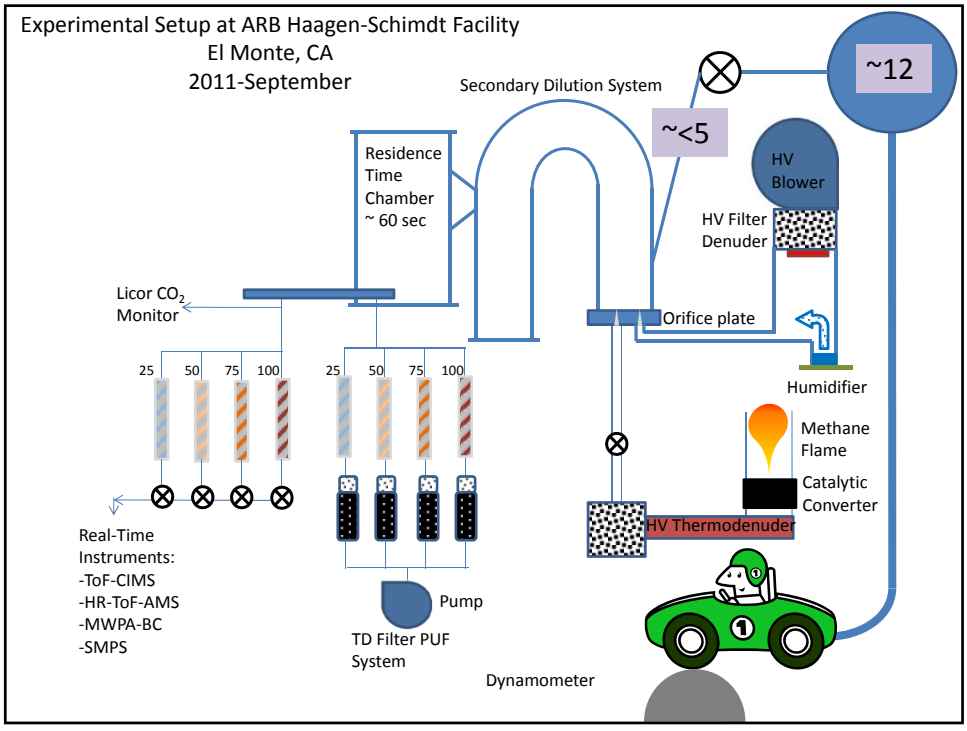
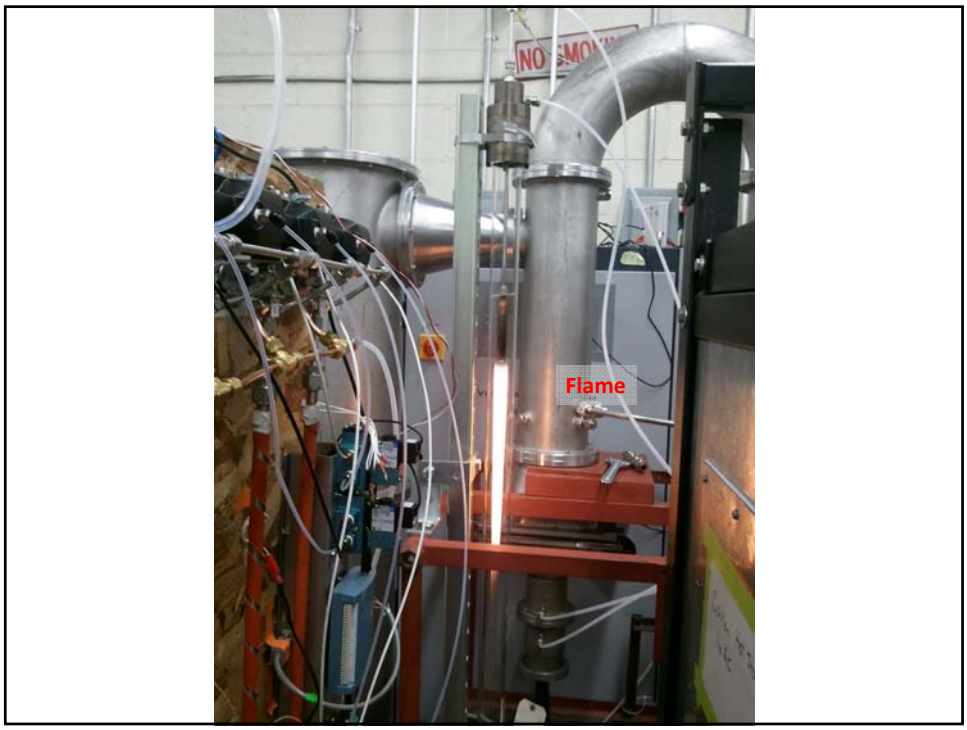
