Identification of sources affecting fog formation using receptor modeling approaches and inventory estimates of sectoral emissions

Bhavin Mehta a, Chandra Venkataraman a, Mani Bhushan a, Sachchida Nand Tripathi b

a Department of Chemical Engineering, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India
b Department of Civil Engineering, Indian Institute of Technology Kanpur, Kanpur 208016, India

Keywords:
Positive matrix factorization (PMF)
Potential source contribution function (PSCF)
Kanpur (80°22′ E, 26°26′ N)
Thermal power plants
Brick kilns
Biofuel combustion

A B S T R A C T

Positive matrix factorization (PMF) was used to identify factors affecting fog formation in Kanpur during the ISRO-GBP land campaign-II (LC-II) in December 2004. PMF predicted factors were validated by contrasting the emission strength of sources in the foggy and clear periods, using a combination of potential source contribution function (PSCF) analysis and quantitative emission inventory information. A time series aerosol chemical data set of 29 days and 12 species was decomposed to identify 4-factors: Secondary species, Biomass burning, Dust and Sea salt. PMF predicted particle mass with a satisfactory goodness-of-fit (slope of 0.83 ± 0.17 and $R^2$ of 0.8), and strong species within 11–12% relative standard deviation. Mean contributions of anthropogenic factors were significantly higher during the foggy period for secondary species (2.9 ± 0.3) and biomass burning (1.2 ± 0.09) compared to the clear period. Local sources contributing to aerosols that mediated fog events at Kanpur, based on emissions in a 200 km × 200 km area around Kanpur city were thermal power plants and transportation (SO2) and biofuel combustion (BC and OM). Regional scale sources influencing emissions during the foggy period, in probable source regions identified by PSCF included thermal power plants, transportation, brick kilns and biofuel combustion. While biofuel combustion and transportation are distributed area sources, individual point sources include coal-fired thermal power plants located in Aligarh, Delhi, Ghaziabad, Jhansi, Kanpur, Rae Bareli and Rupnagar and brick kilns located in Allahabad, Agra, Farrukhabad, Ghaziabad, Kanpur, Ludhiana, Lucknow and Rae Bareli. Additionally, in the foggy period, large areas of probable source regions lay outside India, implying the significance of aerosol incursion from outside India.

1. Introduction

Aerosol particles mediate the formation of fog in the atmosphere (Pandis et al., 1990; Seinfeld and Pandis, 1998) through the preferred heterogeneous nucleation of water vapor on pollution particles, at high RH or low supersaturation. Fog droplets further aid aerosol formation through aqueous-phase reactions of soluble gaseous precursors (e.g. SO2 and H2O2), leading to higher aerosol concentrations of species like sulfate on fog abatement, which then nucleate subsequent fog-smog-fog cycles (Pandis et al., 1990). Fogs lead to atmospheric removal (by dissolution and deposition) of aerosol constituents for which aqueous-phase production reactions are not important (e.g. nitrate, chloride and ammonium).

Fog can occur if the wind is calm and the air is sufficiently moist, cool and descending (e.g. Pruppacher and Klett, 1997). Such conditions are prevalent in the Indo-Gangetic Plain (IGP, 21°75′–31°N, 74°25′–91°50′E) during winter months of November–February (average temperature 17 °C, RH 64% and maximum daily RH > 90%) as evidenced by campaign measurements (e.g. Ali et al., 2004). An increasing frequency of the occurrence of ground fog has been observed during winter in cities in the IGP, for example, foggy days in New Delhi during November–February averaged 43 during 2000–2002, 48 during 2003–2005 and 61 during 2006–2008, with visibility in the range of 0.1–2.3 km (based on airport data from www.wunderground.com). Fog formation in this region has been attributed to meteorological disturbances moving eastward from the west (Pasricha et al., 2003). A recent study, the Indian Space Research Organization-Geosphere Biosphere Programme land campaign-II (ISRO-GBP LC-II), examined the role of aerosols in fog formation during December 2004 (e.g. Tare et al., 2006; Tripathi et al., 2006). Aerosol physical, chemical and optical measurements
were made simultaneously at seven sites in the IGP and at one outside the IGP. Findings include high concentrations of $K^+$, $NO_3^-$, $SO_4^{2-}$, $NH_4^+$ and BC during fog events.

