

Secondary Organic Aerosol: A Comparison between Foggy and Nonfoggy Days

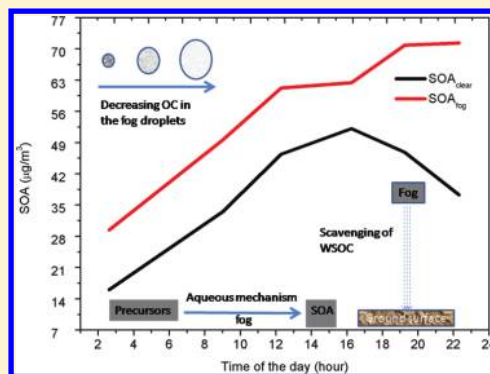
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S Supporting Information

ABSTRACT: Carbonaceous species, meteorological parameters, trace gases, and fogwater chemistry were measured during winter in the Indian city of Kanpur to study secondary organic aerosol (SOA) during foggy and clear (nonfoggy) days. Enhanced SOA production was observed during fog episodes. It is hypothesized that aqueous phase chemistry in fog drops is responsible for increasing SOA production. SOA concentrations on foggy days exceeded those on clear days at all times of day; peak foggy day SOA concentrations were observed in the evening vs peak clear day SOA concentrations which occurred in the afternoon. Changes in biomass burning emissions on foggy days were examined because of their potential to confound estimates of SOA production based on analysis of organic to elemental carbon (OC/EC) ratios. No evidence of biomass burning influence on SOA during foggy days was found. Enhanced oxidation of SO₂ to sulfate during foggy days was observed, possibly causing the regional aerosol to become more acidic. No evidence was found in this study, either, for effects of temperature or relative humidity on SOA production. In addition to SOA production, fogs can also play an important role in cleaning the atmosphere of carbonaceous aerosols. Preferential scavenging of water-soluble organic carbon (WSOC) by fog droplets was observed. OC was found to be enriched in smaller droplets, limiting the rate of OC deposition by droplet sedimentation. Lower EC concentrations were observed on foggy days, despite greater stagnation and lower mixing heights, suggesting fog scavenging and removal of EC was active as well.



I. INTRODUCTION

Frequent and extended fog episodes over the Indo-Gangetic Plain (IGP) during winter make it an ideal site to study the impacts of fog on visibility, health, and climate. One phenomenon of interest is the interaction between fogs and carbonaceous aerosols. Numerous studies on carbonaceous matter in particulate matter (PM_x) (PM ≤ x µm aerodynamic diameter; x = 10, 2.5) have been carried out but few have focused on PM₁.¹ Carbonaceous aerosol is categorized by OC and EC. EC, essentially a primary pollutant, emitted directly to the atmosphere, is produced by various incomplete combustion activities. OC, which has both primary and secondary origins, is a complex mixture of thousands of organic species having a range of chemical and physical properties as well as different sources. OC is emitted directly from various sources such as vehicular exhaust, fossil fuel combustion, biomass burning, and cooking; it can also be formed via gas to particle partitioning of various low volatility products of photo-oxidation reactions.^{2,3} Particulate organic matter produced by gas to particle conversion process is referred to as secondary organic aerosol (SOA). Our understanding about the role of SOA in climate change and its connection to health effects is limited by numerous uncertainties. SOA formation pathways, especially those involving heterogeneous

chemistry, SOA composition, and the contribution of SOA to total particle concentration are all uncertain.⁴ Establishment of ambient air quality standards for fine particles has drawn much attention toward controlling SOA as it mainly contributes to fine particles, has negative health effects, and contributes to haze formation and visibility reduction.^{5–8} SOA also influences climate forcing directly by altering scattering properties of the atmosphere and indirectly by changing cloud properties, both of which affect Earth's radiation balance.^{9–11}

The direct estimation of SOA is complicated due to the complexity of chemical production pathways, the numerous anthropogenic and biogenic precursor species involved in its production, the large number of products produced during oxidation reaction, and resources and costs involved in analytical procedures for their identification and quantification. In order to overcome some of these issues, SOA has been estimated through an indirect method known as the EC tracer method.^{12–15} Although, relative contributions of primary and secondary

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organic carbon can be inferred by OC to EC ratios, quantification of absolute primary organic carbon (POA) and SOA concentrations remain important to assess aerosol predictions made by models. Several methods, including tracer based receptor models,^{16–18} reactive chemical transport models,^{19,20} nonreactive transport models,²¹ and the semiempirical EC tracer method,^{22,23} can all be used to estimate POA and SOA. Only the EC tracer method is used in this study as it is easier to apply and depends only on ambient measurements of OC and EC.

