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Molecular Insights into Gas-Particle Partitioning and Viscosity of Atmospheric Brown Carbon.

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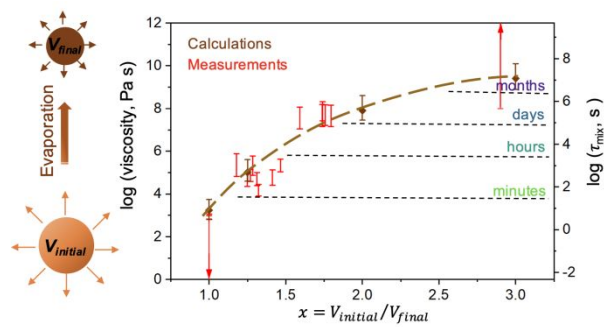
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TOC Art



ABSTRACT. Biomass burning organic aerosol (BBOA), containing brown carbon chromophores, plays a critical role in atmospheric chemistry and climate forcing. However, the effects of evaporation on BBOA volatility and viscosity under different environmental conditions remain poorly understood. This study focuses on the molecular characterization of laboratory-generated BBOA proxies from wood pyrolysis emissions. The initial mixture, "pyrolysis oil (PO₁)," was progressively evaporated to produce more concentrated mixtures (PO_{1.33}, PO₂, and PO₃) with volume reduction factors of 1.33, 2, and 3, respectively. Chemical speciation and volatility were investigated using temperature-programmed desorption combined with direct analysis in real-time ionization and high-resolution mass spectrometry (TPD-DART-HRMS). This novel approach quantified saturation vapor pressures and enthalpies of individual species, enabling the construction of volatility basis set distributions and the quantification of gas-particle partitioning. Viscosity estimates, validated by poke-flow experiments, showed a significant increase with evaporation, slowing particle-phase diffusion and extending equilibration times. These findings suggest that highly viscous tar ball particles in aged biomass burning emissions form as semi-volatile components evaporate. The study highlights the importance of evaporation processes in shaping BBOA properties, underscoring the need to incorporate these factors into atmospheric models for better predictions of BBOA aging and its environmental impact.

Keywords. Volatility and viscosity; atmospheric brown carbon; biomass burning organic aerosol, gas-particle partitioning; non-reactive evaporation, TPD-DART-HRMS.

Synopsis. Molecular characterization of complex biomass burning organic aerosol (BBOA) mixtures enables quantitative analysis of gas-particle partitioning of aerosol components and assessment of viscosity and diffusion within the particle phase.

INTRODUCTION

Biomass burning organic aerosol (BBOA), emitted from wildfires and agricultural burns, contains a substantial amount of gaseous and particulate light-absorbing material known as brown carbon (BrC)¹⁻⁴, contributing to a significant climate warming effect. Exploring the formation, transformation, and removal pathways of BBOA is crucial to understand their impact on air quality and Earth's climate,^{5, 6} particularly as wildfires become more frequent and widespread globally.^{7, 8} Atmospheric ageing alters the composition and optical properties of BrC through various chemical and physical processes, thereby influencing atmospheric chemistry and climate.⁹ The chemically complex components of BrC can be removed from BBOA through evaporation and reaction chemistry, leading to the production of more volatile species.¹⁰ Various multi-phase reactions can darken BrC aerosols within hours of emission, while photobleaching and oxidative whitening may occur a day or more later.^{9, 10} However, the influence of non-reactive evaporation of BBOA remains underappreciated, and little is known about how evaporation affects particle chemical composition and physical properties.^{11, 12} Both volatility and viscosity are important properties of BBOA, as they influence essential processes such as the dynamics of gas-particle partitioning and organic aerosol evolution.¹³ Recent research indicates that BBOA darkens upon volatilization, thereby amplifying its BrC optical absorbance.¹¹ Nonetheless, quantifying the impact of evaporation on volatility and viscosity properties of BBOA remains incomplete. Atmospheric BBOA and its BrC components comprise a diverse mixture of individual species existing in a dynamic equilibrium between gaseous and particulate phases. Through various atmospheric transformations, these complex components undergo multiple processes, with the partitioning of these components between gas and particle phases being central.^{14, 15} Volatility, defined by saturation vapor pressure, is a fundamental property governing the gas-particle

partitioning of individual BBOA components, thereby influencing their atmospheric fate.^{16, 17} The volatility of species is influenced by intrinsic properties such as molecular weights, chemical structures, and intra-molecular forces, as well as external conditions of temperature, pressure, humidity, and total organic mass loading.¹⁸⁻²² However, measuring the volatility values of individual components in BBOA mixtures is challenging due to their chemical complexity and diversity. This complexity complicates the construction and assessment of the corresponding volatility basis sets (VBS) used to model gas-particle partitioning.¹⁶

Recent advances have facilitated this task. A novel experimental approach integrates thermal evaporation of organic aerosol (OA) samples using a temperature programmed desorption (TPD) stage with the direct analysis in real time (DART) ionization source and high-resolution mass spectrometer (HRMS). This method enables the direct measurement of the apparent saturation vapor pressures ($i p_T^*$, Pa) of individual species (i) across a broad temperature (T , K) range.²³ Additionally, these measurements provide values of apparent transition enthalpies ($i \Delta H^*$, kJ/mol), characterizing individual organic molecules as they undergo evaporation or sublimation. Using the records of $i p_T^*$ converted into saturation mass concentration ($i C_T^*$, $\mu\text{g}\cdot\text{m}^{-3}$) and $i \Delta H^*$ values obtained for individual components of OA, the VBS distributions are constructed. These distributions facilitate a quantitative assessment of the gas-particle partitioning of aerosol components, aiding in the prediction of their behavior and evolution in the atmosphere.²⁴

Higher viscosity is associated with slower diffusion, longer characteristic mixing times, and inhibited multiphase chemistry within aerosol mixtures, all of which are influenced by their composition and environmental conditions.^{25, 26} Quantifying particle viscosity is crucial for accurately predicting the phase state of BBOA particles, although viscosity measurements are very

challenging.²⁷ However, the impact of evaporation on temperature- and relative humidity (RH)-dependent BBOA viscosity has not been previously documented.

In this study, samples of BBOA proxies were collected from emissions generated by the pyrolysis of wood chips in a laboratory setup. Afterwards, samples with varying degrees of evaporation were obtained. The TPD-DART-HRMS experiments were employed to measure the values of ${}^i\Delta H^*$ and ${}^iC_T^*$ of individual components, along with their corresponding mass fraction values. Subsequently, VBS distributions were constructed to quantitatively assess the equilibrium gas-particle partitioning of BBOA under atmospherically relevant conditions, including a range of total organic mass loadings (tOM , $\mu\text{g}\cdot\text{m}^{-3}$) and temperatures (T , K). The viscosity values of BBOA mixtures were estimated using the VBS-based prediction of the chemical composition of particle-phase components. These calculated values were then compared with viscosity measurements employing poke-flow experiments to demonstrate their utility and explore viscosity variations during the evaporation processes in the atmosphere.

EXPERIMENTAL AND ANALYSIS METHODS

Generation of BBOA and non-reactive evaporation processes. Smoke emissions resulting from the pyrolysis of hardwood pellets, which mimic the chemical and optical properties of ambient biomass burning aerosols,^{12, 28} were collected using a water-circulating condenser, operated at $T = 293$ K. The collected liquid condensate naturally separated into immiscible “aqueous” and “oily” fractions in a separatory funnel. For this study, the initial oily fraction, designated as wood Pyrolysis Oil (PO_1), was isolated and employed as a proxy for BBOA. Three aliquots of PO_1 , each with a volume of 10 mL, underwent thermal treatment at 350 °C with a flow of N_2 gas passing over the mixtures to facilitate the evaporation of their volatile components for varying durations.

