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Mixing times of organic molecules within secondary organic aerosol particles: a global planetary boundary layer perspective

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15 **Abstract.**

When simulating the formation and life cycle of secondary organic aerosol (SOA) with chemical transport models, it is often assumed that organic molecules are well mixed within SOA particles on the time scale of 1 h. While this assumption has been debated vigorously in the literature, the issue remains unresolved in part due to a lack of information on the mixing times within SOA particles as a function of both temperature and relative humidity. Using laboratory data, meteorological fields and 20 a chemical transport model, we determine how often mixing times are < 1 h within biogenic SOA in the planetary boundary layer (the region of the atmosphere where SOA concentrations are on average the highest). Based on laboratory viscosity measurements, we show that the mixing times are < 1 h most of the time (≥ 94 % of the occurrences) when the SOA concentrations are significant. In addition, we show that a reasonable upper limit to the mixing time for most locations is 30 min. Additional measurements are needed to explore further the effect of oxidation level, oxidation type, and gas-phase 25 precursor on the viscosity and diffusion within biogenic SOA; nevertheless, based on the available laboratory data, the assumption of well mixed SOA in chemical transport models seems reasonable for biogenic SOA in most locations in the planetary boundary layer. On the other hand, slow diffusion in biogenic SOA may still be important in the PBL for heterogeneous chemistry. Slow diffusion in biogenic SOA will also be more important in the free troposphere where both the temperature and RH are lower than in the PBL. Mixing times within anthropogenic SOA can be longer than mixing times 30 within biogenic SOA, at least a room temperature, but additional studies of viscosities or diffusion rates of organic molecules within anthropogenic SOA as a function of both temperature and RH are needed to better constrain how often mixing times are > 1 h within anthropogenic SOA in the PBL.

1. Introduction

Secondary organic aerosol (SOA) is formed in the atmosphere when volatile organic compounds from biogenic and anthropogenic sources are oxidized by a complex series of reactions to form semivolatile organic compounds (SVOCs), followed by condensation of the lowest volatility products or reactions of the SVOCs in the particle phase (Ervens et al., 2011; Hallquist et al., 2009). The term "secondary" indicates the aerosol is formed in the atmosphere rather than emitted directly into the atmosphere. Globally, SOA from biogenic sources dominate, with SOA from anthropogenic sources contributing approximately 10% to the total SOA budget (Hallquist et al., 2009; Spracklen et al., 2011). Major contributors to biogenic SOA are oxidation of α-pinene and isoprene (Hu et al., 2015; Kanakidou et al., 2005; Pathak et al., 2007), and as a result SOA derived from α-pinene and isoprene are the most widely used representatives of biogenic SOA in experimental and modelling studies.

The planetary boundary layer (PBL) is the lowest part of the atmosphere, ranging from the Earth's surface to roughly 1 km in altitude, depending on location and time (Wallace and Hobbs, 2006). Within this region vertical mixing of air masses is rapid and on the order of 30 min (Wallace and Hobbs, 2006). In addition, within the PBL the temperature varies from roughly 265 K to 305 K and the relative humidity (RH) varies from roughly 20 % to 100 % (see below). SOA concentrations are also on average highest in the PBL (Heald et al., 2011; Wagner et al., 2015).

When simulating the formation, growth, and evaporation of SOA particles with chemical transport models, it is often assumed that SVOCs are well mixed within SOA particles on the time scale of 1 h (Hallquist et al., 2009). If SVOCs are not well mixed within SOA particles on this time scale, then chemical transport models could incorrectly predict SOA mass concentrations by up to an order of magnitude (Shiraiwa and Seinfeld, 2012) and incorrectly predict the size of SOA particles (Zaveri et al., 2014), with implications for air quality and climate predictions (Seinfeld and Pandis, 2006). Recent research has shown that mixing times of organic molecules within SOA particles can be > 1 h at room temperature and low RHs (Abramson et al., 2013; Grayson et al., 2016; Liu et al., 2016; Perraud et al., 2012; Renbaum-Wolff et al., 2013; Song et al., 2016; Ye et al., 2016; Zhang et al., 2015). In addition, studies have shown that proxies of SOA particles can form glasses at low RHs and low temperatures (Koop et al., 2011; Zobrist et al., 2008). Nevertheless, the conditions that lead to slow mixing times in SOA may be infrequent on a global scale in the PBL. If this is the case, then the assumption of well mixed SOA particles in chemical transport models should be reasonable. How often mixing times are > 1 h under ambient conditions in the PBL is not well constrained, in part due to the lack of information on mixing times of organic molecules in SOA particles as a function of both RH and temperature.

