Chemistry of Monsoon and Post-Monsoon Rains at a High Altitude Location, Sinhagad, India


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Abstract

Rainwater samples collected at Sinhagad on 65 rain occasions during monsoon season (June – September 2005) and on 23 rain occasions during post-monsoon season (October-November 2005) with standard rain collection instruments, i.e. wet-only (WO) and bulk collectors (BC), were considered for the present study. Sinhagad is a hill station on a mountaintop in the Western Ghats, located about 40 km southwest of Pune. The following ionic components were determined: H+, NH4+, Ca2+, Mg2+, K+, Na+, SO42-, NO32-, Cl- and F-. The pH analyses showed that rainwater in both the seasons were alkaline. The major neutralizing component was associated with Ca2+. In monsoon rains, the major anion was Cl- and the major cation was Na+; whereas in post-monsoon the major anion was SO42- and the major cation was Ca2+. The concentrations of nss SO42-, NO32- and NH4+ were found to be higher during post-monsoon than monsoon. Surprisingly high concentrations of Ca2+ and SO42- were found during the monsoon season. Since no large upwind sources of these compounds are expected, one is led to conclude that long-range transport may be involved, possibly even including African sources. Since the local sources didn’t seem to influence the samples significantly, this rural site is useful for obtaining regionally representative precipitation data.

Keywords: Rainwater; Chemical composition; Seasonal variation; Long-range transport.

INTRODUCTION

Rainfall is one of the most effective ways of removing atmospheric pollutants. The chemical composition of rainfall reflects the quality of the air through which it falls (Hideaki et al., 2008). Consequently, changes in precipitation chemistry are useful indicators of trends in air chemistry. Furthermore, the chemicals carried by the rain can affect ecosystems, sometimes positively but usually negatively. For these reasons, measurements of precipitation chemistry have been a standard feature of many national monitoring programs. It is well documented that precipitation in coastal areas is strongly affected by sea salt (Ozeki

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et al., 2006), while in inland areas it contains proportionately more substances originating from soil (Mouli et al., 2005). Past studies have shown very high concentration of anthropogenic substances like \( \text{NO}_3^- \) and \( \text{SO}_4^{2-} \) in urban or industrial areas compared to other areas (Tu et al., 2005).

Europe and North America have been adversely affected by acidic deposition (Balasubramanian et al., 1999; Rodhe et al., 2002; Hu et al., 2003). Emission of air pollutants is increasing rapidly in many southeastern Asian countries (Granat et al., 1996) and China (Rodhe et al., 2002), due to faster growth in population and the consequent upward trend in agricultural production, industrialization, energy consumption, transport, housing, etc. Systematic observations on the chemical composition of precipitation has been carried out for several years in Europe and North America (Rodhe et al., 2002) but such studies are limited in the rest of the world, especially under non-urban conditions in the tropical region (Granat et al., 1996; Whelpdale et al., 1996; Norman et al., 2001; Rodhe et al., 2002). Rainwater composition data are useful for the validation of Global Chemistry Transport Models (GCTMs) (Langner and Rodhe, 1991; Rodhe et al., 1995) and help in determining global cycling of sulfur and nitrogen compounds.

Several studies on the chemical composition of precipitation in India have been reported in literature. Continuous measurement programs like the Background Air Pollution Monitoring Network (BAPMoN) studies of Global Atmospheric Watch (GAW), (Mukhopadhyay et al., 1992), Precipitation Chemistry Monitoring Program of the Indian Institute of Tropical Meteorology (IITM) in Pune, (Khemani et al., 1989; Rao, 1997; Pillai et al., 2001; Safai et al, 2004; Momin et al., 2005) and the Indo–Swedish collaboration on atmospheric chemistry (Parashar et al., 1996; Granat et al., 2001; Norman et al., 2001; 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 a below cloud scavenging process. Furthermore, variation in composition reflects local or regional characteristics. Researchers have monitored and collected rainwater 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 to rainwater chemistry. As the studies on seasonal variation in precipitation chemistry are sparse, especially at high altitude locations in India, the present study will fill this gap to some extent.