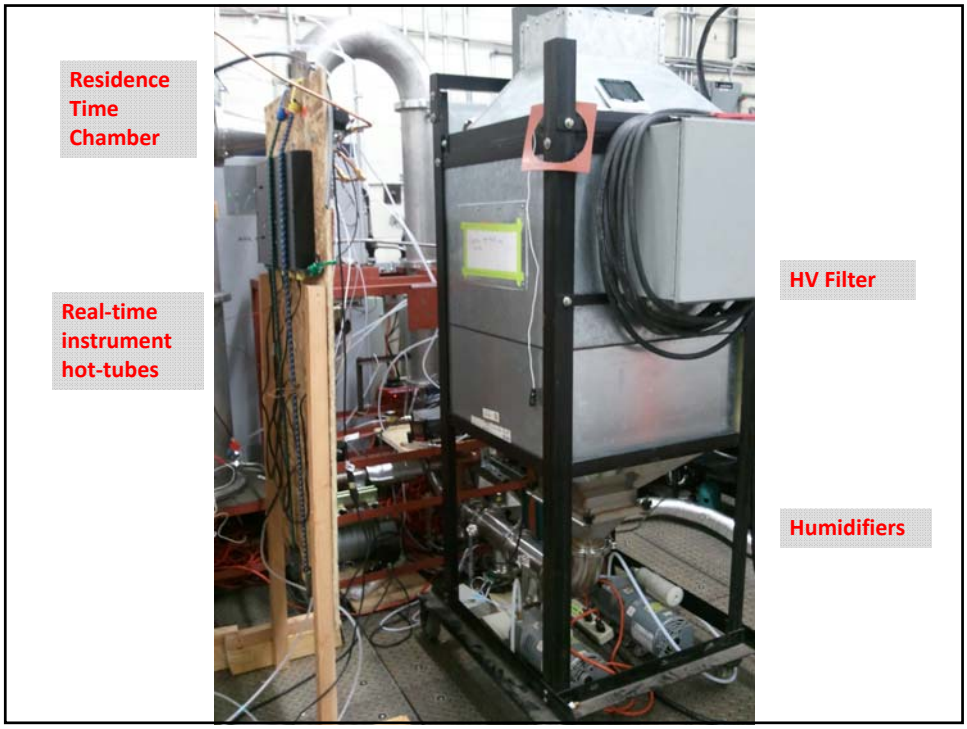
CO_2 Subtraction for Vehicle Emissions Sampled with an HR-ToF-AMS