In the following, we have developed a parameterization for the viscosity of α-pinene SOA particles as a function of both RH and temperature and determined the distribution of RH and temperature in the PBL from an archive of meteorological fields. We also determined the conditions in the PBL when SOA concentrations are significant using a chemical transport model. We then used this combined information to quantify how often mixing times of SVOCs are > 1 h within α-pinene and isoprene SOA for ambient conditions in the PBL. Mixing times within anthropogenic SOA are also discussed. Our study is

complementary to the recent study by Shiraiwa et al. (2017) on the global distribution of particle phase state in atmospheric SOA, although our study focuses on mixing times within SOA in the PBL and uses a different approach to determine physicochemical properties of SOA.

2. Materials and Methods

2.1 Parameterization for the viscosity of α-pinene SOA as a function of temperature and RH.

Recently researchers have measured the viscosity of α-pinene SOA at room temperature (Bateman et al., 2015; Grayson et al., 2016; Zhang et al., 2015) (Table S1) and low temperatures (Table S2) at various RHs. The viscosity of liquid water as a function of temperature have also been measured (Table S3). To develop a parameterization for viscosity within α-pinene SOA as function of temperature and RH, the following equation was fit to these measured viscosities (Table S1-S3):

$$\log(\eta) = 12 - \frac{C_1 * (T - \frac{w_{SOA}T_{gSOA} + w_{H2O}T_{gH2O}k_{GT}}{w_{SOA} + w_{H2O}k_{GT}})}{C_2 + (T - \frac{w_{SOA}T_{gSOA} + w_{H2O}T_{gH2O}k_{GT}}{w_{SOA} + w_{H2O}k_{GT}})} \qquad (1)$$

where C_1 and C_2 are constants, k_{GT} is the Gordon-Taylor fitting parameter, T_{gSOA} and T_{gH2O} are the glass transition temperatures of dry SOA and water, and w_{SOA} and w_{H2O} are the weight fractions of the dry SOA and water in the particles. Derivation of Eq. (1) is discussed in the Supporting Information (Section S1). The weight fractions of the dry SOA and water in the particles were determined from the RH using the following equation (Koop et al., 2011):

$$\frac{RH}{100} = \frac{1}{(1 + i_{SOA}\frac{n_{SOA}}{n_{H2O}})} \qquad (2)$$

where i is the van't Hoff factor and n is the number of moles of dry SOA and water in the particles. We assumed a value of 1 for the van't Hoff factor (Koop et al., 2011) and a dry molecular weight for SOA of 175 g mol^{-1} (Huff Hartz et al., 2005). Since the glass transition temperature of water is known (135 K) (Corti et al., 2008), the unknowns in Eq. (1) (and hence fitting parameters) were C_1, C_2, k_{gt} and T_{gSOA}. The values for these parameters retrieved by fitting the equation to the viscosity data discussed above (using a non-linear curve fitting function in Matlab) are reported in Table S4.

As mentioned above, room temperature viscosities of α-pinene SOA as a function of RH were taken from Bateman et al. (2015), Grayson et al. (2016), and Zhang et al. (2015). We have not included the room temperature results from Renbaum-Wolff et al. (2013) or Hosny et al. (2016) since they only measured the viscosity of the water-soluble component of SOA, while the other studies measured the viscosity of the total SOA (water-soluble and water-insoluble component). In addition, we have not used the estimates of viscosity from Kidd et al. (2014) for α-pinene SOA since the uncertainties in their estimates were too large to help constrain our parameterization. The viscosities reported by Bateman et al. (2015), Grayson et al. (2016) and Zhang et al. (2015) are not inconsistent with most viscosities inferred from diffusion rates within α-pinene SOA (see Fig. S3 in Grayson et al. (2016)) (Abramson et al., 2013; Cappa and Wilson, 2011; Perraud et al., 2012; Robinson et al., 2013; Saleh et al., 2013).

