RESEARCH ARTICLE

# Field performance evaluation during fog-dominated wintertime of a newly developed denuder-equipped PM$_1$ sampler

**Dharmendra Kumar Singh · Lakshay · Tarun Gupta**

**Abstract** This study presents the performance evaluation of a novel denuder-equipped PM$_1$ (particles having aerodynamic diameter less than 1 μm) sampler, tested during fog-dominated wintertime, in the city of Kanpur, India. One PM$_1$ sampler and one denuder-equipped PM$_1$ sampler were co-located to collect ambient PM$_1$ for 25 days. The mean PM$_1$ mass concentration measured on foggy days with the PM$_1$ sampler and the denuder-equipped PM$_1$ sampler was found to be 165.95 and 135.48 μg/m$^3$, respectively. The mean PM$_1$ mass concentration measured on clear days with the PM$_1$ sampler and the denuder-equipped PM$_1$ sampler was observed to be 159.66 and 125.14 μg/m$^3$, respectively. The mass concentration with denuder-fitted PM$_1$ sampler for both foggy and clear days was always found less than the PM$_1$ sampler. The same drift was observed in the concentrations of water-soluble ions and water-soluble organic carbon (WSOC). Moreover, it was observed that the use of denuder leads to a significant reduction in the PM positive artifact. The difference in the concentration of chemical species obtained by two samplers indicates that the PM$_1$ sampler without denuder had overestimated the concentrations of chemical species in a worst-case scenario by almost 40 %. Denuder-fitted PM$_1$ sampler can serve as a useful sampling tool in estimating the true values for nitrate, ammonium, potassium, sodium and WSOC present in the ambient PM.

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## Introduction

Atmospheric aerosols affect climate both by direct and indirect forcing. Aerosols induce direct forcing by scattering and absorption of incoming solar radiation, and indirectly by modifying albedo, lifetimes, and properties of clouds (Takemura et al. 2005). Chemical markers for the particulate matter originating from both natural and anthropogenic sources mainly consist of water-soluble cations (Na$^+$, NH$_4^+$, Ca$^{2+}$, K$^+$, and Mg$^+$) and water-soluble anions (Cl$^-$, SO$_4^{2-}$, and NO$_3^-$), elements, organic carbon (OC), and elemental carbon (EC) (Shen et al. 2010).

The air quality in Kanpur becomes worse during winter season when fog retains tiny particulates, either dissolved or embedded in droplets for longer duration in the atmosphere. During winter season, local additional anthropogenic sources like wood and biomass burning also lead to significantly higher pollution levels. Organic aerosol due to their significant scavenging and removal (both primary and secondary in nature) during fog episodes, are eventually deposited to surfaces with falling droplets (Herckes et al. 2007; Kaul et al. 2011). Thus, physico-chemical characterization of fog during winter season is desired. Chakraborty and Gupta (2010) carried out a study on submicron particulates and their chemical characterization in Kanpur. Trace elements were employed to determine dominant sources of submicron particles in another recent study carried out at the same place (Gupta and Mandariya 2013).

A denuder is a device to separate gases from particles. It is based on the principle of molecular diffusion aided by concentration gradient of the species of interest. Selective membrane sampling involves chemical adsorption of the gases on

the surface of the collecting membrane, which can result in modifying the physical and chemical properties of the aerosol species of interest being sampled (Ashok and Gupta 2012). Also, trapping of various acidic, basic, organic, and inorganic gases on the chemical substrate elevates the chances of interference between two or more species during routine ambient sampling and can result in loss of semi-volatiles due to a drastic change in equilibrium between gas and particulate phases (Ianniello et al. 2007; Chakraborty and Gupta 2010). Due to the above shortcomings, there is a need for sampling ambient suspended particulates in a better manner. In the recent past, researchers have investigated the possibility of using different membrane materials for gas and particle separation (Stern 1994; Ruiz et al. 2006). Also, newer techniques of sampling and extracting gaseous species more efficiently and economically are greatly desired to augment the existing aerosol measuring devices (Gupta et al. 2011). Although absence of denuder will lead to some sampling artifact, such artifacts will be on both clear and foggy days and they will be even higher for organic carbon (OC) (Turpin et al. 1994). The denuder-based sampling system has clear advantages over the filter and adsorbent collection method, particularly for measurement of the particulate phase as residence times in denuders are short (0.1–3.2 s). Thereby they minimize the redistribution of semi-volatile organic compounds between the gas and particulate phases (Turpin et al. 1993). Recently, non-selective-based denuders have been designed and tested for the purpose of sampling ambient particulate matter (Ruiz et al. 2006; Ashok and Gupta 2012).

The current study involves measurement of $PM_1$ during fog-dominated winter season as well as evaluating the performance of a newly developed denuder. The denuder used in this study is a sustainable, compact, lightweight, and eco-friendly device that can ensure the removal of gases present in the ambient air with good efficiency. The membrane used is a non-selective membrane which provides gas removal efficiency over 90 % and particle transmission efficiency above 80–85 % (Ashok and Gupta 2012).

## Methodology

### Sampling site

Sampling was carried out on the roof of a 12-m-high building (Western Lab Extension, WLE) within IIT Kanpur campus. IIT Kanpur (longitude 88°22′ E and latitude 26°26′ N) is an educational institute spread over approximately 4.3 km$^2$, just north-west of the city and having a residential population of more than 8,000 (Fig. 1). There is no commercial or industrial activity prevalent inside the institute. The campus lies about 15 km north of the city in the upwind direction. Within the

campus, vehicular population mainly comprises of two-wheelers and cars. Some construction activities were ongoing during the sampling period. However, there is dense vehicular traffic on a national highway situated about 1.5 km east of the sampling site.

### Materials and sampling schedule

Sampling was carried out for 8 h per day during daytime covering almost all the foggy days during winter season (December 2011–January 2012) with the collocated $PM_1$ sampler and denuder-equipped $PM_1$ sampler, respectively. A total of 25 samples each were collected with both the samplers along with a total of six blanks. Temperature and relative humidity were measured by temperature sensor and relative humidity sensor, respectively. Identification of foggy day was carried out by using information available at IITK Mplnet (http://mplnet.gsfc.nasa.gov/data.html).

### *$PM_1$ sampler*

$PM_1$ sampler consists of a $PM_1$ impactor (calibrated and tested using an aerodynamic particle sizer, APS model 3021; TSI Inc.), rotameter, and a pump. $PM_1$ sampler collects the particles less than 1 μm in diameter. The flow rate (main flow) of the sampler $PM_1$ was 10 lpm (controlled by rotameter, calibrated using a mass flow meter). Whatman QM-A Quartz filter paper with 47 mm diameter was used for $PM_1$ collection. The salient design and performance-related features of the $PM_1$ sampler used here having a $d_{50}=1.0$ μm with a sharp cutoff characteristic (GSD=1.2) are provided elsewhere (Chakraborty and Gupta 2010; Gupta and Mandariya 2013).

### *Denuder-equipped $PM_1$ sampler*

Denuder-equipped $PM_1$ sampler consists of a denuder ahead of $PM_1$ sampler as shown in Fig. 2c along with a rotameter, pump, and compressor. When the mixture of particles and gases are allowed to pass through the denuder, the gases escape through the teflon membrane and the particles are retained at the end of the tube over a filter. It separates gases from aerosol non-selectively through a non-selective PTFE membrane. The working of the denuder is based on the diffusion phenomenon as used in the current study and is shown in pictorial form in Fig. 2a. The denuder was developed and its performance fully optimized in a previous study (Ashok and Gupta 2012). As the gases get separated by the denuder, the particles are then collected by a $PM_1$ sampler on quartz filter paper (Fig. 3). The specification of the $PM_1$ sampler is the same as the one mentioned above (Gupta and Mandariya 2013). The compressor, silica gel, and HEPA filter assembly was used to provide clean air for the flush flow of

**Fig. 1** IIT Kanpur sampling site showing WLE (Western Lab Extension). Source: Google Earth, image 2013 digital Globe



denuder. The flow rate of PM$_1$ sampler was 10 lpm and flush flow of denuder was kept at 20 lpm.

