Intercomparison of Oxygenated Volatile Organic Compound (OVOC) Measurements in the Atmosphere Simulation Chamber SAPHIR

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Oxygenated volatile organic compounds (OVOC) are important players in tropospheric photochemistry. They are emitted from anthropogenic and natural sources but are also formed in the photochemical transformation of other VOCs. A one week experiment was carried out in order to compare different methods for the measurement of OVOCs at ambient concentrations in SAPHIR, the large (270 m^3) atmosphere simulation chamber at the Research Centre Jülich, Germany. This experiment was part of the QA Integration Task of ACCENT, the European Network of Excellence and also supported by EUROCHAMP's networking activities. Twelve groups participated in this intercomparison with fifteen analytical instruments representing a wide range of techniques. The intercomparison was conducted as a formal "blind" intercomparison with an independent referee. Atmospherically relevant OVOC species, in detail formaldehyde, acetaldehyde, butanal, hexanal, methanol, ethanol, 1-propanol, 1-butanol, methacrolein, methyl vinyl ketone, acetic acid methyl ester, acetone, benzaldehyde, and 2-methyl-3-buten-2-ol were added in defined amounts to the SAPHIR chamber. n-Butane and toluene were added as tracers for monitoring the dilution processes in SAPHIR and as reference compounds for gas chromatography. The compounds were measured at different concentration levels with mixing ratios from 0.5 ppb to 10 ppb under three different conditions: 1. OVOCs with no humidity or ozone, 2. OVOCs with humidity added (r.h. ≈ 50%), and 3. OVOCs with ozone (≈ 60 ppbv), and humidity (r.h. ≈ 50%) added. The SAPHIR chamber proved to be an excellent facility for conducting this experiment. Measurements from individual instruments were compared to mixing ratios calculated from the chamber volume and the known amount of OVOC injected into the chamber. Benzaldehyde and 1-butanol, compounds with the lowest vapour pressure of those studied, presented the most overall difficulty because of a less than quantitative transfer through some of the participants' analytical systems (Apel et al, 2008). In addition, formaldehyde measured by 6 different instruments showed the challenges still present when measuring this molecule (Wisthaler et al, 2008). The performance of each individual instrument is evaluated with respect to reference values in terms of time series and correlation plots for each compound under the three measurement conditions. A few of the instruments performed very well, closely matching the reference values, and all techniques demonstrated the potential for quantitative OVOC measurements. However, this study showed that non-zero offsets are present for specific compounds in a number of instruments and overall improvements are necessary for the majority of the techniques evaluated here.

Apel et al., Intercomparison of oxygenated volatile organic compound measurements at the SAPHIR atmosphere simulation chamber, J. Geophys. Res., 113, D20307, 2008.
Wisthaler et al., Technical Note: Intercomparison of formaldehyde measurements at the atmosphere simulation chamber SAPHIR, Atmos. Chem. Phys. 8, 2189-2200, 2008