Estimation of Non-Marine Fractions of Ions in Rainwater at Three Sites of Different Characteristics in Haryana State (India)

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ABSTRACT

Non-marine sulphate (SO₄²⁻) has a significant influence on the pH of rainwater. This study reports the wet deposition of major ions at three sites having different land use and land cover (LULC) characteristics in Haryana state, located in the agriculturally dominated northwestern part of India. The sites Hisar (urban), Bahadurgarh (industrial), and Meham (semi-urban) had an average pH of rainwater of 5.94, 6.32, and 6.38, respectively. The sum of ionic constituents (i.e., Na⁺, NH₄⁺, K⁺, Ca²⁺, Mg²⁺, F⁻, Cl⁻, NO₃⁻, and SO₄²⁻) was found higher at the industrial site (309.9 µeq L⁻¹) as compared to the urban (225.6 µeq L⁻¹) and semi-urban (255.7 µeq L⁻¹) sites with dominant contribution of NH₄⁺ ions. Calculation of ratios of major ions to Na⁺ to compare the standard Na⁺ ratios of seawater at all the sites indicated a significant influence of non-marine sources. Source apportionment was carried out using principal component analysis (PCA) which indicated that anthropogenic activities such as coal combustion or industrial emissions were the key sources at the industrial and urban sites. Fertilizer application and its volatilization was observed as a potential source of NH₃ at the semi-urban site which is expected due to prominent agricultural activities. Ca²⁺ and SO₄²⁻ both were associated significantly with non-marine sources at all three sites. The non-marine fraction was further differentiated into anthropogenic and crustal-associated portions using soil Ca²⁺ ratios. The anthropogenic/crustal ratios of nss-SO₄²⁻ were calculated as 0.41, 0.32, and 0.28 at urban, industrial, and semi-urban sites respectively. These ratios were inversely with pH explaining low pH at higher anthropogenic/crustal ratios. This approach of calculation of non-marine crustal associated and anthropogenic SO₄²⁻ is very important to assess acidification prospects in the region.

Keywords: Non-marine sulphate, Non-marine chloride, Wet deposition, Source-apportionment

1 INTRODUCTION

Wet deposition is the process of removal of gaseous and particulate matter from the atmosphere through clouds, rain, and snow (Tomasi and Lupi, 2017). The wet scavenging of the pollutants strongly influences air quality and atmospheric chemistry (Galloway, 1995; Fuzzi et al., 1996). Both gases and aerosols undergo chemical transformations during the scavenging process (Jacobson, 2010). The wet removal process involves both in-cloud and below-cloud scavenging of air pollutants. When clouds are moved to the terrestrial region and give rise to rain, the below-cloud scavenging process removes atmospheric gases and aerosols from the air column (Possanzini et al., 1988; Kulshrestha et al., 2009). Wet deposition of these atmospheric species has a potential role in altering the pH of rainwater and its subsequent impact on different surfaces. Factors controlling the acidity of natural water are reported by (Charlson and Rodhe, 1982). Acidic pH of rainfall might cause corrosion to buildings, acidification of waterbodies, soil acidification, biodiversity loss, eutrophication, impact on vegetation, climate change, etc. (Ianniello et al., 2011; Erisman et al., 2013; Singh et al., 2017; Liu et al., 2020). Scavenging of anthropogenic solutes from rural,
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urban, and industrial sources can significantly alter the pH and chemical composition of rainwater reflecting the site characteristics (Bertrand et al., 2008; Anatolaki and Tsitourido, 2009). For example, rural and semi-urban areas have more interference of dust particles showing a higher pH of rainwater. Areas with more vegetation cover have less interference of suspended dust particles, and areas with acidic soil have naturally very low pH of rainwater (Kulshrestha, 2020).

There have been several studies on rainwater chemistry worldwide (Rodhe et al., 2002; Hara and Akimoto, 1993; Oberholzer et al., 1993; Asman et al., 1998; Kuylenstierna et al., 2001; Dentener et al., 2006; Galy-Lacaux et al., 2009; Tost et al., 2006; Khemani et al., 1989; Safai et al., 2004). However, there is a lack of availability of new data about the wet deposition of major ions in developing regions of the world including South Asia. Land use and land cover (LULC) patterns are gradually shifting in developing regions, which could alter emissions of air pollutants including NOx, NH3, SO2, and fine particles, and ultimately impact pollutant transport, reaction rates, and deposition in the global ecosystem (Galloway et al., 2003; Tiwari and Kulshrestha, 2018; Erisman et al., 2013; Asman et al., 1998). The Indo-Gangetic Plain (IGP) is considered a hotspot of atmospheric deposition in India due to the high density of population and activities (Kulshrestha et al., 2005; Singh et al., 2017). Rapidly increasing population and their demand for food supply have led to a widespread use of N fertilizers which further contributes gaseous ammonia and ammonium aerosols. Due to this reason, it is important to study the wet deposition of reactive nitrogen (Nr) and sulphur (S) in South Asia.

