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Baker, Stephen; Goel, Rahul; Guttikunda, Sarath K.; Goel, Anubha; Shukla, Anuradha ; Harrison, Roy

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Analysis of Size-Segregated Winter Season Aerosol Data from New Delhi, India

Pallavi Pant[1], Stephen J. Baker[1], Rahul Goel[2], Sarath Guttikunda[2,3], Anubha Goel[4], Anuradha Shukla[5] and Roy M. Harrison[1†]

Corresponding author

Professor Roy M. Harrison
Division of Environmental Health and Risk Management, School of Geography, Earth and Environmental Sciences, University of Birmingham, Edgbaston, Birmingham, B15 2TT United Kingdom
Email address: **r.m.harrison@bham.ac.uk**
Telephone: +44 121 414 3494
Fax: +44 121 414 3709

[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]*TRIPP, Indian Institute of Technology-Delhi, New Delhi, India*

[3]*Division of Atmospheric Sciences, DRI, Reno, Nevada, USA*

[4]*Department of Civil Engineering, Indian Institute of Technology- Kanpur Kanpur, UP, India*

[5]*Environmental Sciences Division, Central Road Research Institute Mathura Road, New Delhi 110025, India*

ABSTRACT

Size distributions of particulate matter and twelve constituent elements were measured at a high traffic site in New Delhi, India during winter 2013. While PM was found to be trimodal, individual elements showed varying size distribution patterns. Three key types of size distributions were observed including unimodal with peaks either in the coarse (Al, Si) or fine (Pb) modes, bimodal with peaks in the fine range (S) and multimodal with peaks in accumulation and coarse (Cu, Sb) modes. Elements such as Al, Si and Fe were found to be in predominantly in the coarse range while Cu, Zn, Pb and Sb were found to be in the fine size range. Two modes dominate the size distribution. One is coarse (ca. 3 µm) and contains mainly crustal elements and hence arises from sources such as soil, road dust, construction dust and possible coal fly ash. The other, more intense mode is fine (ca. 0.6 µm) and appears to comprise sulphate and anthropogenic trace metals which have entered the droplet mode through hygroscopic particle growth in the very high humidity conditions of the Delhi winter. A third, less intensive mode ca. at 0.2 µm probably arises from relatively fresh anthropogenic emissions which have not grown into the droplet mode.

Keywords: Size distributions; India; Aerosols; Metals

1. INTRODUCTION

Particulate matter (PM) is one of the key pollutants found in the ambient air, and despite stringent pollution control programmes, cities across the world often exceed the local and/or national air quality standards. PM is known to have adverse effects on human health including respiratory and heart diseases, circulation disorders and in extreme cases, premature death. Urban air quality features among the major environmental concerns in cities around the globe, and much research has been undertaken to understand the sources and properties of PM. Many sources contribute to PM concentrations in urban areas including anthropogenic sources such as fossil fuel combustion (gasoline, diesel and coal), biomass combustion, building and construction, industrial processes and natural sources including marine aerosol (or sea salt), crustal dust and biological materials. Respiratory deposition and hence the health hazards posed by PM are crucially dependent upon the size distribution (Harrison et al., 2010).

Transition metals (e.g. Cu, Zn) are emitted from a range of sources including traffic (exhaust and non-exhaust), industries and coal combustion. Such elements are thought to be particularly detrimental for health due to their role in reactive oxygen species (ROS) formation (Kelly, 2003). Particle size is characteristic of the emission sources with some sources emitting coarse particles (PM with aerodynamic diameter between 2.5 and 10 μm) and others emitting fine (< 2.5 μm) and ultrafine particles (< 0.1 μm). The size distribution of a particular element or compound not only influences the potential health impact (in terms of respiratory deposition) (Harrison et al., 2010), but also influences the extent of atmospheric dispersion (Allen et al., 2001a). Size distributions can be measured in terms of mass, number or surface area (Harrison et al., 2000). A number of factors can influence the size distribution including, but not limited to, source type, meteorological conditions and extent of atmospheric aging (Zhu et al., 2006; Beddows et al., 2009; Hays et al, 2011).

