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# Roles of Organic Emissions in the Formation of Near Field Aircraft-Emitted Volatile Particulate Matter: A Kinetic Microphysical Modeling Study

*A kinetic microphysical modeling approach that describes the formation of volatile aerosols in the presence of organic emissions in near field aircraft emitted plumes at ground level is presented. Our model suggests that self nucleation of organic species, binary nucleation of water-soluble organic vapors with water, and multicomponent nucleation of water-soluble organic vapors with sulfuric acid and water all have very slow nucleation rates. The formation of new homogeneous particles in near field aircraft plumes is thus considered to be driven by binary nucleation of sulfuric acid and water. Volatile organic vapors emitted from aircraft engines primarily contribute to the nucleation process by condensing on existing homogeneous aerosols and only affect the size and the composition (not the number) of the homogeneous aerosols. Our model also shows that under low ambient relative humidity levels or high ambient temperatures, nucleation mode particles are more organic-rich than soot coatings. Organic mass fraction of nucleation mode particles is more sensitive to organic emissions levels compared to that of soot coatings. Ambient temperature and relative humidity were also predicted to affect the nucleation of sulfuric acid-water cores, where higher ambient relative humidity level and lower ambient temperature strongly favor binary sulfuric acid-water nucleation. The effect of ambient conditions on organic fractions was predicted to be relatively insignificant.*

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## 1 Introduction

Particulate matter (PM) emissions from aircraft engines have gained increasing environmental attention in recent years. When emitted at ground level, these nanosize fine particles can pose potential health risks for workers and residents in airport vicinity [1]. When emitted at cruise, they may affect the climate by changing the amount of incoming and outgoing radiation of earth [2,3]. The impact of aircraft emitted PMs is directly linked to their chemical and physical properties, such as size, concentration, and composition. Typical PMs in aircraft plumes consist of homogeneous liquid aerosols and soot particles coated with liquid mixtures. Characterization of the liquid components of these particles is challenging, since their volatile nature causes constant evolution in the atmosphere. Understanding of volatile PM evolution in near field aircraft exhaust plumes is thus still very limited.

Many field measurements [4–8] were recently conducted to characterize volatile PM emissions from aircraft engines at ground level. It was found that liquid aerosols and soot coatings usually consist of sulfuric acid, water, and condensable organic species. Exact composition and size of these liquid aerosols and soot coatings depend on various factors, including ambient conditions

(e.g., temperature and relative humidity levels), fuel properties (e.g., fuel sulfur and aromatic contents), engine operations (e.g., power settings), and plume characteristics (e.g., plume age and dilution ratio). At low power settings, organics are typically emitted at a higher concentration due to incomplete combustion [5,9,10]. Consequently, volatile PMs emitted at low power settings were observed to have higher organic fractions than those emitted at higher power settings.

The role of sulfuric acid in volatile PM evolution in near field aircraft emitted plumes has been widely studied in the literature [11–14]. However, the role of organic species is still not clear. Recently, we have advanced our model to describe the interactions between aircraft emitted volatile organic vapors and soot particles in near field aircraft emitted plumes at ground level [15]. In this work, we present our latest model development for simulating the formation of homogeneous liquid droplets in near field aircraft emitted plumes at ground level. Our model focuses on the multicomponent interactions between sulfuric acid, water, and organic vapors during the homogeneous nucleation process. The model is exercised to investigate the effects of organic emissions on the formation of aircraft emitted PM with a parametric study on ambient conditions and organic emissions levels.

## 2 Model Development

New particle formation via homogeneous nucleation of liquid droplets can be either homomolecular from one species or heteromolecular from more than one species. In ground level aircraft

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emitted plumes, homomolecular nucleation of aqueous aerosols is very unlikely since it requires very high water supersaturation. As a result, formation of homogeneous water containing liquid droplets is usually through binary heteromolecular nucleation of sulfuric acid and water. In binary sulfuric acid–water nucleation, both species are not required to be supersaturated as long as the participating vapor species are supersaturated with respect to a liquid solution droplet [16]. Many approaches exist to model binary sulfuric acid–water nucleation. In our previous modeling work [13–15], we employed kinetic quasi-unary nucleation (KQUN) theory [17–19] due to its simplicity and accuracy. KQUN theory asserts that sulfuric acid nucleation kinetics is the controlling factor, and that water reaches equilibrium with embryos and droplets immediately. This permits binary nucleation of sulfuric acid and water to be treated as unary nucleation of sulfuric acid, simplifying our model treatment of the whole binary nucleation process.

To model the nucleation processes involving more than two components, several algorithms were developed in the literature. Du and Yu [20] developed a model that extends the KQUN theory of binary  $H_2SO_4$ – $H_2O$  nucleation to ternary systems. An arbitrary third species was assumed to participate in binary nucleation of  $H_2SO_4$  and  $H_2O$ . Similar to the binary nucleation system, sulfuric acid controls the growth and evaporation of the particles, and water affects evaporation coefficients and overall compositions. The third species was assumed to play a similar role to water, reducing the Gibbs free energy of evaporation. The exact amount of reduction in Gibbs free energy affected by the third species, however, can only be determined by fitting experimental data using three empirical coefficients. Although our previous model [13] can be easily extended using this formulation, empirical parameters for the reduction of Gibbs free energy are not readily available for a wide variety of organic species emitted from aircraft engines. Extending this model to treat a system with more than three components is also challenging.

Gorbunov [21] developed a different approach to model the multicomponent homogeneous nucleation process. In this approach, two main species are assumed to be dominant in the nucleation process and the rest are considered minor. The multicomponent nucleation is modeled with two separate steps: (1) binary nucleation of two dominant species and (2) subsequent transformation of minor species from vapor phase to liquid phase. The Gibbs free energy of embryo formation can be calculated as

the sum of Gibbs free energy change for each step. The compositions of aerosols are calculated thermodynamically using Henry's law with respect to the compositions of the two main species. The growth and evaporation rates of the aerosols, which are dependent on the multicomponent composition information, can then be determined.

To expand our binary nucleation treatment to include organic species with different volatility and water solubility, we investigated a total of four possible pathways for new particle formation via multicomponent homogeneous nucleation in ground level aircraft exhaust plumes, as sketched in Fig. 1. These pathways include: (1) unary self nucleation of water-soluble or water-insoluble organic vapors (pathways *a* and *f*); (2) binary nucleation of organic vapors with water (pathways *b* and *g*); (3) multicomponent nucleation of water-soluble organics based on the Gorbunov model using sulfuric acid and water as dominant species (pathway *e*); and (4) condensation of organic vapors on sulfuric acid–water aerosols formed from binary homogeneous  $H_2SO_4$ – $H_2O$  nucleation (pathways *c* and *d*). Each of these pathways will be discussed below.

