

Primary and secondary aerosols from an urban site (Kanpur) in the Indo-Gangetic Plain: Impact on CCN, CN concentrations and optical properties



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HIGHLIGHTS

- First measurements of CCN, CN, chemical composition and optical properties IGP.
- Lower CCN/CN ratios suggesting the dominance of primary and non-hygroscopic particles.
- σ_{abs} of EC during daytime is factor of two higher than that during nighttime.

ARTICLE INFO

Article history:

Received 28 November 2013

Received in revised form

6 January 2014

Accepted 6 February 2014

Keywords:

CCN and CN concentrations

EC

OC

Indo-Gangetic Plain

Mixing state

ABSTRACT

The number concentrations of cloud condensation nuclei (CCN) and submicron aerosols (CN), along with their chemical composition and optical properties, have been studied during October 2008, October–November 2009 and November 2010 from an urban (Kanpur) site in the Indo-Gangetic Plain (IGP). The concentrations of CCN and CN and their optical properties vary with primary emission and secondary aerosol formation. The CCN (at 0.38% super-saturation) and CN concentrations varied from ~ 3900 to $15,000 \text{ cm}^{-3}$ and $\sim 23,000$ to $99,000 \text{ cm}^{-3}$, respectively. The diurnal variability of CCN and CN show peak concentrations during early morning hours (6:00–9:00 AM) and nighttime (7:00–10:00 PM), attributable to variability in source strength of carbonaceous aerosols and secondary aerosol formation. The CCN and CN concentrations are $\sim 50\%$ higher during nighttime with simultaneous increase in organic carbon (OC), elemental carbon (EC) and NO_3^- mass concentrations. However, CCN/CN ratios are similar during day and nighttime suggesting their co-variability with primary and secondary aerosol formation. The CCN/CN ratios are relatively lower (range: 0.11–0.33) than global average value and those over urban areas (with similar chemical composition in China and around the world) suggesting suppressed activation and hygroscopic growth in highly polluted environment of the IGP. The average mass absorption efficiency of EC during daytime ($11.7 \pm 2.5 \text{ m}^2 \text{ g}^{-1}$) is about factor of two higher than that during nighttime ($5.7 \pm 1.3 \text{ m}^2 \text{ g}^{-1}$). These results have implications to study morphological features, mixing state and microphysical properties of aerosols under high acidic environment over northern India.

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1. Introduction

Rapid industrialization, increasing economic growth and emissions from biomass burning and fossil-fuel combustion have led to significant increase in atmospheric concentrations of black carbon (BC) and other anthropogenic aerosols over South-Asia (Adhikary et al., 2007; Carmichael et al., 2009). Recent studies suggest that mass concentration of BC has increased by a factor of six since 1930 (Ramanathan et al., 2005) inducing a significant changes in the

warming trend, hydrological cycle, precipitation pattern and efficiency over south-Asia (Menon et al., 2002; Wang et al., 2009). The extent of warming by BC depends on its optical properties (mainly absorption and absorption efficiency) which are highly dependent on the shape and mixing state of BC in composite aerosols (Bond et al., 2006; Jacobson, 2001).

Freshly emitted carbonaceous aerosols mainly exist as an external mixture as they are least affected by chemical processing in the atmosphere and show their intrinsic optical behavior (Reid et al., 1998). In contrast, chemical and physical (coagulation and condensation) processes and coating of secondary aerosols (mainly water-soluble organic compounds, SO_4^{2-} and NO_3^-) do not only change the mixing state and optical properties but also morphological features and cloud condensation nuclei (CCN) properties of aerosols (Leng et al., 2013; Reid et al., 1998; Wang et al., 2010). Thus, optical properties and CCN activation are governed by composition, chemical processing and hygroscopicity of aerosols. Internally mixed aerosols show an enhanced absorption signal, up to 50% (Bond et al., 2006), for the given amount of BC mass concentration (Chandra et al., 2004; Martins et al., 1998; Schwarz et al., 2008) which can significantly affect the estimation of aerosol radiative forcing (Jacobson, 2001). In addition, chemical and physical processes are important in the evolution of hygroscopicity (from hydrophobic) of organic aerosols (Jimenez et al., 2009), submicron aerosol (CN) to CCN conversion and formation of cloud droplets (Gunthe et al., 2011; Gysel et al., 2004; Rose et al., 2011) and thus, subsequently in the estimation of indirect aerosol radiative forcing as well as precipitation.

In earlier studies, information on mixing state of aerosols was mainly derived using measured aerosol chemical composition and incorporating them into core-shell models (Chandra et al., 2004; Dey et al., 2008). However, real-time observations of changes in optical and microphysical properties were not available to affirm the hypothesis over Indian regions (Patidar et al., 2012). The entire Indo-Gangetic Plain (IGP) is characterized by high levels of primary carbonaceous aerosols and acidic species from secondary aerosol formation (as affirmed by SO_4^{2-} and NO_3^- concentrations) (Behera and Sharma, 2010; Ram and Sarin, 2011; Ram et al., 2010a). The sampling site, Kanpur (longitude: $80^\circ 13'$ E and latitude $26^\circ 30'$ N; 142 m above sea level), an urban location in the central part of IGP provides an ideal environment to study the changes in optical and microphysical properties due to changes in mixing state in a highly polluted environment of northern India. In this study, we have investigated variability and changes in CN and CCN concentrations and CCN/CN ratios during day and nighttime, along with absorption and mass absorption efficiency, in conjunction of primary emissions and secondary aerosol formation at Kanpur.

