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Lability of secondary organic particulate matter

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Atmospheric particulate matter (PM) has significant effects on climate, air quality, and human health (1). Globally, organic compounds constitute 20 to 90% of the submicron PM mass. Most of this mass is produced by the oxidation and subsequent condensation of biogenic and anthropogenic gaseous precursors as secondary organic material (SOM) (2). Parameterizations of produced mass have been developed based on the oxidation of different types of volatile organic compounds (VOCs) in environmental chambers (3, 4). Chemical transport models (CTMs) based on these parameterizations, however, do not successfully account for the PM concentrations measured in the atmosphere (5, 6), and closing the gap between model and measurements is a major research goal (7–10).

The approach to equilibrium for some atmospheric and laboratory scenarios might extend to many hours or even days (30), in some cases exceeding the typical lifetime of PM in the atmosphere. Predictions of atmospheric PM concentrations, implemented in many CTMs for an assumption of equilibrium within an hourly time step, might become inaccurate.

Herein, the evaporation rates of organic films were used to address the foregoing topics, especially the dependence on RH. A quartz crystal microbalance (QCM; SI Appendix, Fig. S1) was used to measure the time course of film mass. Evaporation rates (nanograms per minute) and vapor mass concentrations (micrograms per cubic meter) were obtained from these datasets. RH was regulated inside the QCM cell to affect the water content of the film. Greater water content, in turn, acted as a plasticizer to increase the molecular diffusivities and hence evaporation rates of film constituents (15, 16, 20, 21, 31, 32). The datasets of evaporation rates were inverted by a physical model to infer corresponding molecular diffusivities.

Results

QCM-determined evaporation rates are plotted in Fig. 1 for several different values of RH. Ordinate axes show the observed evaporation rates (Δm/Δt, nanograms per minute) and the corresponding vapor mass concentrations (C, micrograms per cubic meter) (SI Appendix). For films derived from aromatic precursors such as toluene and m-xylene, which are both representative of anthropogenic sources, the evaporation rates were low below 20% RH (Fig. 1 A and B). For this RH regime, the film/vapor interface was isolated from the interior region of the film because of slow species diffusivity in the condensed phase. As a result, after a transient period, the remaining surface species were depleted of...
species diffusivity remained high, even at low RH. Vapor mass concentrations represented global equilibrium. In agreement, SOM particles derived from α-pinene and isoprene did not shatter after poking, even at the low RH (22, 34), implying low viscosities and high species diffusivities.

In line with the foregoing understanding, evaporation rates slowed as the remaining mass fraction decreased (Fig. 2). The most-volatile components evaporated early. For the aromatic-derived films, the vapor mass concentration over the film decreased at low RH (Fig. 2C). Even as the overall remaining mass fraction was high at low RH, the surface region was nevertheless highly depleted of volatile species, and these species were unable to diffuse from the interior to the surface region of the film. For SOM derived from α-pinene and isoprene, because of the high evaporation rates, changes in film composition were significant enough that the overall volatility of the film decreased during the observation time (Fig. 2B and C). The vapor mass concentrations represented the most-volatile fraction (10 to 25%) of the SOM.

Water content did not have an observable effect on the volatility of the biogenic films, at least for the range of experimental conditions from <5% RH to 50% RH.

The results of Fig. 2 were modeled for each film to retrieve the effective diffusivity $D_{eq}$ of the constituent organic molecules of the films. To do so, modeled evaporation rates were constrained...
to the measured evaporation rates in a diffusive multislab model (SI Appendix). The slab representing the surface region was taken as in local thermodynamic equilibrium with the overlying vapor. The compositions of the surface slab and the interior slabs depended on species diffusion. For initialization, model parameters of intrinsic volatility were constrained by the vapor mass concentrations when global thermodynamic equilibrium prevailed at high RH (SI Appendix, Table S1). The intrinsic volatilities were assumed to hold also at low RH. The fundamental assumption is that the effects of shifting water content on intrinsic volatility were not important across the range of investigated RH values. Effective diffusivity was held constant with remaining mass fraction. The model obtained values of \( D_{\text{org}} \) when kinetic factors slowed evaporation at low RH for the aromatic-derived films. At high RH, the model obtained lower limits of \( D_{\text{org}} \) for both the anthropogenic and biogenic films.

