We would like to thank the referee #1 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 #1
Received and published: 12 April 2013

1. What about lubricant contributing to the aliphatic signal at higher temperatures? All of the lower volatility aliphatic signal is attributed to pyrolysis products, but certainly there is some lube oil in the POA. Lube oil consumption rates as a function of engine power should be available for either the DC8 or for another aircraft using a CFM-56 engine. The lube oil signal would be overwhelmed by fuel and 4 and 7%, but could be more important to there overall emissions at higher powers.

The reviewer raises an important point – namely identifying the contribution of lubricating oil (emitted as POA by the engine) to the aliphatic signature that we measure with the current technique especially at higher engine powers. Yu et al., (2010) characterized lubrication oil emissions from the overboard breather vent systems of three aircraft engines as well as laboratory-generated oil droplets. Electron impact ionization mass spectra of the field and laboratory data showed enhanced m/z 85 signal relative to m/z 71 in the case of the lubricant-derived PM (Yu et al., (2012)). Upon close examination of the mass spectra obtained with the technique described here, no 85/71 enhancements were observed suggesting that the contribution of lubricating oil droplets to the measured I/SVOCs at 143 m was relatively minor. Given the thermal and chemical stability of the oil droplets it is possible that any lubricant-derived POA that was sampled into our inlet system remained trapped in the PM filter and did not reach the collector. Although lube oil consumption rates are known as a function of engine power, the correlation between oil consumption and oil droplet POA emissions remains poorly characterized therefore a straightforward estimate of lubricant emissions as a function of engine power remains highly uncertain. We have added the following paragraph to section 3.3 discussing lubricant oil contributions to the I/SVOC measurements presented here:

> "Evaporated POA may also serve as a source of the low volatility organics measured at high engine powers. A significant fraction (5-100%) of aircraft engine POA is attributed to lubricating oil emissions (Yu et al., 2012) but the thermal and chemical stability of the lubricants suggest that these species will remain in the condensed phase even within the heated inlet of the I/SVOC instrument. Lubricant-derived POA would therefore remain trapped in the PM filter of the I/SVOC inlet system and not reach our collector. Further, analysis of the I/SVOC mass spectra collected here do not show enhancement in the ratio of m/z 85 to m/z 71 which as been observed as a characteristic feature of electron-impact mass spectra of lubricant derived POA (Yu et al., 2010, 2102)."

2. The explanation of the behavior of the oxygenated PMF factor is curious. Figure 7 focuses on one engine load and one ion (C2H4O2), and makes it seem like the oxygenated fraction is strictly desorbing at high temperatures. However the PMF indicates that most of the oxygenated factor at 4% load, and maybe half at 7% load, has similar volatility to the fuel. Comparing the 7% data in Figure 7 to the full PMF analysis can therefore be confusing, since the former suggests that the oxygenated material is all lower volatility while the latter says essentially the opposite.

The reviewer is correct to point out that the desorption (and inferred volatility) characteristics of the C2H4O2 ion (for one 7% power collection) and oxygenated PMF factor for all powers do not tell a self-consistent story. We have modified our description of Figure 7 to emphasize more clearly that this single oxygenated ion is not representative of a broader class of hydrocarbons. The revised text reads as follows:

> "The final ion fragment shown in Figure 7 is $C_2H_4O_2^+$, an oxygenated organic ion. This ion is present at lower concentrations than the aliphatic and aromatic fragment ions and occupies the lowest volatility range of organics measured for

> this particular 7% power condition. The source of this class of compound is unclear, though it may be related to the partial oxidation of fuel or lubricant within the combustor. It is important to note that using single ions as proxies for entire compound classes has inherent limitations. For a more complete chemical characterization, the full mass spectral profiles must be examined as described in the following section."

3. Page 8068, Line 25-29: Previous studies have used sorbents and quartz filters to collect I/SVOCs, not just filters. Also, an hour might be overstating the sampling time needed for filters sampling exhaust at low dilution, though the point remains the same - filters have low time resolution, need to be changed between engine loads, etc., and the instrument presented here is an improvement over filter sampling.