2. Analytical methods

2.1. CCN and CN measurements

The number concentrations of CCN (cm^{-3}) were measured during October 2008, October–November 2009 and November 2010 using a continuous flow stream wise thermal gradient CCN counter (Droplet Measurement Technologies, DMT) at three interspersed super-saturation (SS), namely 0.2, 0.5, and 1.0%, each with 12 min intervals. Due to significantly high number concentration of CCN observed at Kanpur, super-saturation depletion correction is applied (Patidar et al., 2012) and thus, CCN concentrations (in this study) are reported at 0.38 and 0.84% SS for 0.5 and 1.0% SS, respectively. The instrument was calibrated by the manufacturer before commissioning and recalibrated again in the laboratory at Indian Institute of Technology (IIT) Kanpur using $(\text{NH}_4)_2\text{SO}_4$ and

NaCl to characterize the performance of the instrument (Patidar et al., 2012; Srivastava et al., 2013). The details of operation, measurements of CCN and error analysis are described in our recent publication (Patidar et al., 2012). The error in the CCN measurements mainly occur due to instrument malfunctioning, instability in temperature, fogged condition in optical particle counter and variation in sheath to aerosol flow ratio (ideally it should be ~ 10) (Patidar et al., 2012). Measurements for all such cases were excluded in subsequent analysis and are not presented here. For SS below 0.2%, analysis show a maximum error of 50% in count rate up to maximum concentration tested (i.e. $30,000 \text{ cm}^{-3}$ in the present study) (Patidar et al., 2012). At SS higher than 0.3% there were minimal losses (10%) and maximum error in CCN counts is less than 10%. Total aerosol number (CN) concentrations and submicron aerosol size-distribution were measured by the Scanning Mobility Particle Sizer (SMPS, TSI Model 3936) between 0.014 and $0.68 \mu\text{m}$ sizes (Srivastava et al., 2013). The detailed measurement protocol and error budget of SMPS has been discussed in detail elsewhere (Baxla et al., 2009; Srivastava et al., 2013).

2.2. Ambient aerosol sampling and measurement of chemical composition

Simultaneous aerosol sampling of $\text{PM}_{2.5}$ and PM_{10} (particulate matter with aerodynamic diameter ≤ 2.5 and $10 \mu\text{m}$, respectively) were carried out during 19–30th October 2008 at IIT campus of Kanpur. The sampling site, located at the center of IGP, represents an urban environment and is significantly influenced by vehicular, industrial and biomass burning emissions. $\text{PM}_{2.5}$ and PM_{10} samples, comprising of day- (7:00 AM to 6:00 PM, Indian Standard Time, IST) and night-time (6:00 PM to 7:00 AM, IST), were collected over the span of two weeks October 2008. $\text{PM}_{2.5}$ and PM_{10} samples were collected separately by operating high-volume samplers with effective cut-off sizes of 2.5 and $10 \mu\text{m}$, respectively. The sampling period was characterized by relatively low ambient temperature (15 – 32°C), calm winds ($< 2 \text{ m s}^{-1}$), enhanced biomass burning activities and secondary aerosol formation (Ram and Sarin, 2011). The meteorological conditions are conducive for the formation of secondary pollutants with a few haze events observed during the sampling period as noticed by the Moderate Resolution Imaging Spectroradiometer (MODIS) images (Ram and Sarin, 2011). Statistical data of measured meteorological parameters and selected optical properties during study period are summarized in Table 1.

Filters and aerosol samples were equilibrated at room temperature of $\sim 22 \pm 2^\circ\text{C}$ and $\sim 35 \pm 5\%$ relative humidity (RH) before and after sampling. Total aerosol mass of $\text{PM}_{2.5}$ and PM_{10} samples was obtained gravimetrically by weighing blank and aerosol loaded filters and volume of air sampled. Mass concentrations of organic and elemental carbon (OC and EC) were measured on a thermo-optical EC–OC analyzer using thermo-optical transmittance (TOT) protocol (Ram et al., 2008). The transmittance of a 678 nm laser source, primarily used for defining the split-point between OC and EC, was used to determine absorption coefficient (b_{abs}) and mass absorption efficiency (σ_{abs}) (Ram and Sarin, 2009; Ram et al., 2010b). The details of measurement of b_{abs} and σ_{abs} and associated uncertainties are described in recent publications (Cheng et al., 2011; Ram and Sarin, 2009; Wang et al., 2013). The root-sum-square error for the determination of b_{abs} and σ_{abs} is estimated to be of the order of $\sim 23\%$ and 32% , respectively, based on the errors in the measurements of optical-attenuation (ATN), area (A), volume of air sampled (V) and corrections due to the multiple scattering and shadowing effects (Ram and Sarin, 2009). The mass concentrations of water-soluble organic carbon (WSOC) were measured using a total organic carbon (TOC) analyzer (Shimadzu, model 5000A), whereas cations (Na^+ , K^+ , NH_4^+ , Ca^{2+} and Mg^{2+}) and anions

Table 1

Statistical data (average ± 1 standard deviation; Av ± 1 sd) of measured meteorological parameters, physical and absorption properties during 19th Oct–30th Oct 2008 at Kanpur ($1 \text{ Mm}^{-1} = 10^{-6} \text{ m}^{-1}$).

Parameters	Units	Day (7:00 AM–6:00 PM)				Night (6:00 PM–7:00 AM)			
		Av \pm sd	median	min	max	Av \pm sd	median	min	max
Temperature	$^{\circ}\text{C}$	27.5 ± 3.4	28.6	16	32.2	18.3 ± 1.5	17.7	15.4	28.3
RH	%	53 ± 16	48	26	100	93 ± 5	95	35	100
Wind speed	m s^{-1}	0.38 ± 0.24	0.4	0.0	1.7	0.12 ± 0.05	0.1	0.0	1.3
Wind direction		258 ± 67	240	10	359	322 ± 22	324	23	359
CCN (@0.38%)	$(\times 10^3)\#\text{cm}^{-3}$	6.6 ± 2.9	5.7	0.2	15.9	9.8 ± 2.5	9.1	5.7	22.7
CCN (@0.84%)	$(\times 10^3)\#\text{cm}^{-3}$	7.9 ± 3.5	7.0	3.0	18.1	12.1 ± 3.0	11.7	7.9	23.1
CN	$(\times 10^4)\#\text{cm}^{-3}$	4.3 ± 2.4	3.2	1.6	11.7	6.6 ± 2.7	6.2	3.2	15.7
CCN/CN	(@0.5%)	0.17 ± 0.05	0.18	0.03	0.33	0.18 ± 0.06	0.16	0.05	0.28
$b_{\text{abs-678 nm}}$	Mm^{-1}	72.1 ± 16.9	69.5	50.5	122.9	63.9 ± 9.9	61.6	48.7	78.1
σ_{abs}	$\text{m}^2 \text{g}^{-1}$	11.7 ± 2.5	12.2	5.6	12.2	5.7 ± 1.3	5.5	3.3	8.1

(Cl^- , SO_4^{2-} and NO_3^-) were analyzed on an Ion-chromatograph (DIONEX[®]) (Ram and Sarin, 2011; Ram et al., 2012; Rengarajan et al., 2007).

