Sources of chemical species in rainwater during monsoon and non-monsoonal periods over two mega cities in India and dominant source region of secondary aerosols

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HIGHLIGHTS

- 76% higher loading of chemical constituents over Delhi than Pune.
- Higher secondary aerosols in RW over Delhi from NW direction.
- ~4 and 26% acidic samples were observed in Pune and Delhi.
- Lower concentrations of ions from the Arabian Sea.

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ABSTRACT

Samples of rainwater (RW) were collected to characterize the chemistry and sources in two representative megacities at Pune (Southwest) and Delhi (Northern) India from 2011 to 2014 across two seasons: monsoon (MN) and non-monsoon (NMN). Collected RW samples were analyzed for major chemical constituents (F\textsuperscript{−}, Cl\textsuperscript{−}, SO\textsubscript{4}\textsuperscript{2−}, NO\textsubscript{3}\textsuperscript{−}, NH\textsubscript{4}\textsuperscript{+}, Na\textsuperscript{+}, K\textsuperscript{+}, Ca\textsuperscript{2+}, and Mg\textsuperscript{2+}), pH and conductivity. In addition, bicarbonate (HCO\textsubscript{3}−) was also estimated. The mean pH values of the RW were >6 at Pune and <6 at Delhi and 4% and 26% were acidic, respectively. The mean sum of all measured ionic species in Pune and Delhi was 304.7 and 536.4 meq/l, respectively, indicating that significant atmospheric pollution effects in these Indian mega cities. Both the Ca\textsuperscript{2+} and SO\textsubscript{4}\textsuperscript{2−} were the dominant ions, accounting for 43% (Pune) and 54% (Delhi) of the total ions. The sum of measured ions during the NMN period was greater than the NM period by a factor of 1.5 for Pune (278.4: NM and 412.1: NMN meq/l) and a factor of about 2.5 for Delhi (406 and 1037.7 meq/l). The contributions of SO\textsubscript{4}\textsuperscript{2−} and NO\textsubscript{3}\textsuperscript{−} to the RW acidity were ~40% and 60%, respectively, indicating that significant atmospheric pollution effects in these Indian mega cities. Both the Ca\textsuperscript{2+} and SO\textsubscript{4}\textsuperscript{2−} were the dominant ions, accounting for 43% (Pune) and 54% (Delhi) of the total ions. The sum of measured ions during the NMN period was greater than the NM period by a factor of 1.5 for Pune (278.4: NM and 412.1: NMN meq/l) and a factor of about 2.5 for Delhi (406 and 1037.7 meq/l). The contributions of SO\textsubscript{4}\textsuperscript{2−} and NO\textsubscript{3}\textsuperscript{−} to the RW acidity were ~40% and 60%, respectively, at Pune and correspondingly, 36% and 64% at Delhi. The concentrations of secondary aerosols (SO\textsubscript{4}\textsuperscript{2−} and NO\textsubscript{3}\textsuperscript{−}) were higher by a factor of two and three when the air masses were transported to Pune from the continental side. At Delhi, the concentrations of SO\textsubscript{4}\textsuperscript{2−} and NO\textsubscript{3}\textsuperscript{−} were significantly higher when the air masses arrive from Punjab, Haryana, and Pakistan indicating the greater atmospheric pollution over the Indo-Gangetic Plain. Positive matrix factorization was applied to the source apportionment of the deposition fluxes of these ions. Three factors were obtained for Pune and four for Delhi. The sources at Pune were secondary aerosols from fossil fuel combustion, soil dust, and marine, whereas, at Delhi, the sources were soil, fossil fuel combustion, biomass burning, and industrial chlorine.

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1. Introduction

The effects of the tropospheric aerosol on climate are not quantitatively understood because of limited information on its chemical composition, physical and optical properties and its geographical distribution (Arimoto et al., 2004). Previously, remotely sensed data and in situ measurements of atmospheric aerosols were applied to investigate their impact on regional as well as global climate, but the effects of washout on climate are not well understood. Airborne particles present in the atmosphere are scavenged by rain in two processes called below-cloud scavenging (washout) which is an efficient pathway to remove the coarse-mode particles and in-cloud scavenging (rainout) that incorporates fine-mode particles and gasses surrounding the cloud droplets (Kajino and Aikawa, 2015; Gong et al., 2011). The composition of RW depends on the particulate or gaseous atmospheric constituents that are emitted by natural or anthropogenic sources locally or transported from distant sources. The acidity, alkalinity, and ionic concentrations of RW depend on the intensity of constituent sources, physical and chemical transformation and their incorporation into the precipitation during the process of cloud formation and drizzle below the cloud (Herrera et al., 2009). It has been observed that RW is contaminated throughout the world due to emissions of various pollutants, and these contaminants can affect the chemistry of rain during the washout process due to its solubilization (Cao et al., 2009). RW chemistry remains a key environmental issue in several parts of the world (North America, Europe and South-East Asia) because of environmental impacts due to acid deposition (acid rain), trace metal deposition, aquatic eutrophication, disturbances of biogeochemical cycling, and global climate change (WMO; Huang et al., 2010).