*Positive sampling artifact*

The accurate measurement of ions, metals, WSOC, and other chemical species is quite difficult due to their complex chemical and physical nature. Various artifacts and uncertainties have been reported during measurement of these species (Huebert and Charlson 2000). It has been observed that the filter used to collect and analyze chemical species may lead to erroneous results due to the adsorption of organic and inorganic gases (positive artifact). These gases can further react with species collected on the filter paper and subsequently alter their true values during measurement. The denuder-equipped PM$_1$ sampler used in the current sampling thus can reduce the gaseous interference and reduce the extent of positive artifact.

The percent of positive artifact is calculated as:

$$\text{Average}(\text{positive} artifact\%) = \left(\frac{(X-Y)}{Y}\right) \times 100$$

$X$   Average concentration of chemical species (without denuder, $\mu g/m^3$)
$Y$   Average concentration of chemical species (with denuder, $\mu g/m^3$)

*Optimization of denuder*

In order to check the performance of the denuder, certain experiments were conducted using a condensation particle counter (CPC, TSI model 3007) to check the particle transmission efficiency at various flow rates. CPC effectively measures particle numbers in the size ranging from 0.01 to 1 μm and provides information about total number of particle suspended per cubic meter of sampled air. As the sampling was carried out at 10 lpm, the main flow (MF) for denuder was the same (10 lpm) and the transmission efficiency was then calculated by using different combinations of flush flow (FF) rates. These experiments were conducted with ambient air. The particle number concentration was measured with CPC at upstream and downstream of the denuder. Particle transmission efficiency ($\eta_p\%$) and the % loss were calculated as:

$$\left(\eta_p\%\right) = \left(\text{PM}_{\text{downstream}}/\text{PM}_{\text{upstream}}\right) \times 100$$

$$\text{Loss}(\%) = 100 - \eta_p(\%)$$

where PM$_{\text{downstream}}$ and PM$_{\text{upstream}}$ are the number concentration of particles at downstream and upstream ends of the denuder, respectively. The performance of the denuder was checked at three combinations of flow rate—FF: 12, MF: 10; FF: 15, MF: 10; and FF: 20, MF: 10 (see Supplementary section).

Collection and storage of samples

Before sampling, each quartz filter paper was pre-conditioned in a controlled environment at 25 °C and 50 % RH for 24 h (Chakraborty and Gupta 2010). Using a Mettler balance
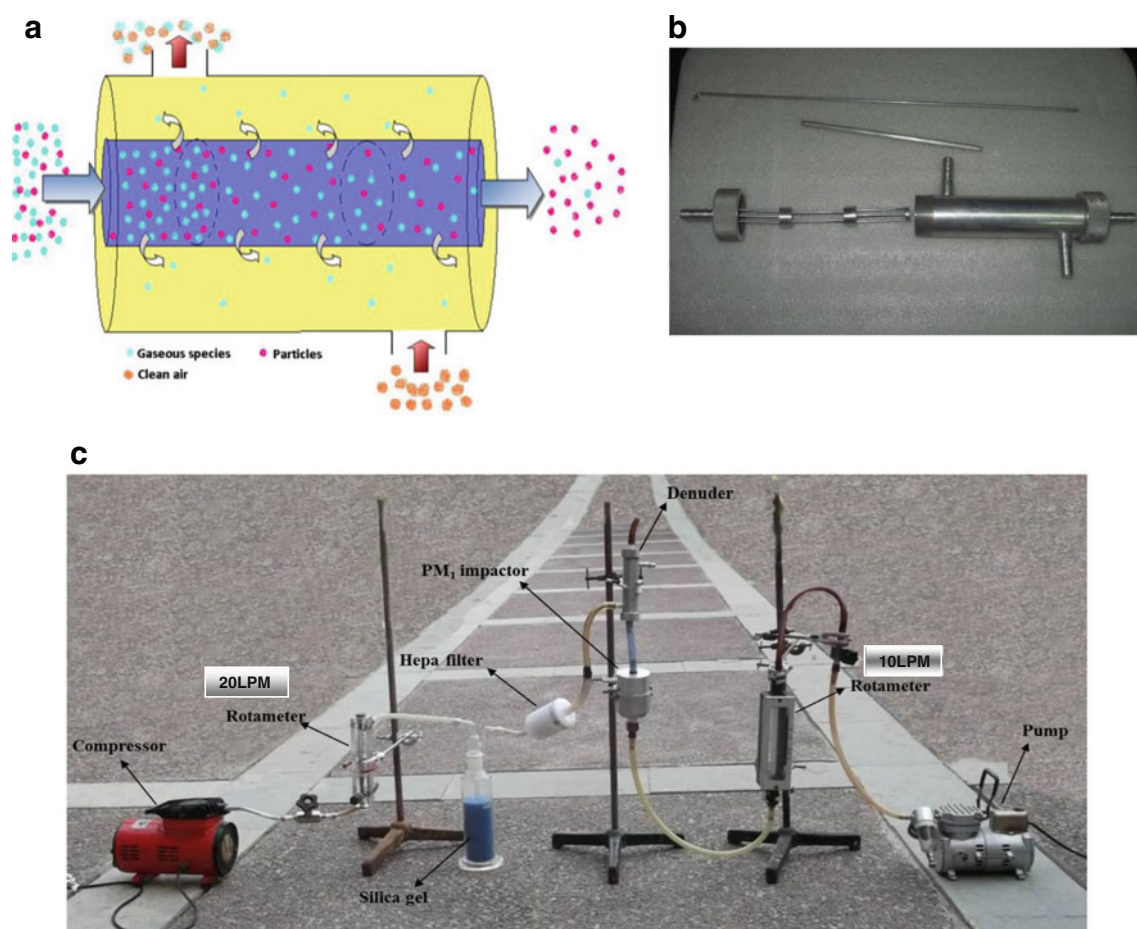
Fig. 2 **a** Schematic diagram of working principle of a diffusion denuder. **b** Internal components of the denuder. **c** Denuder-equipped PM$_1$ sampler on the field

(APM 440, Mettler, least count 1 μg), each pre-conditioned filter was weighed thrice and if for any filter the difference between two consecutive weights was found to be higher than 5 μg then the filter was re-conditioned and re-weighed. Thereafter, the pre-conditioned filters were transferred into sealed plastic containers and placed into the sampler using a clean set of forceps. Filter papers were immediately taken out of the sampler post-sampling using a clean set of forceps and transferred to the sealed plastic container. Collected filter papers were then post-conditioned for 24 h at 25 °C and

50 % RH and weighed under a similar controlled environment to calculate the PM$_1$ mass deposited on them. After weighing the filter papers, they were transferred to the plastic container and kept in the refrigerator at 5 °C till further analysis. Blank filters were subjected to the same procedure.

