We would like to thank both referees for their helpful comments. Our responses to both reviews are included in a single document. The referee comments are in bold type and our responses directly follow each comment.

Referee #1
Comments:

If there is any weakness in this manuscript it is in the omission of a qualitative discussion on how the errors would be expressed in the time series data.
We agree that such a discussion would be helpful, especially for evaluation of our Fig. 8. The calculated levels of interference in the PTR-MS toluene measurements resulting from fragmentation of the monoterpenes via reaction with H_3O^+, O_2^+ and NO^+ in the PTR-MS drift tube depended largely on the mixing ratios of α- and β-pinene relative to those of toluene. This result obtained because (1) the α- and β-pinene mixing ratios accounted for a large fraction (66±7%, on average) of the sum of the mixing ratios of all the measured monoterpenes, and (2) reported values of ϕ(93) for α- and β-pinene were relatively large compared to the other measured monoterpenes. As a result of (1) and (2), the calculated interference from monoterpene fragmentation was highly correlated (r^2=0.99) with the total monoterpene mixing ratio relative to toluene, Δ_{Mon}, which tended to peak during the nighttime hours. In Sect. 3.3 we indicated that interference from monoterpene fragmentation was expected to correlate with Δ_{Mon}, which peaked during nighttime at THF. To Sect. 3.3.1 we added:

"The calculated interference in the PTR-MS toluene measurements from reaction of H_3O^+ with α- and β-pinene was highly correlated with Δ_{Mon} (Fig. 8) due to the relatively large measured abundances for those compounds. Were monoterpene fragmentation an important source of m/z=93 fragment ions in our instrument, error in the PTR-MS toluene measurements, ε_{PTR-MS}, would have closely tracked Δ_{Mon}."

To Sect. 3.3.2 we added the following:

"Reaction of O_2^+ with α- and β-pinene was calculated to make the largest contribution to the O_2^+ mediated monoterpene fragmentation interference due to the relatively large measured abundances and reported ϕ(93) for those compounds. As for the H_3O^+-mediated fragmentation interference the calculated fragmentation interference resulting from reaction of O_2^+ with the measured monoterpenes was highly correlated with Δ_{Mon} (Fig. 8)."

The calculated interference resulting from reaction of H_3O^+ with pinonaldehyde, caronaldehyde and α-pinene oxide was a function of (1) the mixing ratios of α-pinene and Δ^3-carene relative to that of toluene and (2) the local O_3 mixing ratio. The O_3 mixing ratio peaked in the late afternoon, whereas the relative abundances of α-pinene and Δ^3-carene tracked Δ_{Mon} and were highest toward the end of the night. As a result, the calculated oxidation products-mediated interference showed a broad peak between the late evening and early morning. To Sect. 3.4.1 we added the following:

"The calculated interference resulting from reaction of H_3O^+ with pinonaldehyde, caronaldehyde and α-pinene oxide was a function of (1) the mixing ratios of α-pinene and Δ^3-

carene relative to that of toluene and (2) the local O_3 mixing ratio. The O_3 mixing ratio peaked in the late afternoon, whereas the relative abundances of α-pinene and Δ^3-carene tracked Δ_{Mon} and were highest toward the end of the night. The calculated interference resulting from reaction of H_3O^+ with the monoterpene oxidation products showed a broad peak between the late evening (18:00) and early morning (08:00)."

In Sect. 3.4.2 we indicated that for pinonaldehyde produced from reaction of OH with α-pinene the calculated pinonaldehyde mixing ratios attained maximum values in the early morning. The corresponding calculated interference from reaction of H_3O^+ with pinonaldehyde generally tracked the pinonaldehyde mixing ratio. We added the following to Sect. 3.4.2:

> *"The calculated interference tracked the pinonaldehyde mixing ratio."*

Humidity could exert a subtle effect – related to the reactivity of toluene and the monoterpenes to H3O+(H2O). There is no discussion concerning whether this ion is considered as a primary reagent ion. Toluene does not react (at least efficiently) with H3O+(H2O) (Smith and Spanel Int. Rev. Phys. Chem. 15 (1996) 231) while the monoterpenes probably have high enough proton affinities to react with this ion. It would be helpful to include some discussion regarding whether your quantification procedure addresses the influence of humidity on the PTR-MS calibration factors. As per that described by de Gouw and Warneke in their review paper (Mass Spectrom. Rev. 26 (2007) 231).

Our quantification procedure did not address the influence of humidity on the PTR-MS calibration factors. The ratio of the $H_3O^+(H_2O)$ ion current, $I_{H_3O^+(H_2O)}$, to the H_3O^+ ion current, $I_{H_3O^+}$, was on average 10±2% and ranged from 6–15%. Despite a strong diurnal trend in relative humidity (RH), neither the absolute nor relative value of the $H_3O^+(H_2O)$ ion current exhibited a diurnal dependence, indicating that under our operating conditions the reagent ion distribution was not significantly affected by ambient RH. For this reason we did not consider $H_3O^+(H_2O)$ as a reagent ion in our analysis. We recalculated our PTR-MS mixing ratios using our Eq. (7) modified according to the treatment presented by de Gouw and Warneke (2007) (i.e., I_{m93} normalized to $I_{H_3O^+} + X_R \cdot I_{H_3O^+(H_2O)}$; X_R=0.1). The recalculated mixing ratios differed from those calculated according to our Eq. (7) by on average ~1%. Agreement with the GC-FID measurements was not significantly different for the recalculated PTR-MS mixing ratios. To the text in Sect. 2.2 we added the following:

> *"The average H_3O^+ ion current was 2.8±0.2 $\times$ 10^6 cps. The ratio of the $H_3O^+(H_2O)$ ion current to that of H_3O^+ was on average 10±2% and ranged from 6–15%. Because the $H_3O^+(H_2O)$ ion current was low and did not depend on ambient RH, we did not include a term for the water cluster ion current in Eq. (7) as may be necessary under different operating conditions (c.f., de Gouw and Warneke, 2007)."*

To the best of our knowledge, rate data and fragmentation yields for the reaction of $H_3O^+(H_2O)$ with monterpene compounds have not been reported. Thus, we have not attempted to quantify potential interferences in the PTR-MS measurements due to reactions of $H_3O^+(H_2O)$ with the monoterpenes measured at THF. We can reasonably estimate that, at most, reaction of the

measured monoterpenes with $H_3O^+(H_2O)$ would increase the *m/z*=93 yields by ~10% above the yields from reaction with H_3O^+ alone, assuming equal rate constants and yields for reactions with H_3O^+ and $H_3O^+(H_2O)$. Because the proton affinity of $(H_2O)_2$ (808 kJ mole^{-1}) is much higher than that of H_2O (691 kJ mole^{-1}) (Blake et al., 2009), which results in less exothermic proton transfer reactions for $H_3O^+(H_2O)$ compared with H_3O^+, it is likely that the *m/z*=93 yields from reaction of $H_3O^+(H_2O)$ with the monoterpenes measured at THF are significantly lower than those from reaction with H_3O^+. Available kinetic data suggest that proton transfer rate constants for $H_3O^+(H_2O)$ are slower than those for H_3O^+ (Smith and Španěl, 2005). To Sect. 2.2 we added the following:

"It is likely that the proton affinities of the monoterpenes measured at THF are sufficiently high for those compounds to react with $H_3O^+(H_2O)$ in the PTR-MS drift tube (Fernandez et al., 1998; Lindinger et al., 1998; Tani et al., 2004). Such reactions could provide a source of m/z=93 fragment ions in addition to those discussed above. However, in our analysis we did not consider reaction of monoterpenes with $H_3O^+(H_2O)$ due to the low measured ion current for $H_3O^+(H_2O)$ relative to that for H_3O^+ in our instrument and lack of relevant kinetic and product data. We estimated that at most, reaction of the measured monoterpenes with $H_3O^+(H_2O)$ would increase the m/z=93 yields by on average 10% above the yields from reaction with H_3O^+ alone, assuming equal rate constants and yields for reactions with H_3O^+ and $H_3O^+(H_2O)$. Because the proton affinity of $(H_2O)_2$ (808 kJ mole^{-1}) is much higher than that of H_2O (691 kJ mole^{-1}) (Blake et al., 2009), which results in less exothermic proton transfer reactions for $H_3O^+(H_2O)$ compared with H_3O^+, it is likely that the m/z=93 yields from reaction of $H_3O^+(H_2O)$ with the monoterpenes measured at THF are significantly lower than those from reaction with H_3O^+. Available kinetic data suggest that proton transfer rate constants for $H_3O^+(H_2O)$ are generally slower than those for H_3O^+ (Smith and Španěl, 2005)."

Minor comments:

1. Abstract line 24 – Please define "our operating conditions" either in the abstract or in the experimental section. Drift tube pressure and temperature will suffice. These are important details that should be included. It is a lot of work to read through other references just to get this information.
We modified the Abstract text to include the drift tube temperature, pressure and voltage as follows:

"The results from THF suggest that toluene can be reliably quantified by PTR-MS using our operating conditions (drift tube pressure, temperature and voltage of 2.0 mbar, 45 °C and 600 V, respectively) under the ambient conditions probed."

The text in Sect. 2.1 was modified as follows:

"The PTR-MS (Ionicon Analytik GmbH, Innsbruck, Austria) was operated with a drift tube pressure and temperature of 2.0 mbar and 45°C, respectively, and a potential of 600 V applied over the length (9.6 cm) of the drift tube."

2. The statement that the ion transmission efficiency is related to ion concentration (eq 8) is not strictly correct or at least that is not how the transmission efficiency term in PTR-MS is typically discussed. An ion transmission curve is often used to correct for biases associated with the transmission and detection of ions of different masses in the PTR-MS. This curve is used to "correct" all ion masses. Since only a small fraction of the ions within the drift tube are actually sampled it is more convenient to invoke the argument that it is assumed the ion intensity ratio I(93)/I(H3O+) is equal to the ion concentration ratio [93]/[H3O+].
We acknowledge that Eq. (8) is not strictly correct since the analyte ion transmission efficiency is quantified relative to that of the primary reagent ion and transmission efficiency is not defined on an absolute scale. We corrected Sect. 2.2 by substituting the following:

"The toluene volume mixing ratio, VMR(m93) (hereinafter referred to simply as the toluene mixing ratio), is quantified based on the ratio of the background-corrected ion current (counts per second, cps) at m/z=93, I_{m93c}, to the normalized ion current (ncps) for H_3O^+ as shown in Eq. (7),

$$\text{VMR}(m93) = \frac{I_{m93r} - I_{m93b}}{\left(\dfrac{I_{H_3O^+}}{10^6}\right) \cdot C_{Tol}} = \frac{I_{m93c}}{\left(\dfrac{I_{H_3O^+}}{10^6}\right) \cdot C_{Tol}} , \tag{7}$$

where I_{m93r} and I_{m93b} are the raw and background m/z=93 ion currents, respectively, and C_{Tol} denotes the calibration factor (sensitivity) for toluene, typically expressed in units of ncps ppbv^{-1}. In this work the calibration factor was determined from assays of standard gas cylinders as described in Sect. 2.1. Alternatively, the calibration factor can be determined from the instrumental operating parameters, measured ion transmission efficiencies, Tr, and published values of H_3O^+ ion mobility, μ, as described previously (de Gouw and Warneke, 2007). The measured m/z=93 ion current is related to the concentration at the end of the drift tube as shown in Eq. (8) (de Gouw and Warneke, 2007):

$$\frac{I_{m93c}}{I_{H_3O^+}} = \frac{[m93]}{[H_3O^+]} \cdot \frac{Tr_{m93}}{Tr_{H_3O^+}} , \tag{8}$$

where here the expression is given in terms of the background-corrected m/z=93 ion current. In ambient air samples with contributions to [m93] from j as described above the true toluene mixing ratio, VMR(m93)$_t$, and the apparent measured toluene mixing ratio, VMR(m93)$_m$, can be defined as shown in Eq. (9), which follows from Eqs. (6–8):

$$\text{VMR}(m93)_t = \text{VMR}(m93)_m \cdot \frac{1}{\{1 + F\}} . \tag{9}"$$

3. Line 13 page 13 – I am not familiar with the term "increased ventilation of the boundary layer." Are you referring to an increase in the boundary layer height?
Yes, we were referring to an increase in the boundary layer height. We acknowledge that our terminology was ambiguous. We modified the text as follows:

"The observed daytime minima in the monoterpene mixing ratios were likely driven by the increased height of the boundary layer as well as greater oxidation by hydroxyl radical (OH) and O_3 during the daytime despite higher monoterpene emissions during the day owing to warmer temperauture (Guenther et al., 1993)."

4. Line 7 page 26 – Table RD6 must be a typo. I think you are referring to Table 7.
We were indeed referring to Table 7. We replaced "RD6" with "7" in the text.

5. Section 3.5.2 – I think you are giving more bandwidth to the interference from ethanol than it deserves. Proton bound dimers are only formed under very high substrate concentrations and I can't imagine any condition where you would detect this species (EtOHH$^+$EtOH) without seeing exceedingly large signals at m/z 47 (EtOHH$^+$) and m/z 65 (EtOHH$^+$H2O).
Although we monitored m/z=47, the signal was affected by large interferences which precluded its use for monitoring (EtOH+H)$^+$. We did not monitor m/z=65. Our intention with Sect. 3.5 was mostly to review for the reader some additional sources of m/z=93 reported in the PTR-MS literature. We agree with both reviewers that the importance of proton-bound EtOH dimers was overemphasized. We condensed Sect. 3.5 by removing Sect. 3.5.1 and Sect. 3.5.2 and substituting the following text:

"Chloroacetone is not commonly measured in the atmosphere, and its mixing ratios are expected to be low (Warneke et al., 2003). The conditions employed in the laboratory PTR-MS EtOH measurements were not representative of ambient air. We found the m/z=47 signal to be unreliable for measurement of EtOH at THF due to low sensitivity and significant interferences. Interferences in the PTR-MS m/z=93 signal from chloroacetone and $((EtOH)_2+H)^+$ cannot be fully evaluated form our data, but they are not likely to be significant."

6. Figure 3. Is the isopropylbenzene peak the small shoulder or the large adjacent peak? Please clarify this figure. Maybe use a line to point to actual peak or label both peaks.
The isopropylbenzene peak is the small shoulder. To clarify the figure we added a small line to the figure that links the peak label with the shoulder peak (see Fig. 3). The figure caption text can also be modified if necessary.