The present study focuses on the wet deposition of major ions in the agriculturally intensive state of Haryana, India, which is a part of upper IGP. Haryana is one of the pioneering states which supported the Green Revolution in India and has successfully contributed to the food security of the country in light of its increasing population. In the present study, three locations with different LULC patterns within the Haryana region of India were selected, each site having different characteristics (urban, industrial, and semi-urban). The main objective of this study is to differentiate non-marine SO4\(^{2-}\) into crustal-associated and anthropogenic fractions to relate with pH variations. The wet deposition of major ions including inorganic Nr species, calculation of ionic strength, and neutralization factor have also been attempted. The manuscript also provides source identification of major ions in rainwater.

## 2 MATERIALS AND METHODS

### 2.1 Site Description

The study was carried out at three sites having different LULC characteristics. These sites include Hisar (urban), Bahadurgarh (industrial) and Meham (semi-urban). Among these three sites, two (Meham and Bahadurgarh) come under the National Capital Region (NCR) of Delhi, while the Hisar site lies in the state of Haryana. The site characteristics are defined depending on the difference in activities such as agricultural activity, industrial establishment, transportation, residential areas, and surrounding vegetation. The locations of the sites are shown in Fig. 1.

#### 2.1.1 Hisar (Urban Site)

Hisar site was selected as an urban site in the state of Haryana in northwestern India, located 164 km to the west of the capital city of New Delhi (29°09'36″N, 75°43'09″E) in western Haryana. Hisar City has a continental climate with very hot summers where air temperature ranges from 40–46°C (climate-data.org; hisar.gov.in). The annual average maximum and minimum temperatures are 32.3°C and 15.4°C, respectively. Relative humidity conditions range from 5% to 100%. Located just outside the demarcated southwest monsoon regions, Hisar records an average annual rainfall of around 509 mm, mostly during the monsoon (climate-data.org). Temperature extremes with extremely dry air in the winters and low annual rainfall are the defining characteristics of the Hisar climate. Hisar has one of Asia’s largest automobile markets. The area has several industries around. There are two major national highways (NH-9 and NH-52), connecting to Hisar.

#### 2.1.2 Bahadurgarh (Industrial Site)

Bahadurgarh is a town of Haryana in the Jhajjar district, close to the Delhi -Haryana border
commonly known as the Tikri Border (76°56′39″E longitude and 28°41′07″N). The climate of Bahadurgarh is classified as a local steppe climate with an average temperature of 25.1°C and annual rainfall of approximately 655 mm [climate-data.org]. The city covers a total area of 50 square km. Bahadurgarh is also known as an industrial centre, and it is flanked by the NH-9 highway. The NCR Bahadurgarh Industrial Sector is a major Haryana industrial area on the western outskirts of Delhi.

2.1.3 Meham (Semi-Urban Site)
Meham is located in the Rohtak district of Haryana and has been identified as a semi-urban site (28°57′51″N and 76°17′15″E). Meham receives about 649 mm of rain per year on average [climate-data.org]. Temperatures in Meham are extremely variable. During the winter months, the temperature rarely drops below freezing point. The sampling site was located on the national highway (NH-10). Agriculture is the prevalent activity in the surrounding area of urbanized communities of this site. A sugar mill is also situated in this area.

2.2 Sample Collection
Rainwater samples were collected during summer, winter, and monsoon seasons between July 2017 and June 2018. The total number of samples collected was 75, out of which 29 were at the
urban site, 24 at the industrial site, and 22 at the semi-urban site. Sampling was carried out on the
terrace of all three sites by keeping the sampling assembly at 1.5 m above the rooftop with the help
of an iron stand (Fig. 2). The samples were collected manually on an event basis using pre-washed
assemblies of polyethylene bottles and a 20 cm diameter funnel (Kulshrestha et al., 2003c). After
the rain event, the collection assembly was withdrawn and brought to the laboratory. The volume
collected was measured by using a graduated cylinder. Then the sample was stored in a
polypropylene bottle (125 mL). A small amount of thymol as biocide was added to each storage
bottle. Immediately after collecting the samples, pH was measured before decanting to the
cylinder. Then the sample was stored in a refrigerator and analyzed for cations and anions.