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2.2. Organic aerosol concentrations in the planetary boundary layer

To determine the conditions in the PBL when SOA concentrations are significant we used the global chemical transport model GEOS-Chem (http://acmg.seas.harvard.edu/geos/). The version of GEOS-Chem used (v10-01) includes organic aerosol (OA) formation from semi-volatile and intermediate organic compounds (SVOC and IVOC) (Pye and Seinfeld, 2010), plus new
5   aerosol production from nitrate radical oxidation of isoprene and terpenes and NO_x-dependent aerosol yields from terpenes (Pye et al., 2010). In this version IVOC emissions are spatially distributed based on naphthalene. To estimate SVOC emissions we scaled the default GEOS-Chem primary organic aerosol (POA) emissions inventory by 1.27 following Pye and Seinfeld (2010). GEOS-Chem was run at a horizontal grid resolution of 4° latitude by 4.5° longitude using GEOS-5 meteorology with 47 vertical layers with a 3-year spin-up period. Shown in Fig. 1 are the monthly averaged total organic aerosol concentration
10 at the surface for the months of January and July 2006. These monthly averaged total organic aerosol concentrations were used to remove times and locations where SOA concentrations are not expected to be of major importance for climate, health or visibility.

2.3 RH and temperature in the PBL

Information on the RH and temperature distributions in the global PBL in different seasons are also needed to assess mixing
15 times within SOA particles. Temperature and RH in each grid cell within the PBL were determined globally using the 6-h averaged GEOS-5 meteorology fields and PBL heights. To determine if a grid cell was within the PBL, these PBL heights were used. The archive provides temperature and RH at a horizontal grid resolution of 4° latitude by 4.5° longitude and 47 vertical layers.

3. Results and Discussion

20 **3.1 Parameterization of viscosity and mixing times within α-pinene SOA particles as a function of RH and temperature.**

Shown in Fig. 2a (contours) is the RH and temperature dependent parameterization for α-pinene SOA viscosities based on the viscosities measured at room temperature (Bateman et al., 2015; Grayson et al., 2016; Zhang et al., 2015),and low temperature (Järvinen et al., 2016), as well as the viscosity of water as a function of temperature (Crittenden et al., 2012). From the viscosity parameterization, the diffusion coefficients of organic molecules within α-pinene SOA particles were calculated
25 using the Stokes-Einstein equation:

$$D = \frac{kT}{6\pi\eta R_H} \qquad (3)$$

where D is the diffusion coefficient, k is the Boltzmann constant, T is temperature in Kelvin, η is the dynamic viscosity and R_H is the hydrodynamic radius of the diffusing species. For the calculations, a hydrodynamic radius of 0.38 nm was used for the diffusing organic molecules within SOA, based on an assumed molecular weight of 175 g mol^{-1} (Huff Hartz et al., 2005),
30 a density of 1.3 g cm^{-3} (Chen and Hopke, 2009; Saathoff et al., 2009) and spherical symmetry. The Stokes-Einstein equation

should give reasonable values when the radius of the diffusing molecules is roughly the same size as the matrix molecules and when the viscosity of the matrix is relatively small ($\lesssim 400$ Pa s) (Chenyakin et al., 2017; Price et al., 2016). When the viscosity of the matrix is large ($\gtrsim 10^6$ Pa s), the Stokes-Einstein equation can under predict diffusion rates of organic molecules in organic matrices (Champion et al., 1997; Chenyakin et al., 2017; Price et al., 2016). Hence, the diffusion coefficients and

5   mixing times estimated here should be considered lower and upper limits, respectively.

From the diffusion coefficients, the mixing times of organic molecules within an α-pinene SOA particle were calculated with the following equation (Shiraiwa et al., 2011):

$$\tau_{mix} = \frac{d^2}{4\pi^2 D} \tag{4}$$

where τ_{mix} is the mixing time, d is the diameter of an SOA particle, and D is the diffusion coefficient estimated from Eq. (3).

10 For these calculations, it was assumed that the α-pinene SOA particles have a diameter of 200 nm, which is roughly the median diameter in the volume distribution of ambient SOA-containing particles (Martin et al., 2010; Pöschl et al., 2010; Riipinen et al., 2011). Once the mixing time has elapsed, the concentration of the diffusing molecules at the centre of the particle is within 1/e of the equilibrium concentration (Shiraiwa et al., 2011). The calculated mixing times (Fig. 2b) illustrate that, as expected, indirect relationships exist between both mixing time and RH, as well as mixing time and temperature.

