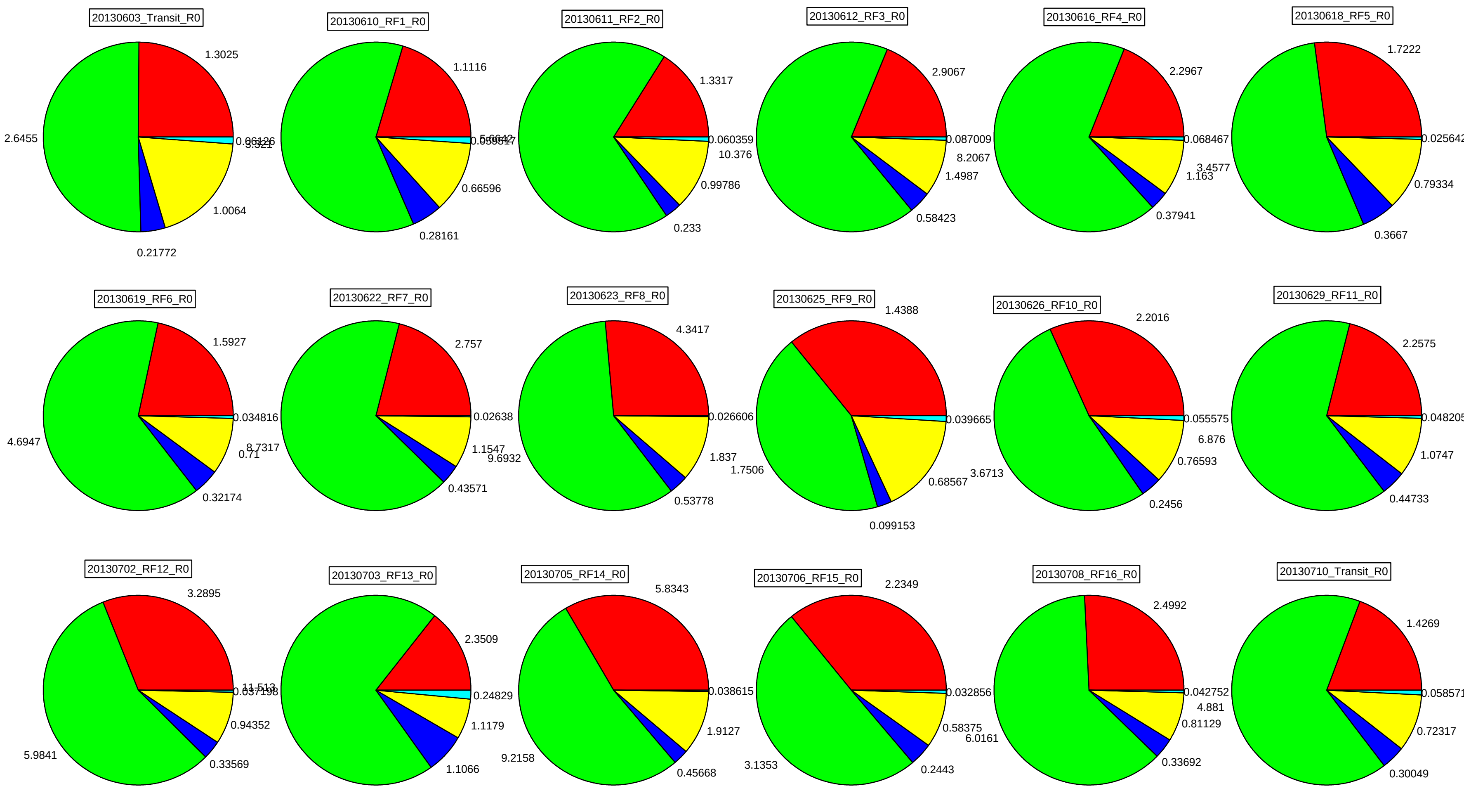
LS-C-ToF-AMS for SENEX: Aerosol Organics, Sulfate, Nitrate, Ammonium, and Chloride



Adapted from Figure 1, Cross et al., ACP, 2009.

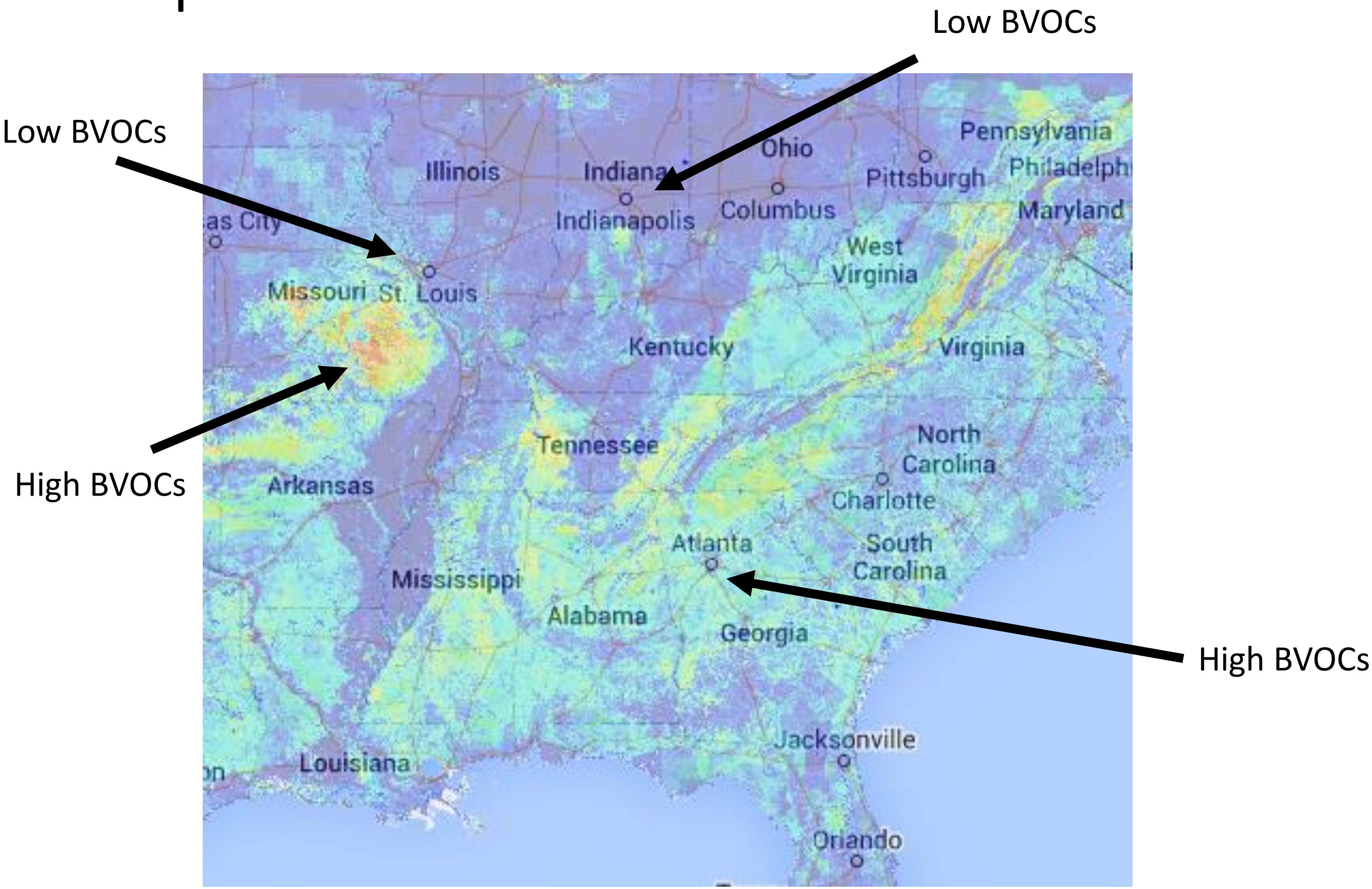
Particles are sampled through an aerodynamic lens which focuses them into a particle beam in the vacuum chamber.
The particle beam impacts a vaporizer at ~600 °C that is hot enough to evaporate non-refractory species.
The resulting vapors are ionized by electron impact and detected by a compact time-of-flight mass spectrometer.
Obtained the first airborne single-particle AMS data (see Jin Liao's poster today).

