RESEARCH ARTICLE

Source apportionment of the ionic components in precipitation over an urban region in Western India

Ramya Sunder Raman · S. Ramachandran

Abstract

Introduction Inorganic ion concentrations in event-based wet-only precipitation samples collected during the southwest (SW) monsoon at an urban location in Western India, Ahmedabad between July 2000 and September 2002 were measured by Rastogi and Sarin (2007).

Methods For the first time at a location in India, an advanced factor analysis model was retrospectively applied to the measured concentrations of ions (Rastogi and Sarin 2007) in precipitation for source apportionment. Positive matrix factorization resolved five factors, including crustal material, sea salt, nitrate/sulfate-rich factor, ammonium-rich factor, and free acidity.

Results and discussion Amongst the model-resolved factors, crustal material was the highest contributor to the total dissolved solids (TDS) accounting for 44.1% on average. Potential source contribution function (PSCF) analysis identified source locations along the eastern coast of Somalia, Yemen, Oman, and the United Arab Emirates for this factor. Sea salt was the second highest contributor accounting for 29.8%. The potential source regions of this factor were also identified in the Arabian Sea and the southern Indian Ocean along the coast of Africa, and the Arabian Gulf. This study also examined the spatial relationships between the source locations of chemical species in precipitation and in ambient aerosol (resolved in an earlier study).

Conclusions Crustal material was the highest contributor to TDS at the study location. Spatial relationships between aerosol and precipitation factor source regions suggested that below-cloud scavenging of aerosol particles was a likely contributor to the chemical species apportioned to various precipitation factors. Additionally, source types of chemical species in precipitation resolved in this study were qualitatively compared with those identified at other locations in India. The comparison showed that soil was an important contributor to the dissolved mass of chemical species in precipitation at all locations in India.

Keywords Ahmedabad · Precipitation · Inorganic ion concentrations · Positive matrix factorization (PMF) · Potential source contribution function (PSCF)

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1 Introduction and purpose

Precipitation is a major mechanism responsible for the removal of ambient particles and gases from the atmosphere. The concentrations of chemical species in precipitation depend on several factors including the sources of particles and gases, chemical transformations in the gas, particle, and aqueous phases, meteorology, and the "in-cloud" and "below-cloud" scavenging efficiencies of precipitation for different species (e.g., Galloway et al. 1989; Tuncel and Ungör 1996; Lehmann et al. 2005). Cloud modeling has demonstrated that, together, in-cloud and below-cloud scavenging mecha-

nisms result in the removal of an appreciable fraction (as high as 90%, depending on the chemical nature and size of the particles) of the ambient aerosol and incorporate it in cloud water (Pruppacher and Klett 1997). Thus, a quantitative estimate of the sources contributing to chemical species in precipitation helps assess the relative importance of natural and anthropogenic sources affecting the air quality of a region. Additionally, source apportionment studies may also help understand the enhancement or suppression of cloud precipitation efficiencies at a receptor site based on the source types and their contribution to pollutants in precipitation.

Several studies across the globe typically assess geographical, annual, and seasonal trends in source contributions to precipitation using individual ion concentrations. This approach can often complicate the attempts to understand the behavior of a particular species when multiple sources with varying strengths contribute to its concentration (Treloar 1993). In an attempt to overcome this difficulty, in the last couple of decades, several investigations in Europe and North America have adopted analytical methodologies that exploit the statistical association between groups of chemical species to identify their origin in precipitation. Such methods include multiple linear regression, principal component analysis, cluster analysis, positive matrix factorization (PMF), and other factor analytic approaches (e.g., Eder 1989 and references cited therein; Hooper and Peters 1989; Kessler et al. 1992; Treloar 1993; Antilla et al. 1995). Air mass back-trajectory ensembles have also been used to identify origin of pollutants in precipitation and their likely geographical locations (e.g., Zeng and Hopke 1989; Lucey et al. 2001).

It is important to point out that the precipitation chemistry in India is quite different from that in North America and Europe. At several locations in India, the pH of precipitation, in contrast to the situation in Europe and North America, was found to be alkaline (e.g., Kulshrestha et al. 1998; Parashar et al. 2001; Safai et al. 2004; Rastogi and Sarin 2005; Salve et al. 2006; Tiwari et al. 2007). This observation was explained by the fact that despite having large sources of oxides of sulfur and nitrogen, neutralization of acidic components by crustal material resulted in alkaline rainwater (e.g., Jain et al. 2000; Norman et al. 2001; Rastogi and Sarin 2005). Thus, the source categories and their "finger prints" resolved for precipitation in Europe or North America cannot be easily extrapolated to precipitation in India.

In India, although several studies report the chemical characterization of precipitation, source apportionment studies are scarce. Further, to our knowledge, just one study broadly classifies the influence of air mass trajectories on the chemical composition of precipitation at four

locations in India (Norman et al. 2001). Thus, there is a need to quantitatively resolve the sources of chemical constituents in precipitation and to identify their source locations. Additionally, given the high loading of dust at several locations in India, Jain et al. (2000) have highlighted the need to identify and differentiate chemical species concentrations from major source types.

This paper presents source apportionment results obtained by the application of an advanced factor analysis technique, PMF to the concentrations of TDS, and its chemical constituents. Thus, this study permits a quantitative assessment of the contribution of chemical species present in various factors to the measured individual species concentration. Potential source contribution function (PSCF) was used to identify the source locations and preferred transport pathways of the ionic species in precipitation. The spatial correlation between ambient aerosol sources resolved in an earlier study Sunder Raman et al. (2010), and sources of ionic species in precipitation were also investigated. Finally, qualitative comparisons of source types resolved in this study with those identified at other locations in India are summarized.

2 Sampling site and chemical analyses

Event-based wet-only precipitation samples were collected during the south-west (SW) monsoon (June–September) during a 3-year period between July 2000–September 2002 at Ahmedabad (Rastogi and Sarin 2005; 2007). A total of 91 samples were collected during the study period. Ahmedabad (latitude 23.03°N, longitude 72.6°E, 49 m asl) is a semi-arid urban city in western India located on the banks of river Sabarmati in the northern part of Gujarat. The city spans an area of about 205 km^2 with a population of about 5.5 million people. Ahmedabad lies south-west of Thar Desert and north-east of the Arabian Sea, with the nearest coastline being about 100 km away. The sampling site itself was located on the terrace of the Physical Research Laboratory building, about 32 m above ground level, with no tall buildings around a 2–3-km radius of the sampling site. The site was surrounded by open fields with a lot of vegetation in the immediate vicinity. A map of the sampling site is shown in Fig. 1a.

