Response to Anonymous Referee #1

We thank the reviewer for her/his supportive and constructive comments. We have revised the manuscript in several instances to address the reviewer's concerns, and believe the paper is stronger overall as a result. This response will address the general concerns raised by this reviewer in the order provided in the review.

General Comments

This is a worthwhile contribution. The discussion of FID response to linalool and myrcene raises some important points and suggests some underestimates in previous studies. The paper indicates the importance of accounting for ECN when analyzed by FID. It also stresses the importance of having an in-house system check for quantitative assessments of more difficult VOCs. ECN's must be taken into consideration when quantifying by FID, especially for more complex bonding structures (1+ double bonds, alcohol, ether, carbonyl, aromatic or tighter cyclic bonding). Confirmation of analytical calibrations is needed, especially for more difficult species like SQTs. This dynamic dilution system seems to be an inexpensive, simple solution.

We appreciate the reviewer's supportive assessment.

MS systems such as TOF PTRMS are ahead of FID in many respects, especially in speed and sensitivity, but response of these systems to individual terpenoids and their isomers is not well characterized, and there is limited data using such systems. The traditional PTRMS systems have been around awhile, but they see only protonated parent ions and can't distinguish between different monoterpenes, for instance.

Regarding the experimental setup, there is concern about the actual SQT concentrations being produced at steady-state. Consider adding more on the following:

- Explain how (or if) the PTR-MS was calibrated.

The PTR-MS response was calibrated by diluting a compressed gas VOC standard (Scott-Marrin) containing a-pinene and 12 other VOCs in dry nitrogen to 19.8 ppbv. The procedures for operating and calibrating this instrument have been detailed previously by Jobson and McCoskey (ACP, 2010). We have added a reference to that paper and a few sentences briefly describing the approach:

> *"Details on the calibration and performance of the PTR-MS used in this study have been described by Jobson and McCoskey (2010). The PTR-MS response was calibrated by diluting a compressed gas VOC standard (Scott-Marrin) containing alpha-pinene and 12 other VOCs in dry nitrogen to 19.8 ppbv."*

It is very important to note though that PTRMS concentration data was never used in our analysis. The PTRMS was used solely to monitor the stability/variability of the analyte signal from the dynamic dilution system. Figure 2 shows PTRMS results as normalized counts per second, not as concentration. Thus the details of that instrument's calibration are extraneous to this study. We have also added text emphasizing this point later in the same paragraph:

"It is important to note that the PTR-MS analyte concentration results (and thus its sensitivity) were not used in our analysis. Only the normalized counts per second from the instrument were used, to determine the stability and variability of the dynamic dilution system."

- Explain how the mixing ratio was determined.

We have added the following sentence to the first paragraph of section 4.1:

"VOC mixing ratios were calculated from the infusion rate and the dilution flow using the density and molecular weight of the liquid standard being injected."

- What types of losses are possible in the dilution system presented?

The primary source of VOC losses within the dilutions system lines is from adsorption onto the PFA tubing walls. Over time, this adsorption would reach a steady state, so that the rate of molecules adsorbing onto the tubing walls matched the desorption rate of the VOC from the walls. Tests indicated that 30 minutes were required for this equilibration to take hold, as noted at the end of section 4.1. After this point, the system's output concentration was stable as illustrated in Figure 2.

To clarify that this equilibration time was taken into account to minimize losses, we have added the following sentence to the end of the last paragraph in section 4.1:

"Based on the results from the PTR-MS, for each experiment the dilution system was allowed to equilibrate for a minimum of 30 minutes prior to sampling."

- Was anything accomplished to ensure limited or no accumulation of moisture (H2O) within the cryotrap etc.? The presence of moisture in these experimental systems can produce inaccuracy.