Secondary OC $[OC]_s$ in PM_1 was estimated using eq 2 assuming that primary OC $[OC]_p$ can be estimated from eq 1

$$[OC]_p = \left[\frac{OC}{EC} \right]_p \times [EC] \quad (1)$$

$$[OC]_s = [OC] - [OC]_p \quad (2)$$

$\left[\frac{OC}{EC} \right]_p$ is the ratio of primary OC to EC observed at a monitoring site,¹⁵ while $[OC]$ and $[EC]$ are measured concentrations. This approach has been used for estimation of primary and secondary contribution to OC aerosols in numerous studies conducted in both urban and rural environments.^{24–28} SOA estimation by the EC tracer method is based on and takes advantage of the fact that OC/EC ratios increase during periods of high photochemical activity,^{29,30} while the ratio of primary OC and EC emissions is assumed to remain constant. $\left[\frac{OC}{EC} \right]_p$ is estimated from the subset of measurements when production of SOA is least likely,^{20,23} an approach that leaves some uncertainty in the true value of this ratio.^{20,31} In this study, $\left[\frac{OC}{EC} \right]_p$ was estimated via linear regression (slope = 4.04, $R^2 = 0.80$) on a portion (~24% i.e. 43 data points) of the data set containing the lowest OC/EC ratios (refer to Supporting Information Figure S2). It was observed that most of these data points were mostly from evening through morning when photo-oxidation and contamination from the SOA was insignificant. Also, these data points were from different days and thus represent the average primary OC/EC ratio for entire the study period. More details are included in the Supporting Information (S3 and Figure S3). A small intercept relative to the slope (Figure S2) suggests minor primary OC contribution from biogenic or other source emissions not containing EC and thus was not accounted for in the estimation of $[OC]_s$. $[OC]_s$ is multiplied by 1.4 to obtain the SOA concentration. The 1.4 multiplier accounts for other noncarbon atoms (e.g., H, O, N, S) in the organic molecules found in organic aerosol particles. The value of 1.4 is based on typical values observed in other urban environments.^{32–34}

Recent studies have suggested that SOA formation through multiphase processes can be important.^{10,35–41} Formation mechanisms have been suggested both in wet aerosols and in fogs and clouds. SOA formation in fog occurs when soluble organic gases dissolve into droplets and are oxidized to yield lower volatility products that remain behind in particles released by evaporating fog droplets. These released particles contain both the initial components present in cloud condensation nuclei and new secondary components consisting of the low volatility products of aqueous phase chemistry.³⁶ Mechanisms of SOA production, which can lead to substantial increase in atmospheric organic aerosol concentration, remain poorly understood partly due to the complex nature of multiphase processes likely involved in SOA production.^{10,23,36} In the case of surface-based fogs, significant scavenging and removal of organic aerosol also occurs as droplets are deposited to surfaces.⁴²

Most work on potential SOA production in fogs has occurred through laboratory studies or numerical modeling. In this study, we compare diurnal changes in atmospheric fine particle OC and EC concentrations, on clear and foggy days, in order to examine the possible influence of regional fogs on particulate organic matter concentrations. Our overall goal is to understand particulate organic matter formation, diurnal changes, enhanced production, and removal mechanisms and how they differ between clear and foggy days.

