Extreme Air Pollution Events Spiking Ionic Levels at Urban and Rural Sites of Indo-Gangetic Plain

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ABSTRACT

The present study is a modest attempt to quantify the water-soluble inorganic ions (WSIIs) in the early morning (fog-forming) ambient air on the central Indo-Gangetic Plain (IGP) during winter via dissolution using a low-cost refluxing mist chamber. The chemical composition of the bulk samples showed significant differences in the WSIIs between the two monitored sites, one urban and the other rural, with NH_4^+ (47% and 37%, respectively) and Ca^{2+} (18% and 8%, respectively) being the major cations and NO_3^- (10% and 16%, respectively) and SO_4^{2-} (9% and 14%, respectively) being the major anions. The WSII concentration spiked during November at both locations ($\Sigma \text{WSII} = 159.6$ and $141.9 \mu\text{g m}^{-3}$) due to two extreme air pollution events, viz., i) the burning of crop residue and ii) the Diwali festival. These changes, which were corroborated by observations of the meteorological conditions, played an essential role in the wintertime atmospheric chemistry. On foggy days, significant scavenging of ions associated with crustal dust (Ca^{2+} , Na^+ , Mg^{2+} and Cl^-) occurred, although the ambient concentrations of other species (K^+ , NH_4^+ , NO_2^- , NO_3^- and SO_4^{2-}) remained relatively unaffected. Furthermore, the relationship between the cations and anions demonstrated that NH_3 and HONO, as the primary gaseous species, were involved in heterogeneous aqueous-phase reactions and the formation of secondary aerosols. Source apportionment based on principal component analysis and the mass ratios also indicated that local anthropogenic sources, in addition to natural ones such as soil/road dust and biogenic emissions, influenced the WSII composition. Vehicular exhaust, solid waste and biofuel burning were identified as the major contributors of WSIIs at the urban site, whereas biomass burning, agricultural activity and coal combustion in brick kilns were the predominant sources at the rural site.

Keywords: Atmospheric chemistry; Mist chamber; Ionic interactions; Fog scavenging; Source apportionment.

INTRODUCTION

The onset of winter season in the Indo-Gangetic Plain (IGP) region has been found to be associated with the formation of a thick blanket of brown clouds within two to three kilometers above the surface (Ramanathan *et al.*, 2005; Chung and Ramanathan, 2006; Nakajima *et al.*, 2007). This seasonal phenomenon is an outcome of the complex interplay between various meteorological and anthropogenic factors. The meteorological factors mainly include calm winds, lower mixing height, temperature inversion, etc. They restrict the dispersion of pollutants and leads to their accumulation in the lower atmosphere (Nair *et al.*, 2007; Gautam, 2014; Pani and Verma, 2014; David *et al.*, 2011; Sen *et al.*, 2017). As to the anthropogenic factors, the increased emissions of harmful pollutants from residential, industrial and transport sectors to meet the energy demands of this densely populated region undermines air quality (Singh *et al.*, 2014; Pan *et al.*, 2015;

Liu *et al.*, 2018). Moving further, another vital connection between the deteriorating air quality and certain extraneous extreme pollution episodes such as stubble burning in the states falling upwind of the IGP and the use of firecrackers during the celebration of Diwali festival needs to be factored in while accounting for the overall atmospheric profile of the region during the winter season (Kulshrestha *et al.*, 2004; Singh *et al.*, 2010; Perrino *et al.*, 2011; Jain *et al.*, 2014; Singh and Kaskaoutis, 2014; Izhar *et al.*, 2018). These cumulatively result in the reduction of visibility, poor air quality and jeopardizing of health indicators (Seaton *et al.*, 1995; Gautam *et al.*, 2007; Balakrishnan *et al.*, 2019).

Furthermore, the winter season is characterized by higher moisture content in the form of fog which provides a potent medium for the chemical reactions of different atmospheric organic and inorganic species (Jain *et al.*, 2000; Rajput *et al.*, 2016; Tie *et al.*, 2017; Bharali *et al.*, 2019). As for the latter, significant concentrations of major inorganic ions have been reported in the non-precipitating clouds and fog (Jacob and Hoffmann, 1983; Jacob *et al.*, 1984; Ram *et al.*, 2012; Straub *et al.*, 2012). Longer residence time and higher scavenging efficiency through aqueous-phase reactions explain the reason behind high concentrations of inorganic

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ions in the cloud and fog water (Jacob and Hoffmann, 1983; Fridlind and Jacobson, 2000). The ambient air chemical composition during winters is assumed to be determined by the following factors: (1) the composition of the activated cloud condensation nuclei (CCN) on which the water droplet condenses, (2) the absorption of atmospheric gases at the droplet's surface, and (3) the subsequent aqueous-phase reactions of homogeneous and heterogeneous species. Such physical as well as chemical interactions among water droplets, gases and aerosols in the ambient air invariably alter the regional-scale atmospheric chemistry (Seinfeld and Pandis, 1998; Raes *et al.*, 2000).

Previous studies conducted in IGP have extensively reported the concentration of ions either in fog water or in the aerosols and gases separately in the atmosphere, which provide vital information regarding the different kinds of phase chemistry during winter period (Kulshrestha *et al.*, 2005; Kaul *et al.*, 2011; Gupta and Mandariya, 2013; Agarwal *et al.*, 2017; Ghude *et al.*, 2017; Nath and Yadav, 2018; Rajput *et al.*, 2018; Izhar *et al.*, 2020). But there are certain interactions going on in the ambient air, particularly during winters owing to aqueous-phase chemistry, which simultaneously includes interactions of gases and aerosol with fog droplets (Waldman *et al.*, 1982; Jacob *et al.*, 1984). Furthermore, the presence of fog, on the one hand, scavenge the aerosols through their dissolution in large droplets and on the other hand also enhance the formation of secondary aerosols, which accentuates the need to look into the overall chemical composition of dominant atmospheric species (Lopez-Hilfiker *et al.*, 2014; Rao and Vejerano, 2018). Ionic composition regulates atmospheric acidity, which helps us understand the partitioning of semi-volatile water-soluble compounds between particulates and gas phase. In such a scenario, the study of bulk air mass samples will be helpful in characterizing the water-soluble inorganic ionic (WSII) species and major reaction chemistry occurring during fog-

forming hours in ambient air. The present study has following research objectives: (1) to quantify overall (bulk) concentrations of WSII and monthly variation at different land use sites during fog-forming hours in winters, (2) to assess the impact of fog scavenging and ionic interactions of different WSII in ambient air and (3) to identify major sources of WSII using principal component analysis (PCA) model at different sites of the IGP.

