

Supplemental Material for:
**Gas-phase CO₂ subtraction for improved measurements of organic aerosol
mass concentration and oxidation degree by Aerosol Mass Spectrometer**

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Table S1: Gas-phase subtraction standard procedure

<p><i>Method 1: Utilization of colocated gas phase measurements</i></p> <ol style="list-style-type: none">1. Include a colocated gas-phase analyzer sampling at similar or higher time-resolution2. Calibrate to AMS using filtered air3. Apply all IE, REI, CE values to data and filter test data<ol style="list-style-type: none">a. Analyze all filtered air runs in single Squirrel/Pika pxpb. Plot average filtered air load for given ion versus average reading from colocated instrument for a given filter period4. Modify fragmentation table to reflect subtraction based on real-time gas-phase data from colocated instrument
<p><i>Method 2: Performing PMF on combined PM and gas-phase signals</i></p> <ol style="list-style-type: none">1. Include gas-phase ion in organic family and generate 2-D matrix2. Input matrix and error matrix into PMF Evaluation Toolkit3. Perform all recommended preparation steps4. Setup PMF calculation with varying fpeak5. Verify that resulting factors separate gas-phase signal from PM signal
<p><i>Method 3. Analysis of PTOF data</i></p> <ol style="list-style-type: none">1. Plot individual ion in PTOF space2. Find percentage in so called PTOF airbeam space compared to that found in PM space

Table S2: Summary of gasoline, spark-ignition, low emission vehicles (LEV) used under base case conditions for the CO₂ subtraction analysis.

Make	Vehicle Type	Vehicle ID	f44 predicted by method			Drive Cycle ³
			Varying CO ₂ Subtraction Method	PMF Subtraction Method	PTOF Subtraction Method	
Ford/Windstar/1998	Van/SI/gasoline	1	0.01	0.014	0.01	UC
Chevy/Cavalier/2001	Sedan/SI/gasoline	2				
Toyota/Tacoma/2003	Truck/SI/gasoline	4				
Jeep/Grand Cher./2002	SUV/SI/gasoline	5				
Nissan/Pathfinder/2003	SUV/SI/gasoline	6				
Chevy/S10/2003	Truck/SI/gasoline	9				
Ford/Taurus/1997	Sedan/SI/gasoline	10				
Toyota/Solara/2003	Sedan/SI/gasoline	11				
Hyundai/Sonata/2011	Sedan/SI/gasoline	ULEV	0.05	0.064 ⁴	NA	ConstV
Hyundai/Sonata/2008	Sedan/GDI/gasoline	GDI	0.015	0.068 ⁴	0.02 ¹	ConstV
VW/Jetta/2008	Sedan/Diesel	DSL	0.045	0.046 ⁴	0.05 ²	ConstV

1. PTOF f44 for GDI vehicle run calculated only for data points where total organic loading was greater than 6 µg/m³.

2. PTOF f44 for DSL vehicle run did not converge to a single value at the high PM loading limit, the number reported here is an average. The same behavior was seen with the varying CO₂ subtraction method.

3. UC refers to Unified drive cycle and ConstV refers to constant velocity driving.

4. The constant velocity PMF values for the alternative vehicles are based on less data points than the gasoline vehicle PMF results and have less variability between the gas-phase and particle-phase. Given that the requirements for data quality are not met, these f44 values should be considered unreliable.