We agree with the reviewer's comment and have modified the text to avoid over-stating the sampling time necessary for off-line based characterization methods in emissions characterization tests. It revised section now reads:

> "Measurements of low-volatility organic emissions from turbine engines are limited to a few studies, all of which have employed off-line analysis techniques to characterize organics collected on sorbents or quartz filters (Agrawal et al., 2008; Presto et al., 2011; 2012; Spicer et al., 1992; 1994). This approach limits the temporal resolution of the measurements and requires steady-state engine operating conditions during sample collection."

4. Page 8070, Section 2.1: it is probably worth noting that these power settings correspond to the ICAO test points. Were the tests done in a standard ICAO LTO cycle, or was each load held until you saw the plume? It seems that some of these questions are answered later in the manuscript in the description for Figure 4. It would be easiest to understand if all of the testing details were placed in one section, rather than split across separate parts of the manuscript.

The reviewer makes a valid point and we have added the following text to section 2.1:

> "The inboard right engine (Engine #3; E3) and inboard left engine (Engine #2; E2) were operated from ground idle (4% maximum rated thrust) through take-off powers (100% thrust) with additional test points at 7% (taxi), 30% (approach), 65% (cruise), and 85% (climb out) power. With the exception of ground idle (4%) and cruise (65%), the power settings tested correspond to the International Civil Aviation Organization (ICAO) landing takeoff (LTO) cycle. The exact sequence and duration of the engine power sweeps did not follow the standard ICAO LTO cycle. In this experiment, each load was held for approximately 10-15 minutes with the exception of the 100% power condition which was held for 2 minutes. The duration of each test was determined by sampling considerations at the 1 m inlet which was translated across the exhaust plume over the course of each test point."

In an effort to explain all of the testing details in one section to improve the clarity of the manuscript we have combined section 2.2 (in the ACPD version) with section 2.1. Each engine load was not held until we captured the plume at 143 m as the experimental matrix was controlled by the sampling specifications of the upstream 1 m sampling platform.

5. Page 8070, Section 2.1: Fuel flow should be reported in SI units to be consistent with other units used in the manuscript.

We have removed the lbs/hr fuel flow rates from section 2.1 in the revised manuscript.

6. Page 8071, Line 4-5: It’s not clear where the 12-ft long sample line went. One end is obviously at the inlet of the instrument. Where was the other end? The sampling manifold for the Aerodyne mobile lab? Or did this line go directly outside? Where was the instrument physically located?

The sampling tip of the heated inlet was located ~ 4 feet above the roof of the sampling trailer. The instrument was located inside of the sampling trailer positioned 143 m downwind of the DC8. We have added the following sentences to section 2.1 to clarify these details in the revised manuscript:

> “The I/SVOC measurements described here were made 143 m downwind of the aircraft, from inside of the NOAA sampling trailer positioned approximately 100 feet from the centerline of the runway (on the E3 side of the DC8).”
>
> “The sampling tip of the inlet was positioned ~ 4 feet above the roof of the trailer along the edge closest to the runway.”

7. I don’t know how to interpret the valve in the inset to Figure 1. It’s not clear which flow is going to or from where in either the trapping or desorbing setup. Perhaps there is a better way to label the valve in the figure.

We agree, the valve inset in Figure 1 fails to illustrate the difference in collection/desorption modes of operation. We have re-drawn and labeled the inset portion of Figure 1 and now show the collection and desorption modes separately.

8. Figure 2a: how did you define C for the n-alkanes? i.e., what was the source data for the compound vapor pressures?*

The source data for the n-alkane vapor pressures was the CRC Handbook of Chemistry and Physics (94th Edition, 2013-2014). C* was calculated at 25C and atmospheric pressure.

9. Figure 4 is very hard to read: the lines, especially for the temperature trace, are too thin, and the labels are hard to read. Zooming in did not make the labels particularly more readable, suggesting that maybe the resolution of the figure is too low. Perhaps indicate wind direction on Figure 4 since it is discussed in the text.

