



## A Comparative Study on Fog and Dew Water Chemistry at New Delhi, India

Supriya Nath, Sudesh Yadav\*

*School of Environmental Sciences, Jawaharlal Nehru University, New Delhi-110067, India*

### ABSTRACT

Fog and dew, formed via different formation mechanisms, are suitable to study the liquid-gas-solid phase chemical interactions in the ambient atmosphere. A total of 24 fog and 19 dew samples were collected using Caltech Active Strand Cloud water Collector 2 and dew condensers, respectively, over New Delhi during winter months of 2014–15 and were characterised for pH and soluble inorganic ion using ion chromatograph. Dew samples were alkaline (pH =  $6.26 \pm 0.37$ ) in comparison to natural rainwater pH of 5.6 and fog collected at rooftop (pH =  $5.38 \pm 1.3$ ) and at ground level (pH =  $5.96 \pm 0.3$ ). The volume weighted mean equivalents of cations followed the order  $\text{NH}_4^+ > \text{Ca}^{2+} > \text{Mg}^{2+} \sim \text{K}^+ > \text{Na}^+$  and of anions as  $\text{SO}_4^{2-} > \text{NO}_3^- \sim \text{Cl}^- > \text{HCO}_3^- > \text{F}^- > \text{NO}_2^-$  in fog whereas the order for dew was  $\text{Ca}^{2+} > \text{NH}_4^+ > \text{Na}^+ > \text{K}^+ > \text{Mg}^{2+}$  and  $\text{SO}_4^{2-} \sim \text{HCO}_3^- > \text{Cl}^- > \text{NO}_2^- > \text{NO}_3^- > \text{F}^-$ . The  $\text{Ca}^{2+}$  ions were higher than  $\text{NH}_4^+$  in dew while  $\text{NH}_4^+$  was higher than  $\text{Ca}^{2+}$  in fog. Nitrite was higher in comparison to nitrate in dew while this was reverse in fog. Alkaline pH of dew samples might have played a role in the gas phase transfer and the base catalyzed transformation of  $\text{NO}_x$  to HONO and subsequent dissolution of HONO in dew in comparison to fog. Acidity was caused more by sulphate ions ( $\text{SO}_4^{2-}/\text{NO}_3^-$  ratio was 2.2 and 4.18 for fog and dew, respectively) but was effectively neutralised. Neutralisation factors were different in fog ( $\text{NH}_4^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$ ) and dew ( $\text{Ca}^{2+} > \text{NH}_4^+ > \text{Mg}^{2+}$ ). The differences in the fog and dew composition are primarily linked to their formation processes. The agricultural fields and fossil fuel combustion were sources for ammonium, sulphates, nitrate and nitrite whereas locally resuspended crustal materials added calcium and magnesium carbonates. Vehicular and plant emissions, biomass burning and the oxidation of volatile organic compounds seems to be responsible for higher organic acids in dew and fog.

**Keywords:** Neutralisation factors; Nitrite; Organic acids.

### INTRODUCTION

Dew water represents the condensation of atmospheric water on a surface whereas fog is suspension of water droplets in the ambient atmosphere. They also play significant role in different ecological and environmental processes (Fisak *et al.*, 2002) and impact air quality by accumulating pollutants (Borthagray *et al.*, 2010). Dew water can be considered as potential water resource in arid and semi arid regions (Sharan *et al.*, 2007; Tomaszkiwicz *et al.*, 2015). Fog reduces visibility and causes disruptions in rail, road and air traffic leading to severe economic losses. Fog intensity is also influenced by climate change phenomenon and air quality (Klemm and Lin, 2016). Both are considered as effective scavengers of gaseous and particulate pollutants and thus their removal from ambient atmosphere. The chemical composition of two is a cumulative outcome of gas-liquid-

solid heterogeneous interactions. However, fog chemistry is influenced by number and composition of the particles, gaseous species (Herckes *et al.*, 2007; Lekouch *et al.*, 2011) as well as by the moisture content and temperature in ambient atmosphere. Dew water chemistry is also influenced by nature of surface on which it is formed (Beysens *et al.*, 2006; Lekouch *et al.*, 2010). Hence, fog and dew are good indicators to understand pollution sources and chemical interactions.

Various studies regarding chemical characterization of dew have been carried at urban places like in France (Beysens *et al.*, 2006), in USA (Mulawa *et al.*, 1986; Pierson *et al.*, 1988), in Chile (Rubio *et al.*, 2002, 2008, 2009), in Poland (Polkowska *et al.*, 2008), in Germany (Acker *et al.*, 2008), in India (Khare *et al.*, 2000; Singh *et al.*, 2006; Lakhani *et al.*, 2012; Yadav and Kumar, 2014), in Japan (Okochi *et al.*, 1996; Chiwa *et al.*, 2003), in Taiwan (Simon *et al.*, 2016). Galeket *et al.* (2016) analysed urban dew water formation efficiency and chemistry at sites near Wroclaw, Poland. These studies remained focused on chemistry determining their acidic or alkaline nature while very few of them (Rubio *et al.*, 2002; Acker *et al.*, 2008; Rubio *et al.*, 2008) have studied about the nitrite in dew and related heterogeneous

\* Corresponding author.

Tel.: +91-11-26704197

E-mail address: sudesh27@hotmail.com

processes. Acker *et al.* (2008) measured nitrite in atmospheric liquid phase fog, dew and rainwater and found them as sink as well as source of  $\text{HNO}_2$ .