*Chemical analysis of collected filters*

After calculating the PM$_1$ mass concentrations, quartz filter papers were analyzed for several elements such as arsenic

Fig. 3 Collected mass of PM$_1$ on the filter
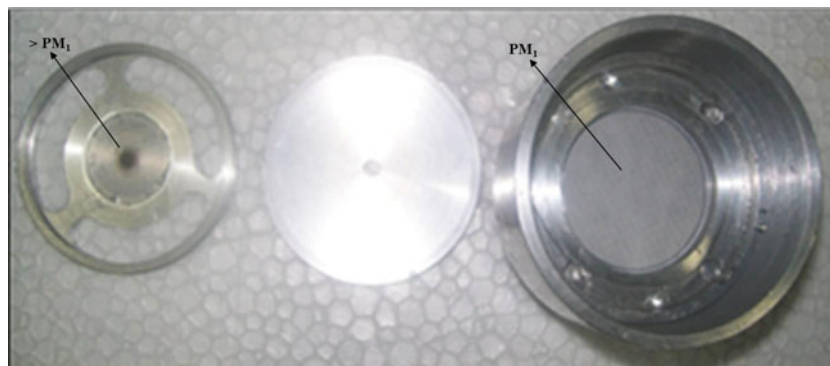
(As), calcium (Ca), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), potassium (K), magnesium (Mg), manganese (Mn), sodium (Na), nickel (Ni), lead (Pb), selenium (Se), titanium (Ti), vanadium (V), zinc (Zn), anions such as fluorine ($F^-$), chlorine ($Cl^-$), nitrate ($NO_3^-$), sulfate ($SO_4^{2-}$), and phosphate ($PO_4^{3-}$), and cations such as ammonium ($NH_4^+$), sodium ($Na^+$), calcium ($Ca^{2+}$), potassium ($K^+$), and water-soluble organic compounds (WSOC). For chemical analysis, each collected quartz filter was punched to obtain a 16.5-mm diameter circular punch. Each filter easily provided four punches, which were used to analyze elemental analysis, cations, anions, and WSOC, respectively.

### Sample preparation and elemental analysis

For elemental analysis, one punch was placed into a round bottom glass digestion vessel, then 15 ml concentrated nitric acid (65 %, GR Merck Supra pure) was poured into the digestion vessel and placed it over a hot plate for 2 h at 180 °C (Fang et al. 1999), but it was made sure that the inside of the vessel did not dry up completely due to the evaporation of nitric acid, and if required, extra nitric acid was added during digestion. After 2 h of digestion, the vessels were allowed to cool to room temperature and the walls of the vessels were rinsed with Milli-Q water (resistivity=18.2 MΩcm at 25 °C) and kept for 30 min for diffusion of acid from the filters into the solution, then the solution in the vessel was filtered through 0.22-μm filters and the final volume was made up to 100 ml using Milli-Q water. Then these aqueous samples were analyzed for elements using an inductively coupled plasma–optical emission spectrometer (ICP-OES; Thermo Fisher, ICAP 6300 Duo). Blank filters were also subjected to the same procedure. Method detection limits for ICP-OES for different elements are previously presented (Chakraborty and Gupta 2010).

### Sample preparation for anions, cations, and WSOC analysis

For anions, cations, and WSOC analysis, one punch of the quartz filter was poured into a test tube with 30 ml of Milli-Q water and then the solution was ultrasonicated for 30 min (Chakraborty and Gupta 2010). Tubes were cleaned with chromic acid, rinsed with Milli-Q water and then they were kept in the oven at 180 °C for 30 min. The digested sample was then filtered with a 0.22-μm filter paper.

The analysis for anions of filtered sample was carried out with the help of ion chromatography (Metrohm compact IC 761) using an electrolyte solution (mixture of 1.3 mmol $l^{-1}$ $Na_2CO_3$ and 1 mmol $l^{-1}$ $NaHCO_3$) at a flow rate of 0.7 ml/min. The analysis for cations of filtered sample was also carried out with the help of ion chromatography (Metrohm compact, IC 761) using an electrolyte solution (mixture of 0.094 ml $l^{-1}$ $HNO_3$ and 0.11698 g $l^{-1}$ dipicolinic acid). Blank filters were also analyzed using the same procedure.

All the glassware used for elemental analysis were washed with diluted (20 %) nitric acid and then washed thrice with Milli-Q water, and then they were sterilized at 180 °C for 30 min. For the anions and cations analysis, glass test tubes were kept overnight into chromic acid solution and then washed thoroughly with Milli-Q water and then sterilized at 180 °C for 30 min; details of the procedure are presented elsewhere (Chakraborty and Gupta 2010; Gupta and Mandariya 2013).

### TOC analyzer

WSOC was analyzed with a total organic carbon analyzer equipped with a high-sensitivity catalyst (model TOC-V CPN; Shimadzu Corporation) (Kaul et al. 2011). Complete TOC method is described in detail in Timonen et al. (2008).

## Results and discussion

### Optimized denuder

It was observed that the particle transmission efficiency of the prototype denuder was around 70 % (on number concentration basis) for all the flow combinations and was slightly higher for FF: 20, MF: 10 lpm. So, this combination was used in current ambient air sampling for foggy and clear days. Percentage loss in particle numbers in the above flow combination lies in the range of 27 % to 31 %, but major particle losses are due to diffusion of particles smaller than 100 nm which contributes very less (~10 % at maximum) to the overall mass of the $PM_1$ (Gupta et al. 2004).

The study was conducted in winter months, so negative artifact due to volatilization of semi-volatile components of PM was negligible. The sampling season usually experiences extremely low wind speeds (~0.2±0.1 m/s) (Kaul et al. 2011). Moreover, the $PM_1$ sampler was designed for a 10 lpm flow rate to minimize pressure drop as well as to have a lower filter face velocity of 10 cm $s^{-1}$ (Kaul et al. 2011; Gupta et al. 2010).

### Variation in mass concentration of $PM_1$

The diurnal variation in mass concentration of $PM_1$ is shown in Fig. 4 for foggy and clear days during the winter season 2011–2012. Fog typically is formed when RH >80 %; in fact at times RH >90 %. The days marked as "F" in Fig. 4 depicts when fog period was overlapping with the sampling duration (8 h). It is important to note that temperature and RH reported here are 24-h average values. It is likely that during fog period (ranging from 3 to 8 h), the hourly temperature and RH were much different from the average values.
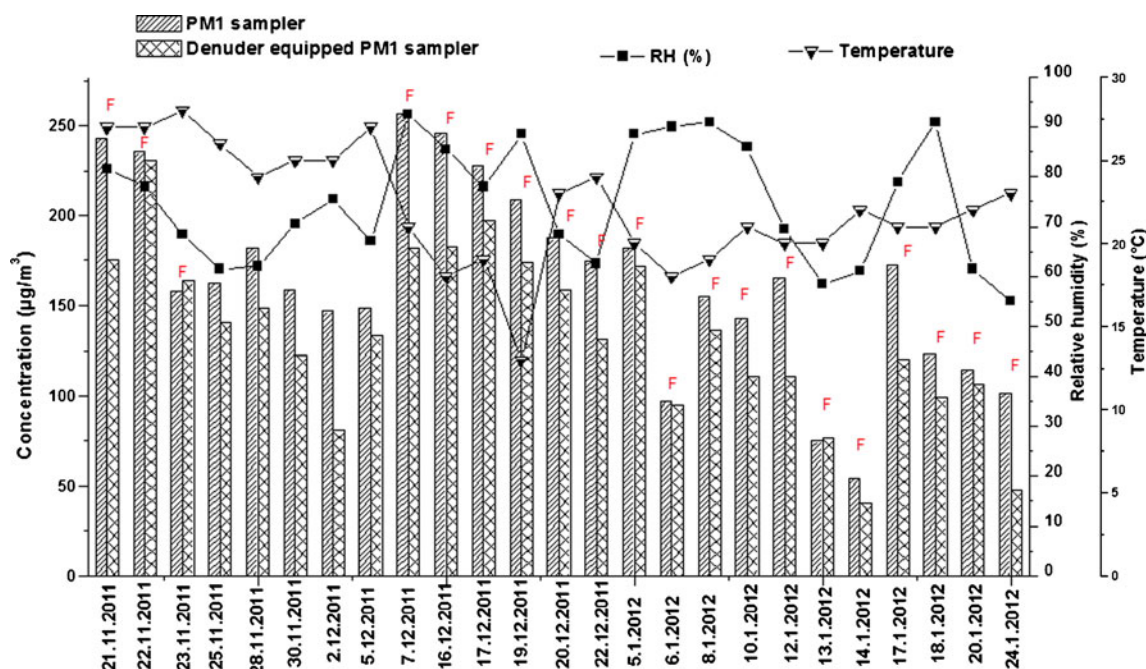
**Fig. 4** Variation in $PM_1$ mass concentration with relative humidity and temperature

Ten percent field blanks were collected and all reported values were blank corrected. The average mass of $PM_1$ on foggy days sampled with the $PM_1$ sampler and the denuder-equipped $PM_1$ sampler was found to be 165.95 and 135.47 $\mu g/m^3$, respectively. The average mass of $PM_1$ on clear days collected with the $PM_1$ sampler and the denuder-equipped $PM_1$ sampler was observed to be 159.66 and 125.14 $\mu g/m^3$, respectively. The maximum and minimum mass concentration on foggy days with the $PM_1$ sampler ranged from 256.45 $\mu g/m^3$ (7 December 2011) to 54.58 $\mu g/m^3$ (14 January 2012), and with the denuder-equipped $PM_1$ sampler from 230.20 $\mu g/m^3$ (22 November 2011) to 40.21 $\mu g/m^3$ (14 January 2012), respectively.

