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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 #2

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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. 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. 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. 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. 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 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. 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. Isoprene is produced mainly in the chloroplast of plants

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but also other organisms do so. Please correct for this in line 292. When discussing methanol mol fractions in ambient air the results of Harley et al. (Biogeosciences, 4, 1083–1099, 2007) should be considered. Technical corrections: Line 102; Apel-Riemer; please correct

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

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