Rain water composition at two BAPMoN stations in India

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ABSTRACT. Six years of rain water composition data from two BAPMoN regional stations in India are analysed using Factor Model Analysis. It gives four factors representing different source type contributing to water soluble pollutants in precipitation. The major influence on rain water composition at both sites are Sea-salt and continental source such as soil dust, ammonia and low levels of sulfate and nitrate which presumably have both natural and anthropogenic components. The long term mean values of pH of rain water at both sites were found to be greater than the pH value of selected polluted northern hemisphere sites.

Key words – Factor model, Precipitation aerosols.

1. Introduction

The study of chemical composition of rain water is very useful to provide an understanding of atmospheric physical and chemical processes and the nature of air pollution sources. The concentrations of chemical constituents is surface precipitation are the consequence of several cumulative processes occurring in and below the clouds. It is well known that the precipitation scavenging is classified into "in cloud scavenging" and "below cloud scavenging" process in accordance with the positions where the scavenging occurs. Thus, rain water samples from different shower events exhibit variable compositions. However, when monthly mixed samples of rain water are chemically analysed and the net deposition accounted for over a long period. It is mainly the ambient atmospheric burden of pollution that gets reflected while the weather-related factors only cause the variations about the mean value.

There are many studies which have reported that acid deposition is increasing and this is mainly due to H\textsuperscript{+} ions associated with anions SO\textsuperscript{2-}, NO\textsuperscript{3-} and Cl\textsuperscript{-} which are generated primarily from anthropogenic emissions. However data on rain analysis for BAPMoN stations suggest alkaline nature of precipitation, attributed to anions associated with cations like Ca\textsuperscript{2+}, Mg\textsuperscript{2+} and K\textsuperscript{+} which originate from natural sources. NH\textsubscript{4}\textsuperscript{+} is also likely to be an important factor in neutralizing the acidity of the precipitation.

The composition of drain water may be affected by ions from both marine and terrestrial sources. But it is often difficult to ascertain the origin of precipitated ions (Eriksson 1958). Larson and Heltick (1956) found that the chemical composition of rain water is influenced by the several factors such as distance of the sampling from sea, topography of the area, wind velocity and contribution from land mass, saline etc. Although it has been inferred (Hutton and Lesile 1958) that terrestrial, rather than oceanic salts predominate at increasing distance from sea. There are reports which suggest that particles of sea salt may travel over long distance.

The objective of this study is to identify the sources of water soluble pollutants contributing to precipitation in a coastal site (Vishakhapatnam, lat.17°41'N, long. 83°18'E) and arid location (Jodhpur, lat.26°18'N, long. 73°01'E).
TABLE 1
Water soluble components in precipitation mg L⁻¹

<table>
<thead>
<tr>
<th>Water soluble component</th>
<th>Vishakhapatnam</th>
<th>Jodhpur</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>SD</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>1.53</td>
<td>1.05</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>7.72</td>
<td>6.50</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>4.88</td>
<td>4.94</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>0.42</td>
<td>0.70</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>3.42</td>
<td>3.71</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>1.44</td>
<td>1.52</td>
</tr>
<tr>
<td>Na⁺</td>
<td>4.59</td>
<td>4.26</td>
</tr>
<tr>
<td>K⁺</td>
<td>1.33</td>
<td>1.43</td>
</tr>
<tr>
<td>pH</td>
<td>6.08</td>
<td>1.88</td>
</tr>
</tbody>
</table>

2. Experimental methods

The rain water samples are collected round the year whenever rainfall occurs at ten BAPMoN stations operated by India Meteorological Department, that forms a part of Global Atmosphere Watch (Global Air Pollution Observational Network). Samples are specially collected under a wet-only sampling programme (i.e., avoidance of any dry deposition in the collector (Krishnanand 1984, Mukherjee et al. 1986). The monthly mixed samples are analysed for determining the concentrations of the cations (Ca²⁺, Mg²⁺, K⁺, Na⁺) using Atomic Absorption Spectrophotometer (PU 9000 Pye Unicam make) and Anions (SO₄²⁻, NO₃⁻ and Cl⁻) and NH₄⁺ using UV-Vis Spectrophotometer (UV-240, Shimadzu make) according to standard and well known techniques.

3. Results and discussions

(i) Chemical analysis

Table 1 gives the average concentrations and standard deviations (SD) of different water soluble species observed in the rain water. The pH values measured are also shown which were used to calculate H⁺ ion concentrations. Sodium and chlorides are major components driven from Sea salt and oxides of Sulphur are the typical pollutants emitted from natural and anthropogenic sources. Major portion of Calcium, Magnesium and Potassium are usually of crustal origin. Other significant pollutants are nitrate and ammonium. It can be concluded that in addition to soil driven components the water soluble species contributed from natural and other man-made sources are also likely to be present in precipitation samples.