Several studies in India have focused on the particle size distributions including mass size distributions (Khemani et al., 1982; Balachandran et al., 2000; Venkataraman et al., 2002; Reddy et al., 2007; Chelani et al., 2010), number size distributions (Mönkkönen et al., 2005), or both (Sharma and Patil, 1992; Mönkkönen et al., 2004; Baxla et al., 2009). However, there is a lack of detailed analysis on size distributions of elements in particulate matter samples from India.

The main objective of this study was to analyse the size distribution of PM mass and associated chemical compounds in New Delhi, India in relation to sources and atmospheric processing. Diurnal properties of $PM_{2.5}$ are also examined.

2. METHODS

2.1 Sampling Sites

Sampling was conducted at Mathura Road (New Delhi, India), one of the major arterial roads in Delhi, with an average traffic flow of 170 000 vehicles per day (Pant et al., 2015). The road also constitutes a part of a major national highway (NH 2) providing connectivity in the northern part of the country. As a result, a large volume of inter-city diesel buses as well as trucks (diesel, BS-III, 350 ppm sulphur) ply on this road. While the sampling location is primarily a traffic site, there are other major sources of pollution located in the vicinity of the site. These include an industrial hub within three kilometres of the sampling site (Okhla Industrial Area) and residential and waste burning in nearby low-income settlements in addition to resuspended dust. Trucks are not allowed between 0730 to 1100 hours and 1700 to 2130 hours, 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 (one of the 14 cities in India with BS-IV fuel) and vehicles from outside Delhi are often BS-III (equivalent of Euro III) because of universal availability of BS-III fuel in India. Similarly, buses plying within Delhi are CNG-based while inter-city buses run on diesel. A summary of the modal variations through the day is presented in Figure 1.

Figure 1 here

2.2 Sampling

Sampling was undertaken from December 16 through December 22, 2013. PM_{10} and $PM_{2.5}$ was monitored using a DustTrak DRX aerosol monitor (Model 8533, TSI Inc., USA). The instrument was pre-calibrated to 29% RH and Arizona Road Dust. Correction factors (internal size-calibration, RH correction and difference between Arizona dust and Delhi aerosols) were applied to the data before analysis. Size-segregated PM samples were collected using 10-stage non-rotating Micro-Orifice Uniform Deposit Impactor (MOUDI) (Model 110, MSP Corporation, Minneapolis, Minnesota, USA) at a flow rate of 30 Lpm. Samples were collected for a period of 6 hours each (0000-0600; 0600-1200; 1200-1800 and 1800-2400) using 47 mm polytetrafluoroethylene (PTFE) filters (pore size of 1.0 μm) as impaction substrates and 37 mm quartz fibre filters as back-up. The samples were collected in the flow-corrected size ranges between 0.06 and 20.2 μm. The sampler was placed at a distance of 2 metres from the main road at a height of two metres from the ground.

It was a dry period (no rainfall during the sampling period) with fog and haze (RH varied from 79-93.5% on average), and wind speeds were less than 5 km/h for most days (lowest wind speed of 1km/h). High relative humidity was observed (> 75% across all days) and the maximum and minimum temperatures were 23ºC and 5.2ºC.

2.3 Chemical Analysis

Gravimetric analysis was performed on the PTFE filter samples using an MC5 Sartorius microbalance. Before weighing, all filters were equilibrated in a humidity (35-45% relative humidity) and temperature (25º Celsius) controlled windowless room for 24 hours. An ionizing blower and an α-particle source (^{210}Po) were used to reduce the effects of static electricity.