METHODOLOGY

Sampling Sites

IGP region is known for its very high population density and stationary sources of pollutant emissions in the environment. Keeping in view the different land use patterns, two sites have been selected: Prayagraj as an urban site and Madhupur, a village in Pratapgarh district of UP, as a rural site as shown in Fig. 1.

Prayagraj (an Urban Site)

Prayagraj ($25^{\circ}54'N$, $81^{\circ}85'E$), formerly known as *Allahabad*, is the administrative headquarters and among one of the most populous cities of Uttar Pradesh state. Located in the southern Uttar Pradesh, at the confluence of the Ganga and Yamuna, the city's area covers 70.5 km^2 area. As per the census 2011, the district has a population density of 1,086 per km^2 . National Highway-130 passes through the city and attracts very high traffic density. Allahabad Development Authority (ADA) continuously focuses on the planning of the suburban areas of the city. As a result, in 2011, it was ranked the world's 130th fastest-growing city. Within the city, sampling was conducted in the Phaphamau area, located in the northern part of the city. The sampler was mounted at 1.5 m above the surface on the terrace of a residential building in a colony situated nearby the highway.

Fig. 1. Description of sampling sites.

Madhupur (a Rural Site)

Madhupur village (25°98'N, 82°04'E) were selected as rural site, which is in Pratapgarh, a district adjacent to the Prayagraj. Madhupur site is located 70 km away in the northeastern side of Prayagraj. Sai and the Ganges are the main rivers flowing through Pratapgarh district. As per the census 2011, the district has a population density of 854 per km². The site comes under one of the most backward districts of India. Primarily an agrarian district, Pratapgarh has risen in ranks as the top producer of *Aonla* or *Amla* fruit, which is used as herbal medicine. The village is poorly developed as hardly any roads pass through the area with two brick kiln units within 5 km² of the site. It has very low vehicle density and high vegetation cover. Biomass burning, soil resuspension, and agricultural activities are the main source of pollution in the area. Sampling was conducted on the terrace of a two-floored house. Similar to the urban site, the fog sampler was mounted approximately 1.5 m above the surface of the terrace.

Sample Collection Using Mist Chamber

Collection of ambient air bulk samples during winter months was carried out using customized low-cost refluxing mist chambers. Very similar mist chamber has been used by Jain *et al.* (1999). A schematic design of the glass mist chamber used in the current study has been shown in Fig. 2. The air inlet sucks the air directly into the mist-forming spherical glass chamber, filled with collecting solution. The spherical glass chamber has a capacity of 250 mL and it consists of an air inlet, a nebulizing nozzle, and a port for the addition and removal of the solution. The collecting solution (Milli-Q water) is drawn from the reservoir into the nozzle, where impaction with the incoming air forms a fine aqueous mist. The fine aqueous drops provide a large surface area for efficient extraction of water-soluble compounds from the air. The mist is drawn upward through the mist chamber where aqueous droplets containing scrubbed atmospheric species collide and are refluxed into the reservoir. The upper side of the mist chamber was designed with a few bends,

Fig. 2. Description of mist chamber used in collecting the bulk samples.

which help to reduce the sample loss and evaporation of the solution. It was connected to the well-calibrated rotameter to maintain the flow rate, which was further connected to the vacuum pump through a silicon tube. Though the flow rate was maintained at 15 L min⁻¹, the pressure drop at each stage was taken into the account (between 12 and 14 L min⁻¹), which was corrected while data calculation and analysis.

The use of such type of mist chambers have been reported in various previous studies, which have shown a very high collection efficiency for gases (Stratton *et al.*, 2001; Spaulding *et al.*, 2002; François *et al.*, 2005; Hennigan *et al.*, 2018). More recently, as in the present study, the mist chambers have also been used for particle plus gas analysis (King and Weber, 2013). Here, the bulk samples which are collected through the incorporation of all the water-soluble components entering with the air stream into the mist drops and their subsequent dissolution in water represents the total concentration of a particular chemical species present in ambient air. The measurement of the collection efficiency of the sample collector was performed with the cations and anions analysis using ion chromatography. Two identical mist chambers were operated in a series similar to prior studies for characterizing their collection efficiency (Spaulding *et al.*, 2002; Hennigan *et al.*, 2018). Collection efficiency (CE) was calculated using the following formula:

$$CE = 1 - C_2/C_1$$

where C₂ and C₁ are the concentrations of the analyte in first and second sampler. For most of the analyzed species, the collection efficiency was found to be very high (> 95%), which strengthened the robust nature of the method. Replicate samples were also collected at each site. The result showed a difference of about 12–18% for all the cations and anions, which is within acceptable limits. However, a slight variation in replicate samples can be attributed to the changing dynamics of analytes in the atmosphere.

Since the winter period, particularly morning hours, has been evident of very high relative humidity (RH), most of the soluble gaseous species also get dissolved onto the water droplets or more precisely on fog droplets and alters atmospheric chemistry, which is the primary reason to use mist chamber during winter months. Along with efficient scrubbing of aerosols, mist chamber also allows the gas- and aqueous-phase diffusion of analytes onto the mist droplets inside the glass chamber. Most of the studies which focus on fog chemical characterization use condensation method, which ultimately gives the species concentrations in per volume of fog (in µeq L⁻¹). However, the current study includes the overall concentration of measured chemical species in ambient air (µg m⁻³) during winters from November 2016 to February 2017. Considering the fog-forming hours in India, the sampling was conducted for 5 h from 03:00 to 08:00. About 60 mL of deionized Milli-Q water was used as collecting solution. Due to high RH, water loss through evaporation was very less and for most of the time it was less than 10 mL, which was corrected before analysis. After the collection of samples, glass chamber was rinsed (20 mL × 3) every time carefully to eliminate contamination in

samples through the detachable lower part. Total 41 and 22 samples were collected at urban and rural sites, respectively. Due to limited power supply in villages, sample size was less at the latter site. Samples were stored using thymol as a preservative and kept in a refrigerator at -4°C to avoid any chemical alterations. Meteorological parameters were reported on a regular basis from online website wunderground.com. Wind speed, temperature and RH are primarily considered for the study.