In Ahmedabad, precipitation events rarely occur outside the SW monsoon. Thus, the samples collected during the SW monsoon account for almost all of the precipitation during a given year. The geographical location of Ahmedabad and predominant wind patterns during different seasons are discussed elsewhere (Rastogi and Sarin 2005; Ramachandran and Rajesh 2007). Briefly, during the summer monsoon, prevailing winds are strong south-westerly/westerly passing over regions of high

Fig. 1 a Map showing the location of the sampling site at Ahmedabad. **b** Seasonal mean surface wind fields (m s^{-1}) at 750 hPa during the monsoon (June, July, August, and September) of 2001
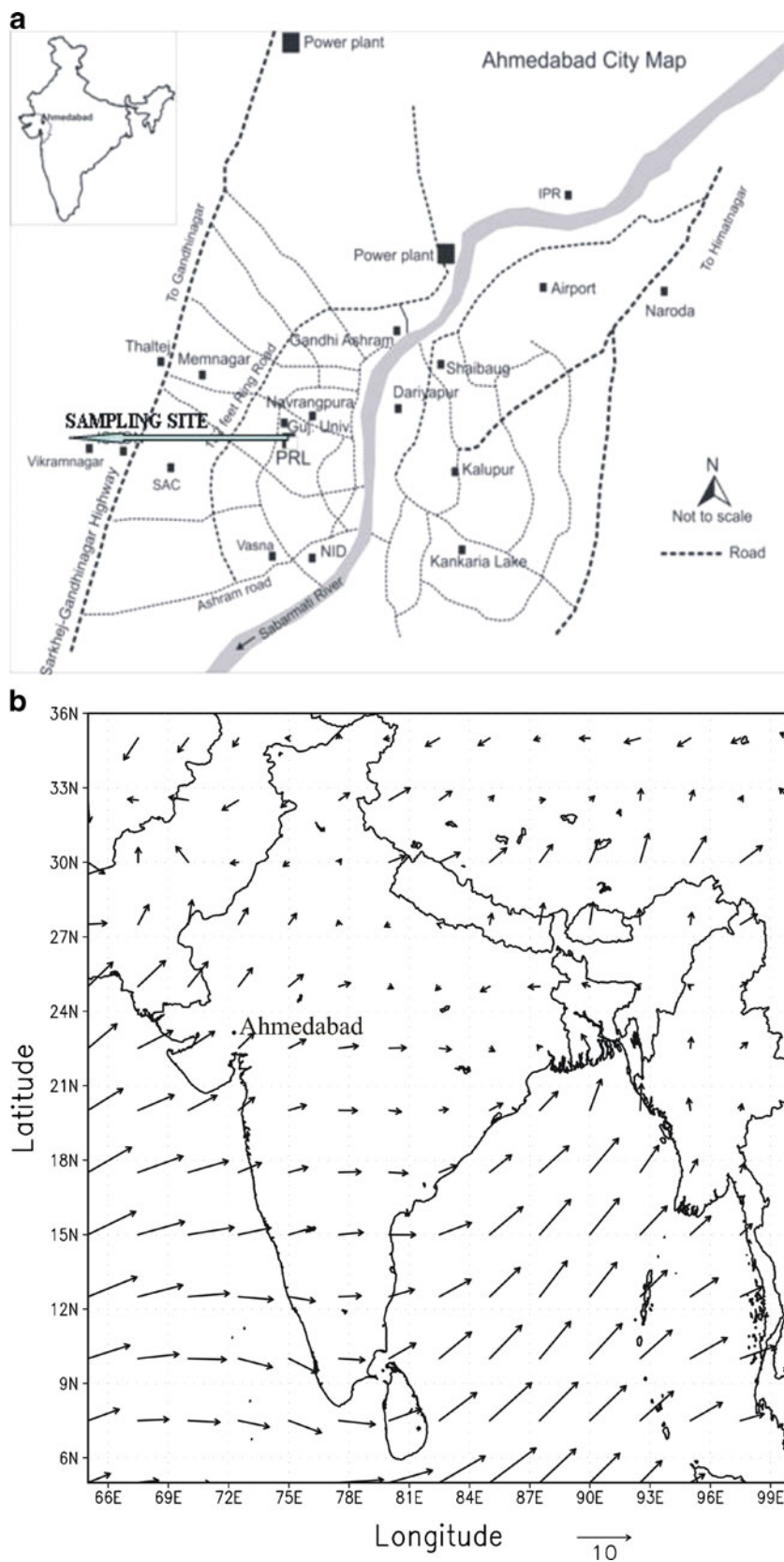
precipitable water content in the southern Indian Ocean and Arabian Sea (Fig. 1b).

Event-based wet-only precipitation samples were collected using a 50-cm-diameter polyvinyl chloride funnel fitted to a 5-L high-density polyethylene bottle. Sampling funnel was kept closed except during the precipitation events. Rainwater samples were immediately transferred to pre-cleaned HDPE bottles (soaked for at least 72 h in 18.2 MΩ Milli-Q water) and filtered using 0.4 μm nuclepore filters. If multiple precipitation events occurred during a day, each individual event was collected separately (Rastogi and Sarin 2007 and references cited therein).

Samples were analyzed for pH, electrical conductivity, and chemical composition. pH was measured immediately after sampling, while the samples were stored in a deep freezer (for about 2–3 weeks) prior to the chemical analyses. The pH was measured using a glass electrode attached to a Auto-titrator system (Metrohm 702 SM Titrino) with a precision on 0.01 pH unit. The pH measurement system was calibrated using buffers ranging from pH 4 to 9.2 using capsules procured from Merck7. A unique feature of this study (study by Rastogi and Sarin 2005) was that HCO_3^- was directly measured. It was measured by acid (0.001 N HCl) titration method using a Metrohm 702 SM Titrino auto-titrator system in combination with a glass electrode by the fixed pH endpoint method (pH=4.3) (Rastogi and Sarin 2005 and references cited therein). Chemical analyses for different species were performed using appropriate techniques which included ion chromatography (Cl^-, NO_3^-, and SO_4^{2-}), UV–Vis spectrophotometry (NH_4^+), flame atomic absorption spectroscopy (Na^+, K^+), and inductively coupled plasma–atomic emission spectroscopy (Ca^{2+}, Mg^{2+}). The sampling methodology and chemical analyses details are presented by Rastogi and Sarin (2005) and Rastogi and Sarin (2007).

3 Data pre-processing

3.1 Data description and quality

All of the chemical species data used in this study were obtained from Appendix I of Rastogi and Sarin (2007). The data set consisted of 10 chemical species including H^+ (reported as pH), NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}, and HCO_3^- (Rastogi and Sarin 2007). No direct measurement of total dissolved solids was made, and it was reported as the sum of all solutes (Rastogi and Sarin 2005). The data quality was tested and reported by Rastogi and Sarin (2005). They found that most of the samples had a charge balance (anion/cation ratio) of within 5% of the equivalent ratio (1.0). Further, they concluded that organic ion contributions to the rainwater composition at Ahmedabad were negligible based on their calculations of anion vs cation regression slope and intercept.