**Location of Sampling Site**

Rainwater samples were collected at Sinhagad, a hill station about 40 km
southwest of Pune (18°21’ N and 73°45’ E, 1450 m amsl) on a mountaintop in the Western Ghats. It’s top is flat with an area of about 0.5 km². Other mountain peaks of comparable heights surround it. This part of the Western Ghats is covered with vegetation, grass and trees. The only noticeable local source of pollution is wood burning for cooking. A few people live at the summit and some tourists visit the area (by foot). A few cars and buses enter the mountain, but cannot come closer to the sampling site than one kilometer. Winds are generally from the west/southwest during pre-monsoon and monsoon; whereas, in the other seasons, easterlies prevail over this region. The Arabian Sea is about 100 km west of this site. Thus, the site is relatively free from major urban pollution sources.

EXPERIMENTAL SECTION

Sampling of Rainwater
Rainwater samples were collected by using standard rain collection gadgets; i.e., Wet Only (WO) and Bulk Collector (BC). “Wet-only collector” means it collects only rain and not dry deposition as its lid remains open only during rain episodes. Bulk collector consists of a polyethylene funnel with a 21-cm diameter fitted onto a 2-liter polyethylene bottle. Bulk and wet-only rainwater samples were collected at Sinhagad on 65 rain occasions during monsoon (June –September) and on 23 rain occasions during post-monsoon (October-November) seasons of 2005. As 90% of the total rain events were collected in both the seasons, the present study represents the rain chemistry of the entire monsoon and post-
monsoon seasons. In order to investigate the sources of pollutants, the data of chemical species obtained in rainwater were compiled season-wise. During the period under study the rainfall at Sinhagad occurred only in monsoon and post-monsoon seasons.

Samples were collected either on an event basis or on a daily basis. Rainwater collection instruments were kept about 2 m above the ground at Sinhagad. Collecting bottles and funnels were cleaned daily with triple-distilled water to avoid dry deposition of gaseous and particulate pollutants. Samples were collected in polyethylene bottles rinsed with triple-distilled water.

Chemical Analysis of Rainwater

Subsequent to the collection of samples, their pH and conductivity were measured as immediately as possible. The pH was measured with a digital pH meter using reference and glass electrodes standardized at pH 4.0 and 9.2. Conductivity was measured with a digital conductivity meter calibrated against a reference KCl solution of analytical grade, E-merk make. The conductivity was measured at actual sample temperature. The time delay between the conductivity measurements and chemical analyses was about two weeks. Thymol was then added to the samples to prevent bio-degradation and the samples were kept in a refrigerator at 4°C until the completion of all the analyses. Anions F⁻, Cl⁻, NO₃⁻ and SO₄²⁻ were analyzed with an Ion Chromatograph. Cations Na⁺, K⁺, Ca²⁺ and Mg²⁺ were measured with an Atomic Absorption Spectrophotometer. NH₄⁺ was measured by Indophenol method. HCO₃⁻ was estimated from the theoretical relationship between pH and HCO₃⁻ (Parashar et al., 1996).

Quality Control Methods

Proper care was taken in collection and preservation of these samples until the completion of all the analyses. Samples that were found to be contaminated with dust or bird droppings were removed. The data obtained by the chemical analyses were then subjected to the quality check which was done by employing the ion balance method. It was found that the ratio between the sums of cations and anions of individual samples varied between 0.8 and 1.2. A significant correlation was observed between the sum of anions and sum of cations as shown in Fig. 2. This indicates the completeness of the analyses; i.e., all the major ionic components were analyzed. The second check was made through comparison between the measured and calculated (EMEP/CCC-Report 1/95, 1996) conductivities of the individual samples as shown in Fig. 3. A good agreement between the measured and calculated conductivities (R = 0.98 and 0.99) further confirms the good quality data of the chemical analyses.

The higher total ionic concentrations in monsoon samples than in post-monsoon samples (Fig. 2) are due to high concentrations of all the ionic components, except NO₃ and NH₄, in monsoon season than in post-monsoon season. In monsoon season the higher rain fall intensities, sea
Fig. 2. Correlation between cations and anions in rainwater at Sinhagad during (A) monsoon and (B) post-monsoon season 2005.

Fig. 3. Relation between the measured and calculated conductivities in rainwater at Sinhagad during (A) monsoon and (B) post-monsoon season 2005.
salt contributions from marine winds, and long-range transport from African countries are responsible for the high loadings of all the ionic components. Also, the difference is substantial in the case of Cl, Na, Ca and HCO₃.

