

Rain water composition at two BAPMoN stations in India

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सार — फैक्टर मॉडल विश्लेषण का प्रयोग करते हुए भारत के दो बेपमन क्षेत्रीय स्थानों के वर्षा के जल संघटन के 6 वर्षों के आँकड़ों का विश्लेषण किया गया है। इससे वर्षा के जल में प्रदूषकों के विलेय होने में सहायक विभिन्न प्रकार के स्रोतों वाले चार कारकों का पता चलता है। दोनों स्थानों पर वर्षा के जल संघटन को मुख्य रूप से प्रभावित करने वाले जिन घटकों का पता चलता है उनमें समुद्री खारापन और महाद्वीपीय स्रोत, जैसे धूल मिट्टी, अमोनिया एवं निम्न स्तर का सल्फेट तथा नाइट्रेट है, जिसमें संभवतः प्राकृतिक और मानवजनित दोनों घटक शामिल होते हैं। दोनों स्थानों पर वर्षा के जल की दीर्घावधि प्रति घंटा औसत मात्रा उत्तरी गोलार्ध के चुने हुए प्रदूषित स्थानों की प्रति घंटा औसत मात्रा से अधिक पायी गयी है।

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 in 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^+ ions associated with anions SO_4^{2-} , NO_3^- and Cl^- 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^{++} , Mg^{++} and K^+ which originate from natural sources. NH_4^+ is also likely to be an important factor in neutralizing the acidity of the precipitation.

The composition of rain 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. $17^{\circ}41'N$, long. $83^{\circ}18'E$) and arid location (Jodhpur, lat. $26^{\circ}18'N$, long. $73^{\circ}01'E$).

TABLE 1
Water soluble components in precipitation mg L⁻¹

Water soluble component	Vishakhapatnam		Jodhpur	
	Mean	S D	Mean	S D
SO ₄ ⁻	1.53	1.05	1.68	2.63
NO ₃ ⁻	7.72	6.50	5.45	6.19
Cl ⁻	4.88	4.94	4.06	5.19
NH ₄ ⁺	0.42	0.70	0.08	0.14
Ca ⁺⁺	3.42	3.71	8.88	7.85
Mg ⁺⁺	1.44	1.52	2.43	2.95
Na ⁺	4.59	4.26	4.49	3.93
K ⁺	1.33	1.43	1.97	3.06
pH	6.08	1.88	7.43	0.44

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 (Ca⁺⁺, Mg⁺⁺, K⁺, Na⁺) using Atomic Absorption Spectrophotometer (PU 9000 Pye Unicam make) and Anions (SO₄⁻, 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 maritime 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 Ca⁺⁺ 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 Ca⁺⁺ 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:

$$C_{ik}^n = \sum_{j=1}^P L_{ij} * (FS)_{jk} + E_{ik} \quad (1)$$

Where, C_{ik}ⁿ 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_{ij} 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

TABLE 2
Correlation coefficients (r) between species

Vishakhapatnam				Jodhpur			
Na ⁺	Vs	Cl ⁻	0.61	Na ⁺	Vs	Cl ⁻	0.60
H ⁺	Vs	NO ₃ ⁻	0.54	Na ⁺	Vs	SO ₄ ⁻	0.50
Ca ⁺⁺	Vs	Mg ⁺⁺	0.65	Na ⁺	Vs	Ca ⁺⁺	0.54
Ca ⁺⁺	Vs	K ⁺	0.47	Cl ⁻	Vs	SO ₄ ⁻	0.74
NH ₄ ⁺	Vs	SO ₄ ⁻	0.42	K ⁺	Vs	Cl ⁻	0.53
K ⁺	Vs	Cl ⁻	0.59	H ⁺	Vs	Ca ⁺⁺	-0.25
Na ⁺	Vs	K ⁺	0.47	K ⁺	Vs	NH ₄ ⁺	0.50

