View metadata, citation and similar papers at core.ac.uk

brought to you by CORE

provided by University of Birmingham Research Portal

UNIVERSITY OF BIRMINGHAM

Research at Birmingham

Characterization of ambient PM2.5 at a pollution hotspot in New Delhi, India and inference of sources

Pant, Pallavi; Shukla, Anuradha; Kohl, Steven D.; Chow, Judith C.; Watson, John G.; Harrison, Roy

DOI:
10.1016/j.atmosenv.2015.02.074

License:
Other (please specify with Rights Statement)

Document Version
Peer reviewed version

Citation for published version (Harvard):
Pant, P, Shukla, A, Kohl, SD, Chow, JC, Watson, JG & Harrison, RM 2015, 'Characterization of ambient PM2.5 at a pollution hotspot in New Delhi, India and inference of sources', Atmospheric Environment, vol. 109, pp. 178-189. https://doi.org/10.1016/j.atmosenv.2015.02.074

Link to publication on Research at Birmingham portal

Publisher Rights Statement:
NOTICE: this is the author's version of a work that was accepted for publication in Atmospheric Environment. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in Atmospheric Environment, Vol 109, May 2015, DOI: 10.1016/j.atmosenv.2015.02.074.

Eligibility for repository checked April 2015

General rights
Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

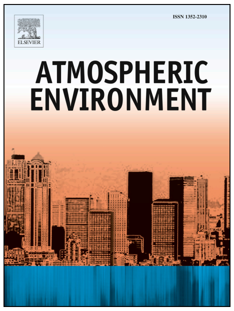
Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy
While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.

Download date: 01. Feb. 2019



Characterization of Ambient $PM_{2.5}$ at a Pollution Hotspot in New Delhi, India and Inference of Sources

Pallavi Pant, Anuradha Shukla, Steven D. Kohl, Judith C. Chow, John G. Watson, Roy M. Harrison

PII: S1352-2310(15)00203-4

DOI: 10.1016/j.atmosenv.2015.02.074

Reference: AEA 13670

To appear in: *Atmospheric Environment*

Received Date: 10 November 2014

Revised Date: 12 February 2015

Accepted Date: 26 February 2015

Please cite this article as: Pant, P., Shukla, A., Kohl, S.D., Chow, J.C., Watson, J.G., Harrison, R.M., Characterization of Ambient $PM_{2.5}$ at a Pollution Hotspot in New Delhi, India and Inference of Sources, *Atmospheric Environment* (2015), doi: 10.1016/j.atmosenv.2015.02.074.

Characterization of Ambient $PM_{2.5}$ at a Pollution Hotspot in New Delhi, India and Inference of Sources

Pallavi Pant[1], Anuradha Shukla[2], Steven D. Kohl[3], Judith C. Chow[3], John G. Watson[3] and Roy M. Harrison[1*†]

[1]Division of Environmental Health and Risk Management
School of Geography, Earth and Environmental Sciences University of Birmingham, Edgbaston, Birmingham, B15 2TT
United Kingdom

[2]Environmental Science Division
Central Road Research Institute, New Delhi, India

[3]Division of Atmospheric Sciences
Desert Research Institute, 2215 Raggio Parkway, Reno, Nevada, USA

---

[*] To whom correspondence should be addressed
Tele: +44 121 414 3494; Email: r.m.harrison@bham.ac.uk

[†]Also at: Department of Environmental Sciences / Center of Excellence in Environmental Studies, King Abdulaziz University, PO Box 80203, Jeddah, 21589, Saudi Arabia

ABSTRACT

Ambient $PM_{2.5}$ samples were collected at a high-traffic location (summer and winter 2013) and characterized for a large suite of elemental and organic markers. Concentrations were found to exceed the Indian $PM_{2.5}$ air quality standard on several occasions, especially in the winter. Winter concentrations of several individual tracer species were several fold higher compared to summer, particularly for some PAHs and trace metals. Enrichment factors relative to crustal material showed significant enrichment for elements such as Ti, Sb, Pb and As, although Ba, often used as a marker for non-exhaust emissions from traffic was not found to be enriched appreciably. Crustal material was found to be an important contributor in the summer (14.3%), while wood burning (23.3%), nitrates (12.4%) and chlorides (12.3%) were found to be major contributors in winter. The contribution of road traffic exhaust emissions was estimated to be 18.7% in summer and 16.2% in winter. Other combustion sources (wood and other biomass/waste/coal) were found to be a significant source in winter, and contribute to the higher concentrations. Secondary sulphates, nitrates and chloride (the latter two in winter) and organic matter also contribute substantially to $PM_{2.5}$ mass.

Keywords: Molecular markers; traffic, India; mass closure; particulate matter

1. INTRODUCTION

Given the rapid rates of urbanization in Indian cities, air pollution is increasingly becoming a critical threat to the environment and to the quality of life among the urban population in India. Particulate matter (PM) concentrations are often found to exceed the Indian National Ambient Air Quality Standards (NAAQS) and recent studies have identified PM as one of the key public health risks, particularly in urban areas (Lim et al., 2012; Guttikunda and Goel, 2013; Trivedi et al., 2014). The primary sources of air pollution in India have been identified as vehicular emissions, industrial emissions, coal combustion, biomass burning, road dust and waste burning, construction activities, oil combustion and sea salt (Chowdhury et al., 2007; CPCB, 2010; Guttikunda and Calori, 2013; Gargava et al., 2014). An overview of PM sources is presented in Guttikunda et al. (2014).

There is a growing body of literature on source apportionment of PM in India which has used receptor modelling with both elements and organic markers, and a detailed review of source apportionment studies in India is presented in Pant and Harrison (2012). A large number of studies have focused on total suspended particulate matter (TSP) and PM_{10} but there is an increasing number of studies focused on fine PM (aerodynamic diameter <2.5 µm) (Chowdhury et al., 2007; Tiwari et al., 2009; Chakrobarty and Gupta, 2010; Khare and Baruah, 2010; Gummeneni et al., 2011; Joseph et al., 2011). In terms of geographic distribution across the country, most studies focus on big cities such as Delhi (Balachandran et al., 2000; Khillare et al., 2004; Srivastava and Jain, 2007; Tiwari et al., 2009; Khillare and Sarkar, 2012; Trivedi et al., 2014), Mumbai (Kumar et al., 2001; Chelani et al., 2008; Kothai et al., 2008), Chennai (Srimuruganandam and Shiva Nagendra, 2011), Hyderabad (Gummeneni et al., 2011; Guttikunda et al., 2013) and Kolkata (Gupta et al., 2007; Kar et al., 2010). The Central Pollution Control Board (CPCB) also conducted a detailed dispersion and receptor modelling analysis in six cities across India (CPCB, 2010). In comparison, there are very few analyses in smaller cities/towns (e.g. Mouli et al., 2006; Kulshrestha et al., 2009;

Chakrobarty and Gupta, 2010; Masih et al., 2010; Giri et al., 2013). Some recent work focused on unique sources (Chakrobarty et al., 2013; Deka and Hoque, 2014; Kirillova et al, 2014; Srinivas and Sarin, 2014).

A majority of the PM source apportionment studies have been conducted using trace element markers (Balachandran et al., 2000; Kumar et al., 2001; Kothai et al., 2008) and in some cases, inorganic tracers have been used in conjunction with organic and elemental carbon (Gupta et al., 2007; Tiwari et al., 2009; Chelani et al., 2010; Sharma et al., 2013). The use of organic molecular markers for PM source apportionment has only been reported in recent years (Chowdhury et al., 2007; Fu et al., 2010; Masih et al., 2010; Giri et al., 2013; Herlekar et al., 2012; Li et al., 2014). In a comprehensive review on receptor modelling of PM in India, several gaps were highlighted including the need for detailed analyses using organic markers, focus on fine particles ($PM_{2.5}$), and the need to characterize the contribution of secondary sources to ambient PM concentrations (Pant and Harrison, 2012).

Delhi is one of the most polluted cities across the world and concentrations of air pollutants are often found to exceed the NAAQS. Delhi is reported to have 29 planned industrial areas and 5 factory complexes with a range of industries including food and beverages, metal and alloys, leather and leather products, chemicals, paper etc. (Delhi Statistical Handbook, 2013). Delhi has two coal thermal power plants and four natural gas power plants and the sulphur content in the coal used in power plants in Delhi typically ranges between 0.35% and 0.50% (Chowdhury et al., 2007). Indian coal is typically high in ash content. Diesel is used for both road transport (cars, utility vehicles, heavy duty vehicles [HDVs]) and industry (power back-up, mobile phone towers, miscellaneous) while gasoline is mostly used for road transport. Public transport in the city runs on compressed natural gas [CNG] while private vehicles run on diesel, gasoline, CNG and liquefied petroleum gas [LPG]. A number of brick kilns are also reported to operate in areas around Delhi (Guttikunda and

Calori, 2013). A range of different cooking fuels are used in Delhi including LPG, kerosene, firewood, cow dung cake, coal, crop residues, biogas and electricity with nearly 90% of households using LPG (Delhi Statistical Handbook, 2013). Estimated source contributions from the different sectors are described in Sahu et al. (2011a) and Guttikunda and Calori (2013). While on one hand, Sahu et al. (2011a) reported road transport as the biggest contributor to $PM_{2.5}$ emissions (30.25 Gg/yr) followed by residential emissions (18.65 Gg/yr), dust (18.35 Gg/yr) and industry (16.29 Gg/yr); Guttikunda and Calori (2013) identified transport, power plants and domestic emissions as the three biggest contributors. Several studies have been undertaken for source apportionment of suspended particulate matter (SPM), PM_{10} and $PM_{2.5}$ using receptor modelling in Delhi and a majority of those have used methods such as principal component analysis (PCA), PCA-MLR (multiple linear regression), diagnostic ratio, enrichment factor etc. However, several recent studies have used positive matrix factorization (PMF) and chemical mass balance (CMB) models for source apportionment. A large percentage of the PM has been attributed to vehicular emissions, road dust, coal combustion and domestic emissions in several studies (Balachandran et al., 2000; Khillare et al., 2004; Chowdhury et al., 2007; Sharma et al., 2007; Chelani et al., 2010; Tiwari et al., 2013). Goyal et al. (2010) have reported diesel vehicles to contribute nearly 28% of the total PM in Delhi. Other sources identified for PM emissions in Delhi include industrial emissions, open refuse burning and construction (Khillare et al., 2004; Mönkönnen et al., 2004; CPCB, 2010; Khillare and Sarkar, 2012; Guttikunda and Calori, 2013). Most receptor modelling studies, however, have focused on characterization of elemental, and in some case ionic species and PAHs, and there is a lack of studies with detailed characterization of molecular marker species in $PM_{2.5}$.

The objective of the current study was to conduct detailed chemical characterization of ambient $PM_{2.5}$ and to assess source contributions to $PM_{2.5}$ including primary and secondary sources.

2. MATERIALS AND METHODOLOGY

2.1 Sampling Location

Mathura Road is one of the major arterial roads in Delhi with an average traffic flow of 170,000 vehicles per day and a modal split shown in Figure 1. Other sources of PM include residential burning and an industrial hub about three kilometres from the sampling site (Okhla Industrial Area). Trucks are not allowed between 07:30 to 11:00 and 17:00 to 21:30 while buses, light duty vehicles (LDVs) and two and three wheelers are not restricted (Delhi Police, 2014). It is important to note that Bharat Standard IV (BS-IV, 50 ppm sulphur) standards are applicable to the vehicles within Delhi; vehicles from outside Delhi are often BS-III (equivalent of Euro III, 350 ppm sulphur).

The samplers were placed at a height of two meters from ground level at a distance of 50 meters from the road. Traffic emissions are the most prominent source. Other sources include biomass combustion in the low-income housing close to the sampling site, emissions from the industrial units located at a distance of ~3 kilometres from the sampling site and a power plant.

New Delhi has a sub-tropical climate with hot summers (April-June) and moderately cold winter (November to January). Typically, S-SW winds are prevalent in summer and N-NW winds are prevalent in winter (Yadav and Rajamani, 2006). During the summer sampling period (June 15-30, 2014), the average temperature and relative humidity (RH) were recorded as 31.4 ± 4.02°C and 67.5 ± 20.5% respectively while during the winter sampling period (December 15, 2013-January 15, 2014), the average temperature and RH were recorded as 13.4 ± 2.7°C and 80.8 ± 8.1 % respectively. During the sampling period in winter, fog/haze was reported on most days with calm wind conditions. Average rainfall in the months of June and December was recorded as 151 and 6.8 mm respectively.

2.2 Sampling

Collocated Minivol samplers (AirMetrics, Springfield, OR) equipped with $PM_{2.5}$ impactors were used to collect two twelve hour $PM_{2.5}$ samples per day (filter change at 12:00 and 00:00 ; n=28 in summer, n= 15 in winter) on 47 mm quartz fibre (Tissuquartz 2500QAT-UP, Pall Life Sciences (7202) (Ann Arbor, MI)) and PTFE teflon membrane (Telfo$^{@}$ PTFE membrane with PMP (polymethypropylene) support ring, 2µm pore size, Pall Life Science (R2PJ047) (Ann Arbor, MI)) filters. Use of a low volume sampler with a flow rate of 5L/min was more suitable in Delhi to minimize clogging since the area records high PM concentrations. Teflon-membrane filters were equilibrated in a temperature (21-23 ºC) and RH (30-40%) controlled room before gravimetric analysis. Pre- and post-weighing of filters was performed with a microbalance (Mettler (Toledo, OH) Model XP-6) with a sensitivity of ± 1µg. Quartz fibre filters were baked at 900 ºC for four hours to remove organic artefacts. All samples were analysed at the Environmental Analysis Facility, Desert Research Institute (Reno, Nevada, USA).

