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Atmospheric aerosols local–regional discrimination for a semi-urban area in India

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ABSTRACT

In the European Integrated project on Aerosol Cloud Climate and Air Quality interactions (EUCAARI), measurements were carried out with a sequential filter-based aerosol sampler and on-line instruments for aerosol composition and behaviour at Gual Pahari, close to New Delhi. In fine mode ($PM_{2.5}$), the secondary organic carbon (SOC) to total organic carbon ratio was 46%. This indicated that condensation of SOC on fine size particles could occur rapidly which may be related to the growth of aerosols and the potential to the size of cloud condensation nuclei in the region.

Source region discrimination was improved significantly through coupling conditional probability functions with receptor modelling, and validation through volume size distribution. The air masses from industrial and dense populated regions show a mix of local as well as regional emissions to fine mode aerosols. The back-trajectory analysis captured the long-range transport of sea-salt aerosols enriched with mineral dust. The surface wind directions identified the influence of local emission activities.

1. Introduction

Atmospheric aerosols affect the quality of human life in many different ways such as health, visibility and climate change. To the climate, aerosol influence the Earth's radiation balance directly by scattering and absorbing solar radiations, and indirectly by acting as cloud condensation nuclei (CCN) (Charlson et al., 1992). However, still the largest uncertainty is in predicting the radiative forcing and future climate due to interaction between atmospheric aerosols and climate system (IPCC, 2013; Andreae and Rosenfeld, 2008). Furthermore, better understanding and quantification of the above aerosol effects requires information on how different sources and atmospheric transformation processes modify the aerosol properties when transport through vertical and horizontal layers in a local, regional and global domain.

The Indo-Gangetic Plain (IGP) region is having large local air pollution emissions from transport, industries, energy production, domestic, residue burning and re-suspended dust (Prasad et al., 2006; Rengarajan et al., 2007; CPCB, 2010; Guttikunda and Calori, 2013). In addition, the IGP is affected by mineral dust in pre-monsoon season. The transport and occurrence of IGP pollutants over foothills of the Himalayan region have also been presented (Raatikainen et al., 2014).

There were local scale initiatives over an air pollution 'hot spot' location in the IGP i.e. Delhi, to control these emissions. Different measures have had been implemented such as conversion of fuel from high sulphur diesel to compressed natural gas (CNG) in year 2000–2002, metro rail system (year 2002–2008), and relocation of industries (year 1996–2000). These initiatives had helped during their inception years. At present, almost all these emission control measures have fallen short in keeping up with the growing local and regional emissions which led to degradation in air quality and increasing health risk. Moreover, when meteorological conditions block the dispersal of aerosols, their high concentration impairs visibility and has a respiratory health threat (HEI, 2010). Thus, there is a need to analyse the aerosol composition to study the behaviour and source-sectors discrimination to control these emissions.

A one-year size-segregated aerosol data was measured at a semi-urban site, Gual Pahari, in IGP from April 2008 to March 2009 as a part of the European Integrated project on Aerosol Cloud Climate and Air Quality interactions (EUCAARI) (Kulmala et al., 2011), that includes particulate mass, elemental and organic carbon, and water soluble ions measured through appropriate techniques to understand atmospheric aerosol behaviour. The purpose of including India along with China, South Africa and Brazil under the EUCAARI project was to expand

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the European activities of aerosol measurements outside Europe and to provide useful reference for evaluating European conditions.

2. Methods

2.1. Site description and aerosol composition

The measurement site was located in Gual Pahari (28°26′N, 77°09′E, 243 m above sea level), Gurgaon, about 25 km south of New Delhi. The 24 h ambient fine ($PM_{2.5}$) and coarse ($PM_{2.5-10}$) aerosols were sampled simultaneously every 6 days using a Dichotomous Partisol-Plus Sequential Air Sampler (Yeatts et al., 2007). The sample was taken at 2 m above the ground. In addition to the filter sampler, the station had a comprehensive set of ground-level *in-situ* aerosol and remote sensing measurements (Hyvärinen et al., 2010; Komppula et al., 2012). In this work, we utilised online $PM_{2.5}$ and PM_{10} measurements (Thermo Scientific SHARP Monitors model 5030), aerosol black carbon measurements (Thermo Scientific Multi-Angle Absorption Photometer, MAAP), and size distribution (TSI Aerodynamic Particle Sizer, APS). Ambient temperature, relative humidity, rain intensity, wind direction and wind speed were also measured (Vaisala WXT 510 weather transmitter) at a height of about 10 m above the ground. A more detailed presentation of the sampling location and instrumentation can be found in Hyvärinen et al. (2010) and Komppula et al. (2012).

The fine and coarse particles were collected on 47 mm quartz filter at a flow rate of 16.7 lpm. Aerosol sampling on quartz filters is subject to negative artefacts (losses of volatile species such as ammonium and nitrate) and positive artefacts (absorption on the collection substrate of semivolatile species such as low molecular weight organics) (Turpin et al., 1994; Vecchi et al., 2009). To correct negative sampling artefacts due to the volatilisation of ammonium and nitrate, a Whatman 41 paper filter was placed on the back of each quartz filter used to sample fine particles. Fine ammonium and nitrate concentration were calculated as the sum of ammonium and nitrate on quartz and on the paper filter concentration (Putaud et al., 2004). To avoid positive sampling artefacts, active carbon honeycomb denuders were placed upstream of the filter to remove semi volatile organic species, while denuders coated with sodium chloride and nitric acid were employed to remove nitric acid and ammonia, respectively (Gilardoni et al., 2011).

