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

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Supporting Information

S1. Derivation of Equation 1 from the main text.

The WLF equation provides a relationship between viscosity and temperature:

$$\log(\frac{\eta}{\eta_g}) = \frac{-C_1(T-T_g)}{C_2+(T-T_g)} \quad \text{(S1)}$$

where C_1 and C_2 are constants, T is the temperature, T_g is the glass transition temperature, η is the viscosity and η_g is the viscosity at the glass transition (10^{12} Pa s). The Gordon-Taylor equation provides a relationship between the glass transition temperature of a mixture and the weight fractions of its components:

$$T_{g,mix} = \frac{w_1 T_{g1} + w_2 T_{g2} k_{GT}}{w_1 + w_2 k_{GT}} \quad \text{(S2)}$$

where w_1 and w_2 are the weight fractions of the solute and water, T_{g1} and T_{g2} are the glass transition temperatures of the solute and water, and k_{GT} is a fitting parameter that describes the interaction between the two species. Equations (S1) and (S2) can be combined to give Eq. (1) in the main text.

Equation (S1) (and hence Eq. (1)) is valid only at or above the glass transition temperature. As a result, we have not used Eq. (1) to predict viscosities > 10^{12} Pa s (which corresponds to mixing times > 5×10^5 h). This is not a concern for α-pinene SOA since the viscosity of α-pinene SOA is rarely > 10^{12} Pa s in the PBL.

S2. Calculations of vertical profiles of temperature and RH in the boundary layer above Hyytiälä (boreal forest) and the Amazon (rainforest)

The monthly average afternoon (13:00-15:00, local time) temperature and RH vertical profiles over Hyytiälä and the Amazon were calculated for the driest month of the year at these locations. For Hyytiälä, the average afternoon temperatures and RHs at the surface were obtained from the SMEAR II campaign data set for 2012, retrieved from Etsin Research data finder (https://etsin.avointiede.fi/dataset) (Aalto, 2012a, 2012b). For the Amazon, the temperature and RH at the surface was obtained from NOAA's National Climate Data Center (http://www.ncdc.noaa.gov/) from 2004 to 2014, and an average from five different stations was used (Alfredo Vasquez Cobo, Itaituba, Tabatinga, Monte Dourado and Iauarete).

The temperature above the surface was calculated using a dry adiabatic lapse rate of 9.8 K km^{-1} and assuming that water vapour was well mixed within the PBL. To determine the RH at different altitudes, the water vapor pressure, water saturated vapour pressure, and atmospheric pressure were calculated. The atmospheric pressure was calculated using the following equation (Seinfeld and Pandis, 2006):

$$P(z) = P_0 \exp(-\frac{Mgz}{kT}) \quad \text{(S3)}$$

where P_0 is the standard pressure at sea level (101325 Pa), M is the molecular mass of the air (28.8 g/mol), g is the acceleration due to gravity (9.81m s^{-2}), z is the altitude in metres, k is the Boltzmann constant and T is the temperature in Kelvin. The water saturated vapour pressure was calculated using the Antoine equation (National Insititute of Standards And Technology, 2016):

$$log_{10}(P) = A - (\frac{B}{T+C}) \quad \text{(S4)}$$

where P is the pressure, A=4.6543, B=1435.264, C=-64.848 and T is the temperature in Kelvin. The values for A, B and C were based on the NIST values for water, which are valid for temperatures between 256 and 373 K (National Insititute of Standards And Technology, 2016).

In Fig. 5, the temperature and RH was plotted until the RH reached 100 %. The height at which RH reached 100 % was only slightly lower than the average height of the planetary boundary layer predicted by GEOS-5 meteorology data for the driest month of the year and for the afternoon (13:00-15:00, local time) above Hyytiälä and the Amazon. For Hyytiälä, 100 % RH was reached at 1605 m, while GEOS-5 predicted an average height of the PBL of 1667 m for this location and time. For the Amazon, 100 % RH was reached at 882 m, while GEOS-5 predicted an average height of the PBL of 1249 m for this location and time. When predicting the height of the PBL using GEOS-5 meteorology, we ran GEOS-Chem at a horizontal grid resolution of 2° latitude by 2.5° longitude rather 4° latitude by 4.5° longitude to provide a better approximation to these single locations. ö

S3. Parametrization for the viscosity of sucrose particles as a function of temperature and RH.