Referee #2
Specific Comments:

Are you performing an "intercomparison" or a "comparison"?
Upon our reevaluation we concluded that the term "intercomparison" may not be strictly correct since the measurements were not performed for the purpose of evaluating the performance of the PTR-MS and GC instruments for measuring toluene. Instead we performed our analysis using measurements made as part of the ICARTT campaign, such that "comparison" seems to better describe the work. We substituted the term "comparison" for "intercomparison" in the text and have changed the title of the paper to:

"A comparison of GC-FID and PTR-MS toluene measurements in ambient air under conditions of enhanced monoterpene loading"

Abstract. Please be more quantitative in the abstract – what was the level of agreement between GC-FID and PTR-MS.

We had intended to keep the abstract brief, but agree that we sacrificed too much in the way of quantitative detail. We added the following quantitative information regarding the level of agreement between the PTR-MS and GC-FID to the abstract text:

> "*A correlation plot of the PTR-MS versus GC-FID toluene measurements was described by the least squares regression equation y=(1.13±0.02)·x−0.008±0.003 ppbv, suggesting a 13% positive bias in the PTR-MS measurements. The two systems agreed quantitatively within the combined 1σ measurement precisions for 60% of the measurements.*"

P6. GC Operation. Was ozone removed? Could ozone reactions be the reason that some of the other monoterpenes were not observed?
Regarding the monoterpenes present at TF, this is the "typical" suite we observe above LOD at this site. As described by Sive et al. (2005), subsequent to sample trapping the sample trap was purged with UHP He, which effectively minimizes O_3-alkene reactions. In Sect. 2.1 we indicated that the loops were flushed with UHP He after sample trapping but did not indicate the purpose. We modified the text as follows:

> "*After sample trapping, the loops were flushed with 100 cm^3 of ultra high purity (UHP) He (Maine Oxy, Auburn, Maine) at 100 cm^3 min^{-1} to reduce O_3-alkene reactions during heating (Sive et al., 2005). Numerous experiments have been conducted in our laboratory, as well as others (E. Apel, NCAR and D. Riemer, University of Miami, personal communication, 2003), which demonstrate that this is a reliable way to quench O_3-alkene reactions for this type of system. To ensure there were no trace contaminants in the UHP He flow stream, it was first passed through a 1/4" (6.35 mm) × 20 ft (6.10 m) activated charcoal/molecular sieve (13X) trap (60/80 mesh) and then through a Valco heated getter helium purifier (HP2).*"

P8. Calibration. How close in agreement were the response factors for C10 compounds and monoterpenes – can you be more quantitative. To what degree of certainty do we know that tertiary carbons and cyclic alkene compounds yield the same per carbon atom response as n-alkanes? How was the FID response to toluene calibrated? How often was the PTR-MS calibrated?
We described our general procedure for calibrating the GC-FID as well as the special treatment for the monoterpenes. We acknowledge that more quantitative detail regarding the toluene calibration should be given. The two whole air standards contained the same suite of compounds at different mixing ratios to partially bracket ambient levels. The toluene mixing ratios in the standards were 1.215 and 0.101 ppbv (±5%). The precisions of the peak area measurements for these standards were ±4% and ±5%, respectively. We took the precision of the ambient toluene mixing ratios to be the greater of ±5% or LOD, which should reasonably describe the mixing ratio dependence of the precision for ambient measurements based on our calibration measurements. We have added the following information regarding the GC-FID toluene response calibration to Sect. 2.1:

> "*The toluene mixing ratios in the whole air standards were 1.215±0.061 and 0.101±0.005 ppbv. The two standards were assayed alternately every 10th run. The precisions of the standard peak area measurements were ±4% and ±5%, respectively.*"

The PTR-MS was calibrated approximately every 4 weeks during the ICARTT campaign because of limited equipment at the time and the need to alternately calibrate a second PTR-MS deployed on Appledore Island, ME. The following text will be added to Sect. 2.1:

"Various classes of hydrocarbons within each carbon number grouping were analyzed and all yielded the same per-carbon response (Table A). For example, the toluene per-carbon response was the same as n-heptane and other C_7 compounds and the individual monoterpene per-carbon response was also the same as n-decane (Tables A, B). This validated the use of a single response factor for each group of compounds (C_7, C_8, etc.), independent of the type of NMHC (alkane, alkene, alkyne, etc.). Furthermore, two of the gravimetric high-pressure synthetic blends from Apel-Reimer Environmental, Inc. used for the PTR-MS calibrations were quantitatively assayed and compared with the whole air standards used for the THF GC system (Table B). The high-pressure synthetic standards were diluted to atmospheric mixing ratios (ppbv to pptv levels) with catalytic converter-prepared zero air adjusted to maintain the humidity of the sampled air."

Additionally, the following excerpt is from Russo et al. (2010) and is now referenced within the manuscript to address the questions raised by the reviewer:

"In order to ensure that the VOC mixing ratios in samples analyzed at different times are comparable, whole air and synthetic standards were routinely analyzed and calibration scales were cross referenced and validated. When conducting the canister sample analysis, one of two whole air standards was analyzed after every eighth sample in order to monitor changes in detector sensitivity and measurement precision and to quickly detect any analytical problems. The whole air working standards employed for this work have mixing ratios representative of clean free tropospheric air and suburban air, thus bracketing the low and high ranges for the measurements at TF. Moreover, linearity studies are regularly conducted to evaluate the detector response over the observed mixing ratio ranges for all classes of compounds. The working standards are part of the larger network of whole air standards maintained by B. Sive at UNH as part of the AIRMAP program. In total, there are currently ten high pressure cylinders, six 36-l electropolished low-pressure pontoons (~350 psi), and three 34-l electropolished high-pressure pontoons (~900 psi) containing whole air standards that have been filled and calibrated by UCI (D. Blake) and UNH. We estimate the upper limit of the absolute accuracy of the calibrated standards to be on the order of ±1–5% for the gases reported here. In addition to the whole air standards, calibrations are conducted using five different high-pressure cylinders containing synthetic blends of selected NMHCs, OVOCs, and halocarbons at the ppbv level (Apel-Reimer Environmental, Inc.). The absolute accuracy for all of the gases in the synthetic standards is <±5%.

Response factors (RF) for each compound in a particular standard were calculated by dividing the detector response (peak area=A) by the mixing ratio (MR) of that compound in the standard (RF=A/MR). Mixing ratios for each gas to be quantified in the ambient samples were subsequently calculated using the average RF determined from the whole air standards during each set of individual analyses. In order to monitor the response of NMHCs with different numbers of carbon atoms, it is useful to evaluate the per-carbon response, particularly when dealing with long-term calibrations. The per-carbon response provides information regarding analytical system performance and standard integrity with time. The per-carbon response factors

(PCRF) were determined by dividing the RF for each NMHC by the number of carbon atoms (C) in each particular hydrocarbon (PCRF=RF/C). While the response for hydrocarbons containing the same number of carbon atoms should be uniform, this should always be verified by analyzing different classes of compounds (e.g., alkanes, alkenes, alkynes). Examples of the PCRFs for several NMHCs are shown in Fig. 2 as representative examples for the analyses when a new standard began to be used and every ~3–6 months when the same two standards were being analyzed throughout 2004–2008. The reference lines are the mean ±1 standard deviation of the PCRF included in each plot. The symbols ±error bars are the mean PCRF±1 relative standard deviation for the individual standard analyzed during the specified time period. While there is some scatter about the mean PCRF over the four years, the PCRF of the two standards analyzed during each analysis period are self-consistent. Moreover, this illustrates the long-term stability of our analytical system.

