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

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ABSTRACT

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 (SO_2) 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. SO_2 and H_2O_2), 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

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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 $60 \pm 11\%$ averaged over the campaign, from atmospheric reactions of SO_2 or NO_x with sea-salt,

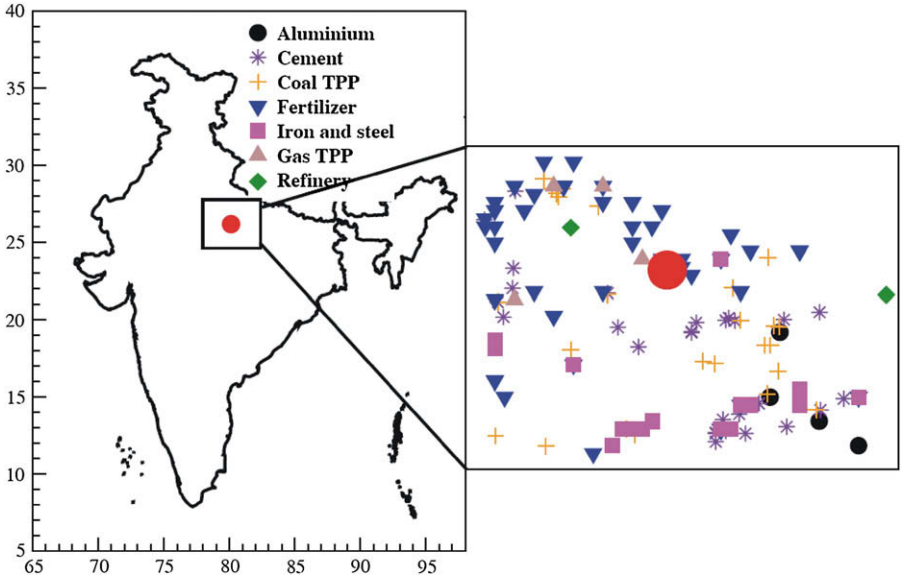

Fig. 1. Map of Kanpur and surrounding areas with location of large point emission sources.