# Supplementary Material

# Online measurements of the emissions of intermediate-volatility and semi-volatile organic compounds from aircraft

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## Positive Matrix Factorization Analysis

To provide a more detailed characterization of the high resolution I/SVOC mass spectra positive matrix factorization (PMF) analysis was applied to the data acquired on the morning of 30 March 2011. Mass spectral and error matrices were prepared following the procedures described in (DeCarlo et al., 2010). As discussed in section 2.3, the acquisition of mass spectra was semi-continuous, resulting in volatility-resolved measurements of I/SVOC mass spectra during each desorption.

The PMF analysis was run using the PMF2.exe algorithm (v 4.2) in robust mode ((Paatero and Tapper, 1994)). The PMF2 results were evaluated using the PMF Evaluation Tool (PET, v. 2.04, (Ulbrich et al., 2009)). The evaluation criteria outlined by (Zhang et al., 2011) was used to interrogate the PMF results and determine the optimal solution.

PMF solutions comprised of 2 to 10 factors (P) were evaluated. To determine the minimum number of factors necessary to adequately describe the data, factor mass spectra and time (volatility) trends for each factor were analyzed. The change in slope of Q/Qexp as a function of P was used to narrow down the range of factors warranting closer inspection (See Figure S1).

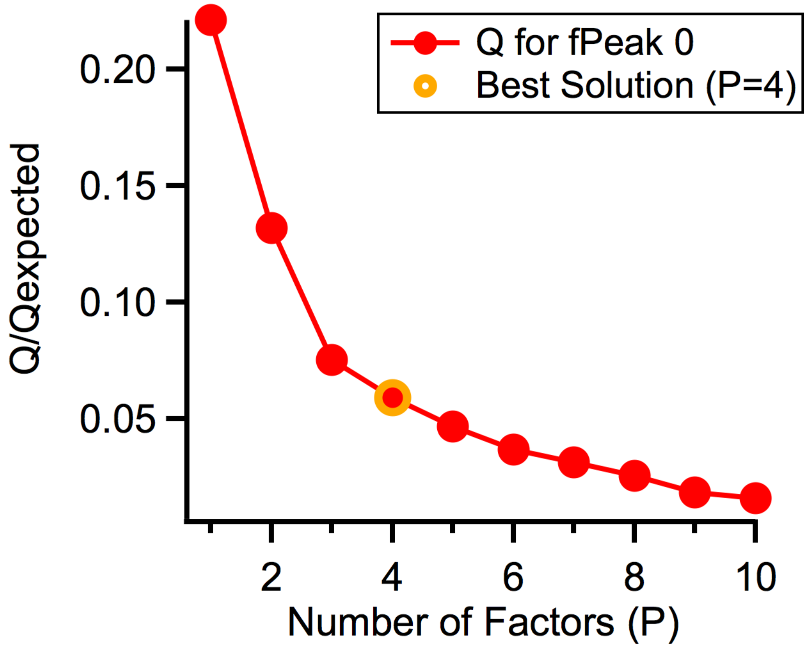


Figure S1. Q/Qexp as a function of the number of factors used in the PMF solution. FPeak = 0 for all cases. The data point highlighted in yellow was chosen as the optimal solution for the aircraft exhaust I/SVOC data obtained on 30 March 2011.

As shown in Figure S1, Q/Qexp decreases substantially between 1, 2, and 3 factor solutions indicating that a substantial amount of the variability in the dataset is accounted for with each additional factor. For P > 3, the slope in Q/Qexp vs P is less severe. The trend in Q/Qexp prompted closer examination of the factor mass spectra and time (volatility) trends for P = 3, 4, and 5. In the case of the 3-factor solution, the aircraft-derived oxygenated hydrocarbon factor was combined with chemical ion signatures indicative of background signal. The 5-factor solution resulted in splitting of the aromatic factor with no discernable difference in volatility or chemical signature between the two aromatics identified in the PMF solution. Additional splitting of the aromatic and aliphatic hydrocarbon factors was observed for PMF solutions for P > 5. The 4-factor solution was chosen as the optimal description of the aircraft I/SVOCs on the basis of clear identification of three distinct chemical classes of low volatility organics: aliphatic, aromatic, and oxygenated hydrocarbon factors. In addition, the 4-factor solution included a factor attributed to instrument background. The background factor was dominant during the ultra-zero air sample desorption and showed little change in response to the aircraft exhaust plume across all engine power conditions tested. A closer examination of the mass spectral features of the background factor is provided in the following section.

