



Source Apportionment for Water Soluble Organic Matter of Submicron Aerosol: A Comparison between Foggy and Nonfoggy Episodes

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ABSTRACT

An extensive filter-based ambient aerosol measurement was carried out at a region that is mostly affected by fog almost every winter. A few fogwater samples were also collected during the study period. Water soluble organic matter (WSOM) was extracted in the aqueous media. The filter extracts and fogwater were analyzed for their chemical constituents using a High Resolution-Time of Flight-Aerosol Mass Spectrometer (HR-ToF-AMS). Data from the HR-ToF-AMS were used in positive matrix factorization (PMF) for the source apportionment to understand the sources of WSOM. Three major sources were identified, namely water soluble biomass burning organic aerosol (WS-BBOA), water soluble oxygenated organic aerosol (WS-OOA), and water soluble primary aerosol (WS-PA). The contributions of WS-BBOA and WS-OOA to WSOM were lower during foggy episodes than during clear (nonfoggy) episodes. The wet scavenging and removal of the aerosols from these sources were the prime causes of their lower contributions. The contribution of WS-PA to WSOM was higher during foggy episodes than during nonfoggy episodes. The higher contribution of this source is attributed to the accumulation of aerosol generated from this source, due to poor dispersion and the calm conditions prevalent during foggy episodes. Surprisingly, the contribution of WS-PA to WSOM was highest among the three sources during both foggy and nonfoggy episodes.

Keywords: Aerosol mass spectrometer; Fog; PMF; Organic aerosol; WSOM.

INTRODUCTION

Water soluble organic matter (WSOM), which constitutes major portion of carbonaceous aerosol, are mostly oxygenated and polar compounds, and their sources of emission are not very well understood. Since WSOM affects the hygroscopic and optical properties of the aerosol, it has significant impact on regional air quality and global climate change (Jung *et al.*, 2011; Ding *et al.*, 2013). Indo-Gangetic plain (IGP) region is affected by fog almost every winter season. The fog episodes have been extensively studied as exemplified by numerous articles due to its effect on the visibility, public health, and global climate change (Charlson *et al.*, 1992; Lee and Sequeira, 2002; Sun *et al.*, 2006; Dall'Osto *et al.*, 2009; Hou *et al.*, 2011; Kaul *et al.*, 2011; Wang *et al.*, 2011). The hygroscopic aerosols act as cloud condensation nuclei (CCN) during the fog formation. The stable meteorological condition, low wind speed and low mixing height accompanying the fog cause accumulation of the primary particles in the fog layer closer to the ground. Fog droplets scavenge gaseous

species which are subsequently oxidized by the dissolved oxidants inside the fog droplets (Lillis *et al.*, 1999). The immersed aerosols inside the fog droplets as well as other aerosols colliding with the falling fog droplets are removed from the atmosphere (Kramer *et al.*, 2000; Moore *et al.*, 2004; Herckes *et al.*, 2007; Pratt *et al.*, 2011; Wang *et al.*, 2011).

To understand the adverse effects of fog and their subsequent reduced visibility, the sources of pollutants contributing to fog formation should be well understood so as to implement appropriate control measures and reduce the fog events. Only a handful of such studies have been carried out over this region (Mehta *et al.*, 2009). The major emission sources dominant in this region include industries, vehicle transport and biomass burning (Mehta *et al.*, 2009; Behera and Sharma, 2010). Previous studies (Bhanuprasad *et al.*, 2008; Mehta *et al.*, 2009) have applied positive matrix factorization (PMF) source apportionment to study the sources over the region and reported relatively higher contribution of secondary and biomass combustion sources during foggy episodes compared to nonfoggy episodes. The apportionment has been based on both organic and inorganic components of the aerosol. The aerosols produced from these sources were indirectly inferred to be the major cause of fog formation over this region (Mehta *et al.*, 2009). Whether fog will clean the atmosphere by removing the aerosols or trap them and increase their concentration depends

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upon the chemical nature of the aerosols and their rate of emission/production and rate of their scavenging. A couple of previous studies (Wang *et al.*, 2012) have reported lower concentration of particulate organic matter during foggy episode due to their scavenging and wet removal whereas others (Ram *et al.*, 2012) have reported higher concentration during foggy episode, possibly due to low boundary layer height, poor dispersion and subsequent accumulation of pollutants. These studies were done mostly on aerosol of size $> 1 \mu\text{m}$. So, effect of fog processing on concentration of WSOM is not lucid.

