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Atmospheric
Chemistry
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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.

C. Jordan et al.

Received and published: 9 June 2009

Response to Anonymous Referee #1

For clarity, in our response we show the referee's comments in italics with our response in regular font.

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.*

We appreciate your point of view, but we do not share it. We believe that novel data is worth publishing in its own right. We are unaware of a data set of this length for these compounds that show their seasonal diurnal behavior. We believe an overview of this kind for such an extensive data set is both intrinsically valuable and essential for providing context for future work that focuses on specific case studies.

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.

We agree that there is always the possibility that the signal observed at m/z 71 is enhanced from the contribution of isobaric ions from various compounds such as pentenes and higher alcohols (Warneke et al., 2003). However, it is not expected that these short-lived compounds would be prevalent in the high mixing ratios observed for m/z 71 at a rural site like Thompson Farm (to date, none of our independent measurements reflect this). It is expected that the isoprene oxidation products methyl vinyl ketone and methacrolein (MVK/MAC) would be produced in significant amounts by local photochemistry (Brasseur et al., 1999). Similarly, m/z 69 could have interferences from a variety of biogenic compound emissions other than isoprene; however, comparison to our canister and *in situ* GC measurements show that isoprene correlates very strongly with the m/z 69 signal (Figure 1.1) as it has in other studies (de Gouw and Warneke, 2007). We do not observe significant interferences at this rural site and the PTR-MS measurements are consistent with two additional independent measurement techniques (Figure 1.1). Other PTR-MS and GC intercomparisons under similar conditions have found very high correlations between the signals at m/z 69, 71, 79, 107, and 121 and those derived from GC measurements for isoprene, MVK/MAC, benzene, and C_8 and C_9 aromatics (de Gouw and Warneke, 2007, de Gouw et al., 2003, Warneke et al., 2005). Elsewhere rural PTR-MS measurements have operated under the assumption that isoprene and MVK/MAC are the dominant contributors at these m/z channels (Karl et al., 2004).

Similarly, for benzene, toluene and the C_8 aromatics, there is good overall quantitative agreement between the different measurement techniques (Figure 1.2). For the aromatics summer data for benzene and toluene and winter data for the C_8 aromatics is shown.

We currently have three additional manuscripts in preparation that specifically address instrument characterization for the PTR-MS. We have and continue to regularly carry out rigorous characterization experiments and intercompare all of our measurement techniques and calibration scales to ensure that we have a self-consistent long-term data set that can be meaningfully compared to others at different times and locations. To illustrate this, we have included an excerpt from a manuscript in preparation by Ambrose et al., “Quantification of Analytical Interferences in PTR-MS Toluene Measurements from Monoterpene Fragmentation”, which will be submitted to AMT sometime in the next month:

. . . “The location of the Thompson Farm observing site in a predominantly forested area as well as the frequent development of low altitude nocturnal inversions during the summer months result in large enhancements of monoterpenes during nighttime. Such conditions have made possible a rigorous field test of the ability of PTR-MS to accurately measure toluene at m/z 93, where several previous studies have suggested the

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potential for analytical interference from ion products of monoterpenes fragmentation in the PTR-MS drift tube. Since the summer of 2004 we have routinely made concurrent measurements of toluene via both PTR-MS and GC-FID. These measurements, together with monoterpenes measurements via GC-FID were used for the present work.”. . .

Although deviations were observed between toluene PTR-MS and GC-FID (not shown), these deviations occur for the lowest toluene mixing ratios of the day (i.e., a large deviation in percent is to be expected when comparing small numbers) and cannot be attributed to monoterpene fragmentation. On the whole good agreement is found between these techniques (Ambrose et al., in preparation).

Referee #2 has also requested more intercomparison data, so we ask you to please see our response to him/her. Finally, we have both formally and informally intercompared with other research groups using similar and different techniques for the trace gases included in this manuscript. Overall, we have intercompared well and the results are topics of the aforementioned manuscripts that members of our group will be submitting in the near future. In the meantime, the following is a list of some of the publications using our PTR-MS data, many of which have also included other groups VOC measurements:

White, M. L., R. S. Russo, Y. Zhou, J. L. Ambrose, K. Haase, E. K. Frinak, R. K. Varner, O. W. Wingenter, H. Mao, R. Talbot, and B. C. Sive (2009), Are Biogenic Emissions a Significant Source of Summertime Atmospheric Toluene in Rural Northeastern United States?, *Atmos. Chem. Phys.*, 9, 81-92.

Cottrell, L. D., R. J. Griffin, J. L. Jimenez, Q. Zhang, I. Ulbrich, L. D. Ziemba, P. J. Beckman, B. C. Sive, and R. W. Talbot (2008), Submicron particles at Thompson Farm during ICARTT measured using aerosol mass spectrometry, *J. Geophys. Res.*, 113, D08212, doi:10.1029/2007JD009192.