The average $PM_1$ mass concentration obtained with our sampler (165.95 $\mu g/m^3$) was found to be in good agreement with the value of 199 $\mu g/m^3$, reported during a study in winter 2008 carried out at IIT Kanpur (Chakraborty and Gupta 2010); 114±80 $\mu g/m^3$, reported during a winter study in November 2009–February 2010 (Gupta and Mandariya 2013); 203 $\mu g/m^3$ ($PM_{0.95}$), reported in a study during December 2004 in IIT Kanpur (Tare et al. 2006); 144 $\mu g/m^3$ ($PM_{1.6}$), reported in a study carried out in Delhi during winter 2005–2006 (Srivastava et al. 2008); and 140.3 $\mu g/m^3$ ($PM_1$), reported in a study during winter 2009 in Raipur (Deshmukh et al. 2011). However, the current values were much lower than the value of 303 $\mu g/m^3$ ($PM_1$) reported in a study during December 2007 in Delhi (Tiwari et al. 2012) and 427.3±209.5 $\mu g/m^3$ ($PM_1$) reported in a study during 16 January 2010 to 20 February 2010 at IIT, Kanpur (Kaul et al. 2012).

Variation in mass concentration of water-soluble ions

### Water-soluble anions

Concentration of water-soluble ions is shown in Fig. 5. Nitrate and sulfate were found to be the most dominating species in the $PM_1$ samples. The average value of $NO_3^-$, $SO_4^{2-}$, and $Cl^-$ was 30.9, 20, and 5.10 $\mu g/m^3$, respectively, with $PM_1$ sampler. For the denuder-equipped $PM_1$ sampler, the average values of $NO_3^-$, $SO_4^{2-}$, and $Cl^-$ were reported as 25.33, 18.49, and 4.67 $\mu g/m^3$, respectively. The concentration of anions was found to be higher during fog episodes than clear days. The highest concentrations of $NO_3^-$, $SO_4^{2-}$, and $Cl^-$ with $PM_1$ sampler was found to be 67.2, 25.6, and 16.72 $\mu g/m^3$, respectively, and were observed during the foggy days. Similarly, the lowest concentrations for $NO_3^-$, $SO_4^{2-}$, and $Cl^-$ with $PM_1$ sampler was 5.69, 13.2, and 0.16 $\mu g/m^3$, respectively, and were observed during clear days. During fog episodes, sulfate, nitrate, and ammonium concentrations increased rapidly as the aqueous phase in the atmosphere (clouds, fogs) acts as a physicochemical processor of gases and particles; these water droplets scavenge soluble gases (HONO, $HNO_3$, $NH_3$, $SO_2$, etc.), and growing and aging aerosol particles accelerate their removal from the atmosphere (Kaul et al. 2011; Gupta and Mandariya 2013). At the same time, the aqueous phase provides a medium for several chemical reactions, like the oxidation of dissolved atmospheric species (Pandis and Seinfeld 1989). The accumulation of $SO_4^{2-}$ and $NO_3^-$ in the fine mode is attributed to gas-to-particle conversion of $SO_2$ and $NO_x$ gas, respectively, and their growth under humid conditions. The
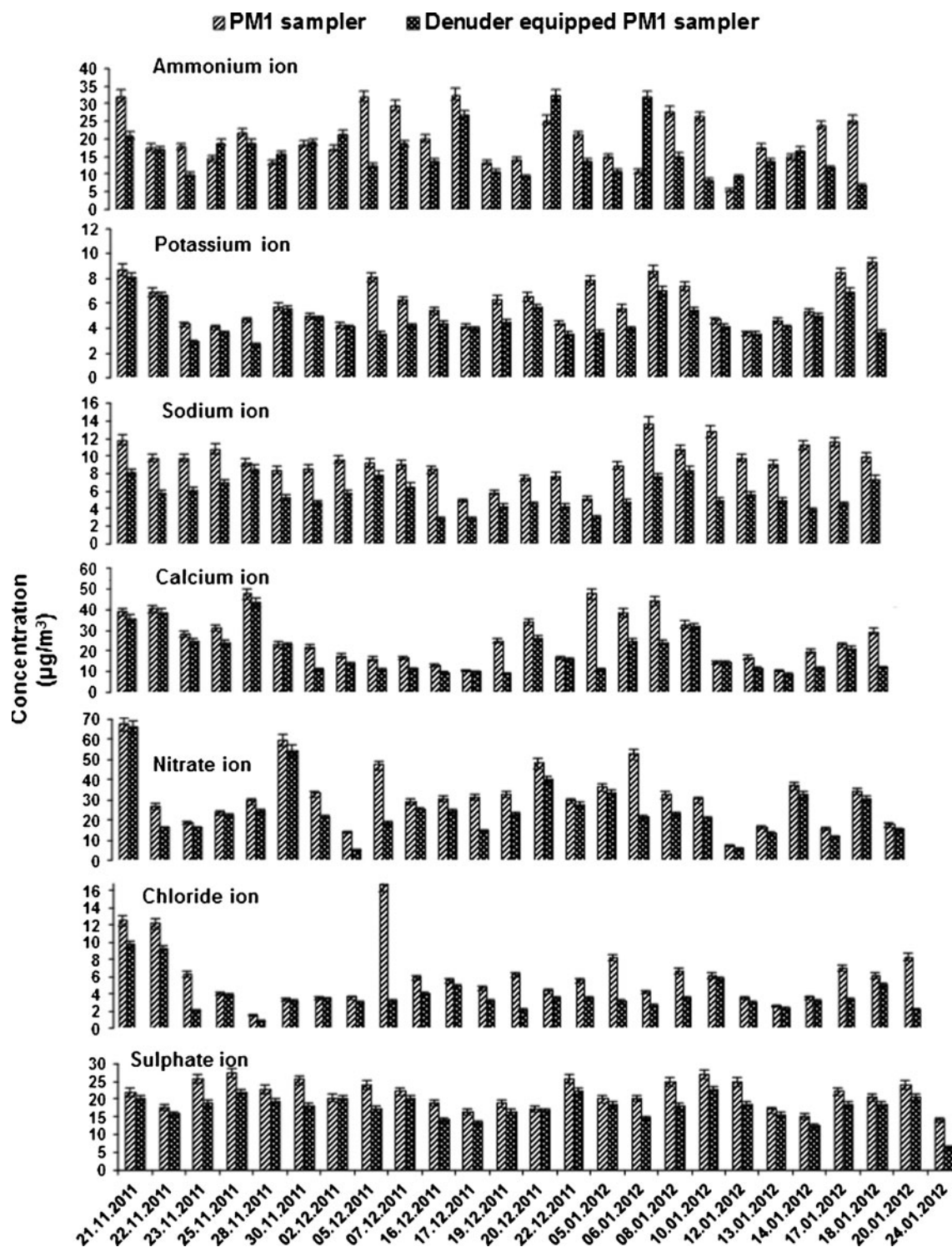
**Fig. 5** Diurnal variation in the mass concentration of major anions and cations sampled with the PM$_1$ sampler and the denuder-equipped PM$_1$ sampler

conversion of SO$_2$ to sulfate and NO$_x$ to NO$_3^-$, in the presence of oxidizing species (H$_2$O$_2$ or O$_3$), are reported to be the dominant pathways for sulfate and nitrate formation (Schwartz 1989; Wang et al. 2006).