15 **3.2 RH and temperature in the PBL**

Shown in Fig. 3a and 3b are the normalized frequency counts of temperature and RH in the PBL for the months of January and July, 2006, respectively, based on the archive of meteorological fields (GEOS-5) used in the global chemical transport model, GEOS-Chem, v10-01. We only included grid points in our analysis if the grid points were within the PBL and the monthly average mass concentration of total organic aerosol was > 0.5 μg m^{-3} at the surface, based on GEOS-Chem, v10-01

20 (Fig. 1). In other words, we included all the grid points in a column up to the top of the PBL when determining frequency counts if the monthly total organic aerosol concentration was > 0.5 μg m^{-3} at the surface. This filtering removes cases where SOA concentrations are not expected to be of major importance for climate, health or visibility. The normalized frequency counts illustrate that the temperature and RH in the PBL is often in the range of 290-300 K and > 50 % RH for the month of January (Fig. 3a) and in the range of 285-300 K and > 30 % RH for the month of July (Fig. 3b).

25 **3.3 Mixing times of organic molecules within α-pinene SOA particles in the PBL**

Also shown in Fig. 3a and 3b are the contour lines produced using our parameterization of mixing times of organics within 200 nm α-pinene SOA particles. These results, together with the frequency counts of temperature and RH throughout the vertical column of the PBL, indicate that the mixing time of organic molecules within α-pinene SOA is often < 1x10^{-1} h for conditions in the PBL.

30 Shown in Fig. 4 are the normalized frequency distributions of mixing times within α-pinene SOA for January and July, based on the data in Fig. 3a and 3b. Figure 4 suggests that the mixing times within α-pinene SOA is < 1 h for 94 % and 99 % of the

occurrences in the PBL during January and July, respectively, when monthly average total organic aerosol concentrations were > 0.5 µg m^{-3} at the surface.

Within the PBL, RH increases and temperature decreases with altitude, with both changes being substantial and impacting mixing times in opposite directions. Shown in Fig. 5a-c are calculated monthly average afternoon (13:00-15:00, local time) vertical profiles of temperature, RH, and mixing times within α-pinene SOA over Hyytiälä (boreal forest), and the Amazon (rainforest) for the driest month of the year at these locations (the method used to calculate vertical profiles is described in the Supporting Information, Section S2). Afternoon vertical profiles were chosen since this is the time of the day when RH is typically lowest and thus mixing times are the longest. Figure 5c shows that mixing times within α-pinene SOA decrease significantly with altitude for these two locations. This is because the plasticizing effect of water on viscosity dominates the temperature effect for these conditions.

Shown in Fig. 6 are global maps of the monthly averaged mixing times of organic molecules within α-pinene SOA for conditions at the top of the PBL for the months of January and July. Figure 6 shows that 83 % and 92 % of the locations for January and July, respectively, have a mixing time < 0.1 h for conditions at the top of the PBL when monthly averaged total organic aerosol surface concentrations are > 0.5 µg m^{-3}. Within the PBL, vertical mixing of air masses occurs on the order of 30 min. Since the mixing times within α-pinene SOA particles for conditions at the top of the PBL are < 0.1 h for most locations where the SOA concentrations are significant (total organic aerosol concentration > 0.5 µg m^{-3} at the surface), a reasonable upper limit to the mixing time within α-pinene SOA for most locations in the PBL is 30 min. During this 30 min interval, mixing times within α-pinene SOA particle can cycle between short and long values, though rarely being > 1 h (Fig. 3 and 4).

3.4 Sensitivity analysis for α-pinene SOA particles in the PBL

The parameterization for the viscosity of α-pinene SOA was based on viscosity measurements from Bateman et al. (2015), Grayson et al. (2016), Zhang et al. (2015), Järvinen et al. (2016) and Crittenden et al. (2012). The measurements by Zhang et al. (2015) and Grayson et al. (2016) were both carried out at room temperature and over a similar range in RH. The viscosities reported by Zhang et al. (2015) were higher than the viscosities reported by Grayson et al. (2016) (see Table S1). As a sensitivity analysis, we developed a second parameterization, using the same procedure as describe above, but excluding the data from Grayson et al. (2016) in the fitting procedure. Based on this new parameterization, for January, 86 % of the conditions in the PBL resulting in mixing times <1 h (previously 93 %) and for July, 96 % of the conditions producing mixing times <1 h (previously 98 %) when the total organic aerosol was > 0.5 µg m^3 at the surface. Using this new parameterization, we also found that the number of locations with mixing times <0.1 h decreased from 83 to 80 % and 92 to 89 % for January and July, respectively. None of these results significantly impact the overall conclusions of the paper.

