Evolution of the complex refractive index in the UV spectral region in ageing secondary organic aerosol

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Abstract

The chemical and physical properties of secondary organic aerosol (SOA) formed by the photochemical degradation of biogenic and anthropogenic volatile organic compounds (VOC) are yet poorly constrained. The evolution of the complex refractive index (RI) of SOA, formed from purely biogenic VOC and mixtures of biogenic and anthropogenic VOC was studied over a diurnal cycle in the SAPHIR photochemical outdoor chamber in Jülich, Germany. The correlation of RI with SOA chemical and physical properties such as oxidation level and volatility was examined. The RI was retrieved by a newly developed broadband cavity enhanced spectrometer for aerosol optical extinction measurements in the UV spectral region (360 to 420 nm). Chemical composition and volatility of the particles were monitored by a high resolution time of flight aerosol mass spectrometer, and a volatility tandem differential mobility analyzer. SOA was formed by ozonolysis of either (i) a mixture of biogenic VOC (α-pinene and limonene), (ii) biogenic VOC mixture with subsequent addition of an anthropogenic VOC (p-xylene-d_{10}), or (iii) a mixture of biogenic and anthropogenic VOC. The SOA aged by ozone/OH reactions up to 29.5 hours was found to be non-absorbing in all cases. The SOA with p-xylene-d_{10} showed an increase of the scattering component of the RI correlated with an increase of the O/C ratio and with an increase in the SOA density. There was a greater increase in the scattering component of the RI when the SOA was produced from the mixture of biogenic VOCs and anthropogenic VOC than from the sequential addition of the VOCs after the approximate same ageing time. The increase of the scattering component was inversely correlated with the SOA volatility. Two RI retrievals determined for the pure biogenic SOA showed a constant RI for up to 5 h of ageing. Mass spectral characterization shows the three types of the SOA formed in this study have significant amount of semivolatile components. The influence of anthropogenic VOCs on the oxygenated organic aerosol, and the atmospheric implications are discussed.

1 Introduction

The interaction between aerosols and incoming solar radiation plays an important role in the radiative balance of Earth's atmosphere. Aerosols containing light-absorbing carbonaceous species are a major contributor to the direct and indirect effects on the climate system (Koren et al., 2008; Andreae and Ramanathan, 2013; Bond et al., 2013). Black carbon, which is the dominant absorber of solar radiation in the atmosphere, has fairly well defined optical properties with an estimate of the industrial-era mean direct radiative forcing of approximately +1.1 W m^{-2} (Bond et al., 2013). However, the optical properties of light-absorbing organic particles, or "brown" carbon (Andreae and Gelencsér, 2006), which may account for 10–40% of the total light absorption in the atmosphere, and on snow and ice (Park et al., 2010; Bahadur et al., 2012; Cappa et al., 2012; Chung et al., 2012; Kirchstetter and Thatcher, 2012; Feng et al., 2013; Bond et al., 2013), are still poorly constrained. Recent studies estimate the global radiative forcing of brown carbon to be 0.10–0.25 W m^{-2}, with higher values on regional scales (Bond et al., 2013; Feng et al., 2013). Brown carbon is mainly produced by combustion sources, especially biomass burning, but it was hypothesized that it can also be produced by atmospheric chemical reactions; for example in the formation of secondary organic aerosols (SOA). SOA can account for 71% of the total organic aerosol (OA) sources, and up to 85% when ageing of primary to secondary OA is included (Spracklen et al., 2011). It is presumed that as SOA ages in the atmosphere, high molecular weight compounds can form, subsequently enhancing light absorption. For example, Lambe et al. (2013) showed that the mass absorption coefficient (MAC) at λ=405 nm of SOA from biogenic and anthropogenic sources oxidized with OH, increases with increasing oxidation level, but has an overall negligible absorption at λ=532 nm.

It is important to understand the production of SOA from atmospheric oxidation of biogenic and anthropogenic volatile organic compounds (VOC). Estimations suggest that globally SOA is dominated by biogenic VOC precursors (BVOC), resulting in 90% biogenic SOA (BSOA) and 10% anthropogenic SOA (ASOA) (Hallquist et al., 2009). However, in many case studies, observations of SOA can only be explained assuming enhancement of SOA production by anthropogenic influences (Spracklen et al., 2011). Several studies have shown that the interaction between biogenic volatile organic compounds and anthropogenic VOCs (AVOCs) can significantly affect the properties of SOA (Kautzman et al., 2010; Glasius et al., 2011; Hoyle

et al., 2011; Spracklen et al., 2011; Emanuelsson et al., 2013a). Two recent studies have shed some light on the chemical behavior of AVOCs and BVOCs. Hildebrandt et al. (2011) studied the mass yields of SOA formed from mixtures of biogenic and anthropogenic precursors and found that the yields can be parameterized by assuming a common organic phase for partitioning, and that the SOA derived from mixtures of AVOC and BVOC (ABSOA) can be treated as an ideal mixture. Similarly, Emanuelsson et al. (2013a) found that the SOA yields and oxidation levels can be described as linear combinations of the corresponding properties of the pure biogenic and anthropogenic systems.

The complex refractive index (RI; $m = n + ik$) is one of the intrinsic optical properties of aerosols. The real (n) and imaginary (k) parts express the extent of scattering and absorption of light by the aerosol, respectively. Several studies retrieved SOA refractive indices in the laboratory (Schnaiter et al., 2003; Yu et al., 2008; Wex et al., 2009; Kim et al., 2010; Lang-Yona et al., 2010; Nakayama et al., 2010; Redmond and Thompson, 2011; Nakayama et al., 2012; Kim et al., 2012; Lambe et al., 2013; Kim and Paulson, 2013; Nakayama et al., 2013); however, recent studies exploring the evolution of the optical properties of SOA formed from mixtures of AVOCs and BVOCs are not available in the literature. Recently, it became possible to retrieve the RI of aerosols as a function of wavelength using broadband cavity enhanced spectroscopy (Washenfelder et al., 2013; Wilson et al., 2013; Zhao et al., 2013). In this paper we report the evolution of the complex refractive index in the UV spectral region of ABSOA formed from mixtures of biogenic (a mixture of α-pinene and limonene) and anthropogenic (p-xylene-d_{10}) precursors at low NO_x levels, by using the approach described in Washenfelder et al. (2013). Additionally, we explore the relationship between the SOA oxidation level, H/C ratio and volatility with the RI, by following the SOA aging process due to OH oxidation reactions in the outdoor atmospheric simulation chamber SAPHIR over a diurnal cycle.

2 Experiments, instrumentation, and methods

2.1 Experiments

The experiments took place in the outdoor atmospheric simulation chamber SAPHIR at the Forschungszentrum Jülich, in Jülich, Germany. The SAPHIR chamber has been previously

described in detail (Bohn et al., 2005; Rohrer et al., 2005); only a short description is given here. SAPHIR is a double-walled Teflon chamber with a volume of 270 m^3. It is operated with synthetic air (Linde Lipur, purity 99.9999%), and kept at a slight overpressure of about 50 Pa. To maintain the overpressure in the chamber and to compensate for the sampling by the instruments, a continuous flow of 7 – 9 m^3 h^{-1} of synthetic air is maintained throughout the experiments. A fan is used to ensure mixing of the injected trace gases, and the chamber is equipped with a Louvre system to either open and expose it to natural sun light or close it to simulate night time processes.

To measure the evolution of the generated SOA, the experiments were performed as follows: after the chamber was flushed throughout the night, synthetic air with about 40 ppm of CO_2 was injected into the chamber and the relative humidity was increased to ~75 %. Then the chosen VOCs were introduced and allowed to mix for approximately 2 hours, followed by injection of 200 ppb of ozone and opening the roof, which marks the beginning of the experiment. The SOA was allowed to age for at least 29 hours and only at the end of the experiment the roof was closed. This allowed simulation of a diurnal cycle through which the aerosols aged. Three experiments were performed in this study: 1) a mixture of biogenic VOCs, 48 ppb of α-pinene (Sigma-Aldrich, 80605-1ML, ≥98.5%; St. Louis, MO, USA) and 48 ppb of limonene (Sigma-Aldrich, 62118, ≥99%) were added as precursors with an initial OH concentration of 7.4×10^6 cm^{-3}, referred to as the BVOC experiment; 2) a sequential addition to the BVOC mixture of 39 ppb of α-pinene and 39 ppb of limonene followed by 51 ppb of p-xylene-d_{10} (Sigma-Aldrich, 175927-5G, 99 atom % D) added 5 h after the BVOCs, with an initial OH concentration of 7.8×10^6 cm^{-3}, referred to as the sequential experiment; and 3) a mixture of 42 ppb of α-pinene, 42 ppb of limonene, and 90 ppb of p-xylene-d_{10} were added as precursors with an OH concentration of 8.0×10^6 cm^{-3}, referred to as the mixture experiment. The three experiments performed are summarized in Table 1, and Fig. 1 shows a schematic of the experimental procedure.