Overall AMS Picture



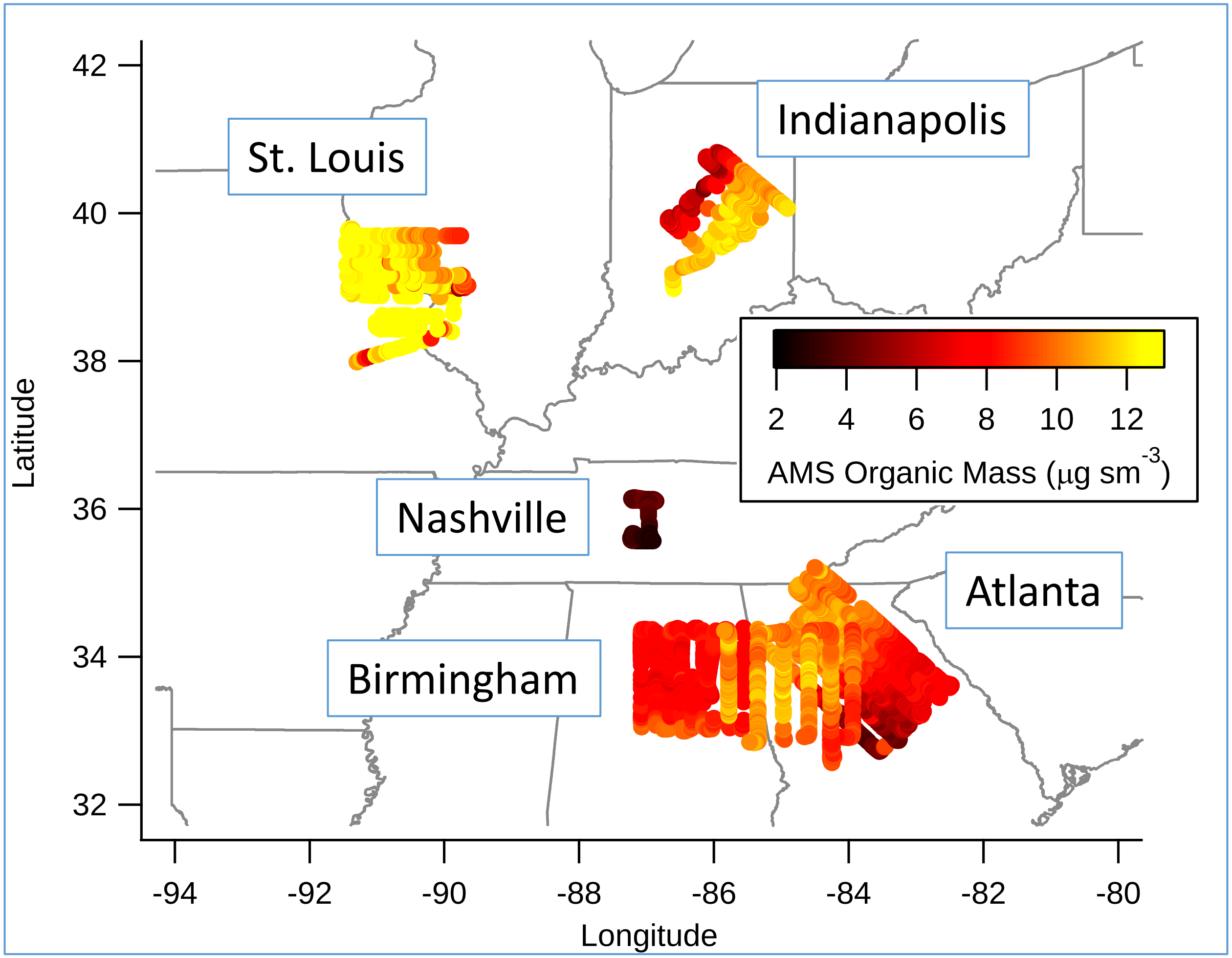
What is the source of the organic aerosol mass?

Isoprene and Cities



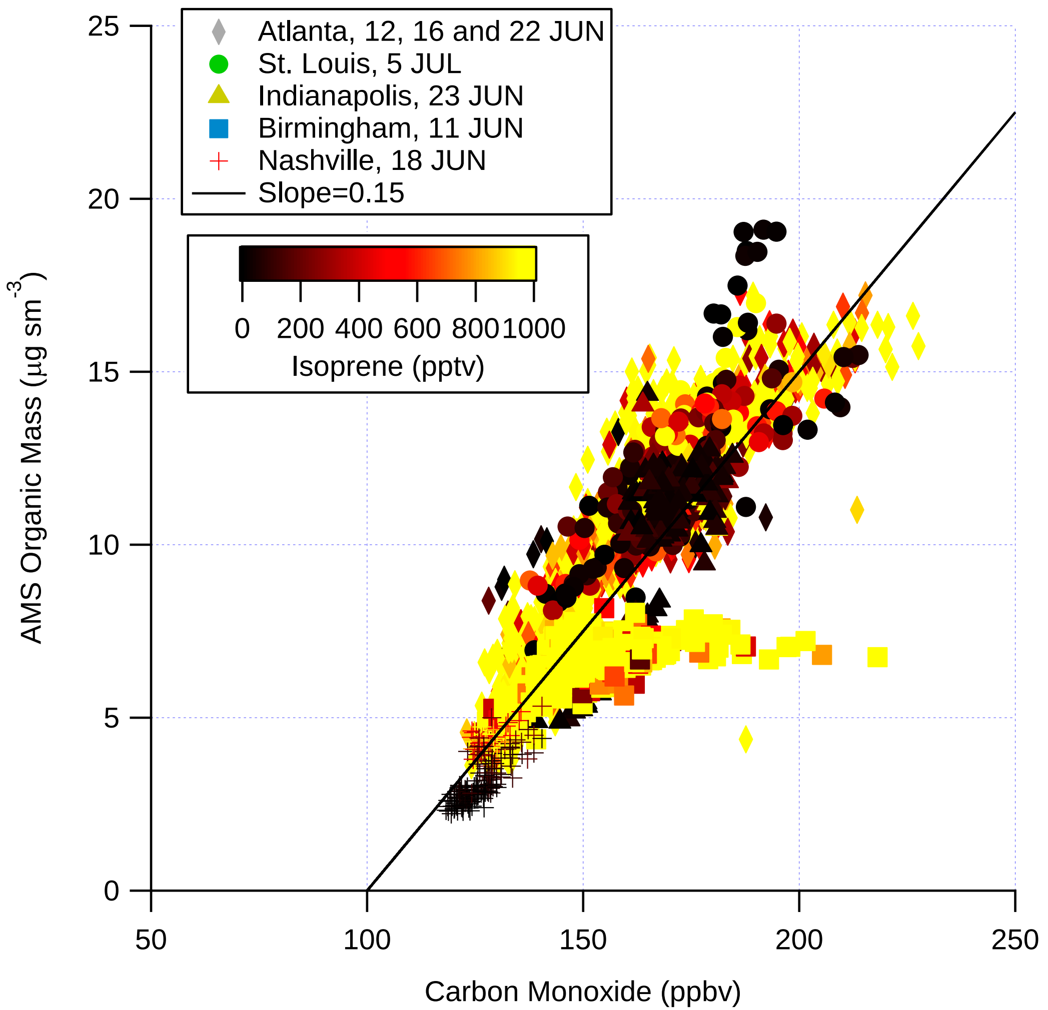
Isoprene emission map from Mapping Tool, Frost, Keane, and Aikin

SENEX Urban Flights



Organic Aerosol Mass Vs. Carbon Monoxide

Urban Data Only from SENEX 2013



Data filtered for low altitude, acetonitrile, and SO2.