**2.1 Unary Nucleation of Organic Vapors.** As stated earlier, self nucleation of water or sulfuric acid to form homogeneous aerosols without the aids from other components is thermodynamically unfavorable in aircraft emitted plumes. To examine if this is also true for aircraft emitted organic vapors, we investigated unary self nucleation of organic species in aircraft emitted plumes using our model. Figure 2 shows concentrations of embryos produced from unary nucleation of organics compared to those produced from binary  $H_2SO_4$ – $H_2O$  nucleation in a plume emitted from a CFM56-2C5 engine at idle (7% power). We initiated this calculation with the same six organic surrogate species described in our recent work [15], including one water-soluble organic (pentanoic acid) and five water-insoluble organics (naphthalene, anthracene, pyrene, perylene, and anthanthrene). The combined emissions level of these organics is 400 ppb, with different fractions were assigned to different species, as listed in Table 1. This initialization is based on the experimental data obtained from recent field measurements, which shows that more volatile species have much higher emissions levels [9,10]. Fuel sulfur content was set at 600 ppm, and 1% of fuel sulfur was

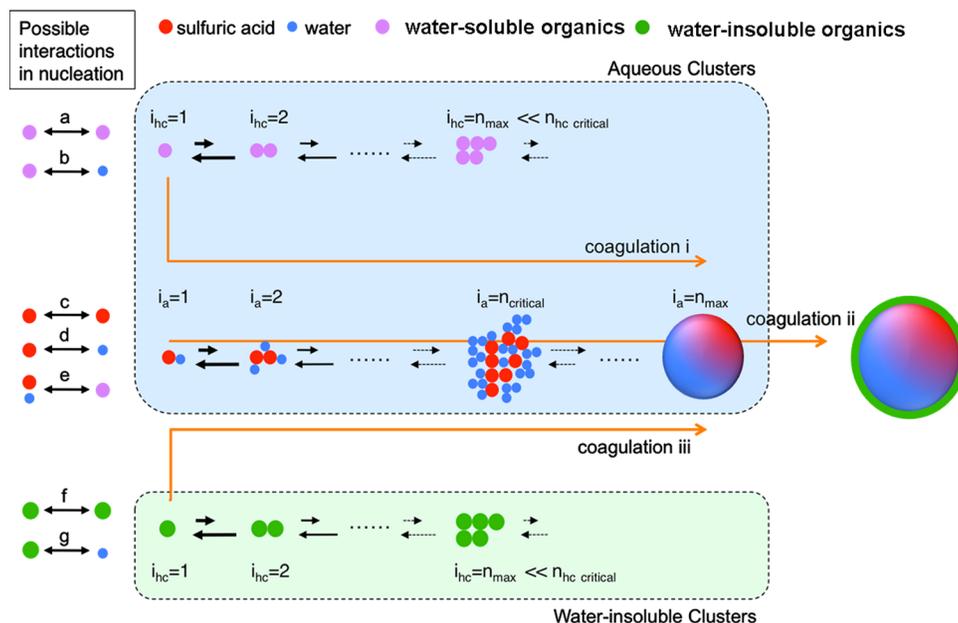
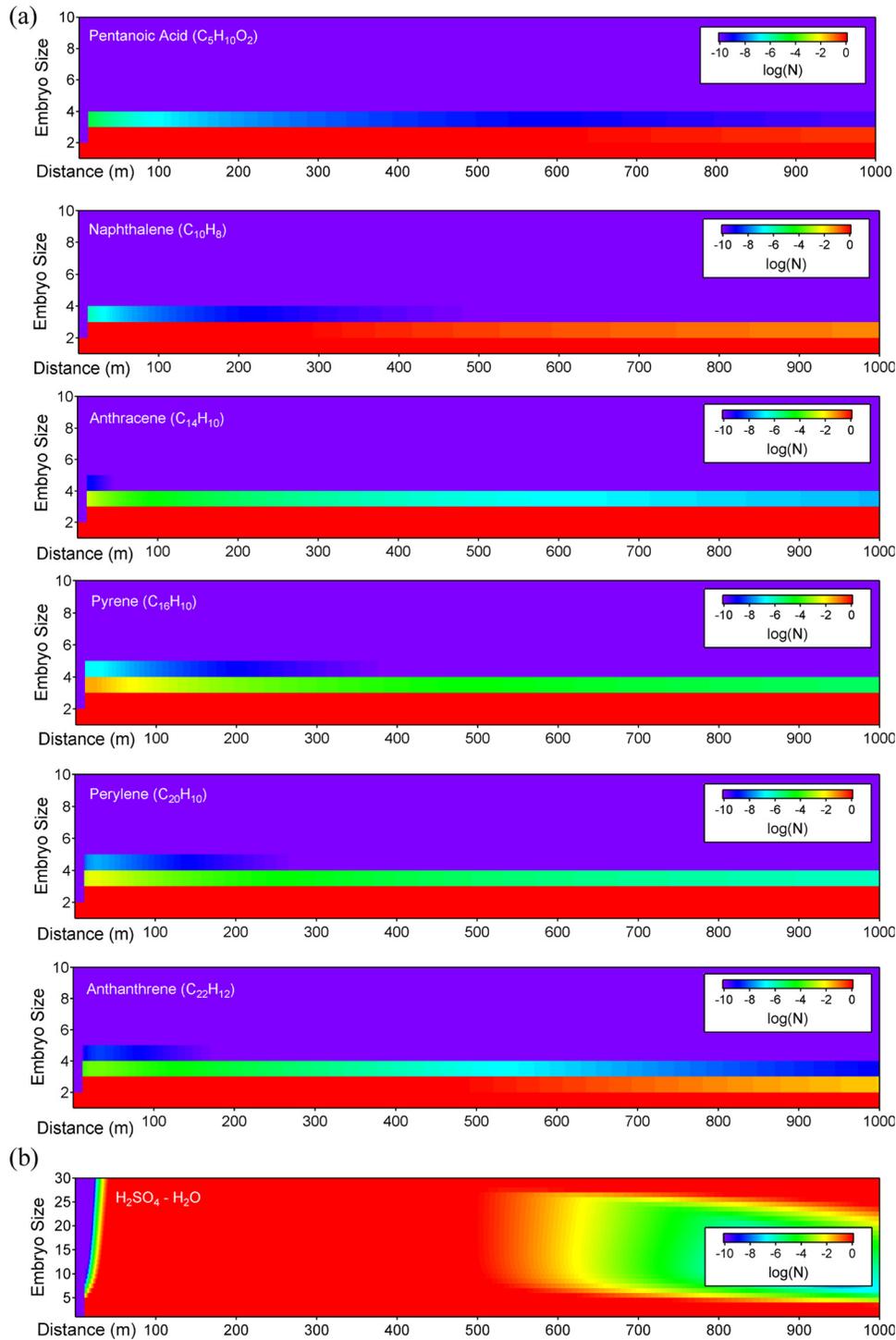


Fig. 1 Possible pathways of homogeneous particle nucleation involving organic vapors considered in our model development



**Fig. 2 Concentrations ( $N$ , in  $\text{cm}^{-3}$ ) of homogeneous liquid embryos produced from (a) unary nucleation of six surrogate organic species and (b) binary  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  nucleation as a function of downstream distance from the engine**

assumed to convert into  $\text{S}^{\text{VI}}$  (sulfuric acid precursor) at the engine exit plane. The ambient temperature was set at 285 K, and the ambient relative humidity was set at 60%. As depicted in Fig. 2, the concentrations of organic embryos produced from unary homogeneous nucleation are many orders of magnitude lower than those produced from binary  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  nucleation. The growth of the self nucleated embryos is also limited to a size of about five monomer units. This suggests that unary homogeneous nucleation of organic vapors is a very minor pathway for formation of new homogeneous aerosols in aircraft emitted plumes.