Sonya Collier, Qi Zhang
UC Davis
10/13/2012

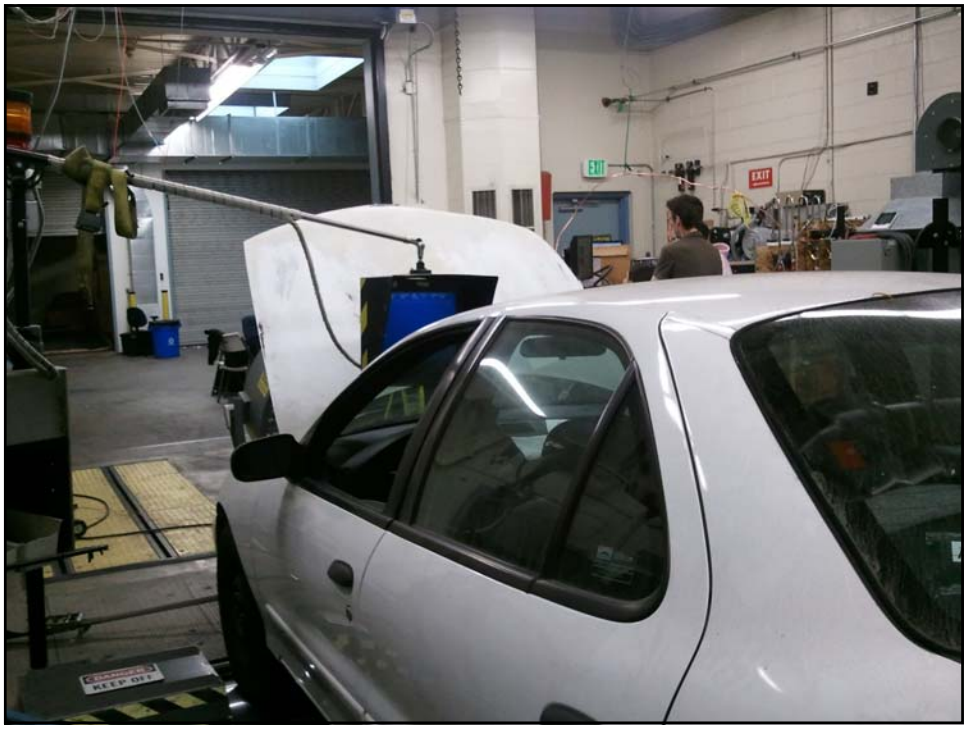


CIMS
HV Blower
ARB CVS Tunnel
HV Filter/Denuder
AMS
MWPA-BC
SMPS


Flame


Residence Time Chamber
Real-time instrument hot-tubes
HV Filter
Humidifiers

Dyno



Summary of Base Case Test Day

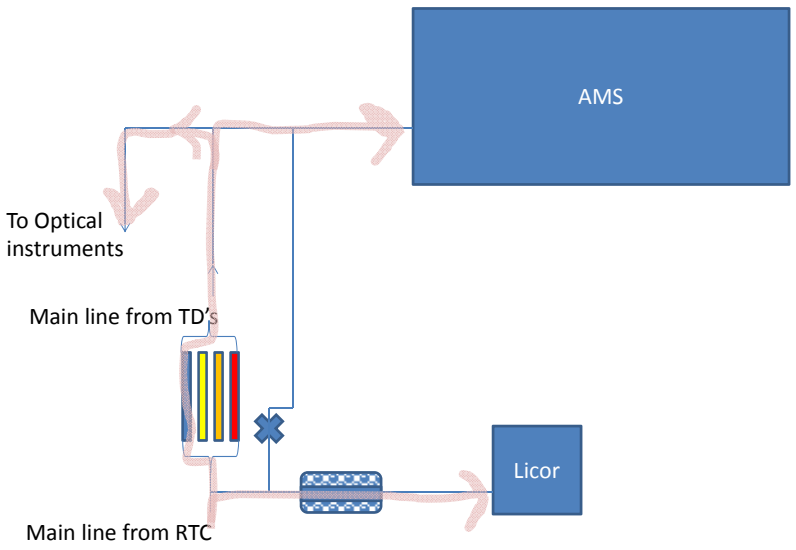
9/20/2011	Tuesday			RH (%)				T (°C)				
EC (0), RH (Ambient)				Ambient		Dilution Air		Ambient		Dilution Air		
Car	Start Time	End Time	Dilution Factor	Mean	Error	Mean	Error	Mean	Error	Mean	Error	Veh ID
Jeep/Grand Cherokee/2002	7:13	7:37	4.82	48.1	2.1	52.0	1.7	25.7	0.6	25.3	0.9	5
Chevy/S10 Pick-Up/2003	8:18	8:42	4.82	47.3	1.0	49.7	0.6	25.8	0.4	26.0	0.2	9
Nissan/Pathfinder/2003	9:13	9:37	4.78	46.3	1.6	48.7	0.6	26.2	0.6	26.3	0.4	6
Toyota/Tacoma/2003	10:26	10:50	4.86	46.9	1.2	49.0	0.0	26.2	0.4	26.3	0.4	4
Ford/Taurus/1997	11:42	12:06	4.80	48.3	1.8	50.3	0.6	25.7	0.5	26.0	0.2	10
Toyota/Solora/2003	13:03	13:27	4.75	48.0	1.4	50.0	0.0	25.6	0.3	26.0	0.2	11
Ford/Winstar/1998	14:06	14:30	4.75	47.0	1.4	49.0	0.0	25.6	0.4	25.8	0.2	1
Chevy/Cavalier/2001	15:19	15:43	4.75	48.1	0.9	49.7	0.6	25.6	0.3	25.8	0.2	2
		Averages:	4.79	47.50	1.43	49.79	0.51	25.80	0.44	25.94	0.35	