We have revised Figure 4 in accord with the reviewers suggestions, increasing the font size on all axis labels, increasing the line thickness on the organic signal and temperature traces, and increasing the overall resolution of the image. We decided to not add an additional axis showing wind speed/direction as we believe this would complicate an already crowded figure.

10. It took me about 10 minutes to determine that the left-hand panels in Figure 8 each represent the time trace for one of the PMF factors. The right-hand panels have the same issue, though I was able to determine what I was looking at based on the mass spectra. It would help immensely to specifically label the panels with "aliphatic", "aromatic", "oxygenated".

We agree with the reviewer on this point and have re-created Figure 8 accordingly. The revised figure is split into two parts, the first showing the desorption profiles for each PMF factor (labeled as aliphatic, aromatic, and oxygenated) with different colored lines representing the engine power. The right panel of figures is provides a zoomed in perspective on the higher power (lower I/SVOC emission) cases.

The revised Figure 8b now shows the average mass spectra for each of the corresponding PMF Factors. For clarity this figure also has aliphatic, aromatic and oxygenated factor labels to identify the different I/SVOC emission types.

11. Did you observe a difference in I/SVOC EF for FT-only 7% versus mixed JP8/FT? It seems the FT-only emissions would be lower, at least based on previous studies.

For the 7% power plume that was intercepted when we were sampling FT-only exhaust at the 143 m position (identified in Figure 4 and discussed in Section 3.6) the total I/SVOC EI was slightly higher than the EI for the mixed-plume 7% runs: ~1.7 g/kg (FT-only) vs. 1.32 g/kg (mixed plume). As discussed in section 3.6, the absence of unburned fuel aromatics for the FT-only 7% plume is consistent with the fuel formulation having lower aromatic content, but newly formed aromatic and aliphatic low volatility vapors are still present in the FT-only plume. The elevated oxygenated HC signature in the fuel-volatility range is also of interest in the case of the FT-only plume. Given the experimental limitations of the AAFEX-II experiment, definitive comparisons of the I/SVOC emission profiles as a function of fuel type aren't possible with the current dataset. As stated in section 2.1:

> "A more detailed investigation of the role of fuel type on low-volatility emissions, which requires a different experimental setup than was used here, is an important area of future research."

There is a section 4.1 but not 4.2, which makes the 4.1 label unnecessary
We have removed the section heading.

References

Yu, Z., Liscinsky, D. S., Winstead, E. L., True, B. S., Timko, M. T., Bhargava, A., Herndon, S. C., Miake-Lye, R. C., and Anderson, B. E. Characterization of Lubrication Oil Emissions from Aircraft Engines, Environ. Sci. Technol., 44(24), 9530-9534, doi: 10.1021/es102145z, 2010.

Yu Z., Herndon S. C., Ziemba L. D., Timko M. T., Liscinsky D. S., Anderson B. E., and Miake-Lye R.C. Identification of Lubrication Oil in the Particulate Matter Emissions from Engine Exhaust of In-Service Commercial Aircraft. Environ. Sci. Technol. 46(17), 9630-9637, doi 10.1021/es301692t, 2012.

