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Citation: J. Appl. Phys. **112**, 024901 (2012); doi: 10.1063/1.4736557
View online: http://dx.doi.org/10.1063/1.4736557
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v112/i2
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Enhanced persistence of fog under illumination for carbon nanotube fog condensation nuclei

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(Received 1 March 2012; accepted 7 June 2012; published online 16 July 2012)

Black carbon (BC) emissions have increased over South Asia and more persistent winter fogs are common during last decade. However, a physical mechanism connecting these two is still unknown. A significant fraction of BC is known to be in the form of carbon-nanotube (CNT). We have investigated the effects of two different sets of fog condensation nuclei, viz., inorganic salts (sodium chloride and ammonium sulphate) and BC (graphite and CNT) on the dissipation of chamber generated fog under dark and halogen lamp illuminated conditions at a controlled temperature, relative humidity, and fog condensation nuclei distribution. We found that, for inorganic salts, fog dissipates at a faster rate under illumination than in dark conditions showing similar trends for both sodium chloride and ammonium chloride. On the contrary, fog is found to be more persistent, for illuminated conditions, in the case of BC. Moreover, fog persistence is found to be more than twice for CNT compared to graphite in illuminated conditions. CNT is known to be an extremely effective absorber of light which leads to microscopic heating and subsequent evaporation which inhibits droplet growth. Small droplets have large residence time leading to longer fog persistence. This hitherto unknown mechanism may be responsible for persistent fog in India during last decade.
 [http://dx.doi.org/10.1063/1.4736557]

INTRODUCTION

Black carbon (BC), a mixture of graphite-like particles and light absorbing organic matter, is presently growing in importance as a major contributor to modern global warming.[1–6] BC emissions have risen linearly since 1950 (Ref. 7) primarily due to bio-fuel consumption. BC may even enhance up to 50% of the atmospheric solar heating[4] in the form of what is now known as brown carbon (BC_e).[2,3] The coating of BC with organic and inorganic material significantly increases the specific absorption cross-sections as compared to uncoated particles.[8] While 93% of the particulate matter in the outdoor is crystalline and 42% contains carbon, ~10% is carbon nanotube (CNT) aggregates of size mostly $<1\ \mu$m (Ref. 9). The strong absorption properties of these CNT conglomerates in the visible wavelengths[10] could lead to the observed increase in the visible optical depth.[4] On the other hand, not only has the occurrence of fog increased over the last decade in the winter months in northern India, fog is also observed to persist for a longer period of time at each forenoon occurrence in tune with the BC distribution.[11] The motivation of this work is therefore to investigate the influence of the above mentioned CNT fog condensation nuclei (FCN) on the persistence of fog.

EXPERIMENTAL SETUP

Experiments were carried out in an in-house fabricated fog chamber, producing different types of fog under an enclosed controlled environment. The fog chamber was made of double walled stainless steel barrel shaped box of dimensions $2 \times 0.3 \times 0.5\ m^3$ with optical windows at both ends as well as in the mid-section sidewalls.[16] Sensors were inserted into the chamber for measuring temperature and humidity. The chamber temperature was controlled to a resolution of 0.1 °C by circulating coolant into the double walled inner jacket to maintain a temperature difference $\Delta T \leq 3\ °C$ between the ambient temperature and the dew temperature for the formation of fog. Water vapor was introduced into the chamber in a uniform and controlled manner via actuator valves. The fog chamber was connected to the following components: i.e., (1) a portable atomizer aerosol generator (TSI Model 3079) used for producing wet aerosol particles; (2) an in-house fabricated dry aerosol generator, consisting of an preset flow valve for varying the dry aerosol particle concentration and to set the air flow rate;[16] (3) two 50 liters chilled liquid circulators with recirculation of isopropyl alcohol (IPA) at −40 to −50 ± 0.1 °C; (4) a humidity and temperature transmitter (HMT, Vaisala model 337); (5) a steam generator of 20 liter capacity; (6) a scanning mobility particle sizer (TSI Model 3936) run with a sheath flow rate of 3.0 lpm and an aerosol flow rate of 0.3 lpm; and (7) a cloud combination probe for the measurement of droplet size consisting

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of (a) cloud droplet probe (CDP), (b) cloud imaging probe, and (c) liquid water content sensor.[12] In addition, a He-Ne laser at 632.8 nm wavelength was installed for visibility measurement of the laboratory generated fog and the experimental data were collected using a data acquisition system at an interval of 0.01 s by a data-logger. Two 500 W halogen lamps (2×500 W) were also installed near the input and output windows to flood the chamber with photons for the investigation of the temporal behavior of the dissipation of dense fog.