AMS Operation and Data Post-Processing Details

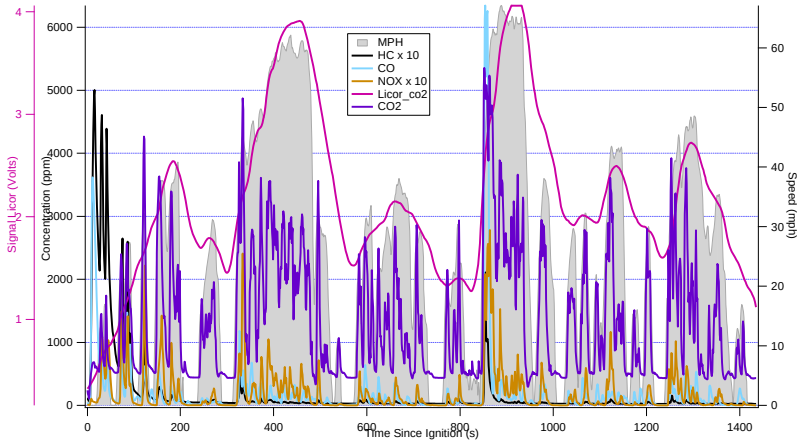
- 10 second averaging, V mode (MS and PToF)
- Thermal conditioning of sample (30 seconds at each Temp)
  - 25-50-25-75-25-100-25-50….
- Onsite IE and size calibrations
- Fit Licor real-time CO_2 data to do proper CO_2 subtraction
- Separate data by driving cycle portion, hot tube temperature, or other relevant parameter
- Fit over 500 ions in HR peak fitting analysis
- Used R^2 analysis to separate background contamination of Si containing ions
  - Screened data points to not include any where contamination was prominent
- Used PMF analysis to separate OA into the components belonging to methane flame, vehicle emissions and background contamination

