Chemical Characteristics of Precipitation during Winter Season over Delhi: Source Identification of Measured Species

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Abstract

The study of precipitation chemistry in the winter season over the northern part of India is vital as the atmosphere is highly loaded with atmospheric aerosols due to emissions and meteorological conditions. Precipitation samples were collected in Delhi and analyzed for major cations (Na^+ , NH_4^+ , K^+ , Ca^{2+} , and Mg^{2+}) and anions (F^- , Cl^- , NO_3^- , SO_4^{2-} and HCO_3^-) along with pH and conductivity. The volume weighted mean pH of rainwater (RW) was 5.76 ± 0.61 , with ~ 42% samples being acidic (mean pH = 5.20 of acidic rain). Specific conductivity was ~16 % (84.93 $\mu\text{S}/\text{cm}$) lower specific conductivity for the acid RW samples as compared to the non-acidic RW samples (101.20 $\mu\text{S}/\text{cm}$). The sum of ionic constituents was $1273.41 \pm 749.91 \mu\text{eq}/\text{l}$, with anion's sum contribution being 17 % lower than the sum of cations. Neutralization factors of major cations were in the order of Ca^{2+} (0.83) > NH_4^+ (0.36) > Mg^{2+} (0.11) over Delhi. Second higher (cation) contribution of NH_4^+ in RW over Delhi may be attributed to the ever increasing vehicular density and the initiation of catalytic converters in public transport. Different source apportionment methods, including principal component analysis (PCA), enrichment factor (EF), and back-trajectory (72 h) analysis were used for estimating the sources of RW. Trajectory analysis indicated three different air masses over Delhi of easterly, westerly and southerly/southeasterly wind regime. The PCA analysis shows three major factors for measured ions and was assigned to mixed source influenced by crustal, anthropogenic and marine origins, whereas, NH_4^+ and HCO_3^- to the local biomass burning and soil dust respectively.

Keywords: Chemical characteristics; Acid rain; Back trajectory, Principle component analysis

Introduction

Global concern about climate change and atmospheric chemistry over the past decades has led to additional investigations on atmospheric aerosols (Menon *et al.*, 2002; Aneja *et al.*, 2006). Ever increasing the quantity of atmospheric aerosols as a function of human and anthropogenic activities, consequently, impart an increasing impact on climate change (IPCC, 2001, 2007). A dynamic association existing between atmospheric aerosols'

sources, transportation trajectories, and their deposition sites vary according to different pollutants in the atmosphere (Kuniyal *et al.*, 2015). Chemical constituency of atmospheric aerosols can be reviewed by evaluating their acidic and alkaline nature (Safai *et al.*, 2010). Investigation of precipitation is one of the appropriate methodologies to access the chemical composition of atmospheric pollutants (Tiwari *et al.*, 2016). High frequency of aerosol fog/haze is prevalent over the North India including Delhi during the winter months (December to February) (Ganguly *et al.*, 2006). It gets abridged due to intermittent precipitation under the influence of Western Disturbances (WD), non-monsoonal precipitation systems in the westerly's (Ali *et al.*, 2004). The areal extension of the winter precipitation increases over the north India when such WD's interacts with southwesterly winds from the Arabian Sea and easterly/southeasterly from the Bay of Bengal (Chand and Singh, 2015).

Rainfall during the prolonged winter fog is a vital process for scavenging atmospheric pollutants (Tiwari *et al.*, 2016). Fog forms in the lower layer of the troposphere where aerosols and gases are most abundant. Rain drops are quite large, almost 100 times higher than fog droplets (Lange *et al.*, 2003; Ali *et al.*, 2004), hence, the concentrations of RW is a considerable determinant of the atmospheric chemical composition during the pre-existing fog aerosols. Atmospheric particles and gases affect the chemistry of rainwater (RW: precipitation) and reveal the air quality of the area where rain occurs (Al-Khashman, 2009). Rainfall is affected by local and transported particles from the vicinity (Chate *et al.*, 2011; Akpo *et al.*, 2015; Tiwari *et al.*, 2016). The dissolved ions in the rainwater give details on both local and long-range transported atmospheric pollutants and alteration in the rainfall's effect on ecosystems through wet deposition (Li *et al.*, 2007). A combination of local and regional pollutants, cloud formation processes, and precipitation amounts affects the chemical composition of RW (Zhao *et al.*, 2008; Calvo *et al.*, 2010). Quantitative measurement of wet deposition compositions determines the relative contributions of the various natural and anthropogenic sources. The scavenging of atmospheric pollutants affects the chemical composition and the pH of rainwater. The acidic rain is primarily caused by incorporation of anthropogenic pollutants such as oxides of sulfur and nitrogen and other acid precursors (Migliavacca *et al.*, 2005; Bisht *et al.*, 2015), whereas, neutralization of acidity in RW can be due to airborne dust and ammonia released from natural and man-made sources (Al-Momani *et al.*, 1995). The amount of the air pollutant reduction by precipitation scavenging effect can be affected by the amount, duration, and intensity of rainfall. Real rainfall events have several characteristics such as rainfall volume, duration, average intensity, inter-event time (IET), peak intensity, and a number of peaks.