The FCNs used in this work were NaCl, $(NH_4)_2SO_4$, uncoated graphite (all research grade reagents of "GR" grade purity from Sarabhai M. Chemicals), and CNT. The CNT FCN was home-grown and purified (99%) single and multi-walled of thickness 10–30 nm and length $\sim$100 μm (supplementary Figure S1).[21] Initially, the chamber was cooled to the desired temperature by circulating chilled IPA. Subsequently, steam and FCN (different type and concentration), at a predetermined flow rate, were introduced simultaneously into the fog chamber through showers provided at the top of the chamber. The dense fog so generated ($V < 2$ m) is then allowed to dissipate at constant temperature and atmospheric pressure. The FCN concentration distribution and droplet size distribution were measured separately, under identical conditions, so as not to disturb the fog condition under dissipation measurements. The FCN flow rate quantifies the air flow through the wet or dry aerosol generators. The flow rates for the different FCN were so chosen that the product of the integral of the FCN concentration distribution, the flow rate, and the total time of flow (i.e., the total number of FCN) remain the same for all FCN under consideration.

The generated fog was qualified by its visibility. Fog visibility (V) was measured from the transmission loss, T ($\lambda = 632.8$ nm) of the He-Ne laser, through the fog chamber along with a silicon photodiode detector and data logger. The formulation for V is adopted from the definition of meteorological optical range (MOR)[13] as

$$V = \frac{L \cdot \ln(0.05)}{\ln(\mathrm{T}(\lambda))} \ [\mathrm{km}], \tag{1}$$

where L is the round trip length of the fog chamber and

$$T(\lambda, L) = \frac{P(\lambda, L)}{P(\lambda, 0)} = \ e^{-\sigma(\lambda).L} \ , \tag{2}$$

where $\sigma(\lambda)$ is the fog attenuation coefficient and

$$\sigma(\lambda) = \alpha(\lambda) + \beta(\lambda), \tag{3}$$

α and β being the absorption and scattering coefficient, respectively. Ideally, visibility should be measured at all visible wavelengths. However, as the wavelength dependence of the transmission losses in fog can be calculated by the empirical formula[14] and the scaling in intensity is proportional to the visible curve, i.e., the ratio of area under the response curve of the human eye for clear environment to the fog condition remains the same. It has been shown that that the meteorological definition of visibility is not altered if measured at only one wavelength;[15] hence, measurement was only performed at $\lambda = 632.8$ nm.

Fog dissipation was measured under two conditions, namely in a dark environment and under illumination with two 500 W halogen lamps. The detector, under fogless condition, reads 6% more due to chamber illumination, translating to a 40% over estimation of the visibility under illumination. This overestimation is found to go down monotonically to be negligible at $V \sim 5$ m. Dense fog was generated in the chamber for each FCN, by introducing a mixture of steam and FCN laden air at predetermined flow rates specific for FNC (steam flow rate is same for all FCN). The FCN and steam flow were switched off, when the fog goes through an initial phase of nonequilibrium state of temperature and relative humidity (RH) (both with and without illumination), where any change in V is smaller than the accuracy of measurement. Thereafter, there is a stable state of $\sim$100 s beyond which it again starts dissipating. This was the onset of our measurement of T, RH, and V variation as a function of time.

RESULTS AND DISCUSSION

Figs. 1(a) and 1(b) show the variation of visibility under dark and illuminated conditions. Broken lines are for dark conditions and solid lines are for illuminated conditions. As shown in Figure 1(b), NaCl and $(NH_4)_2SO_4$ FCN dissipated faster on being illuminated. On the contrary, for uncoated graphite and CNT, the fog was found to be more persistent, Figure 1(a). It should be noted that for the inorganic salts the variation of the dissipation with illumination would actually be closer to the conditions under dark because of the overestimation of "V" at illuminated conditions, whereas for uncoated graphite and CNT the overestimation results in showing up as a reduced effect. It is therefore evident from the measurement that due to BC fog persists for a longer duration under illumination whereas normally it would have dissipated faster. The persistence due to CNT is almost double that due to uncoated graphite.