2.3 Chemical Analysis

The PTFE filter samples were analysed for elements from Na to U at DRI using energy dispersive X-ray fluorescence (ED-XRF) (PANalytical Epsilon 5) and calibration was performed using MicroMatter thin-film standards (Watson et al., 1999) while sulphate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), ammonium (NH_4^+), sodium (Na^+) and potassium (K^+) and carbohydrates (mono- and disaccharides and anhydrosaccharides) were analysed using Ion Chromatography (Thermo Dionex (Sunnyvale, CA) Model ICS 3000 for anions and carbohydrates and Model ICS 2100 for organic acids) (Chow and Watson, 1999). The samples were also analysed for straight chain alkanes, polycyclic aromatic hydrocarbons (PAHs), hopanes and steranes (details in SI) using Thermal Desorption-Gas Chromatography-Mass Spectrometry (Agilent (Santa Clara, CA) Model 6890/5975C TD-GC-MS) with an HP-5MS capillary column in SCAN mode (Ho and Yu, 2004;

Chow et al., 2007a). Internal standards used in the analysis include $nC_{16}D_{34}$ and $nC_{24}D_{50}$ for alkanes and phenanthrene-d_{10} and chrysene-d_{12} for PAHs. Experimental details of the method for hopane and sterane analysis are reported by Ho et al. (2008). The samples were also analysed for carbon fractions (OC1, OC2, OC3, OC4, OP, EC1, EC2 and EC3) using the DRI Model 2001 Thermal/Optical Carbon analyser (DRI (Reno, NV) Model 2001) following the IMPROVE_A thermal/optical reflectance protocol (Chow et al., 2007b). Organic carbon (OC) is defined as the sum of OC1-4 and pyrolyzed carbon (OP), and elemental carbon (EC) is defined as the sum of EC1-3 minus any OP.

2.4 Data Analysis

Data analysis has been carried out using Microsoft Excel and SPSS (Version 21). Several species were detected in less than 20% of the samples and are not included in further analysis. Concentrations below detection limits were replaced with 0.5*detection limit. Correlation analysis of analyte concentrations was conducted using SPSS based on Pearson Correlation and the correlation values reported in the text are for $p<0.01$. Reduced major axis (RMA) regression analysis has been used in most cases due to similar uncertainties of the different species.

3. RESULTS

3.1 Particulate Matter

The average 12h concentration in summer was observed to be 58.2±35.0 $\mu g/m^3$ with a maximum $PM_{2.5}$ concentration of 179.5 $\mu g/m^3$ while in winter; the average concentration was 276.9±99.9 $\mu g/m^3$ with a maximum of 424.9 $\mu g/m^3$ (details in Table 1). Several studies have reported ambient $PM_{2.5}$ concentrations in New Delhi, and most of them report concentrations in exceedance of the Indian $PM_{2.5}$ NAAQS of 60 $\mu g/m^3$ irrespective of site type (Singh et al., 2011; Tiwari et al., 2014; Trivedi et al., 2014). Additionally, studies in other Indian cites, including Chennai have reported higher concentrations in the winter season (Srimuruganandam and Shiva Nagendra, 2012). A summary of relevant studies is presented in Table S1. Continuously monitored $PM_{2.5}$ data for New Delhi are not in the public domain, but these data help to put the concentrations measured during our campaign into context. The summer mean in our study was slightly lower than in most other studies while the winter mean was slightly higher (Table S1). However the broad conclusion is that our site well represented $PM_{2.5}$ concentrations typical of Delhi.

Concentrations in winter were consistently higher compared to summer and this can be due to the differences in meteorological parameters as well as variations in source strengths. Significant differences between PM concentrations in summer and winter have been recorded previously (Guttikunda and Gurjar, 2012; Yadav et al., 2013; Tiwari et al., 2014), and higher winter concentrations are attributed to larger combustion source strength in the winter combined with calm weather conditions and a shallow boundary layer which affects pollutant dispersion adversely.

If the 12-h concentrations are compared (i.e. 00:00-11:59 AM and 12:01- 23:59 PM), the concentrations are ~ 1.2 times higher for the 00:00-11:59 AM period in both seasons (Figure 2). This is expected since this period corresponds with HDV movement across the city at night, and includes the morning traffic peak. EC was found to be higher for the 00:00-11:59 AM period while the OC concentrations were higher during the 12:01- 23:59 PM. EC is typically associated with traffic emissions, and the concentrations are expected to be higher when the volume of heavy duty vehicle traffic increases. On the other hand, OC can be contributed by primary as well as secondary sources, and concentrations are likely higher during the day when combustion activities (e.g. cooking, waste burning), as well as photochemical reactions (i.e. secondary organic aerosol formation) typically occur.

3.1.1 Carbon

In both summer and winter, the high-temperature OC3 (at 480ºC) and OP fractions in helium (He) atmosphere had the highest concentrations among the OC fractions while low-temperature EC (EC1, in 2% O_2/98% He atmosphere) had the highest concentration among the EC fractions. EC3 (at 840ºC) was detected in less than 20% of samples in both seasons. This is in line with the previous studies since EC3 is not associated with gasoline or diesel vehicle emissions. A summary is presented in Table 1. Typically, EC2 (at 740ºC) and OC1 (at 140ºC) are associated with diesel vehicles while EC1, OC2 (at 280ºC) and OC3 are dominant in gasoline vehicle emissions (Watson et al., 1994).

OC and EC were found to be reasonably closely correlated both in summer and winter indicating some common sources such as road traffic and biomass burning. Both OC and EC were also correlated well with $PM_{2.5}$ mass in summer although no correlation was observed in winter. Both OC and EC were correlated well with the carbon fractions. If the concentration of OC is expressed as function of concentration of EC using RMA regression, the OC/EC gradient is significant for both seasons (1.19 for summer and 2.15 for winter) (Figure 3). The intercept is greater than 4 µg C/m^3 in both cases indicating contributions from other sources of OC unassociated with EC.

EC is emitted directly into the atmosphere and can be used to estimate relative amounts of primary OC (POC) and secondary OC (SOC). Higher OC/EC ratios are expected in the conditions where SOC is dominant and the EC-tracer method involves the use of EC as a tracer for POC, allowing SOC to be calculated (Turpin and Huntzicker, 1995; Castro et al., 1999; Pio et al., 2011). Minimum ratios of OC/EC are taken as representative of primary OC (although they may be an over-estimate) (Pio et al., 2011) and OC above that ratio is taken to be SOC. The method as outlined by Castro et al. (1999) was used and estimates of SOC were calculated (Figure 4).

$$Secondary\ OC = Total\ OC - \left(EC \times \left(\frac{OC}{EC}\right)_{\text{minimum}}\right) \qquad \text{Eq (1)}$$

The minimum ratios were estimated as 0.93 for summer and 1.63 for winter, and were used to calculate the contribution from primary and secondary OC for both seasons. The average contribution of POC was estimated to be 41% in summer and 72.3% in winter while the SOC was estimated to contribute 66.7% in summer, and 33.1% in winter.

3.1.2 Ions

$PM_{2.5}$ SO_4^{2-} and NH_4^+ were found to be the most abundant ions in summer with average contributions of 17.1% and 8.5% to $PM_{2.5}$ mass. Higher abundance of SO_4^{2-} in summer and NO_3^- in winter is consistent with previous observations in the region (Satsangi et al., 2013). In winter, NH_4^+ was the most abundant ion followed by NO_3^- contributing 12.4% and 11.8% to $PM_{2.5}$ mass. A summary of the data is presented in Table 1. NO_3^- and SO_4^{2-} were found to be correlated in summer as well as in winter and high correlation was also observed between SO_4^{2-} and NH_4^+ in summer and winter indicating common sources. SO_4^{2-} and NO_3^- were also moderately correlated with $PM_{2.5}$ mass in summer but no correlation was observed in winter. Cl^- was not found to be correlated with any of the other ions in summer while in winter, it was correlated with NH_4^+. Higher concentrations were observed for all ions in winter but Na^+ was present in broadly similar concentrations in both seasons with a winter/summer ratio of less than 2. On the other hand, Cl^-, NO_3^- and NH_4^+ showed the highest winter/summer ratios. It is worth noting that particulate nitrate when present as NH_4NO_3 is semi-volatile (Allen et al., 1989), and at higher temperatures NO_3^- is volatilized from the particle phase. Seasonal variations in concentrations of ions have also been reported by Sudheer et al. (2014), and Tiwari et al. (2013) reported higher chloride concentrations in Delhi during winter.

Cl^- and NO_3^- (or their precursors HCl and NO_x) have been reported to be emitted during wood combustion and K^+ is widely used as a marker for biomass combustion (Kleeman et al., 1999; Simoneit et al., 2004; Watson et al., 2008). In India, Patil et al. (2013) reported a high abundance of Cl^- and K^+ in wood combustion, open burning and coal combustion while NH_4^+, NO_3^- and Cl^- are reported to be abundant in industrial emissions. The high winter concentration of Cl^- could be due to the increased burning (wood, coal, waste) in the winter season, but like ammonium nitrate, ammonium chloride is semi-volatile (Pio and Harrison, 1987a,b) causing loss to the vapour phase during conditions of higher temperature and lower relative humidity in summer.

Ion equivalency was estimated using Cl^-, SO_4^{2-}, NO_3^- (anions) and NH_4^+ (cation) for both seasons to understand the neutralization of the ions in the atmosphere (Figure 5) and the anions were found to be more or less neutralized by NH_4^+ in both seasons.

3.1.3 Elements

S, Si, and Al were found to be the most abundant elements in summer and winter (Table 1). Concentrations of several elements including Cl, Pb, Fe and Zn were found to be more than five times higher in winter compared to summer. Elements typically associated with soil/mineral dust showed the lowest winter/summer ratios (e.g. Si- 0.95; Ca- 0.80) while several other species showed a 1.5 to 4 times increase in concentrations in winter (e.g.- Cr- 1.41; Mn- 2.69; S- 3.14; Zn- 3.27; Cu- 4.74).

Correlation analysis was used to identify associations among different elements. Zn was found to be moderately correlated with Pb and Br in summer, while a strong correlation was observed in winter for Pb. Previous studies have also reported correlation between Zn and Pb and Tiwari et al. (2013) used these as markers for traffic source and Chen et al. (2011) reported association of Fe, Zn, Pb and Br with diesel vehicles. Pb and K^+ have also been used as markers for biomass burning (Cheng et al., 2013) but no correlation was observed between these two species in Delhi.

Al, Si, Ca, Ti, Mn and Fe have been used as markers for crustal dust/soil (Cass, 1998; Chow et al., 2004; Viana et al., 2008; Pant and Harrison, 2012; Tiwari et al., 2013). In summer, Si was strongly correlated with Al, Fe, Ca, Ti, Sr and moderately correlated with Mn and K and weakly correlated with Ni. In winter, Si was strongly correlated with Fe, Ca, Ti but Al was not found to be correlated with the other soil-associated elements but with Cl, Br and moderately correlated with Cu, Zn, and K. This is probably due to anthropogenic sources of Al, particularly from metallurgical industries, coal burning and traffic.

In addition to its correlation with Zn, Pb was correlated with As, K and moderately correlated with S and Na. In summer, Pb was moderately correlated with S, Br, Zn, Cu and V. As was also correlated with Zn in winter though these elements were not found to be correlated in summer. As and Pb are also reported to be emitted from waste burning (Watson et al., 2008). V and Ni are associated with industrial emissions as well as oil combustion (Viana et al., 2008). Pb, Fe, Zn and K have also been associated with industrial emissions (Sahu et al., 2011b; Moreno et al., 2013; Patil et al., 2013; Farao et al., 2014). K and Br have also been reported from wood smoke (Kleeman et al., 1999; Fine et al., 2001) while Zn has been associated with incineration (Harrison et al., 1997; Moreno et al., 2013) and industrial burning (Duvall et al., 2012). Pb and Mg are also reported to be emitted from kerosene combustion (Patil et al., 2013). While the correlations in the summer season are largely indicative of traffic and industrial sources, an additional source, most likely, combustion (including biomass, coal and waste) is affecting elemental concentrations in the winter season. Zn and Cl can both be emitted from coal combustion, and waste incineration (Perrino et al., 2011). In winter, brick kilns are also reported to operate in areas surrounding Delhi, and can contribute to PM concentrations observed in the city (Guttikunda and Calori, 2013).

Elements such as Cu, Ba, Sb and Sn have been associated with brake wear (Pant and Harrison, 2013) but in Delhi, these were not found to be correlated with each other in summer. Species associated with brake wear such as Cu and Ba typically exhibit a coarse mode peak at 3.2-5.6 µm (Gietl et al., 2010). However, in Delhi, these peaks were not observed (unpublished data). This is important for future studies, as this would imply that elements such as Cu and Ba cannot readily be used as markers for non-exhaust emissions in India, and further research is required to characterize appropriate markers for non-exhaust emissions.

3.1.4 Hopanes and steranes

Total hopane concentration was observed to be 1.97±2.47 ng/m^3 in summer and 26.3±7.93ng/m^3 in winter. C31αβR-hopane was the most abundant species in both seasons (Table 1, SI). Hopanes were found to be strongly correlated to alkanes and PAHs in winter although no correlation was observed with OC and EC. In summer, hopanes were strongly correlated with EC and PAHs and moderately correlated with OC and alkanes, indicating a traffic source. While hopanes are typically used as markers for traffic exhaust emissions (Lin et al., 2010; Pant and Harrison, 2013), several hopane species are also found to be abundant in coal burning emissions (Oros and Simoneit; 2000; Zhang et al., 2008). The ratio between S/S+R homohopane isomers was identified as 0.05 for lignite and 0.08 for brown coal (Oros and Simoneit, 2000). In Delhi, the values for this ratio were calculated as 0.11 for summer and 0.05 for winter, indicating the potential contribution from coal/lignite burning as an additional hopane source. Lignite is used for electricity generation in thermal power plants in India, and coal can also be used for cooking and/or heating, particularly in poorer areas and slums.

In the case of steranes, αββ 20R-Cholestane was the abundant sterane in summer while αββ 20S 24R-Ethylcholestane was the most abundant species in winter. Total sterane concentrations in summer and winter were 0.44±1.04 and 3.95±1.49 ng/m^3 respectively. αββ 20S 24S-Methylcholestane showed a very high winter/summer ratio (15.2) while ααα 20R-Cholestane and ααα 20R 24R-Ethylcholestane showed winter/summer ratios less than 2. Steranes were strongly correlated with hopanes and EC in summer and in winter, the correlation was moderate both in the case of hopanes and steranes at $p<0.05$.