Analysis on Ion Chromatography

Five major cations (Na^+ , NH_4^+ , K^+ , Ca^{2+} and Mg^{2+}) and four major anions (Cl^- , NO_2^- , NO_3^- and SO_4^{2-}) in the bulk samples were analyzed using ion chromatography (883 Basic IC Plus; Metrohm). Cation column (Metrosep A Supp 4, 250/4.0; Metrohm) was used for the determination of cations using a mixture of $1.7 \text{ mmol L}^{-1} \text{ NaHCO}_3$ and $1.8 \text{ mmol L}^{-1} \text{ Na}_2\text{CO}_3$ as eluent. Whereas, anion column (Metrosep C4, 100/4.0; Metrohm) was used to determine anions using a mixture of 0.7 mmol L^{-1} dipicolinic acid and 1.7 mmol L^{-1} nitric acid as eluent. MERCK certified standards for anions and cations were used for the calibration. Four standards of 1, 2, 5 and 10 ppm were used to draw the standard calibration curve for cations and anions. The correlation coefficient of standards was observed to be 0.99. Calibration curve was plotted every time the new eluent is prepared and quality was ensured by repeating the analysis of standards on regular interval. Replicate sample analysis has shown a relative deviation within a range of 12–18%. The detection limits (DLs) of Cl^- , NO_2^- , SO_4^{2-} , NO_3^- , Na^+ , NH_4^+ , K^+ , Ca^{2+} and Mg^{2+} for our instrument were calculated as 0.03, 0.75, 0.24, 1.13, 0.35, 0.29, 0.63, 0.85 and 0.33 mg mL^{-1} , respectively. For quality assurance and quality control (QA/QC), procedure field blanks were collected at the start of each month sampling. Blanks were handled and analyzed in the similar way as other samples. Most of the target ions were found below detection limits except Cl^- which was subtracted/corrected at each step while calculations. The final concentration of ions was calculated using following formula:

$$C (\mu\text{g m}^{-3}) = [X (\mu\text{g mL}^{-1}) \times V_s (\text{mL})] / [R (\text{m}^3 \text{min}^{-1}) \times t (\text{min})]$$

where X is the concentration of particular ion obtained from IC, V_s is the volume of sampling solution, R is the flow rate, t is the duration of sampling and C is the final concentration of X ion in the ambient air.

Ion Balance Check

An ionic charge balance is usually performed in aerosols to check the data quality, where the sum of the equivalent ratios of cations and anions are assessed to fulfil the principal of electro-neutrality and characterizing the aerosol acidity (Pani *et al.*, 2017). In the present study, the method does not include exclusively aerosols. The bulk concentration of WSIs in fog-forming air mass simultaneously include fog droplets and diffused gases (mainly NH_3 and HONO) along with the aerosols and their collection in the sampling

solution (Milli-Q water), not filters. The ion balance check revealed an excess cation case as reported by earlier studies in the Indian region (Kulshrestha *et al.*, 2003). According to Kulshrestha *et al.* (2005) bicarbonate measurements substantially fill up the gap in the cation and anion difference in the Indian region. This is because much of the calcium which is a dominant cation is associated with HCO_3^- in the samples which is corroborated with the ion balance studies reported by Satyanarayana *et al.* (2010) and Kumar *et al.* (2016). In the present study we found the ratio of sum of equivalents of anion and cations (Σ^-/Σ^+) in the range of 0.08–0.33 at the urban site and 0.12–0.47 at the rural site (Table 1). The deficiency of unmeasured water-soluble organic anions (such as acetate and formate) might also have led to the lower ratio values, which have been reported to be present in abundance in the wintertime studies of IGP (Verma *et al.*, 2017; Nath and Yadav, 2018). The importance of organic anions in charge balance has been also reported in previous studies (Kerminen *et al.*, 2001; Lee *et al.*, 2003). Furthermore, the lower ratios were identified due to NH_4^+ -rich conditions owing to its efficient collection and higher solubility. In this context, Trebs *et al.* (2005) have also reported an excess in NH_4^+ species due to greater diffusion of gaseous NH_3 , which might be neutralizing the other unmeasured anions in the atmosphere. The ratio of sum of cations other than NH_4^+ and sum of anions was still observed to be in lower range (0.51 and 0.86 for urban and rural sites, respectively), which is probably due to excess in Ca^{2+} concentrations. However, the major limitation of such neutralization process is the unmeasured highly soluble bicarbonate ions formed through the dissolution of CO_2 whose solubility depends on available cation species in the atmospheric samples. In this context higher concentration of unmeasured bicarbonate ions might be compensated with the excess of NH_4^+ and Ca^{2+} ions. Additionally, such interactions with measured ions have been explained using scatter plots in the results.

RESULTS AND DISCUSSION

Variations in pH Values of Samples over the Sites

The pH values are one of the major indicators of dominant

Table 1. Ion balance for the major ions analyzed in the samples ($\mu\text{eq m}^{-3}$).