2.2 Analytical instrumentation

The SAPHIR chamber was equipped with temperature, water content, O_3, NO, and NO_2 monitors. NO and NO_2 measurements were performed with a chemiluminescence analyzer (Eco

Physics AG, TR480, Duerten, Switzerland) equipped with a photolytic converter (Eco Physics AG, PLC760). Ozone was measured by a UV absorption spectrometer (ANSYCO GmbH, Model O341M, Karlsruhe, Germany). The detection limit and accuracy were 0.5 ppbv and 5%, respectively. Hydroxyl radical (OH) concentrations were measured using Laser induced fluorescence (LIF). The uncertainty of the OH measurement, determined by the accuracy of the calibration of the LIF instrument, is 10% (1σ). The LIF instrument is described in detail by Fuchs et al. (2012). The OH radicals in these experiments are predominantly formed from the ozonolysis of the VOCs, and to a minor extent by HONO and ozone photolysis (Rohrer et al., 2005). The absolute water content was measured with a cavity ring down Picarro analyzer (Picarro G2380, Santa Clara, CA, U.S.A), and was used to calculate the relative humidity. A spectral radiometer (Bohn et al., 2005) was used to measure the actinic flux, the VOCs' concentrations were monitored by a PTR-MS (Jordan et al., 2009), and the total particle concentration and number size distributions were measured by a condensation particle counter (UWCPC, Model 3786, TSI Inc., Shoreview, MN, USA) and a scanning mobility particle sizer (SMPS, TSI 3081 and TSI 3786). Fig. 2 shows the time series for the different chamber variables measured for each of the three experiments. The NO_x data is not shown as it was within or below detection limit for all experiments.

2.3 Measurement of SOA chemical composition

The chemical composition of the SOA was measured with a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS, Aerodyne Research Inc., Billerica, MA, U.S.A) (DeCarlo et al., 2006) operated alternatingly between the MS and PToF-mode. The MS mode (in which the ion signals are integrated over all particle sizes) was used to determine the SOA composition. The degree of oxidation of the SOA was characterized by deriving the O/C and H/C ratios (Aiken et al., 2007; Aiken et al., 2008), and by determining the ratios f_{44} and f_{43} (defined as the fractions of the signal at m/z = 44 and 43 of the total organics measured by the AMS) and applying them as suggested by Ng et al. (2010). The corrections for the errors due to gaseous components preceded the calculation of the O/C ratio, f_{44} and f_{43} according to the generalized method by Allan et al. (2004).

The density (ρ) of the particles, assuming that they are spherical, was calculated using eq. 1 (DeCarlo et al., 2004):

$$\rho = \frac{d_{va}}{d_m}\rho_o \quad (1)$$

where d_{va} is the vacuum aerodynamic diameter (obtained from the particle time-of-flight measurements from the TOF-AMS), d_m is the mode mobility diameter from the SMPS size distributions, and ρ_o is the standard density. Calculations of the density are only presented up to 15 h after the experiments began, after that time the vacuum aerodynamic diameter determination became less accurate, probably due to low particle concentrations, and consequently the ρ values became unrealistically variable. However, we do not expect the density trends and values to change significantly after this point.

2.4 Measurement of SOA volatility

The volatility of the SOA was determined with a Volatility Tandem Differential Mobility Analyzer (VTDMA), see Jonsson et al. (2007) and Salo et al. (2011) for details. The VTDMA consisted of a Differential Mobility Analyzers (DMA, TSI 3081), eight temperature controlled ovens, and an SMPS (TSI 3081, TSI 3022). First, a narrow particle size distribution was chosen with the first DMA, then the size selected aerosol was directed through one of the eight temperature controlled oven units under laminar flow conditions, and finally classified with the SMPS. To prevent re-condensation of evaporated gases, activated charcoal diffusion scrubbers were used at the exit of the ovens. Each heated oven consists of a 50 cm diameter stainless steel tube mounted on an aluminum block with a heating element set independently to temperature values between 298 to 563K ±0.1 K. The sample flow of 0.3 lpm was switched between the ovens yielding a residence time in the heated part of the oven of 2.8 s. The aerosol volume fraction remaining (VFR) was calculated assuming spherical particles (Ofner et al., 2011) for the range of elevated temperatures. The VFR decreases with increasing temperature and the data was fitted to a sigmoidal function as has been described by Emanuelsson *et. al.* (2013b). From the sigmoidal fits it is possible to obtain the temperature where 50% of the particle volume has

evaporated, $T_{VFR0.5}$. $T_{VRF0.5}$ was determined every two hours for each experiment, for particles with 100 nm diameter for the first six hours, and 200 nm diameter for the remaining time.

2.5 Measurement of SOA optical properties

A dual channel Broadband Cavity Enhanced Spectrometer (BBCES) was used to measure the aerosol optical extinction and retrieve the complex refractive indices between 360 and 420 nm (at 0.5 nm resolution). This instrument follows the design described in Washenfelder et al. (2013), and only a brief description and main differences are given here. The BBCES consist of two optical cavities and a CPC (TSI 3575) connected in series. One channel covers the 360–390 nm and the other covers the 390–420 nm spectral ranges. Incoherent light emitted from two LEDs with center wavelengths of 370.2 (M365L2, Thorlabs, Newton, NJ, USA) and 407.1 nm (M405L2, Thorlabs) is coupled into each optical cavity with two highly reflective plano-concave mirrors (Advanced Thin Films) situated opposite of each other. The light exiting the cavity is coupled into an optical fiber and transmitted to a 164 mm focal length Czerny-Turner spectrometer (Shamrock SR-163, Andor Technology, Belfast, UK) with a cooled CCD array detector (DU920P-BU, Andor Technology). The spectrometer was calibrated by a reference Hg/Ar lamp. The extinction coefficient (α_{ext}) of the aerosol is determined from the change in light intensity of the filled cavity relative to a particle-free cavity; taking into account the mirror reflectivity and the Rayleigh scattering of the carrier gas (Washenfelder et al., 2013).

It has been previously shown that by measuring several particle diameters (assuming the composition of each selected diameter to be the same) and fitting a theoretical Mie curve to the measured extinction cross sections at a specific wavelength, the RI of the aerosol can be retrieved (Pettersson et al., 2004; Lack et al., 2006; Abo Riziq et al., 2007; Lang-Yona et al., 2009; Miles et al., 2010; Bluvshtein et al., 2012; Flores et al., 2012; Washenfelder et al., 2013). The aerosol optical cross-section, σ_{ext} (cm^2), is determined by eq. 2:

$$\sigma_{ext}(\lambda, D_p, m) = \frac{\alpha_{ext}(\lambda, D_p, m)}{N(D_p)} \quad (2)$$

where λ is the wavelength of the incidence light, D_p is the particle mode diameter, m is the complex refractive index, and $N(D_p)$ is the particle number concentration (cm^{-3}). Particles were size-selected between 175–300 nm in 25nm steps (diameters larger than 250 nm could only be selected towards the end of the experiments). To measure the optical cross section of the size selected SOA from the chamber, aerosol from the SAPHIR chamber was sampled at 1360 cm^3 min^{-1}, passed through a diffusion dryer (RH < 30%), size selected with a DMA (TSI 3081) (with a sheath flow of 11.5 lpm), passed through the BBCES, and counted by the CPC. Each size selection measurement is an average of 150 spectra integrated for 0.3s. The particle concentration was corrected for dilution by the BBCES mirror purge flows (170 cm^3 min^{-1}). The measured extinction cross sections were corrected for multiply charged particles using the closest measured size distributions from the SMPS connected directly to the SAPHIR chamber and the Wiedensohler charge distribution parameterization (Wiedensohler, 1988; with subsequent erratum). Size selection measurements were done, if possible, approximately every two hours and in parallel with the thermal characterization using the VTDMA. To retrieve the real and imaginary components of the RI, the retrieval algorithm was limited to search for $n \geq 1$ and $k \geq 0$, their physical boundaries.