The PCRF of the C2-C4 NMHCs measured with the PLOT-FID column-detector pair decreased with increasing carbon number, but remained approximately the same over the four years and did not vary with standard. Additionally, the PCRFs remained constant for the C3 (mean±standard deviation PCRF=4.12±0.19) and C4 (3.70±0.16) compounds (Fig. 2c–f). The PCRFs of the C4-C10 NMHCs for the VF-1 ms-FID column detector pair have remained essentially constant (1.43±0.03) for compounds with different carbon numbers and for different compound classes since 2005 (Sive, 1998; Zhou, 2006). Periodically, the standards used by the automated GC system at TF were returned to the laboratory and analyzed on the canister analysis system. The PCRFs for the TF standards (e.g., DC2) agreed (within ±5%) with the laboratory standards ensuring that the measurements made by the two independent systems are comparable."

Moreover, to further address the reviewer's comments, we describe our involvement in one of many large scale VOC intercomparison experiments; focusing on NMHC measurements because this has been the largest, most carefully documented, multi-task formal intercomparison experiment conducted to date. B. Sive participated in all five tasks of the NSF sponsored Nonmethane Hydrocarbon Intercomparison Experiment (NOMHICE). Results from each task demonstrate that our analytical procedures consistently yield accurate identification of a wide range of unknown hydrocarbons and produced excellent quantitative results (*Apel et al.,* 1994, 1999, 2003b; *Sive*, 1998). The primary objectives of the NOMHICE program have been discussed previously by *Apel et al.* (1994, 1999, 2003b), and are briefly summarized here. NOMHICE was designed to assess the accuracy and comparability of NMHC measurements from research groups around the globe and has provided confidential feedback to individual laboratories on intercomparison samples that were distributed to all participants. There have been a total of five intercomparisons, called Tasks, with each Task addressing a different question. For Tasks 1 and 2, synthetic standards prepared gravimetrically by NIST, that contained 2 and 16 compounds, respectively, were analyzed by the participating laboratories. A 62 component synthetic standard, not gravimetrically prepared, was analyzed for Task 3. In Tasks 4 and 5, whole air samples were collected by NCAR and reference values were determined by the intercomparison of two analytical laboratories, NCAR and EPA. Unlike Tasks 1, 2, and 3, in which synthetic samples with known concentrations were analyzed, Tasks 4 and 5 involved the analysis of whole air samples whose true compositions were not known. Worth noting, the agreement between B. Sive and NCAR was consistently the best for all five Tasks, with the results from Tasks 2–4 shown in Figure A [*Sive*, 1998; *E. Apel*, personal communication].

Therefore, we conclude that the composition of the whole air samples in Tasks 4 and 5 were accurately quantified and that we have a sound understanding of our system response to various classes of NMHCs. However, we have also included two tables (as figures, Figs. B and C) and one figure (Fig. D) from Apel et al. (2003b) which clearly rank our group's results as having the best agreement for the whole air sample.

P8. What 24 ions were monitored by the PTR-MS – weren't monoterpenes measured at *m/z*=137 or *m/z*=81? Some more information on the operation of the PTR-MS would be useful. What was the H3O+ ion count rate? What was your normalized sensitivity to toluene? What were the background count rates for *m/z*=93? What does the 13% difference represent in terms of m93 count rates? Was the m93 background count rate a function of the toluene mixing ratio?

We agree that the PTR-MS operating parameters should be more thoroughly described. The following 24 ions were monitored (they are listed by *m/z* with the nominal assignment in parentheses): 33 (methanol), 42 (acetonitrile), 45 (acetaldehyde), 47 (ethanol), 51 (methyl chloride), 59 (acetone), 61 (acetic acid), 63 (dimethyl sulfide), 69 (isoprene), 71 (methyl vinyl ketone, methacrolein), 73 (methyl ethyl ketone), 77 (peroxy acetyl nitrate, carbon disulfide), 79 (benzene), 81 (monoterpenes), 87 (pentanal), 89 (pentanol), 93 (toluene), 99 (cyclohexanone, 2,4-dimethyl-2-pentene), 101 (hexenal), 105 (styrene), 107 (C_8 aromatics), 121 (C_9 aromatics), 135 (C_{10} aromatics), 137 (monoterpenes). Many of these channels were selected to explore the possibility of monitoring the indicated compounds. However, after the ICARTT campaign we concluded that several did not yield useful data. The monoterpenes were monitored at *m/z*=81 and *m/z*=137, but only *m/z*=137 was used to quantify mixing ratios. We did not use the PTR-MS monoterpene measurements in the present study. The H_3O^+ count rate ranged from 2.1 to 3.4 × 10^6 cps, with an average value of 2.8±0.2 × 10^6 cps, as determined from the measured *m/z*=21 ($H_3^{18}O^+$) count rate and tabulated isotopic abundances (de Bievre and Taylor, 1993). The normalized sensitivity to toluene was 15.8 ncps ppbv^{-1}. The background count rate for *m/z*=93 ranged from 1.2 to 4.1 cps, with an average value of 2.3±0.6 cps. For the merged data set, a 13% difference represented an average value for the *m/z*=93 count rate of 0.6 cps. Although the background count rate for *m/z*=93 was on average ~4-fold larger than the count rate corresponding to a 13% difference between the GC-FID and PTR-MS toluene measurements, it did not correlate with the toluene mixing ratio. Therefore, it appeared that the PTR-MS bias could not be explained by variations in the background count rate as a function of ambient toluene levels. To the text in Sect. 2.2 we added:

"For the measurements presented below the normalized sensitivity to toluene was 15.8 ncps ppbv^{-1}. The background ion current for m/z=93 ranged from 1.2 to 4.1 cps, with an average value of 2.3±0.6 cps. The average value of the H_3O^+ ion current was 2.8±0.2 × 10^6 cps. The ratio of the $H_3O^+(H_2O)$ ion current to that of H_3O^+ was on average 10±2% and ranged from 6–15%. Because the $H_3O^+(H_2O)$ ion current was low and did not depend on ambient RH, we did not include a term for the water cluster ion current in Eq. (7) as may be necessary under different operating conditions (c.f., de Gouw and Warneke, 2007)."

P10. Equations 8 and 9 are incorrect. The sentence above equation 8 is confusing. The transmission efficiency of an ion is a function of *m/z* and ion optic voltages, detector voltages, and pressure in the mass spectrometer. What you want to account for is the

difference in ion transmission efficiencies for your reagent and analyte ions to calculate a mixing ratio from measured ion count rates and ion-molecule kinetics. You don't have to know the ion transmission efficiency if you determine the instrument sensitivity empirically.