Extraction of the trace metals was performed using reverse aqua regia solution by a quality assured procedure which is described in detail elsewhere (Allen et al., 2001a; Birmili et al., 2006). Briefly,

each filter was extracted using 2 ml of 189 cm^3/L Aristar Grade hydrochloric acid (HCl) and 66 cm^3/L Aristar Grade nitric acid (HNO_3) per sample. The samples were heated followed by mild sonication and were diluted before analysis. Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Agilent 7500ce with an Octopole Reaction System) was used to analyse the samples for Cu, Pb, Zn, Ba, Ca, Sb, Mn and V. This method has a high extraction efficiency for most elements, but the extraction efficiency is lower for aluminosilicates (Harrison et al., 2012). Thus, in order to account for the mass of these species, the filter samples were analysed for Al, Si, Fe and S by Wavelength Dispersive-X-Ray Fluorescence (WD-XRF, Bruker S8 Tiger) prior to filter digestion.

2.4 Data Analysis

Using the data obtained from MOUDI samples, a continuous size distribution was obtained using the numerical inversion method described in Keywood et al. (1999). This approach has previously used in several studies (Allen et al., 2001a; Gietl et al., 2010).

3. RESULTS AND DISCUSSION

3.1 PM Concentration

During the study period, daily average $PM_{2.5}$ concentrations varied from 200 to 550 $\mu g/m^3$. Figure 2 shows the diurnal variation of $PM_{2.5}$ averaged over the study period. The diurnal variation shows high concentrations during night time and early morning hours- from 2100 hrs to 0600 hrs. The time period of high concentrations coincides with the high volume of diesel-based heavy duty trucks and the period typically associated with nocturnal atmospheric stability. A reduction in truck traffic and improved mixing lead to a fall in $PM_{2.5}$ during daytime (Figure 2).

Figure 2 here

3.2 PM Mass Size Distribution

A trimodal size distribution was observed across all four 6-h periods with two modes in the accumulation range (0.15 µm and ~0.55 µm) and one mode in the coarse range (3.0 µm) (Figure 3). Overall, the pattern of the size distribution was found to be similar across all sampling times. PM concentrations were found to be several fold higher than the 24-hour Indian $PM_{2.5}$ air quality standard (60 µg/m^3) across all time periods, and the high concentrations can be attributed to the high volume of traffic, and winter heating (includes combustion of biomass, coal and waste). Low temperature and calm conditions (wind speeds ~0m/s) could have further exacerbated the concentrations due to lack of dispersion. Previous studies have reported bimodal mass size distributions in Indian cities including Pune (Khemani et al., 1982; Ernest Raj et al., 2002; Venkataraman et al., 2002), Mumbai (Sharma and Patil, 1992), Agra (Kulshrestha et al., 1998) and Delhi (Chelani et al., 2010). However, Sharma and Patil (1992) also reported a trimodal mass size distribution at a mixed traffic/industrial site in Mumbai. However, it is important that most of these studies are at least ten years old, and the emission patterns are expected to change over time. Further, the season during which sampling is conducted can also affect the size distributions. For example, several authors have reported higher concentrations of particles in the winter season (Khemani et al., 1982; Venkataraman et al., 2002; Mönkkönen et al., 2005; Baxla et al., 2009; Deshmukh et al., 2012), and it is important to remember that the concentrations as well as size distributions reported in the paper are representative of the winter season. The size distributions are expected to be different in the summer season.

Figure 3 here

A similar size distribution was observed in Prague (Czech Republic) where three peaks (ultrafine, fine and coarse) were observed at a freeway location (Ondracek et al., 2011). However, in New York (USA), Song and Gao (2011) reported a bimodal mass-based distribution (0.32-0.56 and 3.2-

5.6 µm) at a highway site; in Zabrze (Poland), Rogula-Kozlowska et al. (2015) reported a bimodal size distribution for PM at an urban location (0.65-1 and 6.8-10 µm), and in Seville (Spain), Espinosa et al. (2001) also reported a bimodal size distribution (<1 and ~10 µm). At an urban location in Dhaka (Bangladesh), a bimodal (0.63 and 4.37 µm) mass size distribution was reported, and it is interesting to note that the particle sizes are larger for the urban sites compared to high-traffic sites. In Beijing (China), Tian et al. (2014) reported a variable PM mass size distribution dependent on the visibility conditions (i.e. haze vs. non-haze days), and reported higher contribution from fine PM on days with haze.