3 Results

3.1 Refractive indices of SOA from pure BVOC and mixtures of BVOC and AVOC

Oxidative ageing can cause changes in the RI of SOA (Liu and Daum, 2008; Cappa et al., 2011; Nakayama et al., 2012; Lambe et al., 2013; Nakayama et al., 2013), as the chemical speciation, mean molecular weight, density and polarizability of the SOA change with aging. For all retrievals in this study, the imaginary part reached zero $(^{+0.03}_{-0.00})$ at all wavelengths; in other words, there was no detectable absorption under the conditions in this study. Consequently, only the retrieved real part of the RI as a function of wavelength between 360 – 420 nm for the three different experiments performed are shown in Fig. 3. For clarity, the shown retrieved real parts are averaged every 1.5 nm and their individual errors not shown, and, for the mixture experiment, only three out of six retrievals are shown. The averaged errors for the retrievals for

each experiment are shown on the left side of each panel (red symbols; their value has no meaning).

Fig. 3a shows the results for the BVOCs experiment with the ageing induced by OH reactions. Typical NO_X levels were < 0.3 ppbv. For comparison, other studies of α-pinene SOA ageing by ozone and OH reactions are also included. Fig. 3a shows that there is no distinguishable change in the RI, within the calculated error, from the two retrievals taken at 2.5 h and 5h after the experiment began. There is only a slight spectral dependence with n values varying from 1.51 (±0.01) at λ = 360nm to 1.49(±0.01) at λ = 420 nm. Due to technical problems only two retrievals could be obtained for this experiment. The results of the sequential experiment (p-xylene-d_{10} was added five hours after SOA formation from the α-pinene and limonene mixture) are shown in Fig. 3b. For this experiment, the real part increased from a value of n=1.50(±0.01) to n=1.52(±0.01) at λ=360 nm, and from n=1.45(±0.01) to n=1.49(±0.02) at λ=420, from the first measurement at 4.5 h to 29 h of ageing. Contrary to the BVOC experiment, there is a clearer increase in the real part. Fig. 3c shows the results for the mixture experiment (the α-pinene and limonene mixture and p-xylene-d_{10} were added simultaneously). Here there is an increase in the real part of the RI from 1.5 h to 25.2 h of ageing, changing from n=1.49(±0.01) to n=1.54(±0.01) at λ=360 nm, and from n=1.45(±0.01) to 1.49(±0.02) at λ=420 nm. The three experiments show a slight spectral dependence of the real part of the RI with higher values of the real part at shorter wavelengths.

3.2 Refractive indices - literature comparison

In the past few years, several laboratory studies have retrieved the complex refractive indices of SOA generated from biogenic and anthropogenic precursors (Schnaiter et al., 2003; Wex et al., 2009; Kim et al., 2010; Lang-Yona et al., 2010; Cappa et al., 2011; Kim et al., 2012; Nakayama et al., 2012; Kim and Paulson, 2013; Lambe et al., 2013; Nakayama et al., 2013), with only a few retrieving the RIs in the near UV spectral region. For example, for SOA generated from the ozonolysis of α-pinene, Liu et al. (2013) found values of the real part of n=1.517(±0.003) and n=1.509(±0.003) for λ=360 nm and λ=420 nm, respectively, using a variable angle spectroscopic ellipsometer with initial ozone and α-pinene concentrations of 52.2 (±2.2) ppmv and 4.0(±1.4) ppmv, respectively. The imaginary components they found in this range were below $k<10^{-4}$.

Using cavity ring down spectroscopy (CRDS), Nakayama et al. (2012) retrieved values between n=1.463(±0.019) and n=1.475(±0.022) at λ=405 nm, and Nakayama et al. (2010) found values of n=1.458(±0.019) at λ=355nm. The imaginary parts for both studies were found to be below 0.003. Both studies used initial concentrations of 0.1 ppmv of α-pinene, and 1.1 – 2.6 ppmv of ozone. Wex et al. (2009) retrieved only the real part of the RI by using a white light optical particle spectrometer, and found a value of n=1.45 for the visible wavelengths. They used O_3 concentrations of up 2.5 ppmv, and α-pinene concentrations in excess of that of O_3. Similarly, Schnaiter et al. (2003) determined a constant value of n=1.44 for λ>350 nm by measuring the wavelength dependence of the SOA scattering and extinction. They generated the α-pinene SOA by admixing 470 ppb ozone, followed by the addition of 61 ppb α-pinene. Using CRDS and a photo-acoustic sensor to measure RIs Lambe et al. (2013) found values between n = 1.51(±0.02) and n=1.45(±0.04) with imaginary part values of k < 0.001 at λ=405 nm for SOA formed by homogeneous nucleation and condensation following OH oxidation of α-pinene at different oxidation levels, using a potential aerosol mass flow tube reactor.

For SOA formed by ozonolysis of limonene, we could only find one study that measured the RI in the UV spectral region. Liu et al. (2013) measured n values between 1.520(±0.003) and 1.512(±0.003) and imaginary parts below $k<10^{-4}$ for wavelengths between 420 and 360 nm. Recently, Kim and Paulson (2013) measured the real part of the RI for SOA generated from the ozonolysis of α-pinene and limonene with and without an OH scavenger in a Teflon chamber using a polar nephelometer at λ=532 nm. For both SOA products, they found that the real part of the RI increased from 1.39(±0.03) to 1.52(±0.03) as the particles sizes grew in time (up to 4 h), with no discernible effect when an OH scavenger was used.

3.3 Relationship between oxidation level and refractive index

Oxidative ageing changes the SOA's oxidation state, density, mean molecular weight, and polarizability (Katrib et al., 2005; Liu and Daum, 2008; Cappa et al., 2011; Lambe et al., 2013). O/C and H/C ratios are useful metrics to measure the oxidative state of the aerosol (Ng et al., 2010). Fig. 4 shows the change in the retrieved complex refractive index (real part only) for wavelengths between 360–420 nm as a function of the O/C ratio (Fig. 4A1, 4B1 and 4C1), H/C

ratio (Fig. 4A2, 4B2 and 4C2), and $T_{VFR\ 0.5}$ (Fig. 4A3, 4B3 and 4C3) as the SOA evolved with time.

It can be seen that for the mixture experiment, the value of the RI increases with SOA ageing. This is correlated with the SOA increasing oxidation level (Fig. 4C1): the O/C values increase from ~0.34 (±0.10) at 1.5 h to ~0.42 (±0.13) at 29 h of ageing, the H/C ratio decreases (Fig. 4C2) from ~1.55 (±0.16) to 1.49 (±0.15), and the volatility (Fig. 4C3) decreases with $T_{VFR0.5}$ increasing from ~366 K (±2) up to ~388 K (±1). There is a similar trend for the sequential experiment. However, the magnitude of the increase in RI with respect to the O/C ratio is smaller, even though the O/C ratio increased more (~0.44) for approximately the same ageing time. Furthermore, the rate of change of the RI with respect to the H/C ratio is also smaller than for the mixture experiment: the H/C ratio decreased from around 1.50 (±0.15) to ~1.45 (±0.15). There is not a clear difference between the two experiments in the dependence of the real part of the RI on volatility. For the BVOCs experiment it is difficult to assess a relationship with only two retrievals within the first 5 h of the experiment. There is only evidence that the RI remained constant (as seen in Fig. 3) with a small increase in the O/C ratio, and a slight decrease in volatility with $T_{VFR0.5}$ increasing from 365.5 K (±2.7) to 366.7 K (±2.6).