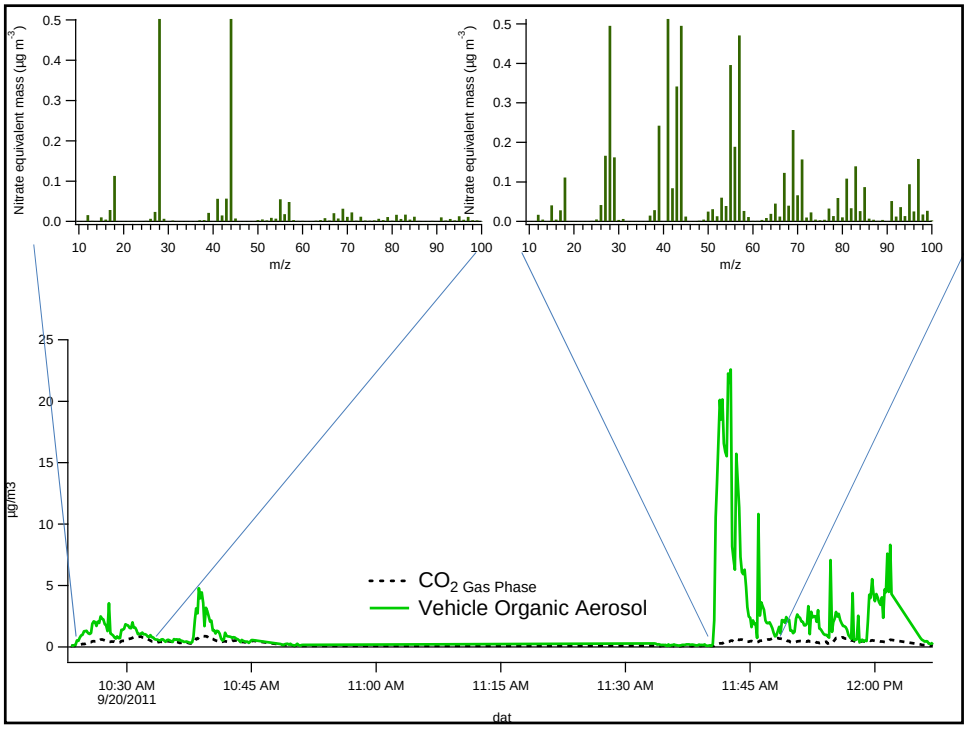
- This analysis
  - Base Case or High RH, ambient (25 ° C) and screened contamination

AMS Measurement setup for vehicle test



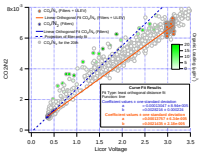
Cold Start Driving Cycle and ARB Emission Results