PM collected on filters was determined gravimetrically with a microbalance in a clean room after conditioning at a controlled relative humidity (20%–30%) and temperature (20–25 °C) for 24 h.

Filters were analysed for organic carbon (OC), elemental carbon (EC), and major water-soluble inorganic ions (sulphate, nitrate, chloride, ammonium, sodium, potassium, calcium and magnesium). OC and EC were quantified on quartz filters with a Sunset Lab Thermal/Optical Carbon Analyser using the EUSAAR-2 protocol (Cavalli et al., 2010). The heating protocol was modified with longer heating step to ensure the complete evolution of the carbon fractions. A punch of each quartz and paper filter was extracted with ultrapure mQ water and the extracts were analysed by ion chromatography to quantify the water-soluble inorganic species (Metrohm 861 Advanced Compact ion chromatographer equipped with an 813 Compact Auto-sampler, Micro Devices Metrohm Limited). For quality control purposes, an aliquot of standard reference material SRM 2694 (simulated rain water) was analysed simultaneously with each sample batch and the agreement between measured and certified concentrations was verified (Gilardoni et al., 2011).

2.2. Source region characterisation

Receptor model (Positive matrix factorization, PMF) (Paatero and Tapper, 1994; Paatero, 1997) a commonly employed method was used for apportionment of source strength using speciation data. EPA PMF 3.0 program (EPA, 2008a) was applied to fine and coarse mode aerosol annual data (11 species, $n = 52$). Each data point was individually weighted using the estimated analytical uncertainty and the method detection limit (Gilardoni et al., 2011; Polissar et al., 1998; Norris et al., 2008). A 7% of fine and 13% of coarse mode aerosol data was below limit of quantification (LOQ) or missing values. Missing values were substituted by medians of the adjacent four values (Huang et al., 1999), and these values were down-weighted by assigning uncertainty with ten times the median concentration. Values below LOQ were replaced with half of the LOQ, and corresponding uncertainty value at 5/6 times the LOQ (Polissar et al., 1998; Evans and Jeong, 2007). A 5% extra modelling uncertainty was used for all species in PMF runs.

Air-mass backward (120 h) trajectories were calculated for every 3 h with the FLEXTRA model (Stohl et al., 1995; Stohl and Seibert, 1998) as described in Hyvärinen et al., 2010 and Raatikainen et al., 2014. Hourly local wind vectors were calculated using local wind direction and speed, similarly as described in Vestenius et al., 2011. Wind direction and trajectories were classified as four main sectors: north (315–45°), east (45–135°), south (135–225°) and west (225–315°).

The conditional probability function (CPF) was applied on resolved source contributions differently for back-trajectories (CPF_T) and wind directions (CPF_W).

CPF is defined with the following equation:

$$CPF = \frac{m_{\Delta\theta}}{n_{\Delta\theta}} \quad (1)$$

where $m_{\Delta\theta}$ is the number of times the average trajectory vectors (3-hourly) and the wind direction vectors (1-hourly) that fall in the sector $_{\Delta\theta}$ in each sampling day and exceed the threshold criteria (80th percentile) of the daily source contribution, while $n_{\Delta\theta}$ is the total number of vectors that fall in the same trajectory sector and the wind direction sector (Kim et al., 2003; Vestenius et al., 2011).

3. Results and discussion

3.1. Trajectories and meteorology

Seasons were classified as summer (March–May), monsoon (June–September), post-monsoon (October–November) and winter (December–February). According to the trajectory analysis, during summer, 43% of the air masses came from the wide western sector between NW (i.e. dust areas) and SW (i.e. Arabian Sea). These mixed air mass patterns have also been similarly seen by Lodhi et al., 2013. In monsoon, air masses were mainly from the W–SW sector (i.e. Arabian Sea) with a small fraction from the E–SE sector (i.e. Bay of Bengal). The post-monsoon and the winter had similar patterns, mainly from the NW sector. The post-monsoon period also had a small contribution from the E–SE sector. The typical seasonal behaviour of air-mass trajectories for summer season (22-04-2008), monsoon season (23-06-2008) and post-monsoon season (27-11-2008) are illustrated in Fig. 4 (discussion in Section 3.4).

In the winter, the coldest nights reached as low as 1.5 °C. The maximum temperature for the hourly data set was 42.4 °C in summer. The diurnal average temperature varied from 8.5 to 34.3 °C during the measurement period. Maximum relative humidity reached nearly 97% during most of the night time in post-monsoon and winter months. On the other hand, the relative humidity in daytime never reached 90%. The average height of planetary boundary layer (PBL) above ground level at Gual Pahari during the measurement period was 540 m (for detailed calculations see Raatikainen et al., 2014). The highest diurnal variation in the temperature during the summer season in the IGP creates a highly dynamic boundary layer and efficient vertical mixing of pollutants (Hyvärinen et al., 2010; Raatikainen et al., 2014).