(ii) Correlation analysis

As expected in a coastal town where aerosols of sea salts are predominant, the correlation between Na⁺ and Cl⁻ is very high (Table 2). High correlation of H⁺ and NO₃⁻ indicates the role of oxide of nitrogen in lowering pH of precipitation.

The strongly correlated group of soil driven species (Calcium, Potassium and Magnesium) are also obvious. The positive correlations of Potassium with Calcium and Sodium indicate that Potassium ions are contributed by both sources (i.e., marine as well as continental). The higher positive correlation coefficient between sulphate and ammonium appears to be due to emission of oxides of sulphur and ammonia gas presumably by both natural and anthropogenic sources.

The pattern of correlations is different at Jodhpur than Vishakhapatnam. It is surprising that Jodhpur which receives meridional air after extensive travel over land has shown a significant positive correlation between Na and Cl. The NaCl is most likely to be of local origin, as also indicated by high Na⁺ to Ca²⁺ correlation (Mukhopadhyay et al. 1992). Thus, in addition to Sea salt particles, terrestrial salt particles also play an important role in the composition of rain water at the station. However the presence of Sea-salt particles in the neighbourhood of Jodhpur has already been reported (S. J. Maske 1982). Interestingly Ca²⁺ is negatively correlated with H⁺, which is suggestive of the importance of dissolution and exchange reaction involving particulate material (calcareous minerals) by which H⁺ ions are consumed.

Although correlation matrix is useful to find out the association amongst the variables. It is very difficult to express relative importance of these variables. The study of correlations shows that one water soluble component has good correlation with many other components. Therefore, the identification of the source contributing to a particular component is very difficult.

(iii) Factor analysis

The objective of "Factor Analysis" is to reduce the dimensionality of the problem so that interpretability increases considerably but no significant information is lost. The basic principle and assumption of classical factor model used in the field of Air Pollution are defined by the following equation:

\[ C_k = \sum_{j=1}^{p} L_{ij} * (FS)_{jk} + E_{ik} \]  \hspace{1cm} (1)

Where, \( C_k \) is the normalised value of concentration of the \( i \)th species in \( k \)th sample. \( FS_{jk} \) is the factor score of the \( j \)th common factor for the \( k \)th sample. \( L_{ij} \) is the factor loading and \( E_{ik} \) is the residual not accounted by the common factors and which is the left out of the solution.

It should also be mentioned that although both Principal Component Analysis (PCA) and Factor Analysis (FA) are
used for data reduction, some difference can be seen between PCA and FA as follows:

(i) Although FA adopts a mathematical model involving data structure

(ii) PCA does not allow the presence of error variance, the error term in FA are assumed to be uncorrelated with each other.

In a familiar Factor Analysis, e.g., Varimax rotated factor analysis model, it is assumed that there is no correlation between the common factors and errors, since Factor Analysis is mathematical model of first place and also the error is taken into consideration. Therefore, Factor Analysis is preferred over the Principal Component Analysis used in this study.

The concentration data of water soluble component and hydrogen ion concentrations (calculated from pH values) were subjected to Factor Analysis. Factor Analysis with Varimax rotated factor matrix (selecting principal factoring technique with eigen value cut off at 1.00) provides a convenient method of scrutinising rain water composition data for patterns in variance which may be used to identify major source of rain water ions (Crawley and Sievering 1986). Certainly factor analysis has some problems when applied as a mean of quantitative source apportionment (for example see Henry 1987). However, it is applied here only as a qualitative tool for identifying grouping of ions which show commonality in variance. Factor loading exceeding about ± 0.5 are generally considered to be significant, although Crawley and Sievering (1986) attributed significance to loading down to ± 0.4.

TABLE 2
Correlation coefficients (r) between species

<table>
<thead>
<tr>
<th>Species</th>
<th>Vishakapatnam</th>
<th>Jodhpur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>VS</td>
<td>Cl⁻</td>
</tr>
<tr>
<td>H⁺</td>
<td>VS</td>
<td>NO₃⁻</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>VS</td>
<td>Mg²⁺</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>VS</td>
<td>K⁺</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>VS</td>
<td>SO₄²⁻</td>
</tr>
<tr>
<td>K⁺</td>
<td>VS</td>
<td>Cl⁻</td>
</tr>
<tr>
<td>Na⁺</td>
<td>VS</td>
<td>K⁺</td>
</tr>
</tbody>
</table>

