

We would like to thank the referee #2 for his/her helpful comments and suggestions. We have incorporated his/her feedback into the revised version of the manuscript and believe that it is a stronger piece of work as a result. Each comment is addressed below (in black, plain text) with the corresponding referee comment shown above (italicized, grey font).

Anonymous Referee #2

Received and published: 22 May 2013

I offer the additional following comments and suggestions:

1) Page 8067, line 16: remove first "of"

We removed the highlighted mistake.

2) Page 8067, line 26: Do the authors of the previous studies suggest the mechanism for this switch?

The authors suggest that the mechanism for the switch to longer chain, higher molecular weight species is due to a shift in the combustion process from a thermal cracking (resulting in mostly alkene emissions) to production of new molecules at the higher temperatures and pressures at higher engine power.

3) Page 8069, line 23: sentence is awkward, please revise for clarity.

The sentence as been revised as follows:

“Differences in the magnitude, volatility, and chemical composition of the I/SVOC emissions are examined as a function of engine power. Results are used to identify potential sources of I/SVOC emissions during routine aircraft operation.”

4) Section 2.2, first paragraph: please explain why 2 fuel types were used for this study then, if you were predicting them to be well mixed at 143m. Were there other investigators closer to the engines to gain information on fuel type differences?

The overall objective of the AAFEX-II experiment was to characterize the influence of alternative aviation fuels on aircraft emissions. Inlet systems were operated at 1 m and 30 m behind each active engine (one burning JP-8, the other often burning an alternative fuel such as FT or HRJ). Our participation in the study was outside of the context of characterizing fuel-specific emission profiles. Our focus was to demonstrate the utility of a new mass spectrometric approach to measuring I/SVOC emissions. Our sampling position 143 m downwind of the aircraft precludes a more detailed analysis of fuel-specific emissions in the current manuscript.

5) Page 8071, line 13: Do you model the conditions to determine the gas/particle split for measured SVOCs?

This is certainly an important topic but is beyond the scope of the present work. Future work should examine gas/particle partitioning of the SVOCs measured with the technique.

6) Page 8072, line 8: What is the i.d. of the collection tube? Have the authors either empirically (using standards) or modeled (using diffusion rates) the collection efficiency over the range of organic compounds of interest? If done empirically, this would include desorption and transfer efficiency as well.

The i.d. of the collection tube is 0.02 inches. This information has been added to section 2.2 describing the technique. The instrument response was calibrated using syringe injections at the inlet tip of C8-C20 n-alkane standard. The peak areas for equal injection concentrations of C13-C20 n-alkanes were approximately equivalent suggesting that for this range of species the collection and transfer efficiencies of the system were comparable. Future work should examine the collection and transfer efficiency of a broader range of I/SVOC species of interest.

7) Page 8072, line 28: specify the masses that are filtered.

As stated in the original manuscript, the quadrupole mass filter was tuned to prevent helium ions from reaching the detector. All masses > 4 amu were transmitted to the detector.

8) Page 8073, line 6: what are the consequences of heating your trap to 280C, and having your transfer line to ToF-MS at a lower 250C?

This is an important consideration. Our decision to heat the trap to 280C was based on experimental observations that showed organics were still desorbing from the collector at temperatures between 250-280C. The concern with this temperature difference is that low volatility organics will re-condense on the walls of the transfer line. We use frequent zeros with ultra-zero-air to diagnose increasing background contributions from the transfer line itself. Results indicate that the background concentrations were not significant and the transfer line was not becoming contaminated over time. There is also a pressure drop along the transfer line that acts to minimize collisions with the wall in the UHP He carrier gas flow to the mass spectrometer.

9) Page 8074, line 1: The hexane peak is never observed tailing into the volatility region > 50C? It has a listed boiling point temperature in the high 60C's.

The collection temperatures were not sufficiently cold to trap the vast majority of the hexane passing through the loop during syringe injections of the n-alkane standard at the inlet tip. This is the main reason why the hexane pulse does not exceed 50C in the resultant desorption.

10) Page 8074, line 28: why is the aromatic signal almost as large as the aliphatic signal for JP-8? Because the aromatic representative fragment here constitutes a large fraction of the total aromatic signal, with the aliphatics fragmenting into more ions? Please clarify.

Figure 3 in the ACPD manuscript shows that in the case of both the JP-8 and FT fuels the aliphatic ion fragment (C6H13) is much larger than the aromatic fragment (C9H7). Perhaps the reviewer is mistaking the C6H13 ion from the FT fuel. To clarify we have added labels for 'aromatic' and 'aliphatic' alongside the corresponding ions in the legend of Figure 3 in the revised manuscript.

11) Clearly this calibration is not ideal, but the authors have tried to recover quantitative information using lab results. Future studies need a more robust calibration.