Ions	$\mu\text{eq m}^{-3}$	
	Urban	Rural
Na^+	0.31	0.12
NH_4^+	3.23	2.84
K^+	0.13	0.35
Ca^{2+}	1.09	0.34
Mg^{2+}	0.15	0.07
Cl^-	0.29	0.06
NO_2^-	0.06	0.02
NO_3^-	0.23	0.19
SO_4^{2-}	0.26	0.18
Σ^-	4.91	3.75
Σ^+	0.84	0.45
Σ^-/Σ^+	0.18	0.25

species governing the aqueous-phase reaction chemistry in the atmosphere (Wang *et al.*, 2005; Morgan, 1982). The pH was analyzed to get the relative difference in the acidity of ambient air bulk samples (Fig. 3). The average pH of the collected urban samples was found to be 5.7 ± 0.1 , which ranged from 5.1 to 6.2. Whereas, rural samples have shown a relatively lower average pH of 5.1 ± 0.1 ranging from 4.5 to 5.6. In the absence of effective neutralization, pH of rural samples indicates the higher concentrations of H^+ ions resulting in greater atmospheric acidity. However, higher pH of urban samples shows the efficient neutralization of acidic species in urban atmosphere which can be attributed to the presence of alkaline species from dust particles emitted from construction activities, deforestation, and road dust and soil resuspension (Kulshrestha and Sharma, 2015). The presence of gases like CO_2 , SO_2 and NO_2 also greatly affect the pH values, depending upon their concentration and dissolution properties in water (Lekouch *et al.*, 2010).

Relative Contribution of WSIs

The relative contribution of different analyzed WSIs has been shown in Fig. 4. NH_4^+ and Ca^{2+} were found as major cations and NO_3^- and SO_4^{2-} as major anions at both the sites. NH_4^+ contributed around 47% of analyzed WSIs at the urban site and 37% at the rural site. NH_4^+ has been reported to be dominating atmospheric species in fog water and wintertime aerosol studies (Ali *et al.*, 2004; Nath and Yadav, 2018; Ge *et al.*, 2019). Since animal/human excreta are one

of the most important sources of NH_3 , densely populated IGP has been observed as one of the major hotspots of ammonia emission in the world (Galloway *et al.*, 2004). Owing to higher solubility, NH_4^+ readily gets scavenged by water droplets present in the air during humid conditions in winter mornings and reacts with the atmospheric acidic components such as chlorides, nitrates and sulfates (Waldman *et al.*, 1982; Jacob and Hoffmann, 1983; Bongartz *et al.*, 1995; Ge *et al.*, 2019). Urban sources of NH_3 include vehicular exhaust, open waste burning and human excreta/sludge degradation, whereas biomass burning, emissions from agriculture and livestock farming remain as major sources in the rural areas (Singh and Kulshrestha, 2014; Singh *et al.*, 2014). At urban site NH_4^+ was followed by $Ca^{2+} > NO_3^- > SO_4^{2-} > Cl^- > Na^+ > K^+ > NO_2^- > Mg^{2+}$. However, at the rural site NH_4^+ was followed by $NO_3^- > SO_4^{2-} > Ca^{2+} > K^+ > Na^+ > Cl^- > Mg^{2+} > NO_2^-$. Ever-growing urbanization, migration and unplanned construction activities are continuously lowering the urban green cover which leads to very high erosion of surface dust and the main sources of Ca^{2+} in urban areas (Gupta *et al.*, 2016). However, in rural areas, high green cover limits the emission of Ca^{2+} in the atmosphere (Tiwari *et al.*, 2016; Mishra and Kulshrestha, 2017). Both NO_3^- and SO_4^{2-} were found to be higher at the rural site as compared to urban site, which primarily can be attributed to the solid fuel burning in the form of wood, crop residues, dung cakes, domestic wastes or low-grade coal burning in the villages (Singh *et al.*, 2014).

Fig. 3. The pH variation of bulk air samples at both the sites.

Fig. 4. Percentage contribution of measured ions at urban and rural sites.

Temporal Variation of WSIs

Since the study includes an overall characterization of WSIs, i.e., without phase differentiation, here samples were not classified based on fog occurrence. The concentration of major WSIs in ambient air bulk samples at urban and rural sites is given in Table 2.

Urban Site

Temporal variation of measured cations and anions at the urban site is shown in Fig. 5. Being dominant species during winters, mean concentration of NH_4^+ at urban site was $58.2 \pm 17.5 \mu\text{g m}^{-3}$ ranging from a minimum $24.7 \mu\text{g m}^{-3}$ to a maximum $123.5 \mu\text{g m}^{-3}$. The IGP has been majorly reported as the hotspot of NH_3 emission (Behera *et al.*, 2013). Apart from natural sources, higher traffic density and vehicular exhausts are the potential sources of NH_3 emission in urban areas. However, being one of the most soluble atmospheric gases, NH_3 readily gets absorbed by fog droplets and get converted into NH_4^+ (Jacob *et al.*, 1984; Shi *et al.*, 1999). It was followed by Ca^{2+} with an average concentration of $21.8 \pm 7.1 \mu\text{g m}^{-3}$ ranging from a minimum $10.6 \mu\text{g m}^{-3}$ to a maximum $35.8 \mu\text{g m}^{-3}$. Construction activities and re-suspended road dust are most important urban sources of Ca^{2+} . Since Ca^{2+} concentration occurs higher in coarse mode and primarily in the form CaCO_3 , these large particulates

provide a surface for the fog water accumulation. Due to the lower mixing height in winters, these particles remain suspended in the lower atmosphere and enhance the fog formation rate (Finlayson-Pitts and Pitts, 2000). Both Ca^{2+} and NH_4^+ have been reported to be crucial for the neutralization of acidic species in the atmosphere (Khemani *et al.*, 1987). Na^+ , K^+ and Mg^{2+} mean concentrations were $7.2 \pm 7.7 \mu\text{g m}^{-3}$, $5.1 \pm 3.6 \mu\text{g m}^{-3}$ and $1.8 \pm 0.7 \mu\text{g m}^{-3}$, respectively. Na^+ and Mg^{2+} mostly come from crustal sources, sea salts or long-range transport (LRT); however, K^+ could have natural (crustal) as well as anthropogenic (biomass burning) sources (Kumar *et al.*, 2016).

Average NO_3^- and SO_4^{2-} concentrations at the urban site were observed to be $14.4 \pm 6.8 \mu\text{g m}^{-3}$ and $12.6 \pm 6.3 \mu\text{g m}^{-3}$, respectively. NO_3^- and SO_4^{2-} generally occur as secondary pollutants formed from their precursor gases NO , NO_2 , volatile HNO_3 and SO_2 . Prayagraj has a very high traffic density due to its large urban population where unregulated engines of local public transports such as *Vikram tempo*, buses and heavy-duty trucks, pass from nearby highways and emit enhanced amounts of these pollutants. During winters mixing height goes as low as 200 m and these exhaust emissions get accumulated in the lower atmosphere. Fog has been reported to intensify in the presence of precursor gases like NO_2 and SO_2 (Klemm and Lin, 2016). In aqueous phase,

Table 2. Concentration of various chemical constituents at urban and rural sites.