TABLE 3(a)
Varimax Rotated Factor Matrix of Vishakapatnam

<table>
<thead>
<tr>
<th>Variables</th>
<th>Factor 1</th>
<th>Factor 2</th>
<th>Factor 3</th>
<th>Factor 4</th>
<th>Commonality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>-0.88</td>
<td>-0.14</td>
<td>-0.11</td>
<td>-0.00</td>
<td>0.807</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>-0.84</td>
<td>0.09</td>
<td>0.28</td>
<td>0.01</td>
<td>0.801</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>-0.36</td>
<td>0.10</td>
<td>-0.03</td>
<td>-0.82</td>
<td>0.847</td>
</tr>
<tr>
<td>K⁺</td>
<td>-0.60</td>
<td>0.45</td>
<td>0.30</td>
<td>-0.11</td>
<td>0.871</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>0.30</td>
<td>-0.03</td>
<td>0.23</td>
<td>-0.84</td>
<td>0.856</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>-0.06</td>
<td>0.90</td>
<td>-0.25</td>
<td>-0.07</td>
<td>0.887</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>-0.22</td>
<td>0.87</td>
<td>0.19</td>
<td>0.02</td>
<td>0.845</td>
</tr>
<tr>
<td>H⁺</td>
<td>0.06</td>
<td>-0.07</td>
<td>0.88</td>
<td>-0.11</td>
<td>0.803</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>-0.34</td>
<td>0.07</td>
<td>0.80</td>
<td>-0.05</td>
<td>0.773</td>
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<tr>
<td>Eigenvalue</td>
<td>2.275</td>
<td>1.825</td>
<td>1.772</td>
<td>1.424</td>
<td>7.296</td>
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<tr>
<td>% Variance</td>
<td>25.27</td>
<td>20.27</td>
<td>19.68</td>
<td>15.82</td>
<td></td>
</tr>
<tr>
<td>Cum. % Var.</td>
<td>25.26</td>
<td>45.54</td>
<td>65.22</td>
<td>81.04</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 3(b)
Varimax Rotated Factor Matrix of Jodhpur

<table>
<thead>
<tr>
<th>Variables</th>
<th>Factor 1</th>
<th>Factor 2</th>
<th>Factor 3</th>
<th>Factor 4</th>
<th>Commonality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>-0.58</td>
<td>0.61</td>
<td>0.05</td>
<td>0.19</td>
<td>0.762</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>-0.90</td>
<td>0.15</td>
<td>-0.29</td>
<td>-0.00</td>
<td>0.923</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>-0.93</td>
<td>-0.08</td>
<td>0.11</td>
<td>-0.03</td>
<td>0.884</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.25</td>
<td>0.25</td>
<td>-0.85</td>
<td>0.04</td>
<td>0.848</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>0.12</td>
<td>-0.15</td>
<td>-0.84</td>
<td>0.08</td>
<td>0.764</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.18</td>
<td>0.76</td>
<td>-0.20</td>
<td>-0.23</td>
<td>0.707</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.16</td>
<td>0.76</td>
<td>0.08</td>
<td>0.16</td>
<td>0.637</td>
</tr>
<tr>
<td>H⁺</td>
<td>0.42</td>
<td>-0.25</td>
<td>-0.22</td>
<td>0.63</td>
<td>0.692</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>-0.15</td>
<td>0.16</td>
<td>-0.00</td>
<td>0.83</td>
<td>0.729</td>
</tr>
<tr>
<td>Eigenvalue</td>
<td>2.354</td>
<td>1.745</td>
<td>1.640</td>
<td>1.212</td>
<td>6.951</td>
</tr>
<tr>
<td>% Variance</td>
<td>26.15</td>
<td>19.38</td>
<td>18.22</td>
<td>13.46</td>
<td></td>
</tr>
<tr>
<td>Cum. % Var.</td>
<td>26.15</td>
<td>45.53</td>
<td>63.75</td>
<td>77.21</td>
<td></td>
</tr>
</tbody>
</table>
4. Conclusions

Correlation studies are useful but not sufficient to explain the association between variables in the observations. Therefore, these should be supported by other statistical analysis. Factor Analysis technique applied to the precipitation chemistry data brought the following conclusions.

(i) Water soluble species are mainly derived from two type of sources. Sea salt aerosols and continental source such as soil dust and ammonia.

(ii) Both the places are relatively little, influenced by the presence of secondary particles as reflected in the last two factors.

(iii) The long term volume weighted mean pH values at both sites are greater than pH values of polluted sites in northern hemisphere suggest that both sites are relatively free from major anthropogenic pollution.

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References