II. EXPERIMENTAL SECTION

Sampling was conducted in the city of Kanpur, India (26.5° N, 80.3° E, 142 m msl). Kanpur is located in the center of the Indo-Gangetic Plain (IGP) region and is a large urban environment (population ~2.6 million). The main particulate and volatile OC sources in the region include industries, domestic fuel combustion, and vehicle transport.³² Time integrated PM_1 samples were collected from January 16, 2010 to February 20, 2010 on 47 mm quartz filters (Whatman, QMA), using a custom designed inertial impaction based sampler⁴³ (operated without a gas denuder) at a flow rate of 10 L min^{-1} , cut off size (d_{50}) of 1 μm , and at a filter face velocity of 10 $cm s^{-1}$. All these filters were heated for 6–8 h at 700 °C to remove any background adsorbed carbon on filters prior to sampling. For every 24 h, a total of six samples were collected: one from 7:30 a.m. to 10:30 a.m., one every 2.5 h from 11:00 a.m. to 11:30 p.m. with a 30 min gap between successive samples (for sample change out), and one night time sample from 12:00 a.m. to 7:00 a.m. The total number of samples collected was 180; 54 of these samples were collected on foggy days.

Filters were analyzed for carbonaceous content by a EC-OC analyzer (Model No: 4F, Sunset Laboratory Inc.) following the NIOSH 5040 method.^{44,45} Filter blank values were subtracted from the measured values. Although absence of denuder will lead to some sampling artifact, such artifacts will be on both clear and foggy days, Turpin's research group⁴⁶ has documented higher correlation of OC with positive artifact. Meteorological data (sampling frequency, 30 min), including pressure and wind speed, were collected from an Atmospheric Weather Station (AWS). The high resolution (one second) temperature (T) and relative humidity (RH) data were collected from a Vaisala Humicap (HMT 337, Serial No: B4050039). A Micro-Pulse-Lidar (Model No: 633SP, Ekto Manufacturing Corporation) Network (MPLNET), a part of the National Aeronautics and Space Administration (NASA), which provides vertical structure of the atmosphere every minute, was used to record information for cloudy and clear days including the precise duration of fog episodes and planetary boundary layer (PBL) height. It transmits a laser at a wavelength of 532 nm vertically into the sky, and backscatter signals are received, processed, and resolved into several products. One of those products is cloud block at ground (L 1.5b) which is a flag for ground level clouds i.e. fogs. A pyranometer (Model No: CM2, KIPP & ZONEN DELFT/HOLLAND), a part of AERONET (Aerosol Robotic Network), was used for incoming solar radiation (F) measurements at 2 min temporal resolution. Trace gas species (SO_2 , O_3 , and CO) concentrations were measured at 15 min resolution using a SO_2 gas analyzer (Model No:43i, Thermo Scientific), an O_3 gas analyzer (Model No: 49i, Thermo Scientific), and a CO gas analyzer (Model No:48i, Thermo Scientific). Fog water was collected using a three stage size-fractionating Caltech Active