We developed a parameterization for viscosity of sucrose particles as function of temperature and RH by fitting the viscosity data listed in Table S5 to the following equation:

$$\log(\eta) = 12 - \frac{C_1 * (T - \frac{w_{Suc} T_{gSuc} + w_{H2O} T_{gH2O} k_{GT}}{w_{Suc} + w_{H2O} k_{GT}})}{C_2 + (T - \frac{w_{Suc} T_{gSuc} + w_{H2O} T_{gH2O} k_{GT}}{w_{Suc} + w_{H2O} k_{GT}})} \quad \text{(S5)}$$

where C_1 and C_2 are constants, k_{GT} is the Gordon-Taylor fitting parameter, T_{gSuc} and T_{gH2O} are the glass transition temperatures of dry sucrose and water and w_{Suc} and w_{H2O} are the weight fractions of the dry sucrose and water in the particles. The weight fractions of dry sucrose and water in the particles were determined from the RH using the following equation (Zobrist et al., 2011):

$$\frac{RH}{100} = \frac{1 + a w_{Suc}}{1 + b w_{Suc} + c w_{Suc}^2} + \left(T - T^{\theta}\right)(d w_{Suc} + e w_{Suc}^2 + f w_{Suc}^3 + g w_{Suc}^4) \quad \text{(S6)}$$

where a-g are fitting parameters, T is the temperature in Kelvin and T^{o} is a reference temperature. The values for T^{o} and a-g can be found in Table S6.

When fitting Eq. (S5) to the viscosity data for sucrose (Table S5), the parameters C_1, C_2, k_{GT} and T_{gsuc} were included as fitting parameters, while the glass transition temperature of water was fixed at 135 K (Longinotti and Corti, 2008). The values for these parameters retrieved by fitting are reported in Table S7. The T_{gsuc} value obtained by fitting was within the range measured experimentally (319-335K) (Dette et al., 2014; Roos, 1993; Simperler et al., 2006).

Equation (S5) was based on the Williams, Landel and Ferry (WLF) equation and the Gordon-Taylor equation, similar to Eq. (1) in the main text. Since the WLF equation is only valid at or above the glass transition temperature, we have not used Eq. (S5) to predict viscosities above 10^{12} Pa s (which corresponds to mixing times longer than 5×10^5 h) (Fig. S2). If the temperature and RH in the PBL was such that the viscosity was greater than 10^{12} Pa s, we assigned a viscosity of 10^{12} Pa s and a mixing time of 5×10^5 hours. This assignment does not affect the conclusions in this manuscript since a mixing time of 5×10^5 hours is already well above the residence time of SOA particles in the atmosphere. However, this assignment did lead to a relatively large frequency count at 5×10^5 hours in Fig. S4.

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Tables

Table S1. Room temperature α-pinene SOA viscosity data used to create a parameterization for the viscosity of α-pinene SOA as a function of temperature and RH.

Reference	Viscosity (Pa s)	RH (%)	Temperature (K)
Grayson et al. (2016) (SOA generated with mass concentration =121 μg m^{-3})	[a]Range=1.8×10^{2} -1.5×10^{4}, midpoint=1.6×10^{3}	50	[c]Range=293-295 Midpoint=294
	[a]Range=9.8×10^{2} -3.0×10^{4}, midpoint=5.4×10^{3}	40	
	[a]Range=4.6×10^{3} -1.4×10^{5}, midpoint=2.5×10^{4}	30	
	[a]Range=1.6×10^{6} -5.9×10^{7}, midpoint=9.6×10^{6}	[b]0	

