Chemical composition of rainwater in a tropical urban area of northern India

Abdul Hameed M. Jawad Al Obaidya, Himanshu Joshi

Abstract

Rainwater samples during the monsoon of 2001 and 2002 were collected from Roorkee urban area, a medium sized “town group” situated on the right bank of Solani River, a tributary of the Ganga River, near the Himalayan foothills and analyzed for EC, pH, TSS, TDS and major ions. The median value of pH was 7.05, well above 5.6, which is the reference pH. The ratios of SO$_4^{2-}$/NO$_3^-$ and Ca$^{2+}$/Mg$^{2+}$ (TA/TC) have been considered for acidity. In this study, ratio of TA/TC is quite below 1.0, indicating alkaline nature of rainwater. The concentration of ions in rain water have been observed to follow the pattern Ca$^{2+}$ > HCO$_3^-$ > NO$_3^-$ > Cl$^-$ > Na$^+$ > Mg$^{2+}$ > SO$_4^{2-}$ > K$^+$. In order to estimate the marine and non-marine contribution, sea salt fraction has been calculated taking Na$^+$ as reference. All ionic ratios have been found to be higher than the recommended sea water ratios in all three types of land use, viz. residential, commercial and industrial, suggesting a significant contribution of non-marine origin for these components. A comparison with the data of the other Indian sites validates the inverse relation of Cl$^-$ and Na$^+$ with distance from the sea and highlights higher Ca$^{2+}$ concentration and lower SO$_4^{2-}$ concentration.

Keywords: Rainwater; Ion balance; Sea salt fraction; Alkalinity

1. Introduction

During last decade, several studies on the chemical composition of rainwater have been carried out in India (Kulshrestha et al., 1996; Satsangi et al., 1998; Srinivas et al., 1999; Jain et al., 2000; Kumar et al., 2002; Kulshrestha et al., 2003). These studies have generally highlighted the alkaline nature of rainwater in India, possibly due to the contribution of soil derived particles in the atmosphere, which are found to buffer its acidity during below cloud scavenging process. Further, variation in composition reflects local/or regional characteristics. The researchers have monitored and collected the rain water samples in many urban and rural areas to determine the composition of the rainwater which may subsequently help in understanding the relative importance of the different contributing sources.

Pollutants like gases and particles present in atmosphere may be dissolved and/or transported by the rain water and brought to the ground. Rainfall is one of the most effective ways of removing atmospheric pollutants. In a study of rainfall contribution to constituent loads in urban areas, the researchers have generally found the
data structure of the rainwater data set determined by three hidden factors, viz. soil dust, sea spray and anthropogenic (Spanos et al., 2002).

The present investigation is the first effort to study the chemistry and the sources for change in quality of rainwater in Roorkee a typical tropical urban area of India. Roorkee town is a medium sized “town group” comprising two units, Roorkee Municipal Board and Roorkee Cantonment Board. It is located in Haridwar district of newly created Uttarakhand state of India (Fig. 1). The town is situated within 29° 51’ N latitude and 77° 63’ E longitude, is on the right bank of Solani River, a tributary of the Ganga River, near the Himalayan foothills. The town is 274 m above the mean sea level. It is situated 172 km to the north of Delhi, capital of India (Arya, 1991). The study area experiences moderate type of subtropical monsoon climate. The rainy season in the area extends from 15th June to 15th September under the influence of south-west monsoon. The average rainfall of the area is about 1100 mm, of which about 85% rainfall is received during monsoon season. The Roorkee town has been famous for its survey and mathematical instrument manufacturing industries. It has 41 sheds covering different industrial activities, viz. electronics, mechanical fabrication, chemical, ceramics, optical lenses and miscellaneous.