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3 111 Additionally, tests were performed using PO₁ evaporation in a vacuum chamber to confirm that
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5 112 compositional changes in the heated samples were attributed to the removal of volatile constituents
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7 113 rather than chemical reactions facilitated by the thermal treatment.¹¹ The resulting evaporated
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9 114 samples were denoted as PO_x, where x represents the ratio of the initial volume to the final volume
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11 115 after evaporation ($x = V_{\text{initial}} / V_{\text{evaporated}}$). For example, if 50% of the initial volume of PO₁ remained
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13 116 after a 40 min evaporation process, it would be referred to as PO₂. In this study, PO₁, PO_{1.33}, PO₂,
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15 117 and PO₃ were utilized. Detailed information on the generation and evaporation methods of PO_x
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17 118 preparations are described in our previous reports.^{11, 12, 28}

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22 119 ***TPD-DART-HRMS experiments and data analysis.*** The detailed description of the TPD-
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24 120 DART-HRMS experimental setup, its operational procedures, the associated methodology for
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26 121 quantitative data analysis, the construction of VBS distributions, and their validation results have
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28 122 been thoroughly documented in our previous publications.^{23, 24} Briefly, small portions of the PO_x
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30 123 bulk samples (~10 μL) were individually placed onto a copper stub heated during each TPD
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32 124 experiment. The temperature ramping profile started at 298 K, held for 0.4 min, followed by a
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34 125 linear ramp at a rate of 70 K min⁻¹ to 773 K, and then maintained at the final temperature for 2
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36 126 min. The temperature profile is shown in Figure S2. The DART ionization source, interfaced with
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38 127 the Q-Exactive HF-X Orbitrap mass analyzer (operated at mass resolution of $m/\Delta m \sim 240,000$ at
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40 128 200 m/z), dynamically ionized the gas-phase species degassing from the PO_x samples during the
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42 129 TPD experimental runs. Progression of the high-resolution mass spectra was recorded to identify
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44 130 individual components. Molecular formulas were assigned based on the ions detected in negative
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46 131 mode, (–)DART-HRMS in the m/z range of 100–1000 Da, with constraints of C₁₋₄₀H₁₋₁₀₀O₁₋₂₅N₀₋
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48 132 ₁ and mass tolerance of ±2.0 ppm.²⁹ In these experiments, the (–)DART ionization mechanism led
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50 133 to the formation of deprotonated molecules [M–H][–] and radical anions M^{•–}. Consequently, the

apparent saturation vapor pressure ${}^i p_T^*$ (Pa) of each component (i) as a function of temperature (T) are determined using the Clausius-Clapeyron equation (Eq. 1).³⁰ The values of saturation vapor pressure are then converted to saturated mass concentrations ${}^i C_T^*$ ($\mu\text{g m}^{-3}$) based on the ideal gas equation (Eq. 2). These calculations require input values of ${}^i T_{max}^*$, ${}^i \Delta H^*$, ${}^i p_{T_{max}}^*$, and molecular weight of $\text{C}_x\text{H}_y\text{O}_z$ species i (${}^i MW$), all inferred from the TPD-DART-HRMS records.^{23, 24} ${}^i T_{max}^*$ corresponds to the peak ion intensity in the extracted ion thermograms of individual species. The values of ${}^i \Delta H^*$ are derived from the slope of Arrhenius plots as discussed below. The reference vapor pressure ${}^i p_{T_{max}}^*$ of the individual species (i) is estimated by assuming the stoichiometry of its formal combustion oxidation reaction, as described in our earlier publication.²³ R denotes the molar gas constant with value of $8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$.

$${}^i p_T^* = {}^i p_{T_{max}}^* \times \exp\left[\left(-\frac{{}^i \Delta H^*}{R}\right)\left(\frac{1}{T} - \frac{1}{T_{max}^*}\right)\right] \quad (1)$$

$${}^i C_T^* = \frac{{}^i p_T^* \times 10^9 \times {}^i MW}{RT} \quad (2)$$

Volatility basis sets constructions. The VBS framework, which segments the volatility spectrum of BBOA components into distinct bins,^{16,31} is utilized to characterize the entire range of saturation vapor pressures of PO_x components based on their ${}^i \Delta H^*$, ${}^i C_T^*$ and mass fraction values of individual components, as described in our previous publication.²⁴ Briefly, individual species i are grouped into a series of $(\log C^*)_j$ bins, where j represents individual bins marked by integer values. The relative heights (H_j) of VBS bins j are calculated as the sum of the molar fractions of species contained within each bin, normalized to the sum of heights across all bins, expressed by the following equation (Eq. 3):

$$H_j = \frac{[\sum_i (S_i \times A_i \times MW_i)]_j}{\sum_j [\sum_i (S_i \times A_i \times MW_i)]_j}, \text{ where } \sum_j H_j = 1 \quad (3)$$

where A_i is the molar fraction of species i , proportional to the area under its TPD-HRMS thermogram; MW_i and S_i are the molecular weight and sensitivity of species i (Figure S1), respectively.

The particle-phase mass fractions of aerosolized PO_x mixtures for each individual bin j is then computed using the constructed VBS distributions. This calculation considers different values of the total organic mass (tOM) loadings in the air (e.g. 1, 10, 100, etc. $\mu\text{g m}^{-3}$) with the following equation (Eq. 4):

$$X_j^P = H_j \times \frac{C_{tOM}}{C_{tOM} + {}^iC_T^*} \quad (4).$$

Viscosity calculations. The glass transition temperature ($T_{g,i}$) of each organic component (i) is estimated using a parameterization method based on the number of carbon (n_C), hydrogen (n_H), and oxygen (n_O) atoms in the corresponding elemental formula. The estimation employs the equation 5 along with parameter values for n_C^0 , b_C , b_H , b_{CH} , b_O , and b_{CO} listed in Table S1.³²

$$T_{g,i} = (n_C^0 + \ln(n_C))b_C + \ln(n_H)b_H + \ln(n_C)\ln(n_H)b_{CH} + \ln(n_O)b_O + \ln(n_C)\ln(n_O)b_{CO} \quad (5)$$

The glass transition temperature ($T_g(\omega_{org})$) of PO_x mixtures in a form of aerosolized particles containing water is estimated using the Gordon-Taylor equation (Eq. 6):^{32, 33}

$$T_g(\omega_{org}) = \frac{(1-\omega_{org})T_{g,w} + \frac{1}{K_{GT}}\omega_{org}T_{g,org}}{(1-\omega_{org}) + \frac{1}{K_{GT}}\omega_{org}} \quad (6)$$

Here, the ω_{org} is the organic mass fraction in the aerosolized PO_x particles containing water, computed as $\omega_{org} = mPO_x / (mPO_x + mH_2O)$, where mPO_x and mH_2O are particle phase masses of PO_x and water, respectively. For each of the environmental conditions of T (K) and tOM ($\mu\text{g}\cdot\text{m}^{-3}$) considered, mPO_x is calculated by summing the particle-phase mass fractions across all bins j comprising the corresponding VBS distribution. Values of mH_2O are subsequently calculated for

PO_x-water aerosol mixtures equilibrated at various RH using the modified Kohler theory,³⁴ assuming an effective hygroscopicity parameter $\kappa = 0.057 \pm 0.07$, as reported for BBOA in the literature.³⁵ The glass transition temperature ($T_{g,org}$) of the aerosolized PO_x mixture is calculated as $T_{g,org} = \sum_i \omega_i T_{g,i}$, where ω_i represents the mass fraction of each component i present in the VBS-calculated particle phase.³⁶ The glass transition temperature of pure water ($T_{g,w}$) and the Gordon-Taylor constant (k_{GT}) were set as 136 K and 2.5, respectively.³⁷ The same Gordon-Taylor constant was used for $T_g(\omega_{org})$ calculations for each of the PO_x mixtures. Additionally, $T_g(\omega_{org})$ values of PO_x mixtures were calculated from experimental values of C^*_{298K} using a separate parameterization approach,³⁸ as detailed in supplementary note 1 (Supporting Information).