RESULTS AND DISCUSSION

Chemical Composition of Rainwater

Chemical composition of wet-only and bulk rainwater samples collected at Sinhagad during monsoon and post-monsoon seasons of 2005 showed that both bulk and wet-only rainwater were alkaline with pH varying from 5.73 to 7.21 for monsoon, and 5.05 to 6.98 for post-monsoon season, with the average values 6.5 and 6.3 respectively. Two events were observed below 5.6 pH during the post-monsoon season; however, no acidic event was observed during monsoon season.

The frequency distribution of pH (Fig. 4) showed that the maximum frequency is in the range of 6.6 –7.0 during the monsoon season. Whereas, during the post-monsoon season the highest frequencies are in two ranges: 5.6-6.0 and 6.1-6.5. This indicates that the rainwater is slightly acidic during post-monsoon compared to monsoon.

The pH is the result of the overall effect of acidic and alkaline components, which originated from their respective sources. Acidic components like NO₃ and SO₄ are generally emitted from industrial and/or vehicular sources. Also, certain sources, such as construction activities give rise to increase in Ca and use of fertilizers that
activate soil microbial reactions, give rise to increase in NH$_4$.

The relative contributions of NO$_3$ and SO$_4$ towards acidification of rainfall during monsoon and post-monsoon seasons were studied by calculating the ratio of NO$_3$/ (NO$_3$ + nss SO$_4$), and by assuming that all the acidity is due to NO$_3$ and SO$_4$. It was observed that SO$_4$ contributed about 75% to the acidity of rain.

Figs. 5 and 6 indicate the composition of bulk and wet-only rainwater samples respectively, collected during monsoon and post-monsoon seasons at Sinhagad. It can be seen that except for NO$_3^-$, all the chemical constituents were found to be higher in bulk samples than in wet only samples. This is because the bulk collector remains open all the time and the large particles falling under gravity (dust-fall) get deposited even if there is no rain. Particles are also deposited through impaction and by sorption of gases on already deposited material in the open collector (Pillai et al., 2001).

During the monsoon season Cl$^-$ showed the highest concentration among all. Concentrations of Na$^+$ and Cl$^-$ were higher (almost two times more) during monsoon than during post-monsoon, which is not surprising with the Arabian Sea as the origin. However, concentrations of NO$_3^-$ and NH$_4^+$ were found to be higher during post-monsoon than monsoon. In the case of SO$_4^{2-}$, even though the total SO$_4^{2-}$ was higher in monsoon season, the non-sea salt sulfate (nss SO$_4^{2-}$) was found to be higher in post-monsoon period. The higher concentrations of nss SO$_4^{2-}$, NO$_3^-$ and NH$^+$ in post-monsoon season may be due to prevailing winds of land origin, which brings pollutants from urban areas. Mg$^{2+}$ showed the similar variation as that of Na$^+$ and Cl$^-$.

Non-sea salt component of Ca$^{2+}$ and SO$_4^{2-}$ was computed by assuming Na as reference element, indicating that about 93% Ca$^{2+}$ and 80% SO$_4^{2-}$ are of non-sea salt origin. Local contribution of Ca$^{2+}$ and SO$_4^{2-}$ are thought to be small due to a small difference between bulk and wet-only samples and also a very close correspondence between the two bulk collectors. Back trajectory plots for the period under study (Fig. 7) indicate that, since there is very little industrial activity between the sampling location and the coast, these chemical species might have been transported from far off distances, such as eastern or northeastern Africa.

**Acidic and Neutralization Potentials**

The difference between acidic potential (AP) and alkaline or neutralization potential (NP) is one of the useful indicators of chemical nature of the precipitation. Acid potential is the sum of NO$_3$ and nss SO$_4$ and neutralization potential is the sum of NH$_4$, Ca, Mg and K. The variation in AP/NP ratio for both monsoon and post-monsoon seasons are studied. This ratio is less than one in both the season indicating the neutralization potential dominates the acidic potential. This ratio is more in post-monsoon season (0.82) than in monsoon season (0.43) indicating the neutralization potential is less in post-monsoon season.
Fig. 5. Comparison between concentrations of chemical ions measured in bulk rainwater samples collected at Sinhagad in 2005.

Fig. 6. Comparison between concentrations of chemical ions measured in wet-only rainwater samples collected at Sinhagad in 2005.
Fig. 7. Seven-day back trajectories at Sinhagad during the: A. Monsoon, and B. Post-monsoon seasons of 2005.

compared to that in monsoon season. The pH has shown an inverse relationship with AP/NP.