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3.5 Mixing times of organic molecules within isoprene SOA particles in the PBL

The discussion in sections 3.1-3.4 is based on SOA generated from the ozonolysis of α-pinene. Another major global source of SOA is photo-oxidation of biogenic isoprene (Hallquist et al., 2009; Hu et al., 2015). The viscosity of isoprene SOA is lower than the viscosity of α-pinene SOA at room temperature (Song et al., 2015). As a result, the conclusions reached above for α-pinene SOA are likely applicable to isoprene SOA as well. A caveat to the discussion above is that the measurements of viscosities used to generate the parameterization shown in Fig. 2a were carried out on SOA samples generated with mass concentrations of $\geq 70 \, \mu g \, m^{-3}$, which is higher than the concentrations of biogenic SOA in the atmosphere. Additional studies of the viscosity of α-pinene SOA generated using lower mass loadings are needed. Additional studies are also needed to further explore the effect of oxidation level (Ng et al., 2010), oxidant type (Pajunoja et al., 2014), and the presence of water during oxidation on the viscosity of biogenic SOA (Kidd et al., 2014). Studies are also need to investigate the viscosity of other types of biogenic SOA (Kanakidou et al., 2005). Nevertheless, based on the data available it is not clear that long mixing times of SVOCs need to be included in chemical transport models when simulating SOA from biogenic sources in the global PBL.

Despite the discussion above, it is important to keep in mind that slow diffusion in biogenic SOA is likely still important in the atmosphere for other reasons. For example, slow diffusion is likely be important for heterogeneous chemistry within biogenic SOA in the PBL (Shiraiwa et al., 2011). Slow diffusion is also likely important when simulating the partitioning of SVOCs into biogenic SOA in the free troposphere where both the temperature and RH are lower than in the PBL (Shiraiwa et al., 2017).

3.6 Mixing times of organic molecules within anthropogenic SOA particles in the PBL

Recently it has been shown that the diffusion rates of organics in SOA from toluene photooxidation is slower than the diffusion rates of organics in SOA from α-pinene ozonolysis and isoprene photooxidation at room temperature (Liu et al., 2016; Song et al., 2016; Ye et al., 2016). These results indicate that that mixing times are longer in some types of anthropogenic SOA than biogenic SOA, at least at room temperature. SOA derived from anthropogenic sources can be a significant contributor to SOA over polluted regions (Hallquist et al., 2009; Spracklen et al., 2011). Viscosity or diffusion rates within toluene SOA or other types of anthropogenic SOA has yet to be measured at temperatures lower than room temperature. As a result, we have used sucrose as a proxy of anthropogenic SOA, since the viscosity of sucrose is similar to the viscosity of toluene SOA at room temperature (Fig. S1) (Power and Reid, 2014; Song et al., 2016), and since a parameterization of the viscosity of sucrose as a function of temperature and RH can be developed using literature data. In the Supporting Information (Section S3, Table S5-S7, and Fig. S2-S5) we carried out a similar analysis for sucrose as for α-pinene SOA above. Assuming sucrose is a good proxy for anthropogenic SOA, the analysis suggests that 70 % and 83 % of the mixing times within anthropogenic SOA in the PBL are < 1 h for January and July, respectively, when SOA concentrations are significant (total organic aerosol concentration > 0.5 $\mu g \, m^{-3}$ at the surface). In addition, 81 % and 87 % of the locations for January and July, respectively, have a mixing

time < 0.1 h at the top of the PBL when surface concentrations of total organic aerosol are > 0.5 µg m^{-3}. These percentages for anthropogenic SOA are likely lower limits since studies have shown that the Stokes-Einstein relation (which is used here to calculate diffusion coefficients of organic molecules from viscosities) can under predict diffusion coefficients of organic molecules in sucrose-water mixtures by at least a factor of 10 to 100 at viscosities ≥ 10^6 Pa s (Chenyakin et al., 2017; Price et

5 al., 2016). Measurements of diffusion rates of organic molecules within anthropogenic SOA as a function of both temperature and RH are needed to better constrain how often mixing times are > 1 h within anthropogenic SOA in the PBL.

Competing interests: The authors declare that they have no conflict of interest.