The relationship between optical properties and chemical composition has been previously explored. Table 2 summarizes the different studies that have related the RI to the O/C ratio. Lambe et al. (2013) measured the real part of the RI at λ = 405 nm for SOA formed from the OH oxidation of α-pinene, naphthalene and tricyclo-decane (anthropogenic surrogate precursors), and guaiacol (biomass burning surrogate precursor). They observed a decrease in *n* with increase in SOA oxidation level. For α-pinene, an O/C=0.42 at the beginning of the experiment, increasing to an O/C=0.93, and an RI decrease from *n* = 1.51(±0.02) to 1.45(±0.04) were obtained. They also observed a slight increase in the imaginary component of the RI from k=0 to 0.001; however, these values are very low. In contrast, Cappa et al. (2011) who studied the heterogeneous OH oxidation of squalane (a saturated hydrocarbon) and azelaic acid (a dicarboxylic acid) particles at λ=532 nm, observed an increasing trend with similar oxidation levels (O/C= 0–0.35) compared with the ones measured in this study. They measured an increase in the real part from about *n*=1.47(±0.02) at O/C=0.0 to about *n*=1.52 at O/C=0.35 for squalene, and from *n* = 1.46 to 1.55 for azelaic acid at O/C ratios from 0.45 to 0.75. Nakayama et al. (2013) also saw an increasing trend studying the RI of SOA generated from the photooxidation

of toluene (an aromatic hydrocarbon). At λ=405nm the real part increased from n = 1.449(±0.030) to n = 1.567(±0.042), and at λ=532nm from n = 1.431(±0.026) to n = 1.498(±0.025) for O/C values from 0.64 to 0.73. Nakayama et al. (2012) retrieved RI values for SOA produced from the ozonolysis and photooxidation of α-pinene, and found values from n = 1.463(±0.019) to n = 1.475(±0.022) at λ=405 nm and n = 1.476(±0.021)–1.458(±0.020) at λ=532 nm for O/C ratios from 0.43 to 0.47. Therefore, it is difficult to assess a decreasing or increasing trend from the Nakayama et al. (2012) study.

3.4 Chemical ageing

To help assess the chemical changes in the different SOA and compare them to literature values, Fig. 5 shows a van Krevelen diagram (van Krevelen, 1950) of the H/C ratio as a function of the O/C ratio. Fig. 5a shows that the H/C ratio for the BVOC and sequential experiment show a similar behavior, the H/C ratio remains nearly constant for the first few hours of the experiment and then decreases. For the BVOC experiment the H/C ratio starts at around 1.50 and decreases to about 1.40, and in the sequential experiment begins at 1.51 that decreases to ~1.43. The mixture experiment, however, shows an increase of the H/C ratio in the first few hours of the experiment, from 1.51 to 1.57, followed by a decrease to ~1.49 at the end of the experiment.

In the evolution of the O/C and H/C ratios there are three distinct features: 1) the initial increase in the H/C ratio, especially seen in the mixture experiment; 2) the increase of the O/C ratio during day time with the H/C remaining almost constant; and 3) the O/C remaining constant, even decreasing, during night time while the H/C decreased. The initial increase of the H/C to O/C ratio occurs in the phase of vigorous chemistry and particle growth at the instance ozone is added. There are two overlapping processes occurring in this stage: chemical ageing, which increases the O/C ratio and lowers the H/C ratio (e.g. pinic acid, multiple ketones), and fast growth by dissolution of semivolatile oxidized products, which maintains the O/C ratio of the precursors (e.g. pinonic acid, pinonealdehyde, hydroperoxides), but has an increasing effect on the H/C ratio. The strongest effect in the initial increase of the H/C ratio, with the simultaneous O/C increase, is clearly seen in the mixture experiment. This may be due to the oxidation conditions, or it could reflect the influence of p-xylene-d_{10}. The difference is not clear as the three experiments began with similar temperatures, RH values, pressure and OH

concentrations (Fig.2). However, the initial ozone concentration and solar radiation exposure were lower for the mixture experiment than for the other two experiments.

Following this initial stage, the mixtures are photochemical aged, with an OH concentration of about 2-3×10^6 molecules cm^{-3} (see Fig. 2 middle panels) for the three experiments. Here there are slight differences in the O/C values between the BVOC and sequential experiment. This might be caused by either the addition of p-xylene-d_{10} 5h after the insertion of the α-pinene-limonene mixture, or the specific oxidation conditions. However, there were no significant differences between the experimental initial conditions, neither the meteorological condition nor the VOC and O_3 concentrations.

During the night the O/C ratio remained constant, showing a slight decrease in the BVOC and sequential experiments, while the H/C ratio decreased. The slight decrease of O/C overnight might be due to reactions in the particulate phase (e.g oligomerization). The observed decrease in the H/C ratio during the night is probably caused by the dilution flow into the chamber which depletes the gas phase, including semivolatile oxidized compounds, leading to their evaporation. The excess of semivolatiles, caused by the high initial load of monoterpenes ceases at the end of the night and onset of the next day. This is seen by the simultaneous decrease of H/C and O/C; at this stage the molecules were converted to higher oxidized generations by OH reactions during the second day.

4 Discussion

By comparing the H/C and O/C ratios measured in this study to values measured in different cities around the world (Fig. 5b), it is clear that the SOA in this study is less oxidized. The fact that the SOA is not as oxidized may explain the lack of absorption observed, though Nakayama et al. (2012) measured similar values of the H/C and O/C ratios and also found negligible absorption. Cappa et al. (2011) with higher values of the H/C ratio and lower values of the O/C ratio assumed purely scattering particles. Lambe et al. (2013) which were able to age BSOA formed from OH oxidation of α-pinene (Fig. 5b, red triangles) up to an O/C = 0.93 and an H/C=1.1 only saw an increase in the imaginary component from k = 0 to k = 0.001. And for ASOA, formed from the OH oxidation of naphthalene, they saw an increase in k up to 0.0035 for an O/C = 1.3 and H/C = 0.84. Only Nakayama et al. (2013) saw slightly higher absorption at O/C

ratios between 0.64 – 0.73, but for SOA generated from the photooxidation of toluene at different NO_x levels, with measured *k* values between 0.0018(±0.0014) and 0.0072(±0.0010) at λ = 405 nm.

The values of the real part retrieved in this study are within the values reported in the literature; however, there is a significant span in the real part, from *n*=1.44 to *n*=1.58, among all the studies (for example, see the values at λ=405nm in Table 2 and Fig.3). The differences in RI values suggest differences in the SOA chemical composition, which can arise from several different factors; for example, the initial VOC and its concentration, oxidant levels, formation temperature and relative humidity, the residence times in either the flow tubes or chamber experiments, and the experimental procedure. The differences in the SOA chemical composition from different initial VOC concentration (which will directly influence the initial mass concentration) seems unlikely; on the one hand, Bateman et al. (2011) and Walser et al. (2008) demonstrated that the composition of limonene + O_3 SOA formed in either a smog chamber with low mixing ratios (<0.1 ppmv) or a flow tube with significantly higher (~10 ppmv) mixing ratios, is similar. On the other hand, Shilling et al. (2009) saw small composition differences of α-pinene SOA when mass concentrations were above 20 μg m^{-3}. All the studies reported here used mass concentration greater than 20 μg m^{-3}; hence, no significant differences in the RIs would be expected. The oxidation level may perhaps explain the differences; however, there are no clear trends from the available studies. For example, Lambe et al. (2013) showed that the real part of the RI decreases with increasing oxidation, and Liu et al. (2013) mentioned that the low oxidation level of their SOA (from Shilling et al. (2009) this would correspond to an O/C < 0.3 as the mass loading was > 140 μg m^{-3}) could possibly explain that their measured *n* values are higher than the other reported values. In contrast, Cappa et al. (2011) and Nakayama et al. (2013) observed the opposite trend; i.e., an increase in the real part with increasing O/C ratio, which is the same trend observed in this study. The initial increase in the real part of the RI in this study might be explained by the change in the SOA density. One form of the Lorentz-Lorentz relation associates the RI to the mean polarizability (α), the molecular weight (MW) and the density of the particle:

$$\frac{(n^2-1)}{(n^2+2)} = \frac{\alpha \cdot \rho}{3 \cdot MW} \quad (5)$$

Furthermore, Liu and Daum (2008) showed that the real part of the refractive index increases with mass density, and Katrib et al. (2005) showed the density of layers of oleic acid increases as the oxygen content also increases. Fig. 6a shows the change in SOA density with time for the three experiments; only values up to 15 h after the experiments began are shown, and Fig. 6b shows the change in RI vs. density. Fig. 6b clearly shows the concomitant increase in the real part of the RI and density for the sequential and mixture experiments, while Fig. 6a demonstrates the ρ increase for all experiments and the distinct differences in change of density with time among the three experiments. For example, the BVOC experiment shows the lowest values up until about 14 h after the beginning of the experiment, when it acquires the same values as the sequential experiment, while the mixture experiment shows consistently higher values than the BVOC and sequential experiments. The increase in ρ seen in Fig. 6b can help explain the increase in the real part of the RI seen in the mixture (Fig. 4C1) and sequential experiments (Fig. 4B1), and assuming the trends between the experiments remain the same up to 30 h after the experiments began, the greater increase in the RI in the mixture experiment. Fig. 6b also demonstrates the influence of the MW due to the addition of p-xylene-d_{10}, as the initial RI for the BVOC experiment is higher than the sequential and mixture experiments.