The viscosity (η , Pa·s) of individual organic components and their mixtures can be derived from $T_{g,i}$ and $T_{g,org}$, respectively, using the Vogel-Tammann-Fulcher (VTF) equation (Eq. 7):³²

$$\log \eta = -5 + 0.434 \frac{T_0 D}{T - T_0} \quad (7)$$

where T_0 is the Vogel temperature ($T_0 = 39.17 \times T_g / (D + 39.17)$) and D is the fragility parameter, assumed to be 10 when $T_g < T$.³² Finally, viscosity values derived for mixtures of interest are used to calculate their corresponding diffusion coefficients (D_b) using the Stokes-Einstein equation (Eq. 8):

$$D_b = \frac{kT}{6\pi a \eta} \quad (8)$$

where k is the Boltzmann constant (1.38×10^{-23} J K⁻¹) and a is the effective molecular radius approximated as 1 nm.^{37, 39}

The mixing time axes (τ_{mix} , s) were calculated with the following equation (Eq. 9):⁴⁰

$$\tau_{mix} = \frac{d_p^2}{4\pi^2 D_b} \quad (9)$$

where d_p is the particle diameter.

Viscosity measurements. Viscosities were measured using the poke-flow method.^{41, 42} PO₁ was deposited on 12 mm glass microscope cover slips by dipping the blunt end of a 0.25 mm diameter needle in PO₁ and then tapping the needle against the cover slip, leaving behind spherical-cap droplets with base diameters ranging from 60 to 120 μm. The cover slips have been coated with a hydrophobic/oleophobic coating (Fluoropel-800, Cytonix) to facilitate the spherical shape of the droplets. The samples were placed in a temperature-controlled flow cell, warmed to 80°C under N₂ gas, and maintained at this temperature to facilitate partial evaporation of the droplets. Before and after heating, the volume of each droplet was measured using a confocal laser-scanning fluorescence microscope (Axio Observer LSM 510MP, Zeiss). The $x=V_{initial}/V_{final}$ of the droplets ranged from 1.2 to 2.9 after heating. Poke-flow viscosity measurements were then carried out as described in detail elsewhere.^{41, 43} In short, the samples were placed in a flow cell located above an inverted microscope and with a fine needle (0.25 mm diameter, 13561-10 Ted Pella) inserted through the top of the flow cell. The samples were conditioned to dry conditions by leaving them under a flow of dry zero-air in the dark for 1 hour before poking. Using a micromanipulator, the needle was lowered into the center of a PO_x droplet, creating a circular deformation. Upon rapid removal of the needle, the PO_x flowed back into the hole to restore its original geometry. The time taken for the hole to close (the recovery time) was then recorded. The initial and final geometries of the droplets and the recovery times were then used in a COMSOL Multiphysics microfluidics simulation to find the lower and upper limits of the droplets' viscosities. Parameters used in the simulations are listed in Table S2. When a droplet was highly viscous, the hole did not recover at all after >12 hours and only a lower limit to the viscosity was established. If the hole closed faster than the camera could capture, then only an upper limit to the viscosity was reported.

RESULTS AND DISCUSSION

Figure 1 illustrates representative results obtained from the TPD-DART-HRMS experiments with PO_1 and PO_3 mixtures, alongside the corresponding data processing workflow. In each experiment, the progression of high-resolution mass spectra is recorded as a TPD thermogram (Figures 1a and 1b). The accurate mass measurements allow for untargeted identification of individual components through assignments of their elemental formulas. Components that evaporate below 300 °C comprise of low-volatility and semi-volatile species, while the extremely low-volatility species that remain after heating at 300 °C are referred to as non-refractory components.^{44, 45} Based on the TPD mass spectra progression, evaporated components of PO_1 and PO_3 samples were detected, with their elemental composition identified, as further detailed in Figures S2 and S3. The distinctions between the PO_1 and PO_3 components are primarily attributable to different relative intensities of HRMS features corresponding to low-volatility and semi-volatile compounds. Specifically, the PO_1 sample exhibits prominent features of relatively low molecular weight species within a mass range of 100–200 Da, whereas the PO_3 sample manifests additional abundant species with higher masses of 150–300 Da. Additionally, organic components within PO_3 exhibit higher fractions of species characterized by longer carbon chain length and lower hydrogen saturation compared to the PO_1 sample (Figure S3).⁴⁶ These observations suggest that the evaporation process primarily depletes low molecular weight components with high saturation levels. Conversely, higher molecular weight species (>150 Da) exhibit minimal alterations upon evaporation, indicating their extremely low volatility and consequent persistence within the particulate matter upon aerosolization.