**2.2 Binary Nucleation of Water-Soluble Organic Vapors With Water.** Since unary self nucleation of organic vapors is unfavorable, the possibility of binary nucleation of organic vapors with water should be considered in our model. Due to their hydrophilicity, only water-soluble organic vapors were considered in this formulation. For binary nucleation of water-soluble organics and water, water-soluble organic vapors were assumed to play a similar role to sulfuric acid in the binary sulfuric acid–water nucleation, which controls the growth and evaporation of clusters. Following this formulation, however, we observed that only a

**Table 1 Organic surrogates and their initial fractions used in this study**

Surrogate species	Initial fraction of the total organic emissions (%)
Pentanoic acid (C <sub>5</sub> H <sub>10</sub> O <sub>2</sub> )	26.5
Naphthalene (C <sub>10</sub> H <sub>8</sub> )	26.5
Anthracene (C <sub>14</sub> H <sub>10</sub> )	32.2
Pyrene (C <sub>16</sub> H <sub>10</sub> )	11.8
Perylene (C <sub>20</sub> H <sub>12</sub> )	2.6
Anthanthrene (C <sub>22</sub> H <sub>12</sub> )	0.4

small fraction of water molecules are attracted to organic clusters due to high activity coefficient of water in organic–water solutions, suggesting that binary nucleation of water-soluble organic vapors and water is essentially the same as unary self nucleation of organic vapors and thus is unfavorable [22]. Furthermore, the high volatility of water-soluble organic vapors in aircraft emitted plumes, causing cluster evaporation faster than cluster growth under most conditions, also prevents this pathway from being dominant.

**2.3 Multicomponent Nucleation of Water-Soluble Organic Vapors.** The last pathway being considered for new particle nucleation involving organic vapors was multicomponent nucleation based on the Gorbunov model. Similar to the previous approach, only water-soluble organic vapors were considered in this formulation. We used sulfuric acid and water as the dominant species in the Gorbunov model, and the composition of binary sulfuric acid and water clusters was first calculated by the quasi-unary nucleation approach. The amount of water-soluble organics transferred from vapor phase to aqueous sulfuric acid–water embryos was then calculated thermodynamically based on the composition of sulfuric acid and water. This calculation assumes that nondominant species in the second nucleation step are relatively insignificant compared to the two species participating in the main nucleation process. This assumption is reasonable, since water-soluble organic vapors in near field aircraft emitted plumes usually have very high volatility.

Following this formulation, our model predicts that water-soluble organics only has a very minor contribution to the formation of new embryos in the first 50 m downstream of an engine. The additional embryo formation due to the assistance of water-soluble organics was less than 1%. As plume age increases, the presence of organics does not affect the amount and the size of the homogeneous embryos. This is because light water-soluble organics have high Henry's coefficients and tend to remain in the vapor phase rather than nucleating with sulfuric acid and water.

The analysis of the nucleation pathways presented in Secs. 2.1–2.3 shows that the contribution of aircraft emitted organic vapors to the formation of new particles via homogeneous nucleation may be negligible under the conditions of interest in this work. Therefore, we conclude that the amount of newly nucleated homogeneous volatile particles in aircraft exhaust plumes is solely determined by the binary sulfuric acid–water nucleation. Organic vapors may only participate in the nucleation process via condensation, which only affects the size and composition (not the number) of the volatile particles. The algorithm to describe condensation of organic vapors on homogeneous sulfuric acid–water particles in our model is presented in Sec. 2.4.

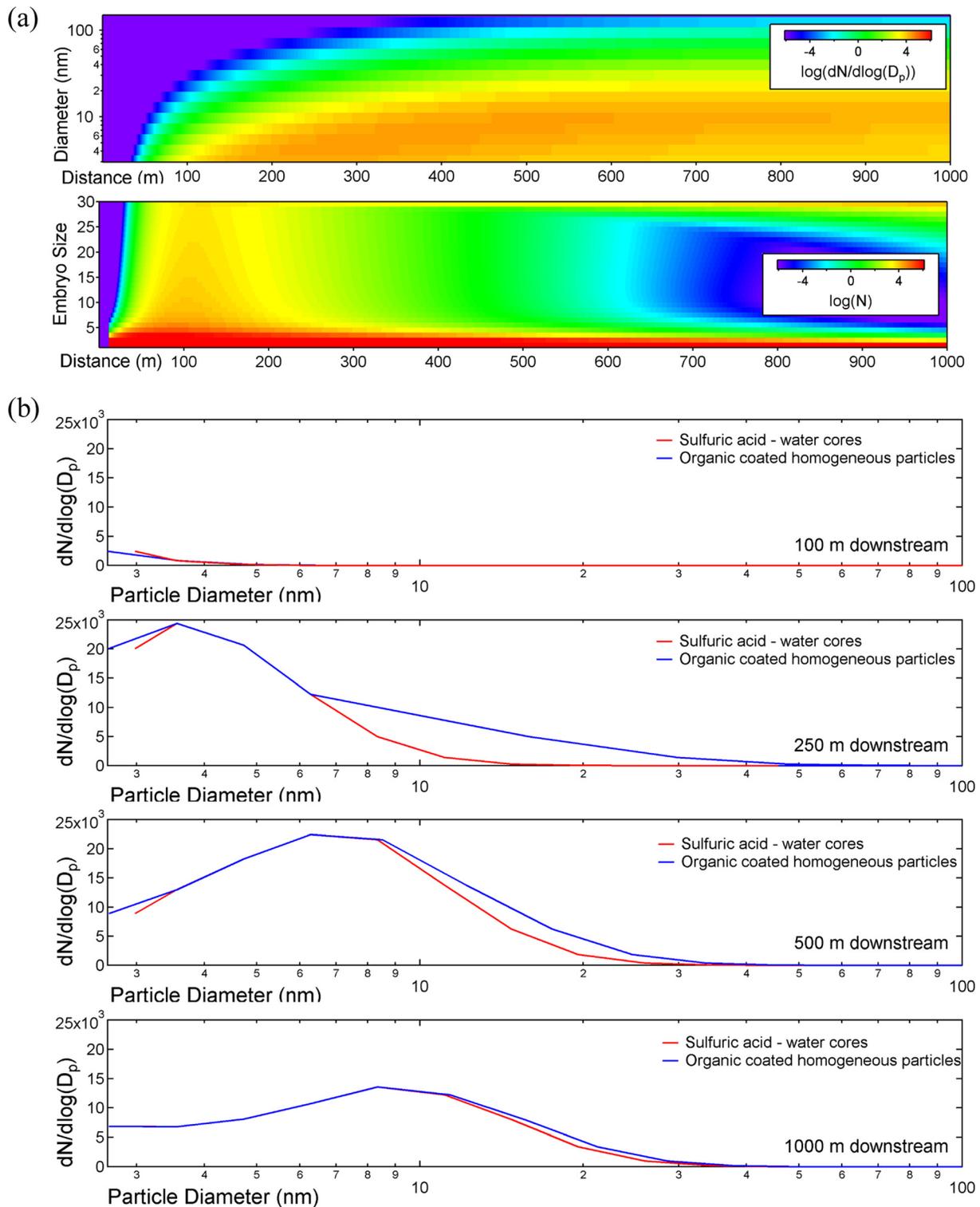
**2.4 Condensation of Organic Vapors on Sulfuric Acid–Water Embryos or Droplets.** Although organic vapors in aircraft emissions may not participate in the nucleation process to promote new particle formation, as discussed in Secs. 2.1–2.3, considerable amount of organics has been measured in aircraft emitted volatile particles during recent field missions [4,5]. Several studies on ambient secondary organic aerosols observed aqueous aerosol cores

with hydrophobic organic surface layers in separate phases [23–25]. We thus assume that aircraft emitted organic-containing volatile particles are present in the same form.