The chemical composition of RW provides information on the atmospheric quality in a specific region that in turn, depends on emission sources, atmospheric chemistry, and meteorological conditions (Zunckel et al., 2003). Thus, the study of RW chemistry has been a global focal point for atmospheric studies during the last three decades (Galloway et al., 1984; Mouli et al., 2005; Vet et al., 2014). The chemical species present in the atmosphere can be transported by wind and travel long distances before being deposited as rain, affecting regional climate and soil, vegetation, etc. (Niu et al., 2014). Generally, RW contains both natural (sea salt and soil dust) and anthropogenic (gases emitted from industrial areas and vehicles) species (Sakihama et al., 2008) that are often enriched in sea salt (Na⁺ and Cl⁻), soil dust (Ca²⁺, Mg²⁺ and K⁺) and acidic constituents (SO₄²⁻ and NO₃⁻) over coastal, continental, and industrial/urban areas, respectively (Li et al., 2007; Huang et al., 2009). In addition, local environmental conditions (meteorology, topography, and geography) also influence the RW chemistry (Zhang et al., 2011). RW chemistry has been widely investigated over the past three decades in a variety of urban, rural, and high altitude environments over India during the Southwest summer monsoon (MN) period. Little evidence of acid rain has been reported except for a few occurrences because alkaline dust generally neutralizes the acidity (Khemani et al., 1994; Rao et al., 1995; Kulsrestha et al., 2003; Momin et al., 2005; Rastogi and Sarin, 2007; Budhavant et al., 2009, 2011; Das et al., 2010; Tiwari et al., 2006, 2007, 2012, 2016a; Bisht et al., 2015a; references therein). However, fewer studies have been conducted during the non-monsoon (NMN) period (Ali et al., 2004; Kumar et al., 2014).

The objective of this study was to characterize the dynamics of RW chemistry during the dry period (NMN) compared to the wet period (MN) in two mega cities in India. The Indian monsoon is the most prominent of the world’s monsoon systems. The wind blows from the northeast (NE) during cooler/colder months (December and January) and reverses direction to blow from the southwest (SW) during the warmest months (April and May) of the year. This process brings significant rainfall to the region during the monsoon months especially from June to September. Our overall goals were (i) to gain an understanding of the nature of RW during two different periods (dry and wet) over highly (Delhi)/less (Pune) populated and polluted region of Northern and Southwestern India, (ii) to identify the sources of natural/man-made chemical species in RW at both sampling sites including air mass transport, and (iii) to determine the possible sources during dry and wet periods.

2. Materials and methods

2.1. Sampling locations and methods

Precipitation samples were collected on the premises of the Indian Institute of Tropical Meteorology (IITM) Pune located in the Pashan area (18°32’N, 73°48'E, 559 m asml) near the National Chemical Laboratory at about 12 m above ground level. In Delhi, samples were collected on the premises of the IITM, Branch Office in Delhi (28°37’N, 77°12’E, ~126 m asml) located near the National Physical Laboratory at 15 m above the ground level (Fig. 1). The Delhi site (urban background with high traffic) is surrounded by a greenbelt on three sides and a major road leading to Gurgaon on the other side (Tiwari et al., 2015). Delhi (semi-arid climate) is located between the rain-washed Indo-Gangetic plains (IGP) and semi-arid tracts of Rajasthan to the East and Southwest, respectively, and distant (~1100 km) from the sea coast (Arabian Sea). It has ~19 million inhabitants and is the fourth most polluted city in the world with respect to suspended particulate matter (PM) (http://www.sciencedirect.com/science/article/pii/S0169809515002197Chelani et al., 2010). The PM originates from many small/large industries, coal-fired power plants (three) and 4.8 million vehicles (http://www.sciencedirect.com/science/article/pii/S0169809515002197Srivastava and Jain, 2009).

Pune (in the state of Maharashtra) is a rapidly expanding city located ~100 km distant from the west coast and is located on the lee (eastern) side of the Western Ghats (Momin et al., 2005). The city spreads over an area of 700 km² and has a population of about 6 million. The Pune sampling site is surrounded by hillocks on three
sides with heights up to 200 m and appears as a shallow valley (Budhavant et al., 2011). On the other side, a major road (100 m away) passes in front of the Institute’s building. There are limited anthropogenic activities including traffic and small scale industries such as bricks manufacturing (kilns) that burn coal. The kilns are located about one kilometer to the west of the sampling site. During the monsoon period, the airflow in the lower troposphere is predominantly south-westerly (Raju et al., 2016). Samples of RW were collected during three consecutive years from 2012 to 2014 (n = 127) in Pune and 2011 to 2013 (n = 106) in Delhi. The annual total precipitation amounts were 536 (2012), 604 (2013), and 713 (2014) mm in Pune. In Delhi, these values were 526 (2011), 468 (2012) and 833 (2013) mm with an average of 618 and 609 mm, respectively.