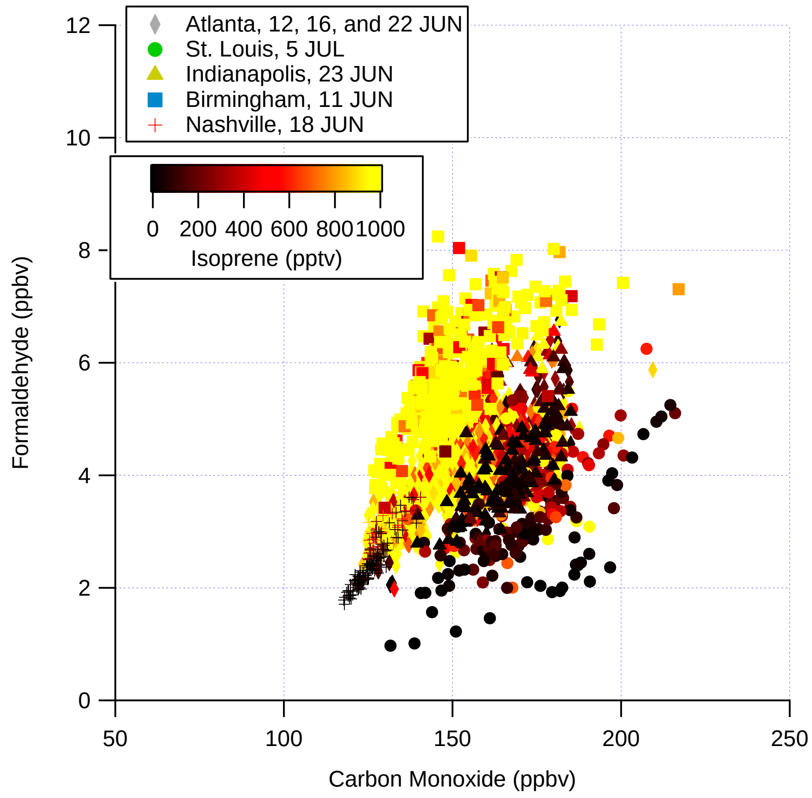
Carbon monoxide values are much smaller than observed in the past – urban areas are getting cleaner.

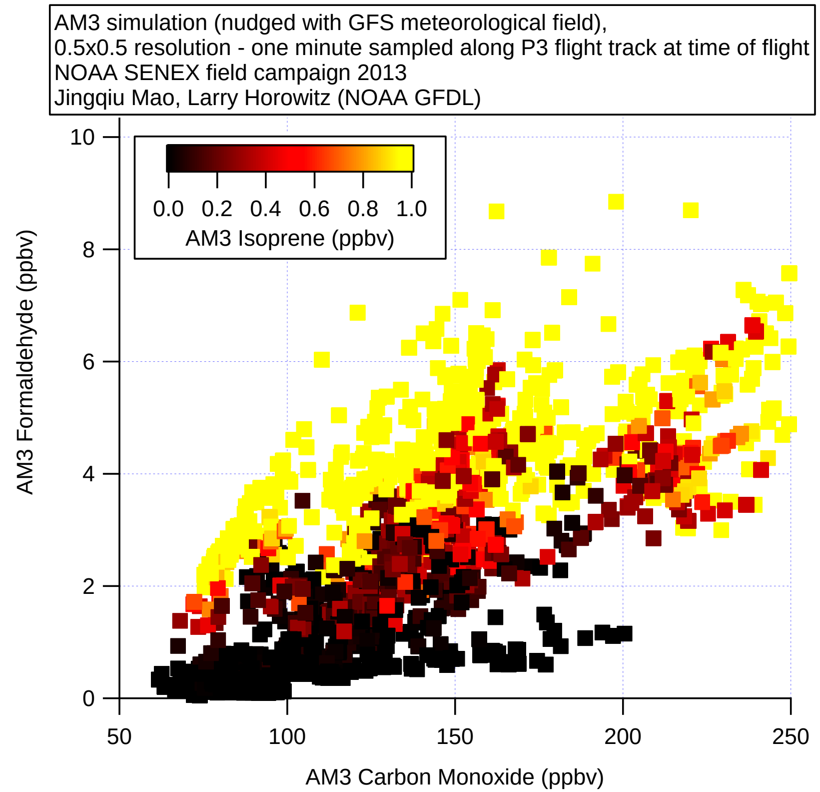
1) No trend with isoprene.
2) Data are highly correlated.
3) Slope is high compared to most urban data.

If the organic mass is from biogenic volatile organic compounds (BVOCs), the slope could be high. It may also be high from biomass burning.

Formaldehyde Vs. Carbon Monoxide

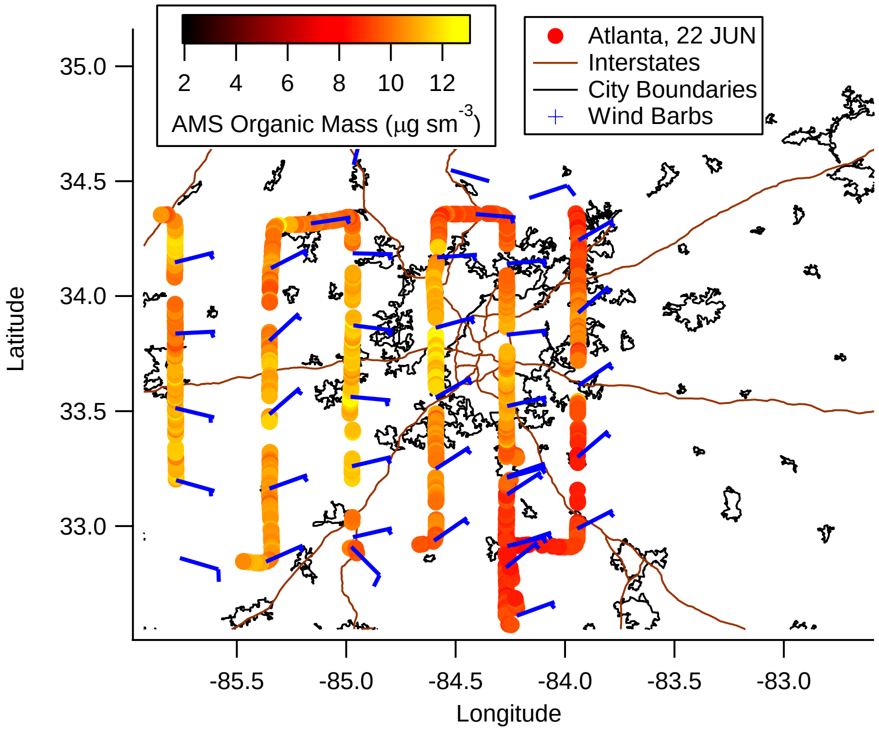
Urban Data Only SENEX 2013

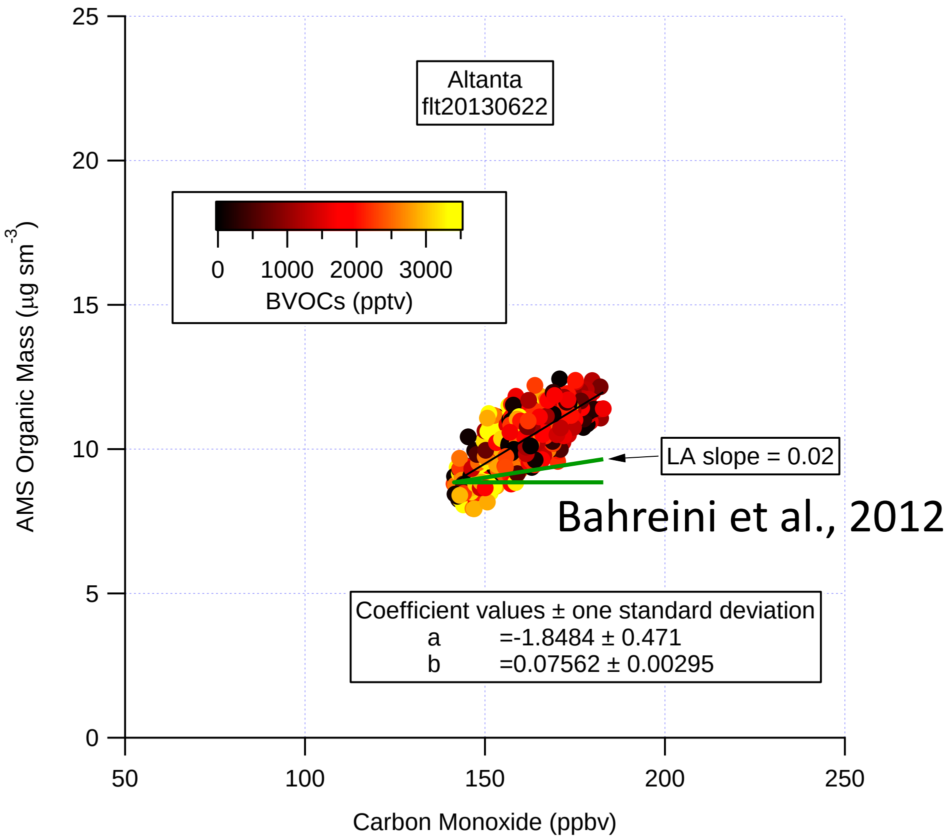




Field data and AM3 model show higher formaldehyde with higher isoprene.
Formaldehyde has a much shorter lifetime than organic aerosol mass.