3.2 Input data for source apportionment

In this study, PMF was applied to the measured chemical species concentrations to identify their sources in precipitation. The key statistics for all of the chemical species used for source apportionment are summarized in Table 1. In this table, BDL indicates number below detection limit, and S/N indicates signal to noise ratio. Detection limit for each ion was reported by Rastogi and Sarin (2005). The S/N ratio and percentage BDL were important criteria in choosing the species included for source apportionment. The S/N ratio and its use for assessing the quality of environmental samples are defined by Paatero and Hopke (2003). They have recommended a suitable downweighting procedure to handle species with 0.2<S/N<2. However, in this study, all species had S/N ratios much larger than 2 and thus were not downweighted. A total of 10 species and 91 samples were retained for the analysis.

Table 1 Summary statistics of inorganic ions measured in precipitation at Ahmedabad

Species	Mean	Geo mean	Max	Min	DL	S/N	BDL N=91	%BDL
	(All concentrations except H^+ in mg/L, H^+ concentration in μg/L)							
H^+	0.33	0.16	6.31	0.01	–	37.52		
NH_4^+	0.91	0.54	3.96	0.03	0.016	14.08	13	14.3
Na^+	2.79	1.14	23.69	0.03	0.01	14.01		
K^+	0.29	0.16	2.07	0.02	0.02	13.70		
Mg^{2+}	0.43	0.21	3.04	0.02	0.005	14.02		
Ca^{2+}	3.90	1.90	21.14	0.11	0.04	14.11		
Cl^-	5.20	2.29	42.25	0.11	0.05	14.08		
NO_3^-	1.70	1.16	7.13	0.08	0.05	13.90	1	1.1
SO_4^{2-}	3.94	2.64	20.69	0.23	0.1	14.05		
HCO_3^-	10.26	6.01	51.00	0.49	0.37	14.03	10	11.1

3.3 Prescription of uncertainties

In addition to the measured values of chemical species, the uncertainties corresponding to each measurement were also included as inputs to the model. In this study, the uncertainties corresponding to each data point were estimated by propagating the reported average measurement uncertainty for each species (5% of the measured value for that species) (Rastogi and Sarin 2005) and uncertainty in the volume of water collected (5% of the sampled volume) because individual data point uncertainties were not reported. This methodology is similar to that successfully applied for the source apportionment of Ahmedabad aerosol reported in a previous study (Sunder Raman et al. 2010). Species concentration (X_{ij}) for measured and BDL values and the corresponding species uncertainty (s_{ij}) for these values were replaced following the procedure recommended by Polissar et al. (1998). Subscripts i and j refer to the sample and species, respectively. The following equations were used to handle measured concentrations, BDL values, and their associated uncertainties.

$X_{ij} = V_{ij}$, for measurements above detection limits, where V_{ij} is the measured concentration

$X_{ij} = d_{ij}/2$, for BDL values, where d_{ij} is the method detection limit

$s_{ij} = u_{ij} + d_{ij}/3$, for measurements above detection limit, where u_{ij} is the analytical uncertainty

$s_{ij} = (5/6)d_{ij}$, for BDL values, where d_{ij} is the method detection limit

4 Receptor modeling methodology—application of PMF to the chemical concentrations measured in precipitation

The fundamental principle of receptor modeling is that mass conservation can be assumed and then a mass balance analysis can be used to identify and apportion sources of chemical species in the atmosphere (Hopke 1985, 1991). Receptor models require no a priori information about source types and profiles. Multivariate receptor models utilize the correlations between measured concentrations of chemical species and their source emissions. Receptor models assume that highly correlated species come from the same source. Further, they assume that the chemical species profile of the sources and the relative source contributions to the samples do not change during the measurement period.

One popular approach to solving the receptor model problem is PMF. A complete description of the mathematical aspects of PMF are discussed by Paatero and Tapper (1994), and the model and its application are extensively described in literature (e.g., Antilla, et al. 1995; Polissar et al. 1998; Paatero 1997). Briefly, the task of PMF is to determine the factor profiles and the corresponding contributions that account for the measured mass with the constraint that all of the elements of the factor profile and contribution matrices be non-negative.

PMF has been successfully applied to apportion airborne particulate matter at various locations across the globe by several investigators (e.g., Lee et al. 1999; Kim and Hopke 2004; Begum et al. 2004; Santoso et al. 2008). However, it is interesting to note that the earliest application of PMF to environmental samples was the source identification of chemical species in bulk wet deposition in Finland (Antilla et al. 1995). The model-resolved factor profile and factor contribution matrices were finally re-scaled to satisfy mass apportionment (Hopke et al. 1980). The scaling coefficients were obtained by a multiple linear regression technique, wherein the model-apportioned factor contribution values were regressed against the total dissolved solids (TDS) concentration. This scaling methodology is discussed by Kim and Hopke (2004).

5 Application of PSCF for identification of geographical source locations

PMF analysis enables the source apportionment of chemical species and identifies temporal variations in the source contributions. However, it does not determine source locations or preferred transport pathways of chemical species from the source to the receptor site. This task is achieved by utilizing PMF-resolved factor contributions in combination with air mass back-trajectory ensembles. A popular trajectory analysis method based on the ideas originally proposed by Ashbaugh et al. (1985) is the PSCF analysis.

The mathematical details of PSCF are described by several authors (e.g., Cheng et al. 1993; Gao et al. 1993; Xie et al. 1999; Liu et al. 2003; Biegalski and Hopke 2004; Begum et al. 2005). In this study, the geophysical region covered by the trajectories was divided into 1° latitude by 1° longitude grid cells. For each factor contribution, the criterion value, or cut-off, was set at the 50th percentile. PSCF was calculated at an altitude corresponding to that of precipitable cloud formation during the SW monsoon in the northern Arabian Sea region. Results from studies characterizing the SW monsoon at several locations in the Arabian Sea, and along its coast, suggested that 1,500 m is the average height for the formation of precipitable clouds (e.g., Rao and Tamin 1995; Rajkumar et al. 1996; Bhaskaran et al. 1998; Fleitmann et al. 2003; Basu and Iyengar 2007).