The modeling framework considered two possibilities for describing intrinsic volatility. Model 1 approximated the composition of the organic film as one volatile component and one nonvolatile component. Model 2 considered a more complex description that the film consisted of one nonvolatile component and four components of decadal volatility from \( 10^3 \) \( \mu \text{g} \cdot \text{m}^{-3} \) to \( 10^5 \) \( \mu \text{g} \cdot \text{m}^{-3} \). The results of model 1, represented by the shaded region in Fig. 2, capture the experimental observations within measurement uncertainty. The associated values of \( D_{\text{org}} \) vary with film type and RH (SI Appendix, Table S2). These values represent an effective diffusivity between the volatile and nonvolatile components. The values obtained for model 2 were the same within the uncertainty ranges as those of model 1 (SI Appendix, Fig. S2 and Table S2), and model 1, as the simpler of the two models, was selected herein for further presentation.

A comparison between the volatilities measured in this study and those predicted based on model 1 parameterizations reported in the literature is shown in Fig. 2 (points and lines, respectively; see SI Appendix, Table S3 for additional information). For appropriateness to the present study, possible literature sources were screened for comparable RH, \( M_{\text{org}} \), NO\(_x\) concentration, and temperature. In the classical approach, the parameterizations are formulated based on the relative mass yield of each species taken to have decadal volatility to infer volatility (4). In this formalism, species are partitioned between the gas and particle phases, depending on particle organic mass concentration \( M_{\text{org}} \). The parameterizations can lead to inaccurate predictions when the underlying assumption of global equilibrium between the vapor and the particle phases is invalid (29). This approach also fails mechanistically when the condensed-phase reactions significantly alter SOM composition and thus volatility (12, 35). By comparison, the QCM-based approach has the advantage that direct measurements of volatility, without inference, are made.

The lines in Fig. 2 representing the literature formalism were initialized by using the \( M_{\text{org}} \) value listed in each panel. For comparison with these values of \( M_{\text{org}} \), mass concentrations of organic PM are typically under \( 10^5 \) \( \mu \text{g} \cdot \text{m}^{-3} \) over relatively unpolluted forested regions (36) but can approach more than \( 100 \mu \text{g} \cdot \text{m}^{-3} \) in polluted megacity regions around the globe (37). The listed values of \( M_{\text{org}} \) in conjunction with the relative mass yields of the different species of decadal volatility (SI Appendix, Table S3) were used to calculate the associated values of vapor mass concentration \( C \) for an initial mass fraction of unity. The lines were then drawn representing the corresponding values of \( C \) as mass evaporated in clean air of infinite volume (SI Appendix).

For the toluene-derived film, for RH < 30%, the literature formalism overestimates the observed evaporation rate or, equivalently, the vapor mass concentration (Fig. 2A). For the highest RH of the present study (55%), the vapor mass concentrations were in the volatility-limited regime, but the literature formalism still overestimates the measured evaporation rates for a remaining mass fraction below 0.9. The explanation can be that the presented literature was developed for RH < 20%; parameters for comparison at higher RH do not appear to be available in the literature. The direct measurements of volatility reported herein suggest that the literature formalism developed under the assumption of rapid mass transfer is not an accurate predictor of actual evaporation rates when kinetic factors regulate rates of dynamic exchange between the vapor and condensed phases. The toluene-derived film has a larger fraction of low-volatility products than that predicted by the literature formalism (SI Appendix, Table S1 and S3).

Based on the review article of Carlton et al. (38) and a survey of more recent literature carried out as part of the present study, there appears to be no literature parameterization available for isoprene photooxidation under low-NO\(_x\) conditions for the high \( M_{\text{org}} \) values (\( 90 \mu \text{g} \cdot \text{m}^{-3} \)) of the present study. In this case, no comparison is shown in Fig. 2B between observations and a literature formalism. Although parameterizations and literature for lower \( M_{\text{org}} \) extrapolation has large uncertainties because the relative mass yields of higher volatility bins are not well constrained by datasets collected at lower \( M_{\text{org}} \).

In contrast to the results for the toluene-derived film, the literature formalism predicts well the observed volatility of the α-pinene-derived film (Fig. 2C). The agreement is consistent with literature observations of volatility, the requirement being that the evaporation did not depend on RH (39), and a revised interpretation was offered that oligomerization, rather than diffusion, may reduce the evaporation rate below that expected by the literature formalism (40).