3. Results and discussion

3.1. CCN and CN concentrations

The temporal variability in ambient temperature, RH, number concentrations of CCN and CN during the study period are presented in Fig. 1. The knowledge of concentrations of CCN in a given population of aerosol is an important parameter to understand the ability of a particle to act as nucleating agent which depends on size and the amount and coating of hygroscopic species (Andreae, 2009; Dusek et al., 2010; Gunthe et al., 2011; Rose et al., 2011). The CCN and CN concentrations at 0.38% super-saturation (SS) are significantly higher compared to those over urban areas with similar condition and varied from ~ 3900 to $15,000 \text{ cm}^{-3}$ and $\sim 23,000$ to $99,000 \text{ cm}^{-3}$, respectively (Fig. 1). The average CCN and CN concentrations at 0.38% SS are $6646 \pm 2981 \text{ cm}^{-3}$ and $44,433 \pm 24,865 \text{ cm}^{-3}$, respectively during daytime whereas those

are $9537 \pm 2690 \text{ cm}^{-3}$ and $65,017 \pm 27,465 \text{ cm}^{-3}$, respectively during nighttime for measurement made during October 2008.

In general, the diurnal pattern of CCN and CN concentrations does not follow that of temperature and relative humidity (Figs. 1a and 2a). The diurnal variability of CCN and CN concentrations show two peaks: first in the early morning (between 6:00 to 9:00 AM) and second in nighttime (between 7:00 to 10:00 PM) (see Fig. 2b for 22nd Oct, 2008 for better clarity). The first peak of CCN and CN concentrations in early morning coincides with higher BC mass concentrations which could be attributed to morning traffic rush hours (Tripathi et al., 2005). In an earlier study, Baxla et al. (2009) have reported that BC and submicron aerosol mass exhibit two peaks at Kanpur, similar to CCN and CN concentration as in this study. The CCN concentrations are provided at two supersaturation levels (namely 0.38 and 0.84%); the CCN concentrations are $\sim 20\%$ higher at 0.84% than those at 0.38% supersaturation. Average CCN (at 0.36 and 0.84% SS) and CN concentrations during day- (7:00 AM–6:00 PM, local time) and night-time (6:00 PM–7:00 AM) are presented in Table 1. The CCN and CN concentrations are higher during nighttime compared to those in day-time. An increase in CCN and CN concentrations can be

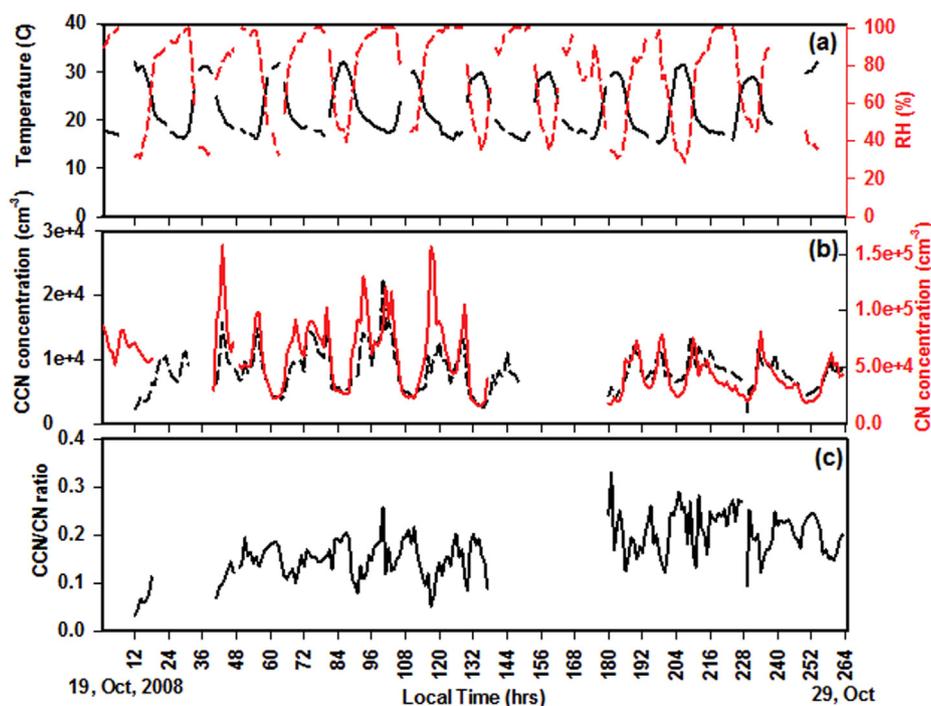


Fig. 1. Temporal variation of (a) ambient temperature and relative humidity (RH); (b) CCN and CN concentrations at 0.38% super-saturation and (c) CCN/CN ratio in aerosol samples collected during 19–30th Oct 2008.

