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Combined volatility and mass spectrometric measurements of biogenic secondary organic aerosol

E. Emanuelsson (1), A. Buchholz (2), M. Hallquist (1), A. Kiendler-Scharr (2), T. Mentel (2), and C. Spindler (2)

(1) Atmospheric Science, Department of Chemistry, University of Gothenburg, Göteborg, Sweden, (2) Forschungszentrum Jülich, ICG-2, Germany

The volatility of secondary organic aerosol (SOA) from the oxidation of mixtures of biogenic Volatile Organic Compounds (VOC) has been investigated in the SAPHIR facility in Forschungszentrum Jülich, Germany, by using a Volatility Tandem Differential Mobility Analyser (VTDMA). The standard VTDMA setup comprises three main parts: 1) An initial DMA, where a nearly monodisperse size fraction of the aerosol particles is selected (typically 100 or 150 nm), 2) the oven unit, i.e. four ovens in parallel where each oven includes a heating and adsorption section where the evaporation and adsorption of the volatile fraction occurs and 3) a final SMPS (Scanning Mobility Particle Sizer) system where the residual particle number distribution is measured. For this measurement campaign the set-up also contained a Quadrupole Aerosol Mass Spectrometer (Aerodyne QAMS). The temperature of the ovens can be varied between 298 and well above 573 K. In parallel to the final SMPS the AMS was used for chemical composition and density measurements. When the system was dedicated for AMS measurements the initial DMA was bypassed to improve the aerosol concentration. However, the produced SOA has a narrow size distribution still making it possible to follow small changes in the aerosol peak diameter. A general feature of the thermo-denuder system is that a less volatile SOA gives a larger residual particle size distribution compared to more volatile SOA.

The experiments conducted were based on photochemical oxidation of selected terpene mixtures. A reference boreal mixture of terpenes, consisting of α-pinene, β-pinene, limonene, δ-3-carene, and ocimene was used as base case. Secondary organic aerosol was formed from the precursor compounds by reaction with $O_3/H_2O/OH$ in SAPHIR on the first day. The particles were kept in the chamber for up to two further days and were exposed to natural sunlight and OH radicals to initiate close to natural chemical ageing.

The VTDMA results show that SOA becomes less volatile during ageing and this ageing was further enhanced when the mixtures were exposed to sunlight. The volatility was also affected by changes in the terpene mixtures.

With the AMS we measured mass spectra of the organic aerosol particles at a reference temperature of 298 K and two additional elevated temperatures. Size distributions of the particles were obtained from the particle-time-of-flight mode of the AMS at sixteen representative m/z values. The residual total mass measured at the elevated oven temperatures was related to the total mass at the reference temperature to obtain the mass fraction remaining (MFR), which is higher for less volatile SOA. In agreement with the decreasing volatility during aging measured with the VTDMA, the MFR increases with time. An effective density of the particles was calculated comparing the mode position of the size distributions measured with the AMS and the SMPS. The effective density increases with ongoing photochemical ageing. In addition, the density of the low volatile residual particles that passed a high-temperature oven is higher than the density of particles at reference temperature. In order to investigate if the observed changes in density and volatility can be attributed to changes of the chemical composition of the particles, the mass spectra obtained at different oven temperatures and different chemical age were compared. We found that the ratio of heavy fragments ($m/z > 90$) increases with higher temperatures. Furthermore the fraction of the CO_2^+-fragment at m/z 44 to the total mass increases during the ageing process.