2.3 Chemical Analysis
The pH was determined by using a pH meter (Mettler Toledo FiveEasy Plus FP20). Before
measurement, pH meter was calibrated using 4.2 and 7.0 buffer. The rain samples were analyzed
for major cations (K⁺, NH₄⁺, Na⁺, Ca²⁺, and Mg²⁺) and anions (F⁻, Cl⁻, NO₃⁻, and SO₄²⁻) by using an ion
chromatograph (Metrohm–883 basic plus model). The anions were determined by using Metrosep
A SUP 4, 250/4.0 column and an eluent of 1.8 mmol L⁻¹ Na₂CO₃ and 1.7 mmol L⁻¹ NaHCO₃ at a
flow rate of 1.0 mL Min⁻¹ with Metrohm suppressor technique. The cation separation was achieved
with the Metrosep C4-100/4.0 column and an eluent of 1.7 mmol L⁻¹ nitric acid and 0.7 mmol L⁻¹
dipicolinic acids at a flow rate of 0.9 mL Min⁻¹ without a suppressor. We have used MERCK reference
standards of 1, 2, and 5 ppm for anions and 2, 5, and 10 ppm for cations to achieve the calibration.
The average concentration of SO$_4^{2–}$ was higher than NO$_3^{–}$ at all three sites indicating the influence of industrial emissions of oxides of S and N. Similar results have been reported in other studies. SO$_2$ is chemically adsorbed onto crustal dust particles, forming calcium sulphate without lowering pH. Samples collected after continuous rain were recorded with relatively lower pH. In general, the ionic components of rainwater varied in the order: NH$_4^+$ > SO$_4^{2–}$ > Ca$^{2+}$ > NO$_3^{–}$ > Cl$^{–}$ > Na$^+$ > Mg$^{2+}$ > K$^+$ > F$^{–}$ at the urban site, NH$_4^+$ > SO$_4^{2–}$ > Ca$^{2+}$ > Cl$^{–}$ > NO$_3^{–}$ > Na$^+$ > K$^+$ > Mg$^{2+}$ > F$^{–}$ at the industrial site and NH$_4^+$ > SO$_4^{2–}$ > Ca$^{2+}$ > Cl$^{–}$ > NO$_3^{–}$ > Na$^+$ > Mg$^{2+}$ > K$^+$ > F$^{–}$ at the semi-urban site. Variations along with the average concentrations of cations and anions for all three sites are shown in Figs. 3(a–c). The sum of ionic constituents was 226.62 ± 16.32 µeq L$^{-1}$ at the urban site, 301.87 ± 23.63 µeq L$^{-1}$ at the industrial site, and 256.63 ± 20.87 µeq L$^{-1}$ at the semi-urban site.

The ionic strength was calculated as follows:

\[
\text{Ionic strength} = \frac{1}{2} \sum \frac{C_i Z_i^2}{eq L^{-1}}
\]

where $C_i$ is the molar concentration of the component and $Z_i$ is the charge.

Table 1 gives ionic strength calculated using the above formula for different sites worldwide. These values include Na$^+$, NH$_4^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, F$^{–}$, Cl$^{–}$, NO$_3^{–}$, and SO$_4^{2–}$. The mean ionic strength was 160.87 µM L$^{-1}$, 212.65 µM L$^{-1}$, and 180.77 µM L$^{-1}$ at the Urban site, Industrial site, and Semi-urban site, respectively which is in the range as reported worldwide.

In general, the concentrations of major ions were found to be higher at the industrial site compared to the other two sites. NH$_4^+$ was the most abundant ion which varied from 16.4 to 132.8 µeq L$^{-1}$ at the urban site, 17 to 93.7 µeq L$^{-1}$ at the industrial site, and 0.11 to 166.5 µeq L$^{-1}$ at the semi-urban site. The mean concentration for SO$_4^{2–}$ was the highest at the industrial site (59.5 µeq L$^{-1}$) as compared to the semi-urban site (49.2 µeq L$^{-1}$) and urban site (44.9 µeq L$^{-1}$). The average concentration of SO$_4^{2–}$ was higher than NO$_3^{–}$ at all three sites indicating the influence of industrial emissions of oxides of S and N. Similar results have been reported in other studies.

2.4 Data Analysis for PCA

PCA is a statistical method that follows a mathematical model of the reduced factor analytical solution to find a few principal components bearing a major part of the existing information from a data set of many correlated variables. PCA was performed using IBM SPSS Statistics, Version: 28.0.1.0 (001) for the selected sites in this study to determine the variables having a factor loading of more than 0.5. Based on the results, the grouping was attributed to potential sources of the investigated major ions at all the sites.

3 RESULTS AND DISCUSSION

3.1 pH, EC, and Ionic Composition of Rainwater

The average values for pH of the rainwater samples were recorded as 5.94, 6.32, and 6.38 at urban, industrial, and semi-urban sites respectively. The average values for electrical conductivity (EC) were 74.78 µS-cm$^{-1}$, 103.48 µS-cm$^{-1}$, and 70.87 µS-cm$^{-1}$ at urban, industrial, and semi-urban sites respectively. These values are in a similar range as reported by previous studies in the region. The suspended particulate matter, which is rich in CaCO$_3$ and MgCO$_3$, buffers the acidity of rainwater. A high-pH value was observed at the urban site, 33.1–84.1 µH at the urban site, 28.0–132.8 µH at the industrial site, and 0.11 to 166.5 µH at the semi-urban site. The average values for electrical conductivity (EC) were 74.78 µS·cm$^{-1}$, 103.48 µS·cm$^{-1}$, and 70.87 µS·cm$^{-1}$ at urban, industrial, and semi-urban sites respectively. These values include Na$^+$, NH$_4^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, F$^{–}$, Cl$^{–}$, NO$_3^{–}$, and SO$_4^{2–}$. The mean ionic strength was calculated as follows:

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Ca$^{2+}$ concentrations varied from 15.5–49.4 µeq L$^{-1}$ with an average of 10.5–118.5 µeq L$^{-1}$ with an average of 39.6 µeq L$^{-1}$ at the urban site, 33.1–84.1 µeq L$^{-1}$ with an average of 56.3 µeq L$^{-1}$ at the industrial site and 20.3–187.4 µeq L$^{-1}$ with an average of 47.8 µeq L$^{-1}$ at the semi-urban site.
Fig. 3. Five summary statistics of analyte ions of all three sites.