2. Sampling and analysis

Rain water samples from the study area in the monsoon season of 2001 and 2002 were collected in polyethylene bottles through funnels (14 cm dia.), which were placed on the roof (top) of the buildings (about 8–10 m from ground level, and 1 m from the floor of the roof) away from surface soil and any specific emission source. To avoid dry deposition, the funnels were washed with distilled water before the rain event; the collectors were deployed as soon as rain began and retrieved immediately after rain stopped. Seventeen rain events were monitored and sampled during the study period. This amounted to about 65% and 35% of the number of rain events occurred in the year 2001 and 2002, respectively, totaling to about 76% and 24% of rainfall in 2001 and 2002, respectively. The sites of the sampling stations were chosen in accordance with general guidelines of the urban characteristics to cover the influence of the major activities in the town. So, the study area was divided in the three main types of land use, viz. residential, commercial and industrial. A total of 36 samples were collected during the study period. Then the samples were brought to the laboratory and analyzed immediately for pH with a digital pH meter, using reference (KCl) and glass electrodes, standardized with pH of 4.0 and 9.2 reference buffers before pH
determination. Electrical conductivity (EC) was measured by conductivity meter. Both pH and EC of the samples were measured at a reference temperature of 25°C, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^- by titration, Na^+ and K^+ by flame photometer, NO_3^- by ion selective electrode, SO_4^{2-} by spectrophotometer TDS and TSS by gravimetric method for total dissolved and suspended solids (dried at 103°C). Procedures followed for analysis have been in accordance with the Standard Methods for Examination of Water and Waste Water of the American Public Health Association, American Water Works Association and Water Environment Federation (APHA, AWWA and WEF, 1998). The calibration for different chemical constituents was done by preparing low-level standard solutions using AR-grade chemicals and were periodically repeated to check the accuracy. The analytical errors were nominal and varied within ±10%.

3. Results and discussion

3.1. Statistical analysis and ion balance

Descriptive statistics for all characteristics have been calculated and presented in Table 1. Ion balance is an important parameter for data quality assessment. It gives an indication of the quality of analysis as well as the possibility of any missing parameter. Quality of data gives an indication of the quality of analysis as well as important parameter for data quality assessment. It calculated and presented in Table 1. Ion balance is an essential parameter for data quality assessment. It is calculated and presented in Table 1.

The anion and cation sums are expressed as milli-equivalents per liter and the typical criteria for acceptance is 5% for anion sum between 10.0 and 800 meq L\(^{-1}\). In this study, the observed difference between cations and anions for all samples (except four samples, which were rejected) fell within the acceptable range.

3.2. General characteristics

The median value of pH has been observed to be 7.05, values of pH in all samples being higher than 5.6, which is the pH of cloud water at equilibrium with atmospheric CO_2 (Charlson and Rodhe, 1982). It should be noted that the urban soil pH in the study area ranges from 7.40 to 7.82. The observed alkalinity of rainwater is due to the high loading of particulate matter in the atmosphere commonly abundant in Indian condition (Khare et al., 2004). The suspended particulate matter that is rich in carbonate and bicarbonate of calcium buffers the acidity of rainwater (Kulshrestha et al., 1996, 2003). In India, pH between 6.0 and 7.5 has been reported in urban areas (Khemani et al., 1989) and 5.22 to 7.65 in forested area (Rao et al., 1995). In contrast, in temperate countries, much lower pH has been reported; 5.10 at Amsterdam Island (remote marine site) (Moody et al., 1991) and 4.96 at Chile, Pacific Ocean (Galloway et al., 1996). It is well known that SO_4^{2-} and NO_3^- are acid contributors and Ca^{2+} acts as acid neutralizer in this region (Saxena et al., 1996).

Assuming that rainwater acidity originates primarily from sulfuric acid and nitric acid and neutralization by Ca^{2+} and Mg^{2+}, so the ratio of \((\text{SO}_4^{2-} + \text{NO}_3^-)/(\text{Ca}^{2+} + \text{Mg}^{2+})\) or TA/TC can be considered as indicator for acidity. If TA/TC is less than 1, it indicates alkaline nature of rainwater and if greater than unity, it indicates the presence of free anions responsible for rainwater acidity. Table 2 shows the ratio of sum of SO_4^{2-} and NO_3^- and sum of Ca^{2+} and Mg^{2+} (TA/TC) from different studies as compared with the ratio TA/TC of