CO_2 Subtraction Method at-a-glance

AMS Data vs Licor Data

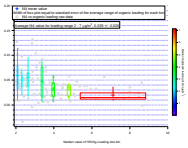


CO_2/N_2 = Slope*Licor ±Intercept

FRAGMENTATION TABLE

Regenerate Vehicle Data

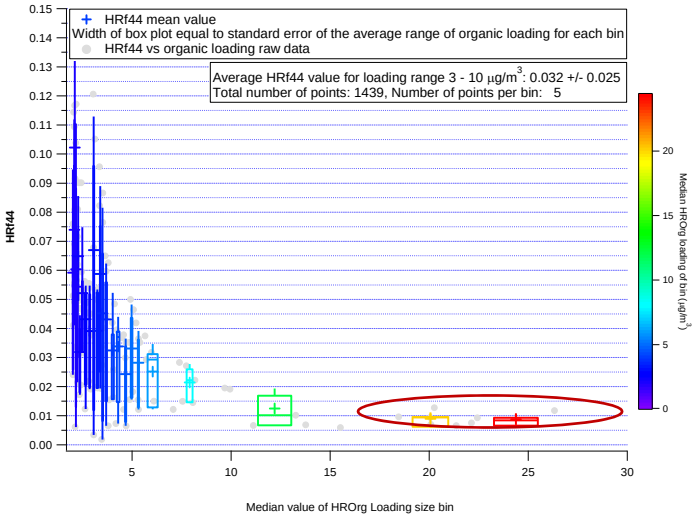
Statistics of f44/Org



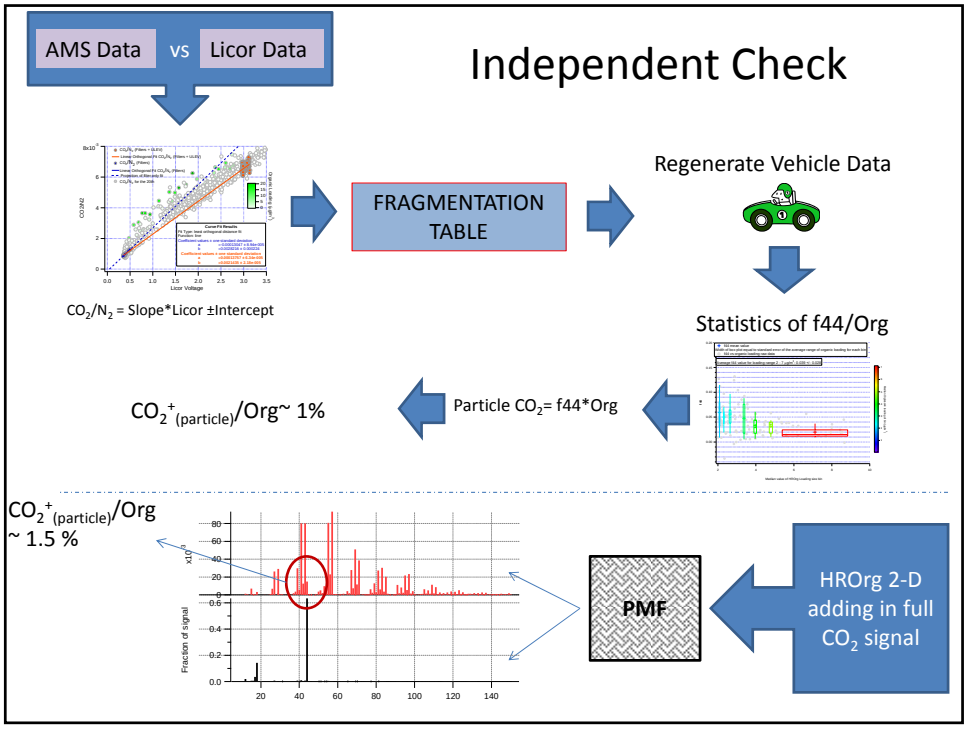
Particle CO_2= f44*Org

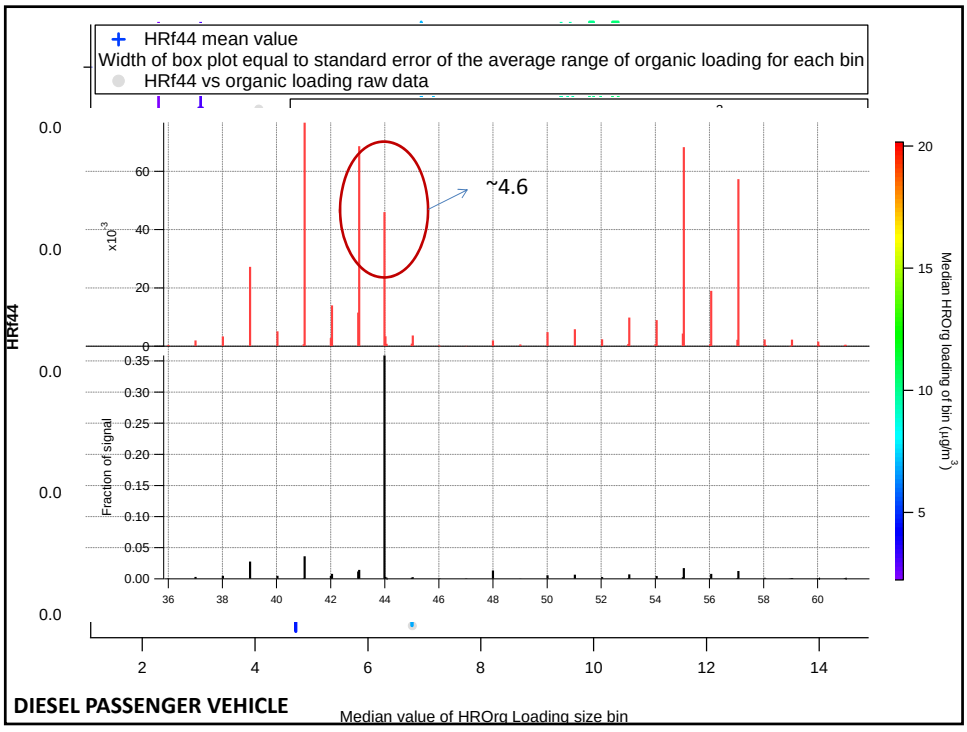
Post-process vehicle data to reflect new particle bound CO_2^+ relative concentration (along with O^+,HO^+,H_2O^+,CO^+)