Grayson et al. (2016) (SOA generated with a mass concentration = 520 μg m^{-3})	[a]Range=$4.2x10^2$ -$3.1x10^4$, midpoint=$3.6x10^3$	50	
	[a]Range=$9.7x10^2$-$7.9x10^4$, midpoint=$8.7x10^3$	40	
	[a]Range=$3.4x10^3$-$2.1x10^5$, midpoint=$2.6x10^4$	30	
	[a]Range=$3.5x10^5$-$1.8x10^7$, midpoint=$2.5x10^6$	[b]0	
Bateman et al. (2015)	$1 x10^1$	70	293
Zhang et al. (2015)[d]	$2.3 x10^8$	5.2	293
	$1.3 x10^8$	13.8	293
	$3.2 x10^7$	22.9	293
	$1.4 x10^7$	36.7	293
	$6.0 x10^6$	44.3	293
	$5.1 x10^6$	54.3	293

[a] Grayson et al. (2016) reported upper and lower limits to the viscosity (i.e. range) at each specified RH. To simplify the fitting procedure, we used the midpoints of the viscosities from Grayson et al (2016).

[b] Grayson et al. (2016) measured the viscosity under dry conditions (RH of < 0.5 % based on measurements). When developing the parameterization we used a value of 0 % RH.

[c] Grayson et al. (2016) carried out experiments at room temperature (293 K-295 K). We used the midpoint of the temperature (294 K) when developing the viscosity parameterization for α-pinene SOA.

[d]Zhang et al. (2015) reported 36 measurements of viscosity over the range of 0 to 60%. For the fitting procedure, we binned their data by relative humidity and used the average viscosity and relative humidity in each bin. The width of each bin was approximately 10% RH. This binning procedure was carried out to give the data from Grayson et al. (2016) and Zhang et al. (2015) similar weights, since both were carried out at room temperature and over a similar RH range.

Table S2. Low temperature α-pinene SOA viscosity data used to create a parameterization for the viscosity of α-pinene SOA as a function of temperature and RH.

Reference	**Viscosity (Pa s)**	**RH (%)**	**Temperature (K)**
Järvinen et al. (2016)	$1x10^7$	[a]Range=22.9-36.3, midpoint=29.6	263.3
		[a]Range=30.5-37.3, midpoint=33.9	262.9
		[a]Range=40.5-46.0, midpoint=43.3	253.3
		[a]Range=44.0-49.8, midpoint=46.9	252.9
		[a]Range=55.0-63.4, midpoint=59.2	243.3
		[a]Range=68.6-80.1, midpoint=74.4	235.5

[a] Järvinen et al (2016) reported upper and lower limits to the RH for a specific temperature and viscosity. To simplify fitting, we used the midpoint of the RH range.

Table S3. Liquid water viscosity data used to create a parameterization for the viscosity of α-pinene SOA as a function of temperature and RH.

Reference	Viscosity (Pa s)	RH (%)	Temperature (K)
Crittenden et al. (2012)	[a]1.002x10^{-3}	100	293
	[a]1.139 x10^{-3}		288
	[a]1.307 x10^{-3}		283
	[a]1.518 x10^{-3}		278
	[a]1.781 x10^{-3}		273

[a] The viscosities values in Crittenden et al. (2012) were reported to 4 significant digits.

Table S4. Initial guess parameters and fitting parameters used in Eq. (1) to predict the viscosity of α-pinene SOA as a function of temperature and RH. The fitting parameters were obtained by fitting Eq. (1) to the viscosity data listed in Tables S1-S3.

Parameter	Guess Value	Fitting Value
C_1	19	31297
C_2	50 K	331446 K
K_{GT}	2.5	5.155
Tg_{SOA}	250	245.17 K

Table S5. Literature viscosity data used to create a parameterization for the viscosity of sucrose particles as a function of temperature and RH.