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Min.</th>
<th>Max.</th>
<th>Median</th>
<th>Mean</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH (standard units)</td>
<td>6.85</td>
<td>7.21</td>
<td>7.05</td>
<td>7.03</td>
<td>0.12</td>
</tr>
<tr>
<td>Specific conductance (µhos cm(^{-1}))</td>
<td>19.00</td>
<td>27.00</td>
<td>22.00</td>
<td>22.33</td>
<td>2.42</td>
</tr>
<tr>
<td>Total dissolved solids (mg L(^{-1}))</td>
<td>11.20</td>
<td>16.59</td>
<td>13.57</td>
<td>13.72</td>
<td>1.50</td>
</tr>
<tr>
<td>Total suspended solids (mg L(^{-1}))</td>
<td>2.00</td>
<td>8.00</td>
<td>6.75</td>
<td>6.33</td>
<td>1.71</td>
</tr>
<tr>
<td>Calcium (Ca^{2+}) (µeq L(^{-1}))</td>
<td>123.00</td>
<td>159.78</td>
<td>145.51</td>
<td>145.13</td>
<td>10.87</td>
</tr>
<tr>
<td>Magnesium (Mg^{2+}) (µeq L(^{-1}))</td>
<td>18.27</td>
<td>29.21</td>
<td>22.42</td>
<td>23.28</td>
<td>3.52</td>
</tr>
<tr>
<td>Potassium (K^+) (µeq L(^{-1}))</td>
<td>6.40</td>
<td>34.53</td>
<td>10.62</td>
<td>14.72</td>
<td>9.41</td>
</tr>
<tr>
<td>Sodium (Na^+) (µeq L(^{-1}))</td>
<td>7.61</td>
<td>78.30</td>
<td>34.32</td>
<td>38.50</td>
<td>17.99</td>
</tr>
<tr>
<td>Bicarbonate (HCO_3^-) (µeq L(^{-1}))</td>
<td>67.36</td>
<td>108.17</td>
<td>85.56</td>
<td>88.34</td>
<td>15.81</td>
</tr>
<tr>
<td>Chloride (Cl^-) (µeq L(^{-1}))</td>
<td>42.31</td>
<td>118.48</td>
<td>54.30</td>
<td>59.38</td>
<td>21.52</td>
</tr>
<tr>
<td>Nitrate (NO_3^-) (µeq L(^{-1}))</td>
<td>9.21</td>
<td>55.33</td>
<td>36.37</td>
<td>33.36</td>
<td>12.75</td>
</tr>
<tr>
<td>Sulfate (SO_4^{2-}) (µeq L(^{-1}))</td>
<td>10.41</td>
<td>33.31</td>
<td>20.82</td>
<td>22.59</td>
<td>6.28</td>
</tr>
</tbody>
</table>
this study. This value is 2.99 for Delhi, where acid rain occurred in 18% of events (Kulshrestha et al., 1995) and 1.06 for Korba (Chandravanshi et al., 1997), where acid rain occurs generally. The value of the ratio TA/TC for this study agrees more with the results in Agra region (Kumar et al., 2002) where the pH value of rainwater is also in the same range.

The concentration of cations follows a general pattern $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$, while the concentration of anions follows a general pattern $\text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-}$, indicating that $\text{Ca}^{2+}$ and $\text{HCO}_3^-$ are the dominant cation and anion, respectively. Comparison with other Indian sites for the relative magnitude of ionic species (concentration) in rain water (Table 3) indicates that in all these results including the present study, and except Chembur study, $\text{Ca}^{2+}$ shows highest concentration due to crustal origin, while the dominance of $\text{Na}^+$ and $\text{Cl}^-$ over $\text{Ca}^{2+}$ ions at Chembur may be attributed to the closeness of city to ocean.

The percentage contribution of each ion towards the total deposition is shown in Fig. 2. The alkaline components ($\text{Ca}^{2+}$, $\text{Mg}^{2+}$, $\text{Na}^+$, $\text{K}^+$) contribute 52%, whereas the contribution from the acid components is 48%.