Different climatic conditions influence trace substance concentrations in the RW and gases like SO₂ and NO₂ are converted into acidic forms after getting dissolved in cloud water (Baron and Denning, 1993). Due to the influence of natural and anthropogenic particles, the chemistry of RW varies from synoptic scale to mesoscale (Kulshrestha *et al.*, 2005; Tiwari *et al.*, 2016); thereby providing the input of anthropogenic as well as natural components of various ecosystems. In recent years, studies on precipitation chemistry over Indian region have been conducted especially during the south-west summer monsoon season (Safai *et al.*, 2010; Das *et al.*, 2011; Salve *et al.*, 2011; Tiwari *et al.*, 2012; Budhavant *et al.*, 2014; Bisht *et al.*, 2015; Tiwari *et al.*, 2016; references therein), however, there is a lack of information on the winter RW chemistry over the northern part of India leaving crucial gaps in the scientific understanding of atmospheric pollutants. Therefore, there is always a larger need to generate new and better quality data on RW chemistry over these Indian regions. Over national capital

region of Delhi, around 13-15 days of rainfall is experienced during the winter season. The present work is envisaged to bridge this knowledge gap of RW chemistry during the winter season over Delhi by estimating the atmospheric deposition and evaluating the characteristics of species over the study region of north India. The second and third objectives are to identify possible sources of the various constituents of RW and comparison of the results with the past studies across India and abroad respectively.

Experimental Setup

Site Description

Rainwater samples collected during the winter season (1st December 2014 to 28th February 2015) in the premises of Indian Institute of Tropical Meteorology (IITM), New Delhi branch (28.62°N 77.17°E), lying in central Delhi. The site is surrounded by a green belt (three sides) and residential colony (one side). The meteorological data of three different meteorological observatories (MO's) spread across National Capital Region (NCR) of Delhi was simultaneously analyzed during the study period. These MO's are located at Indira Gandhi International Palam Airport (PLM) (28.55°N 77.09°E), Hindon Airport (HND) (28.43°N, 77.22°E) and Safdarjung Airport (SFD) (28.35°N, 77.12°E). Delhi is characterized by topographical areas like the extension of the Aravalli ridge, forests, the rivers Ganga, Yamuna, and Hindon, fertile cultivated land, and is a dynamic rural-urban region with a total population of approximately 46 million (Tyagi *et al.*, 2016). The Delhi in northern India is influenced by four major seasons; winter (December to February), SW summer monsoon (July to September.), pre-monsoon (March to June and post-monsoon (October to November) (IMD, 2016). Winter season is the coldest period of the year characterized by low temperatures, poor visibility conditions, and low boundary layer heights. During such conditions, pollutants do not disperse or mix with free troposphere (Tiwari *et al.*, 2008). The impact of such conditions is discernible as poor visibility and high levels of pollutants over Delhi and adjoining region. During the winter season, on an average (monthly) 4 to 6 Western Disturbances (WD's) move across north India and break the spell of the high frequency of widespread fog by causing clouding and precipitation over the region (Kumar and Yadav, 2015).

Sampling Collection Procedure

A total of seven RW samples were collected during the study period by rain collectors at about 15 m above the ground level, on the rooftop of a building of the Institute situated in the thoroughly urbanized central part of Delhi. The sampling area is primarily a residential area, and no large pollutant source exists nearby which could have influenced the sampling site directly (Fig.1). The RW samples were taken on an event-to-event basis. Rain collector consists of a polypropylene funnel (20 cm in diameter) with a 2-l polypropylene bottle (Tiwari *et al.*, 2012). The rain collector was washed with triple distilled water twice daily in the morning and evening and also prior to installation of the new bottle and after the collection of each sample for prevention of any type of contaminations. Immediately after collection, a small portion of collected samples was used for pH and electrical conductivity measurements and those samples were drained after the measurement. The pH was measured

soon after the collection using a digital pH meter (Sartorius Professional Meter, PP20) which was standardized by standard solutions of pH of 4.0 and 9.2. Thymol (200 mg L⁻¹) was added to the samples as a preservative to prevent the decomposition of volatile components and ammonium (Gillett and Ayers, 1991). The samples were then stored in a refrigerator at 4°C until chemical analysis.

Fig. 1: Map of National Capital Region (NCR) of Delhi depicting sampling location at Indian Institute of Tropical Meteorology (IITM) and meteorological observatories: Indira Gandhi International Palam Airport (PLM), Hindon Airport (HND) and Safdarjung Airport (SFD).