System	Viscosity Range (Pa s)	RH (%)	Temperature (K)	Reference
Water	1.002x10^{-3} to 1.781x10^{-3}	100	275-293	Crittenden et al. (2012)
Sucrose-water	3.19x10^{-3} to 4.82x10^{-1}	96.2-80	293	Swindells et al. (1958)
	6.73x10^{-1} to 1.10x10^{3}	80-56.6		Quintas et al. (2006)
	1.97x10^{-3} to 5.67x10^{-2}	99.4-88		Perry and Green (2008)
	1.25x10^{-3} to 8.30x10^{-2}	99.99-87.96		Migliori et al. (2007)
	1.26x10^{-3} to 7.65x10^{-2}	99.89-87.98		Telis et al. (2007)
	1.03x10^{-3} to 5.81x10^{-2}	100-87.98		Forst et al. (2002)

	$3x10^{-2}$ to $6.71x10^{8}$	92-28		Power and Reid (2014)
	$1x10^{12}$	48.53-25.88	255-295 (5 degree increments)[a]	Zobrist et al. (2008)

[a] Zobrist et al. (2008) reported glass transition temperatures as a function of water activity for the range of 160 K to 300 K. These glass transition temperatures were based on glass transition temperature measurements in the range of 240 K to 180 K, water activity measurements, and the Gordon-Taylor equation. To develop our parameterization, we used their glass transition temperatures over the range of 255 K to 295 K from their Fig. 5b, recorded in 5 K increments.

Table S6. Parameters from Zobrist et al. (2011) used in Eq. (S6) to predict the weight fractions of sucrose and water in particles as a function of relative humidity.

Parameter	**Value**	**Parameter**	**Value**
a	-1	e	-0.005151
b	-0.99721	f	0.009607
c	0.13599	g	-0.006142
d	0.001688	T^o	298 K

Table S7. Fitting parameters used in Eq. (S5) to predict the viscosity of sucrose particles as a function of temperature and RH. These parameters were obtained by fitting Eq. (S5) to the viscosity data listed in Table S5 as well as the guess values in the table.

Parameter	**Guess Value**	**Fitting Value**
C_1	19	20.06
C_2	50 K	55.58 K
K_{GT}	4.74	4.531
Tg_{SOA}	336 K	324.5 K

Figures

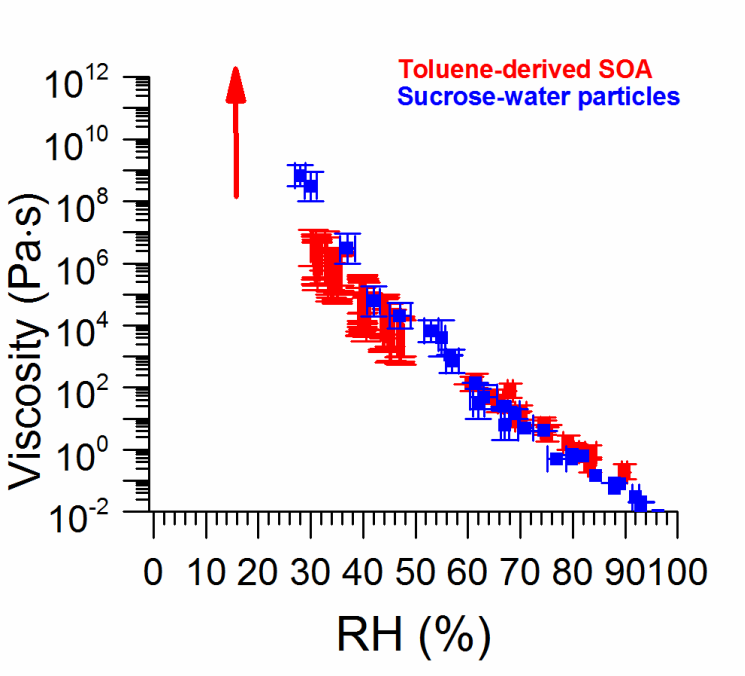

Figure S1. Viscosities of different proxies of anthropogenic SOA as a function of RH. Data for toluene SOA taken from Song et al. (2016). The data for sucrose-water mixtures was taken from Swindells (1958), Quintas et al. (2006), Telis et al. (2007), Forst et al. (2002), Migliori et al. (2007), Perry and Green (2008), and Power and Reid (2014).