Quantitative aerosol source identification contributing to these fog events is yet to be made and has been undertaken in this work. Receptor modeling approaches such as positive matrix factorization (PMF) are effective tools in source identification for aerosols on urban to regional scales (e.g., Bhanuprasad et al., 2008; Pekney et al., 2006). PMF studies typically analyze large data sets of several hundred samples spanning a few years of measurements containing 25–30 chemical species to resolve emission source categories on temporal scales of weeks to seasons. As such large data sets are not available yet in the Indian region, recently, PMF was used to resolve a smaller number (six) of source categories using a relatively small data set, e.g., 23 species in 27 samples (Bhanuprasad et al., 2008). The uncertainty in PMF predictions of factor contributions (based on the relative standard deviation of species with high signal to noise ratio) was satisfactory (5–6%), giving confidence in the application of PMF to smaller data sets towards an understanding of regional scale source–receptor relationships in India.

In this work, we use PMF, PSCF and emissions inventory information to identify sources that affected fog formation in Kanpur during December 2004. We identify potential source regions of the factors during the fog event using PSCF, and combine it with emissions inventory information for source identification.

2. Modeling approach

2.1. Aerosol data set

2.1.1. Data description

Aerosol data were collected at Kanpur during a land campaign by the Indian Space Research Organization (ISRO-GBP LC-II). Kanpur city (80°22'E, 26°26'N) is situated in the southern part of the Indo-Gangetic plain. Sampling was done at Indian Institute of Technology Kanpur (IITK), about 17 km away from Kanpur city, on the roof of a three storey building in the IITK campus at 12 m above ground level. Kanpur city and adjoining areas have a population of over 4 million with a density of 6800 persons per km$^2$ (Gupta, 2006). Foggy periods were identified visually (Tripathi et al., 2006), based on the daily number of hours of fog. On this basis, 9–27 December (except 25 and 26 December) were classified as foggy weather and the remaining campaign period was classified as clear weather.

Emission sources (Fig. 1) include biomass fuel (residential cooking and heating) and fossil fuel burning (mainly coal based thermal power plants and fertilizer plants, transportation, mining) (Reddy and Venkataraman, 2002), and seasonally variable forest and crop waste burning (Venkataraman et al., 2006). The vehicle fleet was estimated at 387,697 vehicles in 2002 and projected to increase by 30,000 every year (Gupta, 2006). Kanpur has over 310,100 cattle (BAHS, 2003), a source of ammonia emissions, with 140 g ammonia emissions reported per head of cattle per day (McGinn et al., 2007). Earlier work gives details of air sampling from December 1–29, 2004 (Tare et al., 2006; Tripathi et al., 2006) and results from size segregated aerosol samples collected for a period of 12 days. In this work, we use daily 8-h-average PM$_{10}$ chemical composition of particles collected on glass fiber filters (Whatmann GF/A) using a high volume sampler operated at a flow rate of 0.7–1.1 m$^3$ min$^{-1}$, from December 1–29, 2004.

Details of anion ($Cl^-$, $NO_3^-$ and $SO_4^{2-}$) measurement using ion chromatography, elemental (Na, Mg, K, Ca, Fe, Al) measurement by atomic absorption spectrophotometry (AAS) and $NH_4^+$ ion measurement by indophenol blue method (Tare et al., 2006) are included in the Supplementary Online Data (Section A, Chemical Analysis Details). AAS measured Na, Mg, K and Ca were designated equal to water-soluble ionic forms by Tare et al. (2006) in earlier published work. Simultaneous measurements of black carbon (BC) were carried out continuously for 24 h using an aethalometer (Model AE-21-ER, Magee Scientific, USA) (Tripathi et al., 2006). The daily average ionic and elemental species in particle samples and aethalometer BC concentration used in the PMF analysis included $NO_3^-$, $SO_4^{2-}$, $Cl^-$, $NH_4^+$, Na, Mg, K, Ca, Al, Fe and BC (Table 1). Chemical concentrations of all measured constituents were above detection limits. Three missing values of BC from December 22–24 were replaced by the geometric mean of measured values (Table 1). A time-series analysis (not shown), gave no extreme values leading to retention of all data for PMF analysis. A low $Cl^-/Na^+$ ratio indicates significant chloride depletion ranging 60 ± 11% averaged over the campaign, from atmospheric reactions of $SO_2$ or $NO_x$ with sea-salt,
indicating significant processing of sea-salt during its transport inland.