We did determine the PTR-MS sensitivity empirically and therefore our analysis did not require that the ion transmission efficiencies be known. We intended to show the relationship between analyte ion concentration in the drift tube and measured ion current. We acknowledge that Eqs. (8) and (9) are not strictly correct since the analyte ion transmission efficiency is quantified relative to that of the primary reagent ion and transmission efficiency is not defined on an absolute scale. We also recognize that the wording in the sentence above Eq. (8) did not properly convey the intended information. We corrected Sect. 2.2 by substituting the following:

"The toluene volume mixing ratio, VMR(m93) (hereinafter referred to simply as the toluene mixing ratio), is quantified based on the ratio of the background-corrected ion current (counts per second, cps) at m/z=93, I_{m93c}, to the normalized ion current (ncps) for H_3O^+ as shown in Eq. (7),

$$\text{VMR}(m93) = \frac{I_{m93r} - I_{m93b}}{\left(\dfrac{I_{H_3O^+}}{10^6}\right) \cdot C_{\text{Tol}}} = \frac{I_{m93c}}{\left(\dfrac{I_{H_3O^+}}{10^6}\right) \cdot C_{\text{Tol}}}, \qquad (7)$$

where I_{m93r} and I_{m93b} are the raw and background m/z=93 ion currents, respectively, and C_{Tol} denotes the calibration factor (sensitivity) for toluene, typically expressed in units of ncps $ppbv^{-1}$. In this work the calibration factor was determined from assays of standard gas cylinders as described in Sect. 2.1. Alternatively, the calibration factor can be determined from the instrumental operating parameters, measured ion transmission efficiencies, Tr, and published values of H_3O^+ ion mobility, μ, as described previously (de Gouw and Warneke, 2007). The measured m/z=93 ion current is related to the concentration at the end of the drift tube as shown in Eq. (8) (de Gouw and Warneke, 2007):

$$\frac{I_{m93c}}{I_{H_3O^+}} = \frac{[m93]}{[H_3O^+]} \cdot \frac{Tr_{m93}}{Tr_{H_3O^+}}, \qquad (8)$$

where here the expression is given in terms of the background-corrected m/z=93 ion current. In ambient air samples with contributions to [m93] from j as described above the true toluene mixing ratio, $VMR(m93)_t$, and the apparent measured toluene mixing ratio, $VMR(m93)_m$, can be defined as shown in Eq. (9), which follows from Eqs. (6–8):

$$\text{VMR}(m93)_t = \text{VMR}(m93)_m \cdot \frac{1}{\{1+F\}}. \qquad (9)"$$

P11. "values of F are obtained…". What are the sources of this information? How valid are the rate constant data and yield data for m/z=93 from the literature since most of the studies (SIFT-MS) are done at thermal neutral conditions?

We realize that this statement is slightly misleading. To be precise, values of F, defined in Eq. (5), were calculated using our monoterpene measurements, as well as kinetic parameters and ion fragmentation yields from the PTR-MS and SIFT-MS literature. Since the monoterpene measurements and literature sources for parameters used as input for calculating F are discussed

in Sect. 3.1 and 3.3, respectively, it should suffice to refer the reader to the appropriate discussion. We made the following revision to Sect. 2.2 for clarity:

"Values of F (Eq. 5) were calculated using monoterpene measurements by GC-FID (Sect. 3.1), as well as published proton and charge transfer rate constants and ion fragmentation yields (Sect. 3.3)."

The use of literature rate data and fragmentation yields rather than empirical values determined with our instrument is a limitation as indicated by the reviewer. However, it was the best approach that we could take given resources available at the time this work was undertaken. Our calibration standard contained a mixture of monoterpenes, whereas standards with individual monoterpenes are necessary to quantify fragmentation patterns. We plan to measure monoterpene fragmentation yields with our PTR-MS instrument in the course of future work. In Sect. 3.3.1 we noted that kinetic parameters and ion fragmentation yields used to evaluate monoterpene fragmentation via reaction with H_3O^+ were taken primarily from the PTR-MS literature (Tani et al., 2003; Warneke et al., 2003; Maleknia et al., 2007), while the rate constant for reaction of H_3O^+ with toluene was taken from the SIFT-MS literature (Španěl and Smith, 1998). The rate constants for reaction of H_3O^+ with α- and β-pinene reported by Tani et al. (2003) were measured relative to the SIFT-MS rate constant for toluene measured by Španěl and Smith (1998). They were in close agreement (to within 15% error) with the SIFT-MS measurements of Schoon et al. (2003) and with the corresponding calculated collisional rate constants (Schoon et al., 2003; Zhao and Zhang, 2004). The accuracy of the SIFT-MS rate constants for reaction of H_3O^+ with α- and β-pinene was estimated to be ±20% (Schoon et al., 2003). As noted in Sect. 3.3.2 and elsewhere (e.g., Blake et al., 2009) a primary difference between PTR-MS and SIFT-MS operating conditions is that ion-neutral collision energies are significantly higher in PTR-MS due to the electric field applied over the drift tube. However, for non-polar compounds with rate constants for reaction with H_3O^+ that are close to the collisional limit the rate constants are expected to be independent of the collision energy, which permits the use of thermal energy values for PTR-MS analyses (Keck et al., 2007). The above discussion suggests that minimal errors should have been incurred in our analysis as a result of using the SIFT-MS rate constant for the reaction of H_3O^+ with toluene and the relative rate data of Tani et al (2003). We added the following to Sect. 3.3.1:

"The PTR-MS rate data of Tani et al. (2003) were derived relative to the SIFT-MS rate constant for the reaction of H_3O^+ with toluene measured by Španěl and Smith (1998). The experimental rate constants agreed to within 15% error with the corresponding calculated collisional values (Španěl and Smith, 1998; Schoon et al., 2003; Zhao and Zhang, 2004). For non-polar compounds with rate constants for reaction with H_3O^+ that are close to the collisional limit the rate constants are expected to be independent of collision energy, which permits the use of thermal energy values for PTR-MS analyses (Keck et al., 2007). Thus, we assumed that the use of the SIFT-MS rate constant for toluene and the relative rate data of Tani et al. (2003) in our analysis was valid."

At this time we are limited to using rate and product yield data from the SIFT-MS literature for reactions of O_2^+ and NO^+ with the monoterpenes and for reaction of H_3O^+ with the monoterpene oxidation products pinonaldehyde, caronaldehyde and α-pinene oxide. In Sect. 3.3.2 we

discussed uncertainties associated with using SIFT-MS fragmentation yields for reactions of O_2^+ and NO^+ with the measured monoterpenes to estimate interferences in our PTR-MS measurements. There we also provided a quantitative comparison between SIFT-MS and PTR-MS monoterpene fragmentation yields, which we used to account for the higher level of fragmentation expected under our PTR-MS operating conditions than reported for SIFT-MS conditions by Schoon et al. (2003). In Sect. 3.4.1, where we estimated interferences from reaction of H_3O^+ with monoterpene ozonolysis products, we similarly accounted for expected higher fragmentation under our operating conditions than reported for SIFT-MS conditions by Schoon et al. (2004). We acknowledge that we could state more clearly how we accounted for expected higher fragmentation yields under our operating conditions. Accordingly, we added the following to Sect. 3.3.2:

"To partly account for higher values of $\phi(93)$ expected under our operating conditions than reported for the SIFT-MS analysis of Schoon et al. (2003), we performed calculations with the SIFT-MS fragmentation yields increased by a factor of 2 as discussed below."

We acknowledge that we neglected to discuss the possible errors incurred in using SIFT-MS rate data for reaction of O_2^+ and NO^+ with monoterpenes and reaction of H_3O^+ with monoterpene oxidation products to estimate interferences under our PTR-MS operating conditions. For reaction of O_2^+ and NO^+ with the monoterpenes, a similar argument applies as given above since the monoterpenes are non-polar and the experimental rate constants are in close agreement (to within 10%) with the collisional values (Schoon et al., 2003). To Sect. 3.3.2 we added the following:

"The experimental rate constants for reaction of O_2^+ and NO^+ with the measured monoterpenes agreed to within 10% error with the corresponding calculated collisional values (Schoon et al., 2004). As described above (Sect. 3.3.1) for reaction of H_3O^+ with toluene, α- and β-pinene the use of the SIFT-MS rate constants for our analysis was assumed to be valid due to the non-polar nature of the monoterpnes."