The average values from PM$_1$ sampler are in good agreement with the values of nitrate (26.82 μg/m$^3$), sulfate (17.90 μg/m$^3$),

and chloride (4.75 μg/m$^3$) obtained in a previous study at Kanpur during foggy days (Tare et al. 2006), but a bit less than the values of NO$_3^-$ (36.61 μg/m$^3$), SO$_4^{2-}$ (33.02 μg/m$^3$), and Cl$^-$ (2.80 μg/m$^3$) reported in the study carried out at the exactly same sampling site in winter season 2007–2008 (Chakraborty and Gupta 2010). The average concentrations of almost all the

anionic and cationic species in the aerosols were higher during foggy days than clear days (Kaul et al. 2012).

Figure 5 shows diurnal variation of the individual concentration of anions sampled with the $PM_1$ sampler and the denuder-equipped $PM_1$ sampler, respectively. Comparison of anionic ($NO_3^-$ and $SO_4^{2-}$) mass concentration along with overall submicrom PM mass between the past winter study (2009–2010) (Gupta and Mandariya 2013) and the current study (2011–2012) is presented in Table 1.

*Water-soluble cations*

$NH_4^+$, $Ca^{2+}$, $Na^+$, and $K^+$ were the major species observed in samples. The average value of $NH_4^+$, $Ca^{2+}$, $Na^+$, and $K^+$ was found to be 20.37, 24.12, 8.57, and 5.69 μg/m³, respectively, with the $PM_1$ sampler and 16.2, 20.99, 6.87, and 4.89 μg/m³, respectively, with the denuder-equipped $PM_1$ sampler. The values from the $PM_1$ sampler were higher than the values of $NH_4^+$ (17.00 μg/m³), $Ca^{2+}$ (0.29 μg/m³), $Na^+$ (1.17 μg/m³), and $K^+$ (5.32 μg/m³) obtained from a fog-dominated study previously carried out at Kanpur (Tare et al. 2006). The values of cations with $PM_1$ sampler was more than the denuder-equipped $PM_1$ sampler. As mentioned previously, the particle mass losses can be of the order of 10 % (on mass basis) for most of the species due to the diffusional losses inside the denuder (Ashok and Gupta 2012). Also, as the particles passes through the denuder they might get stuck to the walls of the denuder due to electrostatic attraction with the walls.

Table 1 shows the comparison of $PM_1$ mass concentration and ionic species between current sampling of fog during winters of 2011–2012 to that for winter days of 2009–2010 (Gupta and Mandariya 2013). It can be observed that mass concentration of $PM_1$ during foggy days was a bit higher in 2009–2010 than in 2011–2012. In terms of ionic species, nitrate dominates more during 2011–2012 than 2009–2010. The values of sulfate and ammonium were quite similar during both the years.

Characteristics of $PM_1$

To better understand the nature of $PM_1$ in fog, ionic balance can be evoked to understand the basic and acidic nature of fog.

The cation and anion microequivalents in $PM_1$ samples were calculated based on the previously established method (Shen et al. 2010; Gupta and Mandariya 2013): C (cation microequivalents/m³)=$NH_4^+/18$ and A (anion microequivalents/m³) = $(Cl^-/35.5)+(NO_3^-/62)+(SO_4^{2-}/48)$ where the ionic concentrations are in micrograms per cubic meter. Equivalent ratios of $NH_4^+/(Cl^- + NO_3^- + SO_4^{2-})$ were calculated for the $PM_1$ sampler. A value of 1.0 for the ratio would indicate neutralization of HCl, HNO₃, and H₂SO₄ by atmospheric NH₃. For the current study, the ratio of 1.07 indicates the slightly basic nature of fog, and hence $PM_1$ was slightly alkaline in nature. The basic nature of PM1 is due to the neutralization of acidity by NH₃, which is in agreement with the value (1.4–1.9) reported in a study carried out in July–September 2004 in Agra, Dayalbagh (Kumar et al. 2007), and with the value (1.1 to 1.4) reported in a previous study carried out at exactly the same sampling site (Gupta and Mandariya 2013).

Variation in WSOC concentration

The average concentration of WSOC measured with the $PM_1$ sampler (21.73 μg/m³) was higher than the value (15.70 μg/m³) obtained using the denuder-equipped $PM_1$ sampler. The highest and lowest concentration of WSOC with $PM_1$ sampler was found to be 53.44 and 5.42 μg/m³, respectively. The denuder-equipped $PM_1$ sampler provided 35.21 μg/m³ and 4.23 μg/m³ as the highest and lowest values, respectively. As shown in Fig. 6 on 21 November 2011, which was the first foggy day of winter 2011, the WSOC concentration was exceptionally high. Similar high concentrations were also observed on 7, 16, and 17 December 2011, and 12 January 2012. The average value of WSOC reported by the $PM_1$ sampler is in agreement with the value of 22.94 μg/m³ obtained during a study carried out during wintertime in Jorhat, India (Khare and Baruah 2011). Kaul et al. (2011) have earlier documented on the basis of Local Standard Time that on clear days the maximum average value of WSOC was ~38 μg C/m³ and minimum was ~23 μg C/m³, whereas on foggy days maximum WSOC was ~33 μg C/m³ and minimum was ~16 μg C/m³. Furthermore, they suggested that highest WSOC/OC ratios were observed in the early morning primarily due to increased nighttime biomass combustion lingering into

**Table 1** Comparison of $PM_1$ mass and ionic concentrations between the previous winter study (2009–2010) (Gupta and Mandariya 2013) and the current study (2011–2012)

| Species | Past study (2009–2010) (Gupta and Mandariya 2013) | | Current study (2011–2012) | |
|---|---|---|---|---|
| | Highest (μg/m³) | Average (μg/m³) | Highest (μg/m³) | Average (μg/m³) |
| $PM_1$ mass concentration (clear days) | 227.3 | 114.0±80.0 (n=37) | 181.8 | 159.7±14.5 (n=5) |
| $PM_1$ mass concentration (foggy days) | 347.8 | 187.0±64.0 (n=14) | 256.5 | 166.0±59.9 (n=20) |
| Nitrate (foggy days) | 56.7 | 18.3±13.8 (n=14) | 67.2 | 30.9±14.3 (n=20) |
| Sulfate (foggy days) | 28.5 | 13.7±10.5 (n=14) | 25.6 | 20.0±5.9 (n=20) |
| Ammonium (foggy days) | 41.9 | 23.7±18.6 (n=14) | 32.7 | 20.4±7.2 (n=20) |