2.2. Chemical analysis techniques and quality control

Rainwater samples at both sites were collected using standard rain collection samplers. The pH and conductivity values were measured immediately after each collection with digital pH meters standardized with 4.0 and 9.2 pH buffer solutions and conductivity meters in the two respective laboratories (see in details: Budhavant et al., 2011; Tiwari et al., 2012, 2016a). After the pH measurement, a small amount of thymol (<5 mg) was added to the collection bottle before transferring the samples to avoid biological degradation. The RW samples were then filtered (through Whatman - 41 filters) and were stored in a refrigerator at 4 °C until performing the chemical analyses. In Delhi, anion (F-, Cl-, NO3 and SO42-) and cation (NH4, Na+, K+, Ca2+, and Mg2+) concentrations were quantitatively analyzed by ion chromatography (Dionex - ISCO2000, USA) (Tiwari et al., 2016a). At Pune, anions were measured by Ion Chromatograph (DIONEX DX-100), and an Atomic Absorption Spectrophotometer was used for the measurement of cations (Na+, K+, Ca2+, and Mg2+) (Budhavant et al., 2011). Ammonium (NH4+) ion was measured by the Indophenol Blue technique (http://www.sciencedirect.com/science/article/pii/S0169809511000093). Weatherburn, 1967). HCO3 was measured by the Indophenol Blue technique (http://www.sciencedirect.com/science/article/pii/S0169809511000093).

2.3. Estimation of volume-weighted mean, wet deposition flux and neutralization factor

The volume-weighted mean (VWM) of ionic constituents in RW was calculated as:

\[
\text{VWM (m eq l}^{-1}\!) = \frac{\sum_{i=1}^{N} C_i P_i}{\sum_{i=1}^{N} P_i}
\]

(1)

where \(C_i\) is the ionic concentration of individual component (m eq/l), \(P_i\) and \(N\) are the rain amount for each rainy event (in mm) and the total number of rainfall event (Akpo et al., 2015).

The seasonal wet deposition (WD) fluxes were also calculated by the following equation:

\[
WD (kg ha^{-1} sn^{-1}) = \text{VWM (m eq l}^{-1}\!) \times \frac{RF}{100}
\]

(2)

where seasonal rainfall (RF) is in mm.

Also, the neutralization factor (NF), an indicator of the neutralizing potential of any component in the RW was calculated as follows (Eq. (3)):

\[
\text{NF}_{\text{Ca}^{2+}} = \frac{[\text{nssCa}^{2+}]}{[\text{NO}_3^-] + [\text{nssSO}_4^{2-}]}
\]

(3)

\[
\text{NF}_{\text{Mg}^{2+}} = \frac{[\text{nssMg}^{2+}]}{[\text{NO}_3^-] + [\text{nssSO}_4^{2-}]}
\]

\[
\text{NF}_{\text{NH}_4^+} = \frac{[\text{NH}_4^+]}{[\text{NO}_3^-] + [\text{nssSO}_4^{2-}]}
\]

\[
\text{NF}_{\text{K}^+} = \frac{[\text{nssK}^+]}{[\text{NO}_3^-] + [\text{nssSO}_4^{2-}]}
\]

The non-sea salt (nss) values of any particular component were calculated from the measured concentrations of the chemical species of interest using sodium ion as the reference element, assuming that all sodium is derived from marine sources (Keene et al., 1986; Singh et al., 2007). The equation for the non-sea salt contribution can be written as

\[
[\text{NSS} - X_i] = [X_i] - [\text{Na}^+] \times \frac{[X_i]}{[\text{Na}^+]} \text{sea salt}
\]

(4)

where \([\text{NSS} - X_i]\) is the concentration of nss concentration of species \(X\) in sample \(i\), \([X_i]\) is the total measured concentration of chemical species \(X\) in sample \(i\), \([\text{Na}^+]\) is the concentration of \(\text{Na}^+\) in sample \(i\), and \([X_i]/[\text{Na}^+]\text{sea salt}\) is ratio of these species as measured in seawater (Keene et al., 1986; Tiwari et al., 2016a).

3. Results and discussion

3.1. pH and conductivity of rainwater over Pune and Delhi

The mean pH values (VWM) (specific conductivity) of the rainwater at Pune and Delhi were 6.05 ± 0.5 (33.2 μS cm⁻¹) and 6.40 ± 0.4 (20.9 μS cm⁻¹), during the monsoon and 5.95 ± 0.71 (53.7 μS cm⁻¹) and 5.97 ± 0.8 (91.42 μS cm⁻¹), during the non-monsoon period, respectively. Generally, conductivity is a broad indicator of the total dissolved solids in precipitation (Giorda et al., 2013). The conductivity at Pune is much lower indicating fewer ions than in Delhi broadly reflecting the better atmospheric quality over the Pune area compared to Delhi. These data may also indicate greater dilution of the pollution due to the most abundant rainfall in Pune (Xu et al., 2015).