Chemical Analysis and Quality Control

The RW samples were filtered using 0.45 μm Millipore filter paper and transferred to 100 ml polypropylene bottles pre-cleaned in Milli-Q water. The major chemical species such as anions (F^- , Cl^- , NO_3^- and SO_4^{2-}) and cations (Na^+ , NH_4^+ , K^+ , Ca^{2+} and Mg^{2+}) were quantitatively determined by Ion Chromatograph (DIONEX-2000, USA). The analytical column IonPac-AS15 with micro-membrane suppressor ASR Sultra II 2 mm, 38 mM Potassium Hydroxide and the IonPac-CS17 column with micro-membrane suppressor CSRS ultra II 2 mm, 6 mM methyl sulfonic acid as eluents and triple distilled water as regenerator were used for anion and cations, respectively. The details of the chemical analysis procedure are discussed elsewhere (Tiwari *et al.*, 2012; Bisht *et al.*, 2015). The data quality was assessed by ionic balance, which is an indicator of the completeness of measured parameters. The ionic ratio between the sum of anions and sum of cations in the present study was 0.83, that is, less than unity, it is due to organics. A significant correlation ($r = 0.82$) at 99 % confidence level was found in between sum of anions and cations (Fig.2), which are within the range of quantitative ionic balance (Sanusi *et al.*, 1996). It indicated the nearby completeness of the analyzed ions. Several field blank samples were also analyzed for the correction of the sample data. The detection limits for Na^+ , NH_4^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , NO_3^- and SO_4^{2-} are 0.05, 0.06, 0.08, 0.1, 0.05, 0.06, 0.08 and 0.07 ppm respectively.

Fig. 2: Regression analysis between sums of anions and sums of cations of winter rainwater.

Results and Discussion

Meteorological Parameters Associated with Rain Occurrences during the Winter Season

Information on meteorological elements namely, dry bulb temperatures, relative humidity (RH), the frequency of fog occurrences and the number of RW samples collected at Delhi during the winter season, 2014 -2015 are presented in Table-1. The monthly occurrence of fog over SFD/PLM/HND MO's in Dec was 21/19/22 days whereas in Jan & Feb was 30/30/30 and 16/20/16 respectively. The monthly average temperatures (°C) over SFD MO in Dec/Jan/Feb were 15.5 ± 4.6 / 12.8 ± 1.6 / 19.1 ± 2.6 respectively whereas PLM MO recorded 13.4 ± 5.8 / 11.9 ± 3.3 / 19.0 ± 5.2 in Dec/Jan/Feb respectively and HND MO recorded 12.7 ± 5.9 / 11.6 ± 3.4 / 17.6 ± 5.3 in Dec/Jan/Feb respectively. The monthly average RH (%) over SFD MO in Dec/Jan/Feb was 69 ± 13 / 78 ± 09 / 65 ± 10 respectively whereas PLM MO recorded 74 ± 25 / 87 ± 15 / 64 ± 22 in Dec/Jan/Feb respectively and HND MO recorded 76 ± 25 / 91 ± 15 / 75 ± 22 in Dec/Jan/Feb respectively. The seasonal rain occurrence in winter season 2014-15 is ≈ 13 ; monthly occurrence being 2/9/2 in Dec/Jan/Feb respectively but only 07 RW samples, (1/5/1 in Dec/Jan/Feb respectively) were selected for analysis. This is because the other samples were discarded either due to their being contaminated in some way or due to their not being enough in the amount needed for a complete chemical analysis.

Table-1: Fog, precipitation and other meteorology parameters during winter 2014-15 of Delhi.

Month	MO	Fog frequency	Rainfall Frequency	Rainfall	Rain Samples	Met Elements			
		(days)	(days)	(mm)	Quantity	Temp (° C)		RH (%)	
						Mean	SD	Mean	SD
Dec 2014	SFD	21	2	13.4	1	15.5	4.6	69	13
	PLM	19	2	17.4		13.4	5.8	74	25
	HND	22	2	6.3		12.7	5.9	76	25
Jan 2015	SFD	30	9	23.9	5	12.8	1.6	78	9
	PLM	30	9	26.7		11.9	3.3	87	15
	HND	30	9	24.2		11.6	3.4	91	15
Feb 2015	SFD	16	4	2	1	19.1	2.6	65	10
	PLM	20	2	5.8		19.0	5.2	64	22
	HND	16	2	0.7		17.6	5.3	75	22