Atlanta: High BVOCs



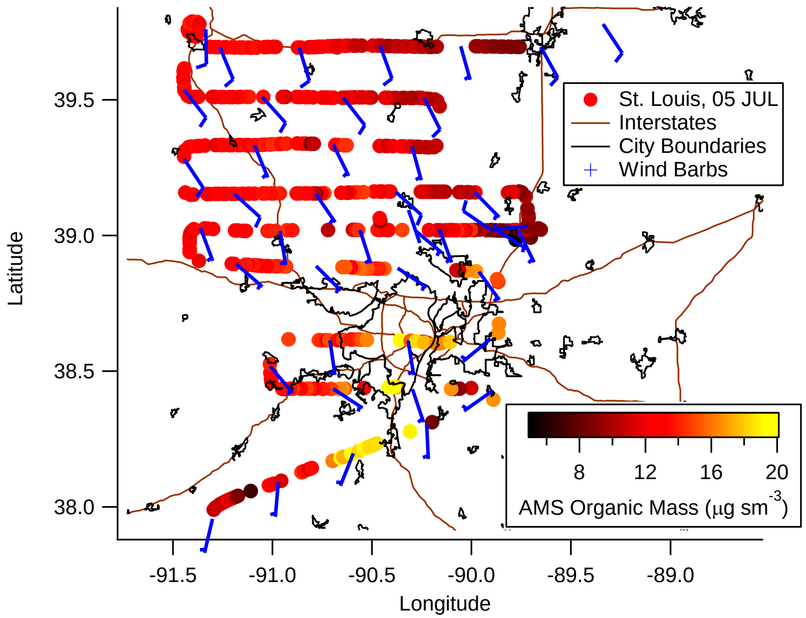


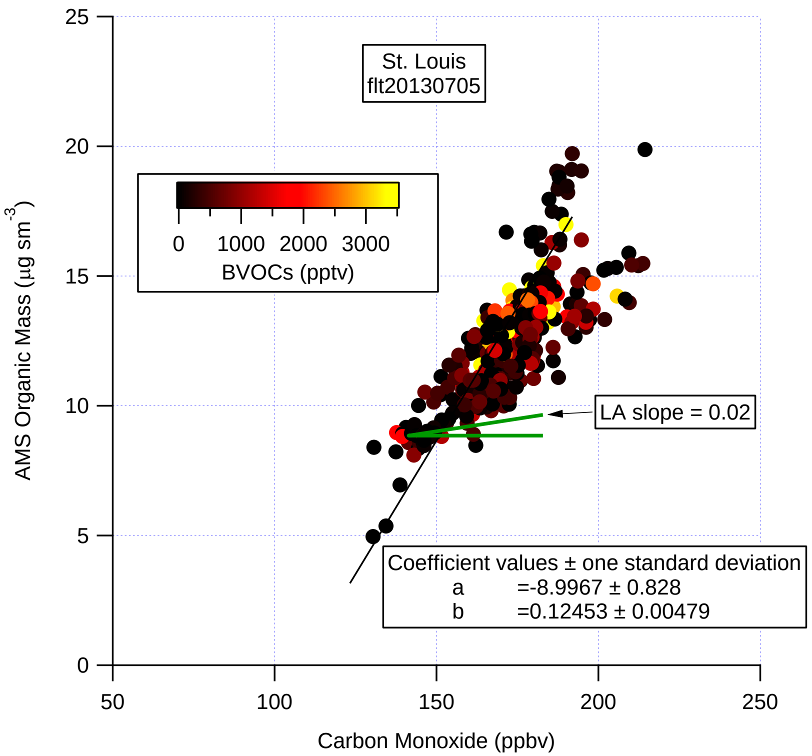
Winds light and from the east and northeast.

Background OA was about 8-13 μg sm^{-3}.

Downwind OA increase maybe a few μg sm^{-3}.

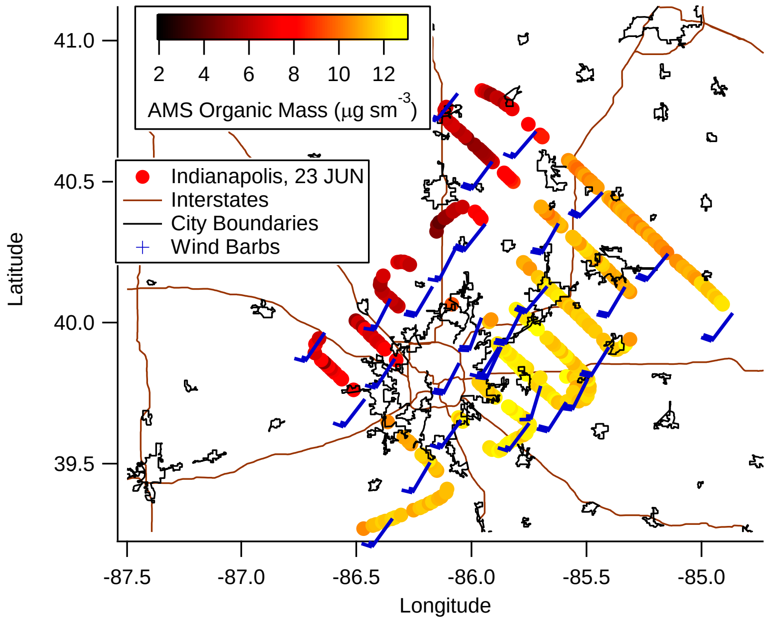
St. Louis: Both High and Low BVOCs

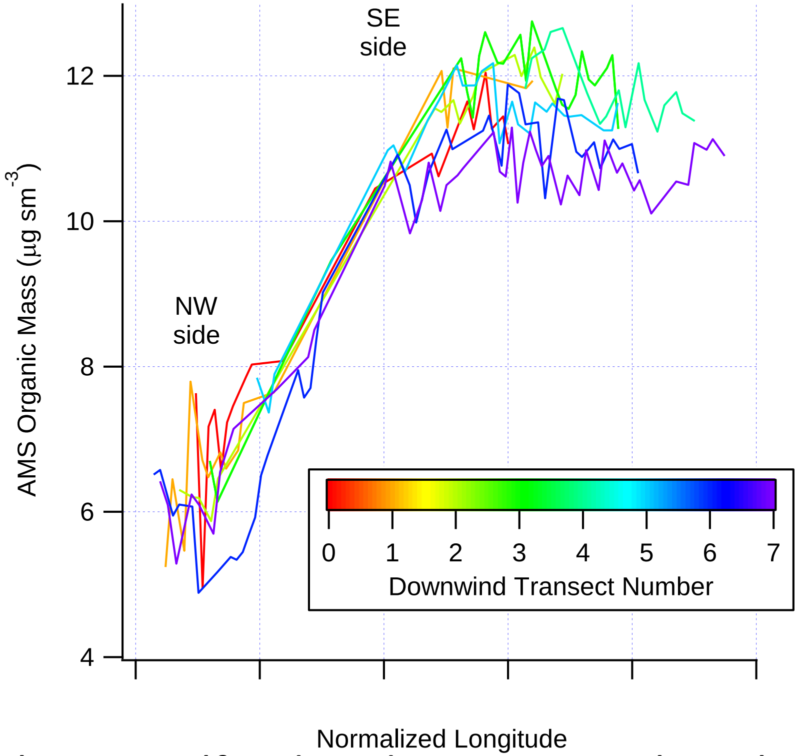




Winds light and from the south and southeast.
Background OA was high, about 12-20 µg sm^{-3}.
OA downwind was lower.