**Fig. 6** Diurnal variation in the mass concentration of WSOC sampled with the PM$_1$ sampler and the denuder-equipped PM$_1$ sampler
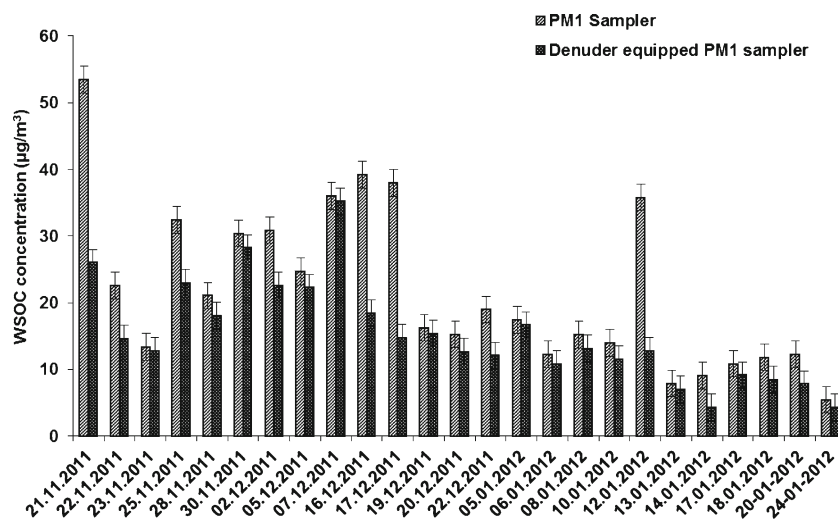
the early morning (Kaul et al. 2011). An increase in WSOC/OC in the afternoon may actually point towards enhanced OC oxidation associated with secondary organic aerosol production. Lower WSOC/OC ratios were attributed to selective scavenging of WSOC by fog droplets and their eventual removal via gravitational settling (Kaul et al. 2011).

Comparison of different chemical species

The sampling included four different sampling events using the PM$_1$ sampler and the denuder-equipped PM$_1$ sampler. These were foggy days without denuder ($n = 20$), clear days without denuder ($n = 5$), foggy days with denuder ($n = 20$), and clear days with denuder ($n = 5$), respectively. Figure 7 shows the comparison of average concentration of different chemical species during foggy and clear days. Sampling was performed on 25 days out of which 20 were foggy and five clear days. As mentioned earlier, the mass concentration of chemical species tend to increase substatially during the fog periods (Kaul et al. 2011; Gupta and Mandariya 2013). The average concentration of $SO_4^{2-}$, $Cl^-$, $NH_4^+$, $Na^+$, and $Ca^{2+}$ with PM$_1$ sampler was higher during the foggy days than those measured on the clear days. However, the average concentration of $NO_3^-$, $K^+$, and WSOC was lower during the foggy days because of higher and preferential scavenging of these species via fog droplets (Kaul et al. 2011).

Chemical analysis of fog water at Agra (Lakhani et al. 2007) shows an alkaline nature with average pH 7.2, and maximum concentrations was observed for $NH_4^+$ followed by $SO_4^{2-}$, $NO_3^-$, $Ca^{2+}$, $Mg^{2+}$, $Na^+$, and $K^+$. The $SO_4^{2-}$/$NO_3^-$ equivalent ratio in fog water was 1.4, indicating a dominant presence of $SO_4^{2-}$ over $NO_3^-$ in fog water. Kapoor et al. (1993) suggested that atmospheric aerosol are taken up in the boundary layer of Delhi, which showed that there is an excess of soil-oriented aerosols ($Ca^{2+}$, $K^+$, $Mg^{2+}$, and $Na^+$) in the region. $Ca^{2+}$, which dominates the particles in the air, can

neutralize the acidic effects of $SO_4^{2-}$ and $NO_3^-$. They found that in nearly all the cases, the dominant ions in the fog water at Delhi were $Ca^{2+}$, $Na^+$, $Mg^{2+}$, and $K^+$, and thus justifying the alkaline nature of the fog.

Variation in mass concentration of elements

Figure 8 shows the concentration of elements obtained with the PM$_1$ sampler and the denuder-equipped PM$_1$ sampler, respectively. Elemental concentration shows good variation from day to day. A total of 20 elements were analyzed using ICP-OES. The elemental concentration was higher with samples obtained from the PM$_1$ sampler than the samples from the denuder-equipped PM$_1$ sampler.

All the detected metals were grouped in two categories: major and minor elements. Major metals include those metals whose concentrations were reported above 2 µg/m$^3$ such as Ca, Fe, K, Zn, Mg, and Na while minor elements were considered as those with concentrations below 2 µg/m$^3$ such as Cr, Mn, Cu, Ni, Pb, etc. Ag, Be, Cd, Co, and V were always found to be below detection limit. This trend is in good agreement with a study carried out in Delhi (Srivastava et al. 2008). The concentrations of metal are usually higher in winter season due to atmospheric stability with low mixing height and less atmospheric turbulence (Chakraborty and Gupta 2010).

Kang et al. 2011 showed that enrichment of metals increases with decreasing particle size since finer particles have the largest diffusional losses (see the Supplementary figure showing submicron PM transmission efficiency measured with CPC). This explains the observed elemental losses (15–20 %) with denuded sampler for submicron particles.

Earlier studies have indicated that Ca, Fe, etc. are present in significant amounts in vehicular emissions (Schroeder et al. 1987; Gangwar et al. 2012), and 80 % of vehicular emissions

**Fig. 7** Comparison between average mass concentration of chemical species present during various events
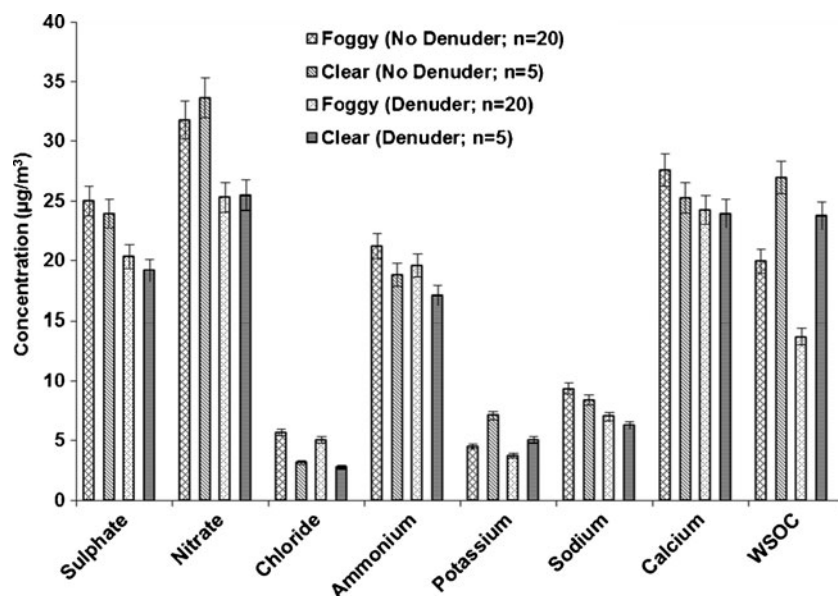


contain particles in ultrafine to fine (0.01–2.8 μm) range (Junker et al. 2000). As, Cr, Cu, Zn, Ni, and Se originate from anthropogenic sources like industries, petroleum and coal combustion, etc. (Kang et al. 2011) and anthropogenic activities like biomass burning. Although compressed-natural-gas-driven vehicles have been running in Kanpur since 2006, over the years Pb emitted by the vehicles driven by leaded fuel has eventually become part of the road dust (Artaxo et al. 1999) and hence it is present in the soil in little but significant concentration. Fe mainly originates from the iron/steel industries and re-suspension of fine soil dust. Potassium concentrations were high during winter time, which is consistent with biomass burning being dominant during the winter period (Sharma et al. 2007; Shen et al. 2010). It may be noted that $K^+$ is released into the atmosphere from vegetation through