2.1.2. Prescription of measurement uncertainties

Uncertainties in the measurement data set were estimated (e.g. Pekney et al., 2006), as shown below:

\[ S_{ij} = p_j X_{ij} \frac{\text{MDL}_j}{3} \]  

(1)

where, \( p_j \) is the uncertainty proportional parameter, \( X_{ij} \) the measured concentration, \( i = 1 \text{--} n \) is index for samples, \( j = 1 \text{--} m \) is index for species and \( \text{MDL}_j \) the method detection limit. PMF literature extensively suggests that the uncertainty assigned to a species must reflect both measurement uncertainty and the variation in source profiles over the measurement period (Kim et al., 2004, 2005a; Kim and Hopke, 2004). In the absence of both measurement uncertainty and source variability information for our campaign, we followed the usual practice in literature of selecting \( p_j \)'s from reported studies and systematically modifying them to obtain sensible solutions (Kim et al., 2005a; Kim and Hopke, 2004; Begum et al., 2004). In the absence of measurement uncertainty and source variability information for our campaign, we used a systematic modification of \( p_j \)'s to obtain sensible solutions (Kim et al., 2005a).

2.2. Positive matrix factorization

Positive matrix factorization models, e.g. the two-dimensional model (PMF-2, Version 4.2) invert a matrix of time-series aerosol chemical concentration measurements using non-negativity constraints to predict source compositions and contributions (Paatero, 1997; Kim et al., 2004, 2005a; Kim and Hopke, 2004; Begum et al., 2004), prescribing individual weights for specific data points. A threshold outlier distance, typically taking a value between 2 and 4, is used to suppress the effect of outlier residuals in unduly distorting the PMF solution. A principal component analysis (PCA) based heuristic for specifying this distance (Bhanuprasad et al., 2008), used in the current work, identified no outliers in the data set leading to adoption of a value of 2 for the threshold distance.

2.3. Potential source contribution function (PSCF)

The PSCF uses back trajectories in combination with atmospheric pollutant concentrations or factor contributions identified by PMF (Hopke et al., 1995) to identify probable source locations or preferred atmospheric transport pathways from source to the receptor. The source domain is divided into a number of grid cells, typically \( 1 \text{"north} \times 1 \text{"east} \) (Kim and Hopke, 2004). The PSCF is the conditional probability of the event that a trajectory endpoint falling in the ith cell arrived at the receptor when the pollutant concentration exceeded a threshold value. A threshold criterion value of 50 percentile (median concentration) was used. The total probability

### Table 1

Summary of aerosol chemical measurements at Kanpur.