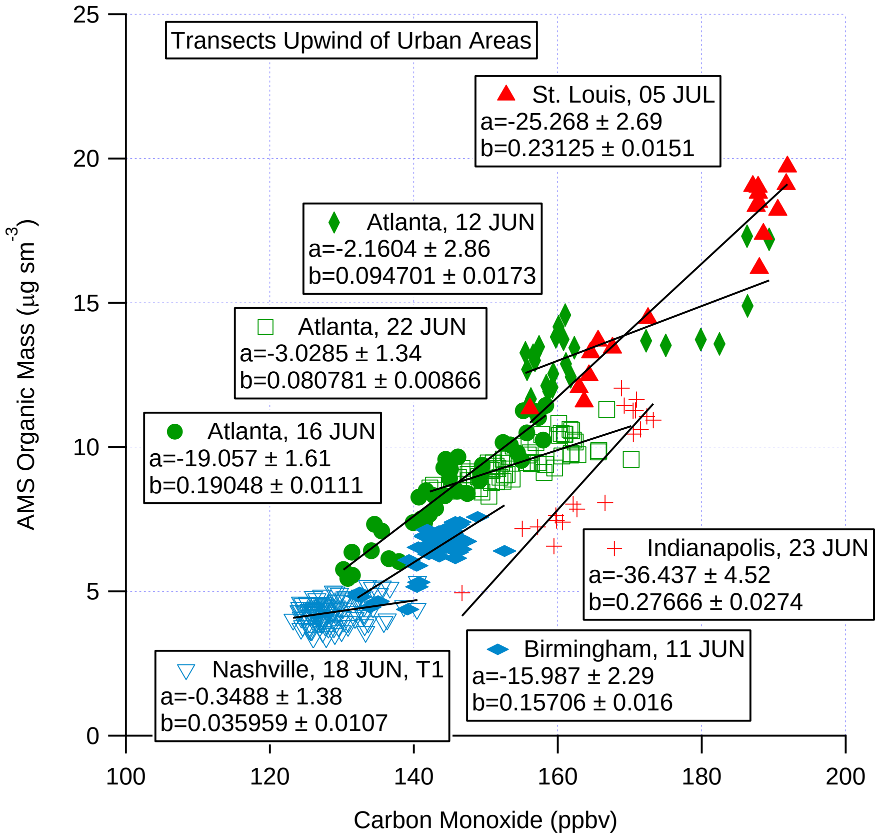
Indianapolis: Low BVOCs





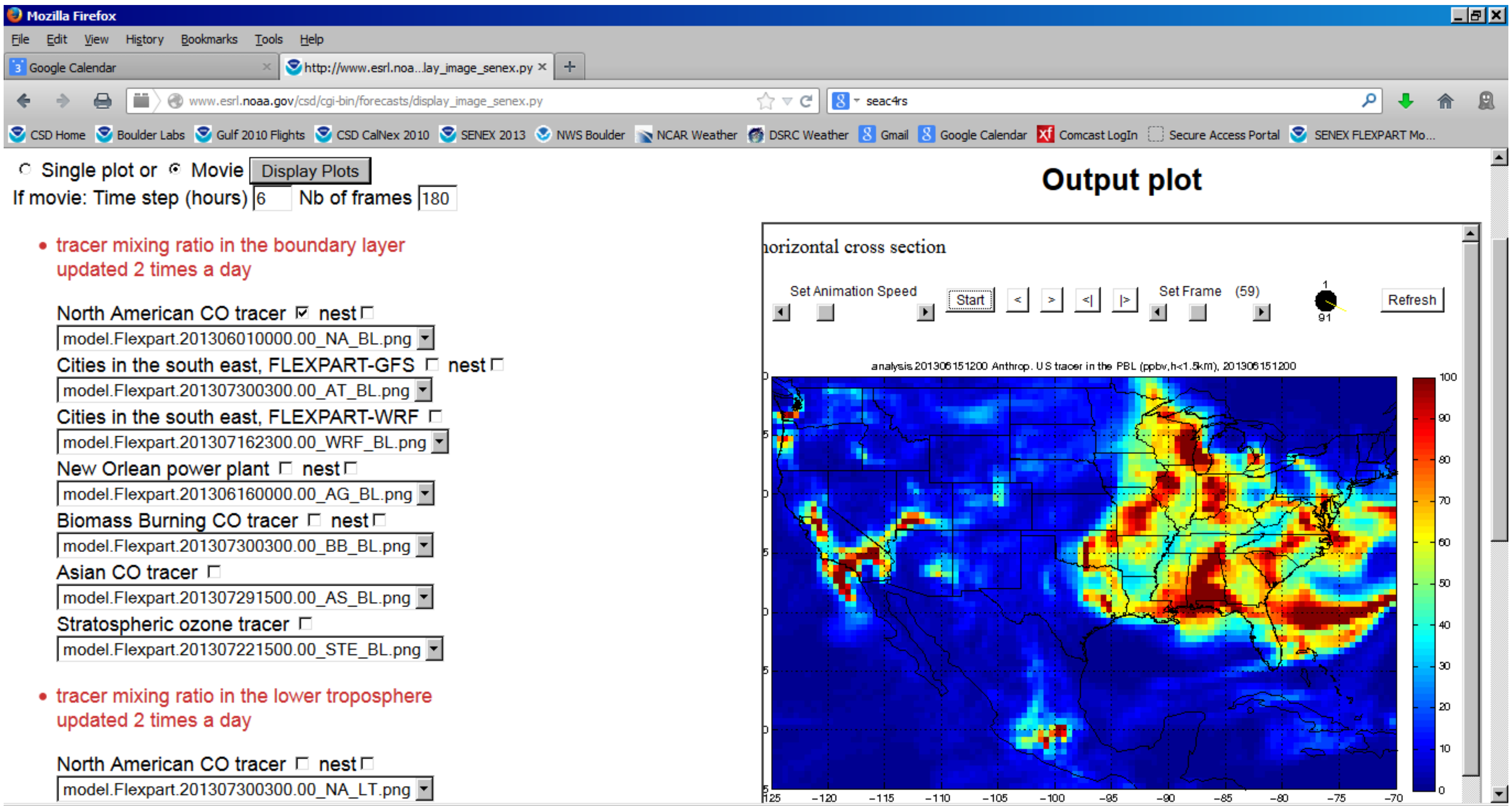
Winds light-moderate and from the southwest, sulfur dioxide sources in the urban area.
Background OA was varied from ~7 (NW side) to ~11 (SE side) μg sm^{-3}.
Difficult to determine changes in OA downwind of the urban area.