Water soluble organic carbon has been used to derive secondary organic aerosol (SOA) as it is mostly considered oxygenated and water soluble (Weber *et al.*, 2007; Ding *et al.*, 2013); although, biomass burning aerosol can also contribute to water soluble carbon. Thus, contribution of biomass is subtracted to estimate the contribution of secondary sources to water soluble carbon (Weber *et al.*, 2007; Snyder *et al.*, 2009; Ding *et al.*, 2013). A few other dominant sources which can contribute to water soluble carbon should be identified such that water soluble organic carbon can be used judiciously to derive SOA, as other sources of water soluble organic carbon will confound the estimate of SOA. Thus, source apportionment of WSOM becomes important from the perspective of estimating SOA accurately.

PMF resolved emission sources were adopted to better understand the influence of different sources and their contribution to water soluble organic matter during foggy and nonfoggy episodes. A reliable knowledge of emission sources will lead to better understanding of aqueous phase processes and mitigation of fog related problems such as health hazard, delay in rail and air transport and traffic related accidents which are caused by the reduced visibility due to fog formation. Source apportionment of WSOM was carried out by innovatively using HR-ToF-AMS for the first time in this region and thus, this study will be useful to the scientific community from this perspective of understanding the sources of production/emission of WSOM and its processing by the fog.

EXPERIMENTAL DETAILS

Sampling was conducted at Kanpur, India which is mostly affected by the fog almost every winter season. PM_{10} samples on 47 mm quartz filter (Whatman, QMA) were collected from January, 2010 to February, 2010 using a custom designed inertial based sampler. Six filter samples were collected every 24 h. The sampling duration was ~ 2.5 h for all the samples except night time samples which was for ~ 7 h. A total number of filters thus collected during the sampling period was 180; 54 of these were collected during foggy episodes. All the filters were heated prior to sampling for 6–7 h at 700°C for removing background carbon present on the filters. Filters thus collected were stored in the freezer until analysis. A few punches (each with area $\sim 2.11 \text{ cm}^2$) from each filter were cut and these punches were further cut into smaller pieces which were dissolved into 20 mL of deionized milli-Q water in test tubes. These sample test

tubes were kept in the ultrasonicator (Fast Clean Ultrasonic Cleaner, 2k909008) for 1 hour duration to extract the water soluble organic carbon into the aqueous solution. The extract was filtered using Millipore filter of pore size $0.22 \mu\text{m}$; similar extraction procedure was also adopted for blank filters and concentration on the blank filters were subtracted from the concentration on the filters samples. Additional detail on schedule of collecting filters samples, particulate matter and aqueous extraction procedure etc. could be found elsewhere (Kaul *et al.*, 2011).

Fogwater samples were collected using a three stage size-selective (having cut-off fog droplet diameters of 4, 16 and $22 \mu\text{m}$, respectively) Caltech Strand Cloudwater Collector which was designed at Colorado State University. The design of this sampler is based on earlier two stage size-selective cloudwater collector (Demoz *et al.*, 1996). 21 (7 for each cut-off size droplet diameter) fogwater samples collected using this sampler were utilized in this study. The collected fogwater was filtered through Millipore filters of $0.22 \mu\text{m}$ pore size.

The aqueous extract of filter samples and fogwater, obtained as described above, were injected into the High Resolution-Time of Flight-Aerosol Mass Spectrometer (HR-ToF-AMS) (Aerodyne Research Inc., USA) using an aerosol atomizer (TSI, Model No:3079). This atomizer produced small droplets of aerosol which entered through a custom built denuder (removes water from aerosol) to HR-ToF-AMS. Similar setup for chemical analysis on liquid extracted samples has been used elsewhere (Crilley *et al.*, 2013). HR-ToF-AMS was run for 10 min in V-mode for each sample and measurement obtained during this duration was averaged. The average data received from the analysis of filters sample thus has been used in positive matrix factorization (PMF) for the source apportionment of WSOM. Analysis on few filters (~ 18) could not be carried out because these filters got consumed in analysis of other species. Thus, measurements obtained from the aqueous extract of 162 filters were used for PMF source apportionment. PMF analysis on the fogwater samples were not performed because of the limited number of samples (21 only). HR-ToF-AMS was calibrated for the ionization efficiency prior to experiment following procedure described elsewhere (Jayne *et al.*, 2000; Drewnick *et al.*, 2004; Huffman *et al.*, 2005). Briefly, ammonium nitrate aerosols from its aqueous solution are generated by the aerosol atomizer and dried by the denuder. The dried aerosols were size selected using differential mobility diameter (DMA) unit of scanning mobility particle sizer (SMPS, TSI Inc.). The aerosols thus produced were measured using AMS and condensation particle counter (CPC, TSI Inc.). The mass of the ammonium nitrate introduced into AMS was estimated using number concentration measured by CPC, bulk density of ammonium nitrate (1.725 g/cm^3) particle and selected size (350 nm) by DMA and was compared with the ion signal of the mass spectrometer to derive the scaling factor. Practically, relative ionization efficiency (RIE) which is ionization efficiency of ammonium relative to ionization efficiency of nitrate is used and RIE was found to be 5.8. Collection efficiency was derived from the comparison of mass size distribution of ambient aerosol