The conductivity showed the highest values (mean: 91.42 μS cm⁻¹) during the dry season (NMN) over Delhi, whereas, in Pune, it was highest during the MN and lower during the NMN season. These results may reflect seasonal differences in the transport of air masses from the sea coast. During the dry period in Pune, winds are generally from the west bringing clean air from the Arabian Sea ~100 km away (Raju et al., 2016). The air masses affecting Delhi during the dry period (NMN) generally originate from the North-western IGP region, a heavily most polluted region.
located in the States of Punjab and Haryana (Kaskaoutis et al., 2014; Tiwari et al., 2015; Bisht et al., 2015a). The India Meteorological Department (IMD, 1982) reported similar high specific conductivity (5–57 μS cm⁻¹) at ten background locations in India. Earlier studies (Kaskaoutis et al., 2014; Tiwari et al., 2016b; http://www.moef.nic.in) of the atmospheric aerosol over the IGP region indicated high PM concentrations produced by natural and man-made sources.

In a clean atmosphere, the RW pH value is ~5.6 (pH) due to the dissolution of atmospheric CO₂ in rain droplets. Thus, the RW with pH values less than 5.6 is commonly classified as acid rain (Charlson and Rodhe, 1982; Oliveira et al., 2012). In this study, the higher acidity of RW in Delhi was observed with ~26% of the samples having pH values below 5.6, while only 4% of the Pune RW samples were acidic. The pH values in Pune were acidic about 1% and 16% during the MN and NMN periods, respectively, while in Delhi, more samples were acidic during the MN period (25%) compared to the NMN period (31%). Tiwari et al. (2016a) reported average pH value across eight different locations in the IGP region was 5.73 ± 0.17 and varied from 5.44 to 6.03 indicating a non-acidic nature of the rainwater over the IGP region. Pinheiro et al. (2014) suggested that the higher pH values are due to higher concentrations of alkaline species that result in basic rainwater.

3.2. Major inorganic constituents in rainwater at Pune and Delhi

Fig. 2 presents the annual percentage distribution of inorganic chemical species in RW collected at Pune and Delhi in India during 2012–2014 and 2011 to 2013, respectively. During these two study periods, the measured ionic concentrations showed high standard deviations (std.) with variations in the ionic concentration distributions. The concentrations of measured ionic species in RW at Pune decreased in the order of Ca²⁺ > SO₄²⁻ > Cl⁻ > Na⁺ > HCO₃⁻ > NO₃⁻ > NH₄⁺ > Mg²⁺ > K⁺ > F⁻. However, in Delhi, the order was Ca²⁺ > SO₄²⁻ > Mg²⁺ > NO₃⁻ > Cl⁻ > Na⁺ > HCO₃⁻ > NH₄⁺ > F⁻ > K⁺. The measured volume-weighted mean (VWM) concentrations of total ionic species in Pune was calculated to be 304.7 μeq/l, and for Delhi, it was 536.4 μeq/l indicating high atmospheric pollution concentrations over these Indian cities. Ca²⁺ and SO₄²⁻ were the dominant ions accounting for 43% (Pune) and 54% (Delhi) of the total ions. Similar characteristics were observed in previous studies in Pune and Delhi (Safai et al., 2004; Budhavant et al., 2011, 2014; Tiwari et al., 2012, 2016a; references therein). Moreover, SO₄²⁻ and Cl⁻ showed the highest anions concentrations (57%) in Pune that may originate from a significant coal burning contribution. In Delhi, SO₄²⁻ and NO₃⁻ had the highest anions concentrations (66%) due to high coal consumption in that area. Ca²⁺ and Na⁺ had the highest concentration in Pune, whereas, in Delhi, Ca²⁺ and Mg²⁺ were the highest concentrations, accounting for 62 and 77%, respectively, of the total measured cations. These ions are a clear indication of suspension of calcareous soils, dust driven by winds and anthropogenic constructional activities combined with sea salt in both locations.

In India, 80% of the rainfall occurs during the summer monsoon period (southwest monsoon winds) and the remaining rainfall occurs during the winter period (north-east monsoon winds). Monsoonal air travels the cooler ocean and is transported towards the warmer land, whereas non-monsoonal air travels over the cool Asian land mass and is transported towards the warmer oceans, respectively. Therefore, rainwater samples were separated into two categories called monsoon (MN) and non-monsoon (NMN) period. For Delhi, the monsoon period was taken from July to September, whereas for Pune, it was considered from June to September and rest of the period were considered as NMN (dry period). The characteristics of the RW at Pune and Delhi during the MN and NMN periods are depicted in Fig. 3 and large variations were seen in both periods at Pune and Delhi. The sum of the measured ions in MN and NMN for Pune were 278.4 and 412.1 μeq/l, for Delhi, they were 406 and 1037.7 μeq/l, respectively. The measured ions were higher during NMN period by about 1.5 and 2.5
times for Pune and Delhi compared to MN period. Overall, the loading of chemical constituents was 76% higher over Delhi than at Pune indicating large particulate matter concentrations during the dry period in both megacities. Individually, the anion and cation concentrations showed large variability (Fig. 3) in concentrations at both sites during the NMN and MN periods reflected by high standard deviations. All analytes showed higher concentrations during the dry period than during the wet period, highlighting the important role of climate conditions. For acidic species during the NMN period, SO₄²⁻ and NO₃⁻ were 1.6 and 2.5 times higher at Pune and 1.3 and 3.5 times higher at Delhi respectively, compared to the MN period. In the case of Ca²⁺ + Mg²⁺, concentrations were 0.4 and 1.8 times higher during the NMN period at Pune and Delhi, respectively. A feature of these data was seen in sea salt (Na⁺ and Cl⁻) contributions, which were 47% lower in Pune in the NMN than MN season. However, in Delhi, sea salt ions were 2.4 times higher in the NMN than MN season. Pune is located near the sea coast, whereas Delhi is located inland and away from the sea.

