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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.

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Response to Anonymous Referee #2

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

General comments: The article of Jordan, et al. on a long-term study of VOCs at a rural site in New Hampshire nicely shows the annual, seasonal and daily variation of VOC in the surface atmosphere. Such a data set with its high temporal resolution in the order of minutes is of high value for the research community investigating chemical processes in the atmosphere. Therefore, this data set should be made available in its full temporal resolution on request.

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We have added a sentence in the Introduction (line 43) to say these data are available upon request.

Specific comments: The paper is well written and has no severe flaws. The authors used the PTR-MS technique to analyse the VOC composition of the atmosphere. For quantification, they used compressed commercial or home-made gas standards of the target compounds. The authors pointed out that when analysing ambient air samples some isobaric compounds other than the target air constituents may be co-detected by the PTR-MS. That feature is a principle problem of the PTR-MS technique when analysing complex matrices as described here.

Please see the response to Referee #1.

In line 117 the authors refer to an in-situ GC system which was also employed at that site. To ensure that the reported mole fractions of the target compounds are not biased by isobaric unknown air compounds, the PTR-MS data should be compared the GC data and the result of that comparison summarized in a graph or table.

Again, please see the response to Referee #1. Additionally, we would like to mention that to date, not all of the GC data has been reduced for the corresponding time period of the PTR-MS data set because of the enormous amount of time and labor involved in processing each individual peak in every chromatogram that we have generated to date. However, we have included some additional figures from Appledore Island (∼30 km from Thompson Farm) to supplement those provided in our response to Referee #1. Here, we provide some intercomparison data with other measurements and techniques to further aid in illustrating that the PTR-MS data are not biased by isobaric interferences in a rural location such as coastal New England. Again, we have several manuscripts specifically addressing these issues that will be submitted for publication in the near future.

During the ICARTT 2004 campaign, VOC measurements by PTR-MS were conducted on the NOAA ship R/V Ronald H. Brown by J. de Gouw and C. Warneke. At various times during the campaign, the Ron Brown (shown as highlighted areas in Figure 2.1) was in the vicinity of Appledore Island (AI) where our PTR-MS was stationed. The time series plots for acetone, methanol and MVK+MACR are shown for July 7-16, 2004, when the Ron Brown (RB) was nearby AI (within ∼1 km) during the campaign. These dates were specifically chosen to compare both instruments during times when there were significant fluctuations in mixing ratios for the compounds shown. Overall, there was good agreement for these gases (and others not shown) by two independently calibrated instruments.

Comparisons between the PTR-MS and other VOC measurements conducted on Appledore Island during the ICARTT campaign were in good agreement overall. Other measurements that were deployed on the island included mist chamber/ion chromatography (MC/IC) for acetic acid, hourly canister samples analyzed by GC-ECD/FID/MS for NMHCs, halocarbons and alkyl nitrates, and an *in situ*, cryo-less GC system for NMHCs, OVOCs, halocarbons and alkyl nitrates. Figure 2.2 shows a time series plot of the acetic acid data from the MC/IC [A. Pszenny and W. Keene] and the Appledore Island PTR-MS. Overall, the MC/IC and PTR-MS measurements tracked each other remarkably well and the calibrated mixing ratios are in very good agreement overall.

Finally, Figures 2.3, 2.4, and 2.5 are from Sive et al. (2005); the results for simultaneous measurements of ambient air at Appledore Island are compared from an *in situ* cryo-less GC system, the PTR-MS, and whole air canister samples analyzed at UNH. Overall, excellent agreement was observed between the three measurement techniques for the majority of compounds at Appledore Island. The numerous intercomparison experiments conducted and the consistently good quantitative agreement for both PTR-MS systems gives us confidence that our long-term Thompson Farm measurements are reliable and robust.

In that context also the frequency of the calibration with the gas standards should be reported. Two PTR-MS instruments were used to generate the data presented. It is stated that the coherence of the data has been is ensured by a rigorous validation *procedure. The coherence of the data sets should be demonstrated.*

Some of the text has been modified as follows (starting at line 108):

from: "Calibrations were conducted periodically (manual calibrations were preformed seasonally in 2005 and 2006, single point calibrations made daily starting in July 2007) to monitor PTR-MS performance, quantify the mixing ratios of target gases and to confirm calibration factors."

to: "Calibrations were conducted periodically (manual calibrations were performed seasonally in 2004, 2005 and 2006 (ranging from every 4 to 12 weeks), daily single point calibrations and bi-weekly multi-point calibrations began in July 2007) to monitor PTR-MS performance, quantify the mixing ratios of target gases and to confirm calibration factors."