<table>
<thead>
<tr>
<th>Species</th>
<th>Geometric mean (µg m(^{-3}))</th>
<th>Arithmetic mean (µg m(^{-3}))</th>
<th>Minimum (µg m(^{-3}))</th>
<th>Maximum (µg m(^{-3}))</th>
<th>MDL (^a) (ng m(^{-3}))</th>
<th>Final P(_b) (%)</th>
<th>Number of BDL values (%)</th>
<th>Number of missing values (%)</th>
<th>S/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO(_3)</td>
<td>15.9</td>
<td>16.9</td>
<td>7.9</td>
<td>29.1</td>
<td>8.7</td>
<td>14</td>
<td>0</td>
<td>0</td>
<td>3.6</td>
</tr>
<tr>
<td>SO(_4)(^2)</td>
<td>14.8</td>
<td>15.6</td>
<td>6.5</td>
<td>27.8</td>
<td>12</td>
<td>30</td>
<td>0</td>
<td>0</td>
<td>1.7</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>2.9</td>
<td>3.0</td>
<td>1.4</td>
<td>4.7</td>
<td>3.1</td>
<td>20</td>
<td>0</td>
<td>0</td>
<td>2.5</td>
</tr>
<tr>
<td>NH(_4)</td>
<td>8.4</td>
<td>3.1</td>
<td>1.6</td>
<td>18.8</td>
<td>17</td>
<td>50</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Na</td>
<td>4.2</td>
<td>4.3</td>
<td>2.7</td>
<td>6.2</td>
<td>30</td>
<td>14</td>
<td>0</td>
<td>0</td>
<td>3.5</td>
</tr>
<tr>
<td>Mg</td>
<td>0.2</td>
<td>0.2</td>
<td>0.05</td>
<td>0.4</td>
<td>8</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>4.5</td>
</tr>
<tr>
<td>K</td>
<td>5.1</td>
<td>5.2</td>
<td>2.9</td>
<td>6.9</td>
<td>14</td>
<td>20</td>
<td>0</td>
<td>0</td>
<td>2.5</td>
</tr>
<tr>
<td>Ca</td>
<td>1.6</td>
<td>1.7</td>
<td>0.95</td>
<td>3.95</td>
<td>1.4</td>
<td>22</td>
<td>0</td>
<td>0</td>
<td>2.3</td>
</tr>
<tr>
<td>Al</td>
<td>0.8</td>
<td>1.0</td>
<td>0.3</td>
<td>2.7</td>
<td>3.6</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>Fe</td>
<td>1.9</td>
<td>2.0</td>
<td>1.2</td>
<td>3.3</td>
<td>0.47</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>BC</td>
<td>10.0</td>
<td>10.6</td>
<td>4.8</td>
<td>19.8</td>
<td>200</td>
<td>200</td>
<td>3 (10)</td>
<td>0.25</td>
<td></td>
</tr>
</tbody>
</table>

\( ^a \) Adapted from Kim et al. (2005a).

\( ^b \) \( p_j \) values are taken as 2 times the values in Kim et al. (2005a) and higher \( p_j \) for NH\(_4\), SO\(_4\)\(^2\), Al and BC.
of material transfer from various heights is calculated from the conditional probabilities associated with each arrival height at the receptor (Hopke et al., 1995). Four arrival height levels of 10, 50, 500 and 1000 m were used in this study. Trajectories were computed using the HYSPLIT4 model and the archived meteorological data from National Oceanic Atmospheric Administration’s (NOAA) Air Resources Laboratory (ARL) website (HYSPLIT4, 1997). Seven-day back trajectories at 2-h intervals (12 per day) were computed for each of the 29 daily samples at the four arrival heights. To correct for anomalously high PSCF values, resulting from low total number of trajectory endpoints in a given cell, a multiplicative weighting function (e.g. Bhanuprasad et al., 2008) is operated on the computed TPSCF for such cells.

3. Source identification using positive matrix factorization

3.1. Base-case solution selection

Ten random runs (corresponding to different starting points) were performed and the run with the minimum estimated Q (Kim and Hopke, 2004) value was retained for 2–6 factors. Estimated Q decreased with increasing number of factors (Fig. S2, Supplementary Online data) and its slope levelled off at 4-factors, with a small decrease on moving to a 5-factor solution. Solutions of 3, 4 and 5 factors were examined. The maximum individual column mean, IM, and the maximum individual column standard deviation IS, of the scaled residual matrix dropped sharply for solutions with 3 or more factors (Fig. S2, Supplementary Online data). Along with these indicators, the physical interpretation of factors in terms of likely number of source categories and model predictions for PM mass were the main criteria for identifying useful solutions. The 3-factor solution had relatively poor factor resolution with mixed factors, such as Secondary species + Biomass burning + Al, Sea salt mixed with Biomass burning + Fe + SO$_4^{2-}$ and Dust with BC, giving poor correspondence with known aerosol sources. The 5-factor solution had insignificant loadings of most of the species in each factor, making it invalid. Additional PMF solutions excluding PM-10 as explicit species had highly mixed factors and negative coefficients on regression of factor contributions against PM mass leading to invalid solutions for 3-, 4- and 5-factors. An attempt to identify other valid solutions, by increasing the uncertainty on BC (by a factor of 4) and SO$_4^{2-}$ (by a factor of 2), was not successful.