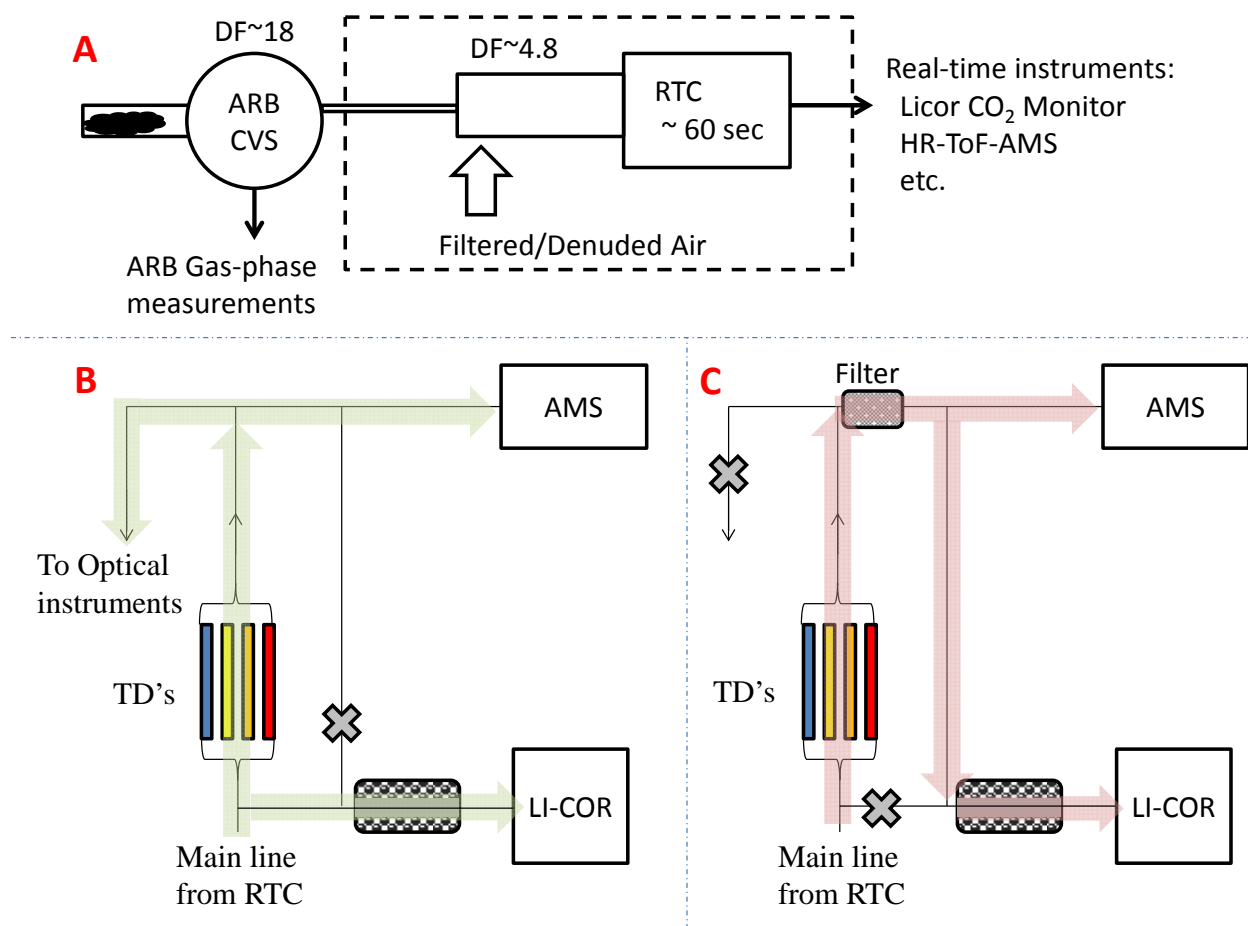


Figure S1 Panel A shows a simplified schematic of the vehicle emissions sampling scheme where vehicle emissions undergo an initial dilution in the constant volume sample tunnel (CVS) and undergo a second dilution in the secondary dilution system (SDS) which includes a residence time chamber (RTC) eventually leading to a suite of real-time instruments. Panel B shows a schematic of the AMS and LI-COR configurations in regular vehicle sampling mode and Panel C shows the filter sampling mode, where air originating from the RTC must pass through a switching valve manifold through one of the thermal tubes and then to the AMS and optical instruments. Upstream of the TD's a tee intersection leads a portion of the flow to the LI-COR instrument.