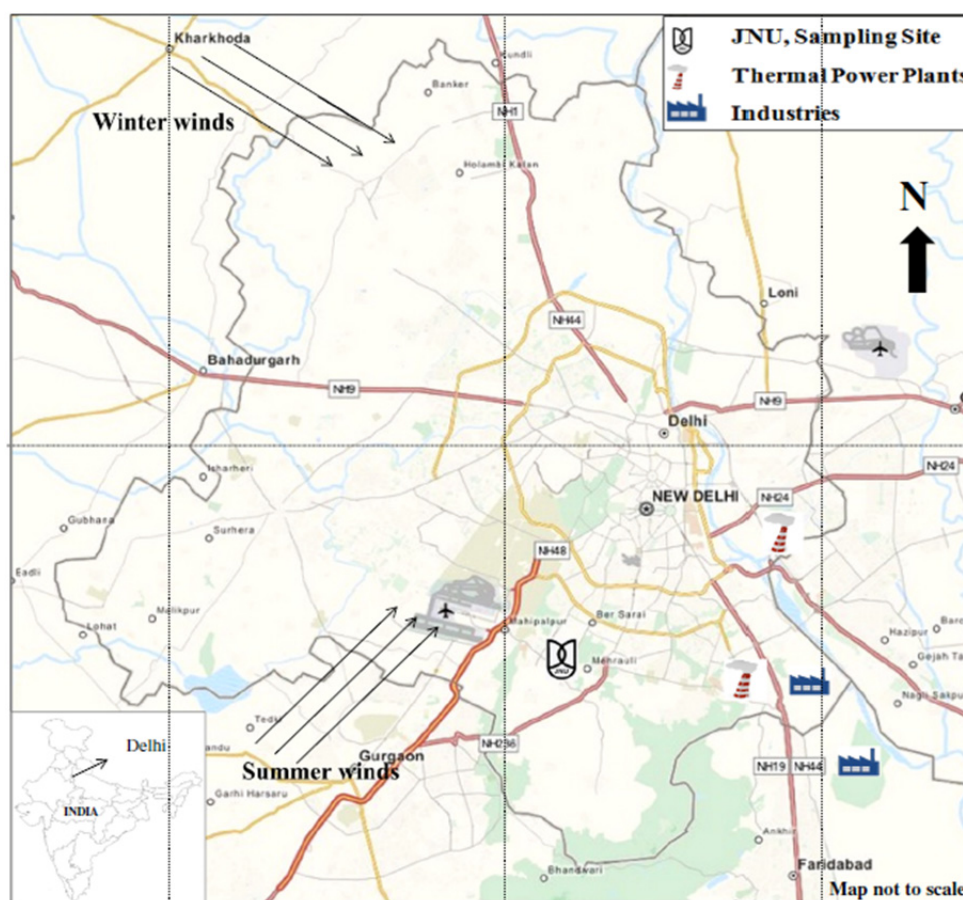
Fog chemistry has been widely studied at California and other locations of USA by Collett *et al.* (2008, 2002, 1999); Herckes *et al.* (2007). They have studied chemical composition, organic acids and buffering capacities of fog water. Other than inorganic soluble ions, formate and acetate ions have also been reported in atmospheric condensate, rainfall or other form of precipitation like fog and dew (Willey and Wilson, 1993; Khwaja, 1995; Khare *et al.*, 2000; Herckes *et al.*, 2013). Formate concentrations are found to be more than acetate in dew water due to more solubility of formate at lower pH in comparison to acetate (Khare *et al.*, 2000; Raja *et al.*, 2008). However, there is a lack of information about tartrate and citrate ions in fog and dew, which could be linked to their limited concentration (in  $\text{ng m}^{-3}$ ) in atmospheric aerosols (Rohrl and Lammel, 2002; Tsai *et al.*, 2013) or otherwise not attempted.

In spite of the fact that fog formation is a frequent phenomenon in north India during winter and have larger environmental and economic implications such as traffic disruptions due to visibility impairment, effects on crops and human health and role in water cycling and storage/recharge, limited information is available about fog chemistry in India (Khemani *et al.*, 1987; Kapoor *et al.*, 1993; Ali *et al.*, 2004). Recent studies in New Delhi on atmospheric

condensate (Kumar and Yadav, 2013) and dew water (Yadav and Kumar, 2014) chemistry and their comparison with rainwater reported high nitrite and lower nitrate in dew when compared with those in rainwater and explained its possible reasons as direct dissolution from gas to aqueous phase or through dissolution of HONO in alkaline dew. Therefore, this study was carried out with the objective to characterize and compare the chemistry of dew and fog in the urban environment of New Delhi, and to understand the chemical process involved.

## SAMPLING DETAILS

Fog and dew samples were collected at height of 15 meters on the roof top of School of Environmental Sciences (SES) building, Jawaharlal Nehru University (JNU), New New Delhi (Fig. 1). Fog samples were also collected near the surface at the ground level in JNU. The campus has limited sources of pollutants and represents a cleaner environment but it receives the atmospheric pollutants from nearby areas (Tandon *et al.*, 2008; Yadav and Kumar, 2014). New Delhi, the capital of India located in the tropical climate zone ( $28^\circ 35' \text{N}$ ,  $77^\circ 12' \text{E}$ ; 218 m MSL), is one of the most polluted cities of world with high population density (12,591 persons per square kilometer; <http://indiapopulation2017.in/population-of-delhi-2017.html>) and remains in news for worst air quality, particularly in winter months.



**Fig. 1.** Study area map showing sampling location and the dominant pollution sources.

Whole north India including the national capital, national capital region and the Indo Gangetic plains (IGP) remain covered with thick fog during winter months and large number of respiratory, asthmatic and cardiac cases are reported to hospital on account of poor air quality and fog. The major pollution sources are emissions from vehicles, coal fired power plants, and natural mineral dust (Yadav and Rajamani, 2004, 2006; Pathak *et al.*, 2013; Yadav and Kumar, 2014). New Delhi represents a climatic transition zone from semi-arid in the west bordering with the Great Indian desert to sub-humid in the east flanked with the River Yamuna. The sampling was carried out during winter season from December, 2014 to March, 2015. This period in New Delhi intermittent foggy condition with reduced visibility due to favourable conditions like low temperature (0–10°C), high relative humidity (close to 100%), stable atmosphere and temperature inversion (Ali *et al.*, 2004; Kumar and Yadav, 2013; Yadav and Kumar, 2014). The contributions from biomass burning increase with increase in combustion activity by general public to get rid of the severe cold during winter season. The average temperature and average relative humidity during the sampling period ranged between 9°C and 32°C and 74% to 95%, respectively.

Fog samples were collected using Caltech Active Strand Cloud water Collector (CASCC2; Demoz *et al.*, 1996; Collett *et al.*, 2008). After reviewing different standard methods for dew water collection (Nilsson, 1996; Takenaka *et al.*, 1999; Beysens *et al.*, 2003; Rubio *et al.*, 2002; Sharan *et al.*, 2007; Rubio *et al.*, 2008), dew samples were collected using pre-cleaned CRSQ-0.25 OPUR Dew Condenser (Beysens *et al.*, 2003, 2006). The samplers were placed after sunset and samples were taken before sunrise on non-rainy and non-foggy days to prevent dilution. For preventing any contamination and change in chemistry, all samples were subjected to the measurement of pH, electrical conductivity (EC), and total dissolved solids (TDS) immediately after the collection and measurement of volume using pH and EC meter of Eutech make. After this, all samples were filtered through 0.22 µm Millipore membrane filters. Filtrate was separated into three aliquots: first part was stored with chloroform for organic acid analysis, second part was stored as such for anion analysis and the third was stored after stabilization with HNO<sub>3</sub> for cation analysis. All samples were refrigerated at about 4°C before further analysis.