To describe the formation of biphasic aerosols present in aircraft emitted plumes, we developed an algorithm for forming a hydrophobic liquid organic coating on a liquid aqueous core in this work. Although liquid films tend to aggregate with liquid of same type of solubility on a partially wetted solid surface (such as soot), hydrophobic liquid films tend to spread on aqueous liquid surfaces after they are in touch. In our algorithm, organic mass will start to have uptake on H<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O clusters after collisions occur between water-insoluble organic vapors and binary H<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O embryos. Coagulation between unary nucleated embryos of different water-insoluble organics is very unlikely due to their relatively low concentrations and is not considered in our work. Our algorithm assumes that water-insoluble organic layers uniformly spread out on the aqueous cores immediately after the collision between the organic vapors and the cores. The presence of the layers also does not affect the thermodynamics and the compositions of the binary H<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O cores, contrary to the Gorbunov model. While some studies have shown that the presence of organic films on aerosol particles can retard the uptake or evaporation of water from aqueous cores [26,27], Garland et al. [28] suggested that this effect is negligible when the hydrophobic films are very thin. In this work, we assume that thin hydrocarbon films do not affect the rapid hygroscopic growth of nanometer-size volatile particles in aircraft exhaust plumes.

Numerically, the above condensation model requires additional variables to track the growth of hydrophobic films compared to our previous implementation [13]. Since tracking all possible sizes and combinations of aqueous cores and organic films covering the size range of interest (up to 100 nm) is numerically expensive, a sectional bin approach was implemented to describe the evolution of both the aqueous cores and the organic coatings. In our previous model [13], we used the fully stationary sectional bin approach for the coagulation between two H<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O embryos or droplets. In this approach, the bin sizes are fixed, and all particles in a bin are assumed to have the same volume. When a particle grows via condensation or coagulation, it is partitioned into two adjacent bins based on its volume. The composition of the particle is then calculated by finding the composition that gives the minimum Gibbs free energy of evaporation at the sizes of the bins it is partitioned into. The fully stationary sectional bin approach is generally practical for simulating coagulation of particles. However, it is difficult to track particles with components in separate phases, such as organic-containing aqueous aerosols considered in this work. To this reason, we implemented a hybrid approach [29] combining fully stationary bins and fully moving bins. The hybrid bin approach tracks aqueous cores and nonaqueous coatings separately, in which the growth of the aqueous cores is tracked with stationary bins and the growth of hydrophobic films is tracked to their exact sizes. When two embryos or droplets coagulate, the new particle is partitioned based on the volume of the aqueous H<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O core into two adjacent bins. The mass of the organic coatings is fractionated into the two bins proportional to how the core is distributed. This approach also allows condensation of organic vapors or coagulation of homogeneous organic embryos onto the organic coatings of an organic–aqueous particle. Detailed description of our coagulation model can be found in the thesis by Jun [22].

In summary, our modeling study found that sulfuric acid and water are the most dominant components in determining the number of new particles formed from this multicomponent homogeneous nucleation process. The presence of organic vapors does not increase the amount of new particles formed via homogeneous nucleation. The water-insoluble organic vapors, however, participate in the nucleation process via condensation, forming organic coatings around binary sulfuric acid–water cores. We conclude that organic emissions in aircraft exhaust plumes do not promote new particle formation via homogeneous nucleation but rather



**Fig. 3 The size evolution of homogeneous nucleation mode particles: (a) concentrations of the sulfuric acid—water cores and (b) homogeneous particle size growth resulted from organic emissions**

affect the composition and size of the homogeneous nucleated aerosols. This result forms the basis of our modeling results presented in Sec. 3.

### 3 Results and Discussion

To use our model to examine the effect of organic emissions on homogeneous particle formation in aircraft emitted plumes, we

selected the conditions described in Sec. 2.1 as our baseline case (CFM56-2C5 engine at 7% power, ambient temperature at 285 K, ambient relative humidity at 60%, 600 ppm of fuel sulfur content, and 400 ppb of total organic emissions at the engine exit plane). Engine exit plane conditions, such as gas-phase species concentrations, soot emissions, exhaust temperature, and jet velocity are user inputs. The values of the inputs were either calculated with an engine cycle simulation tool (e.g., exhaust temperature and jet

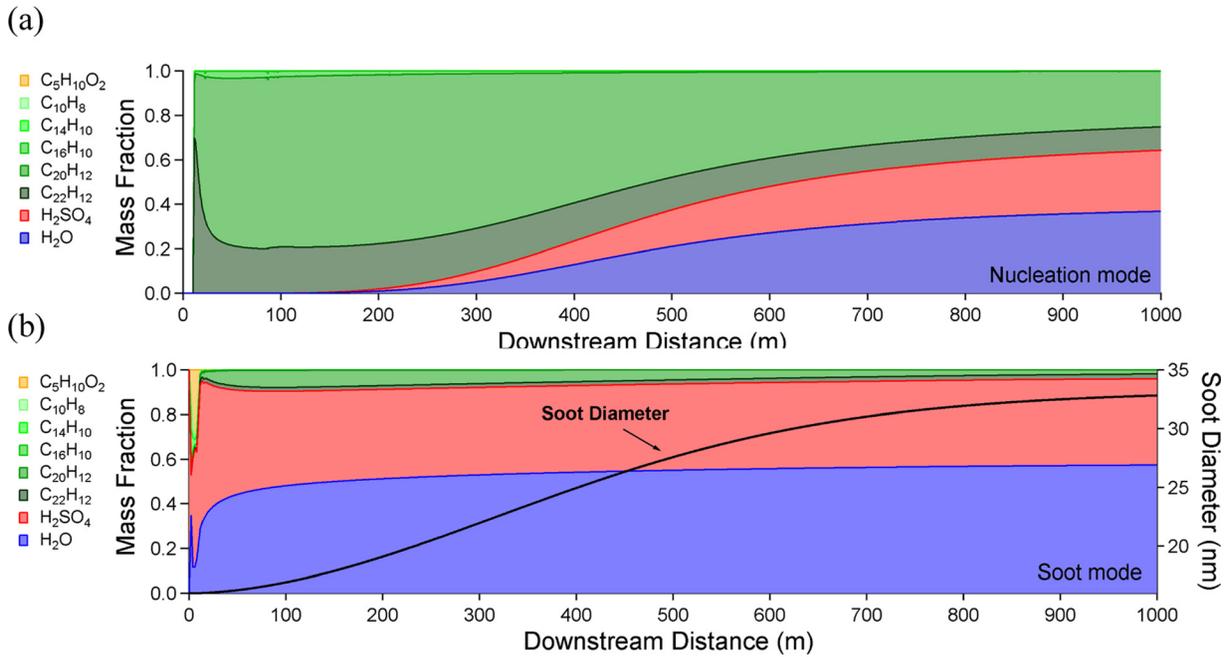


Fig. 4 Predicted composition evolution of aircraft emitted particles: (a) homogeneous nucleation mode particles and (b) coatings of soot mode particles