PSCF was calculated using a combination of the model-resolved factor contributions and 5-day backward trajectories calculated using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model, and FNL meteorological data (Draxler and Rolph 2003). For each sample, back trajectories commencing at seven different times in 3-h intervals between 02 and 20 UTC on the sampling date were calculated. The model-resolved factor contributions obtained corresponding to each sampling date was tagged with the calculated trajectories. Finally, trajectory arrival heights were set at 1,500 m above the ground level for PSCF analysis. The 5-day back trajectories covered a geographical domain extending from 13.5° N to 37.5° S latitude and 34.5° E to 74.5° E longitude. Further, to account for the uncertainties caused in the calculated PSCF values when a grid cell has a small number of total end points (η_{ij}) compared with the average number of end points per cell ($\acute{\eta}_{ij}$), the weighting procedure outlined by Han et al. (2005) was followed in this study. The arbitrary weighting function $W(\eta_{ij})$ applied in this study was as follows:

$$1.00 \text{ when } \eta_{ij} \geq 3\acute{\eta}_{ij},$$
$$0.72 \text{ when } 1.5\acute{\eta}_{ij} \geq \eta_{ij} \leq 3\acute{\eta}_{ij},$$
$$0.42 \text{ when } 0.75\acute{\eta}_{ij} \geq \eta_{ij} \leq 1.5\acute{\eta}_{ij}, \text{ and}$$
$$0.17 \text{ when } \eta_{ij} \prec 0.75\acute{\eta}_{ij}$$

In this study, the average number of end points per cell was 68.8. Examples of PSCF analysis applied to chemical species concentrations in precipitation include studies by Zeng and Hopke (1989) and Lucey et al. (2001).

6 Results and discussion

6.1 Source apportionment and identification

In this study, multiple solutions with different number of factors and values of a PMF tuning parameter "FPEAK" were explored to obtain the most meaningful solution. Robust mode PMF2 implementation was used in this study. Analysis details are summarized in Table S1. A starting point to estimate the number of factors is a comparison of the estimated "Q" value with the theoretical Q. If the uncertainties are well specified, and the model fit is good then the two Q values are approximately equal. Also, the Q value decreases when the number of factors increases. Thus, a drop in Q as function of the number of factors is also examined. In this study, it was noticed that the drop in Q when the number of factors were increased beyond 6 was not appreciable. Also, the difference between five- and six-factor Q was not as high as that between four- and five-

factor solutions. Based on an examination of the scaled residuals for different species, explained variances, factor ion balance checks, and physical interpretability, a five-factor solution was chosen.

PMF solutions, like those from other bi-linear factor analytic models, have some rotational ambiguity. A means of controlling rotations is provided by the FPEAK parameter within PMF2. The mathematical details of how FPEAK controls rotations are discussed by Paatero et al. (2002). Once the five-factor model was chosen, Q values as a function of FPEAK were determined, and the region in which it reached a minimum and was reasonably stable was examined. Further, the need for rotation, and suitable FPEAK values, was determined by examining the G-space plots, following a procedure suggested by Paatero et al. (2005). Despite exploring multiple rotations, a distinct edge was observed between the G-space of two factors (identified as crustal material and sea salt). It appears that the collinearity in these two factors limits the extent to which these factors can be separated. The relationship between these two factors also appears real (discussed in detail in the following sections), taking into account the meteorology, and overlaps in their potential source locations. Thus, based on the G-space plots, and physical interpretability, a FPEAK value of −0.6 was used. Finally, to ensure that the global minimum was attained, several random starts were performed.

PMF resolved five factors, namely, crustal material, sea salt, nitrate/sulfate-rich factor, ammonium-rich factor, and free acidity. The model-resolved factor profiles and the corresponding uncertainties are shown in Fig. 2, while factor contributions are shown in Fig. 3. Figure 3 includes three panels corresponding to the periods during in which samples were collected in 2000 2001, and 2002. Both Figs. 2 and 3 are organized in descending order of the factor contributions to TDS.

A comparison of the reconstructed TDS concentration from all of the model-resolved factors with the reported TDS indicated excellent agreement between the two with an r^2 value of 0.998 and a slope of 0.997 (figure not shown). Further, regression analyses between measured concentrations and model-resolved concentrations for individual ions yielded r^2 values in excess for 0.93 for all species, except K^+ for which it was 0.82. In fact, all species except SO_4^{2-}, NO_3^-, NH_4^+, and K^+ yielded r^2 greater than 0.98. Thus, it can be concluded that the resolved factors effectively reproduce the measured values and account for most of the variation in TDS. The summary statistics of percentage factor contributions to the TDS in precipitation at Ahmedabad are shown in Table 2. Among the model-resolved factors, crustal material was the highest contributor to TDS, while free acidity was the lowest contributor. For each individual ion, in each factor, the percentage

Fig. 2 PMF-resolved factor profiles of chemical species in precipitation at Ahmedabad
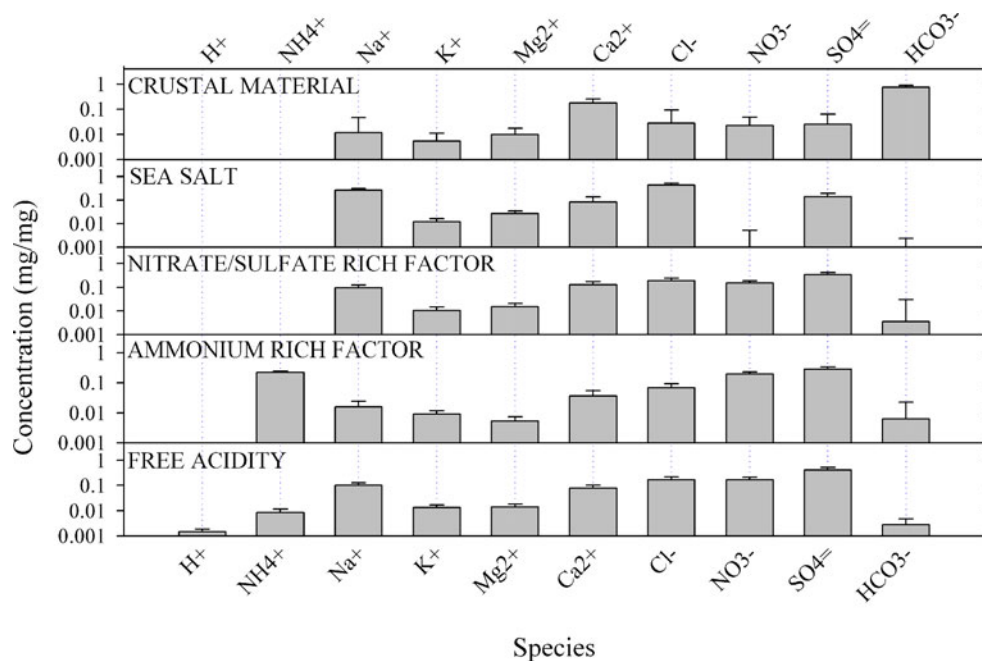
contribution of model-resolved species concentrations to the measured species concentrations is shown in Table 3. The values reported in this table correspond to the ratio of averages.

The PSCF maps indicating the potential geographical source locations of each factor are discussed individually in the following sections corresponding to the identification of the model-resolved factors.