Major cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, and NH<sub>4</sub><sup>+</sup>), anions (F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) were analyzed using Metrohm Ion Chromatograph (IC) model 882 Compact IC pro equipped with conductivity channel. Cations were analyzed using Metrosep C4-150/4.0 column with 1.7 mM nitric and 0.7 mM dipicolinic acid as eluent and 0.9 mL min<sup>-1</sup> flow rate, and Metrosep A Supp 5-150/4.0 column with 3.2 mM sodium carbonate and 1 mM sodium bicarbonate as eluent and 0.7 mL min<sup>-1</sup> flow rate were used for cation and anion analysis, respectively. To check the repeatability of data, a few selected samples were repeated and reanalyzed on different day on the same IC machine. The Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup> ions in samples were also reanalyzed on Atomic Absorption Spectrometer (AAS) of Thermo Fisher Scientific make (model-iCE3000 series). The HCO<sub>3</sub><sup>-</sup> ions

were quantified using Metrohm-877 Titrino Plus.

Field and laboratory blanks were also collected/prepared and analyzed simultaneously with samples. All the physical measurements, sample filtration and storage and ionic analysis were carried out inside positive pressure clean lab having Class 100 airflow at SES, JNU, New Delhi.

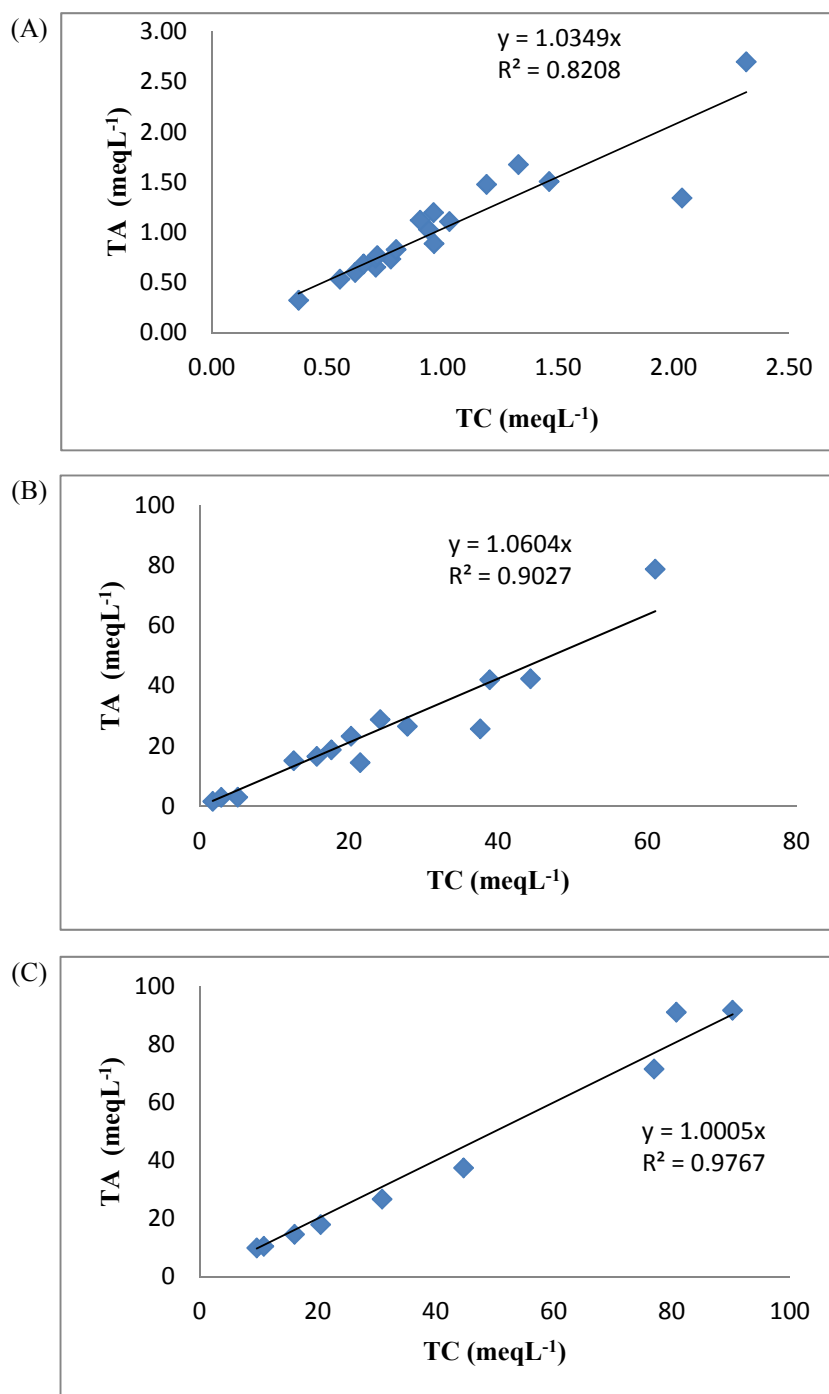
The IC was calibrated using the serially diluted standard stock solutions of ions procured from E-Merck, Germany. The standard, not used in the calibration, was run after every fourth sample to monitor the instrumental stability and precision of the data, if deviation was more than 5% the instrument was recalibrated. The correlation coefficient between total anions (TA) and total cations (TC) was observed in the range of 0.82 to 0.98 for all samples. The TC/TA ratio is well balanced i.e., both contribute almost equally to the total bulk ionic composition of fog and dew water in New Delhi (Fig. 2).

## RESULTS AND DISCUSSION

### pH and Conductivity Measurements

The pH of dew ranged from 5.68–6.99 and was lower than the earlier reported values in the range of 6.5–7.5 (Galek *et al.*, 2015 and references therein). However, a recent study by Galek *et al.* (2016) reported 4.5–6.1 (Avg. pH = 5.0). The dew samples were alkaline (Avg. pH = 6.26 ± 0.37) in comparison to fog samples collected at rooftop (pH = 5.38 ± 1.3) and ground level (Avg. pH = 5.96 ± 0.3) (Table 1). During dew formation on the collection surface, cation (Ca<sup>2+</sup>/Mg<sup>2+</sup>) rich particles could have entrapped within the droplet and therefore, the solubility of these ions from particles was more in dew whereas fog water-particle interactions take place in ambient air. Lekouch *et al.* (2010) have reported higher pH of dew (avg = 6.7) in comparison to rain (avg = 6.4) due to variations in the atmospheric composition of aerosols and gas with altitude and time of exposure by raindrop and dew drop. In addition, pH depends on the dissolution of gases like CO<sub>2</sub>, SO<sub>2</sub>, NO<sub>3</sub> and particles during droplet growth, condensation volume and condensation time (Lekouch *et al.*, 2010), the duration of time of exposure (Beysens *et al.*, 2006) and pollutant concentrations in ambient atmosphere, wind dispersion, rainfall before fog and dew events (Ali *et al.*, 2004). The sample volume of dew water and pH are inversely related (Fig. 3). Assuming that the rate of deposition of particles was constant, the equivalents of neutralizing cations added by dissolution of carbonates of calcium and magnesium were lowered by more volume of water resulting in less neutralization and lower pH in dew water (Lekouch *et al.*, 2011).