3.2. Constraining rotational freedom

PMF can lead to multiple valid solutions as below

$$X = (GT)(T^{-1}F) + E$$

where $T$ is an invertible matrix such that $CT$ and $T^{-1}F$ satisfy non-negativity constraints. Rotations (multiplication of G and F by T and $T^{-1}$, respectively) are prescribed in PMF-2 through a function $f_{\text{peak}}$ (Pekney et al., 2006). The global minimum solution from 10 pseudorandom runs of the 4-factor solution was rotated using $f_{\text{peak}}$ values from 0 to 10 (Fig. S3, Supplementary Online data). Solutions close to the edge ($f_{\text{peak}} = 5–7$) of the stable Q values had an anomalously high PM loading (95–100%) on a single factor (Biomass burning + Secondary species), leading to their rejection. Therefore, the base case 4-factor solution with $f_{\text{peak}} = 0$ was retained.

Fig. 2. Factor profiles and factor contribution time series for PMF predicted factors.
The base case 4-factor solution (fpeak = 0) had a Dust factor (Ca 55%, Fe 54%, Mg 49% loading), Sea salt + Biomass burning + SO4²⁻ factor (Na 54% and Cl⁻ 49% along with 31% SO4²⁻, 30% Fe, 28% K and 24% BC loading), Biomass burning factor contaminated with Dust (52% Al, 42% Mg, 36% Ca, 32% K and 27% BC loading), Secondary species + Biomass burning + chloride factors (NH4 68%, NO3 56%, BC 42%, SO4²⁻ 38%, K 27% and Cl⁻ 27% loading). The fitted straight line between predicted and measured PM had satisfactory goodness-of-fit (slope of 0.92 ± 0.17 and R² of 0.83). Additionally, 8 species were predicted with high (>0.7) R² values: NO3, Cl⁻, Mg, K, Ca, Na, NH4, and Fe, thereby indicating model’s ability to adequately explain most of the measured mass.

When a factor (representing a source) is clearly “contaminated” by a species which is not expected from that source, the function fkey in PMF-2 is used to pull down these unrealistic species. Solutions were obtained by operating fkey only on single factors and then on two, or three factors to resolve mixed sources. The final selected solution had an fkey of 10 on K, BC on Sea salt + Biomass burning + SO4²⁻ factors, fkey of 10 on K on Secondary species + Biomass burning factors and fkey of 5 on K, BC on Dust factor. An fkey value of 5 on Al and Na and 3 on SO4²⁻ on the Biomass burning factor was also used. The solution contained a Dust factor (Mg 73%, Ca 72%, Fe 48% and Al 33% loading), Sea salt factor (Cl⁻ 62%, Na 52%), Biomass burning factor (K 100%, BC 61%) and Secondary species factor (NH4 81%, NO3 74%, SO4²⁻ 61%, BC-39 – Fig. 2). The predicted PM-10 loading on different factors was higher on Secondary species (39%) and Biomass burning (25%) followed by Dust (19%) and Sea salt factor (17%). This solution had satisfactory goodness-of-fit between predicted and measured PM-10 (slope of 0.83 ± 0.17 and R² of 0.8 – see Supplementary Online data Fig. S4; prediction of 7 species with PMF-2 estimated factor contributions for tracer species correlated well with Dust, Biomass burning and Secondary species factors. For example, Mg (R² 0.95) and Ca (R² 0.76) are tracer species for Dust while K (R² 0.95) is a tracer for Biomass burning factor.