Moisture management was considered throughout our experimental design, most obviously by choosing a dilution system carrier gas that was devoid of water vapor. This point was addressed indirectly on page 2426, line 26: "The carrier gas was N_2 blow-off from a liquid nitrogen dewar". At atmospheric pressure, the boiling point of nitrogen is -196 °C; at this temperature, the saturation vapor pressure of water is very, very low. Thus the flow exiting the dilution chamber would have had virtually no water vapor included. We are confident that the carrier gas was dry, and have added the word 'dry' to the sentence in question to improve clarity.

Regarding sampling issues with SQT, myrcene, … could the experimental setup have caused these? Perhaps the syringe pump/dilution system is not the ideal sample generation method for some of these compounds. Why wasn't a capillary diffusion

generation method with gravimetric monitoring used? This latter system is known to be quite robust.

The sesquiterpene sampling issues were challenging, but we are confident that we now understand the nature of the challenges and how to overcome them. Our efforts are described in the text. We saw a good sesquiterpene response with our system after increasing the cryotrapping temperature.

With respect to myrcene specifically, we refer readers to the discussion on page 2433, lines 6-9, of the original manuscript. There we cite the previous work of Komenda et al. (2001), who also had problems quantifying acyclic monoterpenes (ocimene in their case), despite using a capillary diffusion system. Our efforts to understand this led us to the work of Fahlbusch et al. (2003), who state that acyclic monoterpenes may be unstable in the gas-phase (cf. page 2433, line 11 of the original manuscript). These previous works suggest to us that the myrcene sampling issue is not a problem that is specific to our dynamic dilution system design.

The dynamic dilution system is presented in this manuscript as an alternative to capillary diffusion generation methods. We have found that it provides a simple, cost-efficient solution to generate monoterpene and sesquiterpene standards in the lab that may be used for analytical quality control purposes.

Regarding (p. 2432-2433) the discussion about SQT sampling difficulties that suggests homogeneous nucleation of SQTs in the cryo-cooled sample loop, causing them to pass through the sample loop.... what about wall losses or incomplete thermal desorption from the cryotrap during sample generation. Should these and similar possibilities be suggested as well?

We did indeed consider these possibilities, but agree that the original manuscript did not make our thinking sufficient clear. To address the reviewer's concern we have modified the paragraph that begins on page 2432, line 19. The revised version of that paragraph reads as follows:

"Generally, sesquiterpenes are known to be much more difficult to analyze than monoterpenes, due to their high reactivity and low volatility. Similar difficulties were experienced in this study. Initial attempts to sample sesquiterpenes yielded much less signal than was expected; in many cases no analyte peak was observed in either the FID or the MS. We considered several possibilities for what might cause the severe reduction in sesquiterpene transmission through our system, including increased wall adsorption. We discounted wall adsorption as the cause after checking the temperature along the entire heated sampling line and increasing equilibration time for the dynamic dilution system; the sesquiterpenes were still absent from the detector signals. We next tried increasing the cryotrapping temperature from -196 to -130 °C and decreasing the temperature gradient along the loop; this was done by manually adjusting the depth of immersion of the loop in a small liquid nitrogen dewar and by approximately doubling the length of the loop. When testing the system with these modifications the full sesquiterpene peak was

finally observed. This result suggests that homogeneous nucleation of sesquiterpenes was likely occurring within the sampling loop during the initial runs, and that consequently these less volatile, bulkier compounds were not adsorbing onto the cryotrapping loop, but were rather being carried with the sampling flow into the reference volume. Adjustments were made to the system to ensure this would not happen during future analysis."

The change in cryotrapping temperature would not by itself had been effective if the thermal desorption temperature had been the cause of the reduced sesquiterpene signal. If incomplete thermal desorption had been the problem, we would not have seen the peak suddenly appear after increasing cryotrapping temperature while using the same thermodesorption temperature. We feel this reasoning is implicit in the current text.

Figure 4. Change y-axis to reflect ± differences from the respective carbon number of each compound. ie. (Carbon Number) - (Theoretical ECN) and (Carbon Number) - (Measured ECN) plotted on a +3 to -3 y-axis to reflect differences on a more legible scale. Also, place the carbon number in brackets.

This is a good idea. We have modified Figure 4 based on the suggestions outlined here.