3.1.5 Alkanes

Alkanes were the most abundant class among the organic species and the 12-h average alkane concentration was observed to be 48.1±38.9 ng/m^3 in summer and 382±137ng/m^3 in winter. C20-31 homologues were the most abundant while C39 and C40 were not detected in either season. Fu et al. (2010) also did not detect C36-40 homologues in winter and C39-40 in summer in Chennai (India). The dominant homologues were C26, C27 and C25 in summer and C29, C22 and C31 in winter. Dominance of C29 and C31 homologues in winter indicates contribution from vegetative emissions, possibly through burning of biomass. The winter/summer ratios were highest for the lower homologues (C18-C23) and C34-35, probably reflecting greater partitioning into the condensed phase in the cooler months.

Wood and biomass combustion is quite common in Delhi during the winter period when they are used not only as a cooking fuel but also for heating (Fu et al., 2010; Yadav et al., 2013). In addition, tyres, old furniture and waste materials are often burnt in the open. Long chain alkanes (e.g. C36) are also reported to be emitted from open waste burning (Fu et al., 2010; Alves et al., 2012). Alkane emissions ($n<25$) from the vehicles can be attributed to unburnt engine oil in the case of gasoline vehicles and fuel as well as lubricating oil in case of diesel vehicles, and older vehicles are often high emitters of n-alkanes (Rogge et al., 1993).

Alkanes were found to be correlated well with OC, and hopanes and moderately correlated with PAHs and EC) in summer. In winter, however, no correlation was observed with OC and EC although strong correlation was observed with hopanes as well as PAHs ().

Carbon Preference Index (CPI), the ratio of odd to even numbered homologues, can be used to estimate the relative contribution of anthropogenic and biogenic sources. Due to the odd carbon number preference in case of vegetative material, higher ratio values are associated with a biogenic contribution. In this case, the index value was 1.09 for summer and 1.22 for winter indicating a significant contribution from anthropogenic sources in both seasons.

3.1.6 PAHs

PAHs are typically emitted as a by-product of combustion (including road traffic, solid fuel combustion, coal combustion, industries and agricultural burning) and are found both in gas- and particulate-phases (Smith and Harrison, 1996; Cass, 1998; Chow et al., 2004). The total particulate (pPAH) concentration was observed to be 7.73±5.54 ng/m^3 in summer and 119±33.8 ng/m^3 in winter. Several species including picene (Pic), dibenzo(ae)pyrene (DaeP), coronene (Cor) were detected only in winter samples. Acenapthylene (Acy) was the most abundant species in summer followed by acenapthene (Ace), while in winter chrysene (Chr) was the most abundant species followed by benzo(a)pyrene (BaP). PAHs were strongly correlated with OC, EC and hopanes in summer and moderately correlated with alkanes suggesting a traffic source.

HDVs typically emit low molecular weight PAHs including anthracene (Ant), methyl- and dimethyl-phenanthrenes and fluoren-9-one (Rogge et al., 1993; Sjorgen et al., 1996; Miguel et al., 1998). Species such as benzo(b)naphtho(1,2-d)thiophene (BN1NT), fluorene (Flu), phenanthrene (Phe) have been used as markers for diesel vehicle emissions while methylphenanthrenes have been associated with evaporative emissions from fuel (Harrison et al., 1996; Jang et al., 2013). PAHs such as benzo(ghi)perylene (BghiPe), indeno(1,2,3-cd)pyrene (IcdP) and Cor have previously been used as markers for gasoline traffic emissions (Cass, 1998; Phuleria et al., 2007; Pant and Harrison, 2013). Flu, Acy, Ant, Phe, Pyr, benzo(e)pyrene (BeP), BaP, retene (Ret) are typically used as markers for wood combustion (Cass, 1998; Fine et al., 2001; Simoneit, 2002; Jang et al., 2013) while Ant, Phe, benzo(a)anthracene (BaA) and Chr are used as markers for coal combustion (Harrison et al., 1996). Several species such as Ant, cyclopenta(cd)pyrene (CcdP) and BN1NT have been attributed to various sources in different studies. For example, Larsen and Baker (2003) reported the use of CcdP as a tracer for gasoline emissions while Jang et al. (2013) used it as a marker for coal combustion. Previous studies from India have associated pyrene with domestic fuel emissions (kerosene, dung etc.) and coal combustion, BaP with wood combustion and BghiPe and IcdP with traffic emissions (Kulkarni and Venkataraman, 2000; Sharma et al., 2007) while benz(a)anthracene-7,12-dione (BaAQ) has been associated with residential natural gas emissions (Cass, 1998).

If the summer and winter concentrations are compared, species such as Phe (11.6) and BaA (54.7) associated with coal and biomass combustion show very high winter/summer ratios while others associated with traffic such as BghiPe (6.86) and 2-Methyl phenanthrene (2MPhe) (2.50) have comparatively lower winter/summer ratios. This indicates additional sources in the proximity of the sampling site during the winter season which is consistent with emission inventory analyses. High winter/summer ratios have been reported previously by Sharma et al. (2007) for Delhi. In addition to source types, the different temperature regimes across seasons can also influence the partitioning of the species in the gas- and particle- phases for PAHs (Smith and Harrison, 1996).

One of the qualitative approaches for assessment of PAH source is diagnostic ratio (DR) analysis where ratios of different PAHs are used for identification of contributing sources. The ratio of IcdP/IcdP+BghiPe is used as an indicator for diesel/gasoline or coal emissions (Ravindra et al., 2008). The ratio was observed to be 0.38 in summer and 0.46 in winter indicating a contribution from vehicular emissions. The ratio of BaA/BaA+Chr can also be used to distinguish between diesel/gasoline/wood combustion and in the present case, the ratio was observed to be 0.18 for summer and 0.39 for winter which corresponds with diesel emissions (Kavouras et al., 2001). HDVs are reported to emit higher concentrations of lighter PAHs such as Pyr, BaA and Chr compared to heavier PAHs such as BghiPe and coronene (Miguel et al., 1998). The site gets a high volume of interstate HDV traffic, and often the trucks are run on high sulphur fuel.

3.1.7 Sugars

In ambient air, saccharides are typically associated with biological material (e.g. soil organic matter) and arabitol and mannitol have been proposed as markers for fungal spores (Simoneit et al., 2004; Buaer et al., 2008). Glycerol was the only saccharide species detected in both summer and winter with a winter/summer ratio of 26.5. Most of the other saccharides were detected in less than 20% of the samples and are not discussed in detail (Table 1).

Anhydrosaccharides such as levoglucosan and mannosan are typically associated with wood/biomass combustion (Simoneit et al., 2004; Alves et al., 2012). Both levoglucosan and mannosan were only detected in the winter season and had a strong correlation. Levoglucosan was also strongly correlated with OC and Cl^-. Correlation with K^+ was comparatively weaker, and not significant at $p<0.01$. Fu et al. (2010) reported a levoglucosan/mannosan ratio of 16.4 which is comparable to the ratio observed in the current study (16.07). Cow dung burning has also been identified as a source of levoglucosan in India, but K is typically not released from cow dung combustion (Fu et al., 2010). A recent study focused on water soluble organic carbon (WSOC) has also highlighted the importance of biomass combustion as a source of OC in Delhi (Kirillova et al., 2014).

3.1.8 Diacids

Several organic acids including oxalic acid, lactic acid and glutaric acid were found to be present in both seasons. While oxalic acid was found to be the abundant species in both seasons, formic acid had the highest winter/summer ratio of 3.14. Biogenic sources have been reported to contribute to malic acid precursors, and the absence of the compound in this sample set is consistent with the absence or low concentrations of other biogenic material-related molecular markers.

3.2 Enrichment Factors

In order to further understand the sources of the elements (crustal vs. anthropogenic), enrichment factors (EFs) were calculated based on continental crust concentrations using Al as the reference element (Taylor and McLennan, 1995) (selected species are presented in Figure 6).

$$Enrichment\ Factor\ (X) = \frac{\left\{\dfrac{Concentration(X)}{Concentration(Reference)}\right\}sample}{\left\{\dfrac{Concentration(X)}{Concentration(Reference)}\right\}crustal} \qquad \text{Eq (2)}$$

EF values of 10 or higher are considered to indicate significant anthropogenic contribution. High enrichment factors were observed for elements such as Ti, Cu, Zn, Sb, Cd, Sn, As and Pb both in summer and winter, with higher enrichment observed in winter. Ti, typically associated with crustal matter, was also found to be enriched in both seasons although contrary to other elements, the enrichment was higher in summer. Similarly, EFs for Sb and Sn were higher for the summer compared to winter. EF for As was found to be several fold higher in winter (~36 times) compared to the summer. Cr showed similar enrichment in summer and winter seasons. Cd is primarily emitted from industries (smelting), waste incineration and recycling of electronic waste but is also associated with traffic emissions (Amato et al., 2011b). As is used as a marker for coal combustion, and Pb and Zn are also emitted from waste incineration. On the other hand, elements such as Si, Fe, Ca, Ba, Mn, Mg, Sr and Se were present in concentrations similar to the upper continental crust (Taylor and McLennan, 1995).

3.3 Mass Closure

In order to understand the relative contribution of the different species, mass closure was attempted for $PM_{2.5}$ mass with seven key components including woodsmoke, traffic, other OM, secondary aerosol (ammonium chloride, ammonium nitrate and ammonium sulphate) and mineral dust/soil (Table 2). A little over 100% of the measured mass was accounted for in both cases (115.4% in summer and 114.2% in winter) and the results are described in Figure 7.

Crustal material was estimated using concentrations of elements- Si, Al, Ca, Fe and Ti, based on Chan et al. (1997). Organic matter (OM) was estimated from OC using a factor of 1.2 in the case of traffic OM, and 1.5 in the case of other OM, which was considered as largely secondary.

OM was found to be the highest contributor to mass in summer (33.3%) while woodsmoke was the primary contributor to PM2.5 mass in winter (23.3%) (details in Figure 6). Ammonium sulphate (20.5 %) and crustal material (14.3%) had higher contributions in summer while ammonium nitrate (12.4%) had a higher contribution in winter. A lower concentration of nitrate in summer can be explained by the volatility at higher temperatures while higher crustal matter in summer (14.3%) is attributed to desert dust as well as local dust sources which are frequently resuspended in dry and windy conditions. Traffic was found to contribute 18.7% in summer and 16.2% in winter, while woodsmoke was found to contribute 23.3% in winter.

Table 3 summarizes results from source apportionment studies conducted in New Delhi. While most studies report traffic, road dust, coal combustion and biomass as key sources of PM in New Delhi, there is a large variability in the quantitative estimation of source contributions. Some of the variability in introduced by the differences in the computational methods. For instance, while most receptor models use the principle of mass conservation; the CMB model takes into consideration the chemical profiles of individual sources, while the mass closure approach relies on individual tracers. In addition, most of the studies conducted in Delhi have analysed inorganic species (elements and ions) and recent studies have included carbon (OC/EC). In addition, choice of sampling location can often drive differences in the results, especially when site types have significantly different characteristics. In a CMB study in New Delhi, Chowdhury et al. (2007) identified five major sources including road dust, coal combustion, diesel and gasoline exhaust and biomass combustion at an urban residential site. These are in line with the source inferences drawn in this study, and while the quantitative contributions are a little different between the 2007 study and the current study, overall trends with a high contribution from road dust in summer, and biomass combustion in winter are similar. It is important to remember that the site characteristics are not comparable between the two sites, and differences in local source strengths can introduce differences in the overall source contribution estimate. The contribution of secondary aerosol was not estimated in their study. For comparison, a study in 2012 in Mumbai found the contribution of secondary inorganic aerosol to be 23% of total $PM_{2.5}$ mass while crustal material was reported to contribute 11% of $PM_{2.5}$ mass, and in Chennai, the contribution of secondary aerosol was estimated as 42% of $PM_{2.5}$ mass (Joseph et al., 2012).

It is important to note that some of the factors used in the current mass closure calculation are derived from the literature and may not be directly representative of the Indian situation. For example, the woodsmoke estimation factors utilized in this study are based on measurements made in Europe, and due to differences in the wood type, and the burning conditions, the ratios may not accurately represent the contribution of woodsmoke in an Indian city. Also, this can introduce uncertainty in the overall estimation. As a next step, locally developed source profiles (Patil et al., 2013; Matawle et al., 2014) will be tested for a CMB model.

4. CONCLUSIONS

$PM_{2.5}$ samples were analysed for a heavy traffic site in New Delhi, and detailed chemical characterization was conducted including analyses of metals, ions, carbon and molecular markers. PM concentrations were found to be higher than the 24-hour PM2.5 NAAQS (60 µg/m^3) on several occasions in summer and on all days in winter. Several elements including Cu, Zn, Pb, Cd and As were found to be significantly enriched and complex correlations were observed between elemental species. In the case of molecular markers, several combustion-related species were detected only in winter. Alkanes were found to be the most abundant class of organic species followed by PAHs and hopanes.

Concentrations were found to be significantly higher in winter compared to summer. Pollutant concentrations can be affected both by meteorology and source strength. There is an appreciable difference in the average temperature between summer and winter seasons in Delhi, and this could be driving some of the differences between species' concentrations in the two seasons. At higher temperatures, several species can be easily volatilized and reactive species can often undergo chemical reactions in presence of sunlight (e.g. photodegradation of PAHs) (Venkataraman and Friedlander, 1994; Smith and Harrison, 1996; Alves et al., 2012). The combination of higher wind speeds and a deeper mixed layer can lead to better dispersion of pollutants in the summer season. However, in winter, there is much less solar radiation, and the weather conditions are often ‘calm’ in Delhi indicated by zero or very low wind speeds. Further, the inversion layer height is typically much lower in winter. A combination of such meteorological factors can thus contribute to a build-up of pollutants, leading to higher concentrations. Another important aspect is the role of additional sources in the winter season. During the winter season, biomass/waste combustion is often used as a source of heating across the city, a lot of which occurs under uncontrolled conditions in the open areas. An increase in species associated with waste combustion (Pb, Zn, C35 and C36) indicates the potential contribution from this seasonal source at the sampling site. However, in the absence of detailed emission inventories, it is difficult to attribute the elemental concentrations to specific sources. It is also important to characterize the source emissions in detail, in order to separate the contributions from various combustion sources. Lack of enrichment of barium in the samples indicates that the non-exhaust traffic markers typically used in Europe and USA (i.e., Cu, Ba, and Sb) might not be relevant in the Indian scenario.

ACKNOWLEDGEMENTS

Financial support from UKIERI is gratefully acknowledged. Pallavi Pant gratefully acknowledges financial support from the University of Birmingham. Special thanks to the field staff at CRRI for help during the sampling campaign.