Additionally, Table 2.1 lists the calibration factors generated for both PTR-MS instruments from 2004 to present. Over this time period, the upper limit of the precision of the calibration factors was $\pm$ 10%.

Finally, we have included some results to demonstrate the coherence between the two instruments. The results shown (Figures 2.6 and 2.7) are from a manuscript in preparation by Haase et al. addressing long-term instrument operation, calibrations and intercomparisons. While we have numerous “side-by-side” comparisons (results from one are shown in Figure 2.7), for roughly the last year, we have been operating both instruments at our “old” Thompson Farm site and at our “new” site (Figure 2.6), which are approximately 400 m apart from one another. We find the qualitative and quantitative agreement to be quite impressive; however, we are very rigorous in systematically ensuring that each instrument is performing similarly.

The measurements are nicely summarised in the results section. A detailed analysis of the data set is lacking. It must be worthwhile to sort out specific situations in the different seasons years, or even during a day to highlight the value of recording VOC mole

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fractions with high temporal resolution e.g. clean air masses vs. polluted air masses; continental vs. maritime air; biogenic VOC vs. anthropogenic VOC dominated air; old vs. young air masses arriving at the station. Specifically for acetonitrile serving as a tracer for biomass burning the impact of big wild fires to atmospheric trace compound composition should be examined in detail also using trajectory models for classifying the origin or air masses arriving at the station.

This is a similar comment to one made by Referee #1 and we would ask you to see our response to him/her as well. To briefly reiterate, your point is very well taken. However, to dig into specific source regions or particular case studies in this paper would make it prohibitively long for a journal article. We feel strongly that there is value in an overview of the kind we have presented that shows diurnal cycles, seasonal means and interannual variability for this suite of compounds. It is our intention to write further papers to better illustrate the case studies you request. We believe that this paper will be useful to illustrate how such cases (whether means determined on the basis of back trajectory source regions or short-duration event-based case studies that take advantage of the high time-resolution of the data) deviate from the seasonal means.

Critical are deposition rates calculated. Two processes in the atmosphere biasing the result have to be considered: (1) losses by chemical reaction over time and (2) dilution by advection of air masses depleted of the target compound. The first process is discussed and only situations where chemical losses are negligible are considered in the calculation. But the effect of a likely atmospheric dilution has not been addressed properly. It is required that the authors include a description of the selection process of the data used in the calculation of deposition velocities for certain compounds in the methods chapter and demonstrate that advection does not bias the results. Only those data recorded during atmospheric conditions where chemical losses and dilution is negligible must be used in the calculations. It is also recommended to distinguish between dry and wet deposition.

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This is an excellent point and we are grateful to the referee for pointing this out. The approach of Talbot et al. (2005) is very familiar to us, so we were negligent in not describing our approach more fully. We have added a section (2.3 to the Methods section) to address this point. Our analysis is intended to look at mean seasonal diurnal behavior, as a result teasing apart the relative contributions of various removal processes to the overall nocturnal depletion is beyond the scope of this paper. In the new section we have tried to clarify our use of deposition velocities in this context. It is possible however, that one could still make an argument that this term is not entirely appropriate. If the referee is still concerned that a reader may come away from this paper with an erroneous impression of what the calculated deposition velocities represent, then perhaps we may resolve such concerns by only considering rates of depletion (pptv h^{-1}). We would prefer to keep the current approach because the calculation provides a normalization of sorts by dividing the depletion rate by the mean mixing ratio of the compound of interest making comparisons between the species more direct. Perhaps another alternative would be to call the deposition velocities something slightly different, perhaps "equivalent deposition velocity" or some such. That may make it more clear that the calculations here, based on the summer mean diurnal curve encompass all loss processes. We are entirely open to working with the referee further on resolving this issue to his/her satisfaction.

Isoprene is produced mainly in the chloroplast of plants but also other organisms do so. Please correct for this in line 292.

We have added the modifier "mainly" to the sentence you request (now line 331). If you would like us to include more pathways that lead to the release of isoprene to the atmosphere (and can recommend a reference to cite), please let us know and we would be happy to incorporate them.

When discussing methanol mol fractions in ambient air the results of Harley et al. (Biogeosciences, 4, 1083–1099, 2007) should be considered.

Thank you for pointing us to this very helpful reference. We have modified our discussion of methanol (section 4.1.8, beginning at line 475) to include this reference as well as two references they cited (Hüve et al., 2007; and Keppler et al., 2004).

Technical corrections: Line 102; Apel-Riemer; please correct

That has been corrected (now line 103). Thank you for spotting that typo.

As with Referee #1, we appreciate your thoughtful consideration of this manuscript, your comments have helped us improve it. Thank you very much.

Reference

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

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 4251, 2009.

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