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Interactive comment on "Physical Properties of Secondary Photochemical Aerosol from OH Oxidation of a Cyclic Siloxane" *by* Nathan J. Janechek et al.

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Emission Fluxes of Siloxanes in the Urban Atmosphere

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The paper by *Janechek et al.* investigates the atmospheric fate of cyclic volatile methyl

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siloxanes (cVMS) in laboratory (ie. flow reactor) experiments, and highlights the need of a better representation of these compounds in air quality models. While there is already an impressive body of literature on indoor and outdoor concentration measurements of siloxanes, it may not be widely recognized, that recently, urban flux data for D3-D6 siloxanes are also available, allowing to estimate area weighed emissions into the urban atmosphere. Based on these direct eddy flux measurements, urban emission patterns of siloxanes can be clearly separated from conventional combustion NMVOC (e.g. aromatics such as benzene; *Karl et al., 2018*). Based on PTR-qITOFMS eddy covariance measurements we have also observed different emission patterns among various siloxanes suggesting multiple urban sources for these species, in line with the wide application range of cVMS. New data in Innsbruck for the summer of 2018 show typical daytime area weighted emission fluxes of D3+D4+D5+D6 siloxanes around 6 pmol/m2/s (Fig 1 panel A). Siloxane mixing ratios are typically highest during night (up to approx. 6 pptv), when smaller but persisting emissions accumulate in the shallow nocturnal boundary layer (Fig. 1 (B)). Compared to typical combustion related NMVOC (e.g. benzene: Fig 1 C and D), siloxane emission fluxes tend to be more persistent during night, and particularly more pronounced during the weekday rush hour (Fig 2.). While the cyclic D5 siloxane dominates the atmospheric siloxane flux (approx. 50 %), in line with earlier findings, the contributions from D3 and D4 siloxanes (Fig 3) emitted into the urban atmosphere are also significant and seem higher compared to some reported indoor distributions (e.g. *Tang et al., 2015*), which highlights the need to quantify actual emissions into the atmosphere.

Siloxanes were detected on the following mass to charge ratios using PTR: D3 ('m223.0637 ($C_6H_{18}O_3Si_3$)H+'), D4 ('m297.0824 ($C_8H_{24}O_4Si_4$)H+'), D5 ('m355.0699 ($C_9H_{27}O_5Si_5$)+' (fragment) and 'm371.1012 ($C_{10}H_{30}O_5Si_5$)H+' (parent)), D6 ('m445.1200 ($C_{12}H_{36}O_6Si_6$)H+')

References: Karl T., et al. Urban flux measurements reveal a large pool of oxygenated volatile organic compound emissions, PNAS, 115, 1186-1191.

https://doi.org/10.1073/pnas.1714715115, 2018.

Tang, X., et al.: Siloxanes are the most abundant VOC emitted from engineering students in a classroom, Environmental Science Technology Letters, DOI: 10.1021/acs.estlett.5b00256, 2015.

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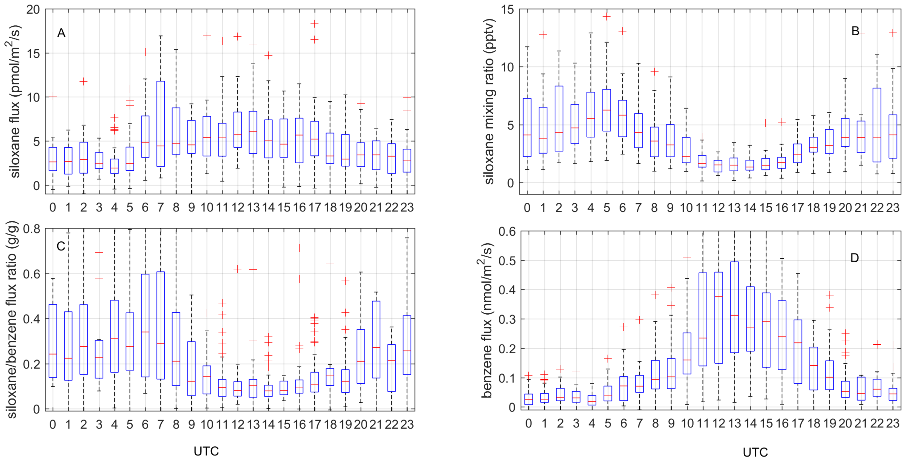

Fig. 1. Diurnal cycles of cVMS and benzene fluxes: (A) the sum of D3, D4, D5 and D6 flux; (B) ambient mixing ratios; (C) the mass flux ratio of siloxanes over benzene, and (D) benzene fluxes.

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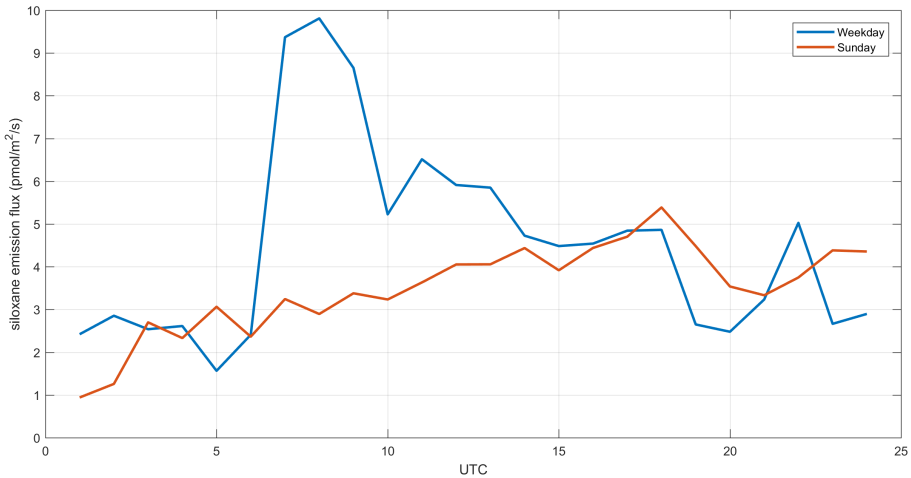

Fig. 2. Median diurnal flux profiles of siloxanes for weekdays (i.e. Tuesday-Thursday) and Sunday.

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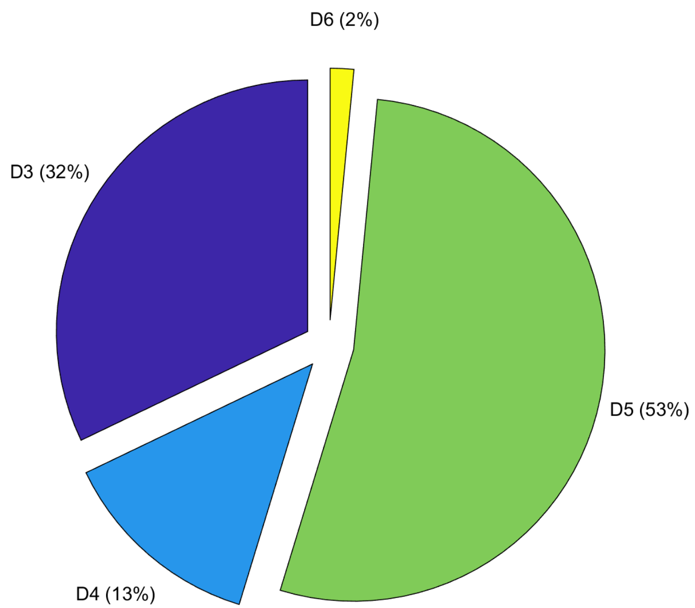

Fig. 3. Relative distribution of molar siloxane fluxes

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