hydathodes and $K^+$ is transported from root to leaves and released into the atmosphere (Parmar et al. 2001). Apart from potassium emission, burning events are also linked to the emission of WSOC. On the specific days when WSOC concentration was high, WSOC and $K^+$ show high correlation ($R^2=0.91$). This indicates that biomass burning or other burning events recorded on 21 November 2011, 25 November 2011, 16 December 2011, 17 December 2011, and 12 January 2012 significantly enhanced WSOC and potassium mass concentration (Fig. 9). It may also be noted that in the upwind side of our sampling site, there are extensive agriculture activities (including crop residue and weed/shrub burning) in rural areas and local area during winter. Hence, it is an ordinary practice to burn agriculture residue in winter to clear the fields of unwanted vegetation. Sodium was present in high
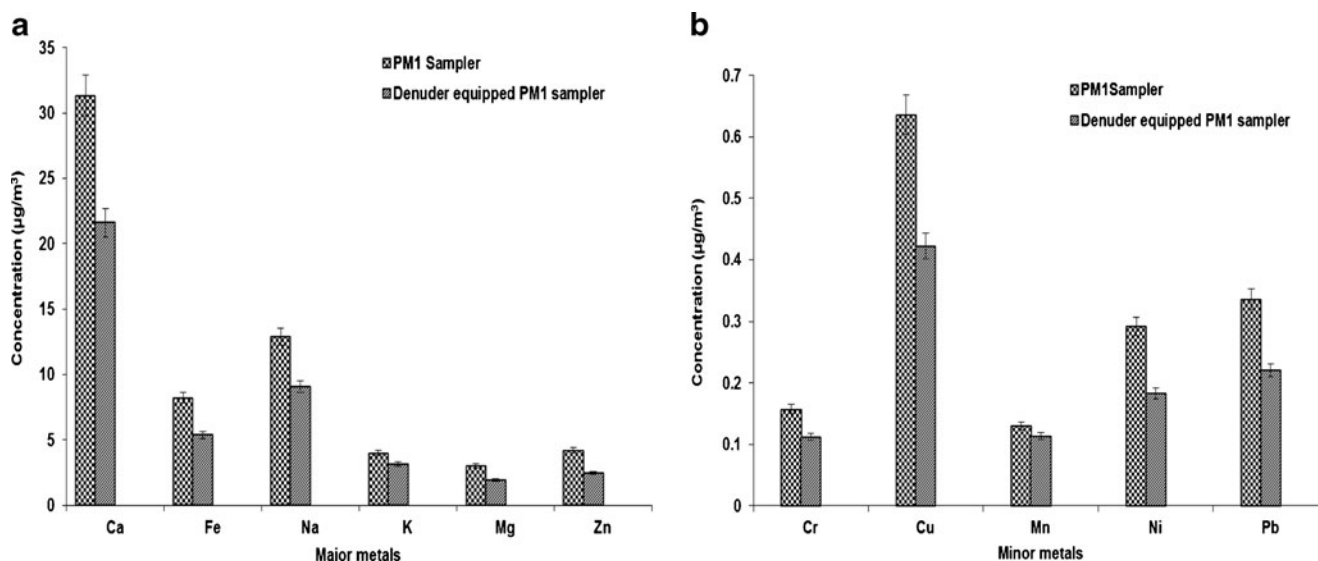


**Fig. 8** Average mass concentration of **a** major metals and **b** minor metals sampled with the $PM_1$ sampler and the denuder-equipped $PM_1$ sampler
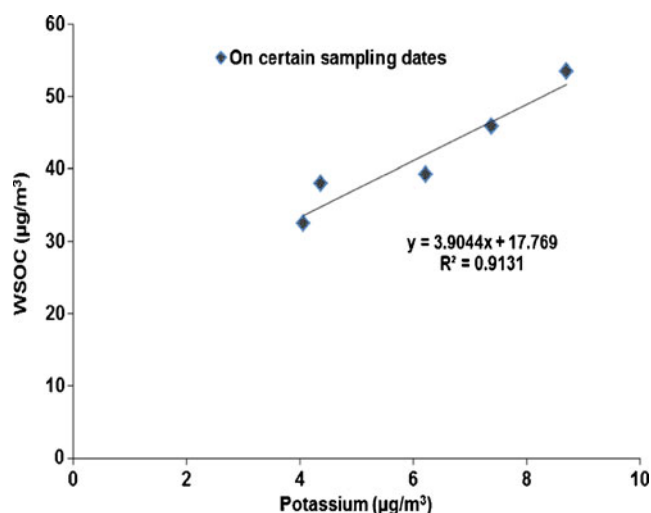
**Fig. 9** Correlation between WSOC and potassium

concentrations, which is attributed to fugitive dust and soil (Kaul et al. 2012). Also, a maximum concentration of Na (79, 569 mg/L) was found in the effluent samples, which, in combination with the above, are high enough to pose serious pollution stress to the environment especially in the proximity of the tanneries (Tariq et al. 2005). Na generated by inciner-ation gets trapped during foggy days in lower boundary layer due to frequent inversion condition during winter time (Baxla et al. 2009).

Sampling artifact

Figure 10 shows the percentage average positive artifact for different chemical species with the $PM_1$ sampler. The amount of positive artifact was observed to be highest in the case of
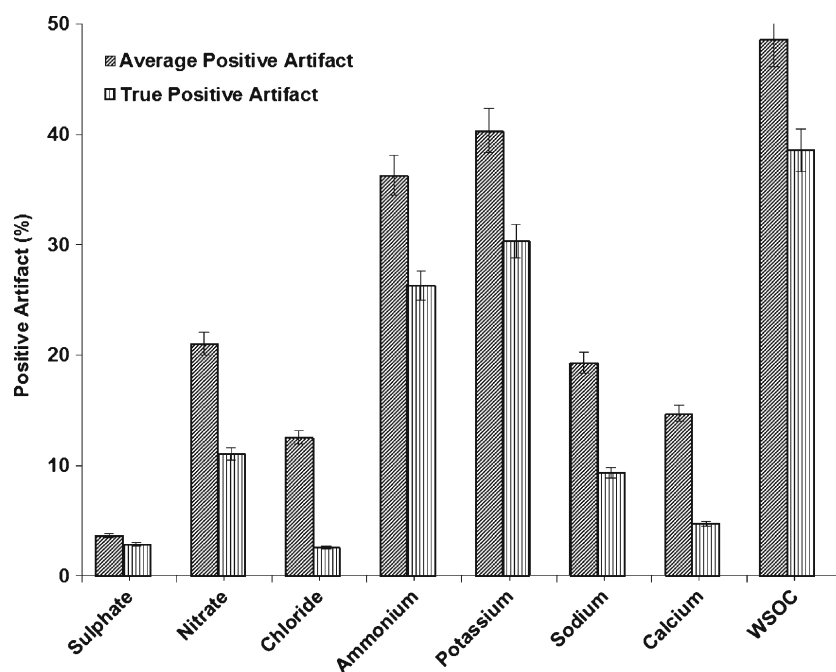
WSOC (48.5 %) followed by potassium (40.3 %). Ammonium and nitrate, two of the most important ionic species in atmospheric chemistry, show high positive artifact values, 36.3 and 21.05 %, respectively. Sulfate, on the other hand, shows lower positive artifact (3.64 %). Calcium and chloride also show lower positive artifact values, 14.7 and 12.55 %, respectively, while sodium shows significantly higher positive artifact value of 19.32 %. As mentioned earli-er, with denuder there were about 30 % losses in $PM_1$ number concentration which may actually correspond to ~10 % losses in terms of mass concentration (Gupta et al. 2004). This is considering the fact that most of the diffusional losses, within the denuder body, will be associated with smallest (ultrafine) particles which contribute significantly to the number concen-tration but have miniscule contribution to the $PM_1$ mass concentration. Also, the particle loss depends on the amount of gas which diffuses to the surface, and the fraction of gas which diffuses increases with the sampling flow (Koutrakis et al. 1993). Fan et al. (2004) applied an Amberlite XAD-coated denuder for ambient air particle-phase OC (organic carbon) sampling in Vancouver and Toronto. The mean OC collected on a non-denuded quartz filter in Vancouver, for example, was 3.59 μg C/m³ and on the denuded quartz filter it was 2.52 μg C/m³, indicating that the non-denuded quartz filter contains 1.07 μg C/m³ of positive artifact (about 42 %).