Table 1. Ionic strength of rainwater at different sites worldwide.

<table>
<thead>
<tr>
<th>Location</th>
<th>Ionic Strength (µM L⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Meham</td>
<td>180.77</td>
<td>Present study</td>
</tr>
<tr>
<td>Bahadurgarh</td>
<td>212.655</td>
<td>Present study</td>
</tr>
<tr>
<td>Hisar</td>
<td>160.875</td>
<td>Present study</td>
</tr>
<tr>
<td>Malaysia</td>
<td>142.305</td>
<td>Tay et al. (2014)</td>
</tr>
<tr>
<td>China</td>
<td>433.35</td>
<td>Cao et al. (2009)</td>
</tr>
<tr>
<td>Singapore</td>
<td>161.94</td>
<td>Hu et al. (2003)</td>
</tr>
<tr>
<td>Korea</td>
<td>116.5</td>
<td>Lee et al. (2000)</td>
</tr>
<tr>
<td>India (Nainital)</td>
<td>279.84</td>
<td>Bisht et al. (2017)</td>
</tr>
<tr>
<td>India (Jaunpur)</td>
<td>68.05</td>
<td>Singh et al. (2017)</td>
</tr>
<tr>
<td>India (Delhi)</td>
<td>191.3</td>
<td>Singh et al. (2017)</td>
</tr>
</tbody>
</table>
3.2 Relative Contributions of Inorganic Ions in Rainwater

The abundance of Na⁺, NH₄⁺, K⁺, Ca²⁺, Mg²⁺, F⁻, Cl⁻, SO₄²⁻, and NO₃⁻ at the three sites is shown in Figs. 4(a–c). At each site, a predominance of NH₄⁺, SO₄²⁻, and Ca²⁺ is evident. Major sources of NH₄⁺ include agricultural activities, domestic sources, and decay processes (Li et al., 2013). The ions such as Na⁺, Cl⁻, and NO₃⁻ were comparatively lower and they showed approximately similar range of percent contributions. The site is away from the sea, and hence, sea salt such as NaCl is expected lower than the marine and coastal sites. Relatively fewer NOx sources might have resulted relatively lower concentration of NO₃⁻. However, their mean concentrations were higher compared to Mg²⁺ and K⁺. The F⁻ showed the lowest contribution among all the ions at all sites indicating its sources are limited. The contribution of NH₄⁺ was comparatively high at the semi-urban site suggesting agricultural sources and decay of organic matter are dominating sources of NH₃ in rural areas. The higher concentrations of NH₄⁺ are also likely due to biomass burning apart from fertilizer emissions from the agricultural sectors, and cow dung cake processing (Kulshrestha et al., 2014).

3.3 Neutralization Factors

Neutralization factors were calculated to evaluate the neutralization extent of acidity generated by SO₄²⁻ and NO₃⁻ in rainwater by Ca²⁺ and NH₄⁺. The neutralization factors (NF) with respect to NH₄⁺, and Ca²⁺ have been calculated for each of the monitoring sites using Eq. (1), and these are given in Table S3. The NF was calculated as (Possanzini et al., 1988):

\[
NF = \frac{X}{SO_{4}^{2-} + NO_{3}^{-}}
\]

(1)

where X represents the neutralizing cation, the neutralization factors with respect to NH₄⁺ were found to be 0.76, 0.83, and 0.85 at urban, industrial, and semi-urban sites, respectively. However, the Ca²⁺ neutralization factors were found to be lower at all the sites. The NF values for Ca²⁺ were 0.60, 0.68, and 0.65 at urban, industrial, and semi-urban sites respectively.

3.4 Origin of Major Ions in the Rainwater

Generally, the ions in precipitation are mainly derived from sea spray, anthropogenic sources,
and atmospheric dust. Further, the chemical composition of precipitation is expected to reflect the relative contribution of the ions from these reservoirs (Kulshrestha et al., 1996; Saxena and Hildemann, 1996; Granat et al., 2002; Safai et al., 2004; Das et al., 2005). Thus, the origin of these ions is categorized into marine and non-marine origins.