4. Interpretation of factors

4.1. Identification of source categories

The Secondary species factor had 81% NH4, 74% NO3, 61% SO4²⁻, 52% Al and 39% BC loading (Fig. 2). Based on the relative mass concentration of different chemical species loading on a factor, termed “factor composition,” the factor had a composition of 35% NO3, 25% SO4²⁻, 21% NH4 and 11% BC. Satisfactory goodness-of-fit was obtained between measured tracer (NO3, NH4) concentrations with both their PMF-2 predicted concentrations and the corresponding factor contributions. Mean Secondary species factor contributions (107 µg m⁻³) were significantly higher during the foggy period and lower (36 µg m⁻³) during the clear period (Table 2), indicating that aerosol constituents of this factor are strongly linked to fog formation, as corroborated by earlier studies on the fog–smog–fog cycle (Pandis et al., 1990). This factor contained a significant loading of Al. There is a cluster of Al smelters to the south-east of Kanpur (Fig. 1), which could explain the association of industrially emitted Al along with sulphate from SO2 emitted by coal combustion in the smelter. The Biomass burning factor had 100% K, 61% BC, 27% Mg and 4% NH4 loadings. The factor had a composition of 53% BC and 43% K. The model predicted K well, sea salt factor (Cl⁻ 62%, Na 52%) and BC moderately well (slope of 0.73, R² of 0.63). The mean Biomass burning factor contributions were somewhat higher (57 µg m⁻³) during the foggy period than (47 µg m⁻³) the clear period (Table 2).

The Dust factor had a high loading of crustal elements (73% Mg, 72% Ca, 48% Fe and 33% Al). The factor had a composition of 14% Ca, 11% Fe, 2% Mg and 2% Al, along with acidic species NO3 (44%) and SO4²⁻ (16%). This is consistent with reported soil composition in the region and surface reactions of acidic species on alkaline soil constituents (Rastogi and Sarin, 2005). Satisfactory goodness-of-fit was obtained between measured tracer (Ca, Mg, Fe) concentrations with PMF-2 predicted concentrations of these species and the Dust factor contribution. Mean Dust factor contributions were lower (32 µg m⁻³) during the foggy period (8–28 December except 26 and 27 December) and higher (57 µg m⁻³) during the clear period (1–7, 26, 27 and 29 December, Table 2), consistent with the expectation that high dust concentrations were probably accomplished by greater dispersion, not conducive for fog formation.

The Sea salt factor had 62% Cl⁻ and 52% Na, 50% Fe and 30% SO4²⁻ loadings. The factor had a composition of 18% Na, 15% Cl⁻ along with 38% SO4²⁻, 11% NH4, 8% Fe and 7% NO3. The significant sulphate loading is consistent with the low Cl⁻/Na⁺ ratio in the observations from Cl⁻ depletion through atmospheric reactions of SO2 or NOx with sea-salt. An electroneutrality check on the factor composition supported these levels of sulphate and gave a cation to anion ratio of 1:0.8. Moderate goodness-of-fit was obtained between measured tracer (Na, Cl⁻) concentrations with PMF-2 predicted concentrations of these species and the Sea salt factor contribution. NaCl has been associated with dust in some locations in India (Rastogi and Sarin, 2005), potentially explaining a part of the loading of Fe on this factor. Additionally, an iron and steel plant near Kanpur and a cluster of plants south of Kanpur (Fig. 1) could be a source of both Fe and SO2 emissions, contributing to the association of both Fe and sulphate with this factor. Iron is a primary pollutant while sulphate results by Cl⁻ depletion from atmospheric reactions of SO2 with sea-salt discussed previously. Mean Sea salt factor contributions were also lower (34 µg m⁻³) during the foggy period than (44 µg m⁻³) the clear period similar to Dust (Table 2).

In view of the small data set available (29 samples and 12 species) we examined the relative standard deviation in the PMF-2 predictions of the mean factor contributions. Only strong species (S/N ratio greater than 2 in Table 1) were considered representative of the errors in PMF model prediction following Bhanuprasad et al. (2008). This was 11–12% for the foggy and clear periods (Table S3, Supplementary Online data) and indicates satisfactory model performance, even with the small data set.

4.2. Validation of factors using the emission strength of sources in the foggy and clear periods

As seen in the previous section, the Secondary species factor had a significantly larger (2.9 ± 0.3) mean concentration during the foggy versus the clear period. The biomass burning factor showed a moderately higher (1.2 ± 0.09) concentration during the foggy period (refer to Section D, Supplementary online data, for details of standard deviation calculation). PMF predicted factors were validated by contrasting the emission strength of sources in the foggy
and clear periods, using a combination of back trajectory modeling and quantitative emission inventory information. A part of the difference in mean concentration would be related to ground-level temperature inversions and a low mixing height during the foggy period. However, the differences in emissions from contributing sources during the foggy and clear periods, especially those responsible for the Secondary species factor are important and are further examined in this section.