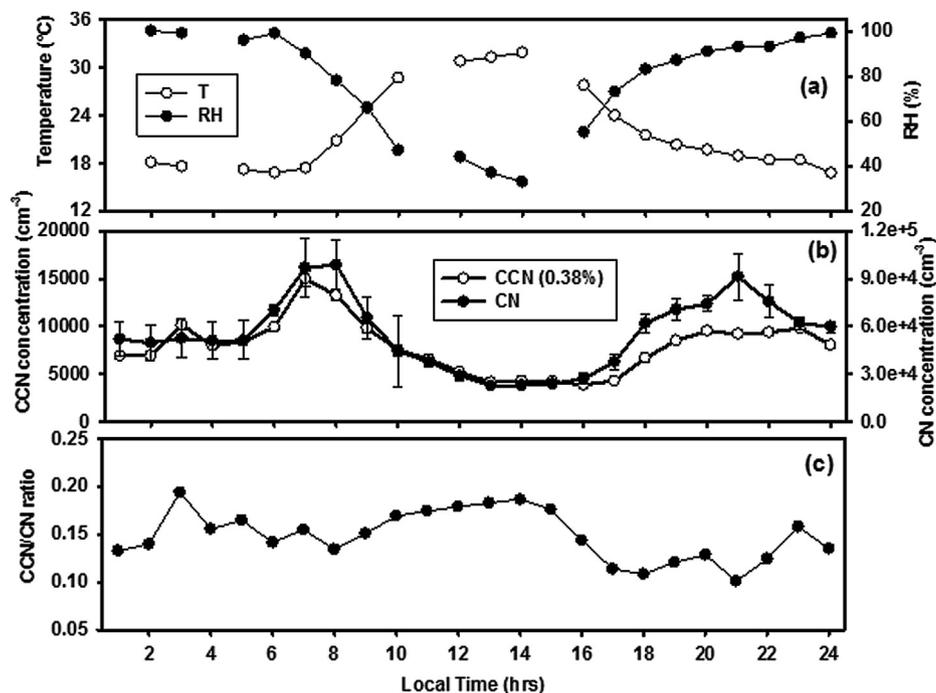


Fig. 2. A typical diurnal variability of (a) ambient temperature and relative humidity; (b) CCN and CN concentrations and (c) CCN/CN ratio at 0.38% super-saturation for the measurement taken on 22nd Oct 2008.

attributed to freshly emitted fine-particles from vehicular emission, mainly from heavy-duty vehicles, which are allowed to enter in the city only during nighttime (as detailed in Section 3.2). Although, we do not have diurnal pattern of secondary aerosols (mainly SO_4^{2-} , NO_3^- and WSOC) at Kanpur and over Indian region, we suggest that secondary aerosol formation, along with primary vehicular emissions, could be a possible cause for the morning peak in the CCN and CN concentrations. This is further corroborated with an enhancement in SO_4^{2-} and secondary organic aerosol formation during daytime and that of NO_3^- during nighttime at Kanpur (Ram and Sarin, 2011).

3.2. Aerosol chemical composition

Aerosol chemical composition of $\text{PM}_{2.5}$ samples during day- and nighttime are given in Table 2 and their fractional contribution to $\text{PM}_{2.5}$ mass and water-soluble inorganic species (WSIS; sum of mass concentrations of cations and anions) are shown in Fig. 3a and b, respectively. Generally, chemical composition of $\text{PM}_{2.5}$ samples is dominated by carbonaceous aerosols followed by major inorganic species (SO_4^{2-} , NH_4^+ and NO_3^-) during day as well as in the nighttime. On average, total carbonaceous aerosol ($\text{TCA} = 1.6 \times \text{OC} + \text{EC}$) contribute $\sim 50\%$ of $\text{PM}_{2.5}$ mass whereas WSIS account for $\sim 18\%$ of $\text{PM}_{2.5}$ mass at Kanpur (Fig. 3a). A conversion factor of 1.6 has been used to account for elements other than carbon present in aerosols (mainly O, N and S), and an average value of 1.6 for OM/OC ratio has been suggested for urban aerosols (Rajput and Sarin, 2014; Ram et al., 2010a; Rengarajan et al., 2007; Turpin and Lim, 2001). A significant correlation between OC and K^+ ($R^2 = 0.59$, figure not shown), along with relatively high K^+/OC (range: 0.04–0.06) and OC/EC ratio (~ 6.0 – 7.0) similar to that of biomass burning emissions was observed which suggest biomass burning as a major emission source of carbonaceous aerosols at Kanpur (Ram and Sarin, 2011). However, fractional contribution of TCA is only $\sim 5\%$ higher during nighttime when compared to that in the daytime. In addition, OC/EC ratios are slightly lower during nighttime which

resulted due to an increased contribution from vehicular emissions. It should be noted that the sampling site at IIT campus in Kanpur is located near the highway and heavy duty vehicles are allowed to enter the city only during nighttime.

The fractional contribution of major inorganic species to WSIS mass in day and night-samples is shown in Fig. 3c and d, respectively. Overall, WSIS mass in $\text{PM}_{2.5}$ samples is dominated by NH_4^+ , NO_3^- and SO_4^{2-} with their fractional contribution of 21.9, 8.7 and 56.1%, respectively during daytime (Fig. 3c) whereas their contribution is 16.6, 28.4 and 40.8%, respectively during nighttime (Fig. 3d). Although there is a significant change in the fractional contribution of individual inorganic species (mainly NH_4^+ , NO_3^- and SO_4^{2-}), attributed to day- and night-time chemistry in an urban environment; fractional contribution of WSIS remains almost similar in day as well as night-samples ($\sim 18\%$ of $\text{PM}_{2.5}$ mass). Secondary aerosol formation, along with aerosols of their primary

Table 2

Average mass concentrations ($\text{Av} \pm 1 \text{ sd}$) of OC, EC, TCA, WSOC, cations, anions and WSIS for $\text{PM}_{2.5}$ samples collected during day- and night-time. Number in the parenthesis represents median values.

Species	Day	Night
$\text{PM}_{2.5}$ mass	133 \pm 61 (122)	192 \pm 83 (178)
OC	36.6 \pm 17.1 (33.7)	55.0 \pm 15.3 (53.3)
EC	6.2 \pm 2.0 (5.9)	10.2 \pm 3.1 (9.8)
TCA	64.7 \pm 29.2 (60.0)	98.1 \pm 26.5 (95.2)
WSOC	25.6 \pm 15.8 (22.0)	25.8 \pm 8.9 (24.8)
Na^+	0.21 \pm 0.12 (0.19)	0.31 \pm 0.13 (0.29)
NH_4^+	5.2 \pm 3.7 (4.5)	5.3 \pm 3.7 (4.5)
K^+	2.2 \pm 1.8 (1.8)	2.6 \pm 0.7 (2.5)
Mg^{+2}	0.05 \pm 0.02 (0.05)	0.04 \pm 0.02 (0.04)
Ca^{+2}	0.34 \pm 0.13 (0.32)	0.32 \pm 0.14 (0.29)
Cl^-	0.05 \pm 0.02 (0.04)	1.28 \pm 1.77 (0.59)
NO_3^-	2.1 \pm 2.1 (1.6)	9.4 \pm 4.6 (8.5)
SO_4^{2-}	13.6 \pm 8.8 (11.8)	13.5 \pm 6.1 (12.5)
HCO_3^-	0.4 \pm 0.5 (0.4)	0.1 \pm 0.2 (0.1)
WSIS	24.3 \pm 16.5 (22.4)	32.9 \pm 13.9 (30.5)