3.4.1 Marine sources

Sea salt is mainly comprised of Na⁺, Cl⁻, and Mg²⁺, with some Ca²⁺, SO₄²⁻, and K⁺ (Keene et al., 1986). For observing the sources of major ions, we compared the Cl⁻/Na⁺ ratios in rainwater to that of seawater (Keene et al., 1986). Further, for estimating the contribution of marine and non-marine sources, sea salt ratios and enrichment factors have been calculated by taking Na⁺ as a reference element with the assumption that all Na⁺ majorly is of marine origin (Keene et al., 1986; Kulshrestha et al., 1996). Table 2 shows the ratios of Cl⁻, Mg²⁺, Ca²⁺, SO₄²⁻, and K⁺ with respect to Na⁺. Results in Table 2 indicate that all ratios were found to be higher than the standard seawater ratios at all sites. Further, average Cl⁻/Na⁺ ratios were very close to seawater for industrial (1.16), semi-urban (1.21), and urban (1.18) sites which showed that Cl⁻ was mostly contributed by the marine sources. However, with a recent understanding of Cl⁻ contributions from plastic waste burning and Na⁺ from soils, the Cl⁻/Na⁺ ratio calculation probably is not the appropriate approach for deciding about marine vs. non-marine contributions (Kulshrestha and Mishra, 2019; Kulshrestha et al., 2003b; Chen et al., 2022). There are some other sources of Cl⁻ as well as for Na⁺ in the region indicating very different sources and mechanisms are working at these sites located very far from the sea (Chen et al., 2022). K⁺/Na⁺, Ca²⁺/Na⁺, and SO₄²⁻/Na⁺ ratios were found to be higher at all three sites as compared to standard seawater Na⁺ ratios, indicating their contribution to non-marine sources. Since the site is around 1400 km away from marine sources, the possibility of non-marine source influence is stronger, especially interference of crustal dust arising from soil suspension and road dust suspension due to which the pH of rainwater remains towards the higher side.

As a standard fraction analysis, the sea salt fraction (ssf) and non-sea salt fraction (nssf) of different components were calculated by using the following formula:

\[
\% \text{ssf} = 100 \times \frac{[X/Na^+]_{\text{seawater}}}{[X/Na^+]_{\text{rainwater}}} \tag{2}
\]

where \([X]\) is the concentration of desired ionic species in µeq L⁻¹; \([X/Na^+]_{\text{seawater}}\) is the standard ratio of seawater (Keene et al., 1986).

\[
\% \text{nssf} = 100 - \% \text{ssf} \tag{3}
\]

[w.r.t., with respect to; ssf, sea-salt fraction; %, percent; nssf, non-sea-salt fraction; EF, enrichment factor; U, urban site; I, industrial site; Semi-U, semi-urban site.

Nearly all components appeared to be non-marine probably originating from anthropogenic and crustal sources. Similar results have been reported by other workers (Khemani, 1993; Kulshrestha et al., 1996; Kulshrestha et al., 2003a; Tiwari et al., 2007). High concentrations of nssf SO₄²⁻ have

<table>
<thead>
<tr>
<th>Ions</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
<th>K⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard Seawater ratios w.r.t. Na⁺</td>
<td>1.160</td>
<td>0.125</td>
<td>0.227</td>
<td>0.022</td>
<td>0.044</td>
</tr>
<tr>
<td>Site type</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U</td>
<td>I</td>
<td>SU</td>
<td>U</td>
<td>I</td>
<td>SU</td>
</tr>
<tr>
<td>Rainwater ratios w.r.t. Na⁺</td>
<td>U</td>
<td>1.16</td>
<td>1.21</td>
<td>2.27</td>
<td>2.25</td>
</tr>
<tr>
<td>ssf %</td>
<td>98.3</td>
<td>99.6</td>
<td>95.9</td>
<td>5.5</td>
<td>5.6</td>
</tr>
<tr>
<td>nssf %</td>
<td>1.7</td>
<td>0.4</td>
<td>4.1</td>
<td>94.5</td>
<td>94.4</td>
</tr>
<tr>
<td>EF</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>18.2</td>
<td>18</td>
</tr>
</tbody>
</table>

Table 2. The equivalent ratios of ions with reference to Na⁺ at urban (U), industrial (I) and semi-urban (SU) sites.
been reported by (Kulshrestha et al., 1999; Granat et al., 2002) due to their contribution from continental sources. In addition, enrichment factors (EFs) of different components with respect to Na+ were calculated using the following formula (Keene et al., 1986):

\[
EF = \frac{X/Na^+_{rain}}{X/Na^+_{seawater}}
\]

where X is the ion of interest. All the components are enriched showing the significant influence of local sources over marine influence at the site (Table 2).

### 3.4.2 Non-marine sources

The non-marine sources of ionic components have been divided into crustal and anthropogenic categories (Table 3) following the approach already been reported in this region having higher influence of mineral dust in the atmosphere (Kulshrestha et al., 1997; Jain et al., 2000). Except for NO3−, the percentage contribution of the other ions (Na+, NH4+, K+, Ca2+, Mg2+, F−, Cl−, and SO42−) with respect to the crustal ratios have been found to exceed the proportions at the industrial site. Comparatively, lower proportions of crustal fraction have been observed at the urban and semi-urban sites than at the industrial sites. A fraction of acidic components (SO42− and NO3−) is found to be associated with crustal fractions (CFs) with Ca2+ possibly as CaSO4 and Ca(NO3)2. In order to calculate CF and anthropogenic fractions (AF), we have used the methodology of (Jain et al., 2000, Kulshrestha et al., 1997; Kumar et al., 2016).

\[
%CF_x = 100 \frac{(nssX/nssCa^{2+})_{soil}}{(nssX/nssCa^{2+})_{rainwater}}
\]

where, nssX is non-sea salt fraction concentrations of ionic species (SO42−, Ca2+, K+, Mg2+, NO3−, NH4+, and F−) in µeq L−1; (nssX/nssCa^{2+})_{soil} is taken as the standard ratio of local soils (Jain et al., 2000).

