

## Formation of anthropogenic secondary organic aerosol (SOA) and its influence on biogenic SOA properties

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Recent field data and model analysis show that SOA is enhanced under anthropogenic influences although the SOA material itself is mainly biogenic (de Gouw et al. 2005; Spracklen et al. 2011). Such anthropogenic enhancement may affect the global SOA loading significantly. However, its mechanism is still not clear. Direct chemical interaction of BSOA and ASOA components may contribute to anthropogenic enhancement.

In order to investigate the interaction of anthropogenic SOA(ASOA) with biogenic SOA(BSOA) we studied mixtures aromatics and monoterpenes as representatives of anthropogenic VOC and biogenic VOC in the large chamber SAPHIR in Juelich, Germany (Emanuelsson et al. 2012). SAPHIR chamber allows for studies under natural OH concentrations. Particle chemistry and properties including volatility were characterized by a High resolution Time-of-Flight aerosol mass spectrometer (TAMS), off-line filter analysis by HPLC-ESI-qTOF-MS(Kristensen and Glasius 2011), and Volatile Tandem Differential Mobility Analyzer (VTDMA, (Jonsson et al. 2007)). Gas phase OH concentration was measured by a Laser Induced Fluorescence (LIF) to quantify the OH dose to which the reaction mixtures were exposed.

We found two major drivers for the time evolution of SOA volatility: OH dose and ASOA fraction. Volatility decreases with OH dose for both BSOA and ASOA (Figure 1). ASOA has lower volatility and higher O/C since its precursor needs higher OH dose before it generate significant amount of materials to condense on the particle due to their low reactivity. Generally, volatility of particle also decreases as ASOA fraction increase (Figure 1). However, ASOA components decrease the volatility of mixed ABSOA more efficient than expected by a simple linear combination of properties of pure ASOA and BSOA systems. Already a very small fraction of ASOA can decrease the volatility of ABSOA significantly likely initiating oligomerization(Kalberer et al. 2004), as shown in Figure 1 for case 10/6.

In contrast, mass yield, f44, O/C can be described by the linear combination of the corresponding properties of pure ABSOA and BSOA systems (Emanuelsson et al. 2012). Decreased volatility increases thermal persistence, suppresses one loss channel, evaporation by heating and dilution and therefore increases the lifetime of ABSOA compared to BSOA

under same conditions. Since aromatic VOCs are mainly anthropogenic (and correlate with CO), this phenomenon may contribute to the anthropogenic enhancement. This phenomenon was further investigated in a second study in order to detect oligomerization and relate it to change of optical properties.

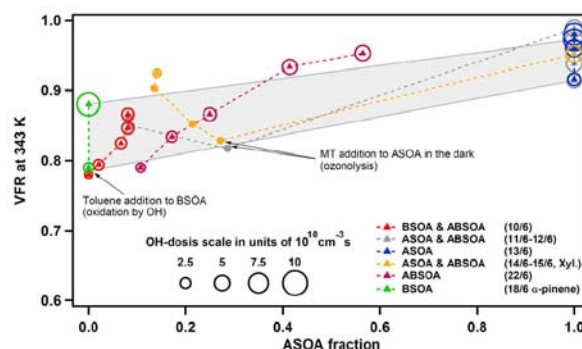


Figure 1 VFR (343K) for ABSOA experiments and BSOA experiment (18/6) as a function of the model derived ASOA fraction (triangles) with OH dose indicate by the size of the circles. The lower boundary of the shaded area is given by VFR (343K) for freshly formed aerosol at OH doses of  $\approx 1\text{-}2 \times 10^{10} \text{ cm}^{-3} \text{ s}$  for pure BSOA and of  $3.6 \times 10^{10} \text{ cm}^{-3} \text{ s}$  for pure ASOA. The upper boundary line connects pure BSOA (18/6) and pure ASOA (13/6) at about the same OH dose  $\approx 9 \times 10^{10} \text{ cm}^{-3} \text{ s}$ .

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