The increase in the density from 4.5 h to 7 h after the beginning of the experiment seen in the sequential experiment occurred practically under dark conditions (see Fig. 2 j(NO2) values). This might be attributed to a combination of a few processes: condensation of ozonolysis products, oligomerization and evaporation of more volatile material from the particles. Between 4.5 h and 7 h the photochemistry and oxidation of p-xylene-d10 stopped due to the lack of sunlight, but O3 and some monoterpenes were still present. Furthermore, the O/C ratio slightly decreased in that period. This indicates that either ozonolysis products with smaller O/C ratios than the products from photo-chemistry condensed onto the SOA, or that non-oxidative liquid phase processes of glyoxal-like structures (i.e., oligomerization) took place at the same time, such as condensation reactions that can lower the O/C ratio, but still compact the particles.

5 Atmospheric relevance and implications

To assess the atmospheric relevance of the SOA measured in this study Fig. 7 shows the f_{44} vs. f_{43} ratio measured for the three experiments presented here. Ng et al. (2010) suggested that the ratio f_{44}/f_{43} can be used to estimate the degree of oxidation and volatility, within the oxygenated organic aerosol (OOA) components; they defined the less oxidized components (lower f_{44}) as semi-volatile OOA and the more oxidized (higher f_{44}) as low-volatility OOA. In other words, a low f_{44}/f_{43} value can be used as an indication of semi-volatile OOA and a higher f_{44}/f_{43} value indicates lower volatility OOA. The triangle in the insert in Fig. 7 shows the area proposed by Ng et al. (2010) which encompasses the majority of the OOA measured in the field. It can be seen that the SOA studied here fall within the lower right section of the triangle and are overall similar, suggesting that the SOA formed in these experiments may be semi-volatile. Furthermore, Fig. 7 shows that for all three experiments the f_{44} signal increases and f_{43} decreases as the SOA age, from approximately f_{44} = 0.05 to ~0.08 to 0.10 and from f_{43} = 0.16 down to ~0.12, confirming that the SOA became less volatile with time, as shown in Figs. 4B3 and 4C3. Moreover, whereas there is no distinguishable difference in the f_{44}/f_{43} signals between the BVOCs and sequential experiment, the mixture experiment has a lower f_{43} signal at a given f_{44} suggesting that BSOA have less volatile components (f_{43}) than ABSOA at the same degree of oxidation (f_{44}). It further suggests that the interaction of p-xylene-d_{10} with α-pinene and limonene in the mixture experiment can change the chemical and volatility properties of the ABSOA formed in comparison to the properties of BSOA; whereas the interaction of p-xylene-d_{10} with BSOA in the sequential experiment does not significantly alter the chemical and volatility properties. However, overall the mass spectral characteristics do not show enough differences to distinguish the influence of anthropogenic VOCs on the oxygenated organic aerosol. Fig. 7 also shows that even though the BSOA and ABSOA were not oxidized significantly and the initial BVOC and AVOC concentrations are higher than atmospherically relevant concentrations, the oxidation and volatility levels of the SOA fall within an atmospherically relevant range; specifically at the edge of large f_{43}, i.e. there is large influence of semivolatiles.

6 Conclusions

We have measured the evolution of the complex refractive index in the UV spectral region, between 360 and 420 nm, of BSOA and ABSOA formed from three different mixtures of

biogenic (a mixture of α-pinene and limonene) and anthropogenic (p-xylene-d_{10}) VOCs at low NO_x levels. Additionally, we have explored the relationship of the oxidation level, H/C, and volatility with the RI as the SOA ages due to OH oxidation in the outdoor atmospheric simulation chamber SAPHIR over a diurnal cycle. One experiment consisted of pure BSOA produced from a 1:1 mixture of α-pinene and limonene, the other two experiments consisted of ABSOA, one with the ABSOA produced from the sequential addition of a 1:1 mixture of α-pinene and limonene followed by p-xylene-d_{10}, and the other with the ABSOA produced from a mixture of α-pinene, limonene and p-xylene-d_{10}. We found an increase in the real part of the RI with ABSOA ageing, and no detectable absorption in any of the experiments. Furthermore, we observed a correlation between the increase in the real part of the RI and the increase of the O/C ratio, with a greater increase in RI when the ABSOA is produced from the mixture of BVOCs and AVOC than from the sequential addition of the VOCs after the approximate same ageing time. This suggests the interaction of BVOCs and AVOCs can make the ABSOA a more scattering aerosol. The increase in the real part points to the fact that it can be associated with an increase in the aerosol density. On the other hand, we only have RI retrievals up to 5 h of ageing for the BSOA and could not assess how much the real part increases, if at all, over a diurnal cycle. We also observed differences in the volatility and the H/C ratio between the BSOA and the ABSOA. From analyzing the f_{44} vs. f_{43} ratios measured for the three experiments, all three types of SOA can be considered semi-volatile oxygenated organic aerosols, and it is suggested that the interaction of AVOC and BVOC can form ABSOA with different chemical and volatility properties than pure BSOA of BSOA that interacts with AVOC. A caveat with respect to generalization of the results obtained in this study is that the SOA measured is less oxidized than SOA measured in different cities around the world. The O/C values in the three experiments ranged from ~0.35 to 0.44, whereas the ones measured in the field are between 0.54 and 1.02.

The results from this study are representative of clean conditions due to the low NOx conditions used. Furthermore, they demonstrate that the optical properties of SOA are influenced by the interaction of BVOCs and AVOCs, are in continuous evolution, and the magnitude of their change depends explicitly on the formation mechanism of the SOA.

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Table 1. Description of the experiments performed in this study

Experiment	Description	VOC (ppb)	Initial [OH] ($\times 10^6$ molec. cm^{-3})	[NO_x] (ppbv)	Local time experiments began	Total duration
BVOCs	BVOCs mix only	α-pinene, limonene (48, 48)	7.4	< 0.25	11:30	~50 h.
Sequential	BVOCs mix & p-xylene-d_{10} (p-xylene-d_{10} added 5h after BVOCs mix)	α-pinene, limonene (39, 39) p-xylene-d_{10} (51)	7.8	< 0.30	11:37	~ 29 h.
Mixture	BVOCs mix & p-xylene-d_{10} (added together)	α-pinene, limonene (42, 42) p-xylene-d_{10} (90)	8.0	< 0.25	11:33	~ 29.5 h.

Table 2. Real parts of the RI for different O / C ratios in this study compared with literature values