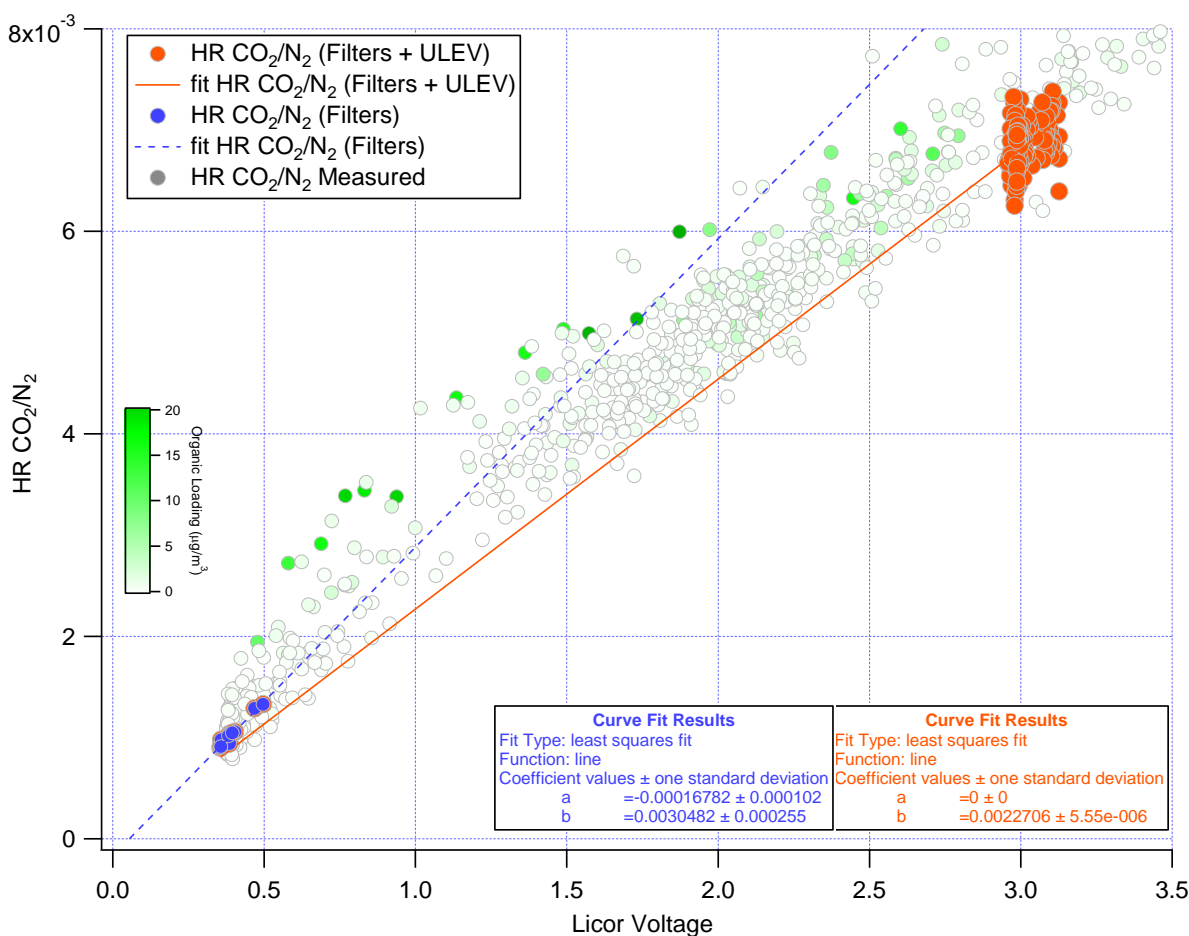


Figure S2 Scatter plot of CO_2/N_2 ratio versus LI-COR instrument voltage signal response during filter tests with orthogonal fit using the filter data plus the ULEV data. The orange fit line includes the ULEV data while the blue dashed fit line is a projection of the linear function using the filter data only. The open circles are colored by organic loading where darker green signifies higher PM loading. The transformation of the real-time LI-COR data was used using the fit described by the orange line, where the ULEV data was included. Furthermore, the orange line traces the lower envelope of the data points, where higher loading periods are farther from the orange fit line, demonstrating that the ULEV data is an acceptable proxy for particle free air.

