

Revisiting the formation of secondary organic aerosol from the photooxidation of anthropogenic precursors

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Atmospheric aerosols are known to affect climate and human health. The organic component of aerosol particles comprises about one half of the fine-particle mass on average. Recent work has shown that most of the organic-aerosol mass is oxygenated organic aerosol (OOA) (Zhang et al., 2007), which is expected to be formed mostly as secondary organic aerosol (SOA) from the oxidation of biogenic and anthropogenic volatile and semi-volatile organic compounds (VOCs and SVOCs). Air-quality models currently under-predict the concentrations of organic aerosol in the atmosphere, especially in the summer and in urban areas (Volkamer et al., 2006), suggesting that anthropogenic SOA formation is still not well understood.

A wide range of SOA mass yield values have been reported in the literature for a number of the most commonly studied anthropogenic VOCs (e.g. toluene and 1,3,5-trimethylbenzene). In this paper, we present results suggesting that the ability of key anthropogenic precursors to form SOA may have been over-estimated in the literature. The paper will discuss a series of smog chamber experiments conducted using single anthropogenic and biogenic precursors, as well as mixtures of anthropogenic and biogenic VOCs at different experimental conditions. Investigated compounds included toluene, 1,3,5-trimethylbenzene (TMB), n-heptadecane, α -pinene, β -caryophyllene and limonene. Among the studied parameters, the influence of different characteristics of chamber light spectrum on SOA formation will be discussed and related to previous anthropogenic SOA studies.

The experiments reported in this paper were conducted at the Manchester aerosol chamber (Alfarra et al., 2012), which is an 18 m³ photochemical batch reactor designed to study atmospheric processes of multicomponent aerosols under controlled and realistic conditions. An array of state-of-the-art instruments measuring aerosol composition and properties as well as

VOC precursors and their oxidation products were employed. The chemical composition of the formed SOA was measured on-line using an Aerodyne Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS). A hygroscopicity tandem differential mobility analyser (HTDMA) and a cloud condensation nuclei (CCN) counter were used to probe the hygroscopic properties and CCN activity of the aerosols in the sub- and super-saturated regimes, respectively. A proton transfer reaction mass spectrometer was used to study the evolution of the gas-phase oxidation products. The phase-state of the formed particles was inferred using a particle bounce method (Virtanen et al. (2010), Saukko et al. (2012)). A thermodenuder was used to study the volatility of secondary organic aerosol at 50 and 75 °C.

Particles from a range of experiments were collected on filters for off-line chemical speciation by liquid-chromatography coupled to mass spectrometry (LC/MS-MS). Results from this detailed analysis will be used to investigate the contribution of specific precursors to the formed SOA, and will also be linked to the particle phase state and precursor type.

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