Ammonium was considerably higher in the NMN period (by a factor of 4) in Pune, whereas in Delhi, ammonium was higher by a factor of 2. The highest concentrations were found in RW samples from the dry season because the collected samples generally reflected several days without rain, suggesting an accumulation of atmospheric pollutants. Generally, meteorological conditions are more favorable for the dispersion and removal of pollutants during the wet season when the weather usually shows great instability, due to continental heating and tropical convection. During the dry period, however, the region showed stability because of the formation of a high-pressure system called an anticyclone, which generates thermal inversions of the atmosphere (lower levels), affecting pollutant accumulation (Rocha et al., 2003). Fontenele et al. (2009) suggested the great variability of chemical species was related to weather changes. Al-Khashman (2009) also observed highest concentrations of elements were observed during the dry season.

The mean concentrations of major chemical constituents in RW of the present study are compared with selected sites in worldwide in Table 1. The acidic species (sulfate and nitrate) in Pune are much lower than in Delhi and in China, Greece, Spain, Jordan, Italy, USA, and Belgium. However, values in Delhi were similar to the other locations except for China and Greece. In the case of soil derived components (potassium, calcium, and magnesium), Delhi has much higher values than Pune, Brazil, Spain, West Africa, Jordan, USA, and Belgium. The higher concentrations of soil derived components in Delhi was likely due to large contributions from the Thar desert that contains a large amount of calcite. However, the higher concentrations of acidic species over Delhi are due to the anthropogenic emissions from industrial sources and thermal power plants in and around the city. The higher concentrations of ammonium in Delhi are due to high fertilizer use in agriculture during monsoon and anaerobic digestion of animal and human wastes that are spread on open fields (Tiwari et al., 2016a).

The calculated total WD fluxes of the total ions in Pune during MN and MN seasons were 48.6 and 14.1 kg/ha/season (annually: 62.7 kg/ha/y), whereas, at Delhi, it was 55.5 and 11.7 kg/ha/season (annually: 67.2 kg/ha/y) respectively. The WD fluxes at Pune and Delhi during MN season were higher by a factor of ~3.5 and 4.5 times compared to NMN season respectively which clearly shows the impact of total rainfall. Tiwari et al. (2016a) reported the similar WD fluxes for multiple location studies in the northern part of India. The highest WD flux at Pune was calcium (8.69 kg/ha/season) in MN season, whereas in NMN, the nitrate was the highest (3.91 kg/ha/season). In Delhi, the calcium was the highest in MN (15.1 kg/ha/season) and NMN (3.2 kg/ha/season). Kulshrestha et al. (2003) reported highest Ca²⁺ WD flux (14 meq/m²/a) at an urban site of south-central India. In a recent study, Akpo et al. (2015) reported lower total WD flux (51.3 kg/ha/y) in West Africa.

### 3.3. Acid neutralization

The acidity of RW depends on the concentrations of acid-forming chemical species and alkaline species to neutralize the atmospheric acidity before depositing on the ground. Considering both SO₄²⁻ and NO₃⁻ (anthropogenic components) as the main acidifying components in precipitation, the capacity of acid neutralization (AN) of the precipitation was calculated as the fractional acidity (FA) according to Balasubramanian et al. (2001). The annual FA values in Pune and Delhi were 0.02 and 0.08, indicating 98% and 92% of the acidity in RW was neutralized by alkaline chemical species. In addition to this, the relative contributions to acidification at both places were calculated by using [(NO₃⁻ / (SO₄²⁻ + NO₃⁻))] and annual mean values were 0.40 and 0.36 for Pune and Delhi respectively. These values demonstrated that ~40% and ~36% acidity in RW were caused by nitrate and 60% and 64% of the acidity was due to sulfates in RW in Pune and Delhi, respectively.

A neutralization factor (NF) was used to evaluate the neutralization of precipitation by major alkaline chemicals species (Ca²⁺, Mg²⁺, NH₄⁺, and K⁺) in RW at both locations by Tiwari et al., 2016a. The NF for Ca²⁺, Mg²⁺, NH₄⁺, and K⁺ was 1.40, 0.29, 0.29 and 0.10 at Pune and 1.40, 0.49, 0.17 and 0.04 at Delhi respectively. These results showed that the dominant neutralization substances in rainwater were Ca²⁺ and Mg²⁺ (crustal components) along with NH₄⁺ ions, whereas, K⁺ has a negligible impact on the neutralization of acidity.