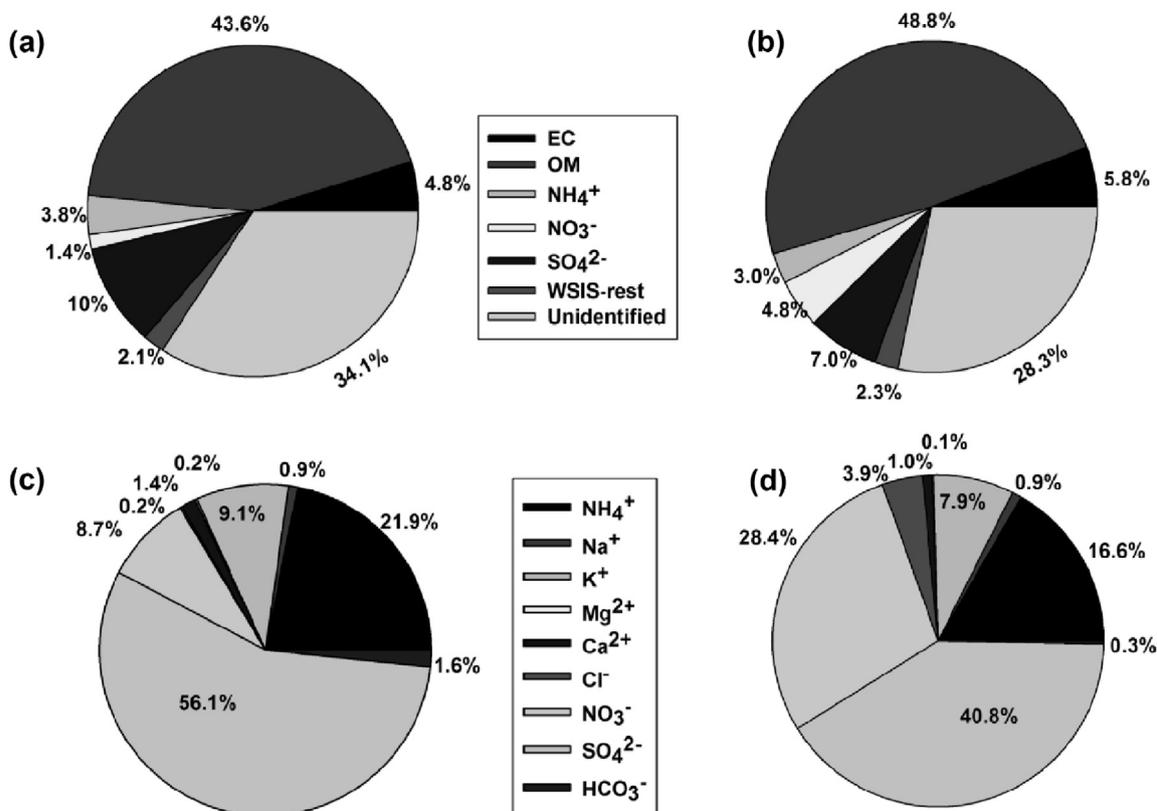


Fig. 3. Fractional composition of $PM_{2.5}$ samples in (a) day- and (b) nighttime; and that of water-soluble inorganic species (WSIS) in (c) day and (d) night samples. OM refers to organic matter abundance ($=1.6 \times OC$), WSIS-rest (sum of ionic species concentrations except SO_4^{2-} , NO_3^- and NH_4^+) and unidentified fraction is defined as $PM_{2.5} - OM - EC - WSIS$.

origin, has been suggested to be a major contributor to PM levels over the entire IGP. This has been inferred based on the elevated mass concentrations of secondary inorganic aerosols (SIA; sum of mass concentrations of NH_4^+ , SO_4^{2-} and NO_3^-) and WSOC/OC ratios (Ram and Sarin, 2011). Several other studies have also reported the presence of high levels of secondary inorganic aerosols in the entire stretch of the IGP during the wintertime (Behera and Sharma, 2010; Ram and Sarin, 2011; Ram et al., 2010a; Rengarajan et al., 2007; Tare et al., 2006).

3.3. Influence of primary and secondary aerosols on CCN and CN concentrations

The diurnal variability of CCN and CN concentrations suggest that concentrations are $\sim 50\%$ higher during nighttime compared to those during daytime (Table 1). Furthermore, CN concentration shows a positive correlation with EC mass concentrations, a tracer for incomplete combustion of biomass and fossil fuel burning emissions (Figure not shown). In addition, it is observed that there is a simultaneous increase in fractional as well as mass concentrations of EC and OC during nighttime (Figs. 3a, b and 4). These primary carbonaceous particles, originating from vehicular and biomass burning emissions, will contribute to submicron aerosols and thus, leading to an increase in CN concentration during nighttime.

The CCN/CN ratio, also called as activated fraction, varied from 0.10 to 0.33 (average: 0.17 ± 0.05) during the sampling period (October 2008). The CCN/CN ratio provides an effective measure for the conversion of submicron aerosol concentrations into cloud condensation nuclei (Gunthe et al., 2011). Primary carbonaceous particles have relatively lower hygroscopicity, compared to those of

water soluble species (Dusek et al., 2010; Petters and Kreidenweis, 2007) and would require larger critical super-saturations to act as CCN. Thus, CCN/CN ratio is expected to be lower during nighttime, provided there is no significant change in the fractional contribution of water soluble species. However, it is observed that average CCN/CN ratios are similar during day and nighttime; although maximum value of CCN/CN ratio is relatively higher during the daytime (i.e. 0.33) compared to that during nighttime (i.e. 0.28; Table 1). This advocates the importance of secondary aerosol formation via day- and nighttime chemistry for CCN activation in an urban environment of the IGP.