For reaction of H_3O^+ with pinonaldehyde, caronaldehyde and α-pinene oxide, the SIFT-MS rate constants likely slightly overestimate the values under PTR-MS operating conditions. The relatively large permanent dipole moments of these compounds, as calculated by Schoon et al. (2004), should contribute significantly to their collisional rate constants (Zhao and Zhang, 2004). The experimental rate constant for reaction of H_3O^+ with α-pinene oxide agreed to within 5% error with the collisional value, while experimental limitations only permitted lower limits to be placed on the rate constants for the pinonaldehyde and caronaldehyde reactions (Schoon et al., 2004). However, as discussed by Schoon et al. (2004) reactions of H_3O^+ with pinonaldehyde and caronaldehyde are also expected to proceed at the collisional limit. In Sect. 3.4 (page 23, line 1) "measured" should be replaced with "collisional". For polar compounds with rate constants for reaction with H_3O^+ that are close to the collisional limit the rate constants are expected to decrease with increasing collision energy (Keck et al., 2007). However, large differences in rate constants are not expected between SIFT-MS and PTR-MS conditions for compounds with thermal ion-molecule rate constants that are close to the collisional limit (Wyche et al., 2005). To Sect. 3.4 we added:

"For polar compounds with rate constants for reaction with H_3O^+ that are close to the collisional limit the rate constants are expected to decrease with increasing collision energy (Keck et al., 2007). However, large differences in rate constants are not expected between SIFT-MS and PTR-MS conditions for compounds with thermal ion-molecule rate constants that are close to the collisional limit (Wyche et al., 2005). We assumed that the rate constants of Schoon et al. (2004) provided upper limits that closely approximated the correct values in our analysis."

To Sect. 4 we added the following:

"An alternative, complementary approach to our methodology for interference estimation would involve direct measurement of fragmentation yields for the relevant monoterpenes. The resources necessary for such measurements were not available to us at the time this work was performed. Measurements under PTR-MS operating conditions of kinetic parameters and ion product yields for reactions of $H_3O^+(H_2O)$, NO^+, and O_2^+ with common atmospheric analytes, including monoterpene compounds, would be highly beneficial to the type of analysis presented here."

P13. I found the reference to Roberts et al., 1985 odd. Is Colorado vegetation relevant to your site?

Our intention in citing the Roberts et al. (1985) study was to highlight that we are not the first to observe consistent daytime and nighttime monoterpene abundances in a forested environment. An important conclusion in Roberts et al. (1985) was that diurnal variability in monoterpene abundances was largely governed by boundary layer dynamics. To clarify the reference we revised the text as follows:

"The daytime and nighttime mixing ratio distributions were in close agreement despite large diurnal differences in the absolute mixing ratios. This is consistent with boundary layer dynamics being a significant factor governing monoterpene abundances at THF as was observed previously in a different forested environment (Roberts et al., 1985)."

P15. How was the precision of the GC-FID and PTR-MS determined as a function of mixing ratio? What is the measurement precision of the PTR-MS and GC-FID at 85 pptv – the median toluene mixing ratio? Usually precision is determined by replicate analysis – trickier to determine with the GC system at low mixing ratios.

As described above in our response to the reviewer's question regarding GC-FID calibration for toluene, the precision of the GC-FID as a function of mixing ratio was determined from replicate measurements of two whole air standards with different toluene mixing ratios that partially bracketed ambient levels. We took the precision of the ambient toluene mixing ratios to be the greater of ±5% or LOD, which should reasonably describe the mixing ratio dependence of the precision of the ambient measurements based on our calibration measurements. The GC-FID precision at 85 pptv was therefore 6 pptv. The PTR-MS precision as a function of mixing ratio was estimated from counting statistics as described by Hayward et al. (2002) and de Gouw et al. (2003a). By this methodology the PTR-MS toluene precision at 85 pptv was 17 pptv. In the manuscript we already gave the GC and PTR-MS precision at the median mixing ratios. We only described the PTR-MS precision determination in a footnote to Table 1; however, this

information would be more accessible if given directly in the text. Accordingly we added the following to the text in Sect. 2.1:

> *"The PTR-MS precision was estimated from counting statistics as described by Hayward et al. (2002) and de Gouw et al. (2003a)."*

P17. You state the 13% bias may be due to calibration or background issues in the PTR-MS. You need to fully explain and eliminate these as factors before spending so much effort investigation interferences.

To be cautious we cited calibration and background issues as potential factors that may have affected the level of agreement between the two instruments. Cross calibration experiments were performed in which the toluene calibration standard used for the PTR-MS was also run on the GC system. The FID response factors for the PTR-MS toluene standard and the whole air standards run on the GC system agreed to within stated uncertainties. Thus, it appeared that the PTR-MS bias could not be explained by calibration error. The calculated values of ε_{PTR-MS} were not correlated with the precision of the PTR-MS background m/z=93 ion current, I_{m93b}. Also, I_{m93b} was not correlated with the ambient toluene mixing ratio. For the merged data set, the precision of I_{m93b} accounted for 10–45% (average, 27±8%) of the PTR-MS toluene mixing ratio precision. The ratio of the background to ambient m/z=93 ion current, I_{m93b}/I_{m93}, ranged from 11–82% (average, 38±16%). Values of ε_{PTR-MS} generally appeared to be more negative at times with the highest values of I_{m93b}/I_{m93}. However, excluding such times from our analysis only partly reduced the PTR-MS bias. For instance, the PTR-MS bias was reduced from 13±2% to 10±2% when the highest 25% of values of I_{m93b}/I_{m93} were removed. This suggested that the PTR-MS bias could not be completely accounted for by error in the PTR-MS background quantification. We edited the manuscript text in Sect. 3.3 by replacing the sentence, "*Although the observed bias is consistent with an additional source of m/z=93 ions in the PTR-MS instrument it could have been introduced in the calibrations or resulted from errors in the blank signal quantification and subtraction.*", with the following:

> *"The FID response factors for the PTR-MS toluene standard and the whole air standards run on the GC system agreed to within stated uncertainties. Thus, it appeared that calibration errors were not the cause of the PTR-MS bias. The PTR-MS instrument background at m/z=93 accounted for on average 38±16% of the total m/z=93 ion current and was therefore relatively high. However, excluding from our analysis times when the largest relative background m/z=93 ion currents were measured did not significantly reduce the PTR-MS bias. Furthermore, although the background m/z=93 ion current was on average ~4-fold larger than the ion current corresponding with the PTR-MS bias, it did not correlate with the toluene mixing ratio. Thus, it appeared that the PTR-MS bias could be only partly accounted for by error in the PTR-MS background quantification."*

In Sect. 4 we replaced the sentence, "*The bias could have been introduced in the calibrations or in quantifying the PTR-MS background.*" with the following:

> *"The bias could only partly be accounted for by error in the PTR-MS background quantification."*

P18. Since monoterpenes can also react with the first water cluster H₃O⁺(H₂O) in the PTR-MS, yields of m/z = 93 for this reaction must also be examined or at least discussed. Was H₃O⁺(H₂O) an important reagent ion in your system?

