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Semivolatile organic compounds monitored using a proton transfer reaction mass spectrometer at 200m above ground in rural Netherlands

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Semi-volatile organic compounds (SVOCs) are anthropogenically and naturally occurring chemical compounds that have vapor pressures such that they exist in both the gas and condensed phase at room temperature. Due to the fact SVOCs condense easily, they are interesting in the context of organic aerosol formation and these compounds impact atmospheric properties and human health. Proton Transfer Reaction Mass Spectrometry (PTR-MS, resolution \sim 1200 FWHM) is a method that facilitates deeper analysis of SVOCs. Our setup, consisting of a PTR-MS with a time of flight mass spectrometer coupled to a denuder sampler (DS) was stationed as part of the European ACTRIS-2 program at 200m

atop the Cabauw tower in the Netherlands as of September, 2016.

The DS consists of three denuders in series. The first two denuders are coated with dimethylpolysiloxane (DB1, OD 4mm, 3cm long) and consists of an assemblage of micro-channels (ID 80 micrometer). The third denuder is an activated charcoal monolith of the same dimensions but with larger (thus fewer) channels (ID 800 micrometer). The air sampled at 800mL/min is pulled through these denuders as laminar flow and the SVOCs will collide and condense on the wall. Undesirable wall losses are minimized by using a short and high flow inlet lines. The collected SVOCs are thermally desorbed under a Nitrogen (N2) gas flow and transferred to the PTR-MS through heated lines to avoid re-condensation.

Evaluation of the full mass spectra revealed over 200 different compounds in the range 15-500 Da. The majority of the mass of SVOCs was contained in m/z > 100 and typical mixing ratios of the detected SVOCs were a few pmol/mol in ambient air. Discernible contamination from the DB1 coating was detected and therefore, different blank methods have been tested and evaluated using a student T-test. Proper blank correction is an important issue of this method and will be discussed in detail.

Data from October 19th, 2016, are used as case studies for analyzing the output and results. On Oct. 19th, the highest average concentrations pertained to m/z 75.028, 219.041, 77.017, 355.100, and 429.119, were 623, 196, 149, 144 and 135 pg/m³, respectively. We observed significant carryover from the first to the second DB1 denuder. For instance, on Oct. 19th, compared to the Nitrogen blank, 193/251 compounds that collected in the first DB1 denuder were enhanced in ambient air, while 181/251 were enhanced in the second DB1 denuder. On the other hand, quantitatively, the carryover was relatively small, with roughly 76% in the first DB1 denuder and 24% in the second when considering m/z 100-475. Ambient SVOC mixing ratios of a two-week period in October 2016 will be discussed.