Variability of pH and Specific Conductivity

The definition of acidic precipitation is a pH less than 5.65. This is the pH associated with the weak solution of carbonic acid (H_2CO_3) that forms when water droplets in clouds are in chemical equilibrium with CO_2 . The increased CO_2 concentration in the atmosphere (~400 ppm) is through the burning of fossil fuels like coal, oil, natural gas etc. (Charlson and Rodhe, 1982). The volume-weighted mean (VWM) of pH value during the present study over Delhi was 5.76 ± 0.61 varying from 4.49 to 6.27 (Fig. 3) indicating the generally non-acidic nature of the RW over Delhi. However, in few cases, the VWM pH values were found to be lower than the threshold value for acidic RW. During the study period, ~ 42% of the RW samples were acidic (mean pH = 5.20) and rest of the samples were more basic than “acid rain.” Very high concentrations of SO_4^{2-} and NO_3^- might be responsible for acidic pH, especially in case of sample V. The episode of acid rain in the winter season indicates that emission of oxides of nitrate and sulphate, precursor gases for acid formation in atmosphere, continues to be high in Delhi despite tough initiatives of Indian government to alleviate pollution by launching of compressed natural gas (CNG) as the primary fuel for public transport in the city and relocation of polluting industries outside New Delhi. Also, organic acids could be boosting acidity in RW over Delhi. The organic acids, in particular, formic and acetic acids play a significant role in precipitation acidity in urban areas (Pen˜a *et al.*, 2002). Tiwari *et al.* (2007) reported alkaline nature of RW having an average pH (6.39) at eight different locations around National Capital Region of Delhi ranging from 5.77 to 6.62. The measured specific conductivity during the study period was 94.22 $\mu\text{S}/\text{cm}$ and varied from 40.33 to 191.90 $\mu\text{S}/\text{cm}$. The specific conductivity was found to be having ~16 % (84.93 $\mu\text{S}/\text{cm}$) lower specific conductivity for the acidic RW samples as compared to the non-acidic RW samples (101.20 $\mu\text{S}/\text{cm}$). Thus, higher concentrations of alkaline species produced such more basic samples (Pi˜neiro *et al.*, 2014; Tiwari *et al.*, 2016).

Fig. 3: Mean pH variation of winter rainwater samples at Delhi. Note Green line indicates the mean pH and Red line indicates the neutral cloud water pH. Samples I (December, 2014), II to VI (January, 2015) and VII (February, 2015).

Ionic Composition of Rainwater

A function of the proportion of acidic and alkaline constituents in the RW sample defines the chemistry of rainwater. The volume weighted means (VWM) of measured chemical components were calculated according to the formula proposed by Galloway et al. (1984) and summarized in Table-2. During the study period, it was found that the sum of volume weighted means (VWM) of ionic constituents over Delhi was $1273.41 \pm 749.91 \mu\text{eq/l}$ which is lower than the value ($1924 \pm 1633.6 \mu\text{eq/l}$) reported in New Delhi during the winter season (December – February) (Kumar *et al.*, 2014). A Large value of standard deviation is due to the small resolution of the data and large sample-to-sample variability. The contribution of anions in the sum of measured ion was 17 % lower than the measured sum of cations. The dominant ions in RW were calcium (Ca^{2+}), sulfate (SO_4^{2-}) and ammonium (NH_4^+), and their weighted mean concentrations were 394.72 ± 193.52 , 353.88 ± 214.91 and $172.91 \pm 83.32 \mu\text{eq/l}$, respectively. The very high concentrations of Ca^{2+} , and SO_4^{2-} could be due to pollution sources, transport of pollutants and windblown dust whereas higher concentrations of NH_4^+ may be attributed to increased humidity levels favoring partitioning into the aerosol phase (Singh and Kulshrestha, 2012). Delhi is considered among the most polluted megacities of the world and the air quality report published by the Central Pollution Control Board (CPCB), Government of India (GoI) reported that Delhi has exceeded the annual average respirable particulate matter (RSPM) concentration limit by more than four times the national annual standards (Maji et al., 2015). The ionic concentrations ($\mu\text{eq/l}$) followed the sequence of $\text{Ca}^{2+} > \text{SO}_4^{2-} > \text{NH}_4^+ > \text{NO}_3^- > \text{Cl}^- > \text{Na}^+ > \text{Mg}^{2+} > \text{F}^- > \text{K}^+ > \text{HCO}_3^-$