### 3.4. Origin of the measured ionic species

#### 3.4.1. Identification of ionic sources by backward trajectory analysis

Air parcel back trajectories can provide indicators of the source regions that contributed to the observed atmospheric pollutant

<table>
<thead>
<tr>
<th>Location</th>
<th>pH</th>
<th>SO₄²⁻</th>
<th>NO₃⁻</th>
<th>K⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>NH₄⁺</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pune, India</td>
<td>6.33</td>
<td>39.7</td>
<td>26.8</td>
<td>5.3</td>
<td>93.4</td>
<td>19.1</td>
<td>19.5</td>
<td>Present study</td>
</tr>
<tr>
<td>Delhi, India</td>
<td>6.35</td>
<td>91.6</td>
<td>50.5</td>
<td>5.3</td>
<td>198.6</td>
<td>69.2</td>
<td>23.7</td>
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</tr>
<tr>
<td>Beijing, China</td>
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<td>42.6</td>
<td>9.17</td>
<td>273</td>
<td>53.3</td>
<td>346</td>
<td>Xu et al., 2015</td>
</tr>
<tr>
<td>Thessaloniki, Greece</td>
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<td>134</td>
<td>41.2</td>
<td>16.4</td>
<td>296</td>
<td>30.5</td>
<td>116</td>
<td>Anatolaki and Tsitouridou, 2009</td>
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<tr>
<td>Southeast, Brazil</td>
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<td>0.6</td>
<td>24.1</td>
<td>14.2</td>
<td>27.2</td>
<td>12.2</td>
<td></td>
<td>Mimura et al., 2016</td>
</tr>
<tr>
<td>Coruna, Spain</td>
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<td>31.5</td>
<td>15.1</td>
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<td>32.5</td>
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<td>9.3</td>
<td>65.7</td>
<td>Staelens et al., 2005</td>
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</table>
concentrations (Huang et al., 2008). During the rainy period, the compositions of RW samples were coupled with back trajectory analysis. Generally, the air masses acquire pollutants as they move through areas in which pollutants are emitted. Back-trajectories were calculated using the HYSPLIT (http://www.arl.noaa.gov/ready/hysplit.html) model (Stein et al., 2015; Draxler and Rolph, 2016) for the study period in Pune and Delhi at a height of 2000 m. This height was selected to be a typical cloud height during rainy periods (Budhavant et al., 2016). Cluster analysis was applied to the daily 120-h back-trajectories. The different clusters represent air masses arriving from different source regions having different environmental and atmospheric characteristics. We classified seven major trajectory clusters for the RW collected at Pune and Delhi (Fig. 4) and the mean concentrations in the related clusters are summarized in Table 2.

The concentrations of secondary aerosols [SO$_4^{2-}$ and NO$_3^-$ (acidic species)] at Pune were observed to be much higher (by a factor of 2 and 3) when the wind passes over the continental (inland) area (clusters: 2 and 7) from Odisha and Telangana States and northern Maharashtra region (Nashik), respectively, compared with those originated over the Arabian Sea (AS) (Clusters: 1, 3, 4 and 5). The acidic species were also higher when the wind passes (cluster 6) over the Gulf of Oman. Sea-salt components (Na$^+$ and Cl$^-$) were significantly higher (by a factor of two) in clusters (1, 3, 4 and 5) (see Supplementary Figure S1) when the air masses pass over the Arabian Sea as compared to clusters: 2, 6 and 7. Recently a study conducted by Budhavant et al. (2016) of cloud water and rainwater chemistry at a mountain site, Sinhagad, located 40 km (aerial) from Pune during the monsoon periods of 2008–2010 found that air masses arriving from the Arabian Sea at Sinhagad had concentrations of acidic species significantly lower than other directions.

For Delhi, the sum of all chemical constituents in cluster 6 was higher by a factor of three (see Suppl. Figure S2 and Table 2) when the wind arrives from the northwesterly direction compared to clusters 2 and 5 (the Arabian Sea and the Bay of Bengal). The concentrations of SO$_4^{2-}$, NO$_3^-$, Ca$^{2+}$ and Mg$^{2+}$ in other clusters (1, 3, and 6) were higher by a factor of 2, 3, 4, and 2, respectively, compared to clusters (2, 4, and 5) when the air masses arrive from Punjab, Haryana, and Pakistan indicating the greater atmospheric pollution over the Indo-Gangetic Plain. The second (third) highest concentrations of acidic species (SO$_4^{2-}$ and NO$_3^-$) were in clusters 1 and 3 (30% and 17% air masses come from this direction). Gurgaon and Faridabad in Haryana are heavily industrialized areas. In cluster 6, the concentrations of SO$_4^{2-}$ and NO$_3^-$ were 2.8 and 5.2 times higher than the other clusters when the air masses originated mainly over northwest IGP region which is among the most highly polluted region in the world (Kaskaoutis et al., 2014) and from Pakistan, Afghanistan, Iran, and Iraq. Lower concentrations in Delhi of all species were obtained when the air masses are transported over very long distances from the Arabian Sea and Bay of Bengal (cluster 4 and 5).