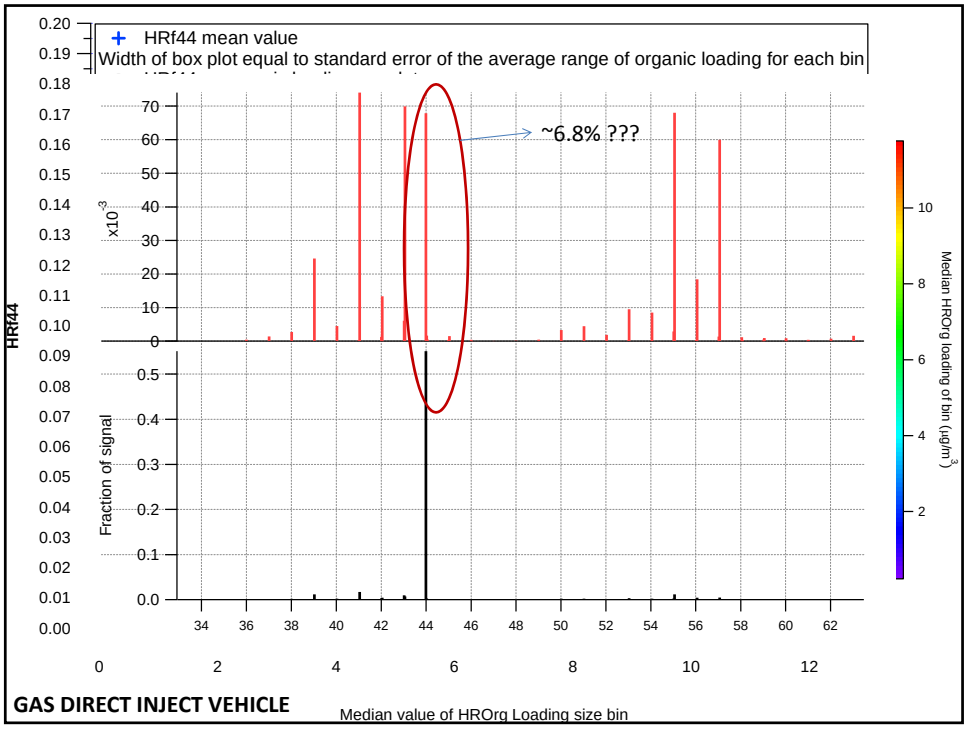
Statistical analysis of subtraction results: convergence of f44 at higher org loading