CCN concentrations exhibit a positive linear relationship with anthropogenic ionic species concentrations in the present study (Fig. 5a). $(NH_4)_2SO_4$ and NH_4NO_3 aerosols have higher hygroscopicity factor (0.6 and 0.7, respectively) whereas freshly formed SOAs have much lower values (~ 0.1) (Petters and Kreidenweis, 2007).

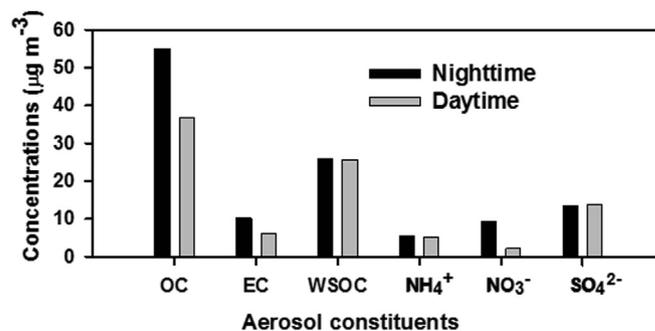


Fig. 4. Average chemical composition of aerosol samples collected during day- and night-time at Kanpur.

The mass as well as fractional contribution of SO_4^{2-} and secondary organic aerosols (SOAs) is enhanced during daytime whereas that of NO_3^- increases during nighttime (Ram and Sarin, 2011). Thus, CCN activation and CCN/CN ratios will depend on the relative fractional contribution and volume fraction of water-soluble species.

We have calculated volume fraction of soluble organics, ammonium sulfate and ammonium nitrate to understand their role in CCN activation. The volume fraction of ammonium sulfate (density = 1760 kg m^{-3}) is relatively higher during the day (average: 0.27 ± 0.04) than that during night-time (average: 0.17 ± 0.03). In contrast, the most soluble species (i.e. ammonium nitrate, density = 1720 kg m^{-3}) has greater volume fraction during nighttime (0.11 ± 0.02) compared to that during daytime (0.04 ± 0.01) which is in accordance with the diurnal variation of NO_x and higher NO_3^- concentrations during nighttime (Ram and Sarin, 2011). The volume fraction of organics, using a density of 1400 kg m^{-3} for soluble organics and 1200 kg m^{-3} for insoluble organics, is ~ 1.5 times higher during daytime than that during nighttime (average: 0.30 ± 0.04). This is also in agreement with higher fractional contribution of WSOC and enhanced WSOC/OC ratios arising due to SOA formation (Ram and Sarin, 2011). Thus, even though volume fractions of soluble organics and ammonium sulfate are higher in the daytime, larger volume fraction of ammonium nitrate in nighttime is compensating and making less difference in activation fractions during two periods. The combination of changes in mass concentrations and volume fractions of chemical species are, thus, responsible for variation in CCN/CN

ratios (at 0.36% SS) during day and nighttime for the measurement made at an urban Kanpur site.

We have also calculated critical diameter (D_c) using measured aerosol chemical composition, mainly water-soluble and insoluble organics and inorganic ions. Multi-component Köhler equation is used to calculate D_c using internally mixed WSOC, $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 as soluble species. It may be noted that high neutralization factor for ammonia, defined as the ratios of equivalent concentration of NH_4^+ to NO_3^- and SO_4^{2-} , were found during day (average: 0.90 ± 0.06) as well as in the night samples (average: 0.76 ± 0.04). This suggest the existence of $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 and NH_4Cl compounds in fine-mode aerosols during wintertime at Kanpur, an observation supported by earlier studies (Behera and Sharma, 2010; Ram and Sarin, 2011). The critical diameter is defined as the diameter above which all particles will be activating and is an important parameter to characterize CCN activation of composite aerosols. For example, Dusek et al. (2010) have recently reported that lower CCN efficiency for particles with diameter $<40 \text{ nm}$ during new particle formation in a forested urban area of Germany and attributed to low hygroscopicity of primary organic material. In the present study, average critical diameter is found to be relatively lower during daytime ($59.4 \pm 2.4 \text{ nm}$) compared to that during nighttime ($64.3 \pm 3.1 \text{ nm}$). However, higher fractional contribution of WSOC and SO_4^{2-} helped in activation during daytime. In addition, an inverse relationship was observed between critical diameter and WSIS/EC ratio (Fig. 5b). The WSIS/EC ratios can provide qualitatively information about the internal mixing state assuming EC as a tracer for incomplete combustion and hydrophobic in nature. The average WSIS/EC ratios in day- and night-sample are 10.3 ± 3.1 and 8.2 ± 2.8 in $\text{PM}_{2.5}$ and 13.0 ± 2.8 and 7.8 ± 2.6 in PM_{10} samples respectively. Thus, change in aerosol size-distribution and WSIS/EC ratios resulted in similar CCN/CN ratios during day- and nighttime.

A comparison of number concentrations of CCN, CN and CCN/CN ratio at Kanpur with other urban locations is shown in Table 3. Unlike CCN and CN concentrations; CCN/CN ratios do not show very clear diurnal variability at Kanpur (Fig. 2c). The CCN/CN ratio, in the present study, varied from 0.10 to 0.33 during 19–30th October 2008 at Kanpur. However, maximum value of CCN/CN ratio (i.e. 0.33) is relatively higher during the daytime compared to those during nighttime (i.e. 0.28) (Table 1). CCN, CN concentrations and CCN/CN ratio, measured during October 2009 and November 2010, are also similar to those observed in October 2008 (Table 3). However, CCN, CN concentrations and CCN/CN ratios are ~ 2 – 3 times higher during November 2010 (Table 3). More recently, Patidar et al. (2012) have studied seasonal variability in concentrations of CCN, CN and CCN/CN ratio at Kanpur during 2008–2009. The authors reported that CCN/CN ratio for the year 2008 varied between 0.12–0.30 in winter season (December–February) and 0.07–0.15 in the pre-monsoon season (October–November), respectively. However, CCN/CN ratios were relatively higher during winter (range: 0.28–0.53) and post-monsoon season (range: 0.20–0.28) in the year 2009 (Patidar et al., 2012). The variation in CCN/CN ratio was explained in terms of the air mass transport, forest fires and accumulation mode particle concentration. It is pertinent to state that CCN/CN ratios at Kanpur are much lower than the global average value of 0.34 (Andreae, 2009) and aged aerosols (e.g. 0.54 ± 0.23 ; Gunthe et al., 2011). However, these ratios are similar to those measured for freshly emitted aerosols in most polluted regions such as China (Gunthe et al., 2011), Mexico (Wang et al., 2010) and other places in the world (Cubison et al., 2008; Quinn et al., 2008) (Table 3). This suggests that CCN/CN ratios, in this study, represent that of freshly emitted aerosols in a highly polluted region of the IGP. The effect of changes in emission strength of primary carbonaceous aerosols (biomass burning vis-a-vis vehicular emissions) and chemical composition (especially secondary