Factor 1: crustal material This factor was identified due to the high loadings of Ca^{2+} and HCO_3^- in the factor profile (Fig. 2). This factor explained nearly 89% of the variance of HCO_3^- and 51% of Ca^{2+}. This factor accounted for 85.3%, 56.5%, 29.9%, and 24.8% of the measured HCO_3^-, Ca^{2+}, Mg^{2+}, and K^+, respectively (Table 3). The factor contribution plots (Fig. 3) showed that there was a lot of event-to-event variability in concentration. However, the
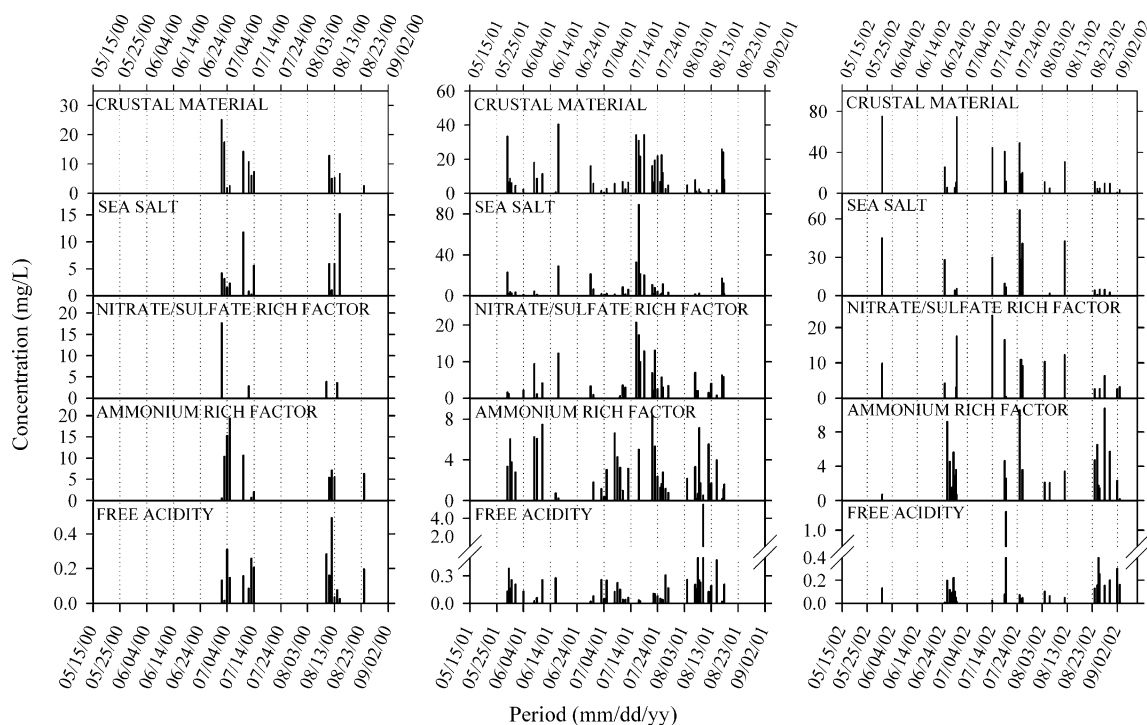
Fig. 3 PMF-resolved factor contributions to precipitation TDS at Ahmedabad

Table 2 Percentage factor contributions to the TDS concentration at Ahmedabad

Factor	Percentage factor contribution to TDS concentration		
	Average	10th percentile	90th percentile
Crustal material	44.08	0.20	66.14
Sea salt	29.81	0.00	43.29
Nitrate/sulfate-rich factor	13.66	0.00	39.25
Ammonium-rich factor	11.62	0.00	62.12
Free acidity	0.78	0.04	5.43
Unresolved	0.05	–	–

factor contribution peaks were concordant with those observed in the time series plots Ca^{2+} and HCO_3^- (not shown), re-affirming the identification of this factor as carbonate-rich material.

The PSCF map for this factor identified source locations along the eastern coast of Somalia, Yemen, Oman, and the United Arab Emirates (Fig. 4). These regions are known to be important contributors of dust over the Arabian Sea (Pease et al. 1998; Prospero et al. 2002). It is also known that dust, specifically that coated with sulfur and other water soluble species, can act as cloud condensation nuclei (CCN) (DeMott et al. 2003; van den Heever et al. 2006). Additionally, based on aircraft measurements made during African Monsoon Multidisciplinary Analysis (AMMA) project, Matsuki et al. (2009) have suggested that the CCN activity of dust particles significantly depends on the chemistry even in the super-micron sizes and that large carbonate particles may be acting primarily as CCN under very low supersaturation. While interpreting the PSCF maps, it must be borne in mind that while local sources, such as re-suspended road dust, may contribute to this factor, such sources cannot be identified since they operate on spatial scales too small to be captured by a $1° \times 1°$ grid trajectory analysis.

Factor 2: sea salt This factor was characterized by high loadings of Na^+ and Cl^-, along with some SO_4^{2-}, Mg^{2+},

and Ca^{2+} (Fig. 2). This factor accounted for nearly 79.9% and 71.8% of the measured Na^+ and Cl^-, respectively. This factor also accounted for 35.1% and 13.6% of the measured Mg^{2+} and Ca^+, respectively (Table 3). Sea salt sulfate contribution was also slightly higher than that reported by Rastogi and Sarin (2005). Thus, it is possible that some crustal material is admixed with this factor. This belief is reinforced by the temporal behavior of factor contributions (Fig. 3). Several co-incident peaks with the crustal material can be observed, especially during 2002.

The PSCF map for this factor (Fig. 5) also showed a remarkable similarity with the carbonate-rich factor maps. The wind direction is south-westerly during the monsoon and transports both marine aerosol and crustal material along the coast of Africa, Yemen, and United Arab Emirates. Studies have shown that sea salt produced by high surface winds during the SW monsoon and the dust from the Arabian peninsula are predominant contributors to the aerosols measured in the Arabian Sea region (e.g., Jones and Christopher 2008). Further, sea salt particles are also believed to act as CCN, although to a lower extent than fine mode anthropogenic hygroscopic aerosols (Pruppacher and Klett 1997 and references cited therein). Thus, the identified source locations for this factor match well with known/expected source regions. The similarity in source locations, and correlation between crustal and marine