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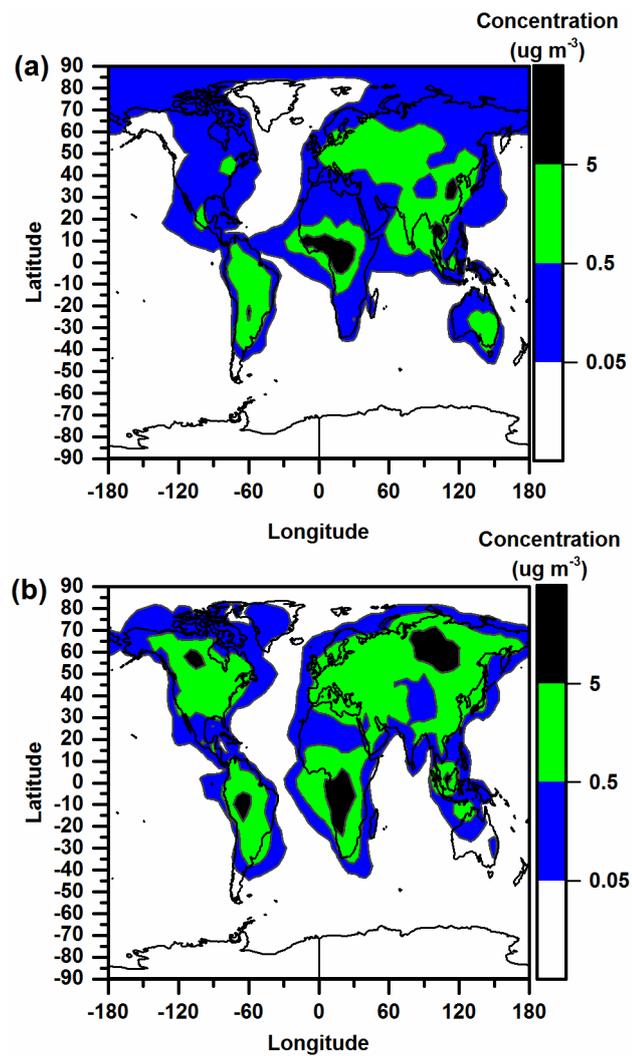Chemistry
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Figures

Figure 1. Total organic aerosol concentrations (color scale) at the Earth's surface in (a) January and (b) July, as calculated using GEOS-Chem.

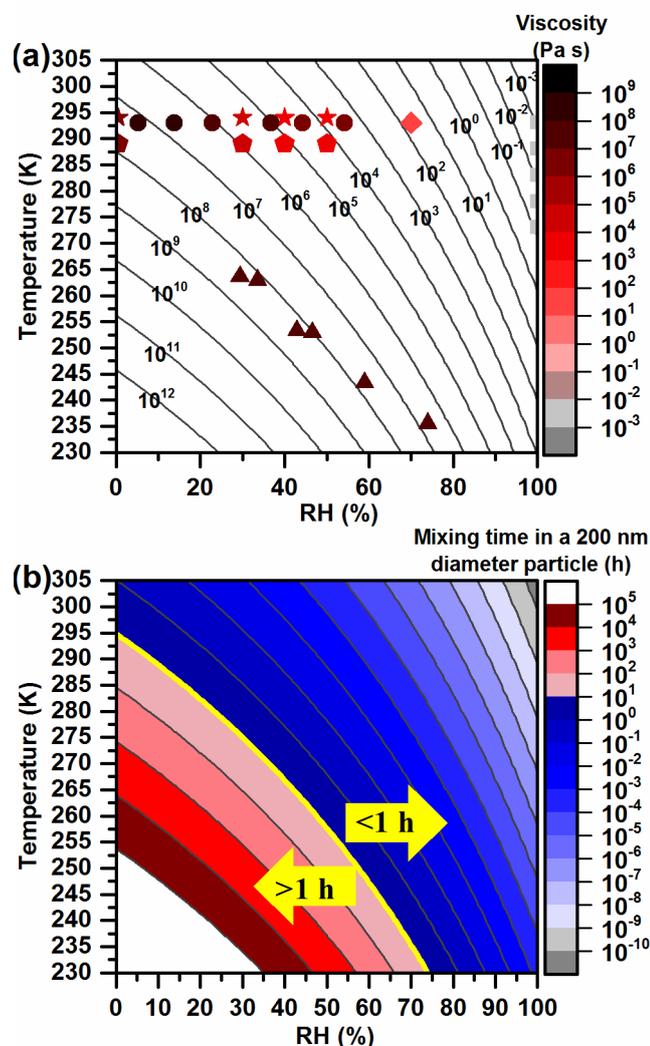Atmospheric
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Figure 2. Plot of RH vs temperature with contour lines representing (a) our viscosity parameterization for α-pinene SOA particles and (b) mixing times calculated for organic molecules with 200 nm diameter α-pinene SOA particles. The symbols in (a) represent the laboratory data used to develop the parameterization: squares represent the water viscosities from Crittenden et al. (2012); triangles represent the viscosity data of α-pinene SOA from Järvinen et al. (2016); circles represent the viscosity data from Zhang et al. (2015), and the stars and pentagons represent the viscosity data from Grayson et al. (2016) measuring using SOA concentrations of 121 and 520 ug m^{-3} respectively. The 520 ug m^{-3} data from Grayson et al. (2016) was offset by 5 K to improve visibility.