whereas the category-wise abundance was in the order of $\text{Ca}^{2+} > \text{NH}_4^+ > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$ for cations and $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^- > \text{F}^- > \text{HCO}_3^-$ for the anions. The percentage contribution of individual cations and anions in RW were calculated and depicted in Fig. 4. It may be noted that among the cations, Ca^{2+} alone contributed to about 57 % of the total cationic strength of wet precipitation, whereas, among the anions, SO_4^{2-} made up about 64 % of total anionic strength. The overall contributions of cations and anions to the ionic strength were 55% and 45%, respectively, indicating nearly equal distribution. Kumar *et al.* (2014) recorded average cations as 52 % and an average anion as 48 % in RW over Delhi during January 2010 – March 2011. Most of the available research work is based on the data sets for annual average (monsoon season); information on the winter season for comparison was not available. Precipitation analysis over Delhi's environment reflects high-soluble ion load compared with other studies. Precipitation of Delhi are enriched in soluble Ca^{2+} and NH_4^+ ions compared with that from other places, and these cations are responsible for alkaline nature of RW, whereas, there have been cases of acid rain in China due to high nitrate and sulfate (Wang and Han, 2011; Kumar *et al.*, 2014). These studies indicate that RW chemistry is subjective and depends on geographical region and confined local pollution sources. The mean values of SO_4^{2-} (353.88 $\mu\text{eq/l}$) and of NO_3^- (120 $\mu\text{eq/l}$) were approximately 35 and 43 times higher than the proposed background hemispheric values (10 and 2.8 $\mu\text{eq/l}$) respectively at remote sites (Galloway *et al.*, 1982; Casimiro *et al.*, 1991). This may be due to secondary particles may be having the highest deposition fluxes. The mean ionic representation in winter RW samples suggests that Ca^{2+} contributed highest (31%) followed by SO_4^{2-} (28%) and NH_4^+ (14%), while NO_3^- (9%) ion makes a relatively moderate contribution compared with Cl^- (6%) and Na^+ (%) ions in RW. The high Ca^{2+} over Delhi may be attributed to the calcareous soil aerosolized into the atmosphere and washed out into the rain (Tiwari *et al.*, 2016). High concentrations of Ca^{2+} are found in the precipitation collected in the initial stages of an event signifying rapid below-cloud scavenging of coarse calcium-containing particles (Chate *et al.*, 2011). Ca^{2+} concentrations could also be linked to suspended road dust (Sanusi *et al.*, 1996). The composition of precipitation over north India during the December to February reflects the marine origin of sea salt such as sodium and chloride as precipitation is due to the WD originating from the Caspian Sea and interacting with feeder moist airmass of Arabian Sea during the transit. The fraction of non-marine constituents could be due to the entrainment of atmospheric particulate matter in the precipitation en route the trajectories of air masses (Bisht *et al.*, 2015). However, NH_4^+ ion makes 14 % of the total cations mass, which was the highest contribution after Ca^{2+} . The concentration of NH_4^+ over Delhi varied from 72.22 to 330.56 $\mu\text{eq/l}$, with the mean of 172.91 ± 83.32 $\mu\text{eq/l}$. The high concentrations of NH_4^+ might be due to agricultural activities and biomass burning (Khattak *et al.*, 2012). The role of ammonium into the atmosphere works as a neutralizing agent of acids caused by H_2SO_4 and HNO_3 in the RW and form as new salts like ammonium sulfate and nitrate (Bisht *et al.*, 2015). The source of acidic species such as SO_4^{2-} and NO_3^- ions may be either from local sources or long-range transport pollutants. The concentration of NO_3^- (120.54 ± 80.09 $\mu\text{eq/l}$) in RW was also found higher at Delhi, which might be due to oxidation of NO_x emitted from various sources such as combustion of fossil fuel, industrial activities, and biomass burning (Seinfeld and Pandis, 2006). Further, significant concentrations of K^+ (13.84 ± 8.35 $\mu\text{eq/l}$) in the air mass confirmed the influence of biomass burning. In general, K^+ is considered as a tracer for biomass burning (Kulshrestha *et al.*, 2004). The high concentrations of soil-originated elements such as Mg^{2+} (50.33 ± 33.04 $\mu\text{eq/l}$) and K^+ (13.84 ± 8.35 $\mu\text{eq/l}$) in the RW during the study period were mainly due to high levels of total suspended particles/dusty soil, which are locally build up or transported from other places. Hence, these constituents

enter into RW by rainout and washout processes. The northern part of India is generally dusty and is a major contributor to total suspended particulate matter in the air (Tiwari *et al.*, 2009).

Fig. 4: Percentage contribution of total ionic composition in rainwater over Delhi during winter season.

Table-2: The volume weighted means (VWM) concentrations ($\mu\text{eq/l}$) of measured ionic species, pH and conductivity in winter rainwater over Delhi in 2014-15.

	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Ca ²⁺	Mg ²⁺	HCO ₃ ⁻	pH	Cond.
Mean	19.59	76.59	120.54	353.88	62.40	172.91	13.84	394.72	50.33	8.62	5.76	94.22
SD	13.74	57.19	80.09	214.91	59.18	83.32	8.35	193.52	33.04	6.55	0.61	50.71
Max	47.68	178.91	243.05	761.20	178.69	330.56	28.57	687.32	113.25	16.60	6.27	191.90
Min	7.74	22.60	36.68	115.69	8.65	72.22	5.56	135.20	19.75	0.35	4.59	40.33

Marine Influence

The influence of marine and non-marine source to the RW during the study period was assessed by calculating the equivalent ratio of measured ions using sodium as the reference element (Table-3). It is assumed that all sodium is of marine origin (Singh *et al.*, 2007). Table-3 shows the calculated enrichment factors (EF) of Cl⁻, Mg²⁺, K⁺, Ca²⁺ and SO₄²⁻ in reference to Na⁺ using following equation $EF = (\chi_c / Na^+)_{\text{Rain}} / (\chi_c / Na^+)_{\text{Sea}}$, where χ_c is the concentration of desired ionic species ($\mu\text{eq/l}$) (Zhang *et al.*, 2007; Bisht *et al.*, 2015). The sea-salt fraction (SSF) and non-sea-salt fraction (NSSF) were also calculated as $100 * [1/(EF)]$ and $100 - \text{SSF} (\%)$ respectively. The analysis of EF reveals that all compounds are enriched with higher than unity, specifying considerable influences of other sources instead