Real part (n) of the RI	O/C atomic ratio	VOC (Initial conc. in ppmv)	SOA formation	Ini. [O_3] (ppmv)	Ini. [OH] ($\times 10^{10}$ molec. cm^{-3})	Exposure time	Wavelength (nm)	Reference
1.50(±0.01) – 1.49(±0.01)	0.37 – 0.38	α-pinene + limonene (0.048 + 0.048)	ozonolysis and OH oxidation	0.2	0.00074	up to 50 h	405	This work
1.46(±0.01) – 1.50(±0.02)	0.39 – 0.44	α-pinene + limonene + p-xylene-d_{10}[a] (0.039 + 0.039 + 0.051)	ozonolysis and OH oxidation	0.2	0.00078	up to 29 h	405	This work
1.46(±0.01) – 1.51(±0.01)	0.35 – 0.42	α-pinene + limonene + p-xylene-d_{10} (0.042 + 0.042 + 0.090)	ozonolysis and OH oxidation	0.2	0.00080	up to 29.5 h	405	This work
1.511 (±0.003)	< 0.3	α-pinene (4.0±1.4)[b]	ozonolysis	52.2±2.2[b]	Scavenger[c]	~38 sec	405	Liu et al. (2013)
1.514 (±0.003)	< 0.3	limonene (3.0)	ozonolysis	30±0.5			405	Liu et al. (2013)
1.51(±0.02) - 1.45(±0.04)	0.42 – 0.93	α-pinene (NA)	OH oxidation	NA			405	Lambe et al. (2013)
1.66(±0.04) – 1.58(±0.06)	0.52 – 1.29	naphthalene (NA)	OH oxidation	NA	22(±11) – 150(±20)	~100 sec.	405	Lambe et al. (2013)
1.55(±0.01) – 1.53(±0.01)	0.70 – 1.14	guaiacol (NA)	OH oxidation	NA			405	Lambe et al. (2013)
1.54(±0.01) – 1.48(±0.01)	0.37 – 0.89	tricycle[$5.2.10^{2,6}$]decane (NA)	OH oxidation	NA			405	Lambe et al. (2013)
1.449(±0.030) – 1.567(±0.043)	0.64 – 0.73	toluene (4.0)	photooxidation	NA	~27	up to 4 h	405	Nakayama et al. (2013)
1.431(±0.026) – 1.498(±0.025)	0.64 – 0.73	toluene (4.0)	photooxidation	NA			532	Nakayama et al. (2013)
1.475(±0.022) – 1.498(±0.030)	0.43 – 0.47	α-pinene (0.1)	ozonolysis and photooxidation	1.1 and 2.6	~27	up to 4 h	405	Nakayama et al. (2012)
1.476(±0.021) – 1.458(±0.02)	0.43 – 0.47	α-pinene (0.1)	ozonolysis and photooxidation				532	Nakayama et al. (2012)
1.47(±0.02) – 1.52(±0.00)	0 – 0.35	squalene (NA)	OH oxidation	NA	0 – ~200	37 sec.	532	Cappa et al. (2011)
1.47(±0.02) – 1.54(±0.00)	0.45 – 0.75	azelaic acid (NA)	OH oxidation				532	Cappa et al. (2011)

[a]p-xylene-d_{10} was added 5h after; [b]Average of four experiments; [c]Butanol was used as an OH scavenger; NA: not available

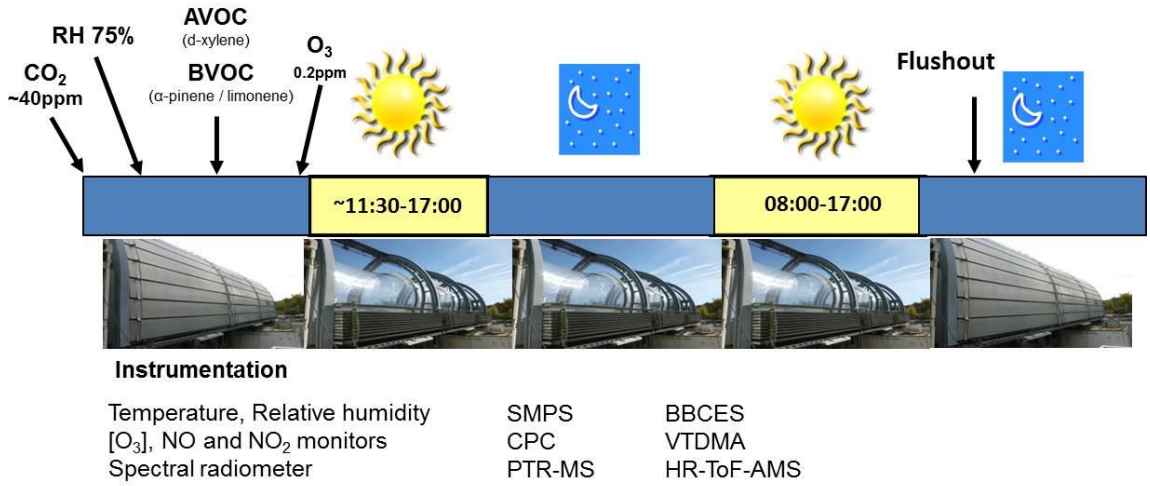

Figure 1. Schematic of the experimental procedure and instrumentation used for measuring the evolution of secondary organic aerosol over a diurnal cycle. All experiments began around 11:30 hrs. local time.
Acronyms:
SMPS – Scanning mobility particle sizer
CPC – Condensation particle counter
PTR-MS – Proton transfer reaction - mass spectrometer
BBCES – Broadband cavity enhanced spectrometer
VTDMA – Volatility tandem differential mobility analyser
HR-ToF-AMS – High resolution – time of flight – aerosol mass spectrometer

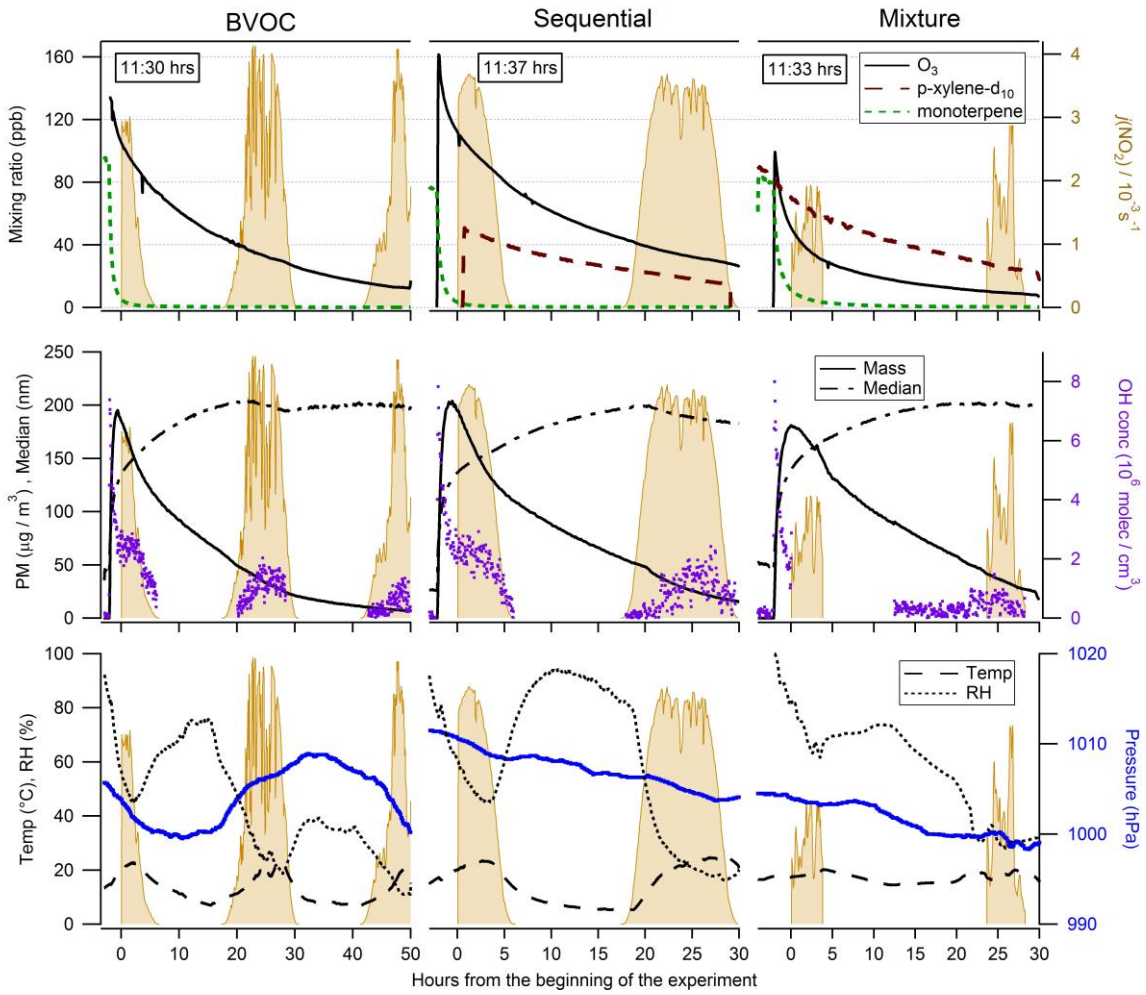

Figure 2. Time series of the three experiments performed. The BVOC experiment is shown in the left panel, the sequential experiment in the middle panel, and the mixture experiment is shown in the right panel. The mixing ratio of ozone (black line), the mixture of α-pinene and limonene (monoterpenes; dotted green line), and p-xylene-d_{10} (red dashed line) are shown in the top panels. The total mass (black line), median diameter (black dash-dot line), and OH concentration (purple dots) are shown in the middle panels. The temperature (black dash line), relative humidity (black dotted line), and pressure (blue dots) are shown in the lower panels. The photolysis rates of NO_2 (orange area) are presented in all panels to indicate the diurnal cycles; the rate values are shown in the right top axis. NO_x levels were below 1ppbv and are not shown here. The local time at which each experiment began is shown in the top panels.