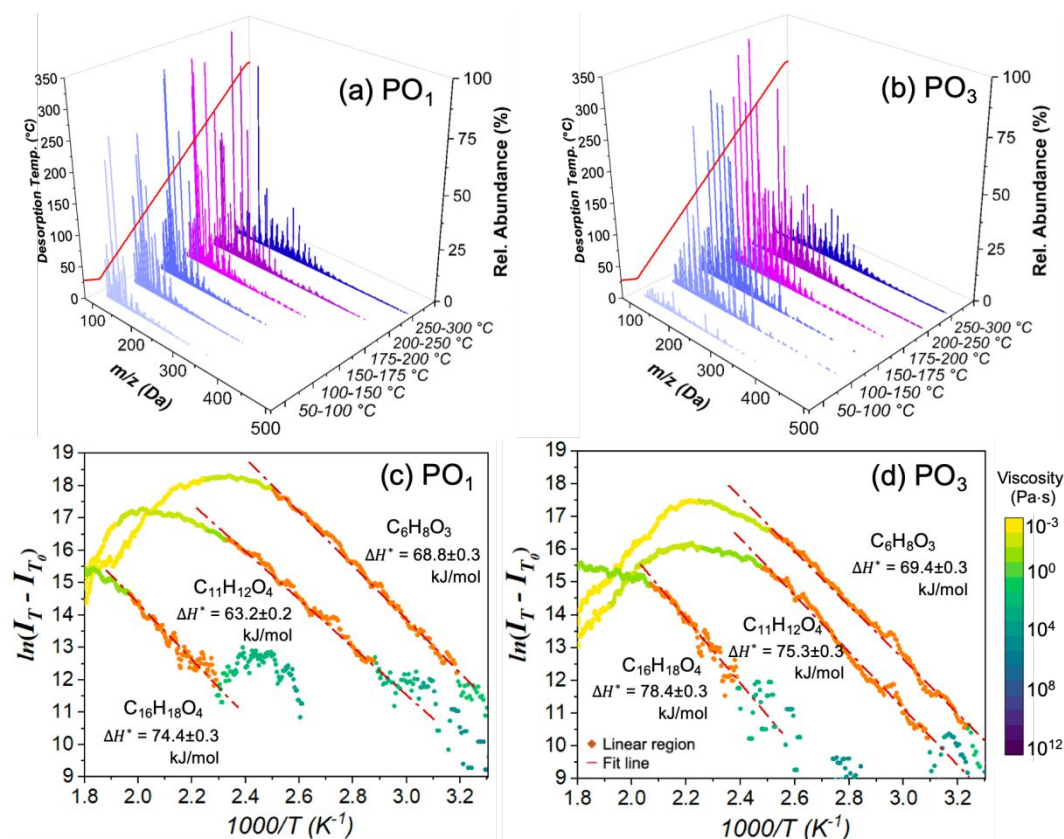


Figure 1. (a-b) Progression of (–)DART-HRMS spectra of PO₁ (a) and PO₃ (b) samples averaged over annotated temperature ranges of the TPD experiment. The temperature profile (red line) is shown along the second y-axis of the plot. The relative abundances of the individual peaks are arbitrarily scaled to the cubic root of the corresponding MS peaks relative intensities to facilitate the comparison. (c-d) The Arrhenius plots of $\ln(I_T - I_{T_0})$ versus $1/T$ (K⁻¹) of three selected species of C₆H₈O₃, C₁₁H₁₂O₄, and C₁₆H₁₈O₄. Orange symbols denote linear regions used to fit (red dashed lines) the data using Clausius–Clapeyron equation and calculate the apparent enthalpies of solid-to-gas transitions, shown in legends. The color scale reflects viscosity values calculated for each species as a function of temperature during the TPD run.

The apparent enthalpies $^i\Delta H^*$ characterizing the transition of individual species from particle to gas phase are determined from the slope of Arrhenius plots, plotting the logarithm of ion intensity ($\ln(I_T - I_{T_0})$) versus the inverse temperature ($1/T$), based on the extracted ion signal recorded during the TPD run.²³ Figures 1c and 1d illustrate examples of the $^i\Delta H^*$ values derived from TPD thermograms for three selected common species of C₆H₈O₃, C₁₁H₁₂O₄, and C₁₆H₁₈O₄ between PO₁ and PO₃ mixtures. The viscosity calculations indicate that at the onset temperatures when each

species starts to evaporate, their viscosity is at the lower values of $<10^1$ Pa·s, indicative of oily liquids. As temperatures increase, their viscosity gradually decreased, eventually reaching values of 10^{-3} Pa·s, comparable to that of water.³⁷ This observation indicates that extensive evaporation of individual PO_x components occurs as they liquefy, implying low kinetic limitations for the evaporated analyte molecules prior to their arrival to the ionization source. In our previous work,²⁴ it has been demonstrated that near-equilibrium conditions are achieved at each TPD stage, allowing for the assumption that the linear sections of the Arrhenius plots can be used to derive the apparent enthalpies $^i\Delta H^*$ characteristic of condensed-to-gas phase transitions of individual species i . In the previous study,²³ the validity of this assumption was confirmed by measuring $^i\Delta H^*$ and $^ip_T^*$ values for a set of carboxylic acids standards, showing close agreement with literature data. Notably, the temperature range of the Arrhenius plots used to determine the $^i\Delta H^*$ values of identified species was below 200 °C (473 K), where most organic species remain stable,⁴⁷⁻⁴⁹ with the exception of peroxides, which may decompose above ~80 °C (353 K).⁵⁰ At elevated temperatures above 300 °C, thermal decomposition products of organic species are observed in our experiments. However, the apparent $^i\Delta H^*$ and $^ip_T^*$ values of species detected at these high temperatures suggest that they are derived from extremely low volatility precursors that do not partition into the gas phase under atmospherically relevant conditions. Consequently, these species have a minimal impact on the gas-phase partitioning.

The apparent $^i\Delta H^*$ values determined for the species $\text{C}_6\text{H}_8\text{O}_3$, $\text{C}_{11}\text{H}_{12}\text{O}_4$, and $\text{C}_{16}\text{H}_{18}\text{O}_4$ detected in the PO_1 mixture are 68.8 ± 0.3 kJ mol⁻¹, 63.2 ± 0.2 kJ mol⁻¹, and 74.4 ± 0.3 kJ mol⁻¹, respectively. The $^i\Delta H^*$ values measured for the same species detected in the PO_3 mixture are 69.4 ± 0.3 kJ mol⁻¹, 75.3 ± 0.3 kJ mol⁻¹, and 78.4 ± 0.3 kJ mol⁻¹, correspondingly. Both experiments exhibit the expected trend of higher enthalpy values for larger molecules. Additionally, the enthalpy values

of individual species observed in the PO_3 experiment are consistently higher than those reported in the PO_1 experiment. The observed disparities in the apparent enthalpies of individual species sharing the same elemental formulas, though reported separately in different PO_x experiments, likely result from a combination of factors. For instance, differences in the number and molar ratios of isomers present in the progression of the PO_x samples could contribute to these variations. Additionally, stronger Raoult matrix effects may play a role, constraining the evaporation of species from mixtures containing larger organic molecules, which is consistent with the higher enthalpies reported in the PO_3 experiment. Consequently, the derived saturation mass concentrations (iC_T^*) showed a general downward trend with increasing molecular weight (Figure S4).

The saturation mass concentrations (iC_T^*) across a wide range of experimental temperatures are determined from the apparent $i\Delta H^*$ values obtained from the experiments, enabling the construction of VBS distributions at varying temperatures.²⁴ Figures 2(a–c) depict the alterations in the VBS distribution of compounds in PO_1 , considering the process of atmospheric cooling exemplified for the aerosol-gas system of total mass loading of $tOM = 1000 \mu\text{g m}^{-3}$, calculated at decreasing temperatures of 473 K, 373 K, and 298 K, respectively. The progression of these VBS plots allows for a quantitative assessment of the gas-particle partitioning in the biomass burning plume as it travels away from the high-temperature emission zone. Assuming the case scenario of $tOM = 1000 \mu\text{g m}^{-3}$, almost all (>92% by mass) of the compounds in PO_1 exist in the gas phase at temperatures higher than 473 K, where saturation mass concentrations of all individual organic species in the plume will be within the ranges of volatile organic compounds (VOC), $6 < \log(C^*, \mu\text{g m}^{-3})$, and intermediate volatility organic compounds (IVOC), $2 < \log(C^*, \mu\text{g m}^{-3}) \leq 6$. As the temperature decreases to 373 K, around 37% of the PO_1 partitions into the particle phase, driven

by the species for which saturation mass concentrations are lowered down to the range of semi-volatile organic compounds (SVOC), $-2 < \log (C^*, \mu\text{g m}^{-3}) \leq 2$, and low-volatility organic compounds (LVOC), $-6 < \log (C^*, \mu\text{g m}^{-3}) \leq -2$.⁵¹ Further decrease of temperature to common ambient 298 K drives 79% of the PO_1 species by mass into the particle phase, where significant fractions of PO_1 species start to exhibit saturation mass concentrations in the range of extremely low volatility organic compounds (ELVOC), $\log (C^*, \mu\text{g m}^{-3}) \leq -6$. Upon further reduction of the temperature to 278 K, approximately 89% of the PO_1 compounds partition into the particle phase. Figures 2(a–c) exemplify that decreasing temperatures shift the VBS distribution towards lower volatility, resulting in larger fractions of BBOA components partitioning into the particle phase. Importantly, the extent of gas-particle partitioning can now be quantitatively assessed based on the bottom-up constructed VBS distributions derived from the temperature dependent values of ${}^iC_T^*$ obtained for individual species i in the TPD-DART-HRMS experiments. However, when calculating VBS distributions at temperatures beyond the experimentally observed Arrhenius range, caution is required. The assumption that ${}^i\Delta H^*$ values remain temperature-independent may not hold true at significantly extrapolated temperatures.