of marine sources. A fraction of non-marine constituents may be contributed to the entrainment of atmospheric particulate matter in the RW along the trajectory path of air masses (Norman *et al.*, 2001). The high values of EF of Ca^{2+} , K^+ , and SO_4^{2-} point towards their anthropogenic origin. The EF of Mg^{2+} indicates the marine source connectivity in RW samples (Zunckel *et al.*, 2003; Migliavacca *et al.*, 2004). The ratios of Cl^-/Na^+ (1.23), $\text{Mg}^{2+}/\text{Na}^+$ (0.81), K^+/Na^+ (0.22), $\text{Ca}^{2+}/\text{Na}^+$ (6.33) and $\text{SO}_4^{2-}/\text{Na}^+$ (5.67) were found to be higher than that of seawater (1.16), divulging that crustal (soil dust) and anthropogenic contribution of these ions are in the precipitation over Delhi. The predominant source of Cl^- in the precipitation is sea spray. The compounds containing Ca^{2+} , Mg^{2+} and K^+ are added to the atmosphere by soil erosion in the form of their carbonate salts (Ali *et al.*, 2004). The NSSF of Cl^- , Ca^{2+} , K^+ , Mg^{2+} , and SO_4^{2-} are 5.48, 99.31, 90.17, 71.86 and 97.80 %, respectively, substantiating the dominance of crustal or anthropogenic sources of Ca^{2+} , K^+ , Mg^{2+} , and SO_4^{2-} . Various studies have sighted similar results (Rastogi and Sarin, 2005; Gobre *et al.*, 2010; Kumar *et al.*, 2014; Bisht *et al.*, 2015). The major source of calcium in Indian precipitation is soil dust particles emitted from the earth's surface (Kulshrestha *et al.*, 2003; Tiwari *et al.*, 2009).

Table-3: Equivalent concentration ratios of ionic components with respect to sodium.

	Cl^-/Na^+	$\text{Mg}^{2+}/\text{Na}^+$	K^+/Na^+	$\text{Ca}^{2+}/\text{Na}^+$	$\text{SO}_4^{2-}/\text{Na}^+$
Rainwater	1.23	0.81	0.22	6.33	5.67
Seawater *	1.16	0.227	0.0218	0.0439	0.125
EF	1.06	3.55	10.17	144.08	45.37
SSF(%)	94.52	28.14	9.83	0.69	2.20
NSSF(%)	5.48	71.86	90.17	99.31	97.80

Keene *et al.* (1986)

Contributions of Sulfuric and Nitric Acid to Total Acidity in the Rainwater

To understand the relative contributions of sulfuric and nitric acid to the total acidity in RW (Chate and Devara, 2009), the ratios between SO_4^{2-} and NO_3^- were estimated and compared with studies undertaken in India and abroad (Table-4). The ratio between SO_4^{2-} and NO_3^- was found to be 2.94 ± 2.64 , suggesting that the contribution to the acidity in RW was about 75% due to sulfuric acid and 25 % from nitric acid. The high influence of sulfur was due to urban industrial activities and vehicular emission. Bisht *et al.* (2015) reported that a low concentration of NO_3^- due very small inputs of nitrogenous fertilizers in the region caused by low crop density in the prolonged period of dry weather. The observed ratio was quite similar to various parts of India (Gobre *et al.*, 2010; Tiwari *et al.*, 2012; Kumar *et al.*, 2014; Bisht *et al.*, 2015; Tiwari *et al.*, 2016; Kumar *et al.*, 2016); however, higher ratios were found overseas in Singapore, Beijing (China), Guaiba (Brazil), Erzurum (Turkey), and Guangzhou (China) (Flues *et al.*, 2002; Yang *et al.*, 2004; Migliavacca *et al.*, 2005; Bayraktar and Turalioglu, 2005; Cao *et al.*, 2009). The relative contributions of the ions to the acidity of RW were variable for the event to event and location to location. Earlier studies reported the contributions of H_2SO_4 and HNO_3 in RW were between 60–70% and 30–40%, respectively (Al-Khashman, 2005; Tiwari *et al.*, 2012; Bisht *et al.*, 2015; Tiwari *et al.*, 2016). The ratios $\text{NH}_4^+/\text{NO}_3^-$ and $\text{NH}_4^+/\text{SO}_4^{2-}$ were 1.43 and 0.48 respectively.

Table-4: Comparison ratio of $\text{SO}_4^{2-}/\text{NO}_3^-$ at various locations in India and abroad.