**Enrichment Factors**

Enrichment factors (EF) are normally applied to identify the origin of an element in precipitation (Zhang *et al.*, 2006). This calculation is based on the elemental ratio found between ions collected in the atmosphere or in precipitation, as compared to a similar ratio for a reference material.

The EF values may imply for information about the source of the element. Commonly, Na is taken as the best reference element for seawater since it is assumed to be of purely marine origin. The EFs were calculated for K, Ca, Mg, Cl and SO₄ by using the following equation and given in Table 1.

\[
EF = \frac{[X/Na^+]_{\text{rainwater}}}{[X/Na^+]_{\text{seawater}}} \quad (1)
\]

Where, X is the concentration of the ion of interest. All the ionic concentrations were taken in µeq/L. In both the seasons, the EFs were found to be high for Ca, SO₄ and K indicating other-than-sea sources; i.e., soil or anthropogenic.
Table 1. Comparison of sea water ratios with rainwater ratios with respect to Na and enrichment factors.

<table>
<thead>
<tr>
<th></th>
<th>K⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seawater ratio</td>
<td>0.022</td>
<td>0.044</td>
<td>0.227</td>
<td>1.16</td>
<td>0.126</td>
</tr>
<tr>
<td>Rainwater ratio</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monsoon</td>
<td>0.06</td>
<td>0.69</td>
<td>0.34</td>
<td>1.02</td>
<td>0.51</td>
</tr>
<tr>
<td>Post monsoon</td>
<td>0.12</td>
<td>0.98</td>
<td>0.31</td>
<td>1.07</td>
<td>1.00</td>
</tr>
<tr>
<td>EF&lt;sub&gt;monsoon&lt;/sub&gt;</td>
<td>2.727</td>
<td>15.681</td>
<td>1.498</td>
<td>1.034</td>
<td>4.047</td>
</tr>
<tr>
<td>EF&lt;sub&gt;postmonsoon&lt;/sub&gt;</td>
<td>5.454</td>
<td>22.272</td>
<td>1.366</td>
<td>0.922</td>
<td>7.936</td>
</tr>
</tbody>
</table>

Percentage Contribution of Ionic Species

The percentage contributions of various ionic species to total ionic content in bulk and wet-only rainwater during monsoon season and post-monsoon season are shown in Fig. 8. During the monsoon season, among the cations, Na⁺ was dominant, and among the anions, Cl⁻ was dominant; whereas, during the post-monsoon season, Ca²⁺ was dominant among the cations and SO₄²⁻ was dominant among anions. This indicates that the sea salt contribution is more during monsoon season, during which the southwest monsoon winds bring sea salt from the Arabian Sea to the sampling location. The percentage contributions of NO₃⁻, NH₄⁺, K⁺, Ca²⁺ and Mg²⁺ were higher in post-monsoon season than those in monsoon. Whereas, the percentage contributions of sea salt components (Na⁺, Cl⁻ and Mg²⁺) and HCO₃⁻ were found to be less in post-monsoon season than those in monsoon. These differences are due to the change in prevailing wind directions during both seasons. The back trajectories at 1400 amsl obtained from Hysplit, NOAA, USA for the monsoon and post-monsoon seasons are shown in Fig 7. It can be seen that during the monsoon season, winds originate from the African countries before passing through Arabian Sea and reaching the sampling location. During the post-monsoon season, the winds were from either the north or northwest and traveled completely over land before reaching the sampling location. Hence, there is a possibility of long-range transport of aerosols over the Sinhagad region when air masses come from as far as the East African Gulf Coast during monsoon season and from northern and northwestern regions of India during post-monsoon.

Factor Analysis

Source identification of different chemical ions present in precipitation samples at Sinhagad was further carried out through Varimax rotated factor analysis (SPSS, 1983), which are shown in Table 2. Factor loadings show that the data synthesized into three factors with Eigen values cut off at greater than unity and explaining about 76% of the total variance. A more-detailed description regarding sources of different
Fig. 8. Percentage contribution of ionic species in rainwater at Sinhagad during monsoon 2005.

chemical species associated with different factors is given below.