Then, % anthropogenic fractions of each ionic species were calculated using the formula:

\[
%{Anthro}_x = % nssx - % CF_x
\]

The SO42− was associated with non-marine sources at all three sites with a small percentage i.e., 5.5%, 5.6%, and 5.9% at the urban, industrial, and semi-urban sites, respectively from marine sources. On the other hand, the K+ fraction was contributed both by the marine (52% at urban, 32% at industrial, and 84% at semi-urban sites) as well as non-marine sources (48% at urban, 68% at industrial, and 16% at semi-urban site). The percent ionic abundance of Ca2+ was primarily contributed from the crustal sources (99%) at all three sites. The ionic species, NH4+ and NO3− are considered mainly from non-marine sources as shown in Table 2. 95% of NH4+ was found to originate from anthropogenic sources at urban sites, 95% at industrial sites, and 95.5% at the semi-urban site. 95% of NO3− was found to originate from anthropogenic sources at urban sites, 95% at industrial sites, and 95.5% at the semi-urban site.

<table>
<thead>
<tr>
<th>Ions</th>
<th>Marine (%)</th>
<th>Non-marine (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>U I SU</td>
<td></td>
</tr>
<tr>
<td>Cl−</td>
<td>98.3 100 95.9</td>
<td></td>
</tr>
<tr>
<td>NO3−</td>
<td>0 0 0</td>
<td></td>
</tr>
<tr>
<td>SO4^{2−}</td>
<td>5.5 5.6 5.9</td>
<td></td>
</tr>
<tr>
<td>K+</td>
<td>51.6 32 84.1</td>
<td></td>
</tr>
<tr>
<td>Ca^{2+}</td>
<td>1.1 1 1.1</td>
<td></td>
</tr>
<tr>
<td>Mg^{2+}</td>
<td>8.3 15.7 13.3</td>
<td></td>
</tr>
<tr>
<td>Na+</td>
<td>100 100 100</td>
<td></td>
</tr>
<tr>
<td>NH4+</td>
<td>0 0 0</td>
<td></td>
</tr>
<tr>
<td>F−</td>
<td>0 0 0</td>
<td></td>
</tr>
</tbody>
</table>
semi-urban site. A small fraction of NH4+ was found to be associated with crustal sources or soils i.e., 4.68% at urban, 4.8% at industrial, and 4.5% at semi-urban sites. NO3− fractions were 65% at urban, 56% at industrial, and 62.5% at semi-urban sites were found to be associated with anthropogenic sources while crustal sources as 35% at urban, 44% at industrial, and 37.5% at semi-urban sites.

3.5 Wet Deposition Fluxes of Reactive Nitrogen

NH3 and NOx are the major reactive nitrogen species. Most NH3 is emitted by agricultural activities, domestic sources, and decay processes, while NOx are emitted by mostly fossil fuel combustion (Asman et al., 1998; Singh et al., 2017). Considering the importance of these reactive nitrogen species and their deposition on the vegetation, waterbodies, and agricultural land, the wet deposition fluxes of their corresponding major components in rainwater (NH4+ and NO3−) were calculated by using the following equation (Singh et al., 2017):

\[
\text{Wet flux (kg ha}^{-1}\text{ yr}^{-1}) = \frac{\text{Conc. of sepcies mg L}^{-1} \times \text{precipitation vol. (l)} \times 10^4}{0.0314 \text{ m}^2 \times 10^6}
\]

A comparison of wet deposition of NH4+ and NO3− in kg ha\(^{-1}\) yr\(^{-1}\) has also been attempted as given in Table S2. The NO3− deposition was observed to be higher at all the sites (Fig. 5). The relative wet deposition flux with respect to NO3− was also found to be higher at the urban sites in previous studies, which is inconsistent with the findings of this work. In addition, Kulshrestha et al. (2003a) have also reported the wet deposition fluxes of reactive nitrogen species such as NH4+ and NO3−. A similar pattern has also been observed in other studies worldwide (Huang et al., 2012; Huang et al., 2015).

3.6 Source Apportionment Analysis Using PCA

PCA results for all the three sites are summarized in the Tables 4–6. Table 4 gives PCA results for urban site Hisar. Four extracted PCs explained a cumulative variance of 74%. PC-1 showed loadings of Cl− and NO3− with a variance of 24%, suggesting transport and waste burning as the major sources. Emissions of Cl− have been associated with plastic waste burning (Kulshrestha and Mishra, 2019). Similarly, NO3− is also released by the combustion of fuels in automobiles. PC-2 showed significant loadings of Ca\(^{2+}\) and SO4\(^{2−}\) and a variance of 22%, consistent with coal combustion and SO2\(^{2−}\) emissions followed by chemical coupling with Ca\(^{2+}\) that led to the formation of CaSO4. SO4\(^{2−}\) is contributed by the oxidation of SO2 from coal combustion of coal power plants and brick kiln activities in this area. The SO2 reacts with crustal CaCO3 forming CaSO4 (Kulshrestha et al., 2003a).

Fig. 5. Wet fluxes of reactive nitrogen species NH4+ and NO3− at the selected sampling sites.
Table 4. PCA analysis for urban site (Hisar).