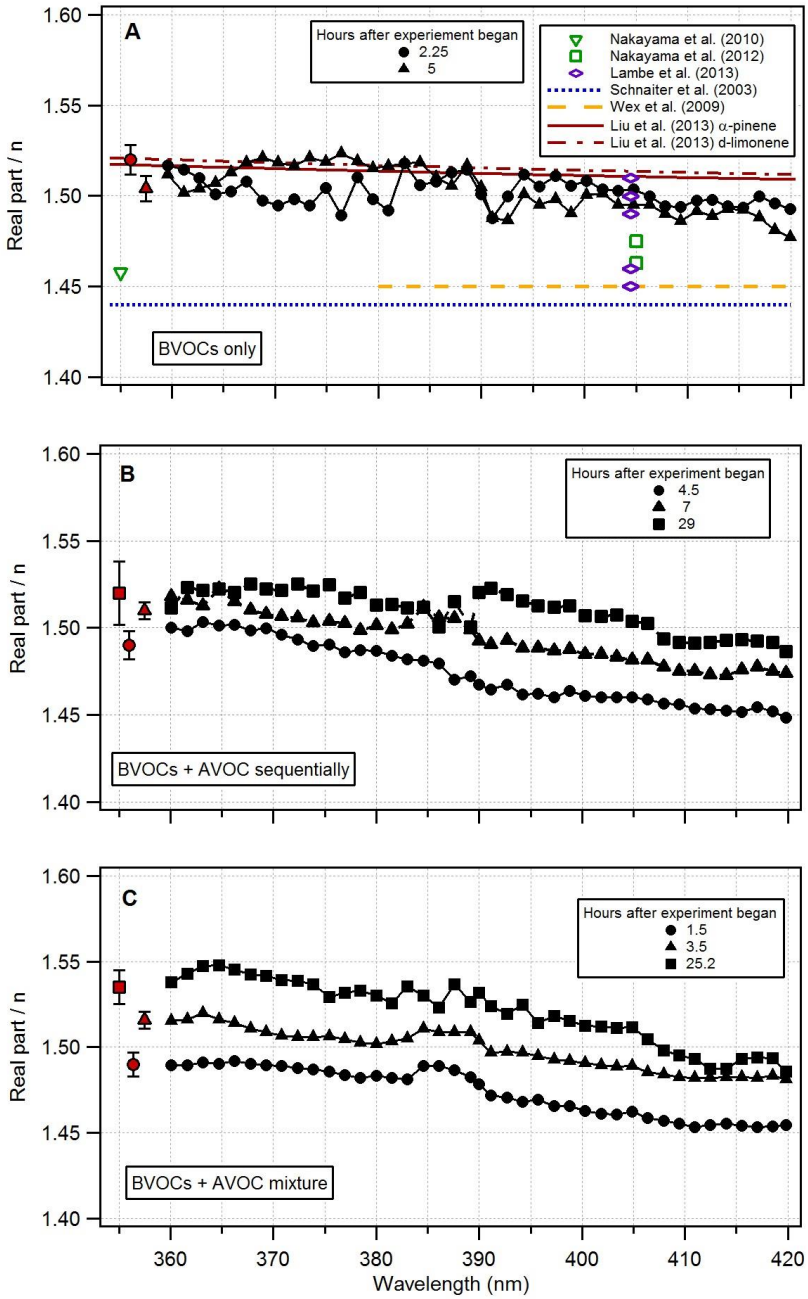

Figure 3. Change of the real part of the complex refractive index vs. wavelength as a function of time for SOA produced from (A) only a mixture of α-pinene and limonene, compared to literature values of the real RI of α-pinene; (B) a mixture of α-pinene and limonene followed by the addition of p-xylene-d_{10} 5 h after, and (C) a mixture of α-pinene, limonene and p-xylene-d_{10} (only 3 retrievals are shown for clarity). The averaged error bars of the retrieved RI values are shown as the red markers on the left for clarity. The average errors for the retrievals in (A) are: 0.008(±0.008), and 0.006(±0.005) for 2.25 h and 5 h, respectively. The average errors for the retrievals in (B) are: 0.005(±0.008), 0.004(±0.001), and 0.018(±0.007) for 4.5 h, 7 h, and 29 h, respectively. The average errors for the retrievals in (C) are: 0.007(±0.006), 0.004(±0.003), and 0.010(±0.004) for 1.5 h, 7 h, and 25.2 h, respectively.

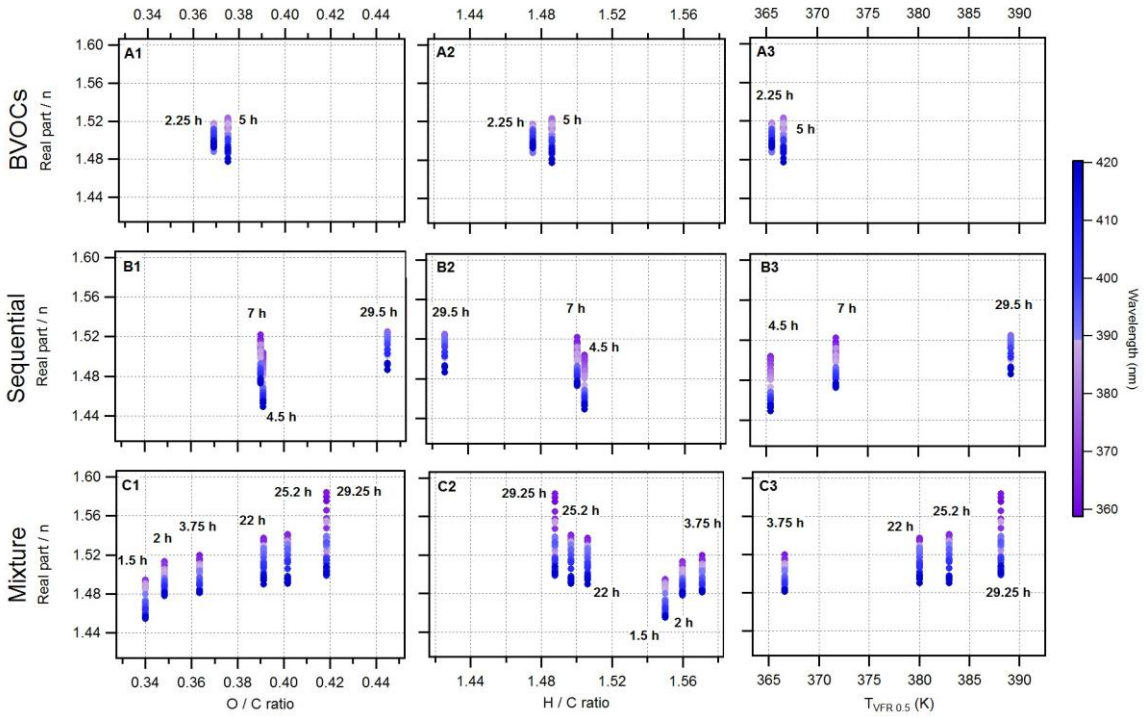

Figure 4. The change in time (given in hours, shown next to the retrieved values) for the retrieved real part of the RI as a function of O / C ratio (panels A1, B1 and C1), H / C ratio (panels A2, B2 and C2), and $T_{VFR\ 0.5}$ (the temperature at which the volume fraction remaining was reduced by half, panels A3, B3 and C3). The top panels – A1, A2 and A3 – show the results for the SOA produced from a 1 to 1 mixture of α-pinene and limonene. The middle panels – B1, B2, and B3 – show the results for the SOA produced from the mixture of α-pinene, limonene, and p-xylene-d_{10}. The lower panels – C1, C2, and C3 – show the results for the SOA produced from the sequential addition of the mixture of α-pinene and limonene followed by p-xylene-d_{10}. The color scale indicates the measured wavelength. The error bars for the O/C (31%), H/C (10%), and $T_{VFR\ 0.5}$ are not shown for clarity. The average error for the $T_{VFR\ 0.5}$ is 2.3 K.