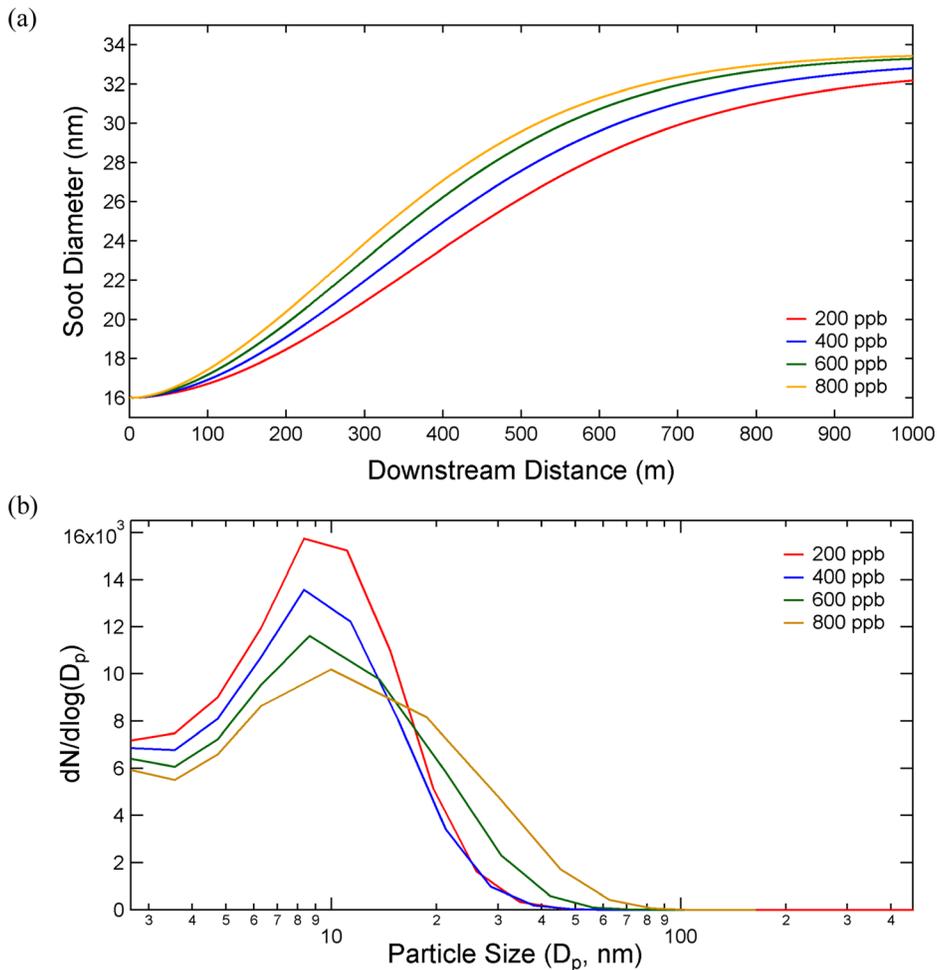
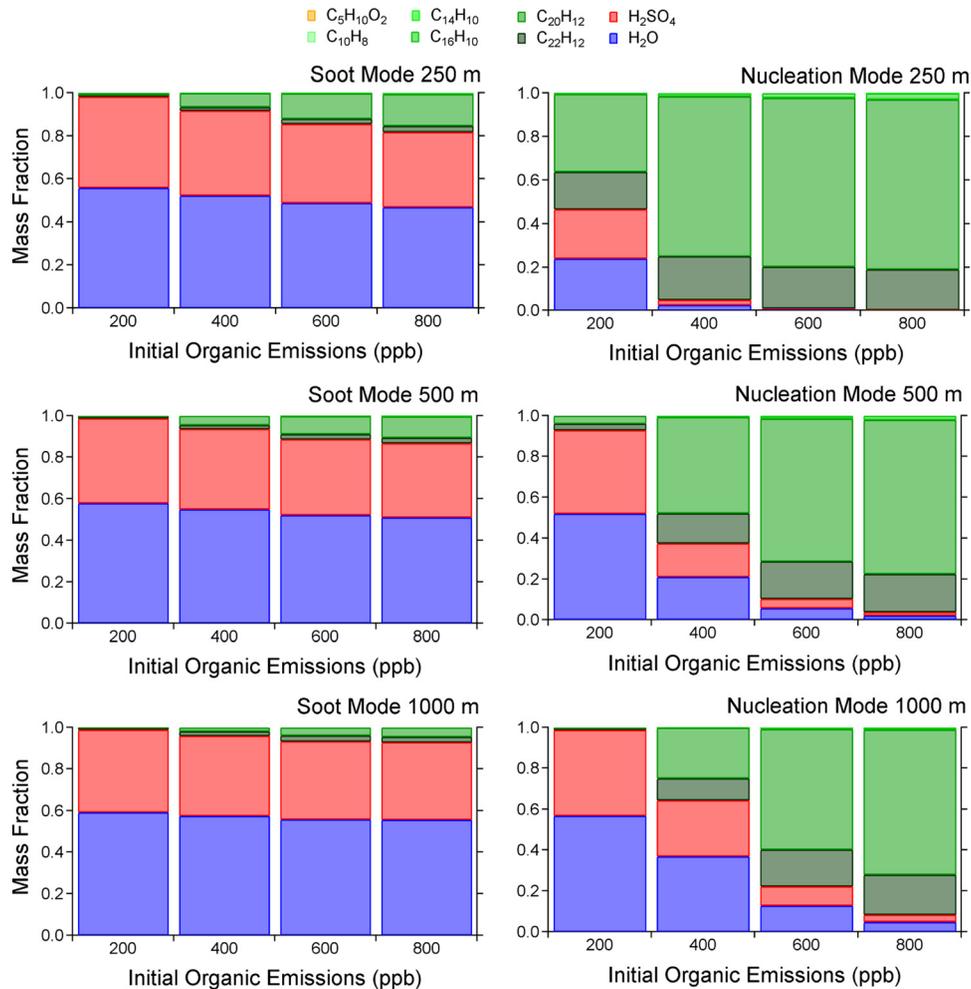


Fig. 5 The effect of organic emissions level at the engine plane on (a) soot particle size as a function of downstream distance and (b) homogeneous particle size distributions at 1000 m downstream



**Fig. 6 Predicted mass fractions of soot coatings and homogeneous nucleated particles at three different downstream distances when initial organic emissions levels were varied from 200 to 800 ppb**