Location	$\text{SO}_4^{2-}/\text{NO}_3^-$	References
NCR of Delhi, India	2.94	Present Study
Indo- Gangetic Plains, India	1.79	Tiwari <i>et al.</i> , 2016
Gulmarg, J & K State, India	1.45	Kumar <i>et al.</i> , 2016
Varanasi, India	2.2	Bisht <i>et al.</i> , 2015
New Delhi (Winter season)	2.21	Kumar <i>et al.</i> , 2014
Kullu, India	1.47	Tiwari <i>et al.</i> , 2012
Goa, India	1.92	Gobre <i>et al.</i> , 2010
Guangzhou, China	3.06	Cao <i>et al.</i> , 2009
Erzurum, Turkey	11.6	Bayraktar and Turalioglu, 2005
Guaiba, Brazil	8.7	Migliavacca <i>et al.</i> , 2005
Beijing, China	2.96	Yang <i>et al.</i> , 2004
Singapore	3.5	Flues <i>et al.</i> , 2002

Acidification and Neutralization Potentials

Sulphuric (H_2SO_4), nitric (HNO_3), and some organic acids are the main contributors to the wet precipitation acidification process (Migliavacca *et al.*, 2005; Zhao *et al.*, 2013). Relative contribution of SO_4^{2-} and NO_3^- toward acidification were computed using the ratio $[\text{SO}_4^{2-}/(\text{SO}_4^{2-} + \text{NO}_3^-)]$ and $[\text{NO}_3^-/(\text{SO}_4^{2-} + \text{NO}_3^-)]$ respectively. H_2SO_4 and HNO_3 contributed 75 and 25 % respectively, to the acidity in winter RW over Delhi, signifying that sulfur-related emissions are a major causal factor for acidity compared with nitrogen oxides. Similar observations have been made in Delhi (Kumar *et al.*, 2014) and over coastal India cities (Das *et al.*, 2010). The source of SO_4^{2-} may be traced back to thermal power plant emissions and crustal sources (Migliavacca *et al.*, 2005; Fang *et al.*, 2013).

The neutralization factors (NF) are calculated for NH_4^+ , Ca^{2+} and Mg^{2+} using formula: $\text{NF}_X = [\text{X}/\text{SO}_4^{2-} + \text{NO}_3^-]$ where X is the cation for which NF is calculated. The winter season average NFs of cations follow the order Ca^{2+} (0.83) > NH_4^+ (0.36) > Mg^{2+} (0.11) over Delhi. In this study, Ca^{2+} was the more important neutralization substance than NH_4^+ . In another study, Kumar *et al.* (2014) also found similar pattern over Delhi in the winter season of year 2010-11 with order of NFs: NH_4^+ (0.82) > Ca^{2+} (0.79) > Mg^{2+} (0.07), however, Ali *et al.* (2004) reported Ca^{2+} as major neutralizing species in RW samples of the winter season collected during 2001–2003 over Delhi. The higher contribution of NH_4^+ the second largest cation in RW over Delhi may be attributed to the ever increasing vehicular density and to the initiation of catalytic converters in public transport. The catalytic convertor-fitted vehicles causing NH_4^+ emissions have been described in previous studies across other parts of the country (Kumar *et al.*, 2014; and references therein). A strong connection between NH_3 and CO emissions and vehicle density has been found in an urban area of Rome (Perrino *et al.*, 2002). For the present study, the implementation of catalytic converters and clean fuel for transport fleet in Delhi may have reduced CO and NO emissions along with a significant positive contribution to NH_3 emissions.

Trajectory Analysis for source Analysis

To investigate the origins of pollutants in RW over Delhi, 72-h air mass backward trajectories were computed for each rain event using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model of the National Oceanic and Atmospheric Administration (NOAA), USA (Draxler and Rolph, 2003). The back-trajectories model was run for 500 m altitude for representing the boundary layer. Based on the backward trajectories and re-analysis of meteorological data, the air masses in the rainy days in the present study may be broadly divided into three different clusters (Fig. 5). Air masses in ‘Cluster 1’ (easterly wind regime) contributed 65.3% of the total rainfall during the winter season observations. This cluster of air masses originated from Himalayan range, traveled through a populated region of Uttar Pradesh accounted for 43.9% of Σ ions during sampling periods. Air masses in ‘Cluster 2’ (westerly wind regime), accounting for 6% of the rainfall, were transferred from Thar desert of central Pakistan and Rajasthan. Air masses in ‘Cluster 2’ accounted for 29.3% of Σ ions during sampling periods. This cluster of air masses, characterized by high loadings of ionic species, was significantly polluted due to low rainfall amount and heavy sand and dust emissions along the passing areas in wintertime. Tiwari *et al.*, (2014) found that back-trajectories coming from Thar Desert region are one of the major sources of enhanced PM mass concentrations over Delhi. Air masses in ‘Cluster 3’ (southerly/southeasterly wind regime) contributing 28.7% of the total sampled rainfall, was primarily from the region of central India. Air masses in ‘Cluster 3’ accounted for 26.8 % of Σ ions. Guttikunda *et al.*, (2014) highlighted that the particulate matter pollution in Central India is highest due to the density of the power plants in the region and high installed generation capacity. The majority of acidic rain events were of ‘Cluster 3’ airmass followed by ‘Cluster 1’; however, the rains were alkaline when the winds were ‘Cluster 2’ type. It may be noted that the trajectory information has certain inherent restrictions due to the chances of resources originated from one location being mixed with others.

Fig. 5: Representative wind directions drawn by HYSPLIT Trajectory Model.