Factor I registered a variance of 50% with high loadings for Cl\(^-\), SO\(_4^{2-}\), Na\(^+\), Ca\(^{2+}\) and Mg\(^{2+}\) indicating natural sources, sea and soil. Na\(^+\) and Cl\(^-\) occur in the form of sea salt, and hence, they appear in the same factor. Although SO\(_4^{2-}\) is not originated from the soil or the sea, it appears in this factor because SO\(_4\) and Ca are brought together in the region by marine wind from the east coast of continental Africa, according to trajectory analyses. As most of the Mg originates from the sea source, it appears in this factor. Factor II contains NO\(_3^-\), K and H\(^+\). This indicates sources as vehicular emissions and biomass burning. Factor III shows loadings for NH\(_4^+\) indicating the anthropogenic source; i.e., manmade activities such as cooking, fertilizers and animal and agricultural wastes, etc.

Sinhagad and Pune Rainwater Comparison

Comparison between chemical composition of wet-only rainwater during monsoon season at Sinhagad (present study) and at Momin \textit{et al.}\ (2005) is shown in Table 3. The pH of rainwater during the monsoon season at Sinhagad is slightly less than that at Pune which is due to the lower concentrations of Ca at Sinhagad, which is a major neutralizing component. Except Na and Mg, all the ionic concentrations were found to be lower at Sinhagad than those at Pune. This comparison indicates that all the ionic species, both soil-oriented and anthropogenic were found to be higher at Pune, which is an urban location.
Table 2. Factor loadings matrix obtained from rainwater samples at Sinhagad during 2005.

<table>
<thead>
<tr>
<th>Chemical Ions</th>
<th>Factor I</th>
<th>Factor II</th>
<th>Factor III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl^-</td>
<td>0.91463</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO_4^{2-}</td>
<td>0.86734</td>
<td>0.90564</td>
<td>0.92313</td>
</tr>
<tr>
<td>NO_3^-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH_4^+</td>
<td>0.92313</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na^+</td>
<td>0.9150</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K^+</td>
<td>0.7352</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca^{2+}</td>
<td>0.66898</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg^{2+}</td>
<td>0.9261</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H^+</td>
<td>0.66684</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCO_3^-</td>
<td>0.79125</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Percentage Variance</td>
<td>50</td>
<td>13.4</td>
<td>12.3</td>
</tr>
<tr>
<td>Eigen Value</td>
<td>4.99943</td>
<td>1.33629</td>
<td>1.26017</td>
</tr>
</tbody>
</table>

Table 3. Comparison between the chemical composition (μeq/L) of wet-only and bulk rainwater samples for monsoon seasons at Pune (2003) and Sinhagad (2005).

<table>
<thead>
<tr>
<th>Location</th>
<th>Cl</th>
<th>SO_4</th>
<th>Nss SO_4</th>
<th>NO_3</th>
<th>HCO_3</th>
<th>NH_4</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pune</td>
<td>75</td>
<td>33</td>
<td>26</td>
<td>20</td>
<td>36</td>
<td>7</td>
<td>59</td>
<td>5</td>
<td>85</td>
<td>15</td>
<td>6.60</td>
</tr>
<tr>
<td>Sinhagad</td>
<td>64</td>
<td>31</td>
<td>23</td>
<td>8</td>
<td>52</td>
<td>2</td>
<td>62</td>
<td>3</td>
<td>43</td>
<td>20</td>
<td>6.41</td>
</tr>
</tbody>
</table>

CONCLUSIONS

1. The average pH values for both bulk and wet-only rainwater samples at Sinhagad were found to be alkaline during both the seasons.

2. The major neutralizing component is associated with Ca. Neutralization by NH_3 in this region is smaller by a factor of ten.

3. The major anions in most of the samples were Cl^- and SO_4^{2-} and the major cations were Ca^{2+} and Na^+.

4. The difference between composition of bulk and wet-only rainwater samples was quite small. It implies that the local sources (within the nearby surroundings) didn't seem to influence the Sinhagad samples significantly. This shows that this rural site is useful for obtaining regionally representative precipitation chemistry data.

5. Surprisingly high concentrations of Ca^{2+} and SO_4^{2-} were measured during the southwest monsoon season. Since no large upwind sources of these compounds are expected on the Indian subcontinent, it is concluded that long-range transport may be involved, possibly from African sources, which is also verified by trajectory analyses.

6. The higher concentrations of NO_3^-; NH_4^+; nss SO_4^{2-} and nss K^+ in post-monsoon season than those in monsoon is due to the differences in the air masses reaching the
sampling location from different regions due to change in wind directions.

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