Revised Figures

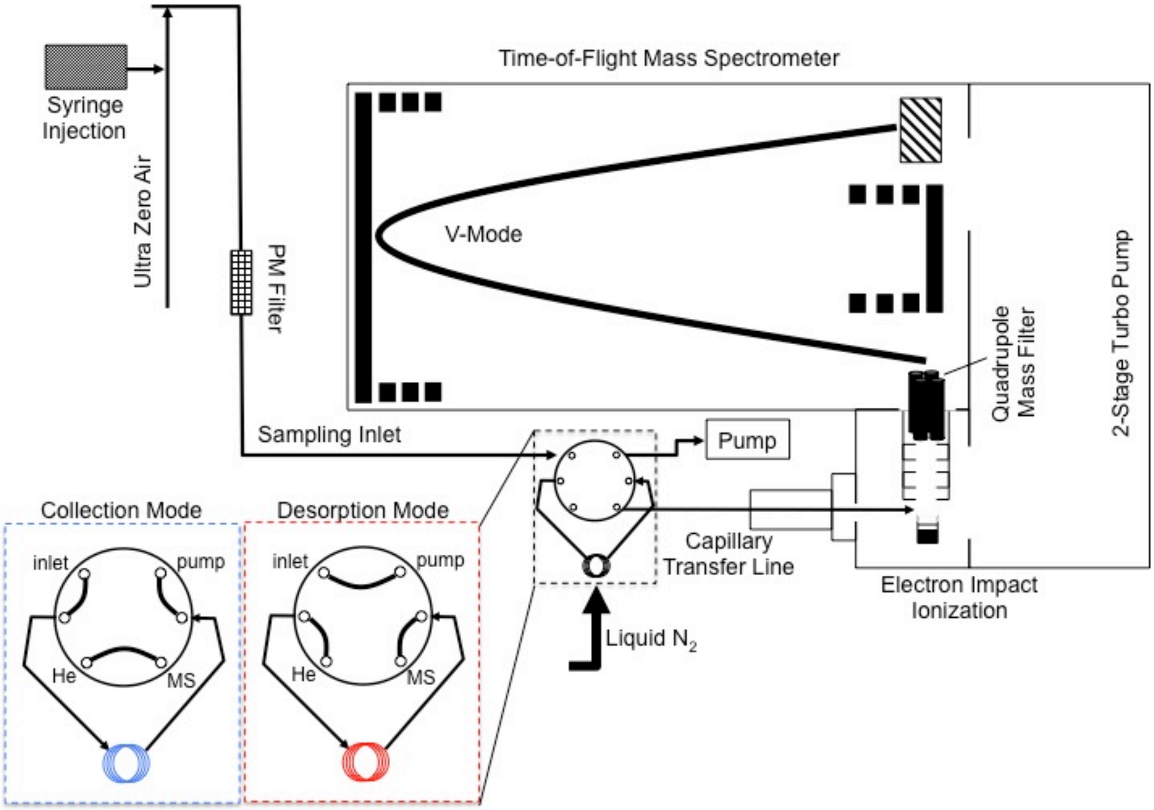

Figure 1. Schematic of the I/SVOC instrument and inlet as configured during the AAFEX-II campaign. The inset shows the 6-way valve orientation for collection (blue) and desorption (red) modes of operation. See text for details.