Table 3 Percentage species contribution of individual ions to the measured species concentration for all factors

|	Crustal material	Sea salt	Nitrate/sulfate-rich factor	Ammonium-rich factor	Free acidity	Unaccounted
H^+	0.04	0.03	0.05	1.46	97.91	0.50
NH_4^+	0.46	1.60	1.01	93.51	0.24	3.17
Na^+	5.21	79.89	11.91	1.91	0.79	0.29
K^+	24.83	25.77	16.50	22.70	3.92	6.28
Mg^{2+}	29.90	35.12	15.83	13.70	3.81	1.64
Ca^{2+}	56.53	13.58	14.55	11.70	2.81	0.83
Cl^-	6.70	71.78	13.97	4.35	0.71	0.83
NO_3^-	17.28	0.01	30.45	46.45	4.56	1.26
SO_4^{2-}	0.03	26.61	27.90	36.86	5.64	2.97
HCO_3^-	85.33	0.00	3.10	8.84	1.28	1.44
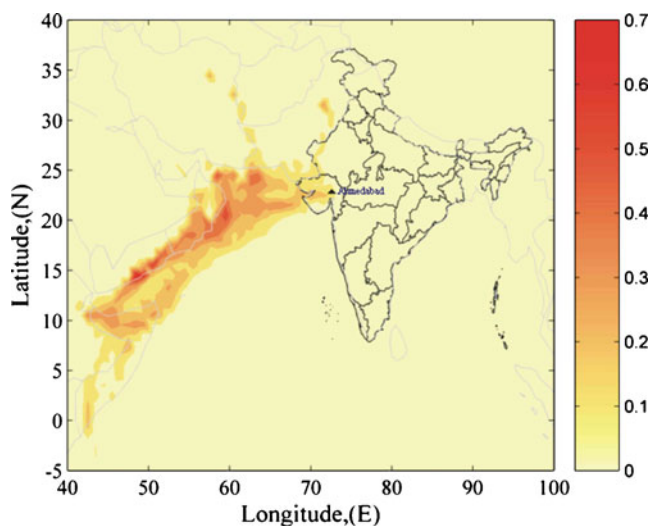
Fig. 4 PSCF map identifying the source locations of PMF-resolved crustal material

species caused due to meteorology and co-location of source regions, limit the ability of receptor modeling techniques to completely separate these two factors.

Factor 3: nitrate/sulfate-rich factor This factor was identified based on the factor profile (Fig. 2) and explained variances (not shown) of sulfate and nitrate. This factor accounted for about 30.5% and 27.9% of the measured concentrations of nitrate and sulfate (Table 3). The apportionment of crustal material along with some Na^+ and Cl^- suggests that this factor is likely to be anthropogenic nitrate and sulfate neutralized by crustal material and sea salt. Sulfate and nitrate particles may displace Cl^- from salt, resulting in the formation of sodium sulfate/nitrate salts. This mechanism supports the observation of excess
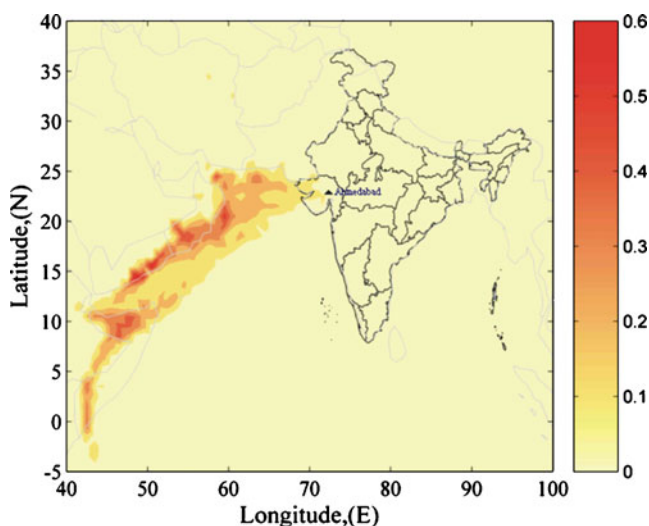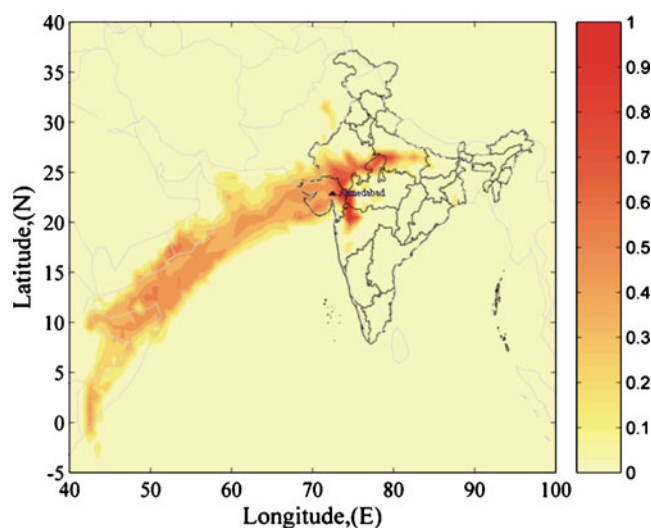

Fig. 5 PSCF map identifying the source locations of PMF-resolved sea salt factor

total measured Cl^- compared with the sea water Cl^-/Na^+ ratio (Rastogi and Sarin 2005). The factor contribution pattern is shown in Fig. 3.

The PSCF map for this factor identified regional source locations that were yet again similar to the carbonate-rich material and sea salt. One explanation for this observation is the in-cloud neutralization of acidic particles by crustal elements and sea salt. The identified source locations include the coasts of Somalia, Yemen, Oman, United Arab Emirates, Iran, and Pakistan (Supplemental Fig. S1). Sulfur-emitting petrochemical industries, off-shore oil rigs, and oil and gas wells are located in the identified source regions. However, since precipitation is restricted almost exclusively to the SW monsoon period in Ahmedabad when the prevailing winds are south-westerly, one can only suggest that the identified regions are a combination of source locations and preferred transport pathways for the identified source material. Only regional source locations have been identified, and there may well be local sources such as traffic and some power plant emissions contributing to this factor, which are not identified in this study. Overall, the meteorology, co-location of regional source regions, and the spatial resolution of the analysis do not permit the sharp separation of geographical source locations of crustal, sea salt, and nitrate/sulfate-rich factors.

Factor 4: ammonium-rich factor This factor was characterized by high concentrations of NH_4^+, NO_3^-, and SO_4^{2-} (Fig. 2). Nearly 89% of the variance in NH_4^+ concentrations was explained by this factor. This factor also explained 39.6% and 31.9% of nitrate and sulfate concentrations. The factor contribution pattern (Fig. 3) showed an event-to-event variation and was also not correlated with any other factor contribution plot. This observation suggests that the sources contributing to this factor are different from the other factors and/or scavenging of gaseous ammonia is a major contributor to this factor. The association of nitrate/sulfate with this factor suggests that ammonium ions account for part of the neutralization of acidic species in precipitation.