We agree. As stated in the manuscript, future work will provide more robust and comprehensive calibrations for subsequent applications of the technique.

12) Equation 1: You're measuring an emission index 143m from the source. How would this index change if you were, for example, at 10m or 1000m?

Given that the emission index is normalized to co-located CO₂ measurements we don't anticipate significant differences I/SVOC emission index at 10 m relative to our measurements at 143 m. The temperature of the exhaust plume as a function of downwind distance from the aircraft is an important detail to consider when evaluating gas-particle partitioning, but a detailed analysis of such factors is outside of the context of the current manuscript.

13) Page 8082, line 3: Q/Q_{exp}=0.06? This is very low. Please explain.

The low Q/Q_{exp} value obtained in the PMF analysis is explained in the supplemental materials (section shown below). We've also moved the reference to the supplemental materials section in the initial discussion of the PMF results as follows:

“Results from the PMF analysis are summarized in Figures 8a and 8b (a more detailed description of the PMF analysis procedures is provided in the supplemental material).”

In the supplemental materials:

“We note that the magnitude of the Q/Q_{exp} 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 $0.2 < \text{SNR} < 2$ are down-weighted ($\times 3$). Since this down-weighting procedure was applied to the majority of ions in the I/SVOC data matrix, a low Q/Q_{exp} value was observed.”

14) PMF analysis: Did the authors try higher factor solutions? If so, did more compound classes appear?

As detailed in the supplemental material 2-10 factor solutions were evaluated. Pertinent discussion is found in the supplemental.

15) Have you tried oxy-IVOC standards to understand what range of oxy-species you may be detecting?

Current laboratory efforts are focused on obtaining a comprehensive calibration suite of oxygenated IVOC species. This research is ongoing and lies outside of the bounds of the present manuscript.

16) Fig 1.: component labels appear washed out. Also, please add label for quadrupole high pass filter.
A quadrupole label has been added and the image resolution has been increased.

17) Fig. 5,7,8: These are really interesting desorption profiles, with lots of information buried in the high resolution mass spectrometry data. It will be exciting to evaluate these types of profiles for many future applications of this technique.

We appreciate the reviewer’s feedback and encouragement. We agree, the data acquired with this new technique contains many layers of information and we look forward to evaluating this complexity more closely in future applications.

18) Fig. 8: Increase size of figure. Maybe include O:C and H:C ratios on the figure?

Figures 8a and 8b have been revised. The O:C and H:C ratios are now included in Figure 8b.

Revised Figures

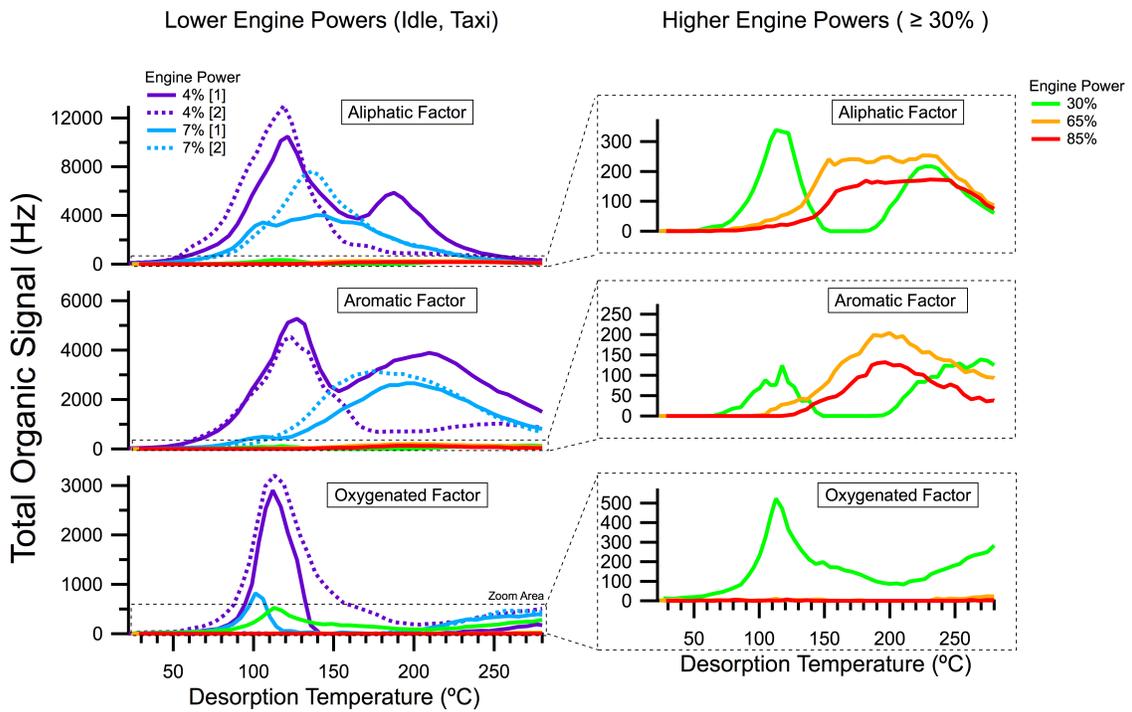


Figure 8a. Desorption profiles for aliphatic, aromatic, and oxygenated PMF factors. Results obtained from higher engine powers ($\geq 30\%$) are re-scaled on the right-hand side of the graph for clarity.