The Electrical conductivity (EC) of dew ranged from 76.7 to 506 µS cm<sup>-1</sup>, with a mean of 200.36 ± 124.76 µS cm<sup>-1</sup> (Table 1). The mean values are similar to that reported by Lekouch *et al.* (2010) (204 ± 177 µS cm<sup>-1</sup>) and are considered to be low due to low total mineralization and smaller than the standard value by European Commission for potable water (400 µS cm<sup>-1</sup>) at 20°C. Similar to pH, EC of dew decreases with the increase in sample volume (Fig. 3) as has also been reported by Lekouch *et al.* (2010), Beysens *et al.* (2006) for dew and Ali *et al.* (2004) for fog. The correlations



**Fig. 2.** Correlation between sum of total cations (TC) and total anions (TA) in A) dew samples B) fog samples of rooftop and C) fog samples of ground level collected over New Delhi.

among pH and EC with volume of the samples show negative trend but statistically non significant. This suggests that the relationship is highly non linear due to complex chemical interactions and require further investigations.

#### ***Ionic Composition of Dew and Fog***

The mean and volume weighted mean equivalents of soluble ions and other statistical details of the data on fog and dew samples are provided in Table 1. The soluble ion data on dew and fog is shown graphically in Fig. 4.

Ammonium and calcium are dominant cations present in dew and fog samples. The general order of abundance of cation in dew is  $\text{Ca}^{2+} > \text{NH}_4^+ > \text{Na}^+ > \text{K}^+ > \text{Mg}^{2+}$  (Fig. 4) while in fog samples collected at the rooftop, the order is  $\text{NH}_4^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ \sim \text{Na}^+$  (Fig. 4). Similarly, the fog samples collected near ground level has cations in the order of  $\text{NH}_4^+ \sim \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$  (Fig. 4). The  $\text{NH}_4^+$  ions were found to be the highest contributor of alkalinity. During winter of December and January, large  $\text{NH}_3$  emission has been reported from fertilizer applications, biomass

**Table 1.** Ionic concentration ( $\mu\text{eq L}^{-1}$ ) of dew (n = 19) and fog samples of rooftop (n = 14) and fog samples of the ground level (n = 10) collected during winter season over Delhi.

	DEW SAMPLES					FOG SAMPLES OF ROOFTOP					FOG SAMPLES OF GROUND LEVEL				
	Mean	VWM	Min	Max	S.D.	Mean	VWM	Min	Max	S.D.	Mean	VWM	Min	Max	S.D.
pH	6.26	6.23	5.68	6.99	0.37	5.38	5.4	5.1	6.98	1.3	5.96	5.81	5.54	6.48	0.3
EC	200.4	175.2	76.7	506	124.76	3501	3862.6	331	6590	2104.3	3454.6	3268.5	129.3	10650	3508.3
Na	69.4	60.6	15.7	162	39.8	782.5	521.3	90	1826.1	626.6	2140.0	695.1	286.6	6037.4	2345.6
NH <sub>4</sub>	352.0	287.1	176	700.5	175.7	12560	13706	465.1	30579	8564	19527	12416	3277	38050	13384
K	47.9	40.3	10.6	114.4	26.7	798.6	808.4	55.5	2055	614.1	2317.2	1257	320.7	5832	1822.5
Ca	493.2	412.5	125	1244	259.5	8789.6	8527.5	986.5	24442	7105.5	19229	10516	2460	37460	13612
Mg	44.3	29.3	5.0	162.2	43.7	1001	839	80.6	2795.6	904.7	2586.1	1184.0	170.3	7726	2507.1
F	39.1	34.7	10.5	80.7	20	735.2	766.7	156.4	1620.9	419.6	818	578.5	221.2	1669.3	472.5
Cl	198.4	158.6	23.6	613	126.8	7808.7	5700.9	333.4	20149	6620.6	13520	4198.9	965.4	32220	13161
NO <sub>3</sub>	85.7	59.2	17.2	389.3	82.5	4545.9	5159.4	253.7	15787	3962.9	9539.3	5168	1153	28927	9458.3
NO <sub>2</sub>	137.6	104.6	42.1	344.6	98.0	448.6	68.4	158.5	738.0	237.5	184.1	105.9	52.8	376.5	144.5
SO <sub>4</sub>	358.0	256.5	64.5	1353	307.1	11725	12794	886.7	40653	10476	17467	11136	2482	33786	12565
HCO <sub>3</sub>	282.9	244.4	121	522.1	106.7	2736.9	1257	1901	4130	1214.4	3740.8	2314.1	2630	4851.1	1570.3

burning and animal breeding (Bouwman *et al.*, 1997), human and animal excretion (Ali *et al.*, 2004) in New Delhi and vegetative emission from agricultural farms (Lekouch *et al.*, 2010; Simon *et al.*, 2016). The temperature inversion conditions and lowering of mixing height during night hours of winter season concentrates the pollutants near the ground level and the low temperature increases the dissolution of ammonia into water in ambient atmosphere (Kapoor *et al.*, 1993; Ali *et al.*, 2004; Cao *et al.*, 2009; Kumar and Yadav, 2013). Source of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  could come via dissolution of the secondary calcium carbonates present in aerosols (Yadav and Rajamani, 2004), construction activities going on around the sampling site and the re-suspension of surface dust (Tandon *et al.*, 2008; Kumar and Yadav, 2013). However, biomass burning and a small contribution from the dense forests nearby sampling sites may contribute to potassium (Ali *et al.*, 2004; Kumar and Yadav, 2013). In addition to contributions from local aerosols, winter time rains on account of winter disturbances bringing moisture from Mediterranean (Dimri *et al.*, 2015) could have added additional  $\text{Na}^+$  ions.