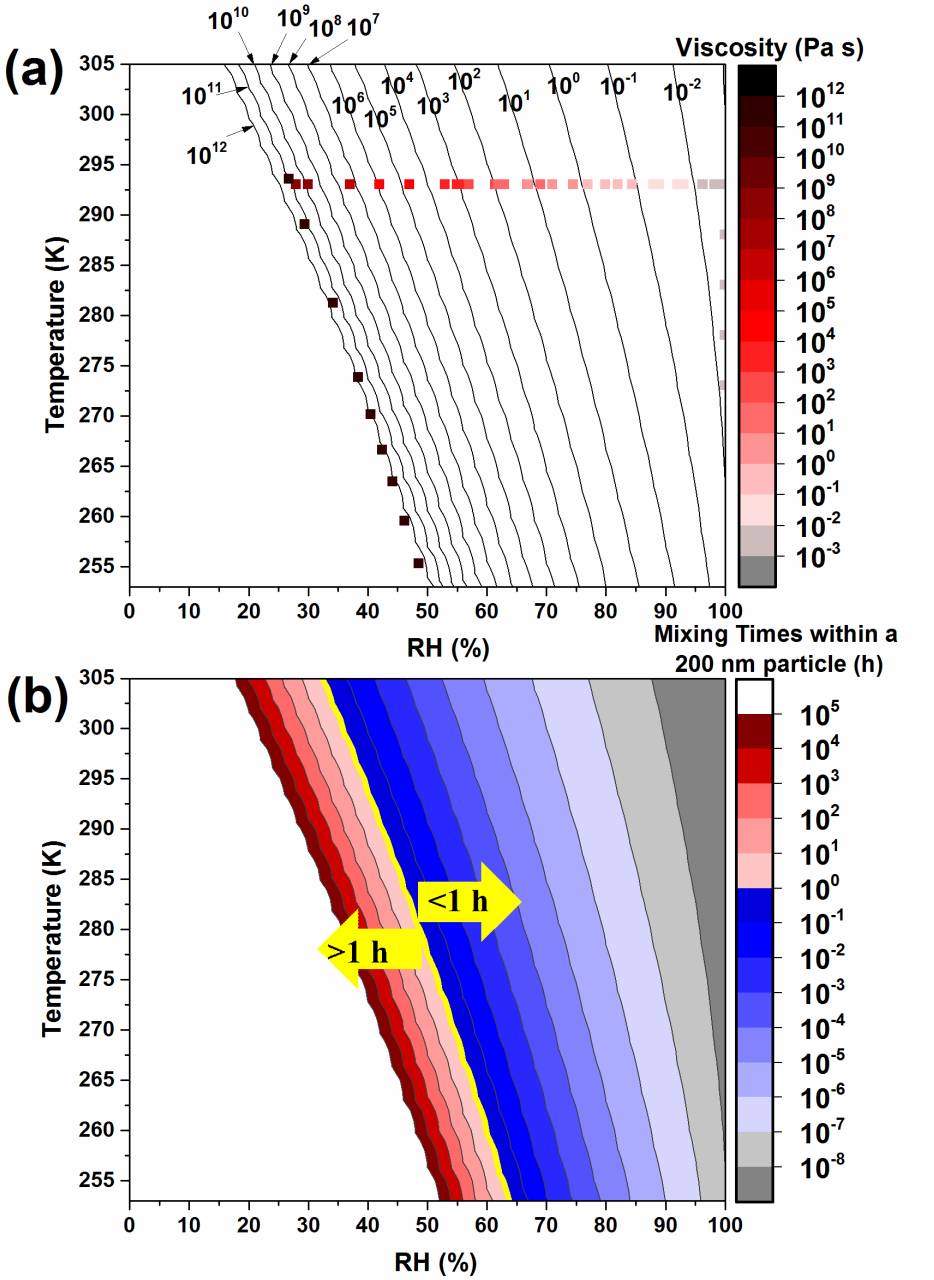

Figure S2. Panel A: Parameterization (contours) for the viscosity of sucrose particles (as surrogates of toluene SOA) as a function of temperature and RH and measured viscosities used to construct the parameterization (symbols). The measured viscosities are listed in Table S5. Panel B: Mixing times (color scale) for organic molecules within 200 nm sucrose particles as a function of temperature and RH. Mixing times were calculated from the viscosity parameterization (Panel A) and Eq. (3) and (4) in the main text.