measured simultaneously by AMS and SMPS and was found to be ~50%.

RESULTS AND DISCUSSIONS

Positive matrix factorization (PMF) analysis was carried out using EPA-PMF V3.0 to better understand the sources of the emission. The detailed information of the EPA-PMF V3.0 is available at <http://www.epa.gov/heads/products/pmf/pmf.html> (Paatero and Tapper, 1994; Paatero, 1997, 1999). It requires concentration profile and related uncertainty profile as input. Model outputs are factor profiles, relative factor contribution, and residuals.

Concentration profile and corresponding uncertainty were obtained from the HR-ToF-AMS. The details on uncertainty estimated by HR-ToF-AMS is provided elsewhere (Lanz *et al.*, 2007). Signal for some values of m/z such as for $m/z = 1$ to 10; $m/z = 21$ to 23; $m/z = 29, 30$; $m/z = 32$ to 36; $m/z = 39, 40$; $m/z = 46$; $m/z = 182$ to 184 were almost zero and thus they were not included in the source apportionment. Guidelines related to the signal to noise (S/N) ratio for assigning the species such as strong or weak depends upon the relative S/N ratio. In the strongest variable, the error is minimal whereas in the weakest variable the data could entirely be noise. Classification of the species as strong or weak was studied by (Paatero and Hopke, 2003) and it was recommended that species having S/N ratio greater than 2 could be assigned as strong, those having less 2 and greater than 0.2 could be assigned as weak and those having less than 0.2 could be assigned as bad. All the species in this study were categorized following their recommendations. It was observed that most of the species appeared in the strong categories with a few in the weak category ($m/z = 24, 37, 38, 47$ – $49, 59$ – $62, 66, 80, 87, 88, 90, 92$ – $95, 97, 99, 106, 108, 112$ – $114, 116, 120, 122, 124, 125, 126, 127, 130, 132, 134, 136$ – $138, 140$ – $146, 150, 151, 153$ – $156, 158$ – $160, 162$ – $170, 172$ – $176, 178$ – $181, 187$ – $190, 194$ – $198, 200$) and none appeared in the bad category.

An appropriate protocol at every step such as choosing number of the factors, observing the similar Q-values of several runs, independency of the factors (G-Space), the regression coefficients between measured and modeled values etc. was followed to arrive at the acceptable solution (Reff *et al.*, 2007) through several trial and errors. An appropriate number of the factors between 3 and 7 was tried and depending upon the Q-values and physical meaning of the profile, 3 factors were chosen which represented the relevant profile of the sources. More than 3 produced too many sources to make any physical sense. Variation in Q-values by changing F-peak values from -1 to 1 was examined for the rotational ambiguity. Q-value was minimum at F-peak = 0 and rotational ambiguity was not observed; thus solution at F-peak = 0 was adopted. The ratio of Q_{true} to Q_{robust} is another parameter to evaluate the PMF modeled results. The Q_{robust} is estimated excluding the outlier data which are samples having scaled residual greater than 4 and Q_{true} is estimated including all the data points (Gupta *et al.*, 2012; Waked *et al.*, 2013). The ratio close to 1 indicates better solution and greater than 1.5 indicates influence of

peak events on the model. The ratio in this study was found to be ~1.1 which indicates satisfactory model fit to the input data. Residual of the species appeared to be normally distributed. The profiles were correlated with the numerous reference spectra available at the website (<http://cires.colorado.edu/jimenez-group/AMSsd/>) to identify the sources (Ulbrich *et al.*, 2009). It was found the two source profile shows higher correlation ($R^2 > 0.85$) with the reference spectra of OOA1 and OOA2-BBOA (Figs. 1(a) and 1(b)). These two emission profile corresponds to SOA and biomass burning aerosols, respectively. In addition, comparatively higher portion (~74%) of $m/z = 44$, which is a tracer of OOA, in the profile of OOA indicates its secondary production. Similarly, comparatively higher portion (~63% and 49%) of $m/z = 60$ and 73, which are tracers of biomass burning aerosol in BBOA profile indicates its origin from biomass combustion.