The soluble anions followed the order  $\text{SO}_4^{2-} > \text{HCO}_3^- > \text{Cl}^- > \text{NO}_2^- > \text{NO}_3^- > \text{F}^-$  in dew and  $\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^- > \text{F}^-$  in fog water (Table 1). Sulphate and chloride are the dominant anions present in the fog samples while sulphate and bicarbonate are dominant anions in dew samples. The higher abundance of  $\text{SO}_4^{2-}$  ion is linked to the emissions of the precursor gas  $\text{SO}_2$  from two coal fired power plants located in the vicinity of sampling site (Kumar and Yadav, 2013). Klemm and Lin (2016) have recently reported intensifications of fog with the presence of precursor gases like  $\text{SO}_2$ ,  $\text{NO}_2$  for formation of hygroscopic particles in ambient atmosphere. The presence of soluble Fe (III) and Mn (II) could accelerate the oxidations of  $\text{SO}_2$  to  $\text{SO}_4^{2-}$  ion and more so in alkaline pH range of dew and fog water (Collett *et al.*, 1999). The tropospheric ozone also provides a pathway  $\text{SO}_2$  oxidation under aqueous conditions (Hunt *et al.*, 2015). The more than one value of Cl/Na ratio indicate that chloride ions find additional sources other than sea salt origin or the salt lakes in the western side of New Delhi (250 km away) which could have come via south westerly's during summer (Yadav and Rajamani, 2004). These sources for chloride ions could be plastic burning as has been reported by Kumar *et al.* (2015). A large number of brick kilns around New Delhi (Tiwari *et al.*, 2007) or coal fired power plants are the possible sources of fluoride ions. Nitrate in samples could have resulted via light-mediated phase oxidation pathway starting from NO to  $\text{NO}_2$  and  $\text{NO}_3$  (Rondon and Sanhueza, 1989; Kumar and Yadav, 2013). The potential sources of NO emissions in this region include vehicular emissions, biomass burnings, agricultural fields as well as from crustal dust/aerosols.  $\text{NO}_2^-$  is major precursor of hydroxyl radicals in radiation fog (Anastasio and McGregor, 2001; Zhang and Anastasio, 2001) despite being less in concentration when compared with  $\text{NH}_4^+$  and  $\text{NO}_3^-$ .

$\text{NH}_4^+$  followed by  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  are dominant ions that contribute nearly 84% and 80% of the analysed soluble ionic content in fog samples of rooftop and near ground level, respectively. The relatively small contribution (9% in the



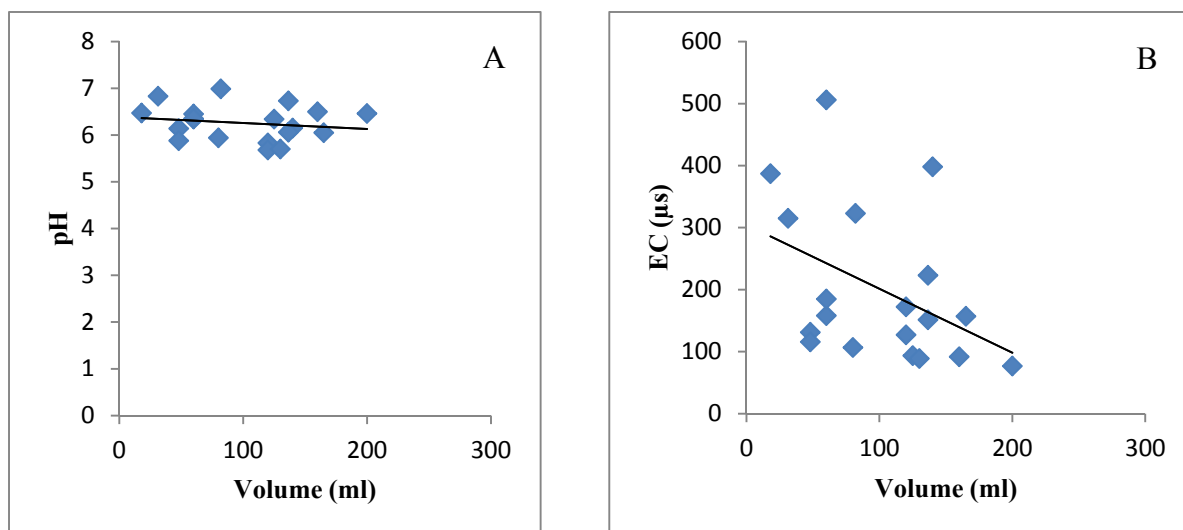


Fig. 3. Correlation plot between sampling volume and pH and EC in dew water collected over New Delhi.

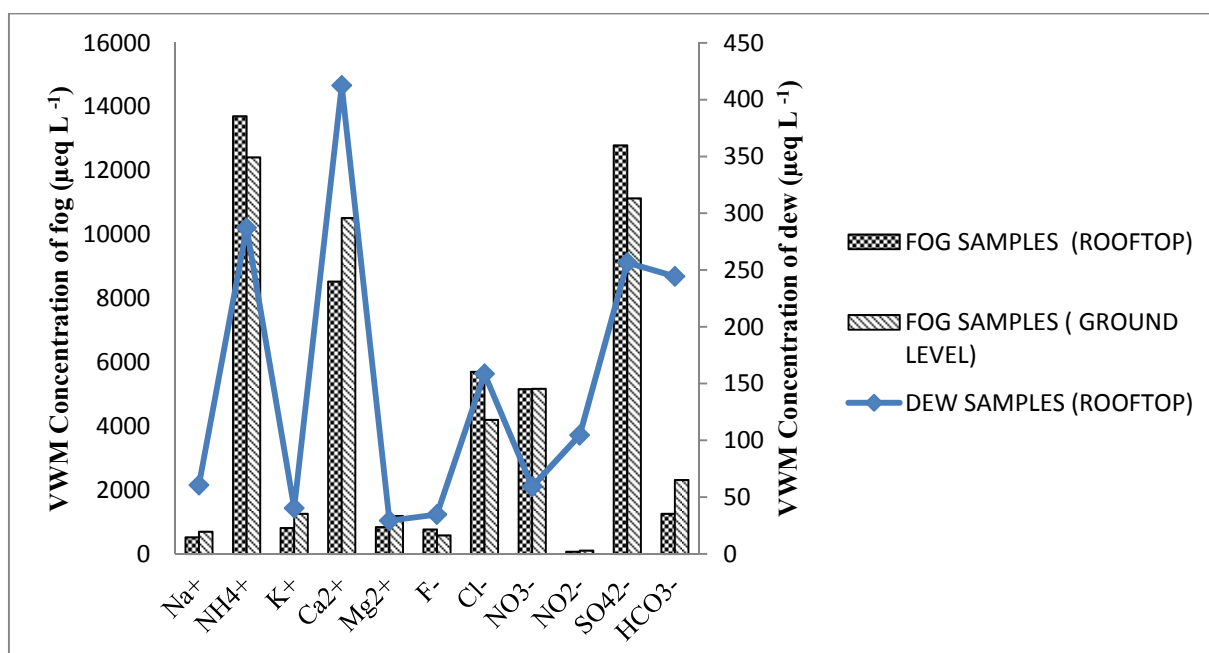


Fig. 4. Ionic composition of soluble ions (in µeq L<sup>-1</sup>) in fog and dew samples collected over New Delhi.