	Urban (n = 41; in $\mu\text{g m}^{-3}$)			Rural (n = 22; in $\mu\text{g m}^{-3}$)		
	Mean $\pm$ SD (σ)	Median	Range	Mean $\pm$ SD (σ)	Median	Range
Na^+	7.2 ± 7.7	5.1	1.1–44.8	6.6 ± 6.7	3.8	0.7–25.1
NH_4^+	58.2 ± 17.5	58.7	24.7–103.5	38.3 ± 13.1	39.8	18.9–62.6
K^+	5.1 ± 3.6	4.1	1.9–21.6	6.8 ± 6.3	4.4	0.6–27.9
Ca^{2+}	21.8 ± 7.1	20.5	10.6–35.8	8.1 ± 2.3	7.6	5.1–14.6
Mg^{2+}	1.8 ± 0.7	1.7	0.7–4.3	1.2 ± 0.5	1.0	0.7–3.2
Cl^-	10.4 ± 7.4	9.0	2.8–46.2	6.4 ± 5.4	4.5	2.0–21.4
NO_2^-	2.5 ± 1.4	2.2	0.5–6.9	1.1 ± 0.5	1.0	0.3–2.3
NO_3^-	14.4 ± 6.8	12.7	3.0–34.2	16.4 ± 7.6	13.9	8.9–36.2
SO_4^{2-}	12.6 ± 6.3	11.4	4.2–30.3	15.1 ± 11.1	10.9	4.7–50.2

Fig. 5. Temporal variation of cations and anions at the urban site.

NO_2 and SO_2 get dissolved in water droplets, where they oxidize into HONO , NO_2^- , NO_3^- and SO_4^{2-} respectively, by oxidizing species such as OH and RH radicals, H_2O , O_3 and O_2 (Seinfeld and Pandis, 1998; Finlayson-Pitts and Pitts, 2000). A higher concentration of HONO in early hours provides the biggest source for hydroxyl radicals, which convert gases into nitrous, nitric, sulfite and sulfuric acids.

Such reactions in the presence of high moisture content and polluted atmosphere promote smog formation and cause thick-haze-like conditions and reduce visibility. Cl^- concentration was $10.4 \pm 7.4 \mu\text{g m}^{-3}$, which can be attributed to alkaline saline soil dust transported from upwind regions, HCl evaporation and municipal waste burning, which is very common for locals (Zhang *et al.*, 2008; Perrino *et al.*, 2011). Mean NO_2^- concentration was found to be $2.5 \pm 1.4 \mu\text{g m}^{-3}$, which could be formed as a result of Eqs. (2) and (3) during morning hours and play as crucial interstitial oxidizing species (Finlayson-Pitts and Pitts, 2000).

Rural Site

Temporal variation of measured cations and anions at the rural site is shown in Fig. 6. NH_4^+ was observed as the dominant species also at the rural site, having an average

value of $38.3 \pm 13.1 \mu\text{g m}^{-3}$ with a minimum of $18.9 \mu\text{g m}^{-3}$ and maximum $62.6 \mu\text{g m}^{-3}$. Agricultural activities and livestock are the major sources of NH_3 emission in rural areas (Singh and Kulshrestha, 2014). Madhupur village has agriculture practice, as their primary source of income. NH_4^+ was followed by NO_3^- and SO_4^{2-} with an average concentration of 16.4 ± 7.6 and $15.1 \pm 11.1 \mu\text{g m}^{-3}$, respectively. Despite having very few vehicles around the village, NO_3^- and SO_4^{2-} concentrations were higher in rural samples. Biomass burning for cooking and heating purposes during winters in the villages of the IGP is a very common practice, which releases harmful primary pollutants NO_2 and SO_2 (Singh *et al.*, 2014; Singh *et al.*, 2016). In the absence of coal burning by local people, two operational units of brick kiln in the nearby area (in the range of 5 km^2) were also observed as a significant source of SO_2 , which use low-grade coal as a fuel for the production. Since these precursor gases are highly hygroscopic, they quickly get incorporated into fog droplets. Also, they lead to the acidity in fog water samples in the absence of effective neutralization by alkaline species such as NH_4^+ and Ca^{2+} (Reactions (1)–(6)). Furthermore, the Ca^{2+} concentration was found to be $8.1 \pm 0.5 \mu\text{g m}^{-3}$ which is about three times lower as compared to urban site and could be associated with the soil dust resuspension. Following these, the mean K^+ concentration was $6.8 \pm 6.3 \mu\text{g m}^{-3}$ and found to be significantly higher as compared to the urban site due to the prevalence of biomass burning in rural areas during winters (Kaneyasu *et al.*, 1999). Average Na^+ concentration was found to be $6.6 \pm 6.7 \mu\text{g m}^{-3}$ and followed by Cl^- concentration with an average of $6.4 \pm 5.4 \mu\text{g m}^{-3}$. Alkaline saline soil dust have been reported to be the primary source of Na^+ and Cl^- over IGP owing to the prevalence of continental air masses from northwestern regions (Ghosh *et al.*, 2014). Mg^{2+} and NO_2^- were also found in a significant amount with average values of 1.2 ± 0.5 and $1.1 \pm 0.5 \mu\text{g m}^{-3}$, respectively.