Another source of PM artifact could be thought as a result of lowered RH of the sampling stream for the $PM_1$ sampler fitted with the denuder. However, our interest here was to sample particulate matter and not gases. Please refer to Gupta et al. (2004) where it has been explained that the RH of the air stream and water bound to the particles are two different things. Silica gel can lower the RH of the air stream

**Fig. 10** Average positive artifact and true positive artifact calculated for different chemical species

quickly, but the water bound to the particulate matter takes significant time to evaporate as the wet particle undergoes metastable form commonly known as hysteresis effect. Aerosol residence time in the denuder residence time was actually less than 0.2 s which is too low to cause any stripping of water molecules from the submicron PM surfaces.

Ding et al. (2002) used a charcoal-impregnated diffusion denuder for ambient sampling and measured 12.28 µg C/m³ OC on the denuded quartz filter and 17.54 µg C/m³ OC on the non-denuded filter. By using the denuder, a 5.26 µg C/m³ (43 %) positive artifact was avoided.

An XAD-coated denuder was coupled with a quartz filter and cartridges or poly urethane foam (PUFs) in diesel emissions sampling work in order to measure the positive artifact and to estimate the distribution of organic compounds in gas and particle phase (Schauer et al. 1999). Only a few studies investigated particle loss through the denuder, such as Temime-Roussel et al. (2004), which examined denuder performance for diesel particle transmission efficiency with a result of 84±14 % at flow rates of 17 L/min and 81±21 % at the flow of 34 L/min. In some ambient sampling applications, particle loss was found to be minor, ranging from about 3 % (Mader et al. 2001) to 0 % no significant difference (Ding et al. 2002; Fan et al. 2004; Cheng et al. 2010). These smaller losses for ambient measurements are not unexpected given that particle sizes even at Kanpur were likely larger with the dominant mass in the accumulation mode (Baxla et al. 2009). Noll and Birch (2008) found 18 % of EC loss in the activated carbon denuder for diesel emission sampling, which is similar to Zhang et al. (2013). However, Schauer et al. (1999) did not find EC loss in denuder-based sampling (XAD-coated glass denuder, four-channel, 40 cm long, at 30 L/min) of diesel emissions.

Fine particle mass collected in this fashion by the filter/ PUF sampling train consisted of 30.4 % organic carbon and 30.8 % elemental carbon. Sulfate and ammonium ion were found to compose 1.0 and 0.73 % of the mass, respectively, accompanied by detectable amounts of silicon and iron. Furthermore, they found sampling artifact with organic and elemental carbon when measured on the quartz fiber filters located downstream of the XAD-coated denuders.

Significantly less organic carbon was collected on filters located downstream of the denuders than for non-denuded filter sample collected in parallel.

Ruiz et al. (2006) showed the effect of varying the diffusion coefficient ($D$) using air mixtures of different gases. These gases were nitric oxide (NO), carbon monoxide (CO), nitrogen dioxide ($NO_2$), sulfur dioxide ($SO_2$), and sulfur hexafluoride ($SF_6$). As the availability of $D$ values for these gases in the literature was limited, they were estimated from their molecular weights using Graham's law:

$$\frac{D_T}{D_{CO}} = \sqrt{\frac{MW_{CO}}{MW_T}}$$

and the $D$ value of CO (0.208 cm² s⁻¹) at 20 °C where $D_T$ and $D_{CO}$, and $MW_T$ and $MW_{CO}$ are the diffusion coefficients and molecular weights of target gas (T) and CO, respectively.

Ruiz et al. (2006) reported that a larger molecule ($SF_6$) has lower removal efficiency (~12 % reduction) than a smaller molecule (CO) through PTFE membrane. Moreover, the pore size of PTFE is 0.2 µm, which is much larger than the size of even the largest gaseous molecule of ambient origin, so their removal is evident. However, if some large gas molecules (organic or inorganic) are removed at a lower efficiency, then the amount of mass collected on the denuded filters might be higher and leads to PM artifact.

Pathak and Chan (2005) have suggested nitrate loss due to the evaporation of $HNO_3$ as significant. On average, the nitrate loss was 55 % (33–79 %) and 36 % (14–64 %) in the samples, respectively. The evaporation of HCl was also significant, with an average chloride loss of 68 % from their samples. According to Pathak and Chan (2005), ammonium artifacts are the result of the evaporation of the ammonia with $HNO_3$ or HCl and the absorption of ammonia. Overall, the average ammonium errors were small (~1 %) in the samples. However, the positive artifact of ammonium was nearly 7 % on average attributed to a much higher ambient $NH_3$ concentration (235 nmol m⁻³). Hence, a denuder/filter pack system is necessary for minimizing sampling artifacts in ambient.

Figure 11 shows the relative contribution of mass concentration of different chemical species sampled with the $PM_1$



Fig. 11 Relative contribution of mass concentration of different species sampled with **a** $PM_1$ sampler and **b** denuder-equipped $PM_1$ sampler
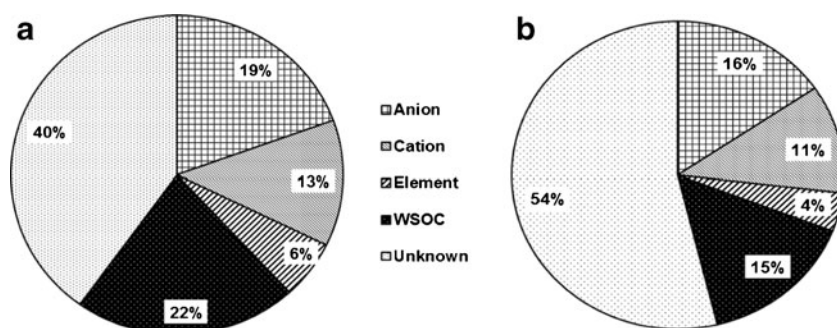
sampler and the denuder-equipped PM$_1$ sampler, which reveals that average mass concentrations of anions, cations, and elements are about 2 to 3 % lower for denuded samples. In WSOC, it has been observed that higher average mass concentration with PM$_1$ sampler (22 %) was observed as compared with denuded sampler (15 %), which also indicates that the amount of positive artifact was observed to be highest in the case of WSOC.

From our results, it can safely be stated that as far as sulfate, chloride, and calcium ion are concerned, denuder is not required. However, in estimating the true values for nitrate, ammonium, potassium, sodium, and WSOC, denuder-equipped PM$_1$ sampler can serve as a useful technique.

## Conclusions

In spite of the fact that IITK is free from industrial activity and vehicle density inside the campus is very low, still very high concentrations of PM$_1$ are observed, indicating its transport by wind or effect of meteorology or further PM processing via gas to particle formation pathway. Significant increase in mass concentration of PM$_1$ was observed during foggy days (165.95±59.9 μg/m$^3$) than the clear days (159.66±14.5 μg/m$^3$). The average mass concentration sampled with a PM$_1$ sampler was found to be higher than the denuder-equipped PM$_1$ sampler. Nitrate, sulfate, ammonium, and calcium were found to be the most dominating ionic species during fog periods. Cation and anion charge balance showed the basic nature of ambient PM$_1$ in fog. Elevated levels of WSOC concentration were found during clear days as compared to the foggy days attributed to preferential scavenging of WSOC by fog droplets. Calcium and sodium were the major metals dominant during the fog periods. Good correlation between K$^+$ and WSOC on specific sampling dates indicates the dominance of biomass combustion. The data obtained in the current sampling carried out during fog-dominated winters was found to be in good agreement with the data previously obtained during winter (2009–2010) at the same sampling site. The difference in the concentrations of chemical species obtained with both the samplers indicates that the use of denuder-equipped PM$_1$ sampler reduces the positive artifact and helps in estimating the true values.

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