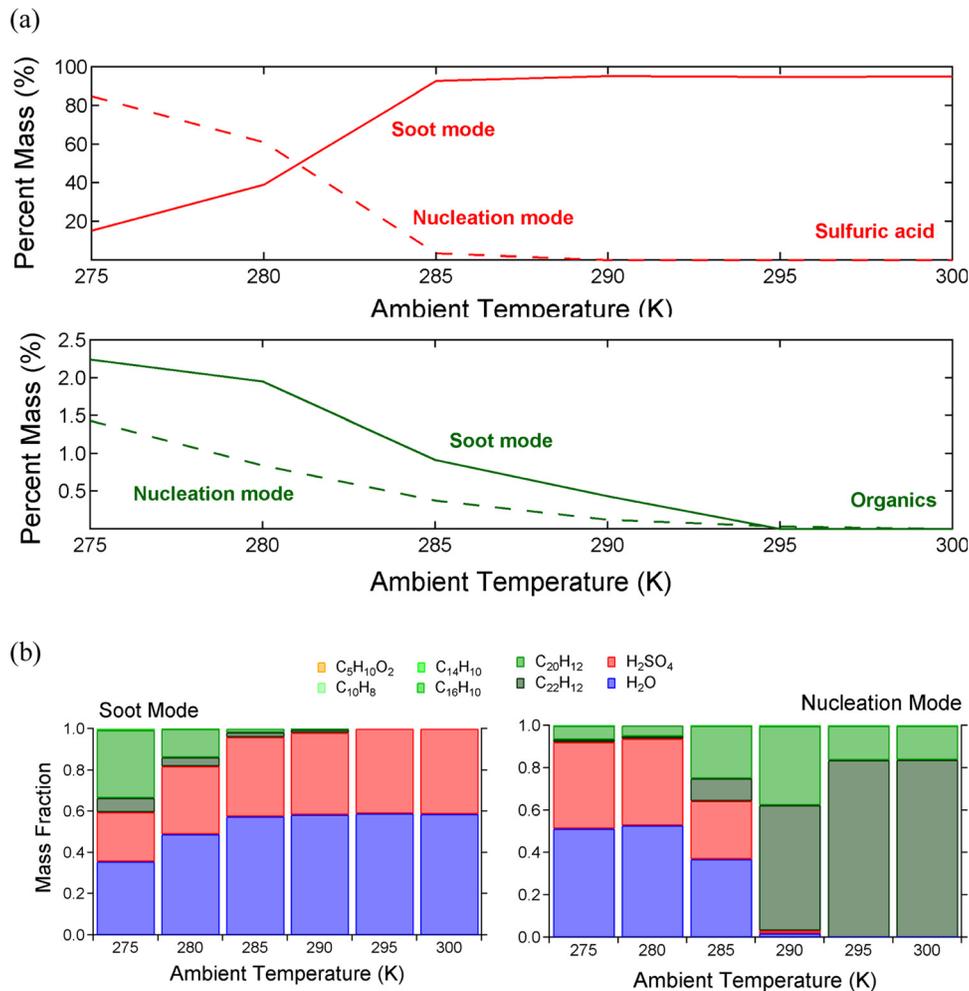
velocity) or derived based on recent field measurement missions performed at the engine-exit plane (e.g., gas-phase and soot emissions). Plume dilution and cooling profiles were calculated with a semi-empirical, self-similar approach developed by Davidson and Wang [30]. To reduce computational cost, we initialized our calculations with monodisperse soot at 16 nm in diameter with a concentration of  $8.5 \times 10^6 \text{ cm}^{-3}$ . This initialization is based on the measurement data collected during the aircraft particle emissions experiment campaign [6]. A total of 15 log-normally distributed bins between 3 nm and 160 nm in diameter were used to describe size distributions of homogeneous sulfuric acid–water cores in the hybrid bin approach described in Sec. 2.4. The sensitivity of homogeneous particle growth to organic emissions levels and ambient conditions was further investigated in a parametric study, also discussed in this section.

**3.1 Representative Modeling Results.** Figures 3 and 4 illustrate the simulation results for the baseline case following an exhaust centerline plume up to 1000 m downstream of an engine. The size evolution of the homogeneous sulfuric acid–water cores tracked in the hybrid bin approach is shown in Fig. 3(a) as binned droplets and embryos. Our modeling results show that sulfuric acid–water cores grow to a maximum size of about 10 nm and a maximum concentration at about 500 m downstream under this condition. No significant particle growth of the homogeneous sulfuric acid–water cores was predicted further downstream, and the

concentration of these homogeneous particles was gradually reduced due to ambient dilution. The presence of the organic emissions resulted in slight increases in particle size, as shown in Fig. 3(b). This is particularly marked between 250 and 500 m downstream before dilution of the particles starts to take effect.

The predicted mass fraction of the homogeneous nucleation mode particles is shown in Fig. 4(a). The majority of the organic species ended up in the particle phase are perylene and anthanthrene. This is because they have low enough vapor pressure to be present in the liquid phase. At 1000 m downstream, about 35% of the homogeneous particle mass consists of organics (about 25% of perylene and about 10% of anthanthrene). The mass fraction of perylene is higher than that of anthanthrene. This is because it has a much higher emissions level at the engine exit plane (10.4 ppb) than that of anthanthrene (1.6 ppb). Although perylene has higher vapor pressure than anthanthrene, it is still low enough to be able to condense. For the remainder of the homogeneous particle mass, about 28% consists of sulfuric acid and about 37% consists of water. The contribution of lighter organic species was found to be insignificant due to their high vapor pressure. Note that in this figure, only mass fractions of the species in the aerosols, not absolute mass, are shown. To this reason, although mass fractions of organics are greater at the engine exit plane than further downstream, the absolute amount of organic mass is greater further downstream, peaks around 250–500 m downstream, as illustrated in Fig. 3(b).

A comparison between the compositions of the homogeneous nucleation mode particles and soot coatings (Fig. 4(b)) shows that



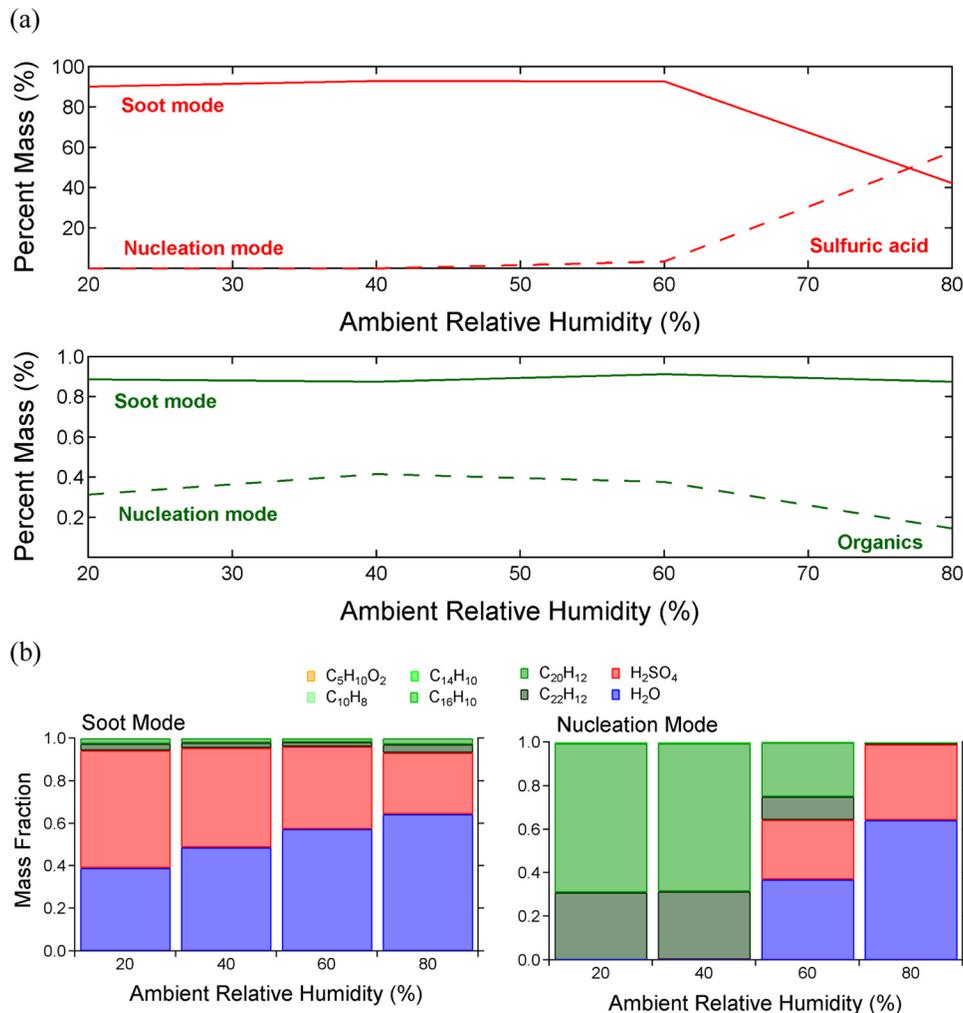
**Fig. 7 Predicted effect of ambient temperature on (a) percentages of sulfuric acid and organics on soot mode and nucleation mode particles and (b) compositions of soot coatings and nucleation mode particles at 1000 m downstream**

homogeneous particles are organic-rich and soot coatings are sulfuric acid-rich. Our simulation predicts that only about 4% mass of soot coatings consists of organics, with the rest consists of sulfuric acid (about 39%) and water (about 57%). This suggests that sulfuric acid and water emissions are more favorable to condense on soot than to nucleate new particles under this ambient condition. This is because our model allows hydrophobic organics, such as perylene and anthanthrene, to have faster condensation on homogeneous sulfuric acid–water droplets than soot surfaces coated with sulfuric acid–water mixtures. Different ambient conditions will result in different split, as will be discussed in Sec. 3.3. The composition difference between the soot mode and nucleation mode particles has not been discussed based on field measurement data, since state-of-the-art instruments for measuring aerosol compositions has a lower bound in particle size of about 40 nm, too high for detecting homogeneous nucleation mode particles with a size no larger than 20 nm. An ongoing measurement activity has been conducted to intentionally promote the growth of the homogeneous particles. The composition difference suggested by our model will be initially verified by this experiment. Future field missions under the conditions favorable for homogeneous particle growth will also be used for model validation.