<table>
<thead>
<tr>
<th>Components</th>
<th>PC-1</th>
<th>PC-2</th>
<th>PC-3</th>
<th>PC-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>.322</td>
<td>-.215</td>
<td>.481</td>
<td>.272</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>-.395</td>
<td>.658</td>
<td>.230</td>
<td>.371</td>
</tr>
<tr>
<td>K⁺</td>
<td>.042</td>
<td>-.214</td>
<td>.691</td>
<td>-.213</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>.215</td>
<td>.824</td>
<td>.017</td>
<td>-.152</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>-.150</td>
<td>.076</td>
<td>.883</td>
<td>.142</td>
</tr>
<tr>
<td>F⁻</td>
<td>-.490</td>
<td>.059</td>
<td>-.223</td>
<td>.714</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>.869</td>
<td>.021</td>
<td>-.076</td>
<td>.262</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>.897</td>
<td>.118</td>
<td>-.013</td>
<td>.294</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>.086</td>
<td>.890</td>
<td>.040</td>
<td>-.224</td>
</tr>
<tr>
<td>Described variance (%)</td>
<td>24%</td>
<td>22%</td>
<td>18%</td>
<td>10%</td>
</tr>
<tr>
<td>Cumulative described variance (%)</td>
<td>24%</td>
<td>46%</td>
<td>64%</td>
<td>74%</td>
</tr>
<tr>
<td>Sources</td>
<td>Waste burning</td>
<td>Coal emission + crustal</td>
<td>Biomass burning</td>
<td>Mixed sources</td>
</tr>
</tbody>
</table>

[Bold values indicate significant factor loading > 0.5 on each PC.

Similarly, PC-3 showed high loadings of K⁺ and Mg²⁺ having a variance of 18% further indicating the possibility of association of this PC with biomass burning. The emission of K⁺ from biomass burning is well known and its association with Mg²⁺ indicates the association of this PC with biomass burning. PC-4 showed contributions of Na⁺, NH₄⁺, Cl⁻, F⁻, NO₃⁻ with 10% variance suggesting mixed source contribution of these chemical components. NH₄⁺ from NH₃ emitted from agricultural activities including fertilizer applications and crop residue burning, and F⁻ from brick kilns showing PC-4 as the mixed source.

PCA of the industrial site Bahadurgarh is given in Table 5. A total of four PCs were extracted which explained 71% of the variance. PC-1 showed significant loadings of Na⁺, Cl⁻, and Ca²⁺ with a variance of 26%. This indicated the influence of crustal components and sea salt dust. PC-2 had contributions in the form of NH₄⁺ and K⁺, which suggested the possible influence of biomass burning. PC-3 accounted for 14% variance with SO₄²⁻ as the significant component which is consistent with the presence of industrial surroundings. PC-4 is identified as the mixed source having moderate loadings of different components.

PCA results of the semi-urban site Meham are given in Table 6. Five PCs extracted explained data loading for 72% cumulative variance. PC-1 showed loadings of Ca²⁺ and NO₃⁻ explaining 24% variance, which suggested the crustal mixed components. PC-2 had high loadings of Na⁺ and Cl⁻ explaining 20% of the variance suggesting sea salt as a potential source. PC-3 explained 15% of the variance having high loadings of NH₄⁺ and K⁺ further suggesting agricultural activities/biomass burning as the source. Due to association with Cl⁻ and SO₄²⁻, PC-4 showed a likely influence of waste burning which is common in this region.

Table 5. PCA analysis for industrial site (Bahadurgarh).

<table>
<thead>
<tr>
<th>Components</th>
<th>PC-1</th>
<th>PC-2</th>
<th>PC-3</th>
<th>PC-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>.70</td>
<td>.04</td>
<td>-.45</td>
<td>-.42</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>-.04</td>
<td>.90</td>
<td>.03</td>
<td>.09</td>
</tr>
<tr>
<td>K⁺</td>
<td>.23</td>
<td>.56</td>
<td>-.58</td>
<td>.23</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>.87</td>
<td>.02</td>
<td>.22</td>
<td>-.12</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>.30</td>
<td>-.33</td>
<td>.12</td>
<td>.56</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>.71</td>
<td>.18</td>
<td>-.03</td>
<td>.15</td>
</tr>
<tr>
<td>F⁻</td>
<td>-.35</td>
<td>-.65</td>
<td>.08</td>
<td>.21</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>-.01</td>
<td>-.13</td>
<td>.06</td>
<td>-.83</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>.22</td>
<td>.08</td>
<td>.86</td>
<td>.08</td>
</tr>
<tr>
<td>Described variance (%)</td>
<td>26%</td>
<td>19%</td>
<td>14%</td>
<td>12%</td>
</tr>
<tr>
<td>Cumulative described variance (%)</td>
<td>26%</td>
<td>45%</td>
<td>59%</td>
<td>71%</td>
</tr>
<tr>
<td>Sources</td>
<td>Sea salt + Crustal dust</td>
<td>Biomass burning</td>
<td>Industries</td>
<td>Mixed sources</td>
</tr>
</tbody>
</table>

[Bold values indicate significant factor loading > 0.5 on each PC.]
Table 6. PCA analysis for semi-urban site (Meham).