The average contribution of PM_1, $PM_{2.5}$ and $PM_{2.5-10}$ to total PM mass was 41.9±7.09 %, 74.9 ±5.36% and 25.1±5.36 % respectively. Other studies have reported broadly similar results in Delhi (82.9% fine and 17.1% coarse), Agra (68% fine at an urban site and 61.4% fine at a rural site), Chennai (PM10 consists of 56% $PM_{2.5}$ and 44% PM_1) and Raipur (60.6% fine and 39.4% coarse) (Balachandran et al., 2000; Kulshrestha et al., 2009; Srimuruganandam and Shiva Nagendra, 2011; Deshmukh et al., 2012). Elsewhere, Zhou et al. (2015) reported a similar observation in Beijing (China) and estimated 70% of PM mass to be in the fine range (<2.5 um) while in Dhaka (Bangladesh), Salam et al. (2012) attributed 52% of the total PM mass to $PM_{2.5}$. In Changsha (China), Liu et al. (2015) found fine PM to account for close to 60% of the total PM mass. Related analyses of detailed chemical composition of $PM_{2.5}$ and source estimation for this site in Delhi is presented in Pant et al. (2015).

The highest relative contribution from $PM_{2.5}$ was at night time (0000-0600) and the morning (0600-1200), while the lowest was during 1800-2400 (Figure 4). On the other hand, the contribution from $PM_{2.5-10}$ was the highest during 1800-2400 hours and lowest during 0000-0600 hours. The highest PM_1 was seen during 1200-1800 and 0000-0600 and corresponds with the movement of HDV traffic. As in the results reported by Srivastava and Jain (2007) and Srimuruganandam and Shiva

Nagendra (2011), PM_1 and $PM_{2.5}$ were strongly correlated ($r=0.99$, $p<0.05$) but contrary to their observation, $PM_{2.5-10}$ was not correlated with either of the fractions. However, Chelani et al. (2010) reported lack of correlation between the fine and coarse fractions a kerbside location, and lack of correlation between the coarse and fine fractions indicates different sources for the coarse and fine fractions. In Beijing (China), Tian et al. (2014) also reported a strong correlation between PM_1 and $PM_{2.5}$.

Figure 4 here

3.3 Element Size Distributions

Elemental size distributions reveal an interesting pattern. Species normally associated with crustal matter such as Si, Al and Fe were observed to have a unimodal mass size distribution with a single peak in the coarse range (~3.0-4.0 µm) while Ca showed a primary peak in the coarse mode and a secondary peak in the accumulation mode (0.9 µm) (Figure 5). The Fe/Al ratios across the different time periods (0.35-0.41) also corresponded broadly with the Fe/Al ratios reported in the literature for Northern India. Similar observations have been reported elsewhere including Vienna (Austria) where Berner et al. (2004) reported a coarse mode peak (4 µm) for PM, and Athens (Greece) where Karanasiou et al. (2007) associated elements such as Al and Fe with a coarse mode. Rogula-Kozlowska et al. (2015) also reported a unimodal size distribution for Fe at an urban site in Poland. In contrast, Cu was found in our study to be trimodal with two the peaks in the accumulation mode (~0.5, 0.15 µm) and one peak in the coarse mode (2.5 µm) (Figure 6). Other species associated with anthropogenic emissions such as Zn and Pb showed a bimodal size distribution with primary and secondary peaks in the accumulation mode (~0.7 µm for Zn and ~0.55 µm for Pb {primary mode}; ~0.15 µm {secondary mode}). Mn showed a bimodal size distribution with the primary mode in the accumulation range and a secondary mode in the coarse range (~3.0 µm) and S had a bimodal distribution with both the primary and secondary peaks in the