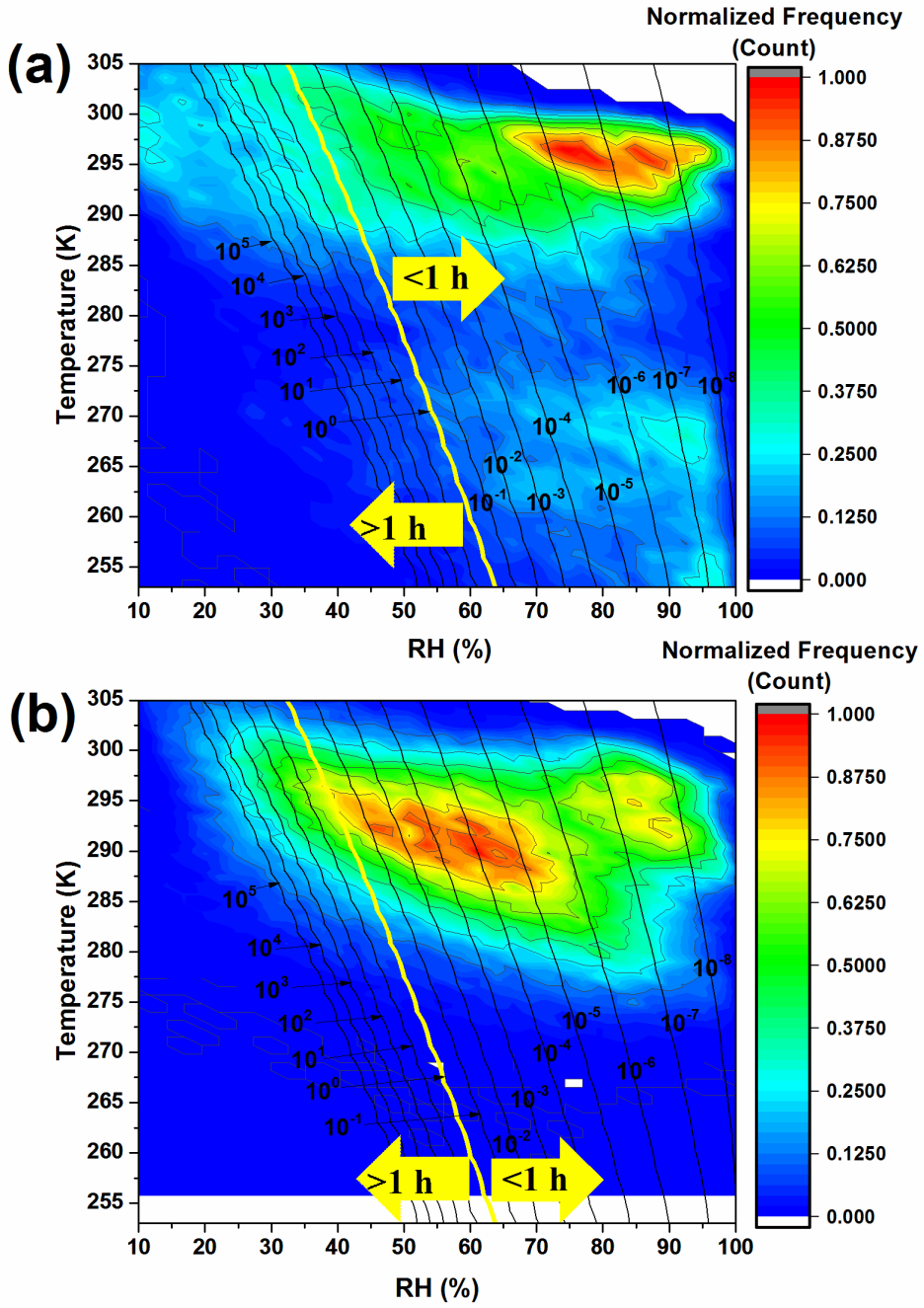

Figure S3. Six-hour normalized frequency counts of temperature and RH in the planetary boundary layer (color scale) together with the mixing times for organic molecules within 200 nm sucrose particles (as surrogates of toluene SOA) (contours). Panel A and B show the conditions for January and July, respectively. Mixing times (contours) are reported in hours. Frequency counts in the PBL were only included for the conditions when the mass concentration of total organic aerosol was > 0.5 μg/m^3 at the surface.