Upwind of Urban Regions

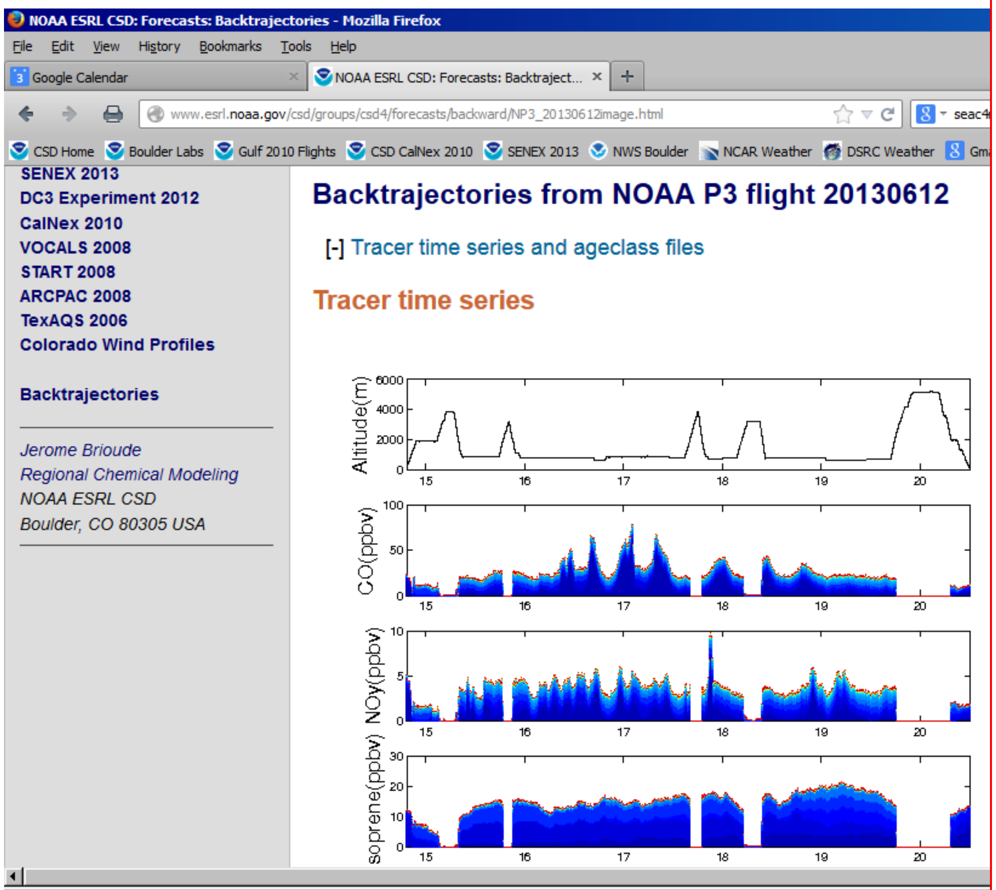


- Upwind transects show a wide range of OA/CO slopes, from 0.036 (Nashville) to 0.28 (Indianapolis)
- Why are the slopes high coming into the urban areas?
- FLEXPART Movie
- Use FLEXPART to understand background air.

Visit this FLEXPART Webpage!
http://www.esrl.noaa.gov/csd/cgi-bin/forecasts/display_image_senex.py



FLEXPART Species:
Urban CO, NOy, SO2, BB CO, Isoprene, and Monoterpenes



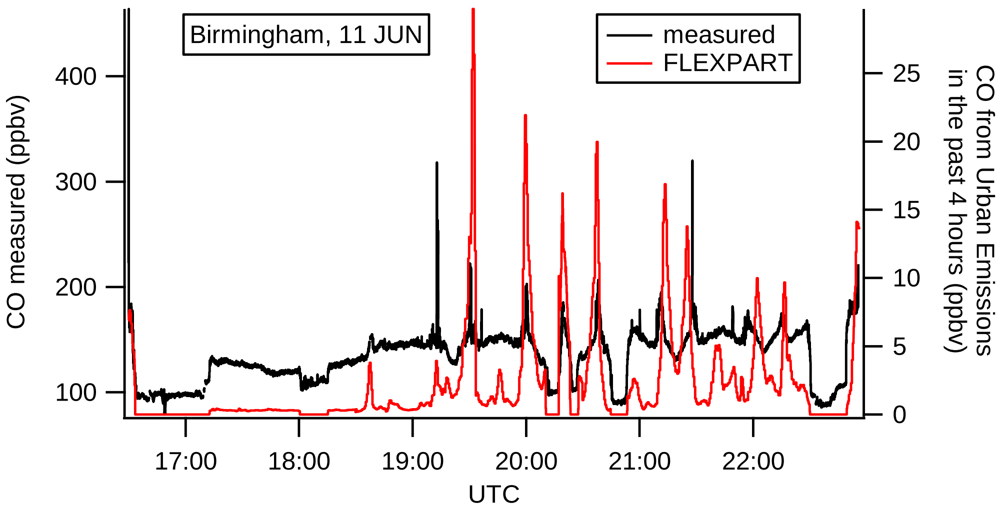
For each point along the flight track, the emissions of each species in the past 4, 8, 12, etc. hours are calculated from the back trajectory and emission inventory, then accumulated into the tracer time series age class for that accumulation time.

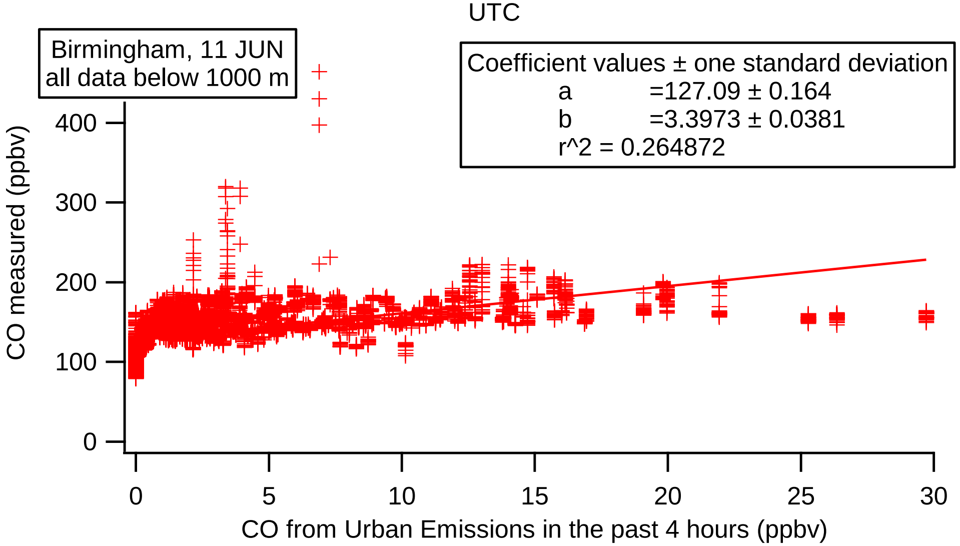
The current set of posted age classes go back 10 days.

Goal: Use FLEXPART to determine source of Background Air

- Organic Aersosol = Urban + Biogenic + Urban*Biogenic+ Biomass Burning
  - Need to consider loss due to rainout, not yet a FLEXPART product
  - J. Brioude revising FLEXPART biomass burning product
  - From C. Blanchard's presentation, biomass burning is about 60-75% and the urban terms were previously dominated by diesel sources
- CO = Urban + Biogenic + Biomass Burning

Measured Carbon Monoxide for an entire flight Compared to One Species and Age Class





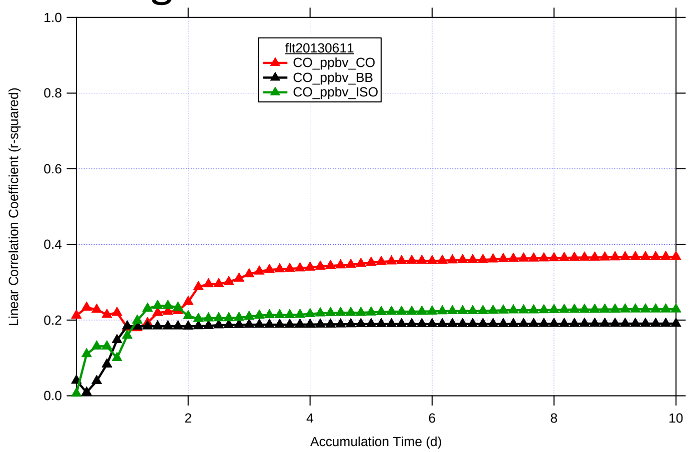
Peaks in the measured time series are slightly correlated with the FLEXPART calculation.

In this example, the measured carbon monoxide is correlated with the carbon monoxide from urban emissions in the past 4 hours with a linear correlation coefficient, r-squared, of 0.26.