Observed concentration of the rainwater constituents have also been compared with data from other Indian sites, and presented in Table 4. It may be noted from the Table 4 that the highest concentration of $\text{Cl}^-$ and $\text{Na}^+$ is at Chembur (coastal site) and the lowest at present site, an inland site, indicating the inverse relation of the distance from the sea with the concentration of $\text{Cl}^-$ and $\text{Na}^+$. The high concentration of $\text{SO}_4^{2-}$ at Chembur, a highly industrialized area and lowest at Dayalbagh and the present site (Roorkee) proves that no significant industrial source of $\text{SO}_4^{2-}$ exists in this area. The concentration of $\text{Ca}^{2+}$ in rainwater at Roorkee is about 1.6 and 1.7 times higher than the concentration reported in rain samples collected from Chembur and Dayalbagh, respectively.

### 3.3. Estimation of marine contribution

It is a standard practice to calculate different ionic ratios in order to estimate the marine and non-marine contribution. For this, $\text{Na}^+$ has been taken as the reference element assuming that all $\text{Na}^+$ is of marine origin (Keene et al., 1986; Kulshrestha et al., 1996, 2003). However, this assumption may not be strictly valid for a typical urban continental site like Roorkee. Sea water concentration given earlier by Riley and Chester (1971) were used as the reference for calculation. Table 4 shows the ratios of $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, $\text{K}^+$, $\text{HCO}_3^-$, $\text{Cl}^-$, $\text{NO}_3^-$ and $\text{SO}_4^{2-}$. All ratios have been found to be much higher at this site than the recommended sea water ratios indicating significant contribution of non-marine source of these components (Khemani, 1993; Kulshrestha et al., 1996). Similarly, the elevated values may be due to the influence of anthropogenic and crustal sources (Kulshrestha et al., 2003).

Further, the sea salt and non-sea-salt fraction have also been calculated as described by Kulshrestha et al.
(1996) by using the following equations:

\[
\% \text{SSF} = \frac{100(Na)(X/Na)_{\text{sea}}}{X},
\]

where X is the component concentration of interest, and

\[
\% \text{NSSF} = 100 - \text{SSF}.
\]

Results presented in Table 5 also indicate that Ca\(^{2+}\), K\(^+\), NO\(_3\)\(^-\) and SO\(_4\)\(^{2-}\) appear to be of non-marine origin. The results also show that Mg\(^{2+}\) concentration in the rainwater is generally affected by both dust and sea-salt particles in the atmosphere, while the highest contribution of Cl\(^-\) appears to be due to a close proximity to sea-salt particles in the atmosphere (derived from cloud movement). The concentration of Mg\(^{2+}\) is dominated by crustal sources in a site far from the sea, but is determined by a marine source at sampling site close to the sea (Crawley and Sievering, 1986).

### 4. Conclusion

The rainwater pH has been observed to be well above 5.6, the reference pH of cloud water at equilibrium with atmospheric CO\(_2\), reflecting a high loading of particulate matter in the atmosphere, commonly abundant in the Indian conditions. The neutral to sub-alkaline nature of rainwater has also been highlighted by the ratio TA/TC, whose value is 0.34 (quite below 1.0). The levels of concentration of rainwater components have been quite similar to those at other Indian sites, and the relative magnitude (concentration) of ionic species follows the order Ca\(^{2+}\) > HCO\(_3\) > Cl\(^-\) > NO\(_3\) > Na\(^+\) > Mg\(^{2+}\) > SO\(_4\)\(^{2-}\) > K\(^+\). The ratios of rainwater components ((X/Na\(^+\))\(_{\text{rainwater}}\)) have been observed to be higher than the sea water ratios ((X/Na\(^+\))\(_{\text{sea water}}\)) indicating the influence of non-marine sources. This finding has been supported by the calculated values of sea and non-sea salt fractions, which indicate that Ca\(^{2+}\), K\(^+\), NO\(_3\)\(^-\) and SO\(_4\)\(^{2-}\) appear to be of non-marine origin, while Mg\(^{2+}\) is generally affected by both dust and sea-salt particles in the atmosphere. Cl\(^-\), however, appears to be significantly influenced by sea salt contribution possibly derived from cloud movements.

### References


Jain, M., Kulshrestha, U.C., Sarkar, A.K., Parashar, D.C., 2000. Influence of crustal aerosols on wet deposition at
urban and rural sites in India. Atmospheric Environment 34, 5129–5137.