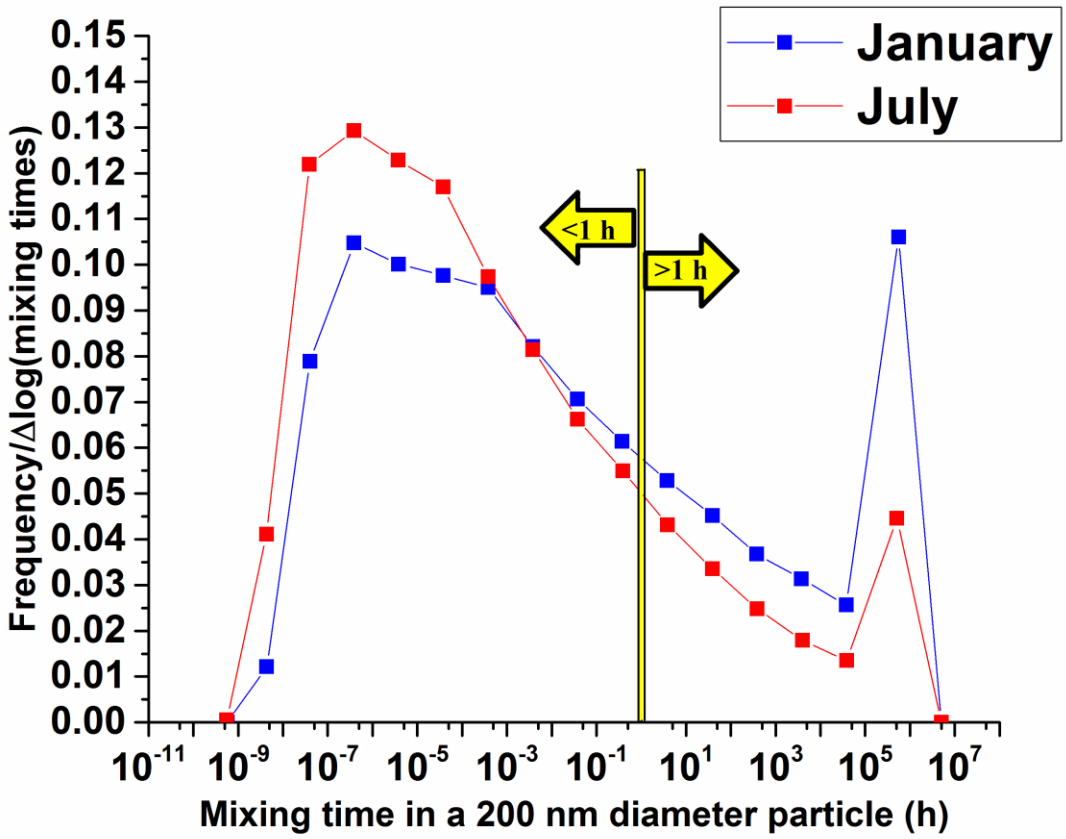

Figure S4. Normalized frequency distributions of mixing times within sucrose particles (as surrogates for toluene SOA) in the planetary boundary layer. Red symbols corresponds to January and blue symbols corresponds to July. Frequency counts in the PBL were only included for the conditions where the mass concentration of total organic aerosol was > 0.5 μg m^{-3} at the surface. The relatively large frequency count at $5x10^5$ h is because all cases that had a viscosity greater than 10^{12} Pa s, it was assigned a value of 10^{12} Pa s. For additional details see Section S3.