rooftop and 11% near ground level) of nitrate could be an outcome of introduction of cleaner fuel (compressed natural gas: CNG) in place of diesel as fuel in public transport and more stringent vehicular pollution control rules in New Delhi. Nitrate contributed only 5% in dew samples while the precursor nitrite contributed 8%, could be linked to aqueous phase chemical reaction leading to the conversion of nitrous acid into nitrite ( $\text{HONO}_{(\text{aq})} \rightarrow \text{H}^+ + \text{NO}_2^-_{(\text{aq})}$ ).

Dew formation coincides with the rise of HONO during night time and fall after sun rise due to degradation by photolysis (Rubio *et al.*, 2002). In absence of the photochemical sink of HONO, this gets trapped in the boundary layer during nighttime and result in high equivalents in dew. The prevailing temperature inversion conditions, high particulate matter from biomass burning and

high pH of dew are favorable conditions for dissolution of nitrite (Yadav and Kumar, 2014). High pH favors the transference of nitrous acid from gas phase to aqueous phase as pKa for HONO is 3.15 (Rubio *et al.*, 2008). The photo dissociation of HONO in dew after sun rise and on evaporation of dew water will release the NO<sub>2</sub><sup>-</sup> in the ambient atmosphere (Takenaka *et al.*, 1999; Rubio *et al.*, 2002; Acker *et al.*, 2008; Yadav and Kumar, 2014) which eventually get oxidized to nitrate. This adds to the nitrate equivalents in fog and results in higher nitrate compared to dew water which is no more in existence. This is to note that dew formation and evaporation of dew water after sun rise have implications to atmospheric chemistry. Dew formation reduces the HONO concentrations in atmosphere and the denitrification process (chemical reaction of ammonium, NO,

NO<sub>2</sub> with nitrite lead to formation of N<sub>2</sub>) suppresses ozone formation (Takenaka *et al.*, 2009) whereas on evaporation dew could be potential sources of ammonia as well as formic, acetic and HONO in early morning (Wentworth *et al.*, 2016). This requires further integrated experiments.

### Comparison of Fog with Dew Samples

The equivalents of soluble cations and anions are more in fog compared to dew (Table 1 and Fig. 4). However, the percentage contribution of each ion to the total ions in both fog and dew samples remains nearly similar. This suggests that both dew and fog chemistry gets the imprints of pollutants (gaseous and particles) from the environment in similar manner whereas their formation, post formation mechanisms and time of collection make the difference in absolute equivalents. Fog formation is near-surface weather phenomenon whereas dew represents condensation of water vapors on a surface. The gas-liquid-solid phase interactions in ambient atmosphere contribute more to fog water as the fog water remain in suspension whereas these interactions are limited to the surface area of the dew droplet (formed on a surface) exposed to the ambient atmosphere. The timing does matter, dew was collected between the sun set and sun rise whereas fog formations persist even after sun rise when the emissions start building up in ambient atmosphere.

Fog samples collected at the rooftop of SES has a greater volume weighted mean equivalents of major ions ammonium, sulphate, chloride and fluoride in comparison to the fog samples collected near the ground level. Whereas, the fog samples collected near the ground level showed higher volume weighted mean equivalents of calcium, sodium, potassium, magnesium, nitrate and bicarbonate ions. These samples probably have a higher input of coarse particles rich calcium, sodium, potassium, magnesium, nitrate and bicarbonate ions relative to rooftop samples, which have contributed more of thee ion in ground level samples.

When we compare percentage contribution of each ion to the total ionic sum of fog water samples studied with the other workers (supplementary Table 3), we find that we have observed higher percentage of nitrate, sulphate, potassium

and calcium but lower percentage of sodium, ammonium and magnesium in comparison to those reported by other studies at New Delhi and at Agra (Ali *et al.*, 2004; Lakhani *et al.*, 2007). The reasons could be representativeness of samples as number of samples studied were very small (2–4 at one site) and increase in the emissions of precursor gases (NO<sub>x</sub> and SO<sub>2</sub>) and sampling techniques.

### SO<sub>4</sub><sup>2-</sup>/NO<sub>3</sub><sup>-</sup> Ratio

SO<sub>4</sub><sup>2-</sup>/NO<sub>3</sub><sup>-</sup> ratio in both types of samples were calculated to find the contribution of anthropogenic sources (Migliavacca *et al.*, 2005; Kumar and Yadav, 2013) and relative contributions of mobile or stationary sources (Zhao *et al.*, 2016, Simon *et al.*, 2016). Coal burnings in power plants located in and around New Delhi are stationary sources and vehicular emissions are possible mobile source (Kumar and Yadav, 2013). The value of this ratio was 2.58 and 1.83 for fog at rooftop and ground level, respectively, and 4.18 for dew samples (Table 2). Relative contribution of SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> towards the acidification was computed using the ratio (SO<sub>4</sub><sup>2-</sup>/[SO<sub>4</sub><sup>2-</sup> + NO<sub>3</sub><sup>-</sup>]) and (NO<sub>3</sub><sup>-</sup>/[SO<sub>4</sub><sup>2-</sup> + NO<sub>3</sub><sup>-</sup>]) respectively. The contribution of H<sub>2</sub>SO<sub>4</sub> in dew samples was found as 81 % and that of HNO<sub>3</sub> was 19% but in fog samples it was 68% and 32%, respectively. The difference in contribution of nitrate (higher in fog samples than dew samples) could be due to higher nitrate of anthropogenic origin in fog as the soil derived nitrate would not add to acidity.