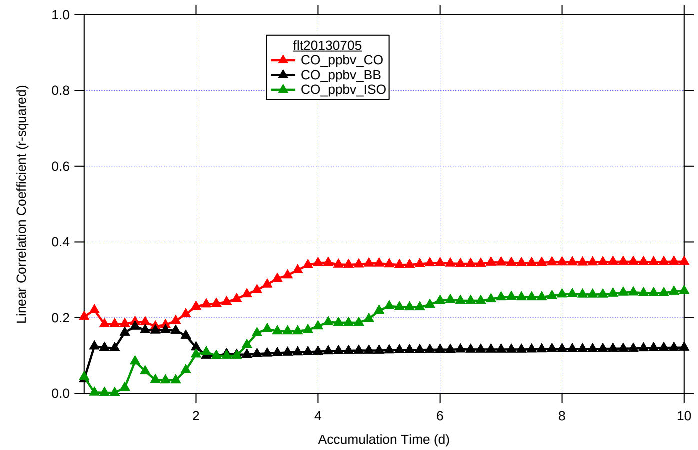
Do these correlations for species that contributed to carbon monoxide and plot the r-squares as a function of accumulation time for each species (next slide).

Compare CO with FLEXPART accumulated urban, biomass burning, and biogenic emissions

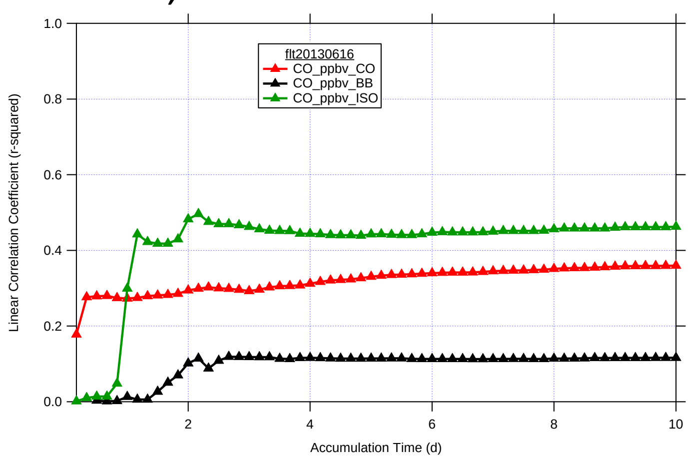
Birmingham



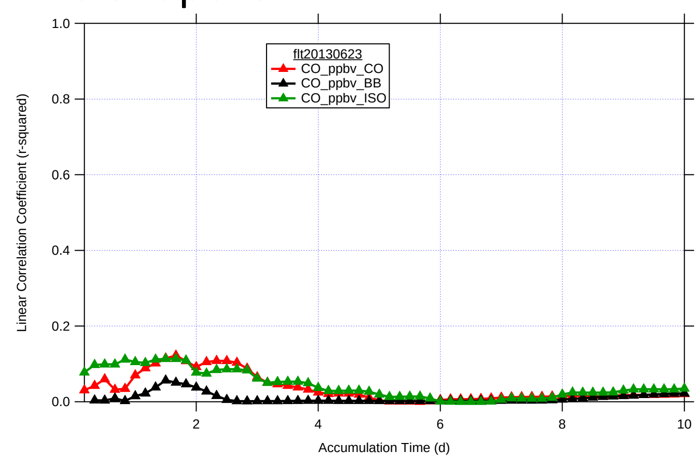
St. Louis



Atlanta, 16 JUN

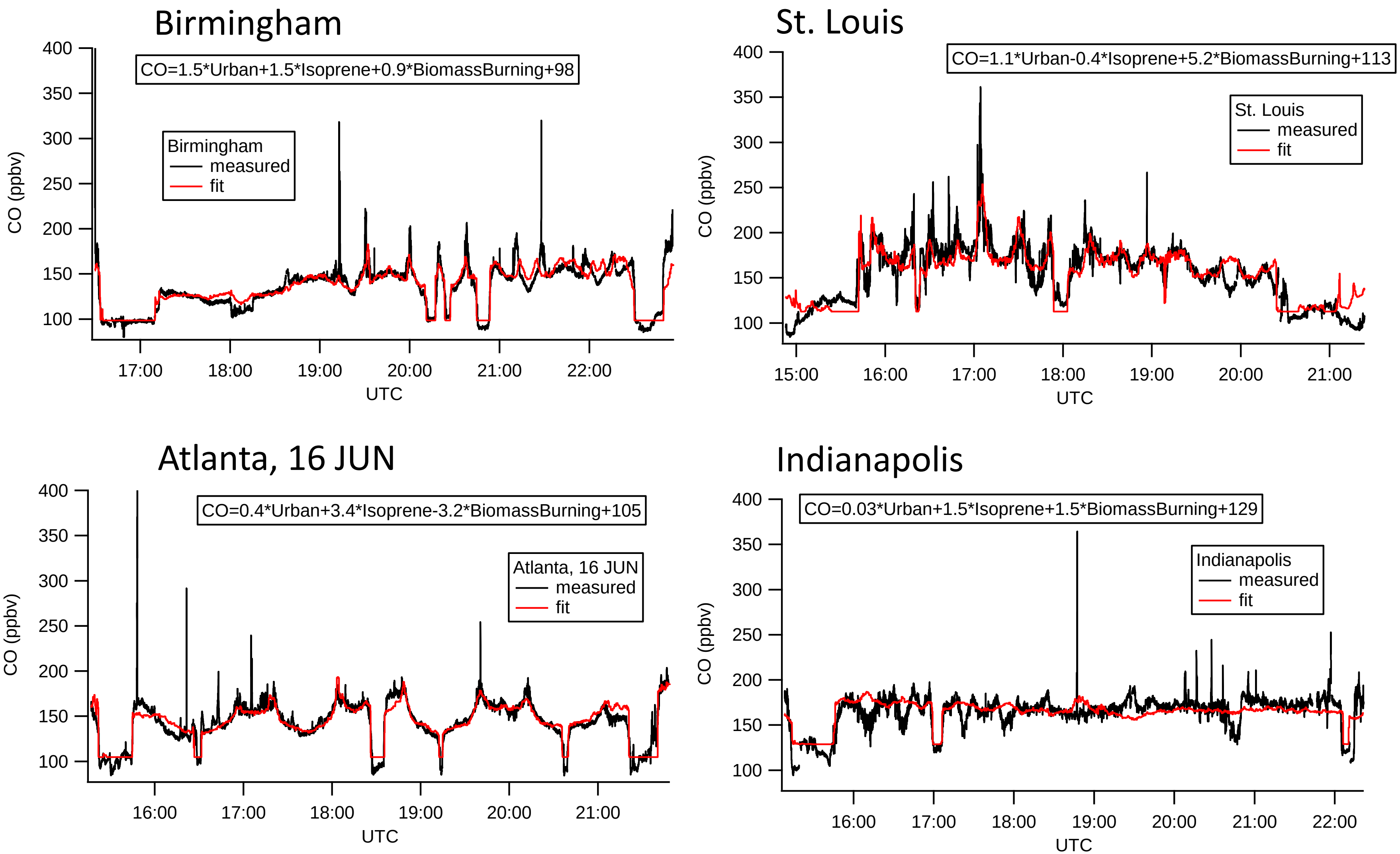


Indianapolis



Emissions important for first 2-4 days. Isoprene diurnal emissions seen. Some flights not OK.

Fit CO with FLEXPART accumulated urban, biomass burning, and biogenic emissions



Some fits are good. Coefficients not always reasonable (e.g. negative and 3.4*Isoprene).

Summary and Future Work

- Organic aerosol (OA) mass around urban areas is highly correlated with carbon monoxide (CO), independent of biogenic volatile organic compound (BVOC) mixing ratios
- In contrast, formaldehyde mixing ratios are higher when BVOC mixing ratios are higher – in measurements and AM3 model.
- Slope of OA to CO in urban data is higher than typically seen in urban areas.
- Urban emissions have decreased over time, such that the areas immediately downwind do not have large increases in primary or secondary pollutants.
- Slope of OA to CO is higher than typically seen in urban areas for several upwind transects.
- Air masses above the eastern US tended to recirculate during the course of the study, mixing fresh emissions with highly aged, polluted air. Overall, the background air masses were already "polluted".
- Unraveling the source of background pollutant levels is the key to understanding pollutant levels in urban areas of the eastern US.
- Not all flights have reasonable results from FLEXPART, so need to validate FLEXPART before using to determine source of background air.
- Future work: incorporate improved biomass burning product and aerosol loss product.

