

Interactive comment on “An intercomparison of GC-FID and PTR-MS toluene measurements in ambient air under conditions of enhanced monoterpene loading” by J. L. Ambrose et al.

Anonymous Referee #1

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Review – An intercomparison of GC-FID and PTR-MS measurements in ambient air under conditions of enhanced monoterpene loading by Ambrose et al.

This manuscript examines the measurement of toluene by the PTR-MS with respect to those determined using a GC/FID in an environment dominated by biogenic emissions. The authors present a nearly complete 3-week data series for toluene (PTR-MS and GC-FID) and speciated monoterpenes (GC-FID) that were collected during the summer of 2004 in rural New Hampshire. They carefully examine the PTR-MS toluene data for potential interferences from the presence of the major monoterpenes, which have been reported (when ionized within a PTR-MS) to produce a fragment ion that

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has the same mass-to-charge ratio (m/z) as protonated toluene. The PTR-MS derived toluene concentrations are observed to compare very well with the corresponding GC-FID measurements – a simple correlation scatter plot shows a slope of 1.16 and correlation coefficient of ~ 0.91 . Considering that all of toluene measurements are below 0.5 ppbV this is very impressive agreement. However, the authors noted that the PTR-MS often exhibited a positive bias during periods when the monoterpene concentrations were at their highest – nighttime periods with calm winds. The authors using ion chemistry (product ion branching fractions and reaction rate constants) reported in the literature have examined whether the observed biases are due to spectral interferences originating from the presence of the monoterpenes or their oxidation products. They conclude that accounting for the fragmentation of α -pinene and β -pinene provides only a marginal improvement in the PTR-MS data.

This is a nice paper and addresses a topic that is appropriate for publication in AMT. It focuses and discusses some important details regarding the interpretation of the m/z 93 signal in the PTR-MS instrument that is typically simply attributed to toluene. The discussion evaluates the data in a pragmatic quantitative approach. Some qualitative discussion of how the interferences from oxidation products would be expected to perturb the data would be useful, but overall I find the authors did a good job of presenting the information. This is an important paper for PTR-MS practitioners as it serves to demonstrate the validity of the PTR-MS to deliver reliable results in an environment dominated by biogenic emissions. After a few minor revisions I feel that is suitable for publication.

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. I like the presentation of the data in Figures 6 and 8 as it allows interested readers (or reviewers) to study the periods when the PTR-MS agrees or diverges from the GC/FID results. For instance if the fragmentation from the monoterpenes dominates, then the error might

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be expected to directly track with the monoterpene concentration. Alternatively, if the terpene oxidation products were influencing the results, then the bias would peak after the monoterpene concentration maximum reflecting their secondary production. The lack of a consistent bias seems important. During some periods of high monoterpene loading (July 30 and August 2) the PTR-MS shows a consistent bias with respect to the GC-FID suggesting an interference from these compounds, while during other periods (August 3 and August 10) there appears to be good agreement between the two methods. This leads me to wonder if some other variable such as humidity is playing a role. Humidity could exert a subtle effect - related to the reactivity of toluene and the monoterpenes to $\text{H}_3\text{O}^+(\text{H}_2\text{O})$. There is no discussion concerning whether this ion is considered as a primary reagent ion. Toluene does not react (at least efficiently) with $\text{H}_3\text{O}^+(\text{H}_2\text{O})$ (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 Spec. Rev. 26 (2007) 231).

A second interesting feature in the time series occurs on August 4 and August 12. On these two days the monoterpene levels are quite low, but the PTR-MS and GC/FID results show poor correlation. It appears that during these periods that the PTR-MS result covaries strongly with wind speed, suggesting the influx of a very different air mass. If the wind direction suggested the presence of marine air, then this could represent the chloroacetone interference. If the wind direction suggested urban air, then one might consider the ethyl toluenes as a potential interferent. This reviewer has no concrete evidence to support that the ethyl toluenes fragment to produce m/z 93, but I find it highly probable. This is drawn by analogy to ethyl benzene that produces m/z 79 (protonated benzene) as a fragment ion. Nothing needs to be done regarding these latter comments unless it adds value to your interpretation. I just found the wind feature interesting.

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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.
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 conventional to invoke the argument that it is assumed the ion intensity ratio $I(93)/I(H_3O^+)$ is equal to the ion concentration ratio $[93]/[H_3O^+]$.
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?
4. Line 7 page 26 – Table RD6 must be a typo. I think you are referring to Table 7.
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 ($EtOHH+H_2O$).
6. Figure 3. Is the isopropylbenzene peak the small shoulder or the larger adjacent peak? Please clarify this figure. Maybe use a line to point to actual peak or label both peaks.

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