Zhou, Y., H. Mao, R. S. Russo, D. R. Blake, O. W. Wingenter, K. B. Haase, J. Ambrose,

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R. K. Varner, R. Talbot, and B. C. Sive (2008), Bromoform and dibromomethane measurements in the seacoast region of New Hampshire, 2002–2004, J. Geophys. Res., 113, D08305, doi:10.1029/2007JD009103.

Millet, D. B., D. J. Jacob, T. G. Custer, J. A. de Gouw, A. H. Goldstein, T. Karl, H. B. Singh, B. C. Sive, R. W. Talbot, C. Warneke and J. Williams (2008), New constraints on terrestrial and oceanic sources of atmospheric methanol, *Atmos. Chem. Phys.*, 8, 6887-6905.

White, M., R. S. Russo, Y. Zhou, R. K. Varner, L. C. Nielsen, J. Ambrose, O. W. Wingenter, K. Haase, R. Talbot and B. C. Sive (2008), Volatile organic compounds in northern New England marine and continental environments during the ICARTT 2004 campaign, *J. Geophys. Res.*, 113, D08S90, doi:10.1029/2007JD009161.

Heald, C. L. et al. (2008), Total observed organic carbon (TOOC) in the atmosphere: a synthesis of North American observations, *Atmos. Chem. Phys.*, 8, 2007-2025.

Ambrose, J. L., H. R. Mayne, J. Stutz, R. S. Russo, Y. Zhou, R. K. Varner, L. C. Nielsen, M. White, O. W. Wingenter, K. Haase, R. Talbot, and B. C. Sive (2007), Nighttime oxidation of VOCs at Appledore Island, ME during ICARTT 2004, *J. Geophys. Res*., 112, D21302, doi:10.1029/2007JD008756.

Chen, M., R. Talbot, H. Mao, B. Sive, J. Chen, and R. J. Griffin (2007), Air mass classification in coastal New England and its relationship to meteorological conditions, *J. Geophys. Res.*, 112, D10S05, doi:10.1029/2006JD007687.

Mao, H., R. Talbot, C. Nielsen, and B. Sive (2006), Controls on methanol and acetone in marine and continental atmospheres, *Geophys. Res. Lett*., 33,L02803, doi:10.1029/2005GL024810.

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.*

We concur that large data sets pose a challenge for presentation in a reasonably concise manner. There have been many studies from observing sites in southeastern NH over the past decade or so that have previously described transport patterns using various trace gases and aerosols influencing this region. In this work we specifically wanted to investigate diurnal behavior at the Thompson Farm site, which yielded some surprising insights into biogenic contributions of compounds (e.g., MEK typically thought to derive from anthropogenic butane). As you suggest DMS and acetonitrile were included as tracers for oceanic air and biomass burning. However, the detection limit for DMS in our PTR-MS proved to be too high for this to be of much use here. Acetonitrile while not used in this study to identify specific air masses influenced by biomass burning, certainly revealed significant seasonal variability. With limited local sources of acetonitrile combined with its relatively long residence time, it proved quite useful as a tracer for surface layer dynamics.

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.

Please refer to the above discussion and figures.

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

To do as you request would require a fundamentally different analysis than the one presented here. We were specifically interested in diurnal behavior, its seasonal variability, and its inter-annual variability. Further, the paper is already quite long, to add specific examples related to transport would make the paper entirely too long. We are currently looking at specific case studies, some of which will investigate such transport related questions. This work provides the context within which to properly evaluate the sort of case studies of interest to you. We look forward to publishing them in the near future.

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?

Your point is well taken. On the one hand PTR-MS provides us with high time-resolution data. However, as you also note this is a large data set, so presenting an overview of the data without some degree of averaging is impractical for a journal article. The one advantage such data does provide is that the hourly means are that much more robust due to the number of data points in the sample. This is why the standard error of the means is so small. From that perspective, yes high time resolution data is advantageous, even when reduced to hourly means.

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.

In mass spectrometry, isobaric ions are different molecules or isotopes that are present at the same measured m/z channel. At unit mass resolution, isomers are isobaric (Sparkman, 2002).

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*

The sentence has been revised as follows (lines 128-130 in manuscript):

Finally, total monoterpenes are measured at m/z137; for most monoterpenes >99% of the signal at m/z137 can be attributed to the C10H16H+ ion (Tani et al., 2003; Lee et al., 2005).

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.

Thank you very much for catching our error. You are quite correct, we misstated their point. We have removed that sentence (and hence, the Holzinger et al. (2001) methanol reference).

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.

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c. If there is enough wood burning to change the observed toluene/benzene ratio then the acetonitrile diurnal should also show a change, since it is tracer for wood burning.

This is a great question. Thank you for bringing the excellent Schnitzhofer et al. (2008) paper to our attention. The three parts to your question are related, so we will address them together beginning with part b. As you note, Schnitzhofer et al. (2008) attribute the seasonal behavior of the toluene/benzene ratio to a strong evaporative source for toluene (i.e. more toluene released in summer than winter), while benzene is formed during combustion and catalytic conversion processes (and hence more uniformly emitted year round). They also investigate the possible influence of domestic wood burning, but find it can only account for $<$15% of benzene observed. They observe an acetonitrile:benzene ratio of 0.077, very close to the ratio from automobile emissions by Holzinger et al. (2001). Schnitzhofer et al. (2008) cite acetonitrile:benzene ratios of 0.18 - 2.66 from biomass burning (Salisbury et al., 2003,Christian et al., 2003). From these numbers they derive only 15% of the observed benzene comes from domestic wood burning. Note, throughout this discussion, they use mean nighttime values (2300 - 0500 CET). Finally they report a toluene:benzene ratio that shifts from about 2:1 in summer to about 1:1 in winter.