The 3rd profile (Fig. 1(c)) did not fairly correlate with any reference spectra available in the database. From the contribution of this source to WSOM, it appeared that this source is strongly local in nature which appears on some days and disappears at other times (Fig. S1, Supplementary Information). The only such local source over the sampling location was found to be spraying of insecticide mixed with smoke of incompletely combusted diesel and petrol. A schematic of machine used in spreading of the insecticide is shown in the supplementary section (Fig. S2, Supplementary Information). Approximately, 15 liter of malathion is mixed with 200 liter of diesel. Petrol is incompletely combusted in the unit –A of the machine which produces considerable amount of smoke. This smoke then travels to unit-B of the machine. The higher temperature of the exhaust of unit-A evaporates the mixture of diesel and malathion. The exhaust from the unit-B consists of trace amount of malathion and considerable amount of incompletely combusted petrol products and partially combusted cum evaporated diesel (Fig. S2). Thus, this source is mostly influenced by the incomplete combustion/evaporation of diesel and petrol. Malathion is almost undetected due to its bare presence in the trace amount. Typically, over 2 h of spreading the insecticide inside the campus, ~150 liter of mixture of diesel and malathion, ~20 liters of petrol is consumed. These quantities are enormous to cause significant air pollution at the local level. The contribution of this source to WSOM is also considerable on specific spraying dates (Fig. S1). The regression coefficients between measured and modeled concentrations of the species were more than 0.90 for all the species.

Having identified the sources, it appears that all the three emission sources, namely WS-OOA, WS-BBOA and WS-PA have contributed to WSOM (Fig. 1). WSOM have been used as a tracer for SOA in numerous studies (Ding *et al.*, 2008; Ding *et al.*, 2013; Timonen *et al.*, 2013) and estimation of the SOA based on mere use of WSOM will certainly confound the SOA estimate. Thus, WSOM should only be used as a tracer when the influence of other sources such as biomass burning, fossil fuel combustion generated organic compounds etc. to the aerosol is almost negligible and existence of such scenario is rare. Therefore, its