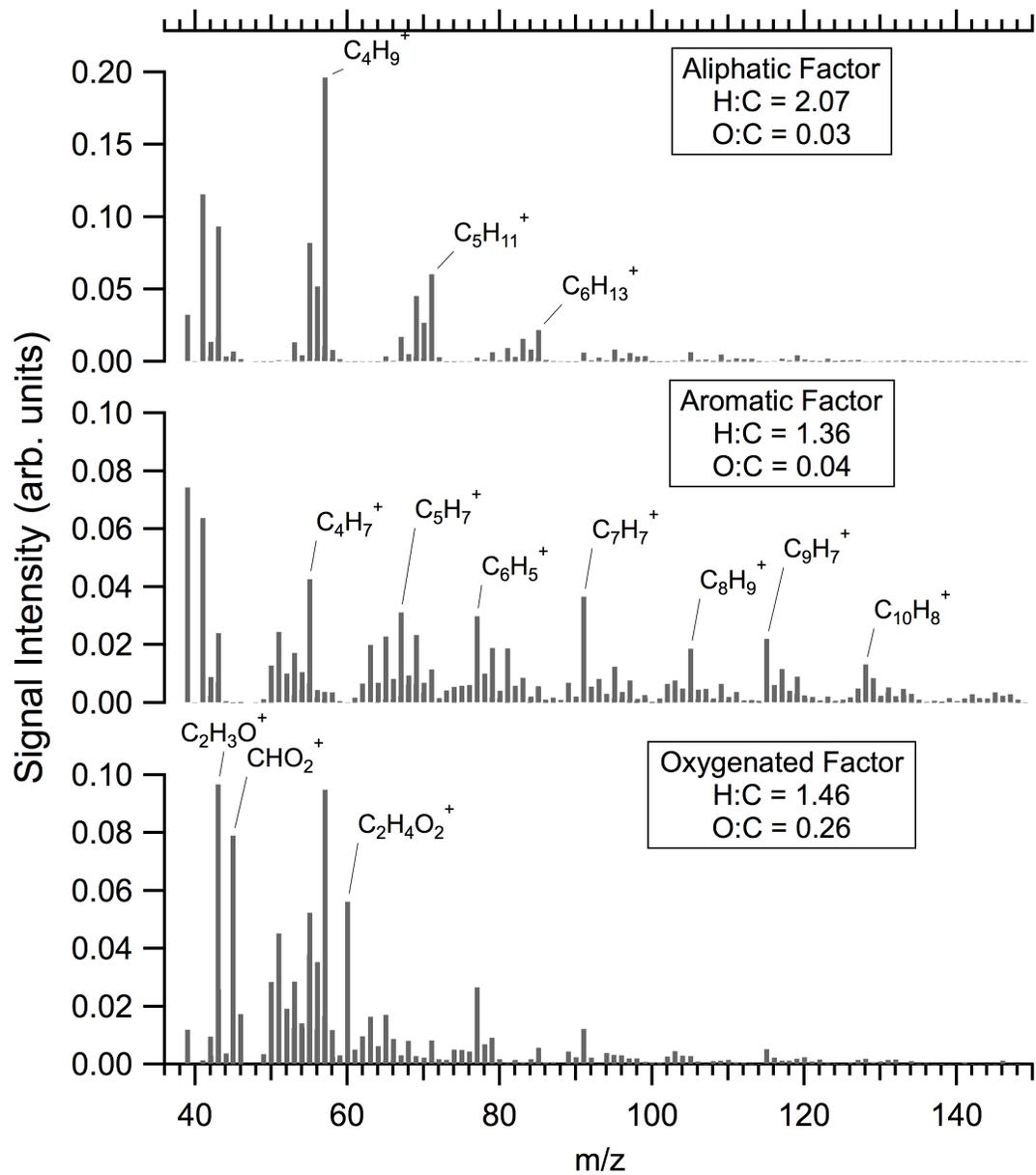


Figure 8b. Aliphatic, aromatic, and oxygenated PMF factor mass spectra and O:C and H:C ratios for each.