Some caveats to the comparisons between observations and parameterizations in Fig. 2 are as follows. The comparisons are based on using \( M_{\text{org}} \) as the singular normalization quantity between the organic films and the chamber-based results. Factors other than \( M_{\text{org}} \) can also influence chemical composition and hence volatility. The extent of oxidation, for example, can vary depending on conditions of production and processing, and these factors can be expected to affect composition and volatility (12, 41, 42). The comparative analysis to the literature formalism also assumes that the film composition corresponds to the particle composition when still suspended as an aerosol at the particle concentration and diffusion rate (29). This approach also fails mechanistically when the condensed-phase reactions significantly alter SOM composition and thus volatility (12, 35). By comparison, the QCM-based approach has the advantage that direct measurements of volatility, without inference, are made.

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Discussion

When considered together, volatility as a thermodynamic parameter and diffusivity as kinetic parameter delineate the lability of atmospheric organic PM. The application can be considered for a scenario representative of the atmospheric dilution of anthropogenic organic particles accompanying the dispersion of an urban pollution plume. At time zero, the volatile and nonvolatile components of an individual particle are completely mixed with one another throughout both the interior and surface regions of the particle, and the surrounding air is clean and of infinite extent. As time evolves, the evaporation of molecules from the particle consists of a sequence of events: diffusion from the
interior region to the surface region of the particle; evaporation from the surface region into the vapor; and transport through the boundary layer surrounding the particle into the infinite extent of the gas, among other possible processes (43). Any one of these processes, as a slow step, can limit the overall evaporation rate.

A numerical approach, using the framework of model 1 for a spherical geometry (SI Appendix), is used herein to simulate these linked processes and respond to the slow step. A characteristic time of evaporation is defined as the time required for depletion of 63% of the volatile component. Fig. 3A displays the temporal evolution of the remaining mass fraction of the volatile component for several different values of \( D_{\text{m}} \). The curves are drawn for a vapor mass concentration \( C^0 \) of 10 \( \mu \)g m\(^{-3}\) for the volatile component in pure form, denoted by the superscript 0.

The diameter of the particle is 100 nm. The characteristic time for 63% loss increases from 10\(^{-2}\) s to 10\(^{-6}\) s as effective diffusivity decreases from 10\(^{-16}\) m\(^2\) s\(^{-1}\) to 10\(^{-22}\) m\(^2\) s\(^{-1}\). In the limit that particle diameter does not significantly change during the course of evaporation, the simulation results are independent of the relative initial concentrations of the two components.

Additional simulations of the characteristic time for evaporation were systematically performed across a matrix of \( D_{\text{m}} \) and \( C^0 \) values for a 100-nm particle. Fig. 3B shows a contour plot of the results. For sufficiently low diffusivity (i.e., to the left of the dashed line), the slow diffusion of molecules within the particle limits the overall evaporation rate. The characteristic time for evaporation decreases for greater \( D_{\text{m}} \). A gradient in composition develops inside the particle, and the concentration of the volatile component in the surface region becomes small (right circle in Fig. 3A). The compositional gradient develops because diffusion from the interior region to the surface region is not fast enough to replace molecules that are evaporating from the surface region.

At a critical juncture, represented by the dashed line Fig. 3B, diffusion becomes fast enough that a different process limits the overall rate of evaporation. This process is transport through the boundary layer surrounding the particle, and it represents the maximum rate of evaporation. This rate is proportional to the vapor mass concentration \( C^0 \) of the volatile component in pure form. Concentrations of the volatile and nonvolatile components remain homogeneously mixed throughout both the interior and surface regions during evaporation (left circle in Fig. 3A).

Delineating the boundary between diffusivity and volatility limitations is important for correctly understanding and accurately modeling the lifecycle of atmospheric particles. The boundary of this curve is defined by the parameter \( \xi \) (\( \xi = D_{\text{m}}/C^0 \)). Riipinen et al. (44) used this parameter to delineate the relative importance of diffusivity in particle growth, but it also holds for the boundary layer surrounding the particle into the infinite extent of the gas. The characteristic time for evaporation becomes small (right circle in Fig. 3A). The compositional gradient develops because diffusion from the interior region to the surface region is not fast enough to replace molecules that are evaporating from the surface region.