In a nutshell, in Schnitzhofer et al. (2008), the winter toluene:benzene ratio boils down to two key points:

1) based on reported emissions of acetonitrile:benzene from biomass burning, too little benzene can be attributed to this source given the observed acetonitrile to account for the observed benzene, and

2) less toluene is emitted in winter than in summer, while benzene remains about the same year round, hence the ratio decreases in winter.

We are not prepared to critique their analysis based on European observations because we are insufficiently familiar with gasoline formulations required by the EU, as well as meteorological conditions in Vomp. However, we can make good comparisons

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with the tunnel studies conducted in Milwaukee, WI reported by Lough et al. (2005). Such studies yield good information on vehicle emissions under real road conditions with a typical representation of a wide range of vehicles (heavy, moderate, and light-duty vehicles, plus cars). Lough et al. (2005), investigated emissions both in summer and in winter in two road tunnels in Milwaukee and a parking structure in Madison, WI (to examine cold-start emissions). Although Milwaukee is in the Midwestern United States, its latitude (43.11°N) is the same as Thompson Farm (43.11°N). Hence the seasonal emissions may be expected to be similar.

Lough et al. (2005) report that the seasonal reformulation of gasoline (to reduce summertime evaporative emissions of light alkanes and alkenes) produces gasoline with a weight percent of toluene that ranges from 1 wt% in winter to 10 wt% in summer, while benzene remains constant year round at about 1 wt%. Toluene in headspace vapors also varies from about 0.3 wt% in winter to 3-5 wt% in summer, while again benzene remains essentially constant at about 1 wt% year-round. So, one would certainly expect lower winter time toluene concentrations in the atmosphere due to evaporation, just as Schnitzhofer et al. (2008) suggest. However, Lough et al. (2005) found that winter and summer emissions of aromatics such as benzene and toluene were comparable: toluene averaged 357±143 mg L^{-1} in summer and 363±232 mg L^{-1} in winter, while benzene averaged 167± 59 mg L^{-1} in summer and 95±26 mg L^{-1} in winter. They attribute the higher winter emissions of toluene to incomplete combustion, cold starts in particular led to higher emissions of both benzene and toluene. Although Lough et al. (2005) do not report toluene:benzene ratios directly, they may be roughly estimated from the mean values provided. From their Table 3, these ratios were approximately 2 year-round.

So this poses a dilemma. If fresh emissions in New Hampshire accumulate at night and mix with background air during the day as is the case for CO, then we would expect to see the toluene:benzene ratio rise at night in the presence of fresh emissions toward a ratio of about 2 followed by a decrease during the day to the background ratio of 0.7.

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This is not the case. The ratio is constant throughout the day and night. This is why we considered domestic heating sources as an alternative source of toluene and benzene with their emission possessing a different ratio than that of vehicle emissions.

Next lets consider the acetonitrile assumption used by Schnitzhofer et al. (2008). They cite a wide range of values 0.18 - 2.66 for acetonitrile:benzene from biomass burning. They do not explicitly state how they calculated the benzene value they report. However, they cite references to open biomass burning conditions, not domestic heat sources. This is almost certainly due to a real lack of data on emissions of these compounds from such sources. As Andreae and Merlet (2001) note there is very little data on wood and dung burning for domestic fuel, so they do not include any estimates for emissions from those sources. They note acetonitrile in particular as a compound for which much more data are needed. They also point out that NO, NO_2, N_2O, and molecular N_2 are emitted during flaming combustion, while nitriles (and NH_3 and amines) are emitted under smoldering conditions. This raises the possibility that less acetonitrile is released in the controlled burning of a wood-fired boiler or stove, than is the case in an open fire. Unfortunately in the one study we could find on furnace emissions (Johansson et al., 2004) no data were reported for N containing compounds. It is worth noting, that although the diurnal variation of acetonitrile in winter is slight, it is at least consistent with the possibility of a wood-fired domestic heat source contribution with higher values at night than during the day (a 17% drop from the nighttime peak of 99 pptv at 2100 h to 82 pptv at 1100 h). Recall CO exhibited a 13% day night difference. Both benzene and toluene exhibit $\approx$30% decrease from their nighttime maxima to daytime minima. And as discussed in the text, benzene and toluene are emitted from oil burners, but the ratio is highly uncertain.

And finally, as requested in part a, I have included the citation for the ratio from the observations made in tunnels.

We thank the referee for their careful consideration of our manuscript. We particularly appreciate this final question. We have reworked this section as recommended and think the paper is much better for it.

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