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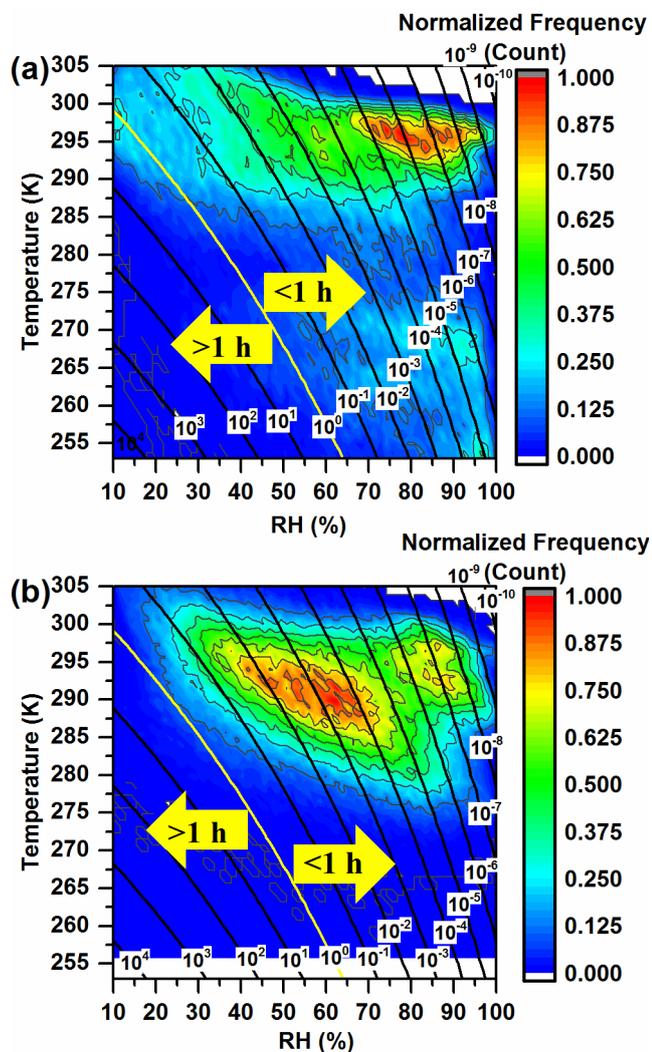and Physics
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Figure 3. Six-hour normalized frequency counts of temperature and RH in the planetary boundary layer (PBL) (color scale) together with the mixing times for organic molecules within 200 nm α-pinene SOA particles (contours). Panel A shows the conditions for January and panel B shows the conditions for July. Mixing times (contours) are reported in hours. Frequency counts in the PBL were only included for the conditions where the mass concentration of total organic aerosol was > 0.5 μg m^{-3} at the surface.
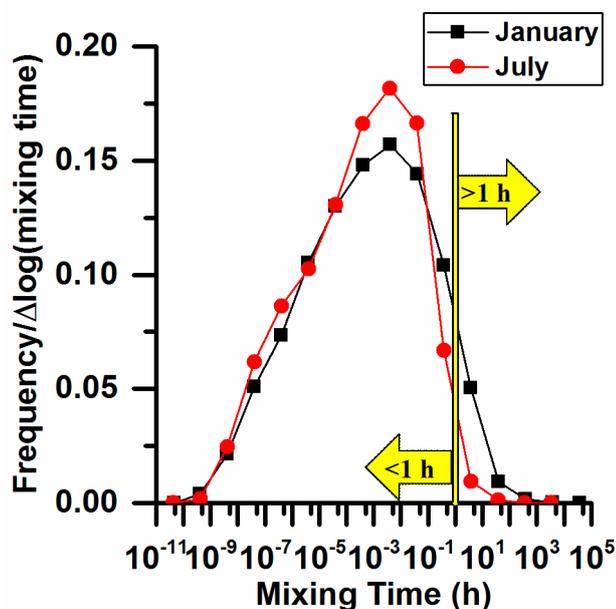
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Figure 4. Normalized frequency distributions of mixing times within α-pinene SOA in the planetary boundary layer (PBL). Black symbols correspond to January and red symbols corresponds to July. Frequency counts in the PBL were only included for the conditions where the mass concentration of total organic aerosol was > 0.5 µg m^{-3} at the surface.
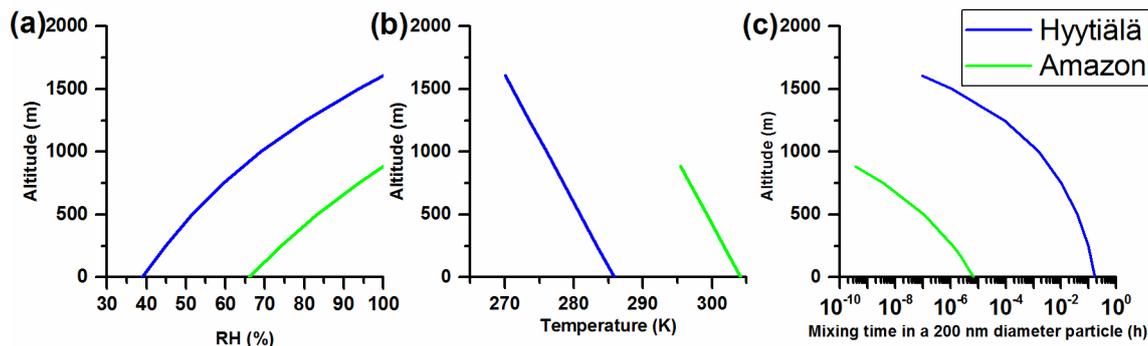