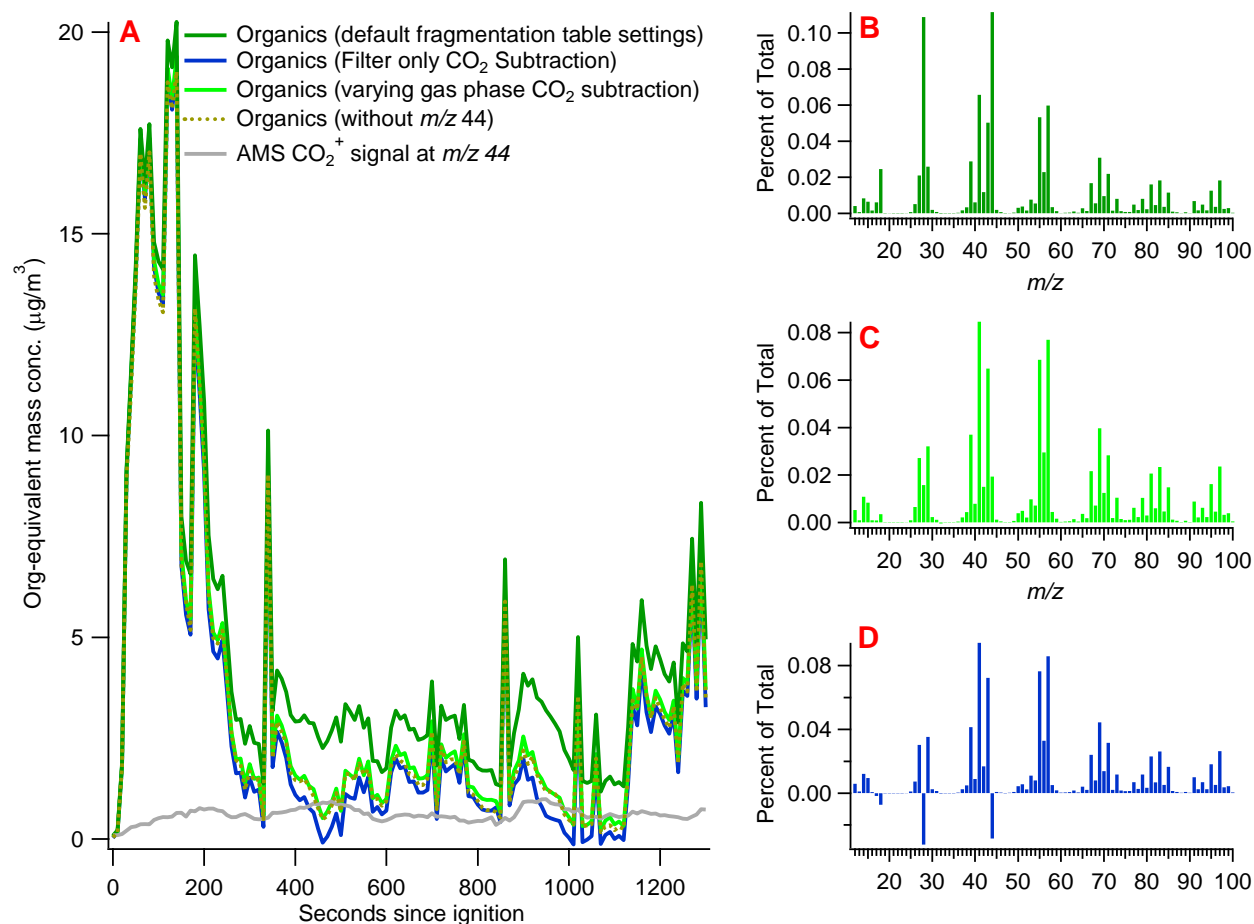


Figure S3. In addition to information provided in Figure 3 of main text, the blue trace in Panel A represents the effect of exclusively using the filter data to perform the gas-phase CO₂ subtraction. Panels B and C are the same as in Figure 3 whereas Panel D shows the resulting mass spectrum, where CO⁺ and CO₂⁺ have negative values, when using only the filter data to define the linear relationship between the LI-COR instrument response and the resulting gas-phase CO₂ measured by the AMS.