The PSCF map for this factor identified "hot spots" in Gujarat, northern Maharashtra, western and northern Madhya Pradesh, southern Rajasthan, and south-central Uttar Pradesh (Fig. 6). The location of several power plants in Rajasthan, Madhya Pradesh, and Uttar Pradesh and their likely contribution to ambient sulfate and nitrate aerosols (formed from the emitted oxides of sulfur and nitrogen) are discussed in detail by Sunder Raman et al. (2010). Further, the agricultural and cattle rearing regions in Uttar Pradesh are also potential sources of ammonia. Both cattle excreta and application of nitrogenous fertilizers result in ammonia emissions. Thus, the identified source regions are indicative of both gaseous ammonia and partially neutralized ammo-

Fig. 6 PSCF map identifying the source locations of PMF-resolved ammonium-rich factor

nium salts of nitrate and sulfate participating in precipitable cloud formation reactions. In the above discussion, likely source regions with reference to regional sources have been identified. However, it is important to note that there may have been some nitrate contribution from local vehicular traffic as well, and the local source regions have not been identified in this analysis.

Factor 5: free acidity This factor was identified due to the apportionment of H$^+$ to this factor along with sulfate and nitrate (Fig. 2). This factor explained nearly 91% of the explained variance of H$^+$ ions and the sum of the explained variances of all of the other species is about 28%. This factor appears to be a "unique factor," and models with factors fewer than five resulted in the H$^+$ ion being very poorly explained. The creation and characteristics of a unique factor are described in detail by Antilla et al. (1995). It is important to note that this factor is a very minor contributor to TDS concentration (Table 2). Given the high dust loadings and the overall alkaline nature of precipitation, this factor may appear to be a modeling artifact. However, a previous study over the Indian region suggests that the acid neutralization is dependent on the environment through which the rain drop travels and that rain drops are acidic just as they leave the clouds but the pH increases by the time they reach the earth's surface (Jain et al. 2000 and references cited therein). Thus, one of the possible explanations for the observation is that regionally transported sulfate and nitrate aerosols and/or dissolved acidic gases are neutralized by calcium carbonate-rich dust in situ, and only samples with acidities too high to be neutralized by dust contribute significantly to this factor. This hypothesis is supported by the observed temporal behavior of this

factor concentration (Fig. 3). The concentration trend of this factor was different from other factors and was mostly anti-correlated with crustal material concentrations. Interestingly, during low dust concentration events, free acidity concentrations show a few co-incident peaks with ammonium-rich factor during all 3 years. This observation suggests that in the absence (or low concentrations) of dust, ammonia is the major acid neutralizing species. The temporal behavior of this factor (Fig. 3) was almost identical to that of the measured pH (r^2=0.99, figure not shown), confirming the identification of this factor as free acidity.

The PSCF map for this factor identifies northern Maharashtra, northern Gujarat, and regions in the Arabian Sea along the coast of Pakistan, Iran, United Arab Emirates, and Oman (Supplemental Fig. S2). As discussed earlier, petroleum drilling and processing operations in Oman, and off-shore oil rigs along the coast of Gujarat may be contributors to the acidic sulfate particles.

7 Spatial relationships between sources of chemical species in precipitation and aerosols over Ahmedabad

Source apportionment of ambient aerosol measured at Ahmedabad between May 2000 and January 2003 was performed in a previous study (Sunder Raman et al. 2010). In that study, six factors including airborne regional dust, calcium carbonate-rich dust, biomass burning/vehicular emissions, secondary nitrate/sulfate, marine aerosol, and smelter were resolved. The source locations of all of the factors were identified using PSCF analysis. The source locations of the regional airborne dust factor were parts of central India, southwestern Pakistan along the Indo-Gangetic Plain (IGP), and southern Iran. Regions in northern India and regions in Punjab, Haryana, and Uttar Pradesh were identified as potential source locations of secondary nitrate/sulfate. Arabian Sea and the Indian Ocean were identified as potential source locations of the marine aerosol, while regions in Gujarat, Rajasthan, Pakistan, and Iran were identified as source locations of the smelters. Sunder Raman et al. (2010) have suggested that lead and zinc, smelting, mining and activities in Rajasthan, and contributions from metal processing industries in Pakistan and Iran may have contributed to the smelter factor.

Thus, it is possible to examine the spatial correlation between aerosol source locations and precipitation source locations as determined by PSCF analysis. PSCF calculated for 500-m trajectory arrival heights for both sources of chemical species in precipitation and aerosol sources (corresponding to SW monsoon period only) (Sunder Raman et al. 2010) were used for this comparison. Since

two crustal factors were resolved in the aerosol study (unlike the precipitation study in which only one was resolved), a probability corresponding to the total aerosol crustal material for each grid cell needed to be estimated for comparison with the precipitation source. Let $P[C1]$ be the PSCF value of airborne regional dust and $P[C2]$ the PSCF value of calcium carbonate-rich dust. Then, the probability of $P[C1]$, $P[C2]$, or $P[C1]$ and $P[C2]$ can be calculated by subtracting the joint probability of both C1 and C2 not occurring (i.e., $\{1-P[C1]\} \times \{1-P[C2]\}$) from 1.

The spatial correlation was assessed using the Spearman rank correlation coefficient "ρ." The results are summarized in Table 4. All of the ρ values are significant at the 99% confidence level.

It can be seen that marine aerosol and precipitation sea salt factors exhibit moderate correlation with each other and with all other factors. These relationships are likely to be due to their relationship with a common third variable, meteorology. The wind directions are predominantly south-westerly/westerly during the SW monsoon period and thus influence the concentrations of all the factors. The relationships between crustal aerosol and sea salt precipitation, and marine aerosol and sea salt precipitation can be interpreted as a reflection of common source material and in-cloud and below-cloud scavenging of particles during precipitation, in addition to the influence of meteorology.

The marine aerosol factor exhibited a moderate correlation with precipitation soil and free acidity factors (Table 4). These relationships suggest that below-cloud scavenging of crustal material, and partial neutralization of acidic species below-cloud by crustal material may contribute to precipitation crustal material and free acidity, respectively. Additionally, crustal material may have been incorporated into a cloud droplet and subsequent oxidation of acidic species may have occurred within this droplet. However, the fact that overall, absolute concentrations of several species were related to the precipitation volume suggests that below-cloud processing may well have been an important part of the precipitation chemistry at the study location (Rastogi and Sarin 2005).

The biomass burning/vehicular emissions factor exhibits moderate correlations with crustal, nitrate/sulfate-rich, and ammonium-rich precipitation factors (Table 4). These relationships also appear realistic given that combustion aerosol is sulfate/nitrate rich. The relationship with ammonium and crustal material may be due to the fact that ammonia and soil are the chief neutralizing species of acidic aerosol and gases at the receptor site.

Secondary sulfate/nitrate aerosol factor is moderately correlated with nitrate/sulfate rich, ammonium, and free acidity factors (Table 4). Yet again, the below-cloud scavenging of partially neutralized acids and completely neutralized secondary inorganic salts (predominantly ammonium sulfate/nitrate, and calcium sulfate/nitrate) may have resulted in the observed relationships. The smelter factor is moderately correlated with all factors (Table 4). The cause of these observed relationships is not clear at this time.