The first water cluster, $H_3O^+(H_2O)$, was not an important reagent ion in our system. We operated our system at a relatively high E/N in order to suppress water cluster formation. The ratio of the first water cluster count rate to the primary ion count rate, $I_{H_3O^+(H_2O)}/I_{H_3O^+}$, was on average 10±2% and ranged from 6–15%. As the reviewer noted, the highest toluene mixing ratios occurred at night. Relative humidity, RH, was typically highest at night as well. However, despite a strong diurnal trend in RH, neither the absolute nor relative value of the $H_3O^+(H_2O)$ ion current exhibited a diurnal dependence, indicating that under our operating conditions the reagent ion distribution was not significantly affected by ambient RH. For this reason we did not consider $H_3O^+(H_2O)$ as a primary reagent ion in our analysis. Nevertheless, as the reviewer noted, reactions of monoterpenes with $H_3O^+(H_2O)$ in the PTR-MS could still contribute to the m/z=93 signal. To the best of our knowledge, rate data and fragmentation yields for the reaction of $H_3O^+(H_2O)$ with monterpene compounds have not been reported. Thus, we have not attempted to quantify potential interferences in the PTR-MS measurements due to reactions of $H_3O^+(H_2O)$ with the monoterpenes measured at THF. We can reasonably estimate that at most, reaction of the measured monoterpenes with $H_3O^+(H_2O)$ would increase the m/z=93 yields by ~10% above the yields from reaction with H_3O^+ alone, assuming equal rate constants and yields for reactions with H_3O^+ and $H_3O^+(H_2O)$. Because the proton affinity of $(H_2O)_2$ (808 kJ mole^{-1}) is much higher than that of H_2O (691 kJ mole^{-1}) (Blake et al., 2009), which results in less exothermic proton transfer reactions for $H_3O^+(H_2O)$ compared with H_3O^+, it is likely that the m/z=93 yields from reaction of $H_3O^+(H_2O)$ with the monoterpenes measured at THF are significantly lower than those from reaction with H_3O^+. Available kinetic data suggest that proton transfer rate constants for $H_3O^+(H_2O)$ are slower than those for H_3O^+ (Smith and Španěl, 2005). To Sect. 2.2 we added the following:

"It is likely that the proton affinities of the monoterpenes measured at THF are sufficiently high for those compounds to react with $H_3O^+(H_2O)$ in the PTR-MS drift tube (Fernandez et al., 1998; Lindinger et al., 1998; Tani et al., 2004). Such reactions could provide a source of m/z=93 fragment ions in addition to those discussed above. However, in our analysis we did not consider reaction of monoterpenes with $H_3O^+(H_2O)$ due to the low measured ion current for $H_3O^+H_2O$ relative to that for H_3O^+ in our instrument and lack of relevant kinetic and product data. We estimated that at most, reaction of the measured monoterpenes with $H_3O^+(H_2O)$ would increase the m/z=93 yields by on average 10% above the yields from reaction with H_3O^+ alone, assuming equal rate constants and yields for reactions with H_3O^+ and $H_3O^+(H_2O)$. Because the proton affinity of $(H_2O)_2$ (808 kJ mole^{-1}) is much higher than that of H_2O (691 kJ mole^{-1}) (Blake et al., 2009), which results in less exothermic proton transfer reactions for $H_3O^+(H_2O)$ compared with H_3O^+, it is likely that the m/z=93 yields from reaction of $H_3O^+(H_2O)$ with the monoterpenes measured at THF are significantly lower than those from reaction with H_3O^+. Available kinetic data suggest that proton transfer rate constants for $H_3O^+(H_2O)$ are generally slower than those for H_3O^+ (Smith and Španěl, 2005)."

P26. Section 3.5 is a bit of a stretch. Proton bound ethanol dimers are only going to be found at unrealistically high mixing ratios of ethanol and chloroacetone is a "specialty"

photoproduct. Since you don't estimate an interference level for chloroacetone anyway I would suggest removing section 3.5 from the paper to shorten the paper.

Our intention with Sect. 3.5 was primarily to review for the reader some additional sources of *m/z*=93 reported in the PTR-MS literature. We agree with both reviewers that the importance of proton-bound EtOH dimers was overemphasized. We also agree that much of Sect. 3.5 can be removed since a full quantitative analysis of the potential interference from chloroacetone and $((EtOH)_2+H)^+$ was not performed. We removed Sect. 3.5.1 and Sect. 3.5.2 and modified Sect. 3.5 as follows:

"Chloroacetone is not commonly measured in the atmosphere, and its mixing ratios are expected to be low (Warneke et al., 2003). The conditions employed in the laboratory PTR-MS EtOH measurements were not representative of ambient air. We found the m/z=47 signal to be unreliable for measurement of EtOH at THF due to low sensitivity and significant interferences. Interferences in the PTR-MS m/z=93 signal from chloroacetone and $((EtOH)_2+H)^+$ cannot be fully evaluated form our data, but they are not likely to be significant."

References

Apel, E. C., Calvert, J. G., and Fehsenfeld, F. C.: The Nonmethane Hydrocarbon Intercomparison Experiment (NOMHICE): Tasks 1 and 2, *J. Geophys. Res.*, *99*, 16,651–16,664, 1994.

Apel, E. C., Calvert, J. G., Gilpin, T., Parrish, D. D., and Fehsenfeld, F. C.: The Nonmethane Hydrocarbon Intercomparison Experiment (NOMHICE): Task 3, *J. Geophys. Res.*, *104*, 26,069–26,086, 1999.

Apel, E. C., Hills, A. J., Leub, R., Zindel, S., Eisele, S., and Riemer, D. D.: A fast-GC/MS system to measure C_2 to C_4 carbonyls and methanol aboard aircraft, J. Geophys. Res., 108(D20), 8794, doi: 10.1029/2002JD003199, 2003.

Apel, E. C., Calvert, J. G., and Gilpin, T. M.: Nonmethane Hydrocarbon Intercomparison Experiment (NOMHICE): Task 4, ambient air, J. Geophys. Res., 108(D9), 4300, doi:10.1029/2002JD002936, 2003b.

Blake, R. S., Monks, P. S., and Ellis, A. M.: Proton-Transfer Reaction Mass Spectrometry, Chem. Rev., 109, 861–896, 2009.

de Bievre, P., and Taylor, P. D. P.: Table of isotopic compositions of the elements, Int. J. Mass Spectrom., 123, 149–166, 1993.

de Gouw, J. and Warneke C.: Measurements of volatile organic compounds in the Earth's atmosphere using proton-transfer-reaction mass spectrometry, Mass. Spectrom. Rev., 26, 223–257, 2007.

de Gouw, J. A., Goldan, P. D., Warneke, C., Kuster, W. C., Roberts, J. M., Marchewka, M., Bertman, S. B., Pszenny, A. A. P., and Keene, W. C.: Validation of proton transfer reaction-mass spectrometry (PTR-MS) measurements of gas-phase organic compounds in the atmosphere during the New England Air Quality Study (NEAQS) in 2002, J. Geophys. Res., 108, D21, 4682, doi:10.1029/2003JD003863, 2003a.

Fernandez, M. T., Williams, C., Mason, R. S., and Costa Cabral, B. J.: Experimental and theoretical proton affinity of limonene, J. Chem. Soc., Faraday Trans., 94, 1427–1430, 1998.