<table>
<thead>
<tr>
<th>Components</th>
<th>PC-1</th>
<th>PC-2</th>
<th>PC-3</th>
<th>PC-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>−.069</td>
<td>.780</td>
<td>.263</td>
<td>−.384</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>−.044</td>
<td>.344</td>
<td>−.801</td>
<td>−.032</td>
</tr>
<tr>
<td>K⁺</td>
<td>−.334</td>
<td>.737</td>
<td>.426</td>
<td>.005</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>.894</td>
<td>.124</td>
<td>.138</td>
<td>−.278</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>−.524</td>
<td>−.280</td>
<td>.372</td>
<td>.152</td>
</tr>
<tr>
<td>F⁻</td>
<td>−.397</td>
<td>.236</td>
<td>−.286</td>
<td>−.458</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>.133</td>
<td>.433</td>
<td>−.392</td>
<td>.506</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>.903</td>
<td>.039</td>
<td>.120</td>
<td>−.052</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>.146</td>
<td>.404</td>
<td>.189</td>
<td>.680</td>
</tr>
<tr>
<td>Described variance (%)</td>
<td>24%</td>
<td>20%</td>
<td>15%</td>
<td>13%</td>
</tr>
<tr>
<td>Cumulative described variance (%)</td>
<td>24%</td>
<td>44%</td>
<td>59%</td>
<td>72%</td>
</tr>
</tbody>
</table>

| Sources                      | Crustal mixed | Sea salt | Agricultural activities/Biomass burning | Waste burning |

[Bold values indicate significant factor loading > 0.5 on each PC].

It can be concluded that anthropogenic activities such as coal combustion or industrial emissions were likely the most influential of precipitation chemistry at the industrial and urban sites. However, the results suggested that activities such as waste and fossil fuel burning, agricultural biomass burning, and secondary aerosol formation also influenced rain chemistry. Effect of fertilizer application and volatilization, emissions from brick kilns, and soil dust were suggested as potential sources in rural/semi-urban areas.

The results indicated that NH₄ was predominantly responsible for the neutralization of rainwater acidity at all the sites; Haryana is dominated by agricultural activities. Hence NH₃ and its secondary compounds abundance are ubiquitous at all selected sites in the state.

3.7 Long-range Transport Using Air Mass Back Trajectory Analysis

The air mass back trajectories were calculated by the NOAA HYSPLIT model (Hybrid Single-Particle Lagrangian Integrated Trajectory Model) to determine the major pathways of transport of pollutants reaching to the receptor sites. These trajectories were calculated for 500 m and 1000 m above ground levels (MAGL) for 120 hours at all three sites. Since most of the rain occurs during the monsoon period, we have plotted typical trajectories for a common date (29 July 2017) at three sites which are shown in Figs. 6(a–c). These trajectories represent the typical movement of air masses in the region. In general, air masses mostly originate from the Arabian Sea passing through the western and central parts of India. All three sites are very close by, therefore, the difference in the air mass routes is not significant. Hence, the measured difference in the chemical composition at three different sites is represented by the below cloud scavenging of the pollutants present in the local air column surrounding the sites. It is to be mentioned that very less frequent precipitation happens during non-monsoon periods including winters. During winters airmass generally originates from the Middle East and Europe and influences the deposition of SO₄²⁻ and NO₃⁻ over the Himalayan region (Sharma and Kulshrestha, 2020; Kumar et al., 2016).

4 CONCLUSIONS

The present study characterized atmospheric deposition at three sites of different characteristics located in different LULC regions in the Haryana state adjacent to Delhi state. Results showed that due to the deep terrestrial location of sites, a non-marine fraction of almost all of the ions were significantly higher. The fraction of nss-SO₄²⁻ was recorded as 94.5%, 94.4%, and 94.1% at urban, industrial, and semi-urban sites respectively. The anthropogenic/crustal ratios of nss-SO₄²⁻ were inversely with pH suggesting relatively low pH at higher anthropogenic/crustal ratios. All the sites had a significant influence of non-marine sources. The non-marine fraction of SO₄²⁻ was further differentiated into crustal associated and anthropogenic SO₄²⁻ fractions using soil Ca²⁺ ratios. A significant fraction of nss-SO₄²⁻ was associated with crustal sources possibly as CaSO₄.
Fig. 6. Typical backward trajectories (120 hours) at an altitude of 500 m and 1000 m using HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory Model. Picture (a) Hisar site, (b) Bahadurgarh site, and (c) Meham site. Source: NOAA Air Resources Laboratory.

The order of anthropogenic/crustal ratios of non-marine fraction of SO$_4^{2-}$ clearly reflected that the method of differentiating nss-SO$_4^{2-}$ is an appropriate approach for explaining pH variation in the region and for estimating the potential damage due to acidity contributed by the anthropogenic fraction of SO$_4^{2-}$.

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SUPPLEMENTARY MATERIAL

Supplementary material for this article can be found in the online version at https://doi.org/10.4209/aaqr.230252

REFERENCES