Meteorological Impact and Monthly Variation

Changing meteorological conditions affect dilution and diffusion, as well as the accumulation and elimination of the

Fig. 6. Temporal variation of cations and anions at the rural site.

air pollutants in the lower atmosphere (Wang *et al.*, 2014; Xu *et al.*, 2018). Pollutants get concentrated in humid and stagnant weather conditions, which are predominant in winters over IGP. Since major properties of atmospheric components are linked to their solubility in water and NH_3 is reported to be highly soluble in increased RH conditions, NH_4^+ was found as the dominant species in the collected bulk samples which varied widely in each month at both the sites (Fig. 7). Despite higher RH at the rural site as compared to urban site in each winter month (Table 3), its concentration remained higher at urban site in all the four months which suggests additional biogenic emissions of NH_3 from the municipal sludge and sewage waste from the urban regions. However, its concentration is recorded to be highest in January at both the sites which can be corroborated with the

high RH, relatively lower temperature and shallow boundary layer in the month of January. Most of the other ions varied widely in each month and did not show any common pattern. Additionally, the mass ratio of $(\text{NO}_2^- + \text{NO}_3^-)/\text{SO}_4^{2-}$ have shown an average value of 1.5 for both the sites and observed to have similar monthly trend (Nov. > Dec. > Feb. > Jan.) as shown in Table 3. This has suggested towards higher emission from stationary sources during January month for both the sites. But on an average November month samples have shown higher concentration of ΣWSII with a spike in combustion-generated ions at both the sites (Table 3), which suggests that firecrackers pollution during Diwali festival and crop residue burning incidents in that period have a significant impact on the atmospheric composition of WSIs. The five days' air mass backward trajectories (plotted

Fig. 7. Monthly variation of analyzed ions. Box plots indicate the 25–27th percentiles and bars indicate the maximum and minimum value along with center line showing median value. Star is denoting the outlier value of the fluxes.

Table 3. Mean temperature, relative humidity (RH) and total WSII at two sites during winter months.

	Temperature (°C)		RH (%)		Σ WSII		$(\text{NO}_2^- + \text{NO}_3^-)/\text{SO}_4^{2-}$	
	Urban	Rural	Urban	Rural	Urban	Rural	Urban	Rural
16 November	21	21	55	63	159.6	141.9	1.7	1.9
16 December	17	16	69	85	119.5	81.7	1.6	1.8
17 January	16	15	71	79	132.5	108.4	1.2	0.9
17 February	21	19	52	63	123.5	87.2	1.4	1.1

using the Hybrid Single-Particle Lagrangian Integrated Trajectory [HYSPLIT] model of sampling duration, classified on a monthly basis, have also been traced to the upwind regions of the sampling sites particularly dominated from northwestern part at both the sites (Fig. 8). The northwestern region of IGP is known for the large-scale crop residue burning in November month which could also be contributing to the higher concentrations of WSII (Jain *et al.*, 2014; Singh and Kaskaoutis, 2014). Monthly comparison of major inorganic ions (Fig. 7) clearly shows that most of the ions were higher at the urban site as compared to the rural site in all the four months except K^+ , NO_3^- and SO_4^{2-} which is primarily due to plant-based combustion sources at the rural site.

Fog Scavenging Using Statistical Analysis

In order to understand the impact of fog occurrence on

ambient concentrations of WSII suspended in the atmosphere, the sample data were classified into *foggy days* and *non-foggy days* to perform a paired *t*-test. Due to unavailability of visibility data, *foggy days* were assumed as the days with more than 80% RH and a temperature less than 20°C combined with visible documentation fog occurrence. High RH values during foggy days promote the wet scavenging of aerosols and gases and subsequently, their deposition in the form of dewdrops (Nath and Yadav, 2018). Result of paired *t*-test at a 95% significance level at urban and rural site is shown in Table 4. The ambient concentrations of NH_4^+ , NO_2^- , NO_3^- and SO_4^{2-} were not affected by fog occurrence at both the sites, suggesting their presence in the form of aerosols or suspended as fog droplets. This can also be attributed to the semi-volatile nature of these ions. However, concentrations of Ca^{2+} and Na^+ were found to be

Fig. 8. Five days' backward air mass trajectories (HYSPLIT) at (A) urban and (B) rural sites (11 November, 12 December, 1 January and 2 February).

Table 4. Details of paired *t*-test, performed to identify the significant difference (at $p = 0.05$) in fog and non-fog days at each site.

WSII	p-value	
	Urban	Rural
Na ⁺	0.04*	0.03*
NH ₄ ⁺	0.88	0.63
K ⁺	0.05*	0.07
Ca ²⁺	0.00*	0.05*
Mg ²⁺	0.00*	0.19
Cl ⁻	0.13	0.02*
NO ₂ ⁻	0.07	0.08
NO ₃ ⁻	0.48	0.50
SO ₄ ²⁻	0.62	0.18

significantly different on foggy and non-foggy days at both the sites, showing greater scavenging by fog droplets and deposition in the form of dewdrops. A significant difference of K⁺ and Mg²⁺ on foggy days at urban site suggests its association with Ca²⁺ in the form of alkaline dust. Unlike urban site, the concentrations of Mg²⁺ and K⁺ were not altered based on fog occurrence at the rural site owing to its continuous emission during sampling period. Cl⁻ was found to be effectively scavenged during foggy days at the rural site but was not affected at the urban site, which can be attributed to its stable sources at the latter site.

Winter Chemistry of WSIIIs

In order to investigate the major interactions of WSIIIs occurring in the atmosphere, correlation coefficients (Table 5) along with the scatter plots (Figs. S1 and S2) were analyzed between each of the major cation with major anions.

Urban Site

Table 5 (Fig. S1) represents the relation of each anion with each of the cations at urban site. Despite being highest in concentration, NH₄⁺ showed least correlation with SO₄²⁻, Cl⁻ and NO₃⁻ ($r = 0.04$, 0.20 and 0.09 , respectively), which are the most important component of secondary aerosols; however, it showed a good correlation ($r = 0.71$ at $p = 0.01$) with NO₂⁻. This can be attributed to the possible heterogeneous gaseous reaction of HONO with NH₃ onto the fog droplets,

which lead to the formation of NH₄⁺ and NO₂⁻ as an end product. HONO has a maximum concentration in morning hours before sunrise during winters which also affects the stoichiometry of atmospheric aqueous-phase reactions (Finlayson-Pitts and Pitts, 2000). However, a good correlation between them is suggestive of their common emission sources in urban areas such as vehicular emission or incorporation of diffused gases into mist during the sampling process. Furthermore, the anions were found to be poorly correlated with Ca²⁺ and slightly positive with NO₂⁻ ($r = 0.27$), showing its limited presence as a secondary aerosol. Rather, it could be directly emitted from excessive road construction activities in the city along with other crustal elements. Ca²⁺ might also act as a surface for fog formation because of its higher solubility in the humid environment. K⁺ and Na⁺ have shown a strong correlation with Cl⁻ ($r = 0.87$ and 0.88 , respectively at $p = 0.01$) and a good correlation with NO₃⁻ ($r = 0.56$ and 0.56 , respectively at $p = 0.05$), which is indicating towards their presence in the form of secondary aerosols as KCl, KNO₃, NaCl and NaNO₃. SO₄²⁻ was also positively correlated with Na⁺ ($r = 0.46$) and K⁺ ($r = 0.44$ at $p = 0.05$), which suggests that they might act as primary alkaline species in the atmosphere for acid neutralization in urban samples.