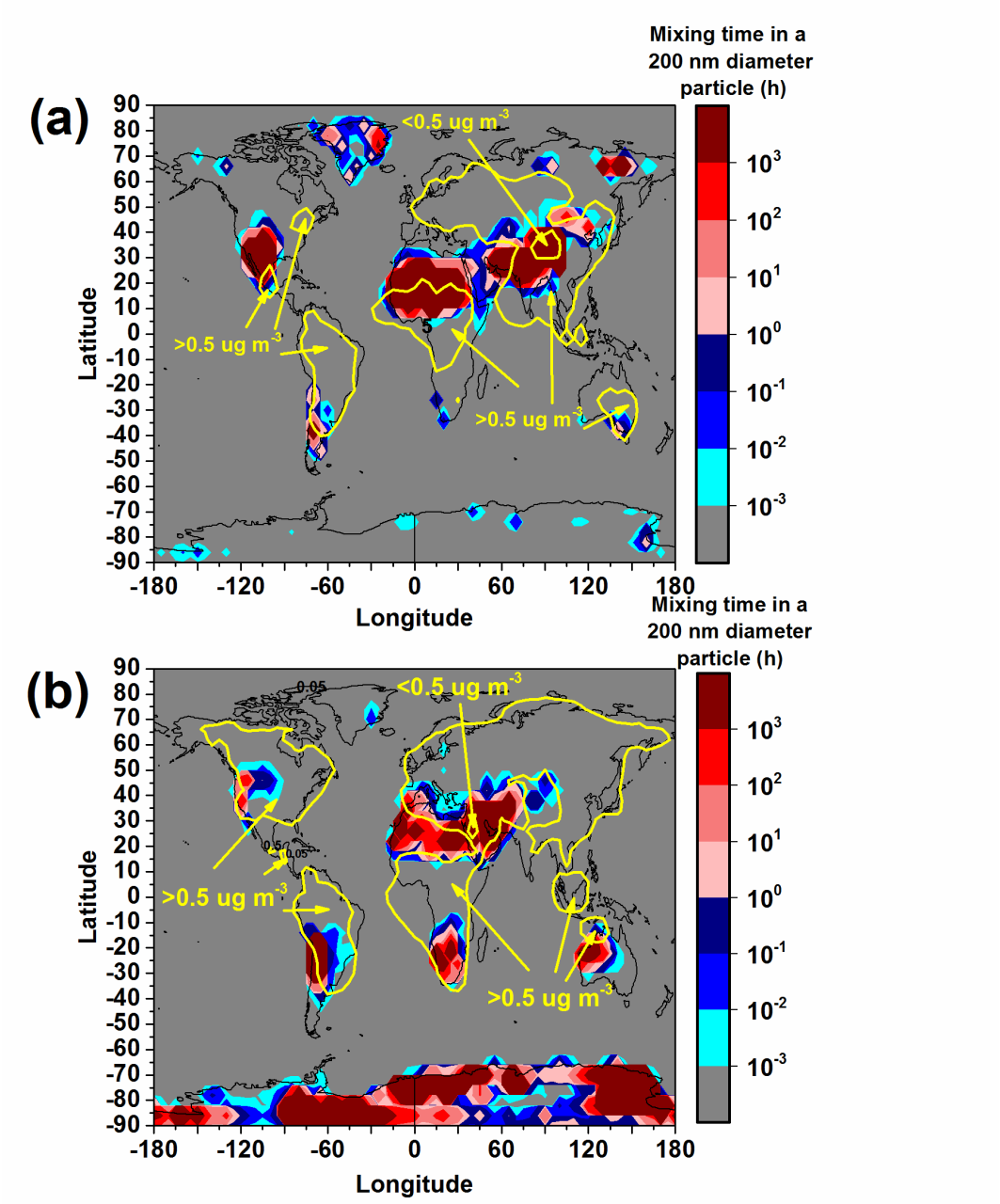

Figure S5. Mixing times of organic molecules within 200 nm sucrose particles (as surrogates of toluene SOA) at the top of the planetary boundary layer as a function of latitude and longitude. The color scale represents mixing times and the yellow contours illustrate when the concentration of total organic aerosol is > 0.5 ug m^{-3} at the surface. Panel A and B correspond to January and July, respectively.