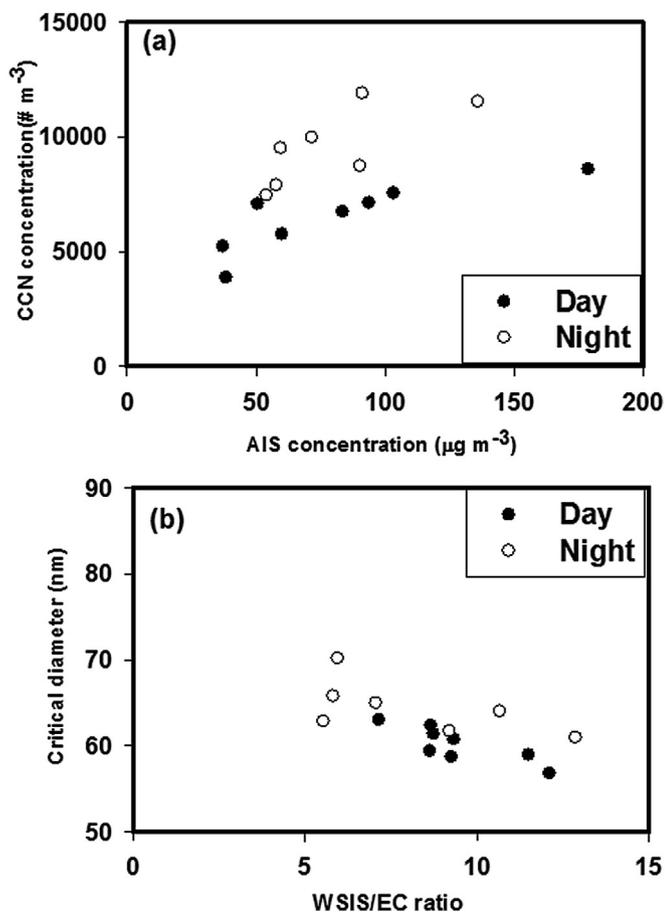


Fig. 5. Scatter plot between (a) CCN and anthropogenic ionic species (AIS) concentration, and (b) critical diameter (D_c) and WSIS/EC ratio.

Table 3
Number concentrations of CCN, CN and CCN/CN ratio at Kanpur and other urban locations.

Sampling period	Type	CCN (@0.38%)	CN	CCN/CN	Reference
		($\times 10^3$)#/cm ³	($\times 10^4$)#/cm ³	(@0.38%)	
Oct 2008 (Day)	Urban	6.6 ± 2.9	4.3 ± 2.4	0.17 ± 0.05	This study
Oct 2008 (Night)		9.8 ± 2.5	6.6 ± 2.7	0.18 ± 0.06	This study
Oct (2009) Day		5.6 ± 2.5	3.1 ± 2.2	0.20 ± 0.06	This study
Oct (2009) Night		5.8 ± 2.0	3.9 ± 2.6	0.24 ± 0.08	This study
Nov (2009) Day		9.3 ± 5.6	2.0 ± 4.2	0.41 ± 0.2	This study
Nov (2009) Night		12.4 ± 6.3	2.3 ± 2.5	0.44 ± 0.25	This study
Nov (2010) Day		4.6 ± 1.3	4.3 ± 2.2	0.15 ± 0.07	This study
Nov (2010) Night		7.3 ± 1.0	6.2 ± 1.4	0.12 ± 0.05	This study
Winter 2008				0.12–0.30	Patidar et al. (2012)
Pre-monsoon 2008				0.07–0.15	
Winter 2009			0.28–0.53		
Pre-monsoon 2009			0.20–0.28		
Aug–Sep 2006	Global average			0.34	Andreae (2009)
Aug–Sep 2006	Entire campaign	7.7 ± 3.5	1.7 ± 0.9	0.54 ± 0.23	Gunthe et al. (2011)
Aug–Sep 2006	Aged	8.8 ± 6.6	1.3 ± 0.3	0.74 ± 0.08	Gunthe et al. (2011)
Aug–Sep 2006	Fresh	5.0 ± 3.4	2.3 ± 0.9	0.25 ± 0.21	Gunthe et al. (2011)
	PRIDE-PRD-06	9.8 ± 5.3	1.8 ± 0.8	0.52 ± 0.19	Rose et al. (2011)
Jul–Aug 2005	Riverside, California		1.5 ± 0.4	0.08 ± 0.03	Cubison et al., 2008
March 2006	Mexico TO		1.2 ± 0.5	0.41 ± 0.15	Wang et al., 2010
July–Sep 2006	Houston, TXc		1.8 ± 1.5	0.45 ± 0.25	Quinn et al., 2008

aerosols) on CCN and CN concentrations and CCN/CN ratios needs to be studied in future.