### Neutralization Factor (NF)

The role of NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> ions in neutralizing the acidity is assessed by calculating neutralization factors (NF) by following an empirical formula, NF<sub>X</sub> = [X/SO<sub>4</sub><sup>2-</sup> + NO<sub>3</sub><sup>-</sup>] where X is the cation for which NF is calculated (Kumar and Yadav, 2013). The strength of neutralization decreases in the order NH<sub>4</sub><sup>+</sup> > Ca<sup>2+</sup> and Mg<sup>2+</sup> for all fog sample similar to that reported by Simon *et al.* (2016) for fog water at four different sites in Taiwan. While dew samples showed the different trend of Ca<sup>2+</sup> > NH<sub>4</sub><sup>+</sup> and Mg<sup>2+</sup> (Table 3). This region has lot of biomass burning, cattle rearing and

**Table 2.** Comparison of average ratio of sulphate and nitrate of fog and dew samples collected at JNU, New Delhi.

	SO <sub>4</sub> <sup>2-</sup> (meq L <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> (meq L <sup>-1</sup> )	SO <sub>4</sub> <sup>2-</sup> /NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup> /[SO <sub>4</sub> <sup>2-</sup> + NO <sub>3</sub> <sup>-</sup> ]	NO <sub>3</sub> <sup>-</sup> /[SO <sub>4</sub> <sup>2-</sup> + NO <sub>3</sub> <sup>-</sup> ]
Dew	0.36	0.09	4.18	0.81	0.19
Fog (Rooftop)	11.73	4.55	2.58	0.72	0.28
Fog (Ground level)	17.47	9.54	1.83	0.65	0.35

**Table 3.** Neutralization factors of three different ionic species in dew and fog water samples analysed during present work and their comparison with previous studies in India.

Precipitation type	NF NH <sub>4</sub> <sup>+</sup>	NF Ca <sup>2+</sup>	NF Mg <sup>2+</sup>	Place	Reference
Dew water	1.06	1.37	0.10	Delhi	This study
Dew water	1.10	0.55	0.05	Delhi	Yadav and Kumar, 2014
Dew water	0.53	0.50	0.34	Rampur	Singh <i>et al.</i> , 2006
Fog water	0.73	0.61	0.07	Delhi	This study
Fog water	0.89	0.61	0.06	Delhi	Nath dissertation, 2013
Fog water	1.45	0.45	0.04	Delhi	Ali <i>et al.</i> , 2004
Atmospheric condensate	2.10	0.81	0.09	Delhi	Kumar and Yadav, 2013

fertilizer application which contribute significant amounts of  $\text{NH}_3$ . Its subsequent conversion to  $\text{NH}_4^+$  neutralizes acidification caused by  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  ions in fog and dew samples (Kapoor *et al.*, 1993; Cao *et al.*, 2009; Kumar and Yadav, 2013). Ammonium, calcium and magnesium in the near surface fog and dew samples get concentrated due to entrapment of ammonia and coarse particles near the surface under temperature inversion and low mixing height conditions (Kumar and Yadav, 2013). Simon *et al.* (2016) have found pH range of 2.27–5.95 in fog water collected from four sites in Taiwan due to limited presence of neutralizing cations. On comparing our fog data with the similar work done by Ali *et al.* (2004) in New Delhi, we found the trend in the strength of neutralization factors remains similar ( $\text{NH}_4^+ > \text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) to that reported by them. In case of dew samples, previous studies reported high neutralization by ammonium ions whereas we report it by calcium ion. This could be either related to lowering of sulphate and nitrate after introduction of CNG in public transport or higher emissions of these cations due to ongoing construction activities which are the possible source of calcium and magnesium (Kumar and Yadav, 2013). The straight comparisons with the previous studies cannot be made due to limited number of samples, lack of representativeness and limited temporal coverage in previous studies.

#### Correlation Analysis

Table 4 depicts correlation coefficients between ionic species in fog and dew samples. A correlation was observed between  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ( $r = 0.88$  for dew and  $r = 0.90$  for fog) suggesting that they have common crustal source.

Similarly, the acid forming anions  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  are closely correlated ( $r = 0.87$  for fog and  $r = 0.88$  for dew) indicating that they are simultaneously released from anthropogenic sources. Correlation coefficient values of  $\text{NH}_4^+$  vs.  $\text{NO}_3^- = 0.81$  and  $\text{NH}_4^+$  vs.  $\text{SO}_4^{2-} = 0.84$ , for fog, show that neutralization reaction forms  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{NO}_3$  while correlation coefficient values of  $\text{NH}_4^+$  vs.  $\text{NO}_3^- = 0.71$  and  $\text{NH}_4^+$  vs.  $\text{SO}_4^{2-} = 0.68$  but  $\text{NH}_4^+$  vs.  $\text{NO}_2^- = 0.94$  in dew samples, show that neutralization reaction forms  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{NO}_2$ . Calcium sulphate and calcium nitrate are also important neutralization product in fog and dew ( $\text{Ca}^{2+}$  vs.  $\text{SO}_4^{2-} = 0.83$  and  $\text{Ca}^{2+}$  vs.  $\text{NO}_3^- = 0.83$  for fog;  $\text{Ca}^{2+}$  vs.  $\text{SO}_4^{2-} = 0.86$  and  $\text{Ca}^{2+}$  vs.  $\text{NO}_3^- = 0.87$  for dew). These correlations indicate multiple neutralization reactions take place in fog and dew in the ambient atmosphere. Ammonium and calcium play important role in neutralizing acidity caused by sulphate and nitrate.

#### Organic Acids

The average level of concentration of formate and acetate in dew were  $124.49 \pm 46.16 \mu\text{eq L}^{-1}$  and  $214.36 \pm 78.74 \mu\text{eq L}^{-1}$ , respectively, which were much higher in comparison with those in previous studies (Willey and Wilson, 1993; Khare *et al.*, 2000; Tsai *et al.*, 2013). This points to the presence of sources of these organic acids in New Delhi, which is one of the most polluted city and further long term study is required to monitor these. It was interesting to find that all the organic acids were higher in concentration in fog samples at rooftop in comparison to those at ground level (Table 5). The dew samples had lower concentration when compared to fog in absolute terms as