Overall, the observed spatial correlations between various factors suggested that precipitation and aerosol samples share several source locations. Further, since precipitable clouds do not typically form at heights as low as 500 m, it seems reasonable to assume that "below-cloud scavenging" of ambient aerosol is an important contributor to the chemical species measured in precipitation.

8 Qualitative comparisons with precipitation sources at other locations in India

Qualitative comparisons of the sources of chemical species in precipitation identified/suggested at other locations in India are summarized in this section (Table 5). This section is not aimed at being an exhaustive review of the literature, but is chiefly intended to lend a regional perspective to the results obtained in this study.

Crustal material is a common source type resolved at all study locations (Table 5). In general, results from this study and other studies in the Indian region suggest that rainwater in India is alkaline and that a large part of the atmospheric neutralizing ability appears to be from crustal material,

Table 4 Spearman rank correlation coefficients characterizing the spatial correlation between precipitation and aerosol factor source locations

Precipitation	Aerosol				
	Crustal	Biomass burning/vehicular emission	Secondary nitrate/sulfate	Marine aerosol	Smelter
Crustal material	0.47	0.47	0.44	0.46	0.52
Sea salt	0.58	0.55	0.64	0.63	0.54
Nitrate/sulfate rich	0.30	0.52	0.49	0.62	0.55
Ammonium rich	0.35	0.48	0.46	0.62	0.50
Free acidity	0.44	0.40	0.45	0.60	0.46

Table 5 Qualitative comparison of the sources of chemical species measured in precipitation over India

Location	Study period	pH range[a]	Major source types	Source identification method	Reference
Multiple urban and rural around Delhi	July–Sept, 1997	Alkaline	Soil, industries, biomass burning	Principal components analysis	Jain et al. (2000)
Nagpur, Maharashtra	SW monsoon 2005	Alkaline	Soil, nitrogenous fertilizers, secondary sulfate and nitrate	Correlation between ionic species	Salve et al. (2006)
Pune, Maharashtra	1984–2002	Alkaline	Soil, sea salt, vehicular emissions, anthropogenic sulfate	Correlation between ionic species	Safai et al. (2004)
Multiple sites around National Capital Region, Delhi	SW monsoon 2003–2005	Alkaline	Suspended soil dust, sea salt, brick kiln, cattle, agricultural emissions	Principal components analysis	Tiwari et al. (2007)
Asansol, West Bengal	SW monsoon June–Sept 2006	Alkaline	Soil, agriculture, cattle, traffic, industrial	Correlation between ionic species	Banerjee (2008)
Bangalore, Karnataka	SW monsoon June–Sept 2005	Acidic	Soil, traffic, cattle, sewage treatment	Correlation between ionic species	Pasha et al. (2008)
Ahmedabad, Gujarat	SW monsoon July 2000–Sept 2002	Alkaline	Soil, sea salt, nitrate/sulfate, ammonium rich, free acidity	Positive matrix factorization (PMF)	This study

[a] With reference to "pure rainwater" pH

chiefly calcium carbonate. However, it is important to note that the high dust loadings in India do not assure immunity against acid rain for the entire sub-continent and that the acidity at a given location is influenced by the source strengths, proximity of sources contributing to acidity at a receptor site, and the relative concentrations of other chemical species, both on local and regional scales. A recent study (Pasha et al. 2008) conducted during the SW monsoon in Bangalore, India (high traffic density and lower dust concentrations compared with semi-arid regions in India) has documented the decrease in pH value of rainwater from an average of 6.61 to 5.40 (Table 5) between 1980 and 2005, and has attributed the decreasing trend in pH to an increase in the local SO_2 and NO_x emissions.

As expected, the identification/resolution of sea salt in precipitation depended on the proximity of the receptor site to the sea. Interestingly, Tiwari et al. (2007) resolve sea salt factors at several locations in Delhi (Table 5). Further, they conclude that a combination of dust and sea salt are major sources influencing the chemical composition of precipitation at the study locations. Their finding is similar to that observed in this study even though Ahmedabad is likely to be influenced by marine salts and dust during the SW monsoon to a greater extent compared with Delhi because of its proximity to the Arabian Sea and the Arabian Gulf countries.

A major source of ammonia at most study locations was emissions from cattle excreta and fertilizer application for agriculture. Other source categories across different locations included local sources such as traffic, brick kiln emissions, and industrial emissions. Thus, the source types resolved in this study agree well with the major sources identified at other locations in India. Further, given that the natural components (dust and sea salt) dominate the ionic composition at sites in western India, it is reasonable to assume that the SW monsoon precipitation pollutant sources resolved in this study will be useful in interpreting atmospheric pollution on a regional scale.

9 Conclusions

Source identification and apportionment of chemical species in precipitation samples collected at Ahmedabad during the south-west (SW) monsoon measured between July 2000 and September 2002 was performed using a combination of PMF and PSCF analyses. Crustal material (44.1%) and sea salt (29.8%) were the major sources contributing to TDS. The source locations of these factors were identified along the west coast of Africa, Yemen, and the United Arab Emirates.

A nitrate/sulfate-rich factor that accounted for approximately 13.7% of the TDS was also resolved. It appeared that this factor represented acidic species neutralized by

crustal material. An ammonium-rich factor was also resolved. This factor was representative of acidic species neutralized by NH_3. The source locations identified for this factor was different from all other factors. In addition to identifying the power plant regions in Gujarat, Madhya Pradesh, and Rajasthan (SO_2 and NO_x source regions), the agricultural and cattle farming dense regions of Uttar Pradesh (ammonia source regions) were also identified.

Free acidity, a minor contributor to TDS, was also resolved. It is hypothesized that a part of the neutralization of the acidic components of precipitation occurs in situ during below-cloud reactions with crustal material. When crustal material concentrations were low and complete neutralization was not possible, the residual acidity resulted in a free acidity factor.

A spatial correlation analysis between precipitation and aerosol factor source locations was performed. The results of this analysis suggested that below-cloud scavenging of ambient aerosol was key mechanism contributing to the ion concentrations measured in precipitation.

A summary of the major sources of precipitation identified at several locations in India was presented. A common source in almost all of the studies was soil. Thus, it can be concluded that crustal species are key participants in precipitation chemistry. Further, it appears that neutralization of acidic aerosol and/or acidic gases by crustal material is a dominant reaction in precipitation chemistry over India. However, several differences in other precipitation sources depending on the study location were observed. Proximity to the sea, industrial activity, biomass burning, on-road traffic, and agricultural/cattle farming influenced the chemical composition of precipitation. Given that several studies have characterized the chemical nature of precipitation in India over the last two to three decades, a comprehensive review of the chemical nature and sources of precipitation for this region is appropriate at this juncture.

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