For the scenario of accumulation-mode particles in polluted suburban regions, SVOC species have volatilities of 1 \( \mu \)g m\(^{-3}\) to 100 \( \mu \)g m\(^{-3}\), and are of most interest for gas-particle partitioning. Partitioning includes both evaporation and condensation. For SVOC species, the characteristic timescales for these two processes are typically similar, although condensation can be more complex than evaporation in some cases (30). For \( D_{\text{m}} \) of 10\(^{-16}\) m\(^2\) s\(^{-1}\) to 10\(^{-10}\) m\(^2\) s\(^{-1}\), or less, the characteristic time for evaporation of SVOC species becomes limited by diffusion (Fig. 3B). Similar transition values have been suggested in previous theoretical studies using more detailed models (30, 45). Associated characteristic times are up to several minutes (Fig. 3B). For comparison, most CTMs have time steps on the order of tens of minutes or longer. The 1-h contour, implying errors in any models making predictions that assume equilibrium of reversible vapor–particle partitioning within each model time step, occurs in Fig. 3B for species having volatilities \( C^0 \) of less than 1 \( \mu \)g m\(^{-3}\) (i.e., LVOC species) or with in-particle diffusivities of less than 10\(^{-19}\) m\(^2\) s\(^{-1}\).
For SVOC species, the foregoing results indicate that the equilibration assumption prescribed in many CTMs is valid when moderate or high RH prevails in the atmospheric boundary layer. Low RH prevails in several megacities during certain times of the year (33). At these times, the gas-to-particle mass transfer of SVOCs can be impeded, and associated oxidation pathways and, ultimately, atmospheric fates can become altered. For extremely low VOC (ELVOC) and some low VOC (LVOC) species, evaporation can generally be considered slow compared with diffusivity for the characteristic timescales relevant to atmospheric processes (Fig. 3B). Condensation, however, can be fast, depending on the species production rates in the gas phase (30), and, in these cases, irreversible uptake should be an appropriate description. Even in these cases, however, diffusivity determines whether the interior composition of the particle becomes well mixed or not, which can influence physical properties and chemical reactivity (16).

The results reported herein, in conjunction with other recent work (16, 21), provide an opportunity to test for possible relationships among transitions with RH in mechanical properties, chemical reactivity, and mass lability. Properties of organic PM can vary with many factors. For example, the viscosity of α-pinene-derived SOM can vary by two orders of magnitude for shifting $M_{\text{org}}$ (46). Comparison of properties for organic PM produced within the same research group, suggesting a possible decrease in variability caused by extrinsic factors, provides one important perspective. Three comparative studies in that regard are summarized herein. For the toluene-α-pinene- and isoprene-derived organic PM, Bateman et al. (21) reported transitions in mechanical properties from semisolid to liquid at 60% to 80%, 70% to 90%, and 40 to 60% RH, respectively. For these same three systems, Li et al. (16) reported transitions in chemical reactivity of 35 to 45%, 35 to 45%, and <5% RH, respectively, meaning that reactivity greatly increased although the particles were not yet liquid. The present study provides directly measured evaporation rates to infer the diffusion limitations in gas–particle partitioning. For the three systems, transitions in evaporation rates occurred at 20 to 50%, 50 to 90%, and <5% RH, respectively, implying that mass lability greatly increased even though the particles were not yet liquid and not yet reactive. A comparison of these RH ranges suggests that correlations among transitions of mechanical properties, chemical reactivity, and mass lability are weak. Hence, based on the collected datasets, using any one of these as a surrogate to predict another is not recommended.