This phenomenon cannot originate from any variation in the FCN number as the measured graphite FCN density distribution, shown in Fig. 2, is somewhat higher than that of CNT. Moreover, the inorganic salts, which show a faster dissipation due to illumination, actually have a slightly higher concentration at lower FCN diameters. Fig. 3 shows the fog droplet distribution for different FCNs at $V \sim 2$ m. The distribution is very similar for all FCN typically being trimodal,[16] as is also shown for the ambient measurements at $\sim$50–100 m visibility. The measured ambient droplet density is lower than that of fog-chamber measurements because of higher visibility in the former.[17] Although the concentration is $\sim$1.4 times in graphite than CNT, at the most, this does not explain the larger persistence in CNT generated fog. The difference in temperature also does not account for the larger persistence for CNT FCN with light as small temperature variations of few degrees do not influence the droplet density for $V \leq 50$ m (supplementary Figure S2).[21]

The relation of aerosol contribution to the frequency of occurrence of fog has been established over Europe.[18] The BC particular content is usually high in India arising out of

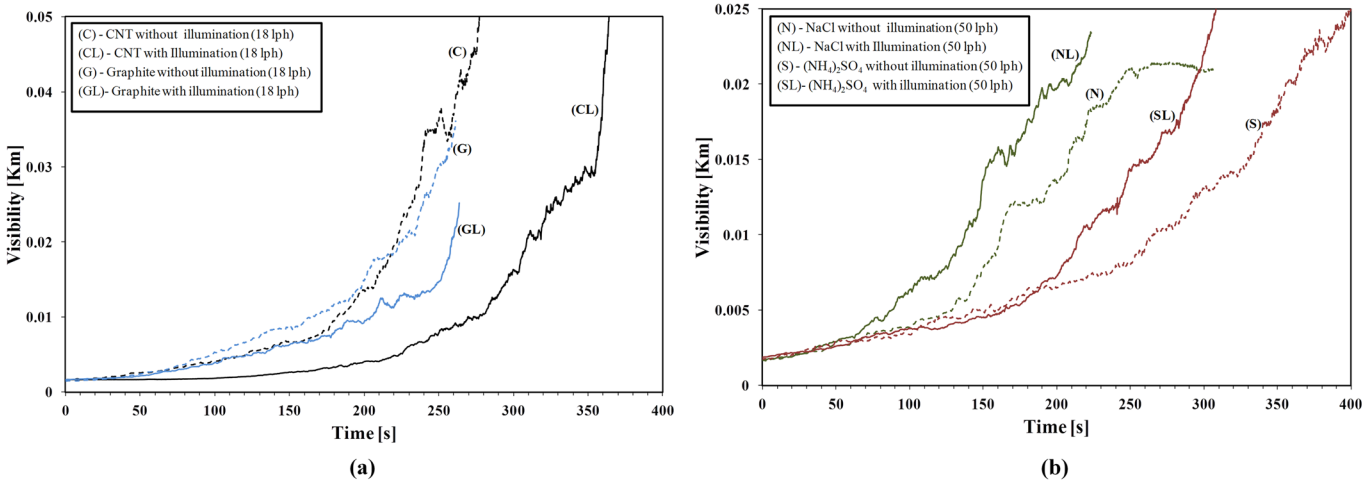

FIG. 1. Variation of visibility under dark and illuminated conditions measured in the fog chamber. (a) Dissipation dynamics for CNT and Graphite, (b) dissipation for NaCl and $(NH_4)_2SO_4$. Broken lines are for dark conditions and solid lines are for illuminated conditions.

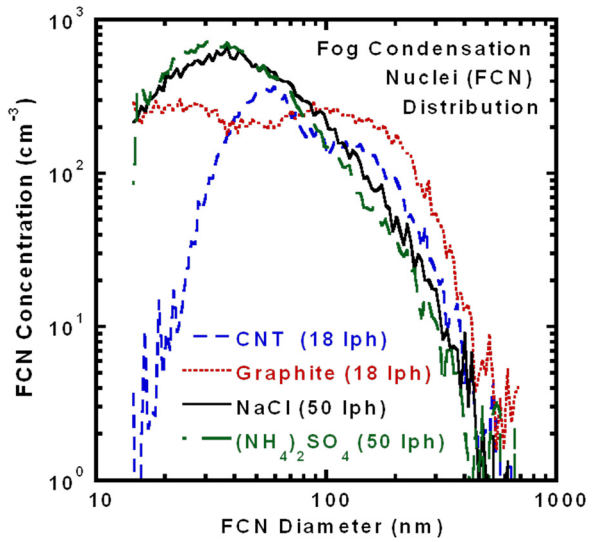

FIG. 2. Fog condensation nuclei size distribution measured for the wet aerosol generator [NaCl and $(NH_4)_2SO_4$] and for the dry aerosol generator [graphite and CNT] using Scanning Mobility Particle Sizer (SMPS).

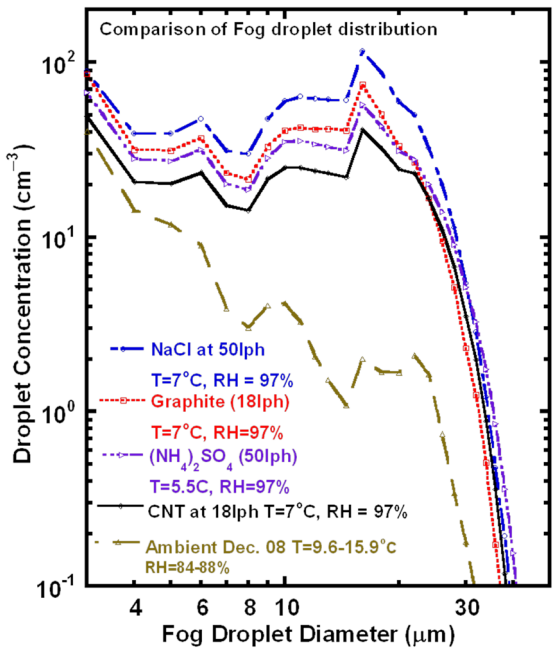

FIG. 3. Fog droplet size distribution measured by CDP for NaCl, $(NH_4)_2SO_4$, graphite, CNT FCN in the fog chamber. Also showed for comparison is the DSD measured for local ambient fog.

both biomass and fossil fuel combustion[19] and it absorbs light over a large continuum spectral range and absorption coefficients have been measured to be as high as 3×10^{-5} m^{-1} at $\lambda = 550$ nm, where the total organic content is 4–5 mg m^{-3}. For $\lambda > 300$ nm, CNTs have been shown to trap thermal energy from photon absorption, resulting in local temperature increase.[20] Extremely high absorption of halogen flash lamps has been observed in ordered CNTs,[10] which is at least 10-fold higher than that of graphite. This may explain the heat generation in fog under illuminated conditions. At diffused light conditions (i.e., early morning), the intensity of light may not be strong enough for the fog to disperse but is sufficient to provide enough energy to the BC/CNT FCN such that the heated droplets reduce in size by evaporation, leading to smaller sedimentation velocity (another mechanism by which fog may dissipate). Smaller sized droplets will also resist the process of collision-and-collection to larger droplets, thus enhancing the fog persistence. On the other hand, the inorganic salt FCN (NaCl and $(NH_4)_2SO_4$) does not absorb visible radiation as does the graphite/CNT FNC; therefore, the droplet's growth is not affected. The large droplets settle down leading to faster dissipation. This hypothesizes the reasons of persistence of fog over the last decade in northern India; however, a detailed microphysical model of this complicated system (fog droplet + CNT FCN along with their optical absorptive effects) needs be established to understand the mechanism.

CONCLUSION

In summary, we have measured the dissipation rates of artificially generated fog in a controlled environment for several fog-condensation-nuclei using fog-visibility as a parameter. Measurements were done under dark and illuminated conditions. For NaCl and $(NH_4)_2SO_4$, fog was found to dissipate at a faster rate under illumination than that in the

dark; whereas, the reverse is true for graphite and carbon nanotube FCNs. CNTs have a more profound effect than that of graphite in the persistence of fog under illumination and may be hypothesized to be due to the optical absorption strength of CNT in the visible spectrum.

ACKNOWLEDGMENTS

We acknowledge the financial support provided by Technology Mission on Railway Safety (TMRS), Ministry of Railways and Ministry of Human Resource Development, Government of India. We also acknowledge the help provided by Mr. Sushil Yadav and Mr. Ramshankar for carrying out the experiments.

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[21]See supplementary material at http://dx.doi.org/10.1063/1.4736557 for scanning electron micrograph of carbon nanotubes used in this work and effect of chamber temperature on the dissipation of fog.