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Figure 5. Temperature, RH and estimated mixing times for α-pinene SOA as a function of altitude for Hyytiälä (boreal forest) and the Amazon (rainforest). The temperature and RH at ground level are the average afternoon values in the driest month of the year for the respective locations. The vertical profiles of temperature and RH are plotted until the RH is 100 % for these locations. The height at which RH reaches 100 % is only slightly lower than the average height of the planetary boundary

10 layer predicted by GEOS-5 meteorology data. For details see the Supporting Information, Section S2.
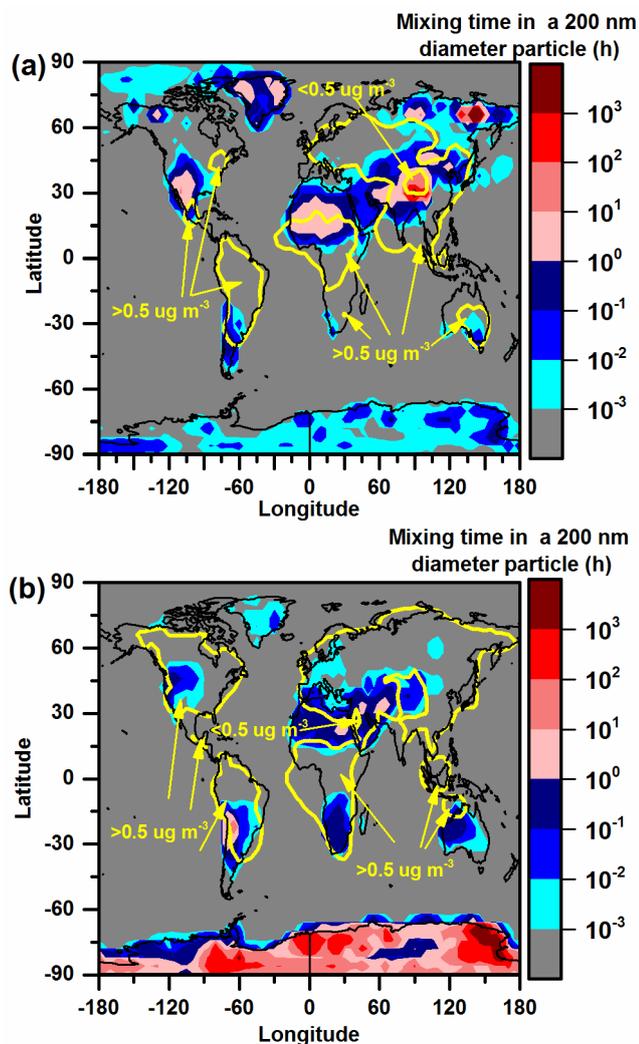
Figure 6. Mixing times of organic molecules within 200 nm α-pinene SOA particles at the top of the planetary boundary layer as a function of latitudes and longitudes in (a) January and (b) July. The color scale represents mixing times and the yellow contours illustrate when the concentration of total organic aerosols is > or < 0.5 ug m⁻³.