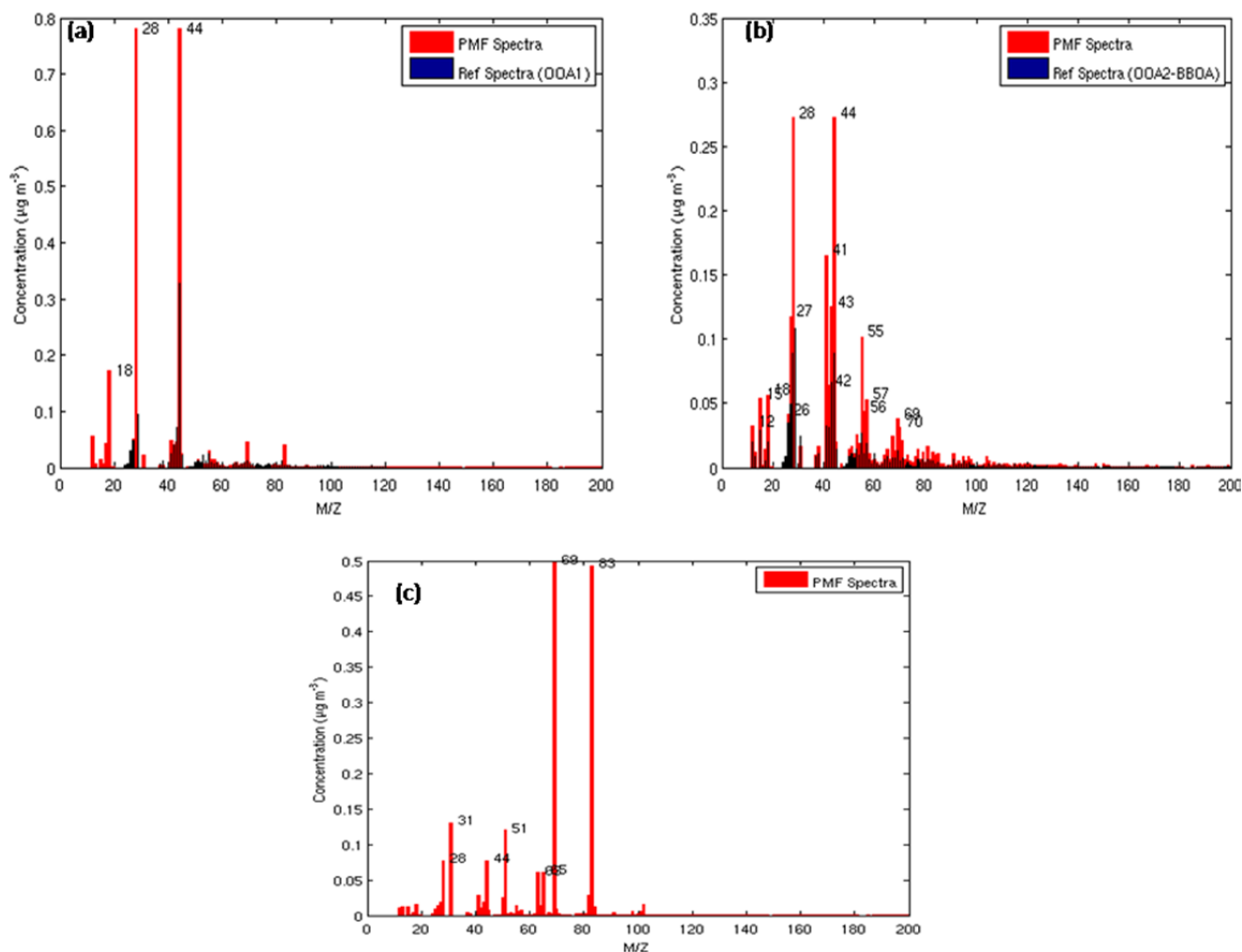


Fig. 1. PMF produced source profile of water soluble secondary organic aerosol (a) water soluble biomass burning generated organic aerosol (b) and water soluble primary generated aerosol (c). The signal of the reference spectrum is in arbitrary unit. The first two profiles compare fairly well ($R^2 > 0.8$) with reference spectra (<http://cires.colorado.edu/jimenez-group/AMSsd/>) of OOA1 and OOA2-BBOA, respectively. The water soluble primary aerosol didn't correlate with any reference spectra available in the database. Thus, no reference spectrum is shown in figure (c). More details on identification of water soluble primary generated aerosol are included in result and discussion section.

predominating use as tracer of SOA can produce unrealistic estimate of SOA. It is also surprising that considerable portion of WSOM is coming from local primary emission (incomplete combustion/evaporation of petrol and diesel) which is mostly thought to be water insoluble. Primary source has considerable effect during foggy episode. It appears that during foggy period when dispersion is minimal due to mostly calm conditions, the primary emitted particles from the machine mostly stayed inside the fog and contributed heavily to WSOM (Fig. 2(b)).

The difference in the concentration during foggy and nonfoggy episode will depend upon the rate of emission and rate of wet scavenging of aerosol. The higher rate of wet scavenging will reduce the aerosol concentration during foggy episode whereas higher rate of emissions of aerosol compared to rate of wet scavenging will cause build up of its concentration. The average contribution of WS-OOA and WS-BBOA to WSOM during foggy episode was ~15%

and ~20% which is lower than that during nonfoggy episode (~28% and ~24%, respectively) (Figs. 2(a) and 2(b)). The lower contribution of WS-BBOA and WS-OOA during foggy episodes could possibly be attributed to relatively higher wet scavenging of biomass and secondary generated aerosol. To examine further their wet scavenging and removal, HR-ToF-AMS produced spectrum of a few fogwater samples were analyzed. PMF on the fogwater samples were not performed due to limited number of fogwater samples (21, 7 for each cut-off sized fog droplet diameter). It was observed that the average spectra of three cut-off sized droplets were almost similar. Thus, a representative spectrum of the fog droplet (4 μm diameter) is presented here (Fig. 2(c)). The sole purpose of providing this spectrum is to confirm the presence of a number of specific tracer species for different sources inside the fog droplets which will substantiate the removal of respective source generated aerosol. Fig. 2(c) indicates that tracer of BBOA ($m/z = 60$ and $m/z = 74$); tracer