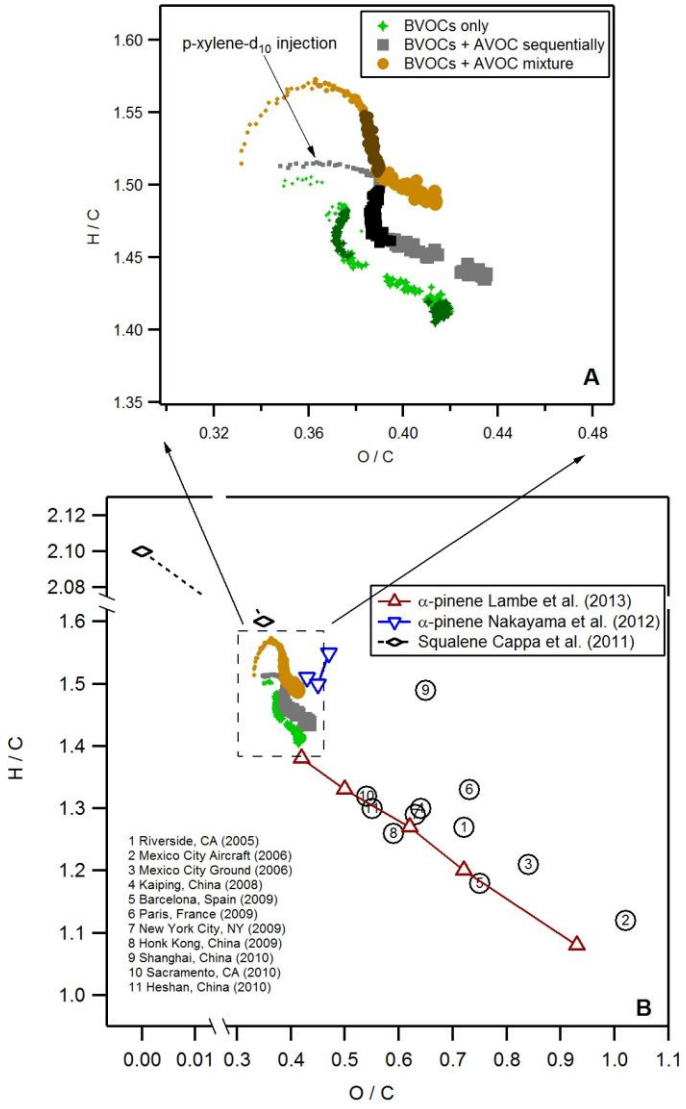

Figure 5. Van Krevelen diagram showing the ratio of H/C to O/C measured for the three experiments performed in this study: a mixture of α-pinene with limonene (green diamons), a mixture of α-pinene with limonene with a sequential addition of p-xylene-d_{10} (grey squares), and a mixture of α-pinene, limonene and p-xylene-d_{10} (orange circles). The change in marker size depicts time; smaller markers refer to the beginning of the experiment, and larger markers to the end. The top panel (A) shows specifically the three experiments performed in this study. The darker colours depict night time. In the lower panel (B), the results are compared to the low volatility oxygenated organic aerosol factors from HR-AMS field campaigns (numbered circles, adopted from Daumit et al. (2013)), results for α-pinene SOA from Lambe et al. (2013) (red triangles), and Nakayama et al. (2012) (blue inverted triangles), and squalene SOA from Cappa et al. (2011) (black rhombus).

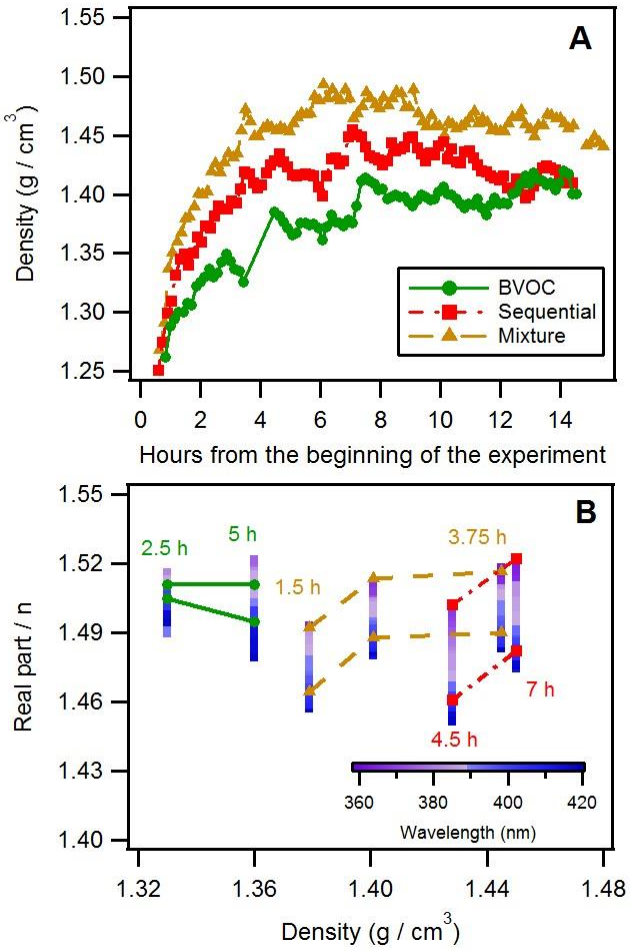

Figure 6. A) Time series of the density measured for the BVOC (green circles), the sequential (red squares); and the mixture (orange triangles) experiment. B) The change in time of the real part of the RI vs. density for each experiment performed. The colour bars show the span in the RI for the wavelengths measured, the time span between the measurements is written above (for the BVOC and sequential experiments) and below (the mixture experiment) each set of measurements.

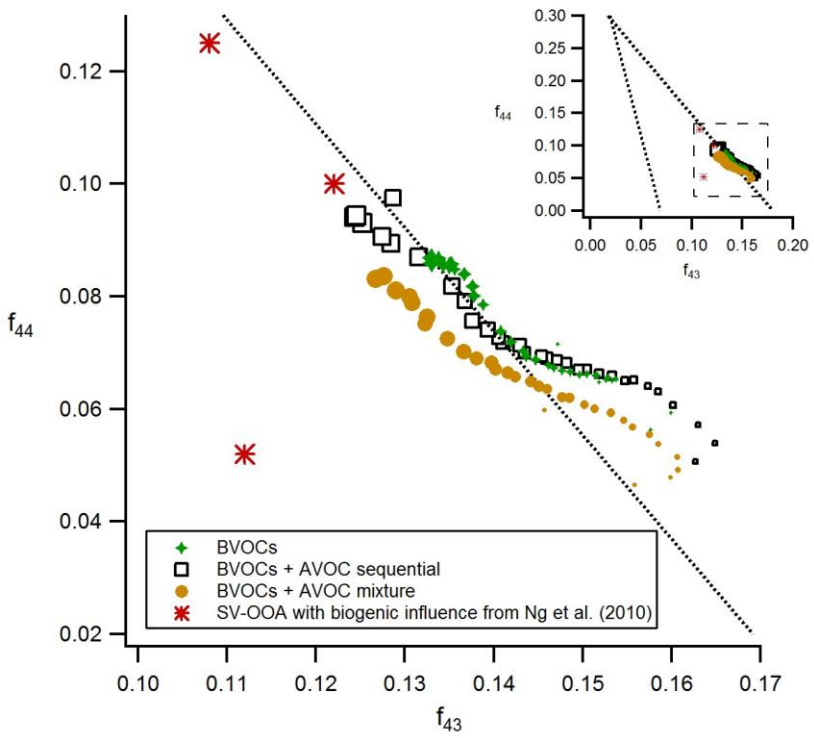

Figure 7. f_{44} vs. f_{43} for the SOA produced from the mixture of α-pinene and limonene (green diamonds), from the sequential addition of the mixture of α-pinene and limonene followed by p-xylene-d_{10} (black squares), and from the mixture of α-pinene, limonene, and p-xylene-d_{10} (orange circles). The change in size of the markers depicts time; smaller markers refer to the beginning of the experiment, and larger markers to the end. The insert shows the total triangular area (dotted lines) that represents the common values of ambient oxygenated organic aerosol components, adapted from Ng et al. (2010).