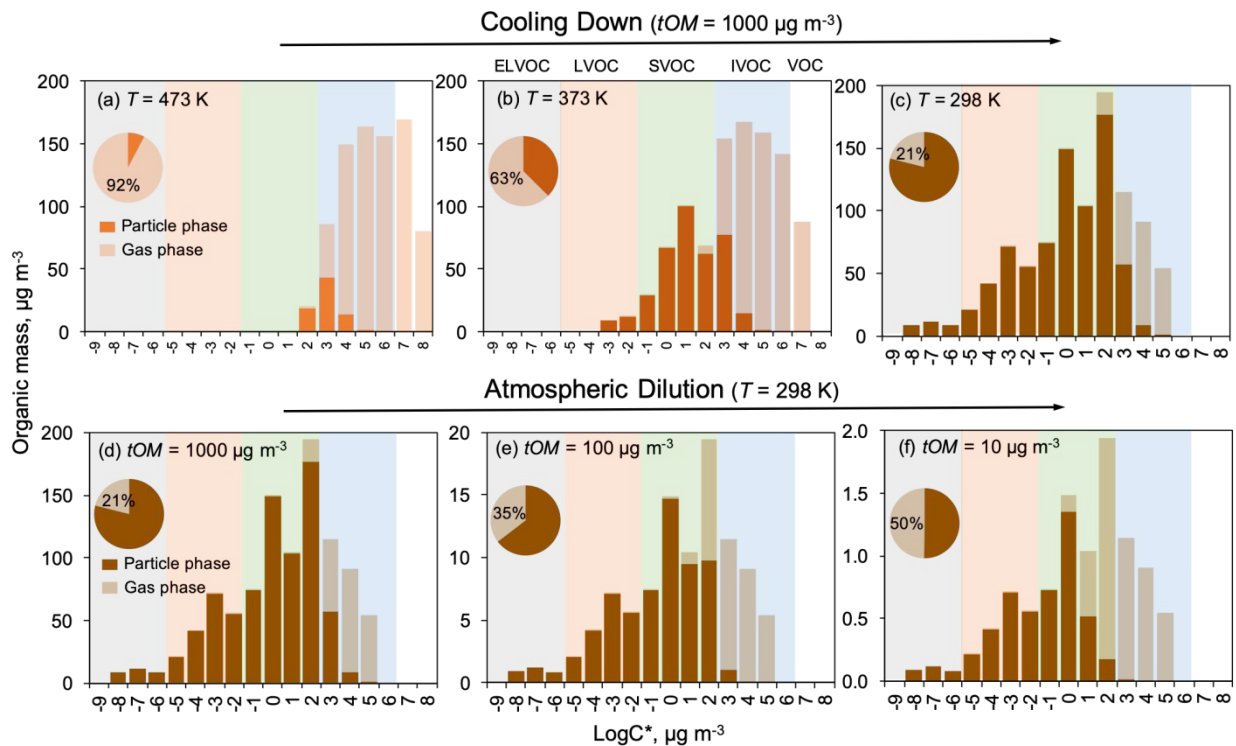


Figure 2. (a–c) Volatility basis set (VBS) distributions for components of the PO₁ mixture considering an atmospheric cooling down process of biomass burning emissions exemplified by decreasing temperatures (473 K, 373 K, and 298 K) and a constant organic mass (*tOM*) loadings of 1000 µg m⁻³. (d–f) VBS distributions for components of the PO₁ sample mixture considering atmospheric dilution exemplified by decreasing values of *tOM* loadings (1000, 100, and 10 µg m⁻³) and a temperature of 298 K. Light colors denote the portions of PO₁ components capable of gas-phase partitioning under these conditions. Pie charts depict the estimated mass fractions percent of gas-phase and particle-phase species summed across all VBS bins.

Gas-particle partitioning in the biomass burning plume is additionally influenced by dilution upon dispersal into the background atmosphere. In addition to the atmospheric temperature, the total mass loadings, which vary during air transport, play a crucial role in shaping the gas-particle partitioning of BBOA compounds. Figures 2(d–f) illustrate the transition between the gas-phase and particle-phase fractions of the PO₁ mixture, as inferred from the VBS distributions constructed for an ambient temperature of 298 K. This transition is exemplified by a progression of decreasing total organic mass loadings of *tOM* = 1000, 100, and 10 µg m⁻³, respectively, considering the

process of atmospheric dilution. Near biomass burning sources, concentrations of all emissions are very high, e.g. $1000 \mu\text{g m}^{-3}$,⁵² where 80% of PO_1 compounds remain in the particle phase, with the remaining 20% released into the gas phase. As the atmospheric dilution progresses, the tOM loadings gradually diminish, and more particle-phase compounds partition into the gas phase. Considering the tOM loadings of $100 \mu\text{g m}^{-3}$, 35% of PO_1 compounds transition into the gas phase. With further dilution during prolonged atmospheric transport where tOM loadings would decrease to $10 \mu\text{g m}^{-3}$, 50% of PO_1 components shift to the gas phase, leaving the other half in the particle phase. A comparison of the VBS distributions for the PO_1 and PO_3 mixtures with those of ambient BBOA from selected field studies^{53, 54} is provided in Figure S5. The VBS distribution of the PO_3 mixture shows significant similarity to that of ambient BBOA, suggesting it may represent a substantially aged aerosol. These observed similarities highlight the potential for future systematic studies, where the measurement approach described here could be used to complement real-time observations.

Figure 3 depicts a two-dimensional (2D) map illustrating the gas-particle partitioning of aerosolized PO_1 mixture, represented by a color gradient. This visualization is based on the constructed VBS distributions, considering a wide range of the tOM loadings from 0.1 to $1000 \mu\text{g m}^{-3}$, and temperatures (T) ranging from 273 to 323 K. The degree of gas-particle partitioning exhibits a significant dependency on both tOM and T . Across the range of conditions considered, particle-phase mass fractions of PO_1 fluctuate from approximately 10% (at low tOM and high T) to around 90% (with high tOM and low T). A similar 2D map constructed for the PO_3 mixture is included in SI (Figure S6). The 2D maps enable a visual assessment of the atmospheric cooling rates, emission sources strength, and dilution effects on the gas-particle partitioning of organic components within aged biomass burning plumes. When original BBOA emissions are rapidly

cooled by the surrounding low temperature environment, the particle fraction initially rises and then decreases throughout the atmospheric dilution process, as depicted in Figure 3 by the blue-line trajectory. However, at warmer ambient temperatures, the particle-to-gas evaporation due to dilution may exceed the gas-to-particle condensation due to cooling, resulting in an overall slow progressive evaporation of species from the particle phase, as illustrated in Figure 3 by the red-line trajectory. Hence, the specific gas-solid distribution of organic compounds is affected by multiple factors, including rates of atmospheric cooling and dilution, as well as the temperature and strength of emission sources. Of note, extensive partitioning from particle to gas phase is particularly prominent when *tOM* loadings are at the level of $10 \mu\text{g m}^{-3}$ and below. This suggests that nascent BBOA particles serve as vital carriers of later gas-phase components, which will facilitate atmospheric gas-phase reactions and SOA formation⁵⁵ in pristine environments located downwind of the BBOA emission sources.