3.4.2. Interrelationships among the measured ions

Correlation analysis is a useful tool to characterize the relationship between the ions which present in RW. To find out the association of measured ions in RW as well as the likely sources of measured ions, Pearson correlations analysis were performed for data at Pune and Delhi during the monsoon and non-monsoon periods as depicted in Table 3 and Table 4. Significant correlations (>0.60) between SO$_4^{2-}$ and NO$_3^-$ were observed at both places and during both seasons except the significant level were higher during MN than NMN, which may reflect similar chemical behavior in rainwater and/or co-emissions of their precursors such as SO$_2$ and NO$_x$. Soil-derived chemical species such as Ca$^{2+}$, Mg$^{2+}$ and K$^+$ also showed strong correlations, indicating a crustal (soil) origin of these ions in RW. The sea-salt components (Na$^+$ and Cl$^-$) also showed significant correlations in both seasons indicating the common marine sources during the monsoon period and a common soil source during the non-monsoon period (Safai et al., 2004; Tiwari et al., 2012). In addition, RW was enriched with Cl$^-$ to a higher equivalence ratio of Cl$^-$/Na$^+$ (0.99–1.24) and (1.16–2.17) for Pune and Delhi (MN to NMN) respectively, with a mean values of 1.01 (Pune) indicating sea salt contribution to 1.64 (Delhi) non-sea salt sources might be derived from other natural sources as well as human activities (Xu and Han, 2009). Significant correlation coefficients between Cl$^-$ and the soil dust component (Ca$^{2+}$, Mg$^{2+}$, and K$^+$) confirmed a contribution from soil dust at both sites. The strong correlation between soil derived (Ca$^{2+}$, Mg$^{2+}$, and K$^+$) and
knowledge of contributing source characteristics (i.e. source sources like biomass burning, agricultural activities etc. (Zunckel

3.4.3. Source contributions estimation of ionic species

Table 4

<table>
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<th>Cluster number (C.N.)</th>
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Table 3

Correlation coefficients among ionic constituents in RW at Pune during MN and NMN period.

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<th>Cl</th>
<th>NO₃</th>
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<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>NH₄</th>
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<td>0.11</td>
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<td>0.26**</td>
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<td>0.15</td>
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<td>Cl⁻</td>
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<td>0.33</td>
<td>0.97**</td>
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<tr>
<td>SO₄²⁻</td>
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<td>0.75**</td>
<td>0.62**</td>
<td>0.82</td>
<td>0.81</td>
<td>0.35</td>
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<td>NO₃</td>
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<td>0.51</td>
<td>0.31</td>
<td>0.39**</td>
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<tr>
<td>Na⁺</td>
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<td>0.79**</td>
<td>0.91**</td>
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<td>0.12</td>
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<td>K⁺</td>
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<td>Mg²⁺</td>
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** Correlation is significant at the 0.01 level (2-tailed).

Table 4

Correlation coefficients among ionic constituents in RW at Delhi during MN and NMN period.

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<th></th>
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<th>Ca²⁺</th>
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<td>F⁻</td>
<td>0.55**</td>
<td>0.46</td>
<td>0.42</td>
<td>0.70</td>
<td>0.08</td>
<td>0.69**</td>
<td>0.32</td>
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</tr>
<tr>
<td>Cl⁻</td>
<td>0.39</td>
<td>0.60</td>
<td>0.70</td>
<td>0.38</td>
<td>0.72</td>
<td>0.59**</td>
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<tr>
<td>SO₄²⁻</td>
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<td>0.83</td>
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<td>0.86**</td>
<td>0.65**</td>
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</tr>
<tr>
<td>NO₃</td>
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<td>0.54</td>
<td>0.47</td>
<td>0.18</td>
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<tr>
<td>Na⁺</td>
<td>0.32</td>
<td>0.74</td>
<td>0.58</td>
<td>-0.16</td>
<td></td>
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<tr>
<td>K⁺</td>
<td>0.06</td>
<td>-0.10</td>
<td>-0.14</td>
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<td>Ca²⁺</td>
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<tr>
<td>Mg²⁺</td>
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</tbody>
</table>

** Correlation is significant at the 0.01 level (2-tailed).

acidic species (SO₄²⁻ and NO₃⁻) is likely caused by atmospheric chemical reactions of the acids (H₂SO₄, HNO₃, and HCl) with alkaline species, and carbonate materials which are enriched in the atmosphere and enter the air by wind-blowing PM. A significant correlation between NH₄⁺ and acidic species (SO₄²⁻ and NO₃⁻) in MN (Pune) and NMN (Delhi) may be due to industrial and automobiles activities. Apart from this, it may be some other anthropogenic sources like biomass burning, agricultural activities etc (Zunckel et al., 2003; Zhang et al., 2012).