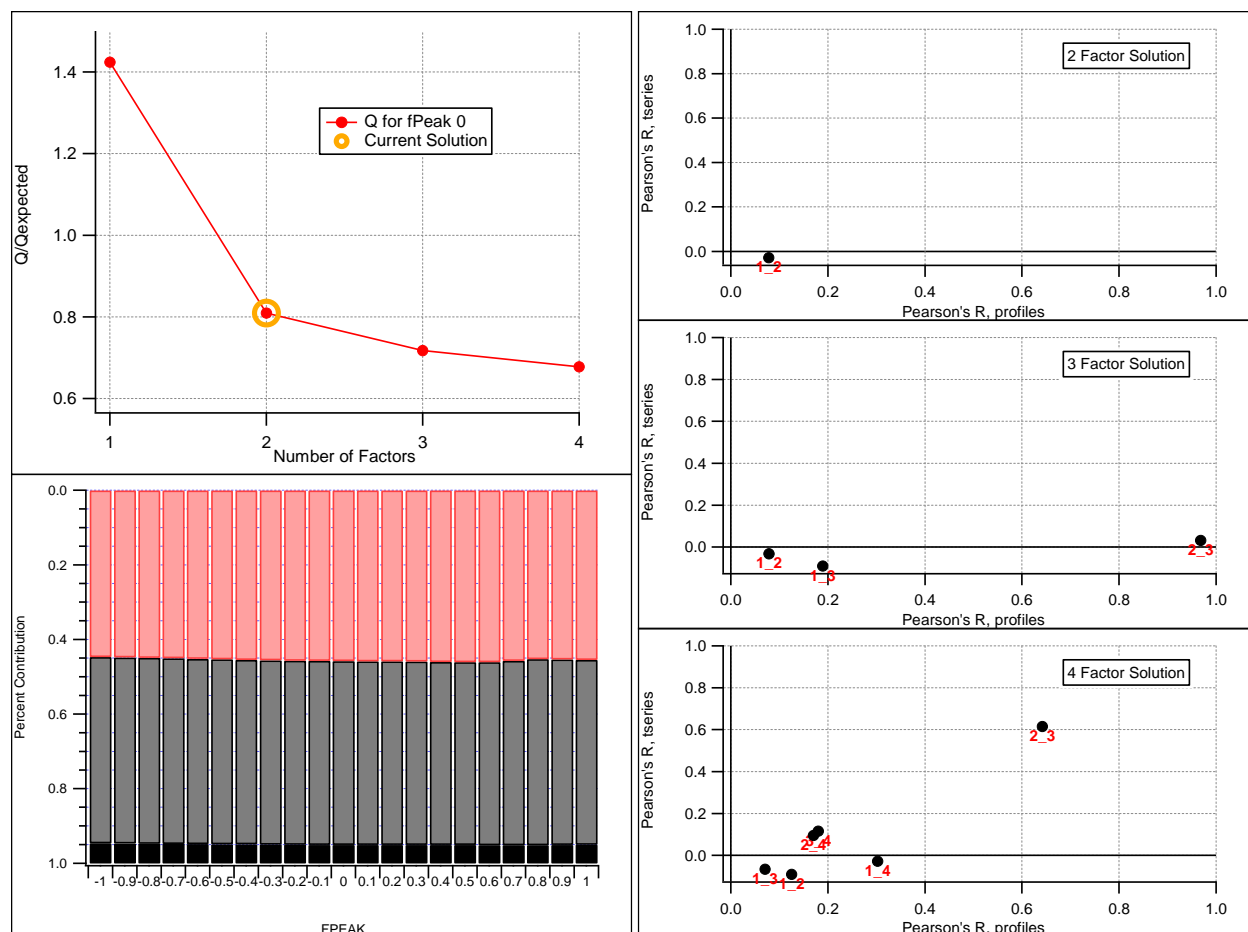


Figure S4. PMF results. Upper left panel shows the Q/Q_{expected} vs. the number of factors. The bottom left shows the fractional contribution for the 2-factor solution of both factors and the residual as a function of FPEAK. The 3 panels on the right show the Pearson's R values for the time-series traces vs. the Pearson's R values for the factor profiles. When the Pearson's R value approaches 1 on either axis it suggests the factors may be split from a single real factor. The top right panel depicts this relationship for the 2-factor solution, the middle right panel is for the 3-factor solution, and the bottom right panel is for the 4-factor solution.

As illustrated in the middle right panel, which corresponds to the 3-factor solution, it is evident that factor 2 and factor 3 correlate well by Pearson's R suggesting that the factor 2 of the 2-factor solution has been split up for the 3-factor solution. In the 4-factor solution factor 4 corresponds to contamination, which was detected early on in the campaign and which has a very unique mass spectrum with prominent ions at $m/z = 73, 149, 207, 221, 401$, etc. This ion series has been correlated with contamination from silicone degassing and was characterized by Timko *et al.* (2009) and also detected by Schneider, *et al.* (2006). Note that no silicone tubing was used for sampling during this study. The signal might come from the rubber connector between the tailpipe and the CVS. Although all the data being analyzed in this manuscript was screened to exclude the contamination, it still had a minor influence in the overall mass spectrum and was factored out in the 4-factor solution. Factors 2 and 3 are still the split version of factor 2 in the 2-factor solution. It is also clear that the rotational ambiguity is more pronounced since changing FPEAK has a larger effect on the overall contribution of each factor to the total signal.