We note that the magnitude of the Q/Qexp values observed in the current experiment are less than unity. Generally, this is an indication that the errors associated with the input data matrix have been over-estimated. After checking the calculation for the ion counting statistical error associated with the high resolution ion signals in the current data set, we confirm that errors were not being over-estimated. Instead, many of the high resolution ion signals comprising the I/SVOC mass spectra had relatively low signal to noise ratios. This is in part due to the acquisition rate (2 Hz) of mass spectra throughout each desorption, ambient dilution of the low volatility organics in exhaust plume itself, and relatively short pre-concentration collection times (120 seconds) used during the AAFEX-II experiment. Prior to generating input matrices for PMF analysis in the current experiment, the 2 Hz mass spectral data were averaged into 4 s time bins to improve the signal-to-noise ratio of many high resolution ions. Although this improved our ability to identify and fit many high resolution ion peaks, the total signal intensity or ion counts/extraction for each identified ion remained relatively low. As part of the PMF analysis, ion signals with $0.2 < \mathrm{SNR} < 2$ are down-weighted (x3). Since this down-weighting procedure was applied to the majority of ions in the I/SVOC data matrix, a low Q/Qexp value was observed.

To ensure rotational ambiguity amongst our optimal 4-factor PMF solution a range of Fpeak or initial seed values were tested ranging from -1 to 1. The change in Q/Qexp with p=4 as a function of different Fpeak values is shown in Figure S2. The results indicate that Q/Qexp is at a minimum for Fpeak = 0, justifying the decision to use Fpeak = 0 in the case of the optimal 4-factor PMF solution.

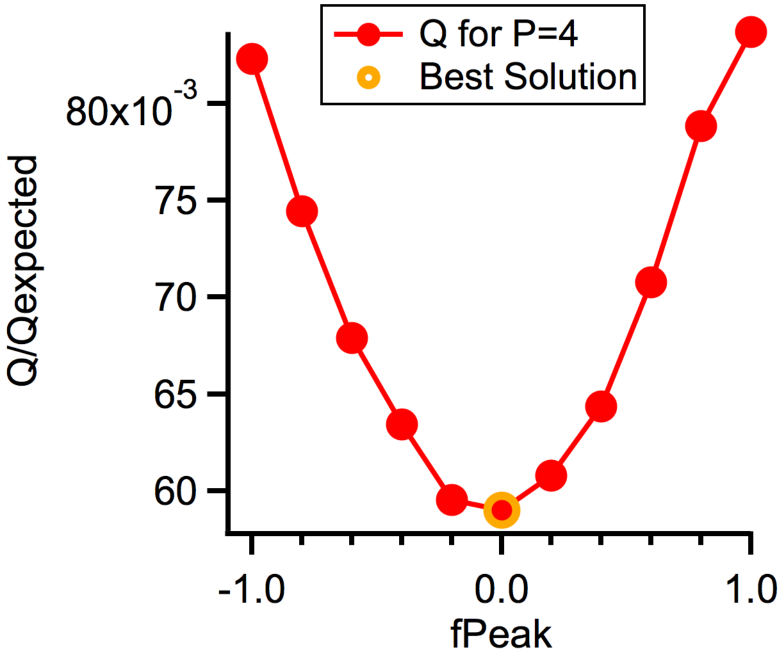
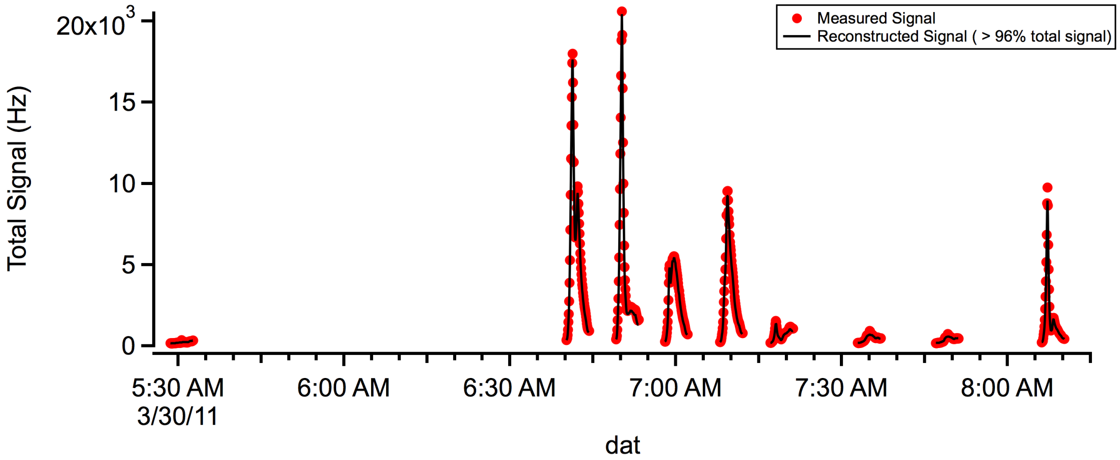