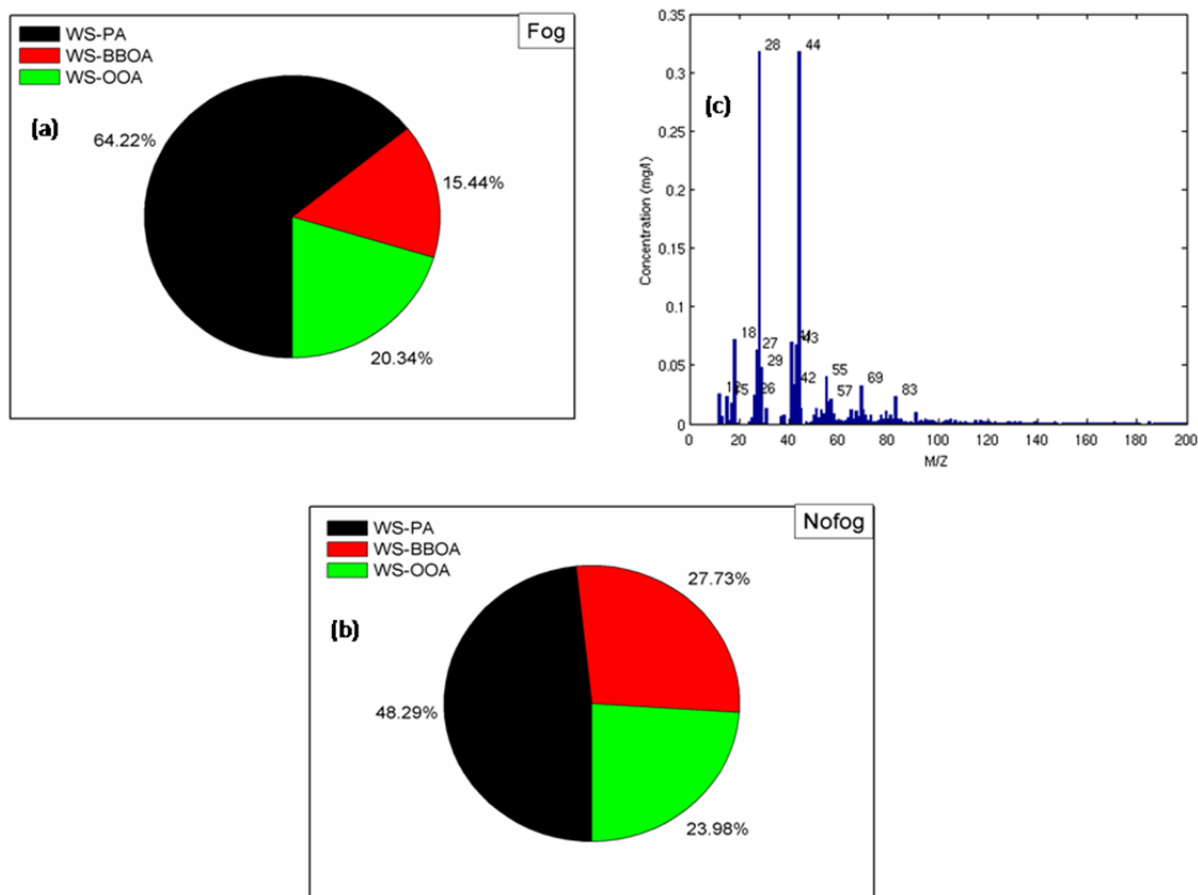


Fig. 2. Average source contribution of water soluble primary aerosol (WS-PA), water soluble biomass burning aerosol (WS-BBOA) and water soluble oxygenated organic aerosol (WS-OOA) to water soluble organic matter (WSOM) for foggy (a) and nonfoggy (b) episode. The comparatively lower contribution of WS-BBOA and WS-OOA to WSOM during foggy episode indicates scavenging and removal of the aerosols generated from these sources. Percentage contribution of WS-PA to WSOM is estimated using only nonzero contribution values of this source. Fig. 2(c): HR-ToF-AMS spectra of fog droplet of cut-off size 4 μm . The presence of tracer species of the sources inside the fog droplets such as $m/z = 44$; $m/z = 60$ and 73 and $m/z = 69$ and 93 does indicate wet scavenging of biomass generated, secondary generated and primary aerosol.

of OOA ($m/z = 44$); tracer of primary aerosol ($m/z = 69$ and 83 in our case) are present in this spectra. This indicates that aerosols generated from these sources get scavenged and removed by the fog droplets. The reduced incoming solar radiation during foggy episode which has been documented elsewhere (Kaul *et al.*, 2011) indicates reduced photochemistry during foggy episodes. The reduced photochemistry during foggy episode could also be the cause of lower WS-OOA. Thus, reduced WS-OOA during foggy episode could be attributed to both wet scavenging as well as reduced photo-chemistry; although, their individual role in reducing WS-OOA could not be segregated in this study. Thus, it appears that lower contribution of WS-OOA and WS-BBOA to WSOM during foggy episode could be attributed to comparatively higher rate of wet scavenging than rate of production/emission of aerosol from these sources. WS-PA appeared to get accumulated in the fog layer during foggy episode as indicated by presence of this source during non-spreading date (Fig. S1) and its relatively higher contribution to WSOM during foggy episode ($\sim 64\%$).