REFERENCES

Allen, A.G., Harrison, R.M. and Erisman, J.W. 1989. Field measurements of the dissociation of ammonium nitrate and ammonium chloride aerosols. Atmospheric Environment 23, 1591-1599.

Alves, C., Vicente, A., Pio, C., Kiss, G., Hoffer, A., Decesari, S., Prevot, A.S.H., Minguillon, M.C., Querol, X., Hillamo, R., Spindler, G. and Swietlicki, E., 2012. Organic compounds in aerosols from selected European sites- Biogenic versus anthropogenic sources. Atmospheric Environment 59, 243-255.

Balachandran, S., Meena, B.R., Khillare, P.K., 2000. Particle size distribution and its elemental composition in the ambient air of Delhi. Environment International, 26, 49-54.

Bauer, H., Claeys, M., Vermeylen, R., Schueller, E., Weinke, G., Berger, A. and Puxbaum, H., 2008. Arabitol and mannitol as tracers for the quantification of airborne fungal spores. Atmospheric Environment 42, 588-593.

Cass, G.R., 1998. Organic molecular tracers for particulate air pollution sources. Trends in Analytical Chemistry 17, 356-366.

Castro, L.M., Pio, C.A., Harrison, R.M. and Smith, D.J.T., 1999. Carbonaceous aerosol in urban and rural European atmospheres: estimation of secondary organic carbon concentrations. Atmospheric Environment 33, 2771-2781.

Chakrobarty, A. and Gupta, T. (2010). Chemical Characterization of Submicron Aerosol in Kanpur Region: a Source Apportionment Study. Aerosol and Air Quality Research, 10, 433-445.

Chakrobarty, R.K., Pervez, S., Chow, J.C., Watson, J.G., Dewangan, S., Robles, J. and Tian, G., 2013. Funeral pyres in South Asia: Brown carbon aerosol emissions and climate impacts. Environmental Science and Technology Letters 1, 44-48.

Chan, Y.C., Simpson, R.W., Mctainsh, G.H., Vowles, P.D., Cohen, D.D. and Bailey, G.M., 1997. Characterisation of chemical species in PM2.5 and PM10 aerosols in Brisbane, Australia. Atmospheric Environment,31, 3773- 3785.

Chelani, A.B., Gajghate, D.G. and Devotta, S., 2008. Source Apportionment of PM_{10} in Mumbai, India Using CMB Model. Bulletin of Environmental Contamination and Toxicology 81, 190-195.

Chelani, A.B., Gajghate, D.G., Chalapati Rao, CV., Devotta, S., 2010. Particle size distribution in ambient air of Delhi and its statistical analysis. Bulletin of Environmental Contamination and Toxicology, 85, 22-27.

Chen, L.W.A., Watson, J.G., Chow, J.C., DuBois, D.W. and Herschberger, L., 2011. PM2.5 source apportionment: Reconciling receptor models for U.S. nonurban and urban long-term networks. Journal of Air and Waste Management Association 61, 1204-1217.

Cheng, H., Deng, Z., Chakraborty, P., Liu, D., Zhang, R., Xu, Y., Luo, C., Zhang, G. and Li, J., 2013. A comparison study of atmospheric polycyclic aromatic hydrocarbons in three Indian cities using PUF disk passive air samplers. Atmospheric Environment 73, 16-21.

Chow, J.C. and Watson, J.G., 1999. Ion chromatography in elemental analysis of airborne particles. In: Landsberger, S. and Creatchman, M., eds. Elemental Analysis of Airborne Particles, Gordon and Breach Science Publishers.

Chow, J.C., Watson, J.G., Kuhns, H., Etyemezian, V., Lowenthal, D.H., Crow, D., Kohl, S.D., Engelbrecht, J.P., Green, M.C., 2004. Source profiles for industrial, mobile and area sources in the Big Bend Regional Aerosol Visibility and Observational Study. Chemosphere 54, 185-208.

Chow, J.C., Watson, J.G., Edgerton, S.A. and Vega, E., 2002. Chemical composition of PM_{10} and $PM_{2.5}$ in Mexico City during winter 1997. Science of The Total Environment 287(3), 177-201.

Chow, J.C., Yu, J.Z., Watson, J.G., Ho, S.S.H., Bohannan, T.L., Hays, M.D. and Fung, K.K., 2007a. The application of thermal methods for determining chemical composition of carbonaceous aerosols: A review. Journal of Environmental Science and Health Part A 42, 1521-1541.

Chow, J.C., Watson, J.G., Chen, L.W.A., Oliver Chang, M.C., Robinson, N.F., Trimble, D. and Kohl, S., 2007b. The IMPROVE_A temperature protocol for thermal/optical carbon analysis: mainitaining consistency with a long-term database. Atmospheric Environment Part A: General Topics 27(8), 1185-1201.

Chowdhury, Z., Zheng, M., Schauer, J.J., Sheesley, R.J., Salmon, L.G., Cass, G.R., Russell, A.G., 2007. Speciation of fine organic carbon particles and source apportionment of $PM_{2.5}$ in Indian cities. Journal of Geophysical Research, 112, D15303, doi:10.1029/2007JD008386.

CPCB, 2010. Air quality monitoring, emission inventory and source apportionment study for Indian cities. Central Pollution Control Board, February 2010. Available at http://www.cpcb.nic.in/Source_Apportionment_Studies.php [Accessed 28 February 2011].

Deka, P. and Hoque, R.R., 2014. Incremental effect of festive biomass burning on wintertime PM10 in Brahmaputra Valley of Northeast India. Atmospheric Research, 143, 380-391.

Delhi Police, 2014. Restriction on the movement of LGV and HGV/MGV vehicles. Available at http://www.delhitrafficpolice.nic.in/restri-lgv-hgv.aspx [Accessed on February 08, 2014].

Delhi Statistical Handbook, 2013. Available at http://www.delhi.gov.in/wps/wcm/connect/doit_des/DES/Our+Services/Statistical+Hand+Book/ [Accessed February 20, 2014].

Duvall, R.M., Norris, G.A., Burke, J.M., Olson, D.A., Vedantham, R. and Williams, R., 2012. Determining spatial variability in PM2.5 source impacts across Detroit, MI. Atmospheric Environment 47, 491-498.

Farao, C., Canepari, S., Perrino, C. and Harrison, R.M., 2014. Sources of PM in an industrial area: comparison between receptor model results and semiempirical calculations of source contributions. Aerosol and Air Quality Research, doi: 10.4209/aaqr.201308.0281.

Fine, P.M., Cass, G.R. and Simoneit, B.R.T., 2001. Chemical characterization of fine particle emissions from fireplace combustion of woods grown in the northeastern United States. Environmental Science and Technology 35, 2665-2675.

Fu, P.Q., Kawamura, K., Pavuluri, C.M., Swaminathan, T., Chen, J., 2010. Molecular characterization of urban organic aerosol in tropical India: contributions of primary emissions and secondary photooxidation. Atmospheric Chemistry and Physics 10, 2663-2689.

Gargava, P., Chow, J.C., Watson, J.G. and Lowenthal, D.H., 2014. Speciated PM_{10} emission inventory for Delhi, India. Aerosol and Air Quality Research 14, 1515-1526.

Gietl, J.K., Lawrence, R., Thorpe, A.J. and Harrison, R.M., 2010. Identification of brake wear particles and derivation of a quantitative tracer for brake dust at a major road. Atmospheric Environment 44, 141-146.

Giri, B., Patel, K.S., Jaiswal, N.K., Sharma, S., Ambade, B., Wang, W., Simonich, S.L.M., Simoneit, B.R.T., 2013. Composition and sources of organic tracers in aerosol particles of industrial central India. Atmospheric Research 120-121, 312-324.

Goyal, P., Jaiswal, N., Kumar A., Dadoo, J.K. and Dwarakanath, M., 2010. Air quality impact assessment of NOx and PM due to diesel vehicles in India. Transportation Research Part D 15, 298-303.

Gummeneni, S., Yusup, Y. B., Chavali, M., Samadi, S.Z., 2011. Source apportionment of particulate matter in the ambient air of Hyderabad city, India. Atmospheric Research 101, 752-764.

Gupta, A.K., Karar, K. and Srivastava, A., 2007. Chemical mass balance source apportionment of PM_{10} and TSP in residential and industrial sites of an urban region of Kolkata, India. Journal of Hazardous Materials 142, 279-287.

Guttikunda, S.K. and Gurjar, B.R., 2012. Role of meteorology in seasonality of air pollution in megacity Delhi, India. Environmental Monitoring and Assessment 184, 3199-3211.

Guttikunda, S. and Goel, R., 2013. Health impacts of particulate pollution in a megacity - Delhi, India. Environmental Development 6, 8-20.

Guttikunda, S. and Calori, G., 2013. A GIS based emissions inventory at 1 km x 1 km spatial resolution for air pollution analysis in Delhi, India. Atmospheric Environment 67, 101-111.

Guttikunda, S., Kopakka, R.V., Dasari, P. and Gertler, A.W., 2013. Receptor model-based source apportionment of particulate pollution in Hyderabad, India. Environmental Monitoring and Assessment 185, 5585-5593.

Guttikunda, S.K., Goel, R. and Pant, P., 2014. Nature of air pollution, emission sources and management in the Indian cities. Atmospheric Environment 95, 501-510.

Harrison, R.M., Smith, D.J.T. and Luhana, L., 1996. Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, U.K.. Environmental Science and Technology 30, 825-832.

Harrison, R.M., Smith, D.J.T., Pio, C.A., Castro, L.M., 1997. Comparative receptor modelling study of airborne particulate pollutants in Birmingham (United Kingdom), Coimbra (Portugal) and Lahore (Pakistan). Atmospheric Environment 31, 3309-3321.

Harrison, R.M., Jones, A.M. and Lawrence, R.G., 2003. A pragmatic mass closure model for airborne particulate matter at urban background and roadside sites. Atmospheric Environment 37, 4927-4933.

Harrison, R.M., Beddows, D.C.S, Hu, L. and Yin, J., 2012. Comparison of methods for evaluation of wood smoke and estimation of UK ambient concentrations. Atmospheric Chemistry and Physics 12, 8271-8283.

Herlekar, M., Joseph, A.E., Kumar, R. and Gupta, I., 2012. Chemical speciation and source assignment of particulate (PM_{10}) phase molecular markers in Mumbai. Aerosol and Air Quality Research 12, 1247-1260.

Ho, S.S.H. and Yu, J.Z., 2004. In-injection port thermal desorption and subsequent gas chromatography-mass spectrometric analysis of polycyclic aromatic hydrocarbons and n-alkanes in the atmospheric aerosol samples. Journal of Chromatography A 1059, 121-129.

Ho, S.S.H., Yu, J.Z., Chow, J.C., Zielinska, B., Watson, J.G., Sit, E.H.L. and Schauer, J.J., 2008. Evaluation of an in-injection port thermal desorption-gas chromatograph/mass spectrometry method for anaysis of non-polar organic compounds in ambient aerosol samples. Journal of Chromatography A 1200, 217-227.

Jang, E., Alam, M.S. and Harrison, R.M., 2013. Source apportionment of polycyclic aromatic hydrocarbons in urban air using positive matrix factorization and spatial distribution analysis. Atmospheric Environment 79, 271-285.

Joseph, A.E., Unnikrishnan, S. and Kumar, R., 2011. Chemical Characterization and Mass Closure of Fine Aerosol for Different Land Use Patterns in Mumbai City. Ambient and Air Quality Research 12, 61-72.

Joseph, A.E., Unnikrishnan, S. and Kumar, R., 2012. Chemical characterization and mass closure of fine aerosol for different land use patterns in Mumbai City. Ambient and Air Quality Research 12, 61-72.

Kar, S., Maity, J.P., Samal, A.C. and Santra, S.C., 2010. Metallic components of traffic-induced urban aerosol, their spatial variation, and source apportionment. Environmental Monitoring and Assessment 168, 561-574.

Kavouras, I.G., Koutrakis, P., Tsapakis, M., Lagoudaki, E., Stephahou, E.G., von Baer, D. and Oyola, P., 2001. Source apportionment of urban particulate aliphatic and polynuclear aromatic hydrocarbons (PAHs) using multivariate methods. Environmental Science and Technology 35, 2288-2294.

Khare, P., Baruah and B.P., 2010. Elemental characterization and source identification of $PM_{2.5}$ using multivariate analysis at the suburban site of North-East India. Atmospheric Research 98, 148-162.

Khillare, P.K., Balachandran, S. and Meena, B.R., 2004. Spatial and temporal variation of heavy metals in atmospheric aerosol in India. Environmental Monitoring and Assessment 90, 1-21.

Khillare, P.S. and Sarkar, S., 2012. Airborne inhalable metals in residential areas of Delhi, India: distribution, source apportionment and health risks. Atmospheric Pollution Research 3, 46-54.

Kirillova, E.N., Andersson, A., Tiwari, S., Srivastava, A.K., Bisht, D.S. and Gustafsson, O., 2014. Water-soluble organic carbon aerosols during a full New Delhi winter: Isotope-based source apportionment and optical properties. Journal of Geophysical Research: Atmospheres, doi: 101.1002/2013JD020041.

Kleeman, M.J., Schauer, J.J. and Cass, G.R., 1999. Size and composition distribution of fine particulate matter emitted from wood burning, meat charboiling, and cigarettes. Environmental Science and Technology 33, 3516-3523.

Kothai, P., Saradhi, I.V., Prathibha, P., Pandit, G.G. and Puranik, V.D., 2008. Source apportionment of coarse and fine particulate matter at Navi Mumbai, India. Aerosol and Air Quality Research 8, 423-436.

Kulkarni, P. and Venkataraman, C., 2000. Atmospheric polycyclic aromatic hydrocarbons in Mumbai, India. Atmospheric Environment 34, 2785-2790.

Kulshrestha, A., Satsangi, P.G., Masih, J. and Taneja, A., 2009. Metal concentration of $PM_{2.5}$ and PM_{10} particles and seasonal variations in urban and rural environment of Agra, India. Science of The Total Environment 407, 6196-6204.

Kumar, A.V., Patil, R.S. and Nambi, K.S.V., 2001. Source apportionment of suspended particulate matter at two traffic junctions in Mumbai, India. Atmospheric Environment 35, 4245-4251.

