Atmospheric Measurement Techniques Discussions

Atmos. Meas. Tech. Discuss., referee comment RC1
https://doi.org/10.5194/amt-2021-85-RC1, 2021

Comment on amt-2021-85

Anonymous Referee #1

Referee comment on "Application of a mobile laboratory using a selected-ion flow-tube mass spectrometer (SIFT-MS) for characterisation of volatile organic compounds and atmospheric trace gases" by Rebecca L. Wagner et al., Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2021-85-RC1, 2021

The authors present measurements using a mobile laboratory equipped with a Selected-Ion Flow-Tube Mass Spectrometer (SIFT-MS) to measure 13 volatile organic compounds (VOCs) including aromatics, monoterpenes, nitrogen oxide, and more abundant species like methanol, ethanol, and acetone together with other instrumentation to measure CO2 and CH4. They provide details on the mobile laboratory setup including the online calibration of compounds. A set of measurements is presented where they perform a correlation analysis of all compounds and hierarchical clustering.

My main concern is that this study is not presenting a new method that isn't already published by previous work. Although the SIFT-MS is a great addition to the mobile lab such measurements have been performed before by higher-resolution instruments. An example is the proton transfer reaction time of flight mass spectrometer (PTR-ToF-MS) measuring hundreds of VOCs at 1-sec resolution that has been extensively used by the NOAA team but not referenced at all in the introduction. Recent example publications are from Coggon et al. (2016); Yuan et al. (2017); Coggon et al. (2018); Shah et al. (2019); Gkatzelis et al. (2021)a; Gkatzelis et al. (2021)b; Stockwell et al. (2020). TOFWERK has also been using the VOCUS for real-time measurements on their mobile lab in Europe (https://www.tofwerk.com/vocus-ptr-mobile-laboratory-video/), Aerodyne in the US e.g. for profiling natural gas production (https://www.tofwerk.com/oil-and-gas-well-emissions/), and the same type of measurements have been performed by Montrose (https://montrose-env.com/services/testing-lab-services/ptr-tof-ms-mobile-laboratory/), and the RJ Lee group (e.g. https://rjlg.com/2019/06/philadelphia-refinery-explosion-air-quality-impact/). Furthermore, a characteristic paper similarly discussing this method was published last year by Richard et al. (2020) on mobile measurements of VOCs using a PTR-ToF-MS and a membrane introduction mass spectrometry (MIMS) where they also perform more detailed Principal Component Analysis (PCA) to source apportion VOCs. This literature can be easily found by just googling "mobile laboratory measurements of VOCs" so I am surprised it is currently not covered by the authors. I am therefore not convinced that this is truly a new method. I could see how this work could be published as a complementary, possibly cheaper (?) way to perform such measurements. Of course, I leave this to the editor to decide. Nevertheless, carefully promoting all the existing work and the benefits and advantages of other studies compared to this one will be crucial, something the paper is currently lacking.

Regarding the scientific analysis of the derived data I find it to be limited to just correlations that are not fully discussed. A benefit I see from the SIFT-MS is that it can measure VOCs but also NO2. The slopes of the correlations of VOCs to NO2 could provide more insights into the pollution source. This correlation analysis would also be more informative when performed at higher resolution as a rolling correlation function. Analysis to prove whether the measurements obtained here are influenced by traffic should focus on comparisons to previous literature. What are the obtained slopes from the correlations for every few minutes of data and how do they compare to a vast literature of traffic emissions? These correlations could be done both for VOCs vs. NO2 but also VOCs vs. CO2. Also, I would expect enhancements of emission when moving to the city center. Did the authors observe that as has been seen before by various other groups (e.g. https://www.fz-juelich.de/iek/iek-8/EN/Expertise/Infrastructure/MobiLab/MobiLab_node.html)? Some timeseries plots or enhancement box-and-whiskers would be great additions here. Furthermore, the authors at points of the manuscript discuss the influence of other sources like paints and in general volatile chemical products. It would be great to compare their results to inventory estimates by McDonald et al. (2018) and paint studies e.g. Stockwell et al. (2021). While this is a measurement technique paper I do consider that science that validates the importance of performing such measurements should be included and in my opinion is currently not sufficient. Statistical methods to separate to different sources would also be valuable e.g. the use of positive matrix factorization. If this is not an option then I would consider discussing in detail the benefits of performing such statistical approaches in the future.

Overall, rewriting the introduction, focusing on what is new from these measurements, discussing the benefits compared to other published work as well as the disadvantages, and performing further analysis of the obtained data would be the main improvements before this publication is suited for AMT. Below some additional specific comments.

Specific comments

Line 211-212: Acetone, methanol, and ethanol are abundant species coming from multiple sources including atmospheric chemistry. This may drive the correlations observed here. Slopes would be interesting to have and compare to other studies. More detailed timeseries of compounds for specific events would be helpful to further conclude on possible sources.