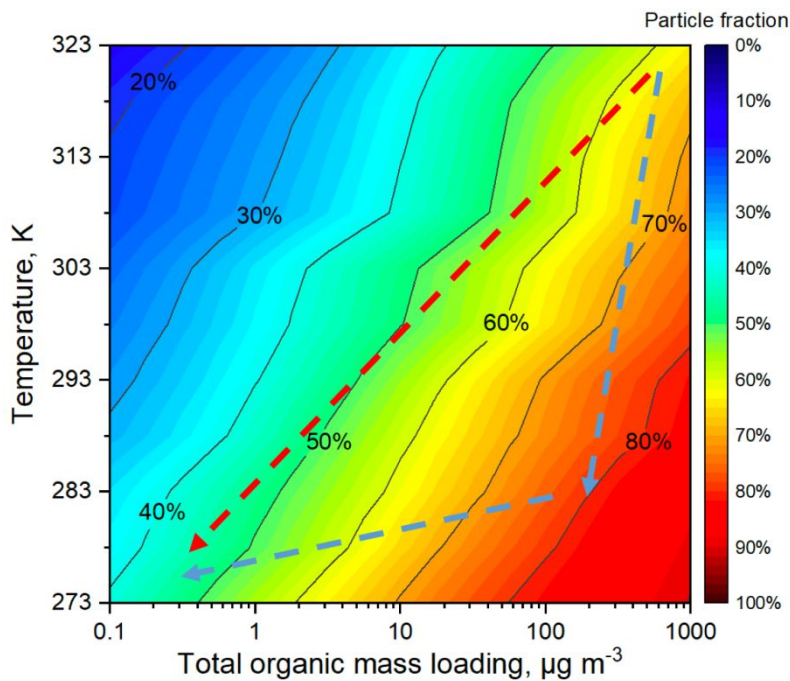


Figure 3. Particle-phase mass fractions calculated for the aerosolized PO_1 components using the constructed VBS distributions and considering broad ranges of ambient temperatures and total organic mass

(*iOM*) loadings. Dash lines showcase the rapid cooling trajectory (blue line) versus gradual cooling trajectory (red line).

The transition of individual components from particle to gas phases can be significantly impeded by transport limitations, particularly slow diffusion within the BBOA particles themselves, especially as they become more viscous and semi-solid. Notably, existing parameterization approaches^{32, 56} allow for the computation of viscosity values for all individual species identified in the TPD-DART-HRMS experiments. This information is then utilized to assess the apparent viscosity of particle-phase mixtures based on the mass contributions of individual species in the particle phase and the degree of gas-particle partitioning, both inferred from the VBS distributions. Figure 4 illustrates the VBS distributions of PO_1 and PO_3 mixtures combined with the component-specific viscosity information, with individual bins color-coded to represent mass fractions of species with different viscosity ranges. Considering a viscosity value of $10^3 \text{ Pa}\cdot\text{s}$, equivalent to the viscosity of paraffin wax, as the boundary between liquid-like and semi-solid materials,^{37, 57} kinetic limitations on the particle-to-gas-phase transition can be evaluated. The plots indicate that IVOC species have viscosity values less than $10^3 \text{ Pa}\cdot\text{s}$, indicating a liquid-like physical state. SVOC and LVOC species exhibit viscosity ranges of 10^3 – $10^7 \text{ Pa}\cdot\text{s}$ and 10^6 – $10^9 \text{ Pa}\cdot\text{s}$, respectively, comparable to highly viscous waxes and semi-solid pitch material. ELVOC species have the highest viscosity of $>10^8 \text{ Pa}\cdot\text{s}$, approaching the viscosity of solid vitreous carbon or amorphous glass.³⁷ Notably, if the characteristic mixing time (*e*-folding time) of BBOA components within individual particles exceeds tens of minutes, the atmospheric particle-to-gas partitioning may be substantially hindered by slow diffusion within the particles. Considering a typical diameter of 200 nm for BBOA particles, a threshold viscosity of $>10^5 \text{ Pa}\cdot\text{s}$ is derived using Eq. 9. At higher viscosities, diffusion within the particle phase becomes the critical limiting factor controlling the kinetics of the particle-to-gas partitioning. Additionally, temperature variations impact the

viscosity of BBOA compounds, inherently affecting diffusion and characteristic mixing times, as illustrated in Figure S7. For the specific conditions of tOM and T , the resulting viscosity of the particle-phase fractions of PO_x can be computed using Eqs 5–7, which require input values of the mass contributions of individual species (i) and their $T_{g,i}$ values.

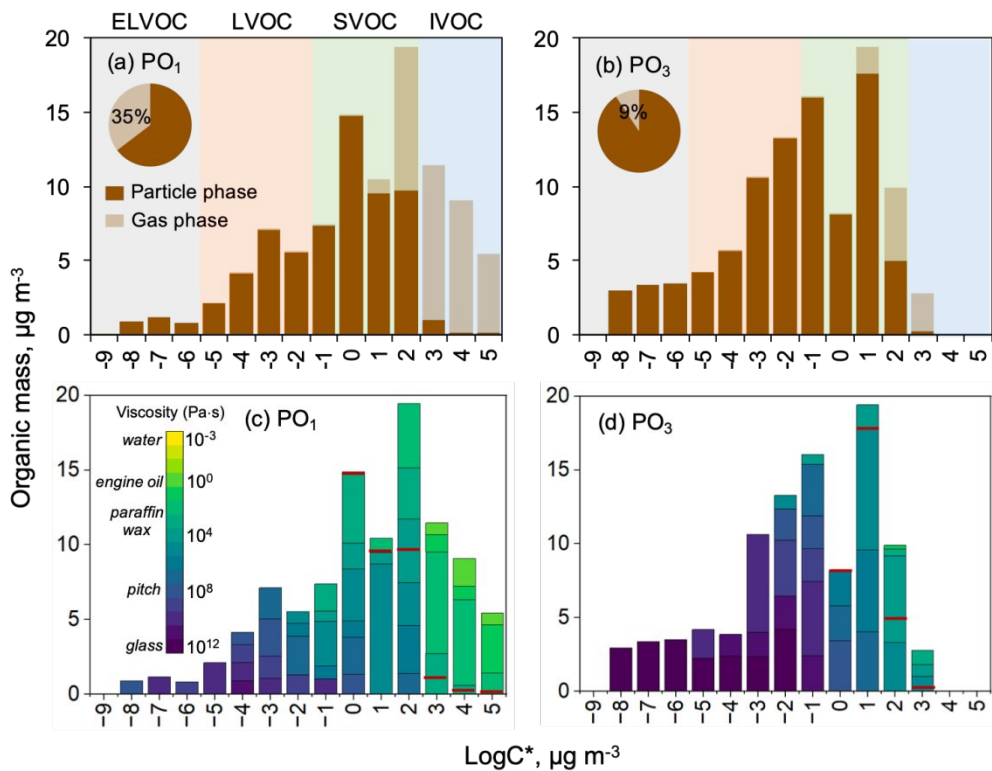


Figure 4. (a, b) Comparison of the VBS distributions constructed for PO_1 and PO_3 mixtures under conditions of $T=298\text{ K}$ and $tOM=100\text{ }\mu\text{g m}^{-3}$. Pie charts depict the estimated mass fractions percent of total gas- and particle-phase species summed across all VBS bins. (c, d) The same VBS distributions as shown above, incorporating information on viscosity values calculated for individual components identified in the mixtures. The viscosity values of individual components are segmented into a series of groups with viscosity ranges that differ by a factor of 10. Each bin in the VBS distributions is color-coded to represent contributions of components with varying viscosity ranges. The color bar denotes the viscosity ranges, with reference materials indicated on the left.