accumulation range. V, interestingly, showed the primary peak in the coarse range (3.0 µm) and two secondary peaks in the accumulation range (~0.18 and 0.55 µm). Based on an emission inventory analysis in Delhi, sources of V in PM_{10} include power plants and industries (Gargava et al., 2014). This could explain the primary peak of V as coming from coal fly ash, with smaller contributions from industrial and traffic emissions in the fine range. Bhanarkar et al. (2008) reported a bimodal size distribution for coal fly ash including a fine particle mode (0.4-0.9µm) and a coarse mode (>1 µm), with significantly higher concentrations in the coarse mode. In the case of Sb, a bimodal size distribution was observed with a majority of the Sb concentration in the accumulation range. A summary is presented in Table 1. Peaks in the 0.1-0.18 µm size range have previously been associated with motor vehicle emissions (Allen et al., 2001b).

Figure 5 and 6 here

Similar to the observations in the current study, Hays et al. (2011) reported erratic size distributions for several elements including Zn and Ni and this was attributed to the variable influence of emission sources including a nearby highway. In Southern Taiwan, Lin et al. (2005) reported trimodal mass size distributions for Cr and V and bimodal distributions for Zn and Pb while in Athens (Greece), Karanasiou et al. (2007) reported unimodal size distributions for Pb and Mn. In the UK, three distinct categories of elements were reported by Allen et al. (2001a) including elements with most of the element mass concentrated in the coarse range (Fe, Sr) and fine range (Sn, Pb) respectively, and metals with several modes (Ni, Zn, Cu). In Poland, Roglowa-Kozlowska et al. (2015) reported bimodal distributions for Ni, Cu, Zn, Pb and Sb while in Changsha (China), while Pb and Cu were found to be dominant in the fine mode, other metals including Mn, Fe and Cd were found to be uniformly distributed between fine and coarse modes (Liu et al, 2015).

Several elements showed distinct time-dependent patterns. For example, the lowest concentrations of S were observed between 1800-2400 hours when the number of HDVs running on high sulphur fuel is low, while Si and Al had the lowest concentrations at night (0000-0600).

It is also important to consider that in Indian cities, land-use is mixed, and as a result, different emission sources are often found in close vicinity of each other, and this can often generate complex size distribution patterns associated with small changes in wind direction. Further, long-range transport of agricultural burning aerosols (Bisht et al., 2015; Sharma et al., 2014), as well as sources such as brick kilns which do not operate within the city limits can lead to higher PM concentrations (Guttikunda and Goel, 2013).

3.4 Fine to Coarse Ratios

The fine/coarse ratios (fine refers to < 2.5 µm and coarse 2.5-10 µm) can help in inference of source contributors, and ratio values can indicate the predominant fraction for individual species. Coarse particles are typically generated due to mechanical processes while fine particles are mainly associated with combustion (fossil fuel, biomass, waste) and industrial activities (Pant and Harrison, 2013). In the current study, fine/coarse ratios were observed to be less than unity for Al, Si, Fe, Ca, V and Mn while the ratio was greater than 1 for the other elements on average (Figure 7). The highest fine/coarse ratio was observed for Pb. In this case, elements typically associated with soil/crustal material such as Si, Al, Ca and Fe were found to be dominant in the coarse range, indicating their origin predominantly in soil and road dust. Aatmeeyata et al. (2009) reported a bimodal (peaks in fine and coarse modes) size distribution for wear and tear of concrete and tyres, and this can be another important source, particularly near roads.

Figure 7 here

Two other elements, Mn and V were also found to have a lower fine/coarse ratio compared to other elements generally associated with anthropogenic activities, which indicates probable dominance of coarse dust sources including soil, coal fly ash and construction dust. In Athens (Greece), Karanasiou et al. (2007) reported fine/coarse ratios of less than one for Cu and Al while the ratios were much higher for Cd, Pb, V, Ni and Mn.