The poor dispersion and calm condition during foggy episode caused the aerosol generated from this source to stay in the atmosphere for longer duration as spreading was performed for only 4 days during foggy episode. This indicates that scavenging has not been the dominating process for removing WS-PA; rather excess emission and calm meteorological conditions have caused its concentration to build up. This could be the reason for higher contribution of WS-PA to WSOM during foggy episode ($\sim 64\%$) as compared with nonfoggy episode ($\sim 48\%$). Primary generated aerosols are comparatively less water soluble compared to biomass burning and secondary generated aerosols (Pratt *et al.*, 2011). Thus, less removal of primary generated aerosol during foggy episodes appears to be consistent with the current findings.

The percentage source contribution to WSOM of WS-PA is more compared to WS-BBOA and WS-OOA which appears to give impression that WS-PA is more water soluble (Fig. 2). Although, this may not be the case as WS-BBOA and WS-OOA are mostly removed from the atmosphere thus the aerosol generated from these two sources are rather

more water soluble. Although, it is surprising that water soluble portion of the aerosol is dominated by WS-PA during both foggy and nonfoggy episode in this study.

CONCLUSIONS

Positive matrix factorization (PMF), as a tool for the source apportionment was used to better understand the emission sources of water soluble organic aerosol. Three major sources namely water soluble biomass burning organic aerosol (WS-BBOA), water soluble oxygenated organic aerosol (WS-OOA) and water soluble primary aerosol (WS-PA) were identified. The contribution of WS-OOA and WS-BBOA to WSOM was comparatively lower during foggy episodes. The possible lower contribution of WS-BBOA and WS-OOA during foggy episodes was attributed to wet scavenging and reduced photo-chemistry. The analysis on collected fogwater has further supported scavenging and removal. The contribution of WS-PA to WSOM was rather high during foggy episode which could be attributed to build up of primary generated aerosol due to reduced wet scavenging and removal. WSOM was composed of all types of aerosol and surprisingly, WS-PA contributed majorly to WSOM during both foggy and nonfoggy episodes. The removal of aerosol generated from these sources indicates that fog to certain level cleans the atmosphere. The contribution of primary and biomass combustion sources to WSOM indicates that WSOM should be carefully used in estimation of secondary organic aerosol.

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SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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SUPPLEMENTARY MATERIALS

Source Apportionment of Water Soluble Organic Matter of Submicron Aerosol: A Comparison between Foggy and Nonfoggy Episodes

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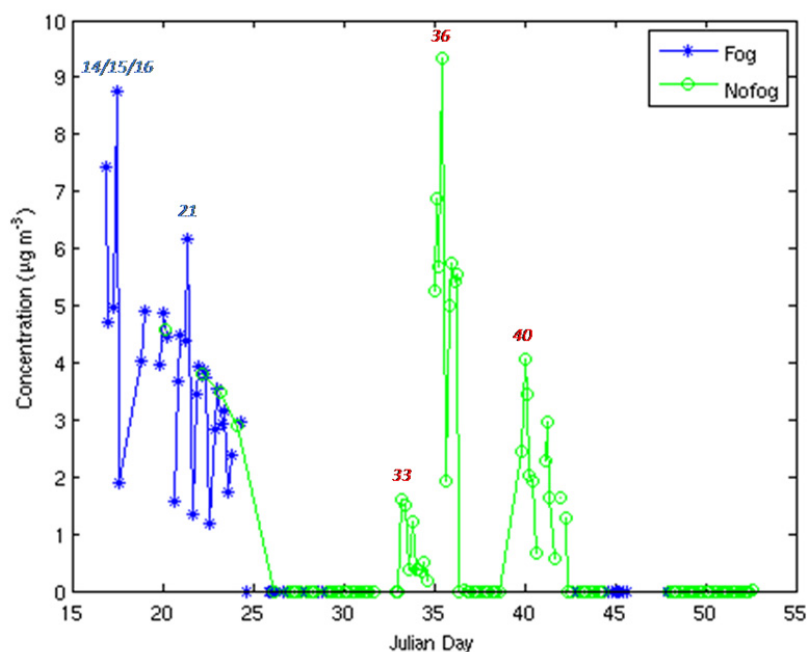