To validate the feasibility of adequate viscosity prediction from the molecular characterization data discussed in this work, we compared the computed viscosity values for the PO_x bulk mixtures

with the corresponding experimental results measured in the poke-flow experiments.⁵⁸ Figure 5a displays the results of this comparison, showcasing the computed and experimentally measured viscosity values at 298K for a series of PO_x mixtures prepared through controlled evaporation in laboratory experiments. The viscosities of PO₁, PO_{1.33}, PO₂, and PO₃ mixtures computed based on the elemental formulas and VTF equation^{32, 33} were 10^{3.2}, 10^{5.0}, 10^{7.9}, and 10^{9.3} Pa·s; viscosities calculated from the C_{298K}^* values³⁸ were 10^{3.3}, 10^{5.1}, 10^{7.8}, and 10^{8.9} Pa·s, increasing significantly as the volume of PO_x decreases upon evaporation. The measured viscosity values were consistent with the computed results. The measured viscosity of PO₁ mixture was at the lower limit of 10³ Pa·s. The measured viscosity increased as the volume of the PO_x mixtures decreased, with the measured viscosity of PO_{1.3±0.1} and PO_{1.8±0.1} corresponding to 10^{5.1±0.4} Pa·s and 10^{7.7±0.1}, respectively. The measured viscosity of the PO_{2.9±0.9} mixture approached the upper measurement limit of >10⁸ Pa·s, where the poked droplets shatter and no relaxation flow can be observed. Both computed and measured results indicate a significant rise in viscosity increase across several orders of magnitude during non-reactive evaporation. While the glass transition temperatures, $T_g(\omega_{org})$, of PO_x mixtures may be influenced by variable matrix effects unique to each mixture, and the use of a single Gordon-Taylor constant in eq. 6 is a simplified approach, the close agreement between the calculated results and poke-flow measurements validates its practical applicability.

The consistent viscosity trend over the set of PO_x mixtures not only demonstrates the utility of the viscosity predictions based on the chemical characterization data from the TPD-DART-HRMS experiments, but also provides means for quantitative assessment of the evaporation processes on the viscosity of atmospheric BBOA. Previous studies have shown that particles collected near a fire, characterized as fresh BB aerosols, exhibit low viscosity. However, as they age within the smoke plume, their viscosities increase significantly, often resulting in the formation of spherical

semi-solid (glassy) particles commonly referred to as ‘tar balls’.^{52, 59} Our work illustrates that when half of the volume of BBOA evaporates (from PO₁ to PO₂), their viscosity increases by four orders of magnitude, potentially resulting in the amorphous semi-solid tar balls. Such drastic viscosity changes can also hinder particle-to-gas transitions through lowering the molecular diffusion rates of BBOA components.⁶⁰

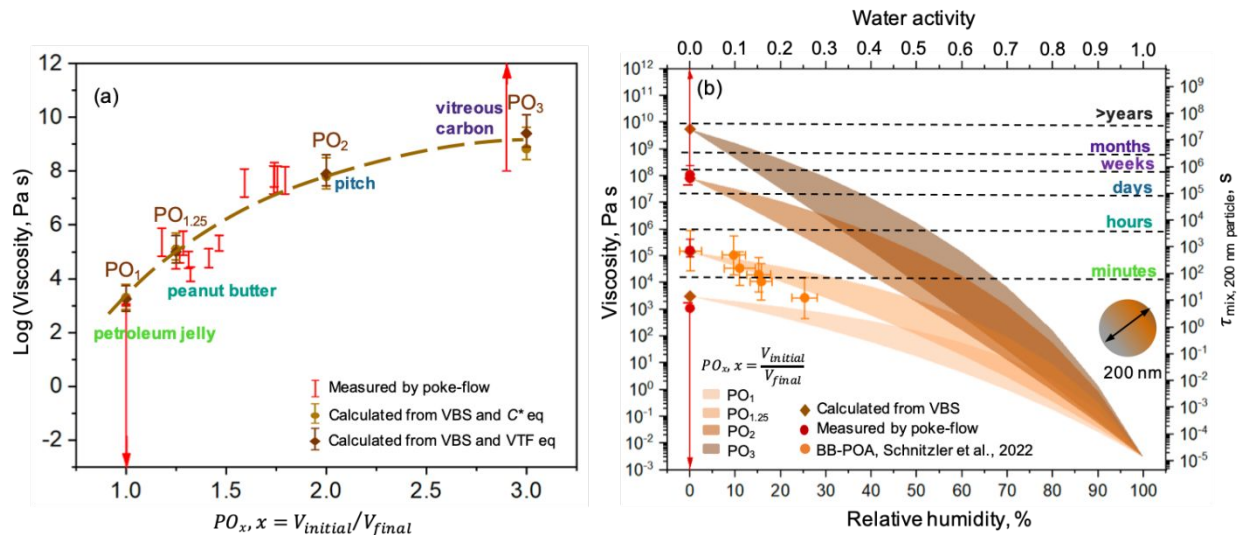


Figure 5. (a) The comparison of viscosity values computed for PO_x mixtures based on the constructed VBS distributions and $T_g(\omega_{org})$ values derived from elemental formulas and VTF equation^{32, 33}, those derived from C^* values³⁸ and experimental viscosity values derived from the poke-flow measurements conducted at room temperature. The dashed line in the plot indicates a polynomial fit of the computed PO_x viscosity values, parameterized as $\log(\eta) = 1.39x^2 + 8.56x - 3.90$ ($R^2 = 0.99$). (b) Viscosity and e -folding times computed for 200 nm particles composed of PO_x mixtures and water content equilibrated at different levels of RH at room temperature.

The viscosity and diffusion in BBOA particles are significantly influenced by their water content equilibrated with external relative humidity (RH),^{33, 61, 62} which can be further quantified for aerosolized PO_x mixtures based on literature reported effective hygroscopicity parameter of $\kappa = 0.057 \pm 0.07$ for BBOA particles.³⁵ Figure 5b illustrates the results of these calculations for particles composed of each of the four PO_x mixtures, showcasing variations in their viscosity predicted for

different atmospheric RH conditions at 298K. Elevated water activity decreases the viscosity of BBOA, and this impact becomes more pronounced as the degree of evaporation (x) increases. Additionally, it is expected that the hygroscopicity of PO_x would decrease substantially with increasing x values, and therefore PO_3 may become hydrophobic with κ approaching 0. Figure S8 showcases variations in viscosity of PO_x mixtures as a function of RH, where variable κ values of 0.15, 0.10, 0.05, and 0.02 were assigned for PO_1 , $\text{PO}_{1.33}$, PO_2 , and PO_3 , respectively. As the degree of evaporation (x) increases, the viscosity of BBOA remains rather unchanged at $\text{RH} < 40\%$ but exhibits more noticeable variations at higher RH. When the viscosity of BBOA increases to a significant level, such as $10^9 \text{ Pa}\cdot\text{s}$ of PO_3 , PO_x likely remains nearly hydrophobic at relatively low RH. Furthermore, as illustrated in Figure S9, lower $t\text{OM}$ loadings and colder temperatures also increase the viscosity and e-folding time of BBOA. These findings underscore the significant influence environmental conditions, such as temperatures, RH, and $t\text{OM}$ loadings during atmospheric dilution, on the viscosity and diffusion within condensed phase of BBOA during transport. In particular, lower temperatures, reduced RH, and the dilution process collectively contribute to an increase in BBOA viscosity.