Larsen, R.K. and Baker, J.E., 2003. Source apportionment of polycyclic aromatic hydrocarbons in the urban atmosphere: a comparison of three methods. Environmental Science and Technology, 37, 1873-1881.

Li, J., Wang, G., Aggarwal, S.G., Huang, Y., Ren. Y., Zhou, B., Singh, K., Gupta, P.K., Cao, J. and Zhang, R., 2014. Comparison of abundances, compositions and sources of elements, inorganic ions and organic compounds in atmospheric aerosols from Xi'an and New Delhi, two megacities in China and India. Science of the Total Environment 476-477, 485-495.

Lim, S.S., Vos, T., Flaxman, A.D., Danaei, G., Shibuya, K., Adair-Rohani, H., et al., 2012. A comparative risk assessment of burden of disease and injury attributable to 67 risk factors and risk factor clusters in 21 regions, 1990–2010: a systematic analysis for the Global Burden of Disease study 2010. Lancet 380, 2224–2260.

Lin, L., Lee, M.L. and Eatough, D.J., 2010. Review of recent advances in detection of organic markers in fine particulate matter and their use for source apportionment. Journal of Air and Waste Management Association 60, 3-25.

Masih, A., Saini, R., Singhvi, R. and Taneja, A., 2010. Concentrations, sources, and exposure profiles of polycyclic aromatic hydrocarbons (PAHs) in particulate matter (PM_{10}) in the north central part of India. Environmental Monitoring and Assessment 163, 421-431.

Matawle, J.L, Pervez, S., Dewangan, S., Tiwari, S., Bisht, D.S. and Pervez, Y.F., 2014. $PM_{2.5}$ chemical source profiles of emissions resulting from industrial and domestic burning activities in India. Ambient and Air Quality Research, doi: 10.4209/aaqr.2014.03.0048, 1-16.

Miguel, A.H., Kirchstetter, T.W., Harley, R.A. and Hering, S.V., 1998. On-Road Emissions of Particulate Polycyclic Aromatic Hydrocarbons and Black Carbon from Gasoline and Diesel Vehicles. Environmental Science and Technology 32, 450-455.

Monkkonen, P., Uma, R., Srinivasan, D., Koponen, I.K., Lehtinen, K.E.J., Hameri, Suresh, R., Sharma, V.P. and Kulmala, M., 2004. Relationship and variations of aerosol number and PM10 mass concentrations in a highly polluted urban environment - New Delhi, India. Atmospheric Environment 38, 57-66.

Moreno, T., Karanasiou, A., Amato, F., Lucarelli, F., Nava, S., Calzolai, G., Chiari, M., Coz, E., Artinano, B., Lumbreras, J., Borge, R., Boldo, E., Linares, C., Alastuey, A., Querol, X. and Gibbons, W., 2013. Daily and hourly sourcing of metallic and mineral dust in urban air contaminated by traffic and coal-burning emissions. Atmospheric Environment 68, 33-33.

Mouli, P.C., Mohan, S.V., Balaram, V., Praveen Kumar, M. and Reddy, S.J., 2006. A study on trace elemental composition of atmospheric aerosols at a semi-arid urban site using ICP-MS technique. Atmospheric Environment 40, 136-146.

Oros, D.S. and Simoneit, B.R.T., 2000. Identification and emission rates of molecular tracers in coal smoke particulate matter. Fuel 79, 515-536.

Pant, P. and Harrison, R.M., 2012. Critical review of receptor modelling for particulate matter: A case study of India, Atmospheric Environment 49, 1-12.

Pant, P. and Harrison, R.M., 2013. Estimation of the Contribution of Road Traffic Emissions to Particulate Matter Concentrations from Field Measurements: A Review. Atmospheric Environment 77, 78-97.

Patil, R.S., Kumar, R., Menon, R., Shah, M.K. and Sethi, V., 2013. Development of particulate matter speciation profiles for major sources in six cities in India. Atmospheric Research 132-133, 1-11.

Puxbaum, H., Caseiro, A., Sanchez-Ochoa, A., Kasper-Giebl, A., Claeys, M., Gelencser, A., Legrand, M., Preunkert, S. and Pio, C., 2007. Levoglucosan levels at background sites in Europe for assessing the impact of biomass combustion on the European aerosol background. Journal of Geophysical Research: Atmospheres, 112, D23S05.

Perrino, C., Tiwari, S., Catrambone, M., Torre, S.D., Rantica, E. and Canepari, S., 2011. Chemical characterization of atmospheric PM in Delhi, India, during different periods of the year including Diwali festival. Atmospheric Pollution Research 2, 418-427.

Phuleria, H. C., Sheesley, R. J., Schauer, J. J., Fine, P. M. and Sioutas, C., 2007. Roadside measurements of size-segregated particulate organic compounds near gasoline and diesel-dominated freeways in Los Angeles, CA. Atmospheric Environment 41, 4653-4671.

Pio, C.A. and Harrison, R.M., 1987a. The equilibrium of ammonium chloride aerosol with gaseous hydrochloric acid and ammonia under tropospheric conditions. Atmospheric Environment 21, 1243-1246.

Pio, C.A. and Harrison, R.M., 1987b. Vapour pressure of ammonium chloride aerosol : Effect of temperature and humidity. Atmospheric Environment 21, 2711-2715.

Pio, C., Cerqueira, M., Harrison, R.M., Nunes, T., Mirante, F., Alves, C., Oliviera, C., Sanchez de la Campa, A., Artinano, B. and Matos, M., 2011. OC/EC ratio observations in Europe: Re-thinking the approach for apportionment between primary and secondary organic carbon. Atmospheric Environment 45, 6121-6132.

Ravindra, K., Sokhi, R. and van Greiken, R., 2008). Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. Atmospheric Environment 42, 2895-2921.

Rogge, W.F., Hildemann, L.M., Mazurek, M.A. and Cass, G.R., 1993. Sources of fine organic aerosol. 2. Noncatalyst and catalyst equipped automobiles and heavy duty diesel trucks. Environmental Science and Technology 27, 636-651.

Sahu, S.S., Beig, G. and Parkhi, N.S., 2011a. Emissions inventory of anthropogenic PM2.5 and PM10 in Delhi during Commonwealth Games 2010. Atmospheric Environment 45, 6180-6190.

Sahu, M., Hu, S., Ryan, P. H., Le Masters, G., Grinshpun, S. A., Chow, J. C. and Biswas, P., 2011b. Chemical compositions and source identification of PM2.5 aerosols for estimation of a diesel source surrogate. Science of the Total Environment 409, 2642-2651.

Satsangi, A., Pachauri, T., Singla, V., Lakhani, A. and Kumari, K.M., 2013. Water soluble ionic species in atmospheric aerosols: Concentrations and sources at Agra in the Indo-Gangetic Plain (IGP). Aerosol and Air Quality Research 13, 1877-1889.

Sharma, H., Jain, V.K. and Khan, Z.H., 2007. Characterization and source identification of polycyclic aromatic hydrocarbons (PAHs) in the urban environment of Delhi. Chemosphere 66, 302-310.

Sharma, S.K., Mandal, T.K., Saxena, M., Rohtash, R., Sharma, A. and Gautam, R., 2013. Source apportionment of PM_{10} by using positive matrix factorization at an urban site of Delhi, India. Urban Climate, doi: http:// dx.doi.org/10.1016/j.uclim.2013.11.002.

Simoneit, B.R.T., 2002. Biomass burning-a review of organic tracers for smoke from incomplete combustion. Applied Geochemistry 17, 129-162.

Simoneit, B.R.T., Elias, V.O., Kobayashi, M., Kawamura, M., Rushdi, A.I., Medeiros, P.M., Rogge, W.F. and Didyk, B.M., 2004. Sugars- Dominant water-soluble organic compounds in soils and characterisation as tracers in atmospheric particulate matter. Environmental Science and Technology 38, 5939-5949.

Singh, D.P., Gadi, R. and Mandal, T.K., 2011. Characterization of particulate-bound polycyclic aromatic hydrocarbons and trace metals composition of urban air in Delhi, India. Atmospheric Environment 45, 7653- 7663.

Sjorgen, M., Li, H., Rannug, W. and Westerholm, R., 1996. Multivariate analysis of exhaust emissions from heavy-duty diesel fuels. Environmental Science and Technology 30, 38-49.

Smith, D.J.T. and Harrison, R.M., 1996. Concentrations, trends and vehicle source profile of polynuclear aromatic hydrocarbons in the U.K. atmosphere. Atmospheric Environment 30, 2513-2525.

Srimuruganandam, B. and Shiva Nagendra, S.M., 2011. Chemical characterization of PM (10) and PM (2.5) mass concentrations emitted by heterogeneous traffic. Atmospheric Environment 45, 3091-3102.

Srimuruganandam, B. and Shiva Nagendra, S.M., 2012. Application of positive matrix factorization in characterization of PM10 and PM2.5 emission sources at urban roadside. Chemosphere 88, 120-130.

Srinivas, B. and Sarin, M.M., 2014. Brown carbon in atmospheric outflow from the Indo-Gangetic Plain: Mass absorption efficiency and temporal variability. Atmospheric Environment 89, 835-843.

Srivastava, A. and Jain, V.K., 2007. Size distribution and source identification of total suspended particulate matter and associated heavy metals in the urban atmosphere of Delhi. Chemosphere 68, 579-589.

Sudheer, A.K., Rengarajan, R., Deka, D., Bhushan, R., Singh, S.K. and Aslam, M.Y., 2014. Diurnal and seasonal characteristics of aerosol ionic constituents over an urban location in Western India: Secondary aerosol formation and meteorological influence. Aerosol and Air Quality Research, doi: 10.4209/aaqr.2013.09.0288.

Taylor, S.R. and McLennan, S.M., 1995. The geochemical evolution of the continental crust. Reviews of Geophysics 33, 241-265.

Tiwari, S., Srivastava, A.K., Bisht, D.S., Bano, T., Singh, S., Behura, S., Srivastava, M.K., Chate, D.M. and Padmanabhamurthy, B., 2009. Black carbon and chemical characteristics of PM_{10} and $PM_{2.5}$ at an urban site of North India. Journal of Atmospheric Chemistry 62, 193- 209.

Tiwari, S., Bisht, D.S., Srivastava, A.K., Pipal, A.S., Taneja, A., Srivastava, M.K. and Attri, S.D., 2014) Variability in atmospheric particulates and meteorological effects on their mass concentrations over Delhi, India. Atmospheric Research 145-146, 45-56.

Tiwari, S., Pervez, S., Perrino, C., Bisht, D.S., Srivastava, A.K. and Chate, D., 2013. Chemical characterization of atmospheric particulate matter in Delhi, India, Part II: source apportionment studies using PMF 3.0. Atmospheric Research 145-146, 45-56.

Trivedi, D.K., Ali, K. and Beig, G., 2014. Impact of meteorological parameters on the development of fine and coarse particles over Delhi. Science of The Total Environment 478: 175-183.

Turpin, B. and Huntzicker, J.J., 1995. Identification of secondary organic aerosol episodes and quantification of primary and secondary organic aerosol concentrations during SCAQS. Atmospheric Environment 29, 3527-3544.

Venkataraman, C. and Friedlander, S.K., 1994. Source resolution of fine particulate polycyclic aromatic hydrocarbons using a receptor models modified for reactivity. Journal of Air and Waste Management Association 44, 1103-1108.

Viana, M., Kuhlbusch, T.A.J., Querol, X., Alastuey, A., Harrison, R.M., Hopke, P.K., Winiwarter, W., Vallius, M.,et al., 2008. Source apportionment of particulate matter in Europe: A review of methods and results. Journal of Aerosol Science 39, 827-849.

Watson, J.G., Chow, J.C., Lowenthal, D.H., Pritchett, L.C. and Frazier, C.A., 1994. Differences in the carbon composition of source profiles for diesel- and gasoline-powered vehicles. Atmospheric Environment 28, 1979-1991.

Watson, J.G., Chow, J.C. and Frazier, C.A., 1999. X-ray fluorescence analysis of ambient air samples. In Elemental Analysis of Airborne Particles, Vol. 1, Landsberger, S., Creatchman, M., Eds.; Gordon and Breach Science: Amsterdam, 67-96.

Watson, J.G., Chen, L.-W. A., Chow, J.C., Doraiswamy, P. and Lowenthal, D.H., 2008. Source Apportionment: Findings from the U.S. Supersites Program. Journal of Air and Waste Management Association 58, 265-288.

Yadav, S. and Rajamani, V., 2006. Air quality and trace metal chemistry of different size fractions of aerosols in N-NW India- implications for source diversity, India. Atmospheric Environment 40, 698-712.

Yadav, S., Tandon, A. and Attri, A.K., 2013. Characterization of aerosol associated non-polar organic compounds using TD-GC-MS: A four year study from Delhi, India. Journal of Hazardous Materials 252-253, 29-44.

Zhang, Y, Schauer, J.J., Zhang, Y., Zeng, L., Wei, Y., Liu, Y. and Shao, M., 2008. Characteristics of particlulate carbon emissions from real-world Chinese coal combustion. Environmental Science and Technology 42, 5068-5073.

TABLE LEGENDS

Table 1: Concentration of the main species measured in the summer and winter campaigns.

Table 2: Estimation factors used for mass closure.

Table 3: Summary of receptor modelling studies for New Delhi.

FIGURE LEGENDS

Figure 1: Modal split at the sampling location in Delhi.

Figure 2: Relationship between OC and EC in summer and winter.

Figure 3: Estimation of minimum OC/EC ratio using the EC tracer method.

Figure 4: RMA regression between ammonium and sum (nitrate, sulphate, chloride).

Figure 5: Enrichment factors for select elements.

Figure 6: Mass closure for $PM_{2.5}$ at CRRI.

Table 1: Concentrations of the main species measured in the summer and winter campaigns (in μg/m^3, organic species in ng/m^3).