Figure S2. Interrogation of range of Fpeak values for 4-factor solution.

Comparing the reconstructed and measured total I/SVOC organic signal provides an additional check on the quality of the 4-factor PMF solution. The reconstructed and measured signals are displayed as a time series in Figure S3. Note that the time series matches the data shown in Figure _ of the manuscript. As shown in the figure, the reconstructed signal closely tracks the total measured signal, accounting for > 96% of the measured signal across all desorptions.



S3. Comparison of the measured (in red) and reconstructed (in black) total organic ion signal intensity for the four factor PMF solution.

The residual (measured – reconstructed) for the 4-factor PMF solution can be examined with a number of different diagnostic plots. Figure S4 shows one diagnostic: the scaled residuals as a function of m/z. This approach allows one to identify which, if any, ions are dis-proportionately contributing to the residual of the 4-factor PMF solution.

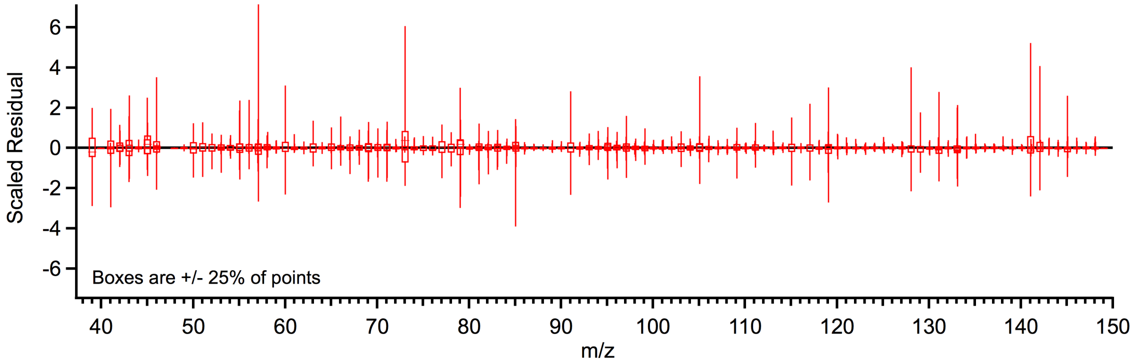


Figure S4. Box and whiskers plot showing the distribution of scaled residuals for each m/z in the 4-factor PMF solution.

Residuals at *m/z* 57.0704 and 73.0473 show the largest positive deviation for the I/SVOC mass spectra. The peak at 57.0704 is the $C_4H_9^+$ peak, which corresponds to one of the largest ion signals observed in the I/SVOC input mass spectra. The peak at 73.0473 corresponds to $C_3H_9Si^+$ a fragment ion due to siloxane. As discussed in the next section, siloxane ions are an important component of the background PMF factor. The scaled residuals suggest that 4-factor solution adequately describes the vast majority of I/SVOC variability in the aircraft exhaust plume with the prominent remaining residuals attributed to ion signal characteristic of the instrument background.