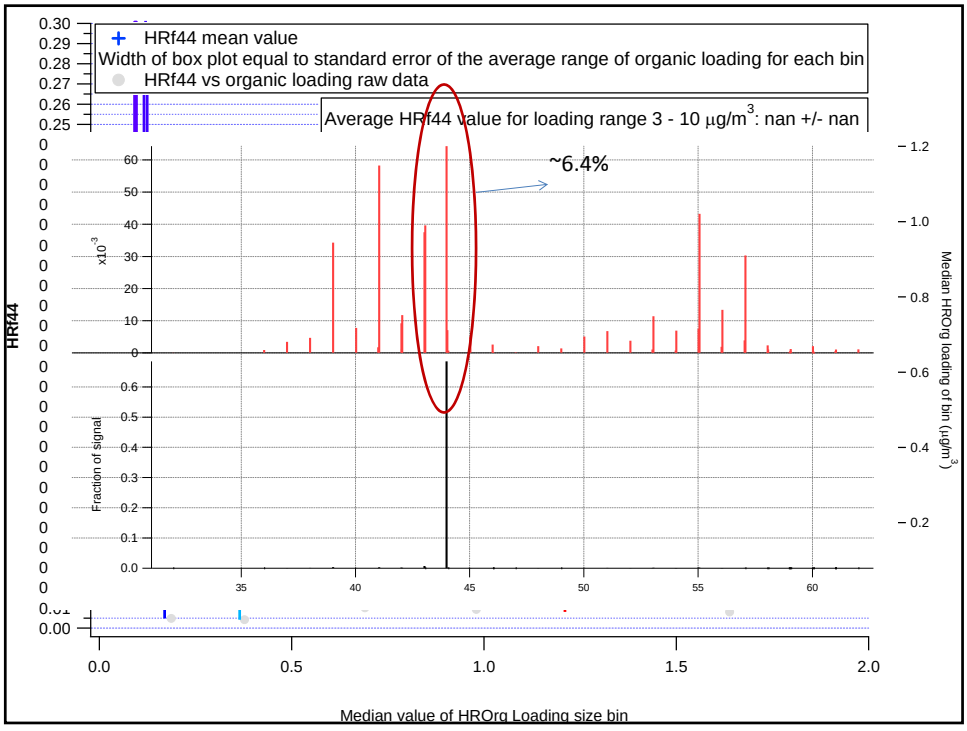


C. Mohr, J. A. H., M.J. Cubison, A.C. Aiken, K.S. Docherty, J.R. Kimmel, I.M. Ulbrich, M. Hannigan, and J.L. Jimenez (2009). "Characterization of Primary Organic Aerosol Emissions from Meat Cooking, Trash Burning, and Motor Vehicles with High-Resolution Aerosol Mass Spectrometry and Comparison with Ambient and Chamber Observations." Environmental Science & Technology **43**: 2443-2449


AMS Data
vs
Licor Data
Independent Check
FRAGMENTATION TABLE
Regenerate Vehicle Data
CO_2/N_2 = Slope*Licor ±Intercept
Statistics of f44/Org
$CO_2^+{}_{(particle)}$/Org~ 1%
Particle CO_2= f44*Org
$CO_2^+{}_{(particle)}$/Org
~ 1.5 %
PMF
HROrg 2-D adding in full CO_2 signal


HRf44 mean value
Width of box plot equal to standard error of the average range of organic loading for each bin
HRf44 vs organic loading raw data
~4.6
HRf44
Fraction of signal
Median HROrg loading of bin (µg/m³)
DIESEL PASSENGER VEHICLE
Median value of HROrg Loading size bin


HRf44 mean value
Width of box plot equal to standard error of the average range of organic loading for each bin
~6.8% ???
HRf44
x10^-3
Fraction of signal
Median HROrg loading of bin (µg/m3)
GAS DIRECT INJECT VEHICLE
Median value of HROrg Loading size bin


HRf44 mean value
Width of box plot equal to standard error of the average range of organic loading for each bin
HRf44 vs organic loading raw data
Average HRf44 value for loading range 3 - 10 µg/m3: nan +/- nan
~6.4%
HRf44
x10^-3
Fraction of signal
Median HROrg loading of bin (µg/m3)
Median value of HROrg Loading size bin

Conclusions

- For cold start days my two methods for CO_2 subtraction seem to correlate
  - For GDI, ULEV, Diesel PMF not ideal since those were tested under constant velocity
- CO_2 subtraction clearly important and has huge effect on oxidation of resulting aerosol