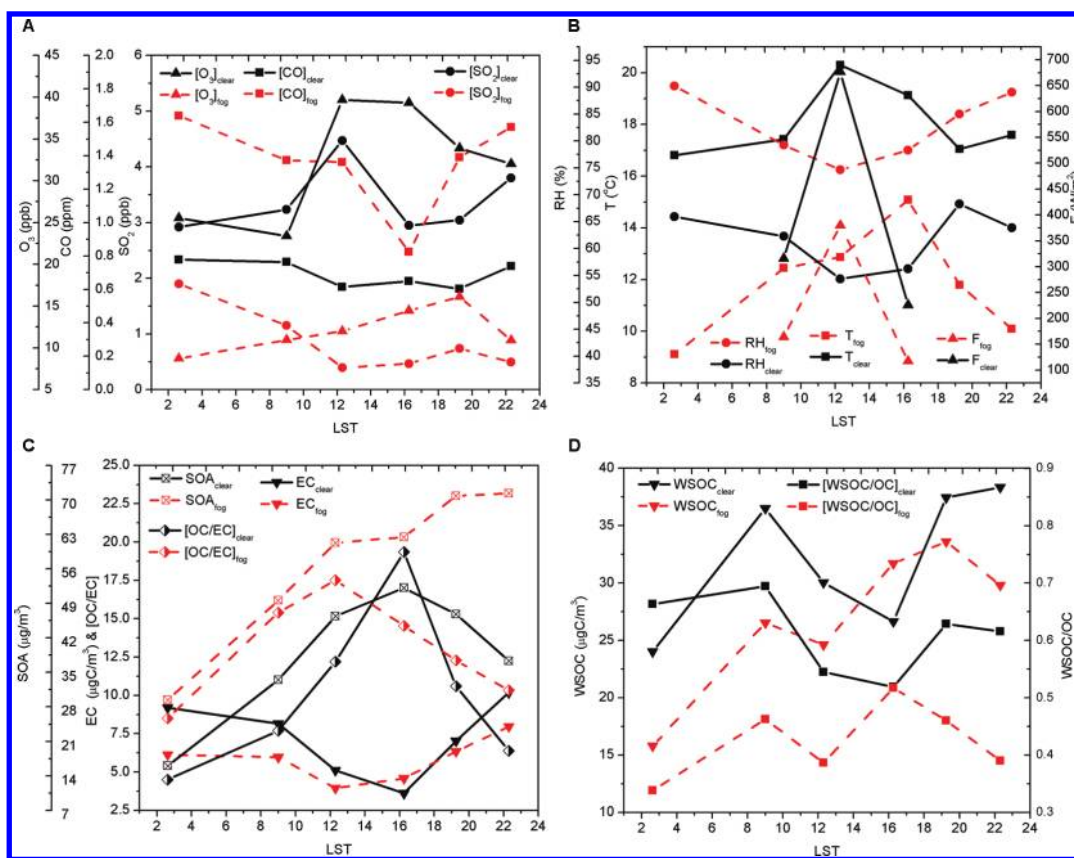


Figure 1. a. Study-average diurnal variation of ozone (O_3), carbon monoxide (CO), and sulfur dioxide (SO_2) concentrations during foggy and clear days. b. Study-average diurnal variation of relative humidity (RH), temperature (T), and solar flux (F), during foggy and clear days. c. Study-average diurnal variation of secondary organic aerosol (SOA) and elemental carbon (EC) concentrations and organic carbon to elemental carbon ratio (OC/EC) during foggy and clear days. d. Study-average diurnal variation of water-soluble organic carbon (WSOC) concentrations and the ratio of WSOC to organic carbon (WSOC/OC), during clear and foggy days.

Strand Cloudwater Collector (3-stage-sf-CASCC)⁴⁷ built at Colorado State University following the earlier 2-stage sf-CASCC design principle described by Demoz et al.⁴⁸ Droplets are collected in each stage by inertial impaction onto Teflon cylinders and then flow down through a Teflon trough into a polyethylene sample bottle. The 3-stage sf-CASCC features size cuts (droplet diameter) of 4, 16, and 22 μm . The fog sampler was cleaned, and blanks were collected prior to sampling. Fog water was refrigerated until analysis.

All the filters were analyzed for the inorganic biomass tracer, water-soluble K^+ by ion chromatograph (Metrohm 882 Compact IC plus). Analysis of fogwater from 11 days is included in this study. TOC analyses on all filters and fogwater samples were carried out using a TOC analyzer (Model No: TOC-V CPN, Shimadzu Corporation). This instrument provides total carbon and inorganic carbon measurements separately. Only organic carbon, determined as total carbon minus inorganic carbon, is reported in this study. Aliquots of fogwater samples for TOC analysis were filtered by Millipore filters with pore size of 0.22 μm . Filter samples for TOC and K^+ analysis were prepared through aqueous (deionized milli-Q water) extraction with ultrasonication (Fast Clean Ultrasonic Cleaner, 2k909008). Aliquots for analysis of TOC and K^+ were refrigerated until analysis. pH of fogwater samples were measured using a pH meter (pH200, Orbeco Hellige), with a pH electrode, calibrated using pH of 4, 7, and 10 buffers. pH measurements on fogwater were carried out directly (i.e., on unfiltered fogwater).