## Background PMF Factor

As stated in the text and highlighted above, the 4-factor PMF solution successfully isolated a background factor from the total measured I/SVOC signal. This factor did not vary with changes in engine power and was therefore, not included in the analysis of aircraft I/SVOC emissions presented in the manuscript. For completeness, the mass spectrum of the background factor is shown in Figure S5. It shows that the vast majority of ion signal intensity is located in *m/z* < 47. The inset in Figure S5 shows the region of the mass spectrum for *m/z* > 47 amu. Prominent ion signals corresponding to siloxane fragment ions are labeled in the graph. The minor siloxane contributions are believed to be due a contaminated section of the inlet system used during AAFEX-II. Given that the inlet itself is the likely source of these species, it is not surprising that the temporal variability in the background factor was not changed between UZA and aircraft engine exhaust desorptions. In fact, although the siloxanes are generally considered a nuisance, their presence in low concentrations was helpful in identifying the optimal, 4-

factor PMF solution. Additionally, the siloxane ions were used to check the *m/z* calibration throughout the experiment.

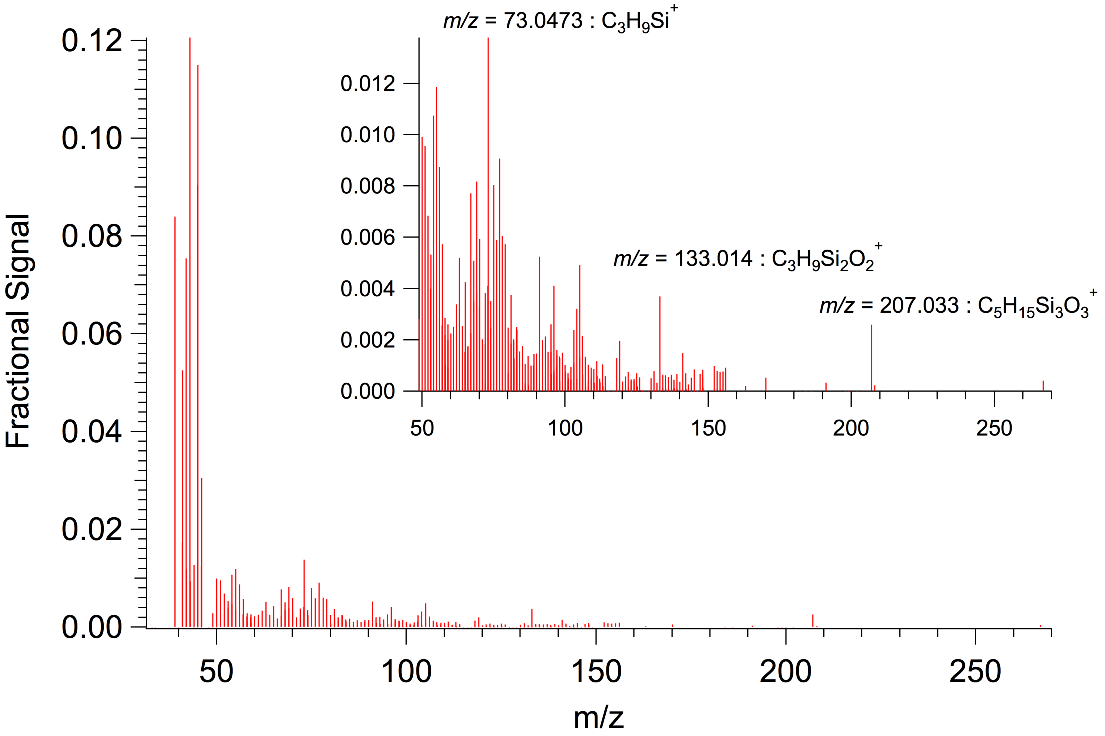


Figure S5. Mass spectrum of background PMF factor.

## References

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