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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Long-term study of VOCs measured with PTR-MS at a rural site in New Hampshire with urban influences" *by* C. Jordan et al.

Anonymous Referee #1

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General Comments: This manuscript reports concentrations of a selected set of compounds determined using Proton Transfer Reaction Mass Spectrometry (PTR-MS) for long-term multiple-year study. The results are reported as seasonal medians and as diurnal averages and subsequent discussion of the data is focused on interpretation of the diurnal trends in qualitative terms. This manuscript has a number of serious shortcomings. What are we the readers to derive from this work? The manuscript lacks a clearly stated scientific purpose, beyond reporting their measurements. Secondly, given that the measurements have been derived using the PTR-MS technique the authors need to provide some assurance that the measurements themselves are valid and reasonable before embarking on atmospheric interpretation. A central tenet

in applying PTR-MS to any system is that one knows what is being measured. Not to belabor the point, but it is not appropriate to interpret every signal at m/z 69 as arising from isoprene. Similar arguments can be made for the interpretation of the m/z 71 signals. These signals are not always due to the presence of methyl vinyl ketone and methacrolein. While these are reasonable mass assignments when measuring summertime biogenic emissions, there is no precedence for applying this same interpretation when the air mass represents urban anthropogenic emissions. Given that the measurements reflect the analysis of air masses representing very different emission sources there needs to be conscious effort to validate the PTR-MS measurements.

Long-term studies such as this are very important as they provide valuable information about diurnal, seasonal and annual variability but the shear volume of data collected presents real challenges in terms of presentation and discussion. Diurnal profiles may reduce the data into a manageable format, but it is not clear that this an appropriate decision for examining the atmospheric behavior of tracer species like DMS or acetonitrile. These tracers should be used in a logical manner to identify when the air masses are being influenced by oceanic air, large-scale forest fire emissions or seasonal domestic wood burning.

General Recommendations:

1) Provide some discussion and validation of the PTR-MS mass assignments. Some PTR measurements such as methanol, acetonitrile and DMS are generally well accepted others such as isoprene, the sum of methyl vinyl ketone and methacrolein, benzene, C8 and C9 benzenes can have interferences. Canister measurements appear to have been made routinely over portions of the measurement period. Comparisons with between the GC methods and the PTR-MS are needed to establish the reliability and validity of the PTR-MS measurements.

2) Select specific examples to highlight in the discussion section. Consider the presentation of some data as function of air mass type: marine, clean continental or polluted

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continental. The data set must have some fascinating results. Focus on the most significant ones and avoid over analyzing small details.

Specific Comments and Questions:

1) Page 4253 lines 5-9. Does the high time response of the PTR-MS really matter when the data is reduced to diurnal averages?

2) Page 4256 line 13. Isobaric is not the correct term. All of the mixtures stated are isomers. There are isobaric interferences that are not mentioned. Benzaldehyde is an isobaric interference to the C8-benzenes and the aromatic aldehyde and ketone species (C8H8O) can interfere with the C9-benzenes.

3) Page 4256 line 18. The terpenes all fragment upon ionization to form an ion at m/z 81. What is meant by the statement that for most monoterpenes >99

4) Page 4267 line 26. The Holzinger et al reference states that emission patterns of isoprene and methanol are similar when biogenic emissions are dominant. It is not correct to state that the diurnal cycles are similar.

5) Section 4.1.12. This section should be reworked to address the comments below.

a. One should reference toluene/benzene ratios from engine exhaust studies (Schauer et al. Environ. Sci. Tech. 36, (2002) 1169, Heeb et al. Atmos Environ. 33 (1999) 205) or modern tunnel studies (Legreid et at Environ. Sci. Tech. 41 (2007) 7060). The Warneke reference reflects city outflow measurements, which represents the sum of all the anthropogenic emissions of these two compounds.

b. The seasonal changes in the toluene/benzene ratio reported here have been observed and reported previously, see Schnitzhofer et al. Atmos. Environ. 42 (2008) 1012. In that study the authors argued that the seasonal change was due to a temperature dependence in the evaporative emissions.

c. If there is enough wood burning to change the observed toluene/benzene ratio then

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the acetonitrile diurnal should also show a change, since it is tracer for wood burning.

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