The viscosity of BBOA undergoes significant changes caused by evaporation during atmospheric transportation. As illustrated in Figures 4c and 4d, there is a notable increase in the contribution of highly viscous species in the PO_3 sample, compared to PO_1 . In PO_3 , the liquid-like species with viscosity values less than $10^3 \text{ Pa}\cdot\text{s}$ are largely depleted, while the highly viscous semi-solid species persist, particularly those with viscosity values exceeding $10^8 \text{ Pa}\cdot\text{s}$, comparable to pitch tar.³⁷ As indicated in Figure S10, the PO_3 mixture exhibits substantially higher viscosity compared to PO_1 under identical environmental conditions, including $t\text{OM}$ loadings, temperatures, and RH. These findings suggest that as BBOA particles gradually evaporate in emission plumes

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3 479 due to atmospheric dilution, their low-viscosity components vaporize, leaving behind high-
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5 480 viscosity components, and leading to the solidification of aged BBOA particles, commonly
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7 481 referred to as tar balls. Additionally, the condensed-phase reactions inside particles may also lead
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9 482 to the formation of oligomers, contributing to the increased viscosity of PO_3 . This solidification
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11 483 significantly impedes condensed-phase diffusion, resulting in much longer characteristic *e*-folding
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13 484 mixing times of species equilibrating within the particles. Considering 200 nm as a typical
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15 485 diameter for BBOA particles and assuming that fresh and aged particles are represented by the
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17 486 PO_1 and PO_3 proxies, respectively, trends in their characteristic mixing times can be evaluated.
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19 487 Specifically, as PO_1 transforms into PO_3 upon evaporation, the viscosity of BBOA particles would
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21 488 change from 10^3 Pa·s to 10^8 Pa·s under dry conditions, corresponding to changes in mixing times
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23 489 from seconds to months. At more atmospherically relevant conditions of 50–60% RH, the viscosity
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25 490 of BBOA particles may range from 10^1 Pa·s to 10^5 Pa·s, still significant enough to slow down
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27 491 mixing times from milliseconds to hours. Lower atmospheric temperatures of BBOA plumes from
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29 492 wildfires transported aloft would further facilitate solidification, leading to the formation of tar
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31 493 balls as illustrated in Figures S10 and S11. Electron microscopy imaging of individual BBOA
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33 494 particles sampled during aircraft transects at varying distances downwind from a wildland fire
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35 495 revealed that tar balls form within approximately three hours of ageing, driven by transformation
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37 496 and solidification of the initially emitted liquid-like particles.^{52, 59} These studies reported a
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39 497 significant increase in tar ball mass fractions, rising from less than 1% near the fire to 31–45%
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41 498 downwind,⁵² and an increase in tar ball number fractions from nearly zero in young smoke to
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43 499 approximately 80% in aged smoke.⁵⁹ While atmospheric aging of BBOA is synergistically
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45 500 influenced by both reactive chemistry and physical processes,^{63, 64} the evaporation of semi-volatile
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environmental conditions of 283–288 K and 40–50% RH, the viscosity of fresh BBOA particles is 10^2 – 10^3 Pa·s, but rapidly increases to 10^9 – 10^{10} Pa·s in aged BBOA particles, supporting tar ball formation. During atmospheric transport, as *tOM* loading decreases from $\sim 1000 \mu\text{g m}^{-3}$ to $\sim 100 \mu\text{g m}^{-3}$ or less, the viscosity of BBOA particles increases from 10^2 to 10^9 Pa·s, highlighting the role of evaporation in this transformation. It is important to note that humidity-driven hydration and dehydration effects can lead to irreversible particle transformations, which are not accounted for in the estimated values presented above. The resulting uncertainty in composition and optical properties of the real-world BBOA particles due to humidity fluctuations should also be considered. Furthermore, variability in the mixing states of BBOA particle ensembles may introduce additional complexity to the effects of volatilization.

ATMOSPHERIC IMPLICATIONS

The atmospheric aging of BBOA involves a series of physical and chemical transformations, with evaporation and solidification playing a pivotal role. Understanding the impact of evaporation on BBOA is essential for assessing its broader implications on atmospheric chemistry and climate. During atmospheric transport, evaporation prompts highly volatile and low-viscosity compounds to transition into the gas phase.⁵⁵ Consequently, compounds with low volatility, high viscosity, and stronger light-absorbing properties¹¹ remain in BBOA, enhancing the BrC absorption and thereby affecting climate. The TPD-DART-HRMS measurement platform offers unique capability to measure the apparent volatility of individual compounds, enabling the acquisition of valuable temperature-dependent volatility profiles of complex mixtures. This advancement facilitates the quantification of solid-gas partitioning and viscosity under varying environmental conditions. Specifically, our results indicate that BBOA typically undergoes a process of becoming more

viscous during regional or vertical transport in the atmosphere. This increase in viscosity can prolong the atmospheric lifetimes of various BBOA components, thus amplifying their impact on radiative forcing and air quality.⁶⁵⁻⁶⁷ Additionally, the enhanced viscosity of BBOA can facilitate their propensity to act as cloud ice nuclei.⁶⁸ Importantly, the gas-particle partitioning of BBOA throughout its atmospheric transport is highly sensitive to environmental conditions. Our study demonstrates how variations in temperature and atmospheric mass loadings may influence the gas-particle partitioning of BBOA particles, leading to significant alternations in their viscosity and optical properties. Furthermore, our study provides quantitative insights into the origin and formation mechanism of the highly viscous tar ball particles commonly observed in aged biomass burning emissions.^{52, 59, 69} We suggest that tar balls form through the solidification of BBOA particles upon the evaporation of their semi volatile components. We emphasize the profound influence of environmental conditions, such as humidity, on these transformations. However, the aging of atmospheric BrC involves not only volatilization but also other processes such as photochemical aging and oxidation. Future research should explore the combined effects of these aging mechanisms, as they have distinct impacts on BBOA.

ASSOCIATED CONTENT

Supporting Information

The following supporting information is available free of charge.

Additional information as mentioned in the text; Volatility basis sets constructions, viscosity calculations and viscosity measurements, Progression of TPD-DART-HRMS spectra and molecular characteristics of PO_x samples , The comparison of VBS distribution of PO_x mixtures with literature ones, Gas-particle partitioning of PO₁ mixtures under variable *T* and *tOM*

conditions, VBS distributions and viscosity of PO_1 mixtures under variable T conditions, Viscosity and e -folding time of PO_x mixtures as a function of RH under variable T and tOM conditions (Supplemental Notes S1–S6); additional Text S1, Figures S1–S11, and Table S1 illustrating supplemental notes (PDF).

VBS distribution template of PO_x mixtures (XLSX).

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Notes

The authors declare no competing financial interest.

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