4.2.1. Influence of proximate/local sources

Aerosol and SO$_2$ emission fluxes were calculated in a box around Kanpur (79.5–81.25°E and 25.5–27.25°N) aggregated from sources in our India emissions inventory (Reddy and Venkataraman, 2002; Venkataraman et al., 2006). The inventory is on a monthly mean temporal scale and therefore cannot diagnose differences in emissions from local sources between the foggy and clear periods. We therefore identify dominant local sources based on the monthly mean emission flux of four pollutants: SO$_2$, particulate inorganic matter (PIM) which includes water-soluble ions and mineral matter like fly-ash, particulate organic matter (OM), and black carbon (BC). Among these pollutants, the atmospheric reactions of SO$_2$ to sulfate are known to affect fog formation (Pandis et al., 1990). PIM would contain soluble inorganic ions (Cl$^-$, NO$_3^-$, SO$_4^{2-}$, NH$_4^+$) present in combustion aerosols (e.g. Habib et al., 2008), which could also mediate water uptake and fog formation. The role of organic matter in water uptake by aerosol particles is still uncertain. Secondary organic matter from atmospheric reactions of hydrocarbons is believed to increase hygroscopicity beyond ionic content (Saxena et al., 1995), but primary organic matter, e.g. from forest biomass burning (Carrico et al., 2005) is believed to inhibit hygroscopic growth. BC may be associated with other hygroscopic compounds and provide condensation nuclei to mediate fog formation.

Among sources that affect the Secondary species factor, coal based thermal power plants (TPPs), transportation and other large...
point sources (LPSs) were dominant accounting, respectively, for 2428, 841 and 675 ton mon\(^{-1}\) of SO\(_2\) and 1240, 23 and 40 ton mon\(^{-1}\) of PIM, respectively (Fig. 3). There are 2 coal based thermal power plants, 5 fertilizer plants, 1 cement plant and 1 iron and steel plant, close to Kanpur. Transportation (diesel powered vehicles) influences BC emissions (74 ton mon\(^{-1}\)) and brick kilns influence OM emissions (349 ton mon\(^{-1}\)). Among source categories that affect the Biomass burning factor, biofuel combustion and crop waste burning were significant, respectively, emitting 2049 ton mon\(^{-1}\) and 483 ton mon\(^{-1}\) of OM and 339 and 94 ton mon\(^{-1}\) of BC. In summary, local sources of significance are thermal power plants to SO\(_2\) and PIM emissions, biofuel combustion to PIM, BC and OM emissions, transportation to SO\(_2\), PIM and BC emissions and crop waste burning and brick kilns to OM and BC emissions.

4.2.2. Influence of sources in PSCF identified source regions in the foggy and clear periods

The TPSCF (Section 2.3) identifies probable source regions and transport pathways that affect the predicted factor contributions during a given time period. Distinct potential source regions were identified by TPSCF for the foggy and clear periods for the Biomass burning and Secondary species factors. Areas with PSCF between 0.5 and 1.0 in each period were designated as probable source regions during that period (Fig. 4). We aggregate the emission fluxes in the probable source region for each period (foggy and clear) for each source to estimate its relative emission strength. Median or 50th percentile values of PMF predicted factor contribution were used as the criterion value for the PSCF calculations.

During the foggy period, TPSCF plots (Fig. 4) for the factors of anthropogenic origin, the Biomass burning and Secondary species factors, both had probable source regions in the northwestern IGP (Indian states of Uttar Pradesh, Uttaranchal, Haryana, Punjab and Himachal Pradesh) and in parts of west-Asia, i.e., Pakistan, Iran, UAE and Oman. In addition, the Secondary species factor had probable source regions to the south-west of Kanpur in the Indian states of Rajasthan, Gujarat and Madhya Pradesh (Fig. 4). During the clear period, probable source regions for both factors lay to the north and north-west of Kanpur.