Rural Site

Table 5 (Fig. S2) represents the relation of major anions with each cation at the rural site. Na⁺ has shown a strong positive correlation with Cl⁻ ($r = 0.60$ at $p = 0.01$), which shows the influence of alkaline saline soil dust or in the form of secondary salts as NaCl in the ambient air during sampling hours at rural site. Na⁺ has also shown a strong correlation with NO₂⁻ ($r = 0.66$ at $p = 0.01$), which implies to the formation of NaNO₂. Being dominant inorganic ion in the rural samples, NH₄⁺ has shown a good correlation with the NO₂⁻, NO₃⁻ and Cl⁻ ($r = 0.46$, 0.48 and 0.51 , respectively at $p = 0.05$) suggesting efficient neutralization of acidity and the formation of secondary aerosols, viz. NH₄NO₂ and NH₄NO₃. However, it was least correlated with SO₄²⁻ ($r = 0.17$). SO₄²⁻ has shown a strong correlation with K⁺ ($r = 0.63$ at $p = 0.01$), which suggests their common sources and strongly indicating towards biomass burning in rural areas. Furthermore, the good correlation of K⁺ with Cl⁻

Table 5. Correlation matrix representing *r*-value between the cations and anions of both the sites.

	Na ⁺	NH ₄ ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	NO ₂ ⁻	NO ₃ ⁻	SO ₄ ²⁻
Urban	Rural								
	Na ⁺	0.27	0.42	0.85**	0.80**	0.60**	0.66**	0.47*	0.17
	NH ₄ ⁺	0.03	0.26	0.32	0.37	0.51*	0.46*	0.48*	0.17
	K ⁺	0.93**	0.17	0.42	0.23	0.71**	0.29	0.16	0.63**
	Ca ²⁺	0.03	0.41*	0.16	0.82**	0.57**	0.80**	0.36	0.25
	Mg ²⁺	0.41*	0.25	0.48*	0.81**	0.59**	0.66**	0.23	-0.18
	Cl ⁻	0.88**	0.20	0.87**	0.17	0.45*	0.52*	0.30	0.40
	NO ₂ ⁻	0.30	0.71**	0.36	0.27	0.23	0.32	0.12	0.03
	NO ₃ ⁻	0.56*	0.09	0.56*	-0.19	0.08	0.58*	0.43*	0.23
	SO ₄ ²⁻	0.46*	0.04	0.44*	-0.15	0.20	0.39	0.12	0.51*

** Significant correlation at $p = 0.01$ level.

* Significant correlation at $p = 0.05$ level.

($r = 0.71$ at $p = 0.01$) suggests that the waste burning could be taking place for heating or cooking purposes during winters. Ca^{2+} and Mg^{2+} have shown highest correlation with NO_2^- ($r = 0.80$ and 0.66 at $p = 0.01$, respectively) as compared to other anions which suggest that crustal components might be providing active sites for nitrogenous gases oxidation.

Source Apportionment

Factor analysis is a statistical method, based on a mathematical model of the reduced factor analytical solution, to find small number of factors from a dataset of many correlated variables which explains a major part of the result thereby extracting latent information. To analyze factors, the original data matrix gets decomposed into the number of factor loading and a matrix of factor scores along with variance of dataset, i.e., analytical uncertainties. SPSS version 20.0 for Windows was used to analyze the principle components for each site. PCA was performed in order to determine the factors underlying the inter-correlations between the measured species, having a factor loading more than 0.5. In accordance with this, the grouping of ions in each factor was attributed to physical, chemical, meteorological reasons as well as to the common sources.

Urban Site

PCA of WSIs at urban site ($n = 41$; Table 6) identified four principle factors, which explains data loading for 91% (cumulative variance) where most of the components have significant loading, i.e., more than 0.5 values. The first factor explains about 45% of dataset, with the major loading of Na^+ , K^+ , Mg^{2+} , Cl^- , NO_3^- and SO_4^{2-} . This suggests the common emissions of K^+ , Cl^- , NO_3^- and SO_4^{2-} from municipal solid waste and biomass burning during winters as the dominant sources at urban site which are responsible for about half of the ambient levels of WSIs. Such attributions can be further corroborated with the higher ratios of Cl^-/K^+ (2.2) for municipal waste burning and $\text{SO}_4^{2-}/\text{K}^+$ (3.3) for biomass burning (Fourtziou *et al.*, 2017). The presence of Na^+ and Mg^{2+} in Factor-1 is indicating towards their existence in the form of NaCl and MgCl_2 salts. Second factor explains about 23% of dataset with a heavy loading of Ca^{2+} and NH_4^+ and light loading of Mg^{2+} and NO_2^- . This

suggests the oxidization of gases like NH_3 and NO_2 into NH_4^+ and NO_2^- on the dust particles, which is providing a surface for heterogeneous aqueous-phase interactions. NH_3 sources in urban areas mainly include biogenic emission from sewage microbial degradation (Jain *et al.*, 2000; Tiwari *et al.*, 2012; Behera *et al.*, 2013). Furthermore, the mean ratio of $\text{Mg}^{2+}/\text{Ca}^{2+}$ (0.08) has shown to have a crustal origin following the previously reported winter season ratio by Mu *et al.* (2019). Third factor explains 15% of dataset and primarily loaded with NO_2^- and NH_4^+ which indicates their common gaseous emission from vehicular exhausts. Fourth factor included only SO_4^{2-} and explains 8% of the dataset which suggests the SO_2 sources around the sampling sites. Coal burning in local food *dhabas* (restaurants) and heavy-duty (diesel) vehicles are the primary sources of SO_2 in urban areas. Vehicular emission of SO_4^{2-} was further supported by the lower mean ratio (1.2) of $\text{NO}_3^-/\text{SO}_4^{2-}$ (Rajput, 2018). PCA clearly indicates that primary sources at urban sites are solid waste burning, biomass burning, soil dust, vehicular exhausts and biogenic emissions.