3.4. Absorption coefficient (b_{abs}) and mass absorption efficiency (MAE, σ_{abs})

Aerosol absorption coefficient (b_{abs}) and mass absorption efficiency (σ_{abs}) was derived from the optical-attenuation measurements at 678 nm in a thermo-optical EC–OC analyzer (Ram and Sarin, 2009). The measured b_{abs} and σ_{abs} values (at 678 nm wavelength) are presented in Table 1. Aerosol absorption coefficient varies from 43.7 to 122.9 Mm^{−1} (av: 68.7 ± 14.8 Mm^{−1}; 1 Mm^{−1} = 10^{−6} m^{−1}) whereas mass absorption efficiency ranged from 3.3 to 15.6 m² g^{−1} (av: 9.3 ± 3.6 m² g^{−1}) for the samples collected during 19–30th October 2008. The average b_{abs} value during daytime (72.1 ± 16.9 Mm^{−1}) is similar to those during nighttime (63.9 ± 9.9 Mm^{−1}), however average σ_{abs} value during daytime (11.7 ± 2.5 m² g^{−1}) is factor of two higher than that during nighttime (5.7 ± 1.3 m² g^{−1}). Furthermore, σ_{abs} values in PM_{2.5} and PM₁₀ are similar at Kanpur suggesting that σ_{abs} is independent of size, mainly due to association of EC and absorption coefficient with fine-mode fraction of aerosols. It is also observed that ~85% of EC mass and absorption coefficient is found to be associated with fine-mode aerosols (i.e. <2.5 μm) (Ram and Sarin, 2011). The average value of σ_{abs} for the entire sampling period (9.3 ± 3.6 m² g^{−1}) is similar to the most accepted value of 10 m² g^{−1}; however, Bond and Bergstrom (2006) have suggested a value of 7.5 ± 1.2 m² g^{−1} at 550 nm for freshly emitted aerosols.

The scatter plot between mass absorption efficiency (σ_{abs}) and EC mass concentration is shown in Fig. 6. In general, σ_{abs} values show an inverse relationship with EC concentrations and σ_{abs} values are factor of two lower for the samples collected during nighttime. In addition, samples collected during nighttime have lower OC/EC and WSOC/OC ratios suggesting freshly emitted aerosols from vehicular emissions. On the contrary, relatively high OC/EC and WSOC/OC ratios were observed for the daytime samples and are attributed to higher photochemical production of secondary organic aerosols (Ram and Sarin, 2011). For example, Moffet and Prather (2009) have found that freshly emitted soot particles account for the majority of absorption in the early morning and at night whereas aged soot particles were responsible for the majority

of the midday absorption when the solar irradiance is higher. In a recent study, mass absorption efficiency for fresh soot aggregates was found to be in the range of 6.7 ± 0.7 to 8.7 ± 0.8 m² g^{−1} for particles with mobility diameters from 155 to 320 nm (Khalizov et al., 2009). However, MAE was found to be as high as 12.6 m² g^{−1} for 320 nm particles at 80% RH after exposure of soot to sulfuric acid when soot particles acquires 10–40% mass fraction of sulfate by coating. These observations are in line with the results of the present study. Fine-mode particles in the atmosphere are more prone to chemical aging with reactive gaseous species because of the larger availability of surface area. As a consequence, fine-mode aerosols mainly exist as a complex internal mixture of ammonium, sulfate, organics and soot inclusions (Reid et al., 1998). The presence of high concentration of secondary aerosols and WSIS/EC ratio during daytime further substantiates our observations. Thus, higher σ_{abs} values obtained during daytime can be attributed to formation of internal mixture produced by coating of secondary aerosols (Ram et al., 2010b; Shamjad et al., 2012).

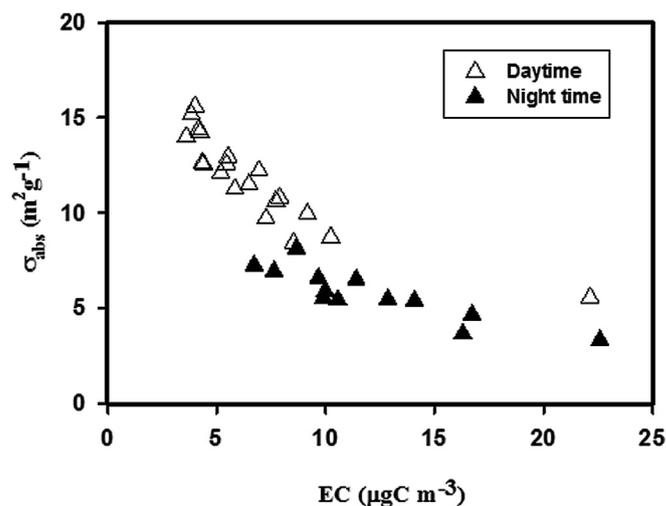


Fig. 6. Scatter plot between mass absorption efficiency (σ_{abs}) and EC mass concentration.

4. Conclusion and implication

This study provides the first field observational evidence on the impact of primary and secondary aerosols on CN, CCN and optical properties of aerosols at an urban site (Kanpur) in the Indo-Gangetic Plain. The CCN (at 0.38% super-saturation) and CN concentrations varied from ~ 3900 to $15,000 \text{ cm}^{-3}$ and $\sim 23,000$ to $99,000 \text{ cm}^{-3}$, respectively during the study period. The CCN and CN concentrations are $\sim 50\%$ higher during nighttime, with simultaneous increase in OC and EC mass, suggesting an increase in emission of carbonaceous aerosols from vehicular emissions. The lower CCN/CN ratios (range: 0.11–0.33) at Kanpur represent less hygroscopic nature of both freshly emitted primary and secondary aerosols in a highly polluted region of the IGP. The coating of secondary aerosols leads to formation of internal mixture and higher mass absorption efficiency during daytime. The presence of significant amount of water soluble species in the IGP can convert hydrophobic EC into hygroscopic species during aging and transport. The understanding of the role of chemical composition (especially secondary aerosol formation), microphysical properties (e.g. aging and mixing with hygroscopic particles) and factors which control CCN activation and droplet growth is necessary to constrain their impact on hydrological cycle and uncertainties from the aerosol indirect effect over northern India.

Acknowledgments

The authors thankfully acknowledge the funding support received from Indian Space Research Organization-Geosphere Biosphere Programme (Bengaluru, India). KR thanks Department of Science and Technology (DST), India for providing financial support under the scheme of INSPIRE Faculty award (IF-EAS-02). SNT was supported under the program Changing Water Cycle funded jointly by Ministry of Earth Sciences, India, and Natural Environment Research Council, UK. This work in part is supported by National Academy of Sciences and USAID. The views expressed here are of authors and do not necessarily reflect of NAS or USAID. Kirpa Ram also thankfully acknowledges Director, CSIR-NEERI, Nagpur.

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