Elements such as Cu, Zn, Pb and S were predominantly found in the fine range, and can be associated with traffic and industrial emissions as well as emissions due to waste burning. In contrast, Karanasiou et al. (2007) reported Cu to be present primarily in the coarse mode while Pb, Mn, Ni and V were reported to be predominant in the fine range. Both intrastate and interstate traffic is allowed on Mathura Road, and some of the interstate vehicles, particularly HDVs run on high sulphur fuel (350 ppm) and can be a source of primary sulphate. The highest fine/coarse ratio was observed for Pb across all time periods (8.6-19.6). Interestingly, Gargava et al. (2014) reported wood combustion as the dominant source for Pb. In addition, there is an industrial zone within a distance of three kilometres from the sampling site as well as a waste-to-energy plant. Pb was found to be present in very high concentrations, and possible sources include industrial emissions, waste incineration and small-scale Pb-battery recycling units. Additionally, burning of plastic and electronic waste can contribute to lead in ambient air, and in Delhi, aerosols generated due to burning of plastic could be a significant source of Pb. Since unleaded petrol is used in India, exhaust emissions are not considered to be a significant source of ambient Pb.

A notable feature of the data is the absence of peaks for elements such as Cu and Sb in the coarse range (3-4 μm) which have been associated with non-exhaust emissions from road vehicles (Iijima et al., 2007; Karanasiou et al., 2007; Gietl et al., 2010). However, preliminary analyses of brake pads from India suggest a markedly different composition to those from the UK and United States (unpublished data).

3.5 Enrichment Factors

In order to further understand the sources of the elements (crustal vs. anthropogenic), enrichment factors (EFs) were calculated for the fine and coarse PM modes based on continental crust concentrations using Al as the reference element (Taylor and McLennan, 1995) as described by equation 1. Results appear in Figure 8.

$$Enrichment\ Factor\ (X) = \frac{\left\{\frac{Concentration(X)}{Concentration(Reference)}\right\} sample}{\left\{\frac{Concentration(X)}{Concentration(Reference)}\right\} crustal} \qquad Eq\ (1)$$

Figure 8 here

Al has been used as a reference element in several studies, and typically, EFs less than 10 are associated with species with soil-related sources whereas EFs greater than 10 indicate contribution from anthropogenic sources. Corresponding to the other observations, highest EFs were observed for Cu, Zn, Sb, Pb, V and Mn while EFs for Si, Fe and Ca were observed to be less than 10 for both modes. However, it is important to note that the EFs for the elements associated with anthropogenic emissions were lower in the coarse mode compared to the fine mode (e.g. in the case of Cu, the EF for the fine mode was 122 while for the coarse mode, it was 5.87). This further confirms that while Si, Fe and Ca are primarily associated with crustal material, other elements including Cu, Zn, Sb, Pb and V are contributed by anthropogenic sources.

3.6 Impact of Meteorology

High levels of relative humidity lead to hygroscopic growth of water-soluble particles, which can then uptake soluble gases and be a medium for chemical reactions (Meng and Seinfeld, 1994; Wilson and Suh, 1997). This mode, referred to as the droplet mode, is often observed during fog

episodes when the RH levels are high. In the current study, meteorological conditions during the sampling period were conducive for formation of droplet-mode particles, since observed RH levels were high. Tian et al. (2014) observed this phenomenon on days with high RH in Beijing (China). Average daily relative humidities ranged from 82-97%, with a maximum of 100% on all days of the sampling. The droplet mode has also been observed in China under similar meteorological conditions (Yu and Yu, 2011).