The present study highlights the low evaporation rates and hence low effective diffusivity for organic PM derived from aromatic precursors. By implication, aromaticity of the precursor and, by extension, of highly conjugated products appears to be important. Many chamber experiments for aromatic-derived SOMs were conducted at low RH and with observation times measured in hours (3, 9, 47–50). For toluene-derived material for RH < 5%, the characteristic time for SVOC equilibration is estimated as on the order of 1 wk for a 100-nm particle, based on the results of the present study (Fig. 3B). The estimated value of $3.0 \times 10^{-22}$ m$^2$ s$^{-1}$ for $D_{\text{org}}$ is at least 10$^3$ times smaller than that of the isoprene- and α-pinene-derived PM at low RH (SI Appendix, Table S2). The mechanism of particle growth from aromatic precursors can then be inferred as adsorptive partitioning and layer-by-layer growth (51). By comparison, for biogenic precursors derived organics, particles tend to grow by adsorptive partitioning, although some in-particle diffusion limitation remained possible in large particles at low RH. All other factors being equal, growth by adsorptive partitioning tends to be faster than by adsorptive partitioning. Parameterizations based on an assumption of equilibrium in adsorptive partitioning for datasets that were collected when adsorptive or diffusion-limited partitioning prevailed can be biased. When used in CTMs, these parameterizations may erroneously represent partitioning and PM production at elevated RH. Atmospheric measurements appear to suggest that models are most inaccurate in urban regions for which aromatic species contribute significantly to the production of atmospheric organic PM (6).

The solubility of aromatic-derived SOM at low RH may also bias the measured particle mass yield in chamber experiments. In chamber experiments, wall loss competes with the growth of particles for the scavenging of low-volatility oxidation products from the vapor phase (9). The possible importance of wall loss compared with particle growth depends on relative mass transfer rates, which determine the timescales for vapor–particle and vapor–wall interactions. In agreement with the low effective diffusivity reported in the present study, Zhang et al. (9) reported slow mass transfer of vapor species to the particles relative to the wall for toluene photodissociation, resulting in more pronounced vapor wall loss, and particle mass yield was underestimated by a factor of 2 to 4. Because of the kinetic limitations of species diffusion inside the particles, the low-volatility oxidation products in the vapor preferentially deposited on the chamber walls instead of contributing to the mass concentration of organic PM. In contrast, for α-pinene ozonolysis, Nah et al. (52) reported that condensation of organic vapors is dominated by quasi-equilibrium growth, and the extent of wall loss is smaller than that of the toluene system. The findings of the present study are consistent with this report.

In summary, the results presented herein suggest that effective diffusivity can influence the solubility of atmospheric organic PM in different ways for particle type derived from biogenic precursors. Natural biomes compared with particles associated with regions of urban and industrial development. An RH-dependent behavior was observed for the toluene-derived SOM, indicating that diffusion limitations strongly influence this model system of anthropogenic PM. A study by Ye et al. (53), carried out independently at the same time as this work, reached a similar conclusion by using a different methodology, and the two studies thus complement and reinforce one another. For RH below 20%, organic PM produced from aromatic precursors in urban atmosphere is effectively nonlabile, implying extended residence times for semivolatile species in this type of organic PM. The behavior can be delineated within regional and global CTMs by consideration of the presented ratio quantity $\phi$ to simplify prediction of diffusivity compared with volatility-limited regimes. This quantity can be used in simulations of gas–particle partitioning of SVOCs to take into account the diffusivity of organic PM (30, 45). The simulated mass concentrations, particle sizes, and physiochemical properties of atmospheric organic PM can change, ultimately influencing predictions of associated climate and health effects. Quantifying the effective diffusivity of organic PM, as a key factor for kinetic modeling, can potentially reduce uncertainties in the assessment of these effects. More broadly, the QCM technique used in this study provides an approach for measuring volatility and diffusivities for thin-film samples of tens of nanometer thickness, and this approach can be useful in various fields of research, such as material science, biomedical science, and physical chemistry.

Materials and Methods

Different types of SOM were produced in aerosol form through oxidation reactions of gaseous biogenic and anthropogenic SOM precursors in an oxidation flow reactor (OFR) (SI Appendix, Table S4) (54, 55). The aerosol particle populations were characterized by a scanning mobility particle sizer (SMPS; TSI Inc.) and an aerosol mass spectrometer (HR-ToF-AMS; Aerodyne Research Inc.). Organic films were grown by electrostatic precipitation of aerosol particles exiting the OFR onto QCM substrates (TSI 3089) (56). The evaporation rates and vapor mass concentrations of the organic films were analyzed by a QCM (Q-sense E4) equipped with a flow cell (Q-sense QX 303). RH-regulated nitrogen gas flowed across the surface of the film. The plug flow residence time of the gas inside the QCM cell varied between 0.3 s and 0.4 s. Detailed additional information about the measurements and associated modeling is provided in SI Appendix.

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