Fig. S1. Contribution of water soluble primary aerosol (WS-PA) to water soluble organic matter (WSOM). The contribution is observed during emission of the primary aerosol emitted from the incomplete combustion of petrol and evaporation of diesel from the insecticide spreading machine; other times, contribution is zero. Numbers inside the figure are Julian date on which machine for spreading insecticide was run. Contribution of this source on non-spread days during foggy episode is mostly due to the accumulation of primary aerosol emitted from this machine in the fog layer characterized which is mostly calm conditions. Machine was also run 2 days (14 and 15 Julian Day) prior to sampling start day (Julian day 16 morning). Machine is run mostly during evening from ~5:00 PM to ~10:00 PM.

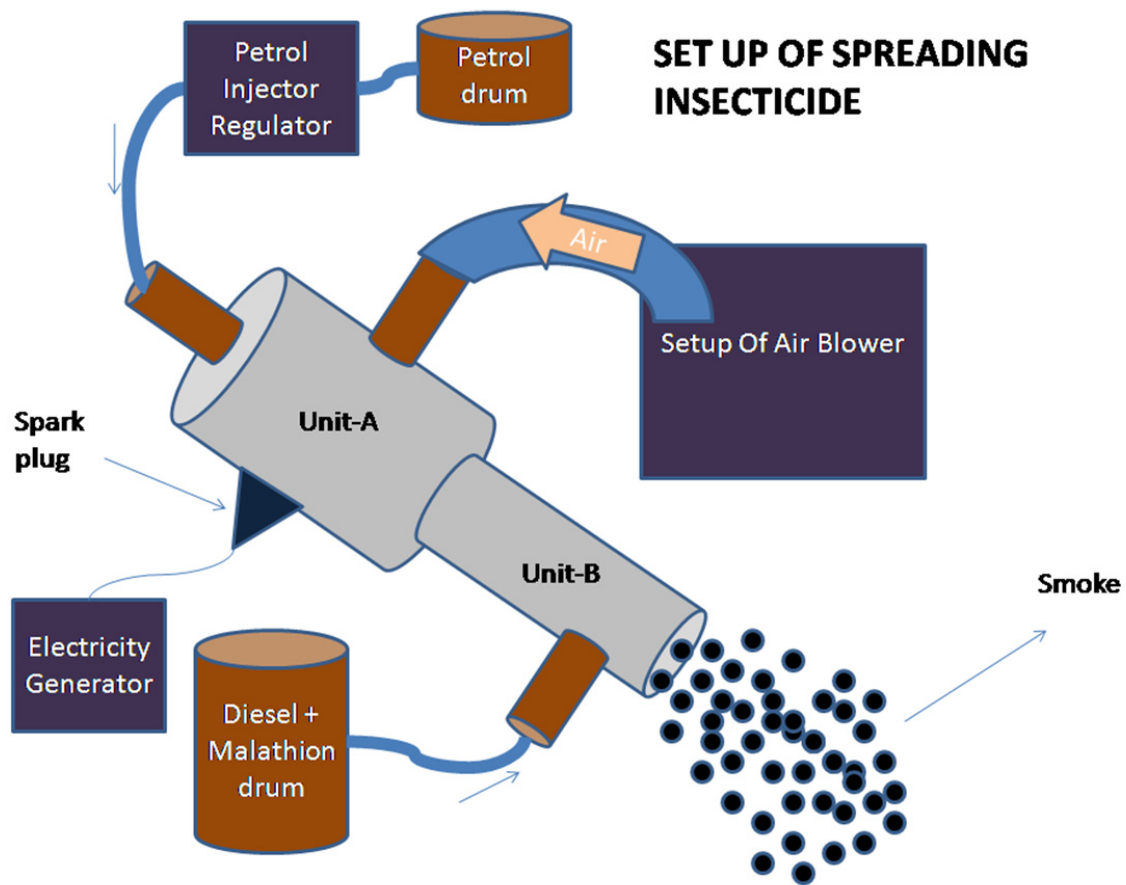


Fig. S2. Schematic of the machine used to spread insecticide. Insecticide is in the trace amount. Enormous emission of primary aerosol from the incomplete combustion of petrol and evaporation of diesel occurs.