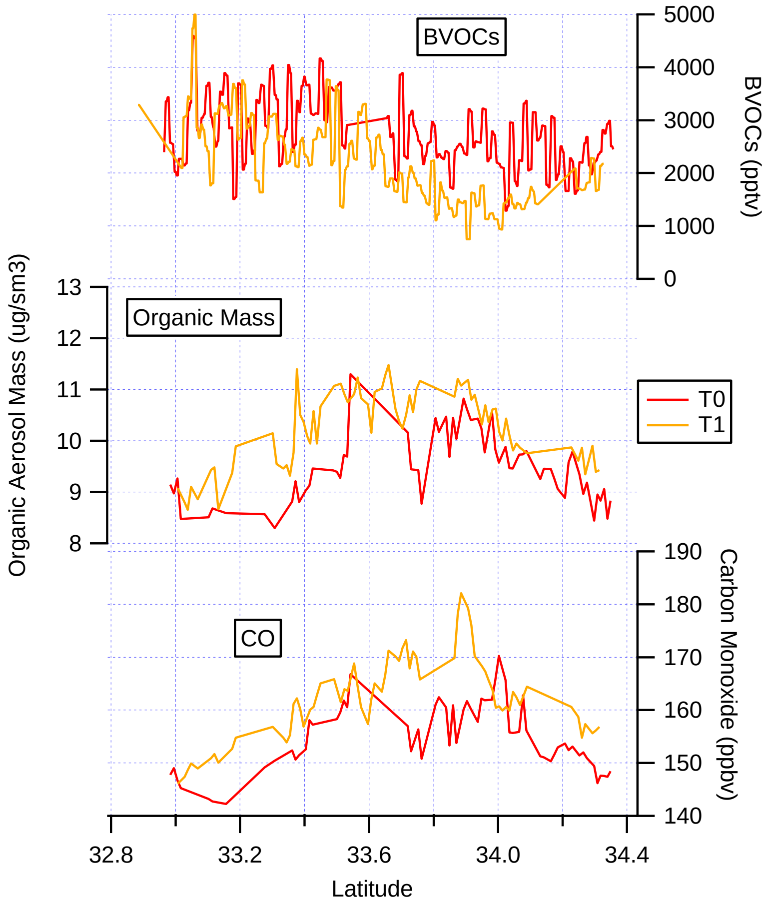
Special Thank You
for helping collect a RICH data set.

Dr. André Welti

Dr. Jin Liao

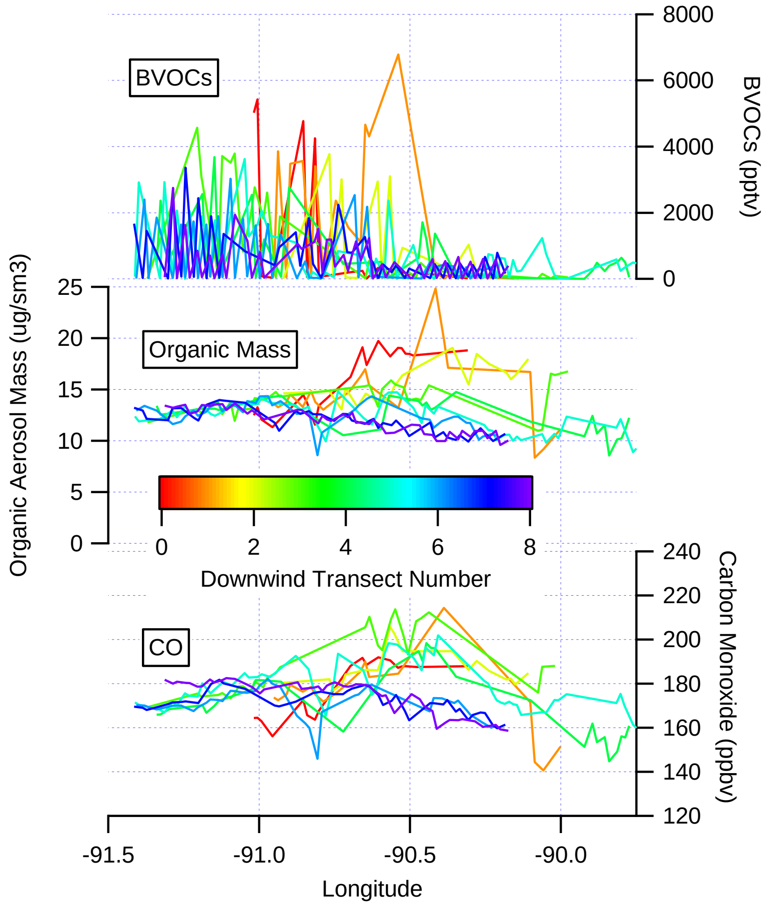
Dr. Milos Markovic

Individual Transects for Atlanta



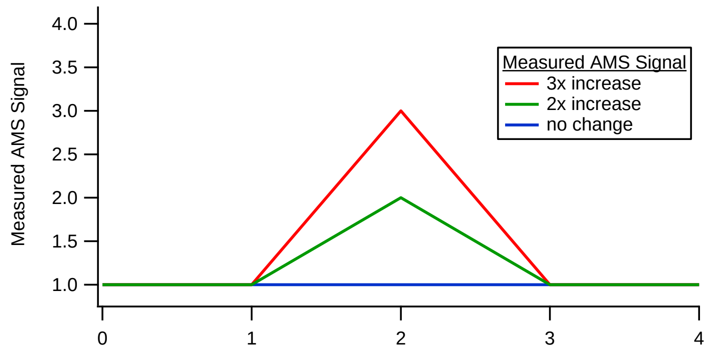
- Upwind air contained high carbon monoxide, organic aerosol mass, and BVOCs.
- Very little CO and OA added downwind of the urban area
- OA is not correlated with BVOCs.

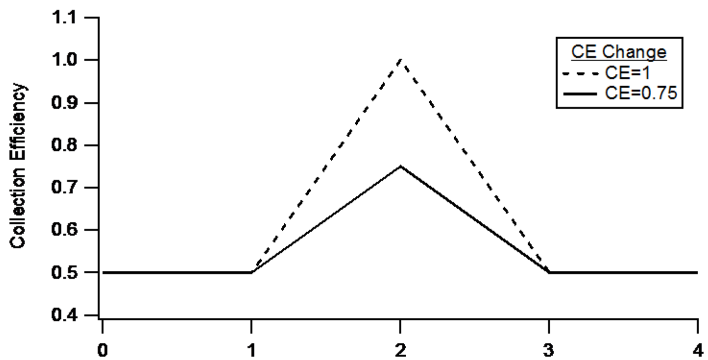
Individual Transects for St. Louis

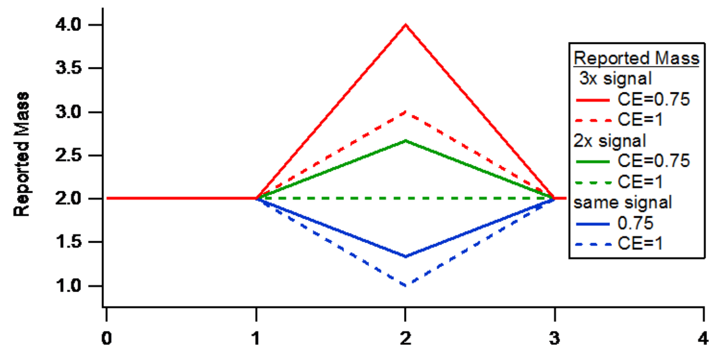


- Upwind air contained high carbon monoxide, organic aerosol mass, and some BVOCs.
- Very little CO and OA added downwind of the urban area
- OA is not correlated with BVOCs.

Reported AMS Mass ∝ Signal/CE: Case of Power Plant Plumes







Note that CE ~ 0.5 for most ambient data, so most reported mass is 2x the signal.

- Peaks in reported mass indicate that signal/CE > 2.
- Valleys in reported mass indicate that signal/CE < 2.

- Need to verify that the derived CE is appropriate for each case.
- Please contact me for assistance.

- Collection efficiency (CE) increases in power plant plumes due to increased detection of acidic sulfate particles.
- CE change is determined by NH4 measured/neutralized (Middlebrook et al., 2012).