III. RESULTS AND DISCUSSIONS

Fog episodes during the winter season (Dec-Feb) often affect the whole IGP region. They sometimes affect visibility of the region severely^{49,50} and can cause traffic related accidents, airport closures, and health hazards. The region is typically under a synoptic influence of high pressure during winter (1000.3 ± 1.8 mbar during sampling period) resulting in periods of poor dispersion. An image of a typical fog event (Jan 09, 2010 at 05:10 a.m. UTC, obtained by the Moderate Resolution Imaging Spectrometer (MODIS) and MPL (L 1.5b data) can be seen at <http://aeronet.gsfc.nasa.gov/>, clearly indicating the large spatial and temporal scale to which this area ($\sim 7-15\%$) can be affected. Temporal and spatial scales of other foggy days can also be obtained at <http://aeronet.gsfc.nasa.gov/>. Several such episodes, extending from 2 to 48 h duration, occurred during the study sampling period. Periods were classified as foggy when fog persisted for approximately 100% of the sampling duration. Periods were classified as clear when fog was absent during most of the sampling period, although some influence from fog ($\sim 5-20\%$ of sampling duration) was unavoidable in some cases due to our fixed sampling schedule.

The EC-OC analyzer measures thermal OC, thermal EC, and optical EC. Optical OC is obtained as Optical OC = (thermal OC + thermal EC) - Optical EC. Excellent regression parameters between thermal OC vs optical OC ($R^2 = 0.99$, Slope = 1.01) and thermal EC vs optical EC ($R^2 = 0.96$, Slope = 0.86) ensured good

quality of the data from the EC-OC analyzer. High regression coefficients and slope values close to 1 imply that use of either thermal or optical method data would not significantly influence other derived quantities; thermal OC and EC values were chosen for use in the analysis here.

Meteorological, trace gas, and carbonaceous aerosol concentration data were averaged to the sample time intervals of the PM1 samples, separately for foggy and clear days, and plotted as a function of time of day in Figure 1 (refer to Tables S4-a, S4-b, S5-a, S5-b for data). A calm condition persisted for most of the sampling duration during both foggy and clear days. Foggy days were calmer than clear days. Thus, contamination of parameters studied over this region from the distant emission sources is mostly unlikely; for more details refer to the Supporting Information (S7, Figure S7-a and S7-b). Figure 1a,b shows the study average diurnal variation of trace gas concentrations and meteorological parameters during foggy and clear days. O₃ and SO₂ concentrations are both much higher, on average, throughout the day and night on clear days; study average CO concentrations are higher on foggy days during most of the day and night, although similar values are seen in late afternoon (Figure 1a). Higher O₃ concentrations during clear days are indicative of greater photochemical activity which results in enhanced oxidant production; during foggy days lower solar fluxes (Figure 1b) suppress ozone production. The ozone diurnal trend is similar to those documented earlier,²⁵ with the daily concentration peak on foggy days (~1900 LST) lagging the peak (~1200 LST) on clear days. Higher CO concentrations on foggy days most likely reflect greater atmospheric stagnation due to lower PBL (~0.73 ± 0.03 km) and lower wind speed (~0.17 ± 0.05 m/s) conditions, whereas greater dispersion on clear days (PBL ~ 0.84 ± 0.06 km, wind speed ~0.21 ± 0.05 m/s) helps to disperse emitted CO both vertically and horizontally away from sources. The similarity between late afternoon (~1600 LST) CO concentrations on both clear and foggy days likely reflects enhanced vertical mixing associated with a deepening boundary layer in the afternoon, even on foggy days, when reduced fog optical depths are likely to permit an increase in surface heating.

Lower concentrations of SO₂ are expected during foggy days, due to uptake of SO₂ into fog droplets (or wet aerosols) followed by aqueous oxidation to sulfate. The extent of sulfur dioxide uptake and the rate of reaction in the aqueous phase depend on the droplet pH and the availability of key oxidants, such as hydrogen peroxide and ozone. As observed in fogs elsewhere,^{51,52} the rate of sulfate production in the aqueous phase can be very fast, especially when fog pH values climb above 6 where oxidation of dissolved SO₂ by ozone is rapid. The pH of the fogwater observed in this study ranged from 6.03 to 8.07 and averaged 7.24. Similar oxidation during fog episodes and deposition of sulfate has been previously documented.^{53–57} Sulfuric acid production through SO₂ oxidation can produce acidic aerosol. High concentrations of sulfate over this region have been documented earlier.⁵⁰