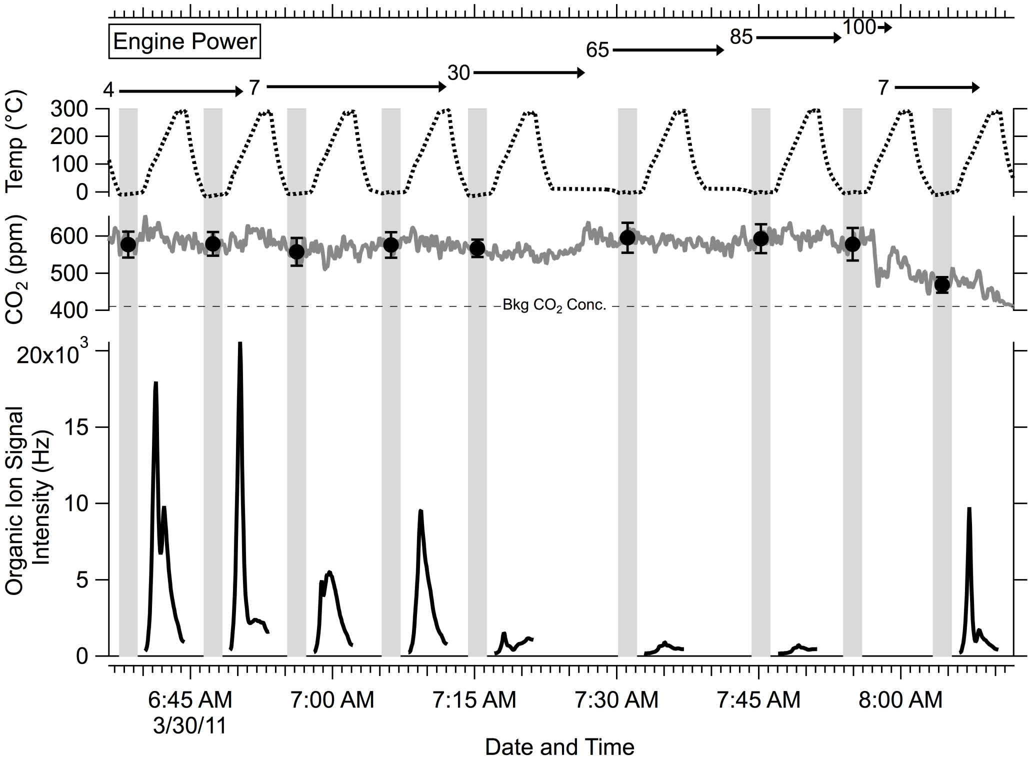

Figure 4. Timeline showing the sample collection/desorption cycles during the 30 March 2011 power sweep: jet engine power setting, measured CO_2 level at 143 m, collection temperature, collection period and total organic ion signal. Elevated CO_2 levels recorded at the 143 m inlet position are shown in the middle panel with the dashed line demarcating the ambient CO_2 background concentration.

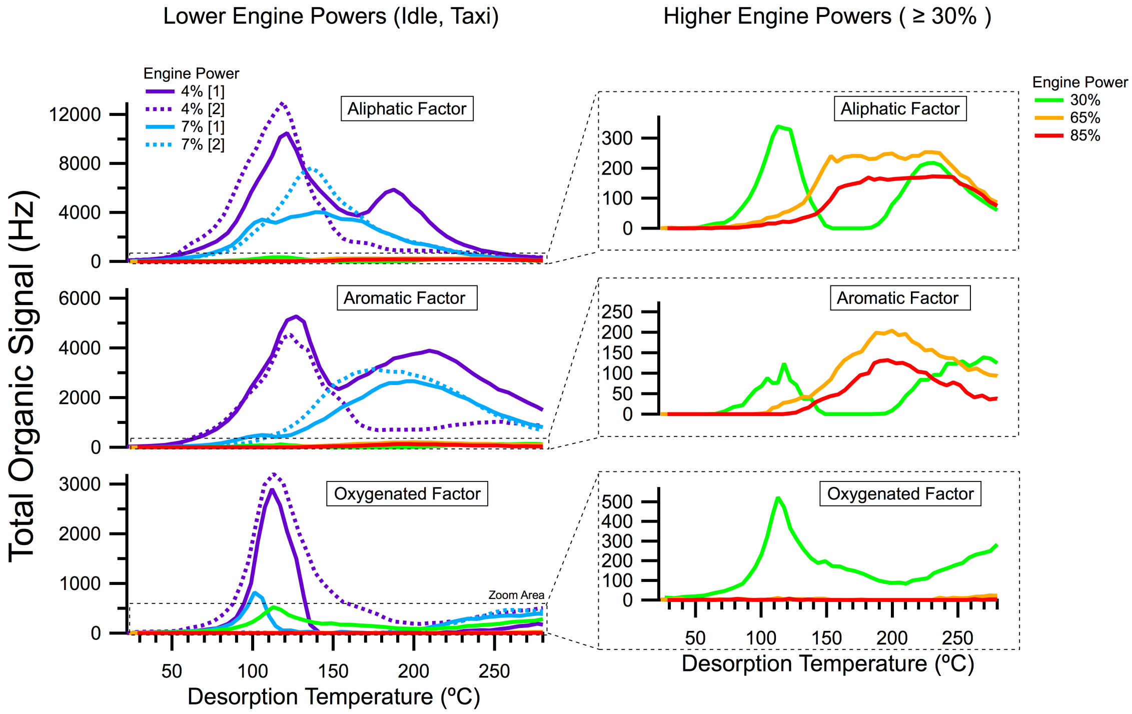

Figure 8a. Desorption profiles for aliphatic, aromatic, and oxygenated PMF factors. Results obtained from higher engine powers (≥ 30%) are re-scaled on the right-hand side of the graph for clarity.