TABLE 3(a)
Varimax Rotated Factor Matrix of Vishakhapatnam

Variables	Factor 1	Factor 2	Factor 3	Factor 4	Commonality
Na ⁺	-0.88	-0.14	-0.11	-0.00	0.807
Cl ⁻	-0.84	0.09	0.28	0.01	0.801
SO ₄ ⁻	-0.36	0.10	-0.03	-0.82	0.847
K ⁺	-0.60	0.45	0.30	-0.11	0.671
NH ₄ ⁺	0.30	-0.03	0.23	-0.84	0.856
Mg ⁺⁺	-0.06	0.90	-0.25	-0.07	0.887
Ca ⁺⁺	-0.22	0.87	0.19	0.02	0.845
H ⁺	0.06	-0.07	0.88	-0.11	0.803
NO ₃ ⁻	-0.34	0.07	0.80	-0.05	0.773
Eigenvalue	2.275	1.825	1.772	1.424	7.296
% Variance	25.27	20.27	19.68	15.82	
Cum % Var.	25.26	45.54	65.22	81.04	

TABLE 3(b)
Varimax Rotated Factor Matrix of Jodhpur

Variables	Factor 1	Factor 2	Factor 3	Factor 4	Commonality
Na ⁺	-0.58	0.61	0.05	0.19	0.762
Cl ⁻	-0.90	0.15	-0.29	-0.00	0.923
SO ₄ ⁻	-0.93	-0.08	0.11	-0.03	0.884
K ⁺	-0.25	0.25	-0.85	0.04	0.848
NH ₄ ⁺	0.12	-0.15	-0.84	0.08	0.764
Mg ⁺⁺	0.18	0.76	-0.20	-0.23	0.707
Ca ⁺⁺	-0.16	0.76	0.08	0.16	0.637
H ⁺	0.42	-0.25	-0.22	0.63	0.692
NO ₃ ⁻	-0.15	0.16	-0.00	0.83	0.729
Eigenvalue	2.354	1.745	1.640	1.212	6.951
% Variance	26.15	19.38	18.22	13.46	
Cum % Var.	26.15	45.53	63.75	77.21	

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 .

(a) *Vishakhapatnam*

The pattern of factor loadings in Table 3(a) clearly identifies two major source of ions. The first factor represents sea salt source, dominated by the major sea salt ions Na^+ , K^+ and Cl^- as expected at the coastal site, where the absolute concentrations of sea salts are higher. The second factor seems to express soil particles, since it is correlated with Ca^{++} and Mg^{++} . These elements are usually found in crustal components. Moreover, this factor appears to have weak correlation with nitrates (NO_3^-) and it can, therefore, be estimated that this factor is also associated with the emission of nitrogen. Third factor corresponds to the emission of oxides of nitrogen, which is converted in to secondary particles by further chemical reactions. This factor also indicate that nitrate combined with Hydrogen ions have major effect in determining the pH of rain water. Fourth factor depends upon NH_4^+ and SO_4^{--} . These are the predominant chemical components of secondary particles. It may also be suggested that a major origin of secondary particles is the Sulphur Dioxide, Ammonium ions are the results of ammonia gas emitted by natural and man-made activities.

(b) *Jodhpur*

Sodium, chloride and sulphate have higher factor loadings for factor 1. Calcium, Magnesium and Sodium for factor 2, Ammonium and Potassium for factor 3 and Hydrogen and nitrate for factor 4. Factor 1 may be considered to represent Sea salt particles and emission of sulphur. The second factor corresponds to soil particles as it is correlated with Ca^{++} and Mg^{++} . The station is known to be rich in the Ca^{++} and Mg^{++} (Krishnanand 1984). Factor 3 also seems to express continental source dominated by ammonia and some crustal contributions. Fourth factor represents emission of oxides of nitrogen.

The variance explained by the last two factors which indicate the presence of secondary particles is small in comparison to first two factors at both sites. This suggests that contribution from the continental source and the sea salt aerosols is more compared to anthropogenic sources at both the sites. B. Mukhopadhyay *et al.* 1993, found that sulphates and nitrates are more homogeneously distributed and may, therefore, have gaseous precursors from the natural emissions.

It is also found that the long term volume-weighted mean pH values 6.08 and 7.43 at Vishakhapatnam and Jodhpur respectively are above 5. Moreover, these figures can be contrasted with mean values of 4.5 and below at polluted northern hemisphere sites (*e.g.*, NAPAP 1990 and reference therein). The conclusion suggested by these data is that both sites may be considered to be relatively free from major anthropogenic pollution.

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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