Guenther, A. B., Zimmerman, P. R., Harley, P. C., Monson, R. K., and Fall, R.: Isoprene and monoterpene emission rate variability: model evaluations and sensitivity analyses, J. Geophys. Res., 98, D7, 12,609–12,617, 1993.

Hayward, S., Hewitt, C. N., Sartin, J. H., and Owen, S. M.: Performance characteristics and applications of a proton transfer reaction-mass spectrometer for measuring volatile organic compounds in ambient air, Environ. Sci. Technol., 36, 1554–1560, 2002.

Keck, L., Oeh, U., and Hoeschen, C.: Corrected equation for the concentrations in the drift tube of a proton transfer reaction-mass spectrometer (PTR-MS), Int. J. Mass Spectrom., 264, 92–95, 2007.

Lindinger, W., Hansel, H., and Jordan, A.: Proton-transfer-reaction mass spectrometry (PTR-MS): on-line monitoring of volatile organic compounds at pptv levels, Chem. Soc. Rev., 27, 347–354.

Maleknia, S. D., Bell, T. L., and Adams, M. A.: PTR-MS analysis of reference and plant-emitted volatile organic compounds, Int. J. Mass Spectrom., 262, 203–210, 2007.

Roberts, J. M., Hahn, C. J., Fehsenfeld, F. C., Warnock, J. M., Albritton, D. L., and Sievers, R. E.: Monoterpene hydrocarbons in the nighttime troposphere, Environ. Sci. Tech., 19, 364–369, 1985.

Russo, R. S., Zhou, Y., Talbot, R., and Sive, B. C.: Seasonal variation of nonmethane hydrocarbons and halocarbons in New Hampshire: 2004–2006, Atmos. Chem. Phys. Discuss., 10, 1083–1134, 2010.

Schoon, N., Amelynck, C., Vereecken, L., and Arijs, E.: A selected ion flow tube study of the reactions of H_3O^+, NO^+ and O_2^+ with a series of monoterpenes, Int. J. Mass Spectrom., 229, 231–240, 2003.

Schoon, N, Amelynck, C., Vereecken, L., Coeckelberghs, H., and Arijs, E.: A selected ion flow tube study of the reactions of H_3O^+, NO^+ and O_2^+ with some monoterpene oxidation products, Int. J. Mass Spectrom., 239, 7–16, 2004.

Sive, B. C., Atmospheric nonmethane hydrocarbons: Analytical methods and estimated hydroxyl radical concentrations, University of California, Irvine, Irvine, Ph.D. Thesis, 1998.

Sive, B. C., Zhou, Y., Troop, D., Li, Y., Little, W., Wingenter, O. W., Russo, R. S., Varner, R. K., and Talbot, R. W.: Development of a cryogen-free concentration system for measurements of volatile organic compounds, Anal. Chem., 77, 6989–6998, doi:10.1021/ac0506231, 2005.

Smith, D., and Španěl, P.: Selected Ion Flow Tube Mass Spectrometry (SIFT-MS) for on-line trace gas analysis, Mass Spectrom. Rev., 24, 661–700, 2005.

Tani, A., Hayward, S., and Hewitt, C. N.: Measurement of monoterpenes and related compounds by proton transfer reaction-mass spectrometry (PTR-MS), Int. J. Mass Spectrom., 223/224, 561–578, 2003.

Tani, A., Hayward, S., Hansel, A., and Hewitt, C. N.: Effect of water vapor pressure on monoterpene measurements using proton transfer reaction-mass spectrometry (PTR-MS), Int. J. Mass. Spectrom., 239, 161–169, 2004.

Warneke, C., de Gouw, J., Kuster, W. C., Goldan, P. D., and Fall, R.: Validation of atmospheric VOC measurements by proton-transfer-reaction mass spectrometry using a gas-chromatographic preseparation method, Environ. Sci. Technol., 37, 2494–2501, 2003.

Wyche, K. P., Blake, R. S., Willis, K. A., Monks, P. S., and Ellis, A. M.: Differentiation of isobaric compounds using chemical ionization reaction mass spectrometry, Rapid Commun. Mass Spectrom., 19, 3356–3362, 2005.

Zhao, J., and Zhang, R.: Proton transfer reaction rate constants between hydronium ion (H_3O^+) and volatile organic compounds, Atmos. Environ., 38, 2177–2185, 2004.

Tables

Table A. Mixing ratio in pptv, per-carbon response factor (PCRF) and standard deviation (StDev) of the PCRF for the Thompson Farm GC system whole air working standards (Std0 and DC2). For DC2, the pre-ICARTT and ICARTT PCRFs are listed to show the change in the monoterpene mixing ratios over the course of the campaign but the consistency of the n-decane PCRF.

	ICARTT				Pre-ICARTT		ICARTT	
Compound	Std0 (pptv)	Std0 PCRF	Std0 StdDev	DC2 (pptv)	DC2 PCRF	DC2 StdDev	DC2 PCRF	DC2 StdDev
toluene	101	1.41	0.06	1215	1.42	0.04	1.41	0.06
n-octane	33	1.43	0.07	356	1.40	0.04	1.40	0.06
ethylbenzene	30	1.41	0.07	304	1.40	0.04	1.41	0.05
1,2,4-TMB*	54	1.40	0.08	285	1.42	0.04	1.41	0.06
n-decane	38	1.42	0.07	290	1.41	0.04	1.42	0.09
α-pinene	-	-	-	469	1.41	0.06	1.36	0.11
β-pinene	-	-	-	99	1.41	0.08	0.40	-

*1,2,4-trimethylbenzene

Table B. The per-carbon response factor (PCRF) and standard deviation (StDev) of the PCRF for the Thompson Farm GC system whole air working standard (DC2) and for two of the Apel-Riemer Environmental, Inc. gravimetric standards used for PTR-MS calibrations (Monoterpenes and Aromatics) during the ICARTT campaign. These results further validated the use of a single response factor for each group of compounds, specifically C_7 and C_{10} NMHCs.

			Apel-Riemer Gravimetric Standards			
	DC2 PCRF	DC2 StDev	Monoterpenes PCRF	StDev	Aromatics PCRF	StDev
toluene	1.40	0.02	-	-	1.42	0.02
ethylbenzene	1.40	0.05	-	-	1.39	0.02
1,2,4-TMB*	1.42	0.02	-	-	1.41	0.02
n-decane	1.42	0.03	-	-	-	-
α-pinene	1.43	0.03	1.39	0.03	-	-
β-pinene	1.42	0.02	-	-	-	-
camphene	-	-	1.43	0.04	-	-

*1,2,4-trimethylbenzene

Figure Captions

Figure 3. Portion of a chromatogram recorded at THF on 3 August, 04:23 LT during a period of enhanced monoterpene mixing ratios.

Figure A. Average absolute percent deviation of each investigator's reported values from NCAR values for (a) Task 2, (b) Task 3 and (c) Task 4 of NOMHICE, respectively. The numbers above each bar represent the number of compounds reported by each investigator; the red stars designate the results of B. Sive. The results for select compounds showing the NIST (Task 2 only), NCAR before send, B. Sive and NCAR after return values are shown for (d) Task 2, (e) Task 3 and (f) Task 4, respectively.

Figure B. Table 4 of Apel et al. (2003b).

Figure C. Table 5 of Apel et al. (2003b).

Figure D. Figure 9 of Apel et al. (2003b)