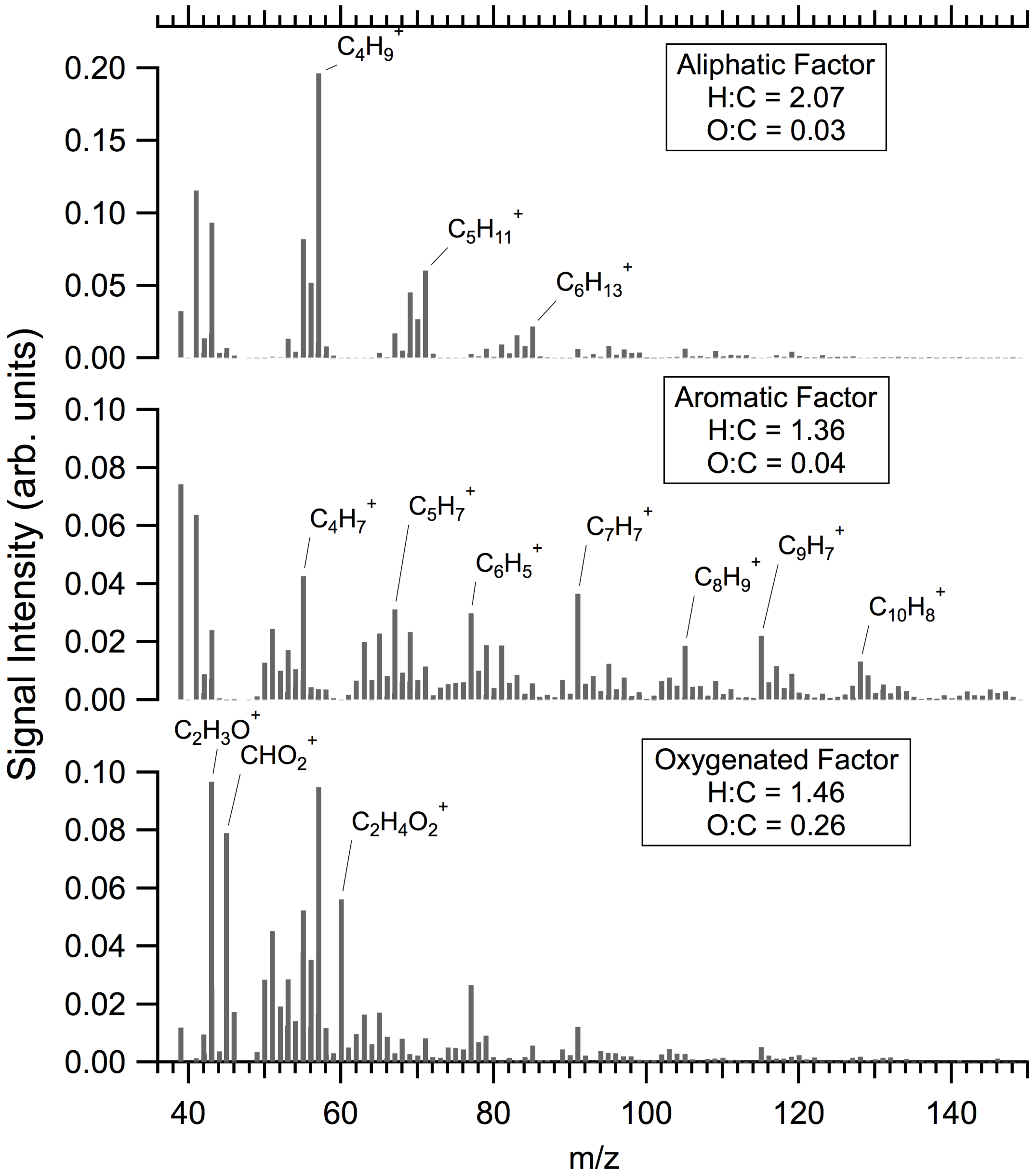

Figure 8b. Aliphatic, aromatic, and oxygenated PMF factor mass spectra and O:C and H:C ratios for each.