Species	**Summer**				**Winter**			
	Mean	**S.D.**	**Min**	**Max**	**Mean**	**S.D.**	**Min**	**Max**
Mass	58.2	35.0	3.30	179.5	276.9	99.9	111.9	424.9
OC	17.6	8.38	5.17	36.4	104.4	40.6	53.3	195.5
EC	7.77	7.06	0.60	31.4	46.3	18.9	12	78.9
Ions								
Chloride	2.14	1.54	0.56	6.70	27.8	18.1	7.21	68.1
Nitrate	4.37	2.14	1.04	8.79	32.8	20.1	0.21	76.7
Sulphate	9.97	6.25	1.74	27.5	26.1	15.3	7.66	59.1
Ammonium	4.94	2.87	0.94	12.4	34.2	17.0	13.0	64.0
Na^+	0.41	0.38	0.01	1.56	0.64	0.30	0.20	1.18
K^+	0.86	0.49	0.13	2.40	3.83	1.63	1.51	6.50
Anhydrosaccharides								
Levoglucosan	*detected in <20% samples*				6.57	3.23	2.15	12.0
Mannosan	*detected in <20% samples*				0.42	0.27	0.06	1.04
Molecular Markers								
Sum of Hopanes (C27-C35)	1.97	2.47	0.00	9.26	26.3	7.93	15.6	40.4
Sum of Steranes (C27-C29)	0.44	1.04	0.00	4.81	3.95	1.49	1.63	6.79
Sum of Alkanes (C14-C40)	48.1	38.9	1.52	145	382	137	168	617
Sum of PAHs (C12-C24)	7.73	5.54	0.82	25.8	119	33.8	84.1	188
Sum of Saccharides (C3-C12)	0.05	0.01	0.03	0.08	1.63	1.77	0.54	7.21
Sum of Diacids (C1-C5)	1.43	0.49	0.65	2.41	3.76	3.12	1.00	9.55
Elements								
Al	0.81	0.72	0.08	3.03	1.73	0.87	0.63	3.74
Si	1.88	1.87	0.02	7.80	1.79	0.67	0.77	2.94
S	3.02	2.20	0.01	9.67	9.49	7.27	2.42	26.9
Ca	0.78	0.75	0.004	3.27	1.11	0.46	0.33	1.85
Cu	0.02	0.01	0.001	0.05	0.07	0.07	0.01	0.28
Zn	0.20	0.19	0.01	0.75	0.64	0.38	0.23	1.47
Mn	0.03	0.03	0.0003	0.11	0.08	0.07	0.01	0.29
Fe	0.71	0.63	0.02	2.52	1.15	0.33	0.53	1.57
Ba	0.03	0.03	0.004	0.13	0.01	0.01	0.01	0.04
Pb	0.08	0.06	0.003	0.27	0.60	0.65	0.08	2.51
Ni	0.004	0.003	0.0003	0.01	0.01	0.01	0.0003	0.02
Ti	0.07	0.06	0.003	0.25	0.07	0.04	0.005	0.13
V	0.01	0.01	0.0004	0.02	0.01	0.01	0.001	0.03
Cr	0.01	0.01	0.0003	0.05	0.01	0.02	0.00	0.06

Table 2: Estimation factors used for mass closure.

Source	Component	Estimation factor	Reference
Woodsmoke	Mass	11.2*levoglucosan	Harrison et al. (2012) In summer, since levoglucosan was not detected, this calculation was not included for mass closure.
	OC_w	7.35*levoglucosan	Puxbaum et al. (2007)
	EC_w	0.2*woodsmoke $PM_{2.5}$	Harrison et al. (2012)
Traffic	EC_t	Total EC- EC_w	In summer, since levoglucosan was not detected, EC mass was not corrected for woodsmoke EC.
	OC_t	0.35* EC_t	Pio et al. 2011
	$PM_{2.5}$	1.35* EC_t	
	OM ($PM_{2.5}$)	Traffic $PM_{2.5}$*1.2	Chow et al. (2002)
Other OM		Other OC = Total OC – (OC_t+ OC_w) Other OM= Other OC*1.5	Puxbaum et al. (2007), Pio et al. (2011)
Secondary Ions	$(NH_4)_2SO_4$	1.38*Sulphate	Harrison et al. (2003) Based on molar ratios
	NH_4NO_3	1.29*Nitrate	
	NH_4Cl	1.51*Chloride	
Dust	Crustal Mass	1.16(1.90Al+ 2.15Si+ 1.41Ca+1.67Ti+ 2.09Fe)	Chan et al. (1997)
Total PM	SUM (Woodsmoke, Traffic OM, Other OM, $(NH_4)_2SO_4$, NH_4NO_3, NH_4Cl, Crustal mass)		

EC_t- EC associated with traffic; EC_w- EC associated with woodsmoke, OC_w- OC associated with woodsmoke, OC_t- OC associated with traffic

Table 3: Summary of receptor modelling studies for New Delhi.

Reference	**Location**	**Method**	**Results (%)**
Current study	$PM_{2.5}$ Mathura Road	Pragmatic Mass Closure (elements, ions, OC, EC, molecular markers)	Woodsmoke- 23.3 (w) Traffic- 18.7 (s)/ 16.2 (w) Dust- 14.3 (s)/ 3.9 (w) Sulphate- 20.5 (s)/ 10.6 (w) Nitrate- 8.4 (s)/ 12.4 (w) Chloride- 4.8 (s)/ 12.3 (w) Other OM- 33.3 (s)/ 21.4 (w)
Sharma et al. (2013)	PM_{10} CSIR- NPL Campus	PMF (elements, ions, OC and EC)	Soil (20.7) Vehicles (17.0) Secondary-inorganic (21.7) Fossil fuel-coal/heavy oil (17.4) Industry (4.5) Sea salt (4.4)
Li et al. (2014)	TSP (winter) CSIR- NPL Campus	Mass Balance (elements, ions, OC, EC, molecular markers)	Crustal material (48) Organic matter (23) Sulphate (4.9) Nitrate (4.5) Ammonium (2.7) Other (7.2)
Tiwari et al. (2013)	PM_{10} IITM Campus (Central Delhi)	PMF/UNMIX (elements, ions)	Road traffic Crustal dust SIA Chloride
Khillare and Sarkar (2012)	PM_{10} Residential sites	PCA-MLR (elements)	Crustal (49-65) Vehicular (27-35) Industrial (4-21)
Singh et al. (2011)	PM_{10} and $PM_{2.5}$ GGSIP University Campus	Qualitative- diagnostic ratios, enrichment factor (elements, PAHs)	Vehicles, road dust, industries
CPCB (2010)	$PM_{2.5}$ Various sites	CMB (elements, ions, OC and EC)	Vehicles- 7-40 (s)/ Industry- 10-19 (s) Construction- 16-41 (s) Resuspended dust- 17-56 (s)
Tiwari et al. (2009)	$PM_{2.5}$ Two sites in New Delhi		Biomass and fossil fuel burning (80); natural and soil derived particles (~6) *[refers to % variance explained]*
Srivastava and Jain (2008)	SPM (fine and coarse) Residential	CMB (elements)	Diesel vehicles, industries, paved road dust, gasoline vehicles, solid waste, and soil and crustal dust *[in descending order]*
Chowdhury et al. (2007)		CMB (elements, ions, OC, EC, molecular markers)	Diesel- 22 (s)/ 10 (w) Gasoline- 2 (s)/ 9 (w) Road Dust- 42 (s)/ 11 (w) Coal- 2 (s)/ 14 (w) Biomass- 7 (s)/ 20 (w) Sulphate- 10 (s)/ 8 (w) Nitrate- 3 (s)/ 7 (w) Ammonium- 3 (s)/ 5(w) Other Mass- 11 (s)/ 17 (w)
Khillare et al. (2004)	SPM Residential/industrial/commercial sites in Delhi	PCA (elements)	Vehicular and industrial emissions (60) Crustal (22) *[refers to % variance explained]*

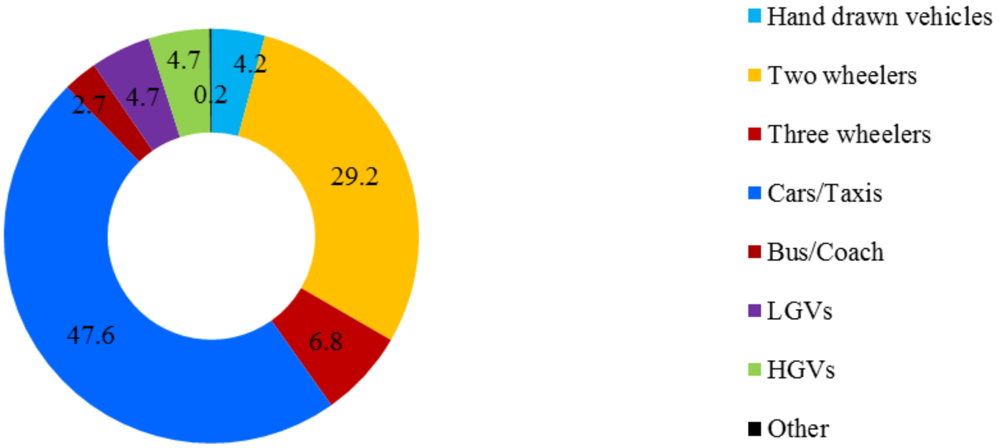
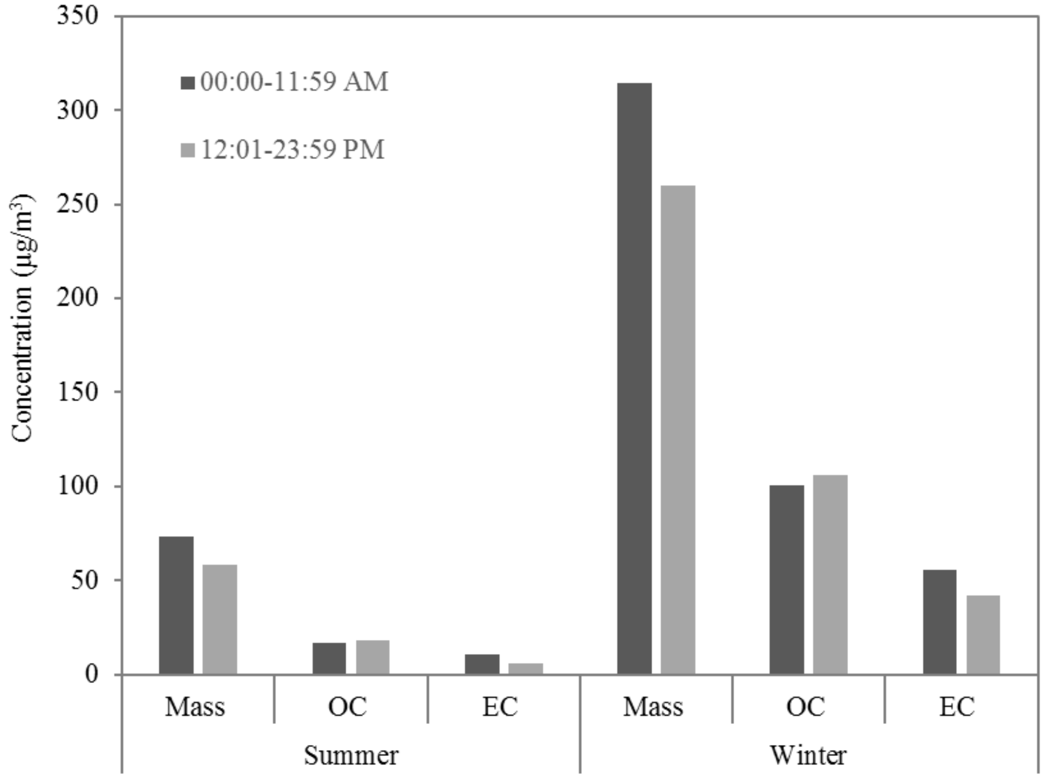