**Table 4.** Correlation coefficient of all ionic species studied in fog samples (above) and dew samples (below).

	$\text{Na}^+$	$\text{NH}_4^+$	$\text{K}^+$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{F}^-$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{NO}_2^-$	$\text{SO}_4^{2-}$	$\text{HCO}_3^-$
$\text{Na}^+$		.70(**)	.85(**)	.81(**)	.876(**)	.44(*)	.62(**)	.68(**)	.55(**)	.48(*)	-0.21
$\text{NH}_4^+$	.50(*)		.68(**)	.94(**)	.81(**)	.81(**)	.85(**)	.81(**)	0.18	.84(**)	-0.15
$\text{K}^+$	.95(**)	.63(**)		.80(**)	.89(**)	.49(*)	.65(**)	.76(**)	0.3	.58(**)	-0.26
$\text{Ca}^{2+}$	.83(**)	.67(**)	.86(**)		.90(**)	.74(**)	.81(**)	.83(**)	0.27	.83(**)	-0.22
$\text{Mg}^{2+}$	.87(**)	.65(**)	.91(**)	.88(**)		.66(**)	.74(**)	.91(**)	0.27	.72(**)	-0.22
$\text{F}^-$	.54(*)	.70(**)	.58(**)	.64(**)	.58(**)		.76(**)	.80(**)	-0.16	.88(**)	-0.09
$\text{Cl}^-$	.65(**)	.47(*)	.68(**)	.86(**)	.68(**)	.58(**)		.79(**)	-0.05	.76(**)	-0.17
$\text{NO}_3^-$	.68(**)	.71(**)	.75(**)	.87(**)	.75(**)	.50(*)	.82(**)		-0.03	.87(**)	-0.16
$\text{NO}_2^-$	.57(**)	.94(**)	.66(**)	.75(**)	.73(**)	.74(**)	.47(*)	.68(**)		-0.16	0.28
$\text{SO}_4^{2-}$	.58(**)	.68(**)	.67(**)	.86(**)	.66(**)	.56(*)	.88(**)	.88(**)	.64(**)		-0.13
$\text{HCO}_3^-$	-0.22	-0.18	-0.31	-0.27	-0.38	-0.19	-.48(*)	-0.30	-0.08	-0.43	

\* Correlation is significant at the 0.05 level (2-tailed).

\*\* Correlation is significant at the 0.01 level (2-tailed); Bold: significant correlation  $> 0.8$ .

**Table 5.** Ionic concentration ( $\mu\text{eq L}^{-1}$ ) of organic acids of dew and fog samples of rooftop and fog samples at ground level collected during winter season over Delhi.

	Fog Samples (Rooftop)				Fog Samples (Ground level)				Dew Samples (Rooftop)			
	Tartrate	Formate	Citrate	Acetate	Tartrate	Formate	Citrate	Acetate	Tartrate	Formate	Citrate	Acetate
Mean	489.69	350.96	43.98	557.32	362.20	423.32	45.14	482.53	23.57	124.49	30.23	214.36
VWM	474.51	237.02	27.81	506.93	289.50	419.65	12.33	499.84	22.60	118.88	13.21	185.17
Min	55.59	63.42	20.08	32.66	25.36	32.68	31.65	32.00	4.07	21.24	17.31	132.30
Max	736.14	852.72	157.93	1781.33	685.37	964.15	58.64	887.16	87.84	241.66	108.99	404.62
S.D.	237.90	294.28	56.92	641.13	257.91	386.99	19.08	352.33	19.51	46.16	31.86	78.74



dew being a surface phenomenon captures much lesser pollutants as the surface area of dew drop in contact with the surface of samplers is not available for exchange of gases or particles in the ambient atmosphere. Volume weighted mean concentration of fog samples collected near the ground level and dew samples collected at rooftop show similar trend of acetate > formate > tartrate > citrate while fog samples collected at rooftop acetate > tartrate > formate > citrate. The higher percentage of acetate (41% in fog samples and 54% in dew samples) may indicate the effect of vehicular emission and biomass burning (Tsai *et al.*, 2013) or it may be emitted from vegetation and soil as reported by Wang *et al.* (2007). Formic and acetic acids are of local origin since there is lack of long range transport of acetic acid and formic acid (Raja *et al.*, 2008).

The formate and acetate ratio in all the studied fog and dew samples were less than 1 indicating that vehicular emissions being dominant source. Vehicles emits more of acetic acid compared to formic acid (Avery *et al.*, 2001; Raja *et al.*, 2008 and references therein). The high pH of samples further helped dissolution of more acetate than formate which could be possibly as formic acid ( $pK_a = 3.75$ ) dissolves more when pH is low (Khare *et al.*, 2000; Raja *et al.*, 2008).

Tartrate was present in quite significant percentage among organic acids in fog samples (38% in rooftop and 24% in ground level samples) but only 7% in dew. A possible source of tartrate is biomass burning as tartaric acid is present in plants. Tsai *et al.* (2013) reported the percentage of tartrate (2.93%) as well as citrate (3.4%) amongst the studied carboxylates in atmospheric aerosol. Citrate contributed least compared to other organic acids (2% and 1% in fog at rooftop and ground level, respectively, and 4% in dew). Citrus fruits are potential source of citrate and it is also released from molds like *Aspergillus niger* and *Penicillium*. Similar to soluble ions all organic acids were in higher concentration if fog compared to dew. The other pathway for formation of organic acids could be oxidation of volatile organic compounds.

## CONCLUSIONS

The fog and dew samples collected during winter of 2014–15 at a receptor site in New Delhi were alkaline in nature (Avg. pH = 6.26) compared to natural rainwater pH of 5.6. Though New Delhi encounters enough emissions of acid forming nitrogen and sulphur oxides but the dominance of cations ( $Ca^{2+}$  and  $NH_4^+$ ) could effectively neutralize the acidity. The collected fog and dew showed variations in ionic compositions within the samples. The observed order of ions of species in dew samples was  $Ca^{2+} > NH_4^+ > Na^+ > K^+ > Mg^{2+}$  for cations and  $SO_4^{2-} > HCO_3^- > Cl^- > NO_2^- > NO_3^- > F^-$  for anions.  $NH_4^+$  followed by  $SO_4^{2-}$ ,  $Ca^{2+}$  and  $Cl^-$  are dominant ions that contribute nearly 84% and 80% of the total soluble ionic content in fog samples of rooftop and ground level, respectively. The higher values of  $SO_4^{2-}/NO_3^-$  ratio in both fog and dew suggests the  $SO_4^{2-}$  emissions dominates over  $NO_3^-$  in the study area and the role of  $SO_4^{2-}$  in determining the acidity of the fog. The

strength of neutralization decreases in the order  $NH_4^+ > Ca^{2+}$  and  $Mg^{2+}$  in fog samples while this order for dew was  $Ca^{2+} > NH_4^+$  and  $Mg^{2+}$ . It may be concluded that the ammonia released from agricultural activities and the coarse particles due to re-suspension of dust are trapped near surface the surface under temperature inversion and low mixing height conditions during winter season and neutralize the acidity caused by nitric and sulphuric acids in fog and dew water. The nitrite concentration was found to be higher in dew in comparison to fog samples. The organic acids could come from biomass burning, vehicular emissions and plant emissions as well as could have been formed by oxidation pathways of volatile organic compounds in ambient atmosphere. The dew formation and evaporation of dew water can have implications to other atmospheric reactions in ambient conditions and require further investigations.

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