**3.2 Effects of Initial Organic Concentrations.** The most uncertain parameter in near field aircraft emissions is the amount of organic emissions at the engine exit plane. To investigate the

effect of initial organic concentration, a sensitivity study was performed using our model. In this set of calculations, total initial organic emissions levels were varied from 200 to 800 ppb, while other conditions were set the same as the baseline case. The predicted particle growth resulted from increased organic emissions is shown in Fig. 5. When organic emissions at the engine exit plane was varied from 200 to 800 ppb, our calculations show that the monodisperse soot size tracked in the model increased slightly from 32 nm to about 33.5 nm at 1000 m downstream. Slight increase of peak size of particle size distributions was also predicted for homogeneous nucleation mode particles when initial organic emissions increased. One interesting finding is that higher organic emissions levels at the engine exit plane cause homogeneous aerosol particle size distributions to be broader, rather than shifting the whole distributions to a larger size, as illustrated in Fig. 5(b).

The compositions of soot coatings and homogeneous nucleation mode particles were also tracked as a function of downstream distance of the engine in our simulations. Our results show that higher initial organic emissions result in higher organic mass fraction for both soot and nucleation mode particles, as shown in Fig. 6. The change of organic mass fraction on soot is predicted to be more linearly dependent on initial organic concentrations, whereas the change of organic mass fraction in homogeneous aerosols is much more sensitive to the concentration change. This is because organic vapors are allowed to condense at faster rates on homogeneous particles in the model, as described in Sec. 3.1.



**Fig. 8 Predicted effect of ambient relative humidity on (a) percentages of sulfuric acid and organics on soot mode and nucleation mode particles and (b) compositions of soot coatings and nucleation mode particles at 1000 m downstream**

This is also similar to the nonlinear dependency of the homogeneous sulfuric acid–water aerosol growth on the initial concentration of sulfuric acid at the engine exit plane described in our previous work [13].

**3.3 Effects of Ambient Conditions.** Our previous work on binary nucleation of sulfuric acid–water shows that homogeneous particle formation is very sensitive to ambient temperature and relative humidity, where lower ambient temperature and higher ambient relative humidity level strongly enhance nucleation rates of homogeneous aerosols [13]. In the presence of the organic emissions, our model still predicts the same behavior. As shown in Figs. 7(a) and 8(a), the percentage of total emitted sulfuric acid mass in nucleation mode particles at 1000 m downstream dramatically drops when ambient temperature is higher than 285 K or the ambient relative humidity is lower than 60%. When ambient conditions become unfavorable for binary sulfuric acid–water nucleation, most of the sulfuric acid mass ( $\sim 95\%$ ) condenses as soot coatings due to its low vapor pressure. For organic species, higher ambient temperature slightly suppresses condensation as expected, as illustrated by the decline of the percentage of total organic emissions in the particle phases in Fig. 7(a). The effect of ambient temperature on organics, however, is not as nonlinear as sulfuric acid, since organic vapors only participate in the nucleation process by condensation, rather than binary nucleation. The effect of ambient humidity level on the amount of organic mass in

both condensed modes is insignificant, as shown in Fig. 8(a). This is because our model turns off any direct interactions between organic vapors and water during the nucleation process. Since ambient conditions only have minor effects on the vapor to particle process for organic species, decreased organic mass fractions in nucleation mode particles were predicted at lower ambient temperatures or higher ambient relative humidity levels due to increased amount of sulfate mass fractions in the particle phases, as shown in Figs. 7(b) and 8(b). These figures also show increased organic mass fractions in soot coatings at these conditions (lower temperature, higher relative humidity) due to the smaller amount of sulfate condensed on soot. In summary, our model suggests that nucleation mode particles are more organic-rich than soot coatings under low ambient relative humidity levels or high ambient temperatures, and are sulfate-rich otherwise.

#### 4 Conclusions

In this work, a new modeling approach is presented to describe the homogeneous aerosol nucleation process in near field aircraft emitted plumes at ground level when condensable organic vapors are present. Our model and simulation results suggest several key findings:

- (1) Formation of new homogeneous particles in near field aircraft plumes is driven by binary nucleation of sulfuric acid and water. Self nucleation of organic species and binary

nucleation of water-soluble organic vapors with water were all found to have very slow nucleation rates. Multicomponent nucleation of water-soluble organic vapors with sulfuric acid and water was found to be not significantly different from binary nucleation of sulfuric acid and water. Therefore, we conclude that the presence of organic vapors do not promote the nucleation of new particles.

- (2) Volatile organic vapors emitted from aircraft engines primarily contribute to the nucleation process by condensing on existing homogeneous aerosols. Our results suggest that aircraft emitted organic vapors only affect the size and the composition (not the number) of the homogeneous aerosols in aircraft emitted plumes.
- (3) The presence of aircraft emitted organic species results in slightly larger homogeneous particles and soot coatings, and our model suggests that nucleation mode particles are more organic-rich than soot coatings under low ambient relative humidity levels or high ambient temperatures.
- (4) Higher organic emissions at the engine exit plane results in higher organic mass fraction for both soot and nucleation mode particles. Organic mass fraction of nucleation mode particles is more sensitive to organic emissions levels compared to that of soot coatings.
- (5) Ambient temperature and relative humidity primarily affect the nucleation of sulfuric acid–water cores, where higher ambient relative humidity level and lower ambient temperature strongly favor binary sulfuric acid–water nucleation; the effect of ambient conditions on organic fractions is relatively insignificant.