Rural Site

PCA of WSIs at the rural site ($n = 22$; Table 7) identified three principal factors, which explains data loading for 80% cumulative variance where each factor has a variable loading more than 0.5 values. The first factor explains about more than half of the total variance, i.e., 51% with a high loading of Na^+ , Ca^{2+} , Mg^{2+} , Cl^- and NO_2^- which suggests the influence of natural sources like crustal dust and salts including dominant oxidation processes induced by HONO as a primary factor during early hours in winters. However, a higher ratio of $\text{Mg}^{2+}/\text{Ca}^{2+}$ (0.14) as compared to the urban site is indicating towards additional plant-based sources of Mg^{2+} . The dominance of K^+ and SO_4^{2-} in the second factor explains about 17% of the dataset, which is clearly indicating towards the biomass burning sources used for cooking and heating purposes in winters in rural areas. However, the brick kiln units have also been observed as an additional source of SO_2 , since none of the other coal-burning sources were observed in the area. Furthermore, the lower mean ratio of Cl^-/K^+ (1.3) due to increased levels of K^+ and a higher ratio of $\text{SO}_4^{2-}/\text{K}^+$ (4.4) due to increased concentration

Table 6. PCA results of urban site.

Components	Factor-1	Factor-2	Factor-3	Factor-4
Na^+	0.884	-0.288	-0.190	-0.212
NH_4^+	0.364	0.619	0.584	0.052
K^+	0.920	-0.150	-0.152	-0.187
Ca^{2+}	0.291	0.862	-0.327	0.090
Mg^{2+}	0.591	0.555	-0.493	0.211
Cl^-	0.897	-0.137	-0.139	-0.231
NO_2^-	0.460	0.377	0.654	-0.074
NO_3^-	0.677	-0.415	0.327	0.078
SO_4^{2-}	0.542	-0.403	0.035	0.711
% of variance	45	23	15	8
% cumulative	45	68	83	91
	Solid waste and biomass burning	Road dust, biogenic NH_3	Vehicular exhaust gases	Coal burning

Table 7. PCA results of rural site.

Components	Factor-1	Factor-2	Factor-3
Na ⁺	0.874	−0.219	−0.069
NH ₄ ⁺	0.473	0.087	0.687
K ⁺	0.515	0.727	−0.303
Ca ²⁺	0.896	−0.229	−0.150
Mg ²⁺	0.808	−0.433	−0.102
Cl [−]	0.822	0.176	−0.086
NO ₂ [−]	0.774	−0.364	−0.148
NO ₃ [−]	0.479	0.149	0.744
SO ₄ ^{2−}	−0.166	0.805	0.320
% of variance	51	17	12
% cumulative	51	68	80
	Soil dust, gaseous HONO	Biomass burning, brick kilns	Agriculture emissions, NH ₄ NO ₃

of SO₄^{2−} ions cumulatively indicated towards biomass and coal burning as their primary sources (Mu *et al.*, 2019). Third factor dominated with NH₄⁺ and NO₃[−] explains 12% of the dataset. This can be attributed to their common sources such as agriculture activities, gasoline vehicles and secondary aerosol formation as NH₄NO₃. Summing up, the PCA at rural site have shown that biomass burning, soil dust, coal combustion in brick kilns, agricultural emission (livestock and fertilizers) and light-duty vehicles as primary sources.

Overview of Research Conducted and Implications

Atmospheric abundance of WSIs has been assessed from an urban (Prayagraj) and a rural location (Madhupur) in Indo-Gangetic Plain. The study has identified the sources of contamination in fog water. The urban site was highly influenced by the emissions of automobiles, solid waste and biofuel combustion while the rural site was influenced by biomass burning, agricultural activities and brick kilns. The crustal sources also contributed significantly. The study suggests to develop the regulations for pollution control accordingly. The levels of sulfates and nitrates in fog water give an idea about their role in visibility reduction during foggy days. The knowledge of gas-to-particle transformation can partially be utilized in understanding the scavenging of cloud condensation nuclei in the region.

CONCLUSIONS

This study investigated the interactions of the major water-soluble inorganic ions (WSIs) in the early morning ambient air during winter and their principal causative factors at an urban and a rural site on the IGP. We found significantly high concentrations of cations and anions at both of the sites, largely owing to the higher humidity during wintertime and consequent aqueous-phase chemistry, which played a crucial role in the scavenging of pollutants and resulted in the rapid condensation and evaporation of water droplets on preexisting particles during the morning/foggy period. Compared to the urban site, the rural site displayed higher ambient concentrations of acidic species, which were primarily responsible for the lower pH at this location. In general, NH₄⁺, Ca²⁺, NO₃[−] and SO₄²⁺, as the dominant ionic species, clearly governed the ambient chemistry of the

WSIs. Furthermore, the higher mean concentration of ΣWSI during November (based on the collected samples) indicated that extreme pollution episodes arising from festivities and crop residue burning in this month may have altered the atmospheric ionic composition. Fog scavenging significantly influenced the levels of the dust-associated components but did not affect the other species (e.g., K⁺, NH₄⁺, NO₂[−], NO₃[−] and SO₄^{2−}). Natural sources of WSIs, such as crustal dust and biogenic emissions, were apparent at both sites. However, fossil fuel combustion, and solid waste and biofuel burning were the major anthropogenic contributors at the urban site, whereas biomass burning, brick kiln combustion and agricultural activity were the predominant ones at the rural site. The increased pollution, which is emitted by various sources, and the occasional spike in pollutant concentrations on the IGP is a serious concern in terms of both human health and regional ecosystems.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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