Principal Component Analysis

Principal components analysis (PCA) was performed on the RW data set comprised of major ions to identify and associate their possible sources. The software used for PCA

analysis was SPSS 16.0 for Windows. All data used for PCA analysis were the first auto-scaled, as they had the same importance for sample discrimination (Cerqueira *et al.*, 2014). Factors with an eigenvalue >1 were retained. PCA yielded in total three significant factors, explaining about 95.6% of the total data variance. Loadings of the varimax rotated factors are presented in Table-5. The first factor (Factor 1) explains 73.5% of the total variance, characterized by a high loading of the most ions (F^- , Cl^- , NO_3^- , SO_4^{2-} , Na^+ , K^+ , Ca^{2+} and Mg^{2+}) except ammonium and bicarbonate. It indicates a well-mixed source influenced by crustal, anthropogenic as well as marine origins, possibly localized as well as transported over a long distance. The second factor (Factor 2) is shown by a high loading of NH_4^+ accounting for 11.4% of the total variance and engaging a local biomass burning and agricultural activities because of low wind speed and temperature along with lower boundary layer heights. The third factor (Factor 3) is highly loaded by HCO_3^- with a variation of 10.7%. The higher HCO_3^- loading at this factor can be associated to Ca^{2+} and Mg^{2+} neutralization process of rain acids, by suspended $CaCO_3$ and $MgCO_3$ in air, originated mostly from soil dust (Shrestha *et al.*, 2013; Cerqueira *et al.*, 2014).

Table-5: Factor analysis on the chemical species of rainwater.

Variable	Factor 1	Factor 2	Factor 3
F^-	0.899*	0.095	0.318
Cl^-	0.973*	-0.069	-0.187
NO_3^-	0.925*	-0.138	-0.233
SO_4^{2-}	0.951*	0.185	0.108
HCO_3^-	0.329	-0.188	0.904*
Na^+	0.972*	-0.116	-0.041
NH_4^+	0.156	0.976*	0.027
K^+	0.954*	-0.201	-0.202
Ca^{2+}	0.938*	0.178	0.01
Mg^{2+}	0.985*	-0.02	-0.07
Eigen values	7.356	1.14	1.068
Variance %	73.56	11.40	10.68
Cumulative %	73.56	84.96	95.64
Probable Origin	Mixed Sources	Biomass burning	Roadside dust

*Bold data indicate that the loading for the variables is higher than 0.50.

Conclusions

Chemical characteristics of precipitation were investigated during the winter season of 2014-15 at an urban site in Delhi. The weighted mean pH and specific conductivity of RW were 5.76 ± 0.61 and $31.6 \pm 31.0 \mu S/cm$, respectively with ~ 42% samples being acidic (mean pH = 5.20). The contribution of SO_4^{2-} and NO_3^- to the acidic rain samples were 74%

and 26 % respectively. The specific conductivity was found to be having ~16 % (84.93 $\mu\text{S}/\text{cm}$) lower specific conductivity for the acid RW samples as compared to the non-acidic RW samples (101.20 $\mu\text{S}/\text{cm}$). The sum of the measured VWM of ionic constituents was $1273.41 \pm 749.91 \mu\text{eq}/\text{l}$, with the contribution of anions in the sum of the measured ion being 17 % lower than the measured sum of cations. The mean values of SO_4^{2-} (353.9 $\mu\text{eq}/\text{l}$) and of NO_3^- (120 $\mu\text{eq}/\text{l}$) were approximately 35 and 43 times higher than the proposed background hemispheric values (10 and 2.8 $\mu\text{eq}/\text{l}$) respectively at remote sites. NH_4^+ ion makes 14 % of the total cation mass, which was the highest contribution after Ca^{2+} . The high concentrations of NH_4^+ might be due to agricultural activities and biomass burning. Equivalent ratio (EF) method was used to identify the influence of marine and non-marine source to the RW. The ratios of Cl^-/Na^+ (1.23), $\text{Mg}^{2+}/\text{Na}^+$ (0.81), K^+/Na^+ (0.22), $\text{Ca}^{2+}/\text{Na}^+$ (6.33) and $\text{SO}_4^{2-}/\text{Na}^+$ (5.67) were found to be higher than that of seawater, divulging that crustal (soil dust) and anthropogenic contribution of these ions are in the precipitation over Delhi. Neutralization factors of cations follow in the order of Ca^{2+} (0.83) > NH_4^+ (0.36) > Mg^{2+} (0.11) over Delhi. Second higher contribution of NH_4^+ in RW over Delhi may be attributed to the ever increasing vehicular density and the initiation of catalytic converters in public transport. Back-trajectory analysis (72 h) indicated that the air masses over Delhi can be divided into three clusters, prevailing from easterly, westerly and southerly/southeasterly wind regime respectively. PCA was performed, grouping the major analyzed cations and anions into three different factors and were assigned to mixed source influenced by crustal, anthropogenic and marine origins whereas NH_4^+ to local biomass burning and HCO_3^- to soil dust.

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