## Acknowledgment

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## References

- [1] Levy, J. I., Woody, M., Baek, B. H., Shankar, U., and Arunachalam, S., 2012, "Current and Future Particulate-Matter-Related Mortality Risks in the United States From Aviation Emissions During Landing and Takeoff," *Risk Anal.*, **32**(2), pp. 237–249.
- [2] Brasseur, G., and Gupta, M., 2010, "Impact of Aviation on Climate," *Bull. Am. Meteorol. Soc.*, **91**(4), pp. 461–463.
- [3] Lee, D. S., Pitari, G., Grewe, V., Gierens, K., Penner, J. E., Petzold, A., Prather, M. J., Schumann, U., Bais, A., Berntsen, T., Iachetti, D., Lim, L. L., and Sausen, R., 2010, "Transport Impacts on Atmosphere and Climate: Aviation," *Atmos. Environ.*, **44**(37), pp. 4678–4734.
- [4] Onasch, T. B., Jayne, J. T., Herndon, S. C., Worsnop, D. R., Miake-Lye, R. C., Mortimer, I. P., and Anderson, B. E., 2009, "Chemical Properties of Aircraft Engine Particulate Exhaust Emissions," *J. Propul. Power*, **25**(5), pp. 1121–1137.
- [5] Timko, M. T., Onasch, T. B., Northway, M. J., Jayne, J. T., Canagaratna, M., Herndon, S. C., Wood, E. C., Miake-Lye, R. C., and Knighton, W. B., 2010, "Gas Turbine Engine Emissions—Part II: Chemical Properties of Particulate Matter," *ASME J. Eng. Gas Turbines Power*, **132**(6), p. 061505.
- [6] Wey, C. C., Anderson, B. E., Wey, C., Miake-Lye, R. C., Whitefield, P., and Howard, R., 2007, "Overview on the Aircraft Particle Emissions Experiment," *J. Propul. Power*, **23**(5), pp. 898–905.
- [7] Presto, A. A., Nguyen, N. T., Ranjan, M., Reeder, A. J., Lipsky, E. M., Hennigan, C. J., Miracolo, M. A., Riemer, D. D., and Robinson, A. L., 2011, "Fine Particle and Organic Vapor Emissions From Staged Tests of an In-Use Aircraft Engines," *Atmos. Environ.*, **45**(21), pp. 3603–3612.
- [8] Timko, M. T., Fortner, E., Franklin, J., Yu, Z., Wong, H.-W., Onasch, T. B., Miake-Lye, R. C., and Herndon, S. C., 2013, "Atmospheric Measurements of the Physical Evolution of Aircraft Exhaust Plumes," *Environ. Sci. Technol.*, **47**(7), pp. 3513–3520.
- [9] Knighton, W. B., Rogers, T. M., Anderson, B. E., Herndon, S. C., Yelvington, P. E., and Miake-Lye, R. C., 2007, "Quantification of Aircraft Engine Hydrocarbon Emissions Using Proton Transfer Reaction Mass Spectrometry," *J. Propul. Power*, **23**(5), pp. 949–958.
- [10] Yelvington, P. E., Herndon, S. C., Wormhoudt, J. C., Jayne, J. T., Miake-Lye, R. C., Knighton, W. B., and Wey, C., 2007, "Chemical Speciation of Hydrocarbon Emissions From a Commercial Aircraft Engine," *J. Propul. Power*, **23**(5), pp. 912–918.
- [11] Kärcher, B., 1998, "Physicochemistry of Aircraft-Generated Liquid Aerosols, Soot, and Ice Particles: 1. Model Description," *J. Geophys. Res. Atmos.*, **103**(D14), pp. 17111–17128.
- [12] Kärcher, B., and Yu, F., 2009, "Role of Aircraft Soot Emissions in Contrail Formation," *Geophys. Res. Lett.*, **36**(1), p. L01804.
- [13] Wong, H.-W., Yelvington, P. E., Timko, M. T., Onasch, T. B., Miake-Lye, R. C., Zhang, J., and Waitz, I. A., 2008, "Microphysical Modeling of Ground-Level Aircraft-Emitted Aerosol Formation: Roles of Sulfur-Containing Species," *J. Propul. Power*, **24**(3), pp. 590–602.
- [14] Wong, H.-W., Yu, Z., Timko, M. T., Herndon, S. C., De La Rosa Blanco, E., and Miake-Lye, R. C., 2011, "Design Parameters for an Aircraft Engine Exit Plane Particle Sampling System," *ASME J. Eng. Gas Turbines Power*, **133**(2), p. 021501.
- [15] Wong, H.-W., Jun, M., Peck, J., Waitz, I. A., and Miake-Lye, R. C., 2014, "Detailed Microphysical Modeling of the Formation of Organic and Sulfuric Acid Coatings on Aircraft Emitted Soot Particles in the Near Field," *Aerosol Sci. Technol.*, **48**(9), pp. 981–995.
- [16] Seinfeld, J. H., and Pandis, S. N., 1998, *Atmospheric Chemistry and Physics—From Air Pollution to Climate Change*, Wiley, New York.
- [17] Yu, F., 2005, "Quasi-Unary Homogeneous Nucleation of H<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O," *J. Chem. Phys.*, **122**(7), p. 074501.
- [18] Yu, F., 2006, "Binary H<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O Homogeneous Nucleation Based on Kinetic Quasi-Unary Nucleation Model: Look-up Tables," *J. Geophys. Res.*, **111**(D4), p. D04201.
- [19] Yu, F., 2007, "Improved Quasi-Unary Nucleation Model for Binary H<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O Homogeneous Nucleation," *J. Chem. Phys.*, **127**(5), p. 054301.
- [20] Du, H., and Yu, F., 2009, "Kinetic Modeling of Nucleation Experiments Involving SO<sub>2</sub> and OH: New Insights Into the Underlying Nucleation Mechanisms," *Atmos. Chem. Phys.*, **9**(20), pp. 7913–7922.
- [21] Gorbunov, B., 2001, "From Binary and Ternary to Multicomponent Nucleation: Atmospheric Aerosol Formation," *J. Chem. Phys.*, **115**(6), pp. 2641–2651.
- [22] Jun, M., 2011, "Microphysical Modeling of Ultrane Hydrocarbon-Containing Aerosols in Aircraft Emissions," Ph.D. thesis, Massachusetts Institute of Technology, Cambridge, MA.
- [23] Ellison, G. B., Tuck, A. F., and Vaida, V., 1999, "Atmospheric Processing of Organic Aerosols," *J. Geophys. Res.*, **104**(D9), pp. 11633–11641.
- [24] Gilman, J. B., Tervahattu, H., and Vaida, V., 2006, "Interfacial Properties of Mixed Films of Long-Chain Organics at the Air–Water Interface," *Atmos. Environ.*, **40**(34), pp. 6606–6614.
- [25] Tervahattu, H., Juhanaja, J., Vaida, V., Tuck, A. F., Niemi, J. V., Kupiainen, K., Kulmala, M., and Vehkamäki, H., 2005, "Fatty Acids on Continental Sulfate Aerosol Particles," *J. Geophys. Res.*, **110**(D6), p. D6207.
- [26] Gill, P. S., and Graedel, T. E., 1983, "Organic Films on Atmospheric Aerosol Particles, Fog Droplets, Cloud Droplets, Raindrops, and Snowflakes," *Rev. Geophys. Space Phys.*, **21**(4), pp. 903–920.
- [27] Xiong, J. Q., Zhang, M., Fang, C., Chen, L. C., and Lippmann, M., 1998, "Influence of Organic Films on the Hygroscopicity of Ultrafine Sulfuric Acid Aerosol," *Environ. Sci. Technol.*, **32**(22), pp. 3536–3541.
- [28] Garland, R. M., Wise, M. E., Beaver, M. R., Dewitt, H. L., Aiken, A. C., Jimenez, J. L., and Tolbert, M. A., 2005, "Impact of Palmitic Acid Coating on the Water Uptake and Loss of Ammonium Sulfate Particles," *Atmos. Chem. Phys.*, **5**(7), pp. 1951–1961.
- [29] Jacobson, M. Z., and Turco, R. P., 1995, "Simulating Condensational Growth, Evaporation, and Coagulation of Aerosols Using a Combined Moving and Stationary Size Grid," *Aerosol Sci. Technol.*, **22**(1), pp. 73–92.
- [30] Davidson, M. J., and Wang, H. J., 2002, "Strongly Advected Jet in a Coflow," *J. Hydraul. Eng.*, **128**(8), pp. 742–752.