Complementary studies of the chemical composition and source apportionment of $PM_{2.5}$ in Delhi (Pant et al., 2015) have revealed high concentrations of sulphate, chloride and nitrate in winter campaign samples. The ion balance of these data suggest that, as is normally the case, the sulphur measured in this study is predominantly sulphate. The stoichiometry of the particles is consistent with ammonium sulphate, ammonium chloride and ammonium nitrate comprising a substantial proportion of $PM_{2.5}$ mass (Pant et al., 2015). These compounds are all highly water soluble and will undergo substantial hygroscopic growth at the high humidities experienced during this sampling campaign. The aqueous droplets will also take up sulphur dioxide, which undergoes oxidation forming further sulphate. The presence of trace metals such as Pb, Zn, Cu, Sb and Mn also in the droplet mode suggests that these are either emitted as water soluble salts, or present in particles internally mixed with soluble material which enters the droplet mode. Past research (Sturges et al., 1989) has highlighted the presence of several metal ammonium sulphate salts in the atmosphere, which would be consistent with the formation mechanisms suggested above. The less prominent finer particle mode at ca 0.2 μm seen for most metals is therefore likely to arise from fresh emissions which have not undergone hygroscopic growth, or emissions in a hydrophobic form. This hypothesis needs further analysis, and measurements from sampling locations with different characteristics and pollutant loads across seasons can help shed light on the role of meteorological parameters, particularly humidity, in particle formation and growth.

4. CONCLUSIONS

PM size distribution revealed predominance of fine particles in the ambient air. Elemental size distributions indicate the dominance of crustal material and other dust sources (including road dust, construction dust) in the coarse mode, and anthropogenic (particularly combustion-associated) activities dominate in the fine mode. PM was observed to be trimodal with two peaks in the accumulation mode and one peak in the coarse mode. However, it is important to bear in mind that the concentrations and size distribution patterns reported here are representative of the winter season, and the patterns are expected to differ in the summer, particularly coarse particles. Previous studies have highlighted the differences between size distributions in summer and winter (Zhu et al., 2006).

Two modes dominate the particle size distribution. The most intense is centred around 0.6 μm and is a droplet mode containing sulphate and anthropogenic metals emitted as fine particles. The coarser, less intense mode centred around 3 μm contains mainly crustal elements and arises from coarse dust sources such as soil, road dust and construction dust, with a possible contribution from coal fly ash. The least intense mode which appears at around 0.2 μm in the mass distribution and as a shoulder in the distribution of some metals probably arises from recent emissions which have not grown into the droplet mode.

Future studies should focus on analysis on spatial as well as seasonal variability of size distributions for PM and its constituents, particularly near residential areas.

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TABLE CAPTION

Table 1 Summary of elemental size distribution data.

FIGURE CAPTIONS

Figure1 Temporal variation of traffic at the sampling site.

Figure 2 Mean diurnal variation of $PM_{2.5}$ during the study period.

Figure 3 Average mass size distribution for PM at the sampling site.

Figure 4 Average contribution (in %) of various size fractions to total PM mass.

Figure 5 Average mass size distribution of crustal elements.

Figure 6 Average mass size distribution of non-crustal elements.

Figure 7 Percentage of elements in fine (< 2.5 µm) and coarse (> 2.5 µm) ranges.

Figure 8 Enrichment factors for metals in fine and coarse fractions.

Table 1

Element	PSD type	Primary Peak	Secondary Peak(s)	Other references
Si	Unimodal	Coarse (4 µm)		
Al	Unimodal	Coarse (~3.5 µm)		
Fe	Unimodal	Coarse (~3.5 µm)		Coarse mode peak (4 µm) reported in UK (Allen et al., 2001a)
Ca	Bimodal	Coarse (4 µm)	Accumulation (0.9 µm)	
Cu	Trimodal	Accumulation (~0.55 µm)	Accumulation (0.15 µm), Coarse (~2.5 µm)	
Zn	Bimodal	Accumulation (0.7 µm)	Accumulation (0.15 µm)	
Pb	Bimodal	Accumulation (~0.55 µm)	Accumulation (0.15 µm)	Accumulation mode peak (0.5 µm) reported in UK (Allen et al., 2001a, Taiwo et al., 2014)
Mn	Bimodal	Accumulation (~0.65 µm)	Coarse (3 µm)	
S	Bimodal	Accumulation (0.9 µm)	Accumulation (~0.15 µm)	
V	Trimodal	Coarse (3 µm)	Accumulation (~0.15,0.55 µm)	
Sb	Bimodal	Accumulation (0.7 µm)	Accumulation (~0.15 µm)	