Table 4 should be a box and whiskers figure with the y-axis representing the compound names and the x-axis the concentrations. In-city and out-of-city box and whiskers would be valuable and provide urban enhancements during the COVID-19 pandemic. Also, a more detailed discussion on the lockdown conditions during the period of the measurements would be great. A suggested reference could be the stringency index (https://ourworldindata.org/grapher/covid-stringency-index).

Technical comments:

Line 10: correct to “sources”

Line 22-32: The authors could further discuss here VOC emissions from other pollution sources in more detail. Volatile chemical products, cooking emissions, residential wood burning, and industry with their respective citations would be of value here. Also, studies that focus on the contribution of different sectors of VOC emissions would be valuable too.

Line 29: Add references. Examples for volatile chemical products could be McDonald et al. (2018), Stockwell et al. (2021), Gkatzelis et al. (2021)a,b.

Line 57-58: Many recent studies use PTR-ToF-MS in mobile laboratories that are currently not discussed. See comments above.

Line 123: Correct to “formulas”.

Line 161: delete “instrument”

References:

Coggon, M.M., Veres, P., Yuan, B., Koss, A., Warneke, C., Gilman, J., Lerner, B., Peischl, J., Aikin, K., Stockwell, C., Hatch, L., Ryerson, T., Roberts, J., Yokelson, R., and de Gouw, J. (2016). Emissions of nitrogen-containing organic compounds from the burning of herbaceous and arboraceous biomass: fuel composition dependence and the variability of commonly used nitrile tracers. Geophs. Res. Lett., 43, DOI:10.1002/2016GL070562.

Coggon, M.M., McDonald, B., Vlasenko, A., Veres, P., Bernard, F., Koss, A., Yuan, B., Gilman, J., Peischl, J., Aikin, K., DuRant, J., Warneke, C., Li, S-M., and de Gouw, J.A. (2018). Diurnal variability and emission pattern of decamethylcyclopentasiloxane (D5) from the application of personal care products in two North American cities. Environ. Sci. Technol., 52, 5,610–5,618, DOI:10.1021/acs.est.8b00506 .

Gkatzelis, G.I., Coggon, M.M., McDonald, B.C., Peischl, J., Gilman, J.B., Aikin, K., Robinson, M., Canonaco, F., Prevot, A., Trainer, M., Warneke, C. (2020) Observations confirm that volatile chemical products are a major source of petrochemical emissions in

U.S. cities, Environ. Sci. Technol., DOI: 10.1021/acs.est.0c05471.

Gkatzelis, G.I., Coggon, M.M., McDonald, B.C., Peischl, J., Aikin, K., Gilman, J., Trainer, M., Warneke, C. (2020) Identifying volatile chemical product tracer compounds in U.S. cities, Environ. Sci. Technol., 55 (1), DOI: 10.1021/acs.est.0c05467.

McDonald, B. C., de Gouw, J. A., Gilman, J. B., Jathar, S. H., Akherati, A., Cappa, C. D., . . . Trainer, M. (2018). Volatile chemical products emerging as largest petrochemical source of urban organic emissions. Science, 359(6377), 760-764. doi:10.1126/science.aaq0524.

Richards, L. C., Davey, N. G., Gill, C. G., & Krogh, E. T. (2020). Discrimination and geo-spatial mapping of atmospheric VOC sources using full scan direct mass spectral data collected from a moving vehicle. Environmental Science: Processes & Impacts, 22(1), 173-186. doi:10.1039/C9EM00439D.

Shah, R.U., Coggon, M.M., Gkatzelis, G.I., McDonald, B.C., Tasoglou, A., Huber, H., Gilman, J., Warneke, C., Robinson, A.L., Presto, A.A. (2019). Urban oxidation flow reactor measurements reveal significant secondary organic aerosol contributions from volatile emissions of emerging importance, Environ. Sci. Technol., 54 (2), 714-725, DOI:10.1021/acs.est.9b06531.

Stockwell, C.E., Coggon, M.M., Gkatzelis, G.I., Ortega, J., McDonald, B.C., Peischl, J., Aikin, K., Gilman, J.B., Trainer, M., Warneke, C. (2020) Volatile organic compound emissions from solvent- and water-borne coatings: compositional differences and tracer compound identifications, Atmos. Chem. Phys. Discuss., in review.

Yuan, B., Coggon, M.M., Koss, A.R., Warneke, C., Eilerman, S., Peischl, J., Aikin, K., Ryerson, T.B., and de Gouw, J.A. (2017). Emissions of volatile organic compounds (VOCs) from concentrated animal feeding operations (CAFOs): chemical compositions and separation of sources. Atmos. Chem. Phys, 17, 4,945–4,956, DOI:10.5194/acp-17-4945-2017.