Fogs are often effective scavengers of organic carbon with more widely varying scavenging efficiencies (~5–90%) observed for elemental or black carbon.^{53,58–60} The concentrations of OC measured in fogwater were very high in this study. The average concentrations (±one standard deviation) in the large, medium, and small drop size fractions collected with the 3-stage-sf-CASCC were 49 ± 25.6, 98.2 ± 101, and 423.8 ± 479.8 mgC/L, respectively. The observed pattern indicates an enrichment of organic carbon in smaller droplets, as observed previously,^{60,61}

while the large standard deviations indicate substantial variability in concentrations across the studied fog events. Enrichment of OC in smaller fog droplets could reflect a combination of effects. Smaller droplets often form on smaller particles that are more likely to be enriched in OC. Uptake of highly soluble volatile organic compounds might also occur preferentially in smaller droplets.⁶² Finally, it is possible that aqueous phase SOA production might occur more rapidly in small droplets which are less likely to be limited by finite rates of mass transfer of reactants or oxidants from the gas phase. The enrichment of OC in smaller fog droplets will reduce its removal from the atmosphere by droplet sedimentation,⁴² since deposition velocities for smaller droplets are much lower than for larger droplets.

Figure 1c shows study-average diurnal variations of EC, SOA, and OC/EC during clear and foggy days. SOA concentrations on both foggy and clear days are higher, on average, during the afternoon and evening than in the morning. This trend is consistent with photochemical production of SOA during daytime. SOA concentrations on foggy days are higher, on average, than on clear days, with the difference most pronounced in the afternoon. A direct comparison of SOA concentrations is, however, perhaps not especially illuminating, since fogs actively deposit scavenged organic matter to the surface (especially at night) while enhanced dispersion on clear days is expected to reduce SOA concentrations under those conditions. It may be more useful, in considering the possibility of aqueous phase SOA formation, to look at OC/EC ratios instead. These are likely to be less influenced than SOA concentrations by fog deposition and atmospheric dispersion processes, although a preference in OC vs EC scavenging by fog drops could still lead to some depression in the OC/EC ratio through deposition. Comparing OC/EC ratios on foggy days vs clear days, one sees much higher ratios from midnight through noon on foggy days (13.81 ± 4.70 vs 8.14 ± 3.86), while similar OC/EC ratios are observed from noon to midnight (12.63 ± 3.53 on foggy days and 10.61 ± 5.78 on clear days). Given the tendency for fog to be present most often during the overnight and early morning hours, the enhanced OC/EC ratio during this time period on foggy days could be an indication of aqueous phase SOA production. A possible alternate explanation of this trend could be an increased prevalence of biomass burning at night. The study occurred during winter when overnight heating by fires is likely to be important. Depending on combustion fuels and burn conditions, relatively high OC/EC ratios can be found in particle emissions from open biomass burning.⁶³ On clear days, WSOC/OC concentration ratios tend to be highest in the early morning hours (Figure 1d). This is consistent with increased biomass burning overnight into the morning, since WSOC/OC ratios in biomass burning aerosols tend to be high (A. Sullivan, unpublished data). An increase in WSOC/OC in the afternoon may reflect increased oxygenation of the organic aerosol associated with SOA production or an evening increase in biomass burning activity. Lower WSOC/OC ratios at all times, except ~1600 LST, on foggy days could reflect preferential scavenging and deposition of WSOC by fog droplets during the nighttime and morning hours when fogs commonly occur (Figure 1d). Previous studies of organic aerosol scavenging by radiation fogs in California⁶⁰ clearly indicate differences in scavenging across aerosol source types, with particle emissions from biomass burning showing especially high scavenging efficiencies. Similar EC diurnal concentration profiles on clear and foggy days suggest that fogs are not actively interacting with atmospheric EC. An unpaired *t* test of foggy day EC values vs

clear day EC values was also performed to compare EC levels during foggy and clear days. A relatively large p-value (~ 0.14) suggests the observed difference is not statistically significant. EC removal by fogs, through scavenging and sedimentation, may still be important, as suggested by difference in average EC concentrations on clear and foggy days during overnight and afternoon periods (Figure 1c).