We contrast the mean emission fluxes from different sources located in these probable source regions during foggy versus clear period to identify significant sources. Thermal power plants, other LPS, transportation and brick kilns located in probable source regions had significantly larger emission fluxes of SO\(_2\) during the foggy versus the clear period (factor of 1.93, 3.53, 2.35 and 3.69, respectively). Individual point sources likely to have contributed to SO\(_2\) emissions during the foggy period are coal-fired thermal power plants located in Kanpur, Ghaziabad, Aligarh, Jhansi, Rupnagar and Delhi, iron and steel plants located in Kanpur and Bulandshahar and fertilizer plants located in Kanpur, Ghaziabad, Buduan, Bulandshahar, Firozabad. Black carbon could be associated with fog formation, if coated with hygroscopic aerosol species. The emission flux of BC and OM from brick kilns in probable source areas was substantially larger during the foggy period (Fig. 5). These include brick kilns located in Kanpur, Ghaziabad, Agra and Ludhiana districts. Since brick kilns use a mixture of locally available biomass and powdered coal, the BC and OM emissions from this source may also be associated with SO\(_2\) emissions (from the coal) and therefore have sufficient hygroscopicity to be potential fog nuclei. Large areas of probable source regions for both Secondary species and Biomass burning, lay outside India (Pakistan, Iran, Oman and UAE) in the foggy period, while few probable source regions lay outside India during the clear period. This implies the significance of aerosol transport from outside India to fog formation in the IGP. However, lack of detailed emission inventory information for these regions does not permit further analysis of sources which may have contributed to the fog events.

5. Conclusions

PMF identified factors were analyzed to explain influence of source categories on fog formation in Kanpur during the ISRO-GBP land campaign-II (LC-II) in December 2004. PMF predicted factors were validated by comparing the emission strength of sources during the foggy and clear periods, using a combination of PSCF analysis and quantitative emission inventory information. The time series of 29 days and 12 species was decomposed to identify 4 factors: Secondary species, Biomass burning, Dust and Sea salt.

The ratios of mean contribution during the foggy to the clear period were significantly larger than unity for the anthropogenic Secondary species (2.9 ± 0.3) and Biomass burning (1.2 ± 0.09) factors. The larger predominance of the secondary species factor than the biomass burning factor during fog events is somewhat surprising. Significant emission fluxes from biomass burning sources in the Indo-Gangetic plain are estimated in emission inventories (e.g. Venkataraman et al., 2006). The predominance of secondary species during fog events therefore suggests significant secondary aerosol formation through aqueous-phase reactions in fog droplets. Further understanding of aerosol composition before, during and after fog events is needed to investigate such mechanisms. Since the Secondary species factor had high loadings of sulfate, nitrate and ammonium, sources of these aerosol precursors (thermal power and fertilizer plants, transport and cattle rearing) would have a large bearing on fog formation.

Based on their relative emission flux strength, thermal power plants and transportation emissions, on both local and regional scales, brick kilns on a regional scale and local biofuel combustion are the likely contributors to aerosols that mediated fog events at Kanpur during the ISRO-GBP land campaign. Biofuel combustion and transportation are distributed area sources. Contributing point sources include coal-fired thermal power plants located in Aligarh, Delhi, Ghaziabad, Jhansi, Kanpur, Rae Bareli and Rupnagar and brick kilns located in Allahabad, Agra, Farrukhabad, Ghaziabad, Kanpur, Ludhiana, Lucknow and Rae Bareli. This identifies industrial and transport emissions of SO\(_2\) and NO\(_x\), and cattle-related emissions of NH\(_3\) as a relevant factor in fog formation. A more complete inventory especially for NH\(_3\) from industrial sources and cattle
rearing activities is needed to understand sources in more detail. Large areas of probable source regions for both Secondary species and Biomass burning factors in foggy period, lay outside India (Pakistan, Iran, Oman and UAE), suggesting the significance of regional scale aerosol transport from outside India to fog formation in the Indo-Gangetic Plain.

Acknowledgments

We thank the Indian Space Research Organisation’s Geosphere Biosphere Programme (ISRO-GBP), Bengaluru, India, for enabling this collaborative work and Ribu Cherian for assistance with emissions data processing and figure preparation.

Appendix A. Supplementary information


References