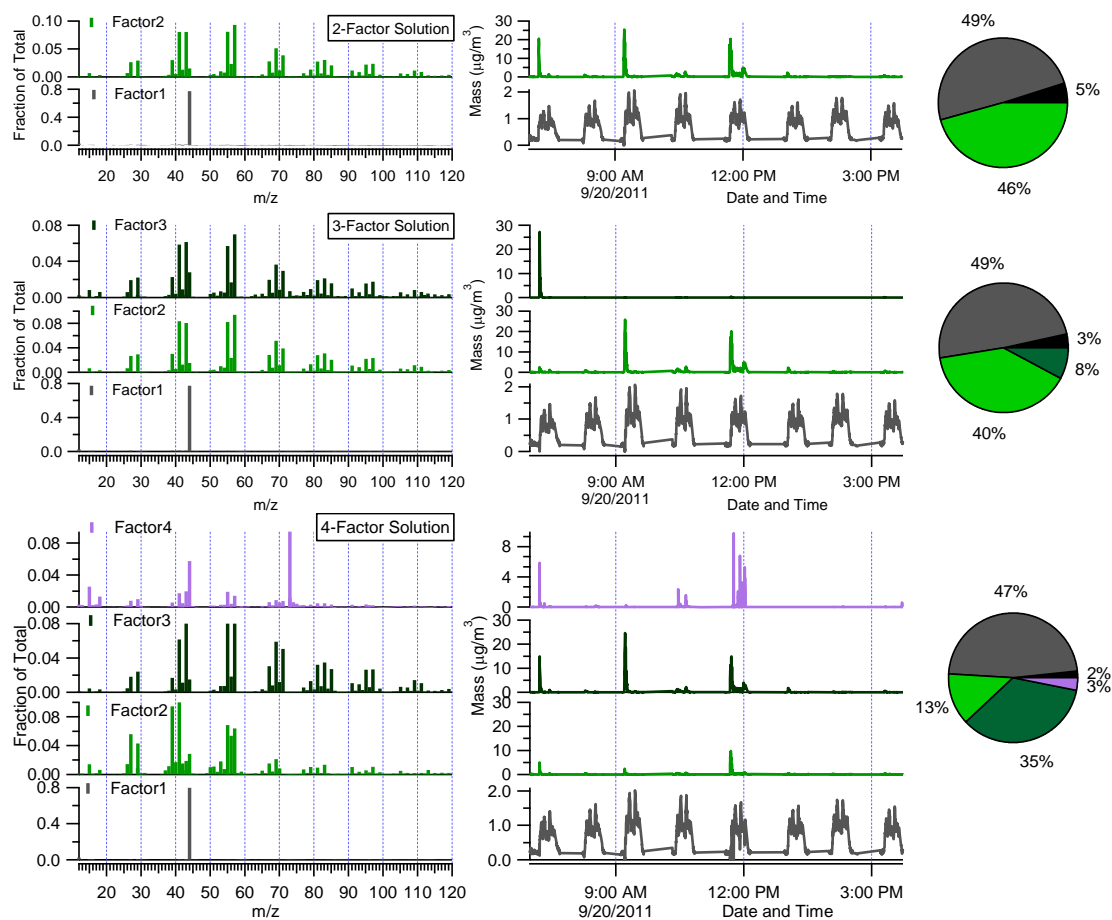


Figure S5: Results of solution spaces with 2,3 and 4 factors. The main manuscript text discusses primarily the 2-factor solution. The 3-factor solution appears to split the factor 2 from the 2-factor solution. Pearson's R^2 analysis further alludes to this in Fig. S4. For the 4-factor solution factor 4 corresponds to silicon contamination which was discussed also in Fig. S4 caption and only contributes 3% by mass to overall mass in that solution space. The gas-phase factor, factor 1 in all solution spaces, has a stable factor profile and contributes roughly the same mass overall.