3.4.3. Source contributions estimation of ionic species

Positive matrix factorization (PMF) is widely used source apportionment method for air pollutants (Anttila et al., 1995; Begum et al., 2004; Lee et al., 2008; Pervez et al., 2012; Tiwari et al., 2016a). PMF requires only measurements and associated uncertainty values of the environmental samples without prior knowledge of contributing source characteristics (i.e. source profiles) and is described in detail by Hopke (2016). US EPA’s PMF version 5.0 was applied to investigate possible sources of the ionic components associated with the RW samples described previously. The uncertainty values associated with species were calculated using the method described by Anttila et al. (1995) and used previously by Tiwari et al. (2016a). Missing values were replaced with associated geometric mean values (Murillo et al., 2013). All variable species had S/N ratios higher than >1 and all species were categorized as “strong” weighted (Norris et al., 2014). US EPA PMF 5.0 model was run for 2 to 6 factors separately for the data for the two sites. Finally, three factors for Pune and four factors for Delhi contributions were selected because they provide good fits to the data as shown by the distributions of scaled residuals and physically interpretable source contribution profiles. The PMF 5.0 extracted chemical stacked source profiles are depicted in Fig. 5 (Pune) and Fig. 6 (Delhi) and the corresponding source contribution plots are presented in Figure S3 and S4, respectively. The factor loadings of
chemical species are also given in Table S1 and S2. The source profiles show different source compositions with only one similar crustal/soil dust factor for both sites (factor 1 for Pune and factor 3 for Delhi). These factors were dominated by crustal species such as Ca$^{2+}$ and Mg$^{2+}$. These species are markers of local calcareous soils, suspended road dust, and civil construction activities (Tiwari et al., 2012; Matawle et al., 2015). Secondary inorganic species (SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$) contributions were identified at the Pune site only in Factor 2 with high explained variations of SO$_4^{2-}$ (51.6%), NO$_3^-$ (79.4%), and NH$_4^+$ (89.5%). These species are markers of secondary aerosol particles [NH$_4$NO$_3$ and (NH$_4$)$_2$SO$_4$] formed from the oxidation of SO$_x$ and NO$_x$. A marine source (Factor 3) also contributed significantly to the Pune RW with high explained variations of Na$^+$, Cl$^-$, Mg$^{2+}$, and K$^+$. This factor may represent effective sea salt cloud condensation nuclei from the Arabian Sea in this region (Tiwari et al., 2016a). For Delhi, fossil fuel combustion (F-1), biomass burning (F-2) and industrial chlorine (F-4) factors show major contributions along with the crustal factor (F-3). Significant increases in SO$_2$ and NO$_x$ emissions from coal combustion activities were reported in earlier studies in the IGP region (Ghude et al., 2008; Tiwari et al., 2016a; references therein). An industrial chlorine source around the Delhi region was reported earlier (Tiwari et al., 2013). Tsai et al. (2007) reported Cl$^-$ emissions from the raw material used in sinter processes in steel manufacturing. Contribution from biomass burning emissions with the high mass loadings of K$^+$ and NH$_4^+$ is likely to be the impact of crop residue burning in the IGP region on the chemical characteristics of Delhi rainwater (Bisht et al., 2015b).

4. Conclusions
A study was conducted on RW chemical composition during 2011–2014, which allowed the classification and evaluation of the RW quality at two representative megacities in Southwestern (Pune) and Northern (Delhi) India across the monsoon (MN) and non-monsoon (NMN) seasons. Mean pH values of the RW were $>6$ at Pune and $<6$ at Delhi with 4% and 26% classed as acidic (pH $<5.6$), respectively. The mean sum of all measured ionic species in Pune and Delhi were 304.7 and 536.4 meq/l, respectively, indicating the role of atmospheric pollution over these mega cities in India. Both the Ca$^{2+}$ and SO$_4^{2-}$ were dominant ions, accounting for 43% (Pune) and 54% (Delhi) of the total ions. The sum of measured ions was greater during NMN than MN by a factor of 1.5 for Pune (278.4: MN and 412.1: NMN meq/l) and by a factor of 2.5 for Delhi (406 and 1037.7 meq/l). The contribution of SO$_4^{2-}$ and NO$_3^-$ to the acidity of RW were $-40$ and 60% in Pune and 36 and 64% in Delhi, respectively. The annual fractional acidity values in Pune and Delhi
were 0.02 and 0.08, indicating that 98% and 92% of the acidity in RW was neutralized by alkaline species. The concentrations of secondary particulate matter (SO\textsubscript{2} \textsuperscript{-} and NO\textsubscript{3} \textsuperscript{-}) were higher by a factor of two and three when the air masses were transported to Pune from the continental side. At Delhi, the concentrations of SO\textsubscript{2}, NO\textsubscript{3}, Ca\textsuperscript{2+}, and Mg\textsuperscript{2+} were significantly higher when the air masses arrive from Punjab, Haryana, and Pakistan indicating the greater atmospheric pollution over the Indo-Gangetic Plain. Positive matrix factorization was applied to the deposition fluxes values, and factors for Pune (three) and Delhi (four) were obtained. The major sources at Pune were secondary aerosols from fossil fuel combustion, soil dust, and sea salt particles. In Delhi, sources were from soil, fossil fuel combustion, biomass burning, and industrial chlorine.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2016.06.069.

References