Figure 1: Modal split at the sampling location in Delhi

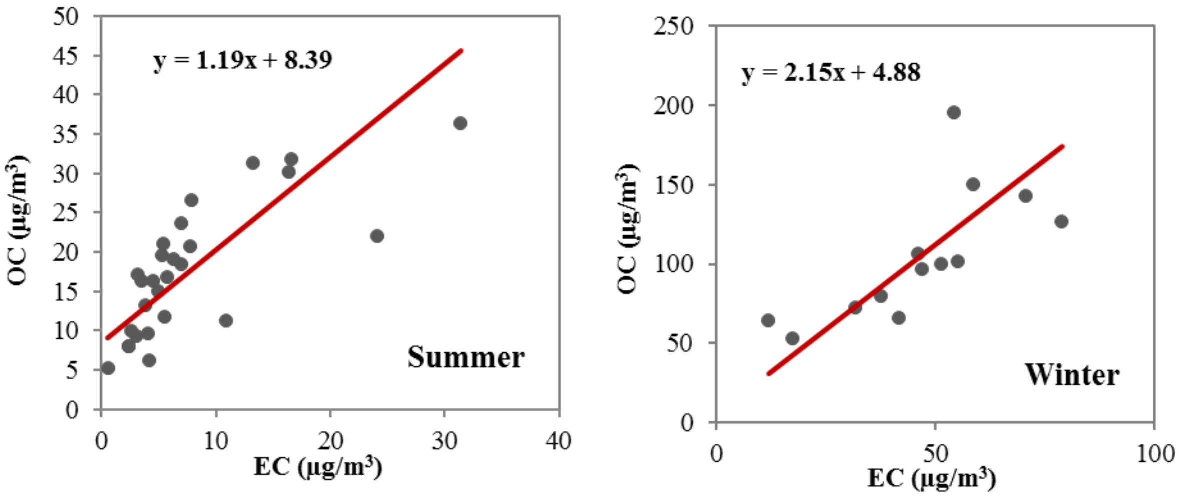


1044

1045

1046 **Figure 2**: Average 12-h concentrations in summer and winter seasons

1047



1048

1049 **Figure 3:** Relationship between OC and EC in summer and winter

1050

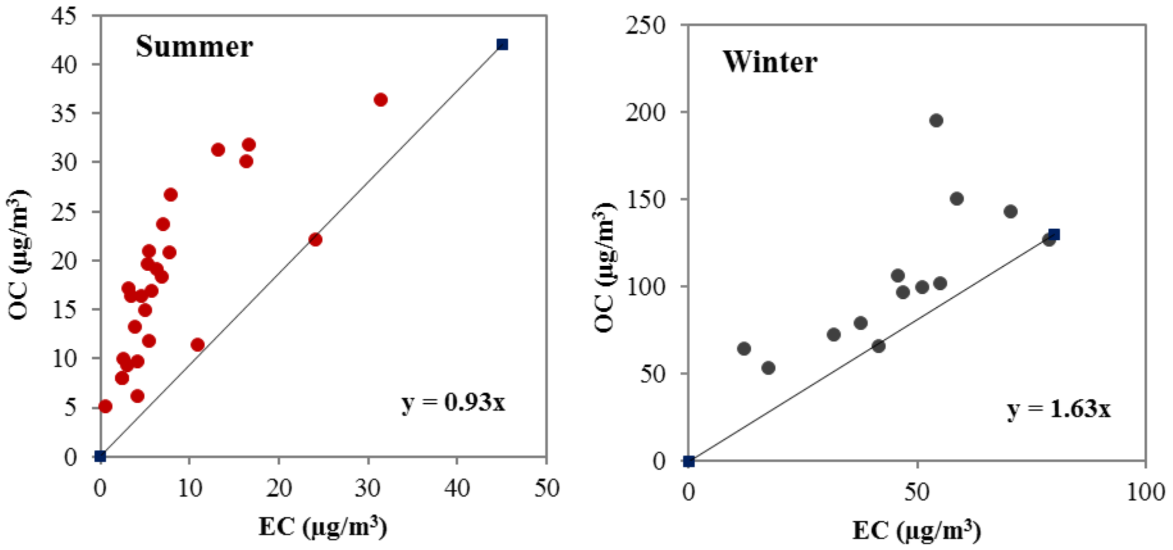


Figure 4: Estimation of minimum OC/EC ratio using the EC tracer method

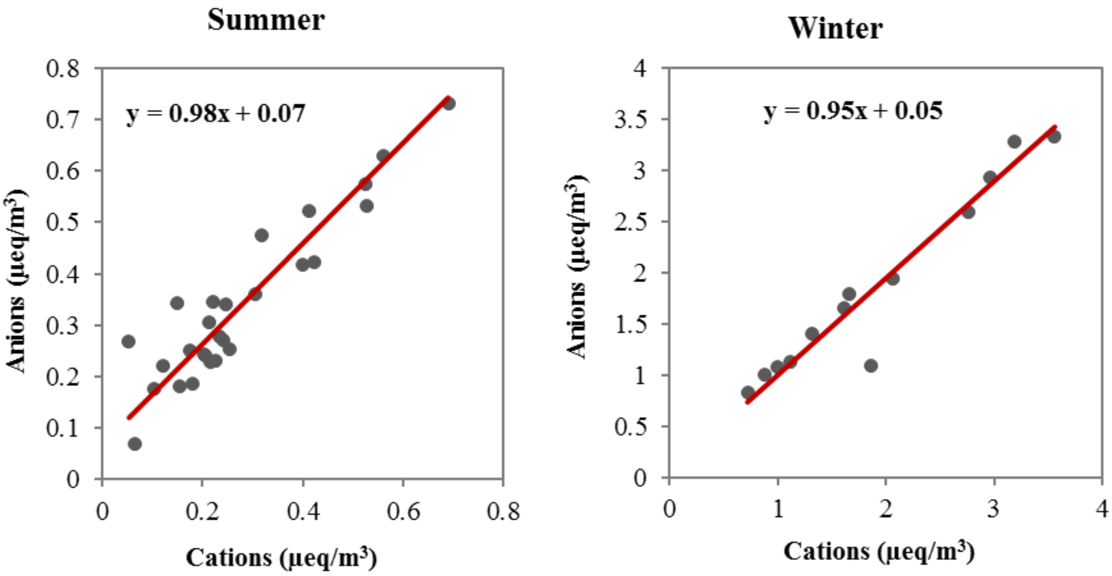
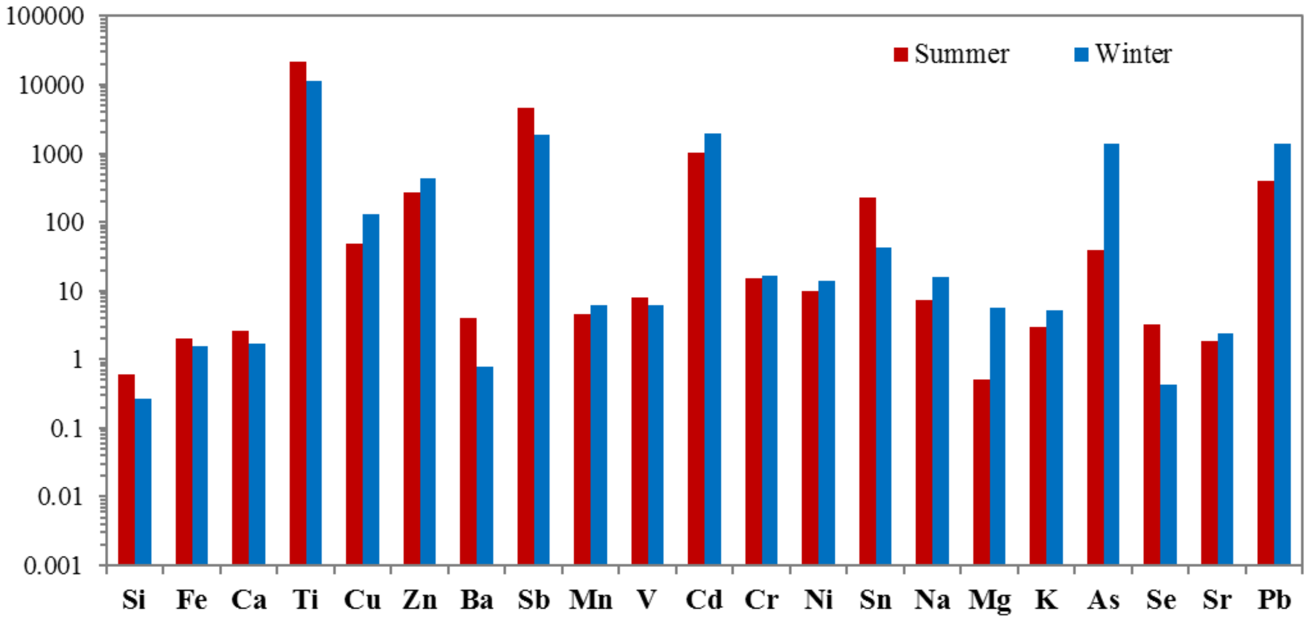


Figure 5: RMA regression between ammonium and sum of anions (i.e. nitrate, sulphate, chloride)