Previous investigators⁶⁴ have reported fair correlation of OC with EC at two sites in India, implying common sources of their emissions. A poor linear correlation between OC and EC ($OC = 2.22EC + 40.13$, $R^2 \sim 0.20$) concentrations in the current study suggests that concentrations of these species are not solely due to a common set of source emissions, consistent with substantial contributions from secondary production. Several investigators^{65–68} have used OC/EC ratios as indicators of sources of their emissions; higher ratios are indicative of biomass burning sources while lower ratios are associated with fossil fuel combustion emissions. Measurements in a European Alpine valley⁶⁷ indicated an average OC/EC ratio of 7.3 for wood burning and 1.1 from traffic (vehicular) emissions. A second study in northern Europe⁶⁹ determined an OC/EC ratio of 6.6 for biomass combustion, 12 for aerosol from long-range transport, 3.3 for secondary organic carbon, and 0.71 for traffic emissions, based on measurements made in an urban environment. The OC/EC ratio in this study ranged from ~ 3 to 18 on clear days and ~ 8 to 17 on foggy days (Figure 1c). These high ratios are consistent with values reported above from biomass burning, long-range transport, or a mixture. Low wind speeds during the study (speed = 0.2 ± 0.1 m/s) and the observed diurnal variation of OC/EC concentrations, however, suggest that long-range transport is unlikely to dominate the measured aerosols. The high OC/EC ratios observed in this study appear, therefore, to reflect important contributions from both biomass burning and SOA production. SOA production on foggy days, in particular, appears to be important, as OC/EC ratios during overnight fog periods are higher than on clear days. Overnight WSOC/OC ratios are lower on foggy days than on clear days, suggesting that the enhancement in OC/EC ratios is probably not due only to increased biomass burning contributions. Contributions of biomass burning were further investigated with biomass tracer, K^+ analyzed in PM_{10} aqueous extracts. A lower average value of K^+ during foggy days ($4.45 \pm 1.00 \mu\text{g}/\text{m}^3$) than clear days ($5.26 \pm 0.54 \mu\text{g}/\text{m}^3$) was observed. The night time K^+ average value during foggy days ($4.43 \pm 2.64 \mu\text{g}/\text{m}^3$) was also smaller than during clear days ($5.55 \pm 3.76 \mu\text{g}/\text{m}^3$). The day time K^+ average value during foggy days ($4.20 \pm 2.76 \mu\text{g}/\text{m}^3$) was also smaller than during clear days ($4.88 \pm 3.73 \mu\text{g}/\text{m}^3$). While these differences may not be statistically significant, they clearly suggest that biomass burning was not a bigger contributor to OC on foggy days than on clear days. Evaporation of individual fogs and the subsequent change in the OC/EC ratio was further investigated. In almost all the fog episodes, an increase in OC/EC ratio as fog evaporated (more details in S8, Table S9) was observed. Findings in the current study suggest that aqueous production mechanisms are likely an important component of regional SOA production in winter.

Poor regression coefficients for OC/EC vs temperature and relative humidity for the entire sampling period ($R^2 = 0.002$; 0.032) were also observed (Supporting Information Figure S6-a and Figure S6-b). Although, various chamber studies have documented stronger correlation with these parameters.^{4,70}

This study shows that fog episodes in Kanpur were associated with enhanced production of SOA. It is hypothesized that enhanced SOA production is due to aqueous phase chemistry. Biomass burning did not appear to be a substantial contributor to

observed increases in OC/EC ratios that are interpreted as evidence of SOA production. The temperature and relative humidity had no detectable influence on SOA production. Fogs are also active at cleansing the atmosphere of carbonaceous aerosols. Water-soluble organic carbon is scavenged from the atmosphere during fog episodes; smaller fog droplets were more enriched with carbon than large droplets that counter their removal rates by droplet sedimentation. EC, which typically interacts less strongly with fog, was also observed on average to be lower during fog episodes, in spite of lower mixing heights and reduced dispersion. However, unpaired t test showed statistically insignificant difference between EC concentration for foggy and clear days.

■ ASSOCIATED CONTENT

S Supporting Information. Figures, tables, and text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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