1059



1060
1061

1062 **Figure 6:** Enrichment factors for select elements

1063

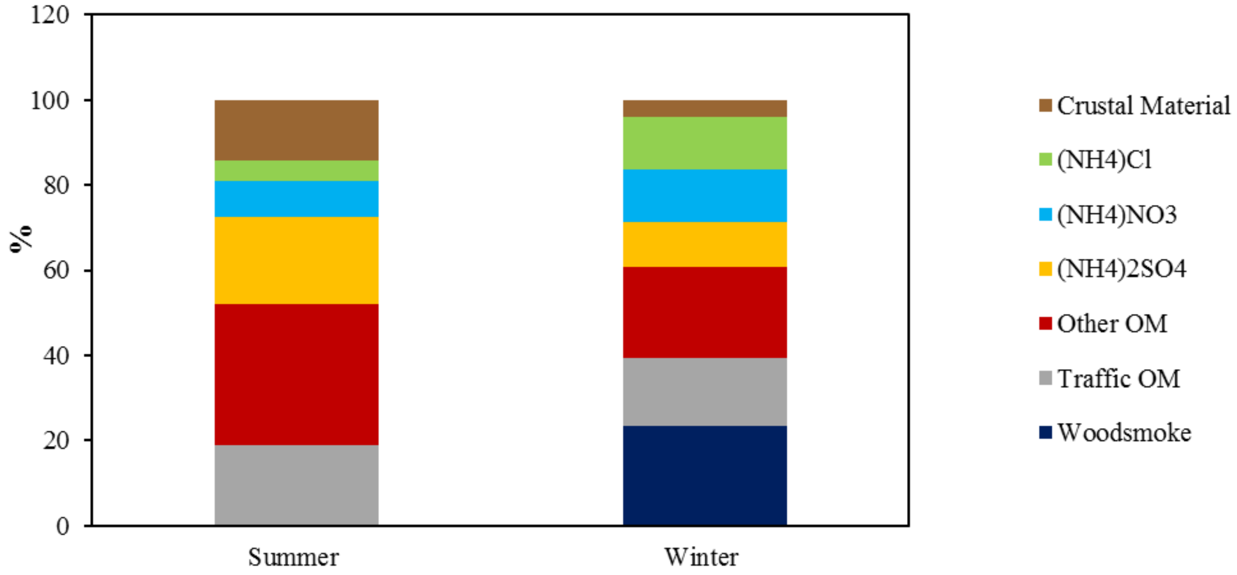


Figure 7: Mass closure for $PM_{2.5}$ at CRRI

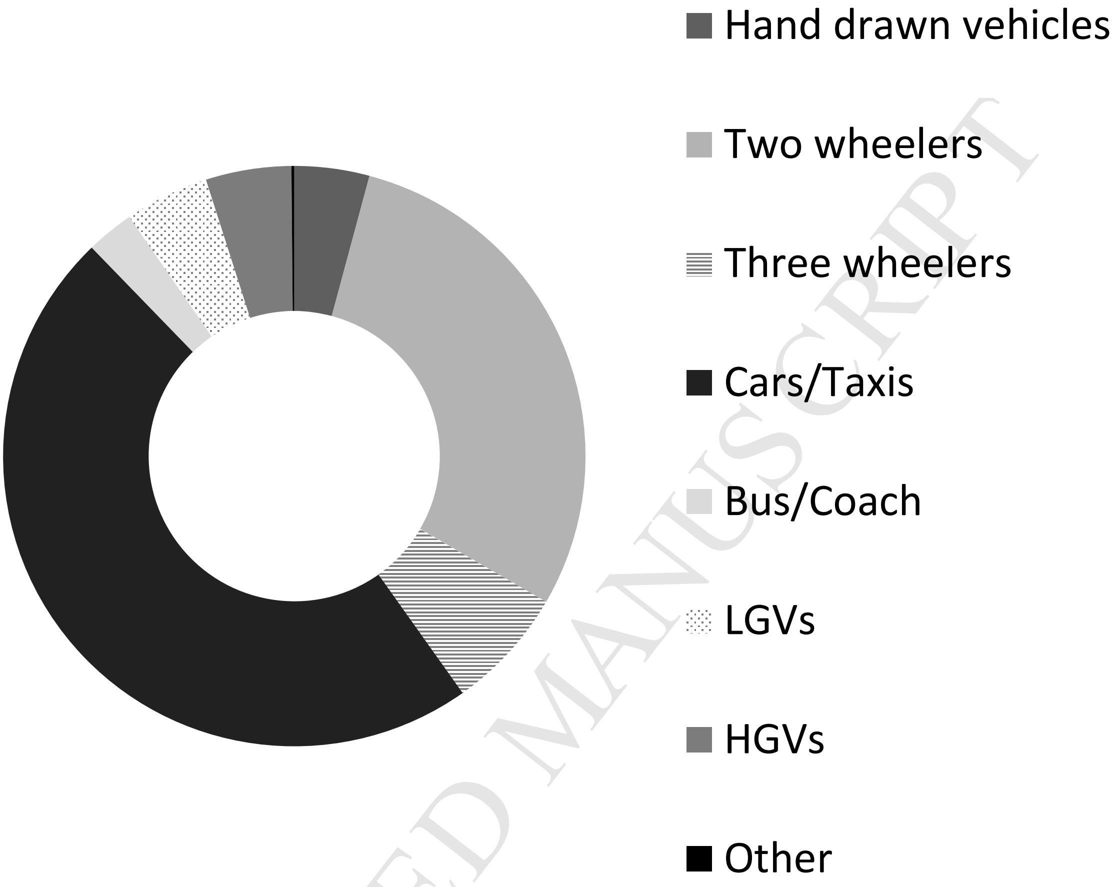


Figure 1: Modal split at the sampling location in Delhi

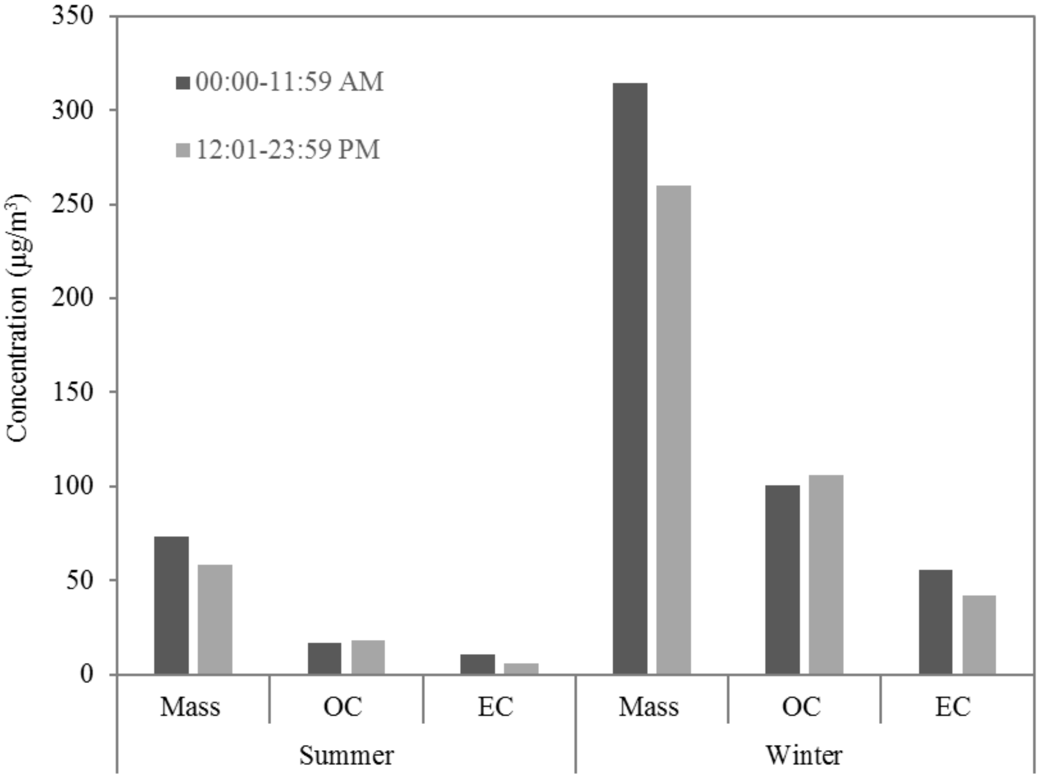


Figure 2: Average 12-h concentrations in summer and winter seasons

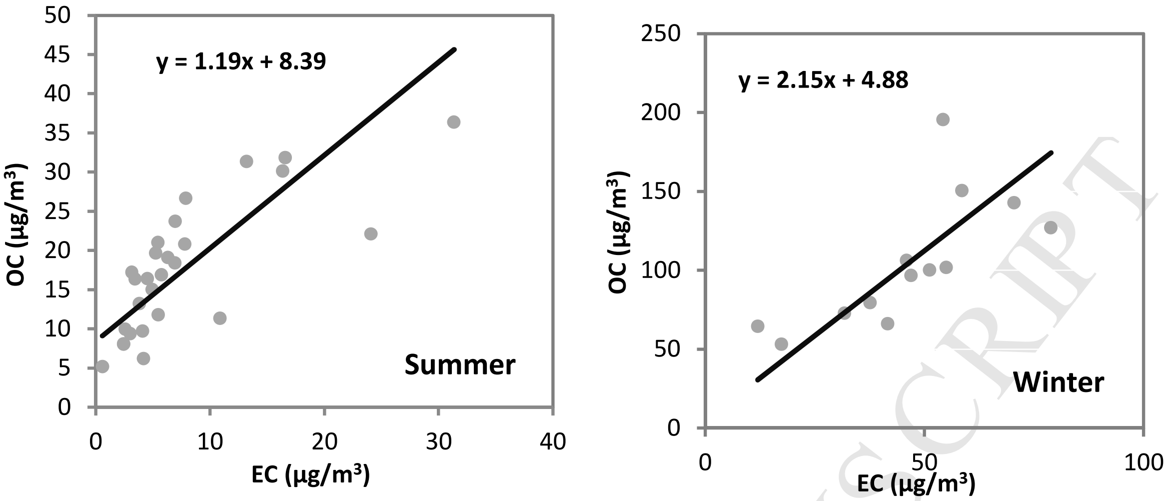


Figure 3: Relationship between OC and EC in summer and winter

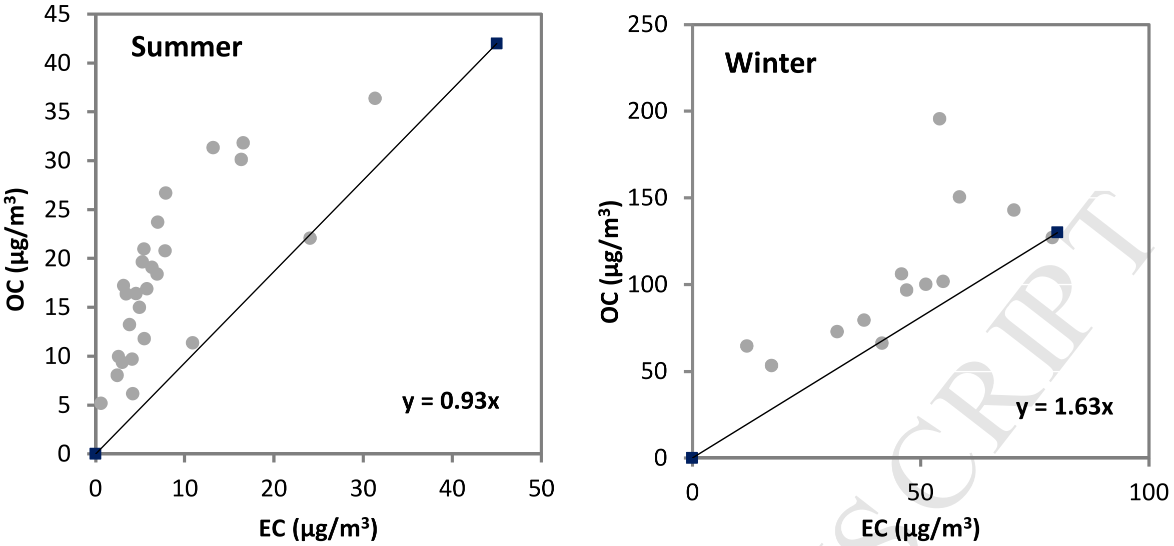


Figure 4: Estimation of minimum OC/EC ratio using the EC tracer method

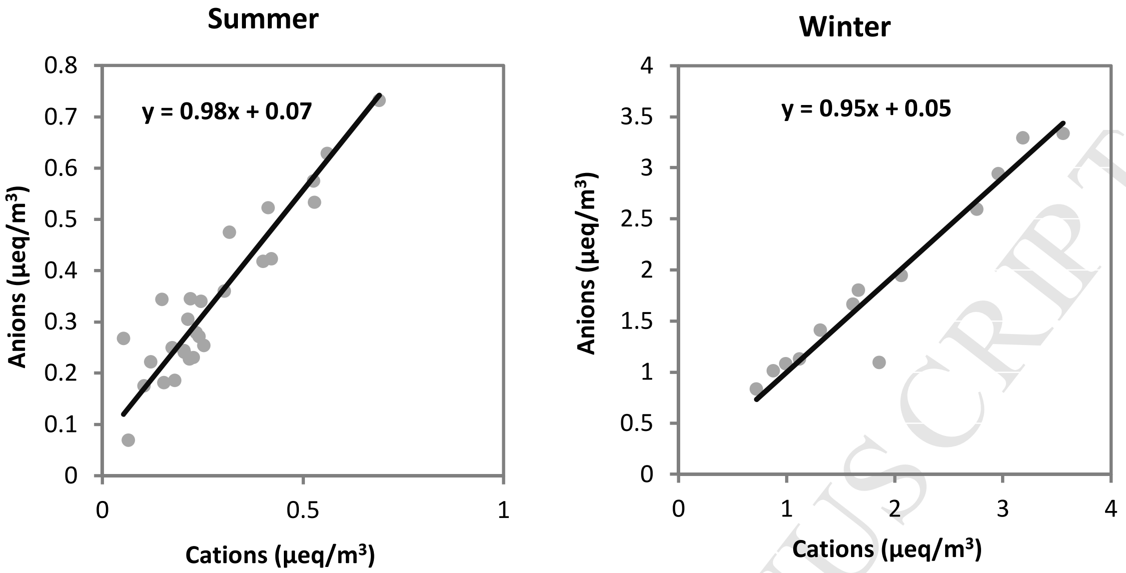


Figure 5: RMA regression between ammonium and sum of anions (i.e. nitrate, sulphate, chloride)

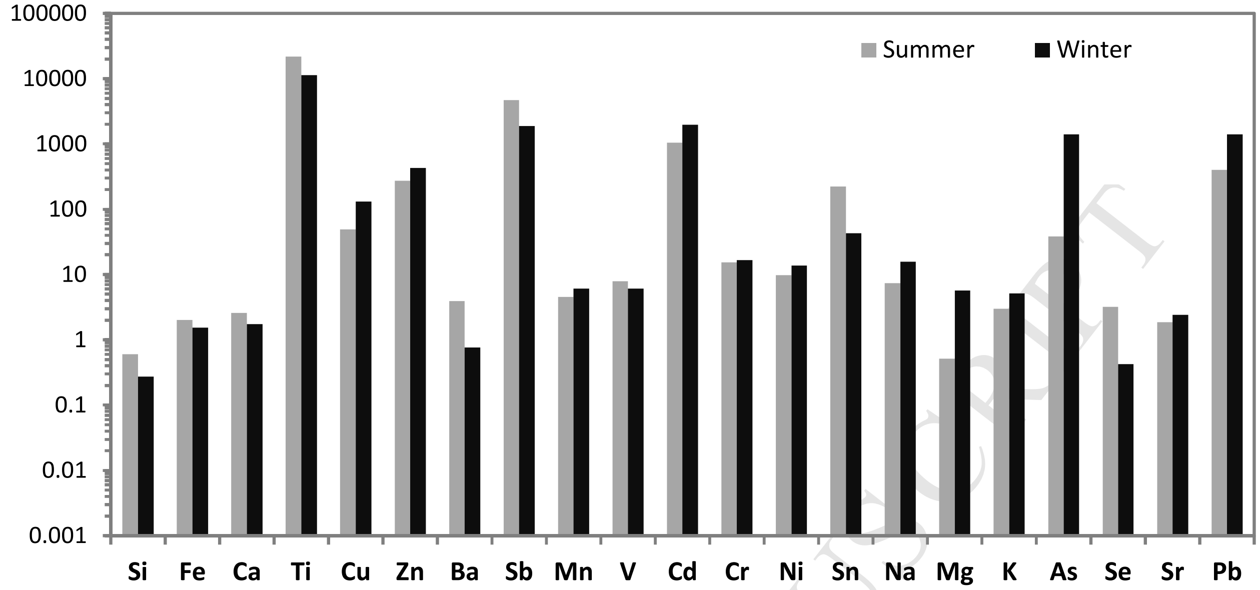


Figure 6: Enrichment factors for select elements

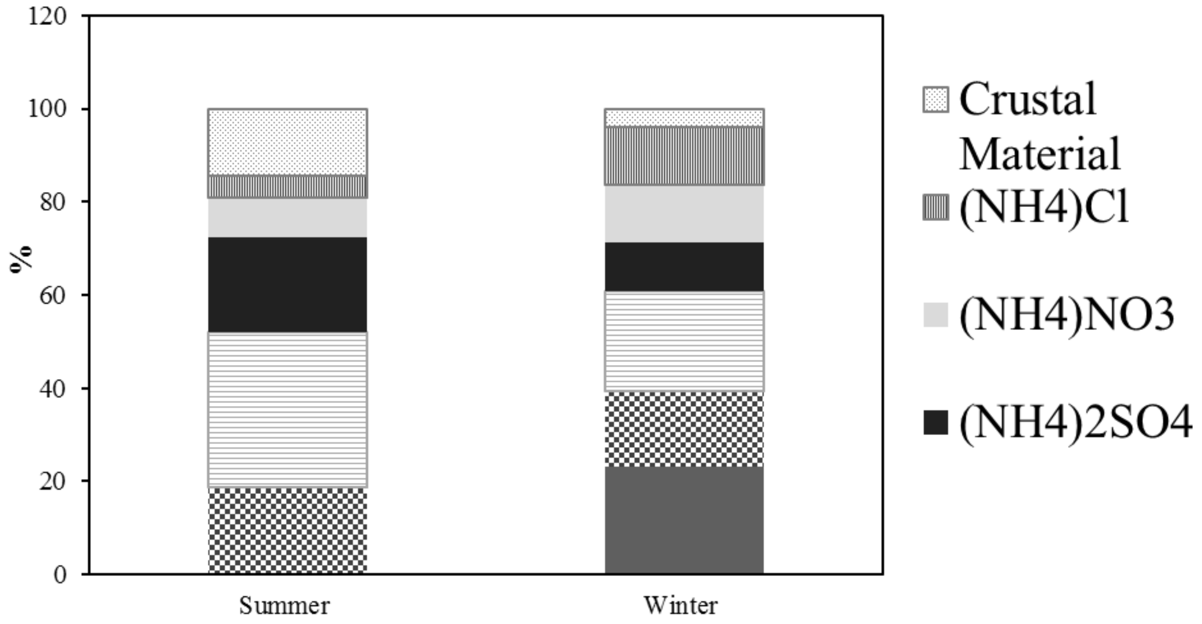


Figure 7: Mass closure for $PM_{2.5}$ at CRRI

Characterization of Ambient $PM_{2.5}$ at a Pollution Hotspot in New Delhi, India and Inference of Sources

Pallavi Pant, Anuradha Shukla, Steven D. Kohl, Judith C. Chow, John G. Watson and Roy M. Harrison

HIGHLIGHTS

- Chemical composition measured in summer and winter campaigns
- Analyses of many elements, ions, OC/EC and organic molecular markers
- Winter campaign mass concentrations far exceed those in the summer campaign
- Major components (ammonium salts, woodsmoke, traffic, crustal) are quantified
- Good mass closure achieved

SUPPLEMENTARY INFORMATION

Characterization of Ambient $PM_{2.5}$ at a Pollution Hotspot in New Delhi, India and Inference of Sources

Pallavi Pant[1], Anuradha Shukla[2], Steven D. Kohl[3], Judith C. Chow[3], John G. Watson[3] and Roy M. Harrison

Table S1: Previous studies reporting concentrations of PM$_{2.5}$ at sites in India

Reference	City	Site Type	Measurement Technique	Year	Season	PM$_{2.5}$ concentrations (µg/m^3)
Trivedi et al., (2014)	Delhi	Residential	Beta Attenuation Monitor (BAM), real-time data	2010-2011	Summer	86.4 ± 26.8 (a) 40.6 - 144.7 (r)
					Winter	221.1 ± 94.7 (a) 80.7 – 470.1 (r)
Tiwari et al. (2014)	Delhi	Residential	Beta Attenuation Monitor (BAM), real-time data	2010-2011	Summer	91.0
					Winter	169.4
Saraswat et al. (2014)	Delhi	Various locations	TSI DustTrak 8250 aerosol monitor, real-time data	2010	Spring/Summer	96 – 232 (r)
Bisht et al. (2013)	Delhi	Ten different locations across Delhi	Beta Attenuation Monitor (BAM), real-time data	2010	Post monsoon	112.1 ± 56.0
Singh et al. (2011)	Delhi	Roadside	APM 550 Fine Particle Samper, offline data	2007-2008	Winter	61.8 ± 11.7 (a) 30.92 – 73.5 (r)
					Summer	39.4 ± 13.9 (a) 16.3 – 63.2 (r)
Srimuruganandam and Shiva Nagendra (2012)	Chennai	Urban roadside	Envirotech APM 550 Fine Particle Samper, offline data	2008-2009	Winter	74.1 ± 14.4 (a)
					Summer	67.4 ± 20.2 (a)
Joseph et al. (2012)	Mumbai	Control	AirMetrics Minivol Sampler	2007-2008	Average of summer, winter and monsoon	69 ± 20 (a)
		Kerbside				84 ± 31 (a)
		Industrial				95 ± 36 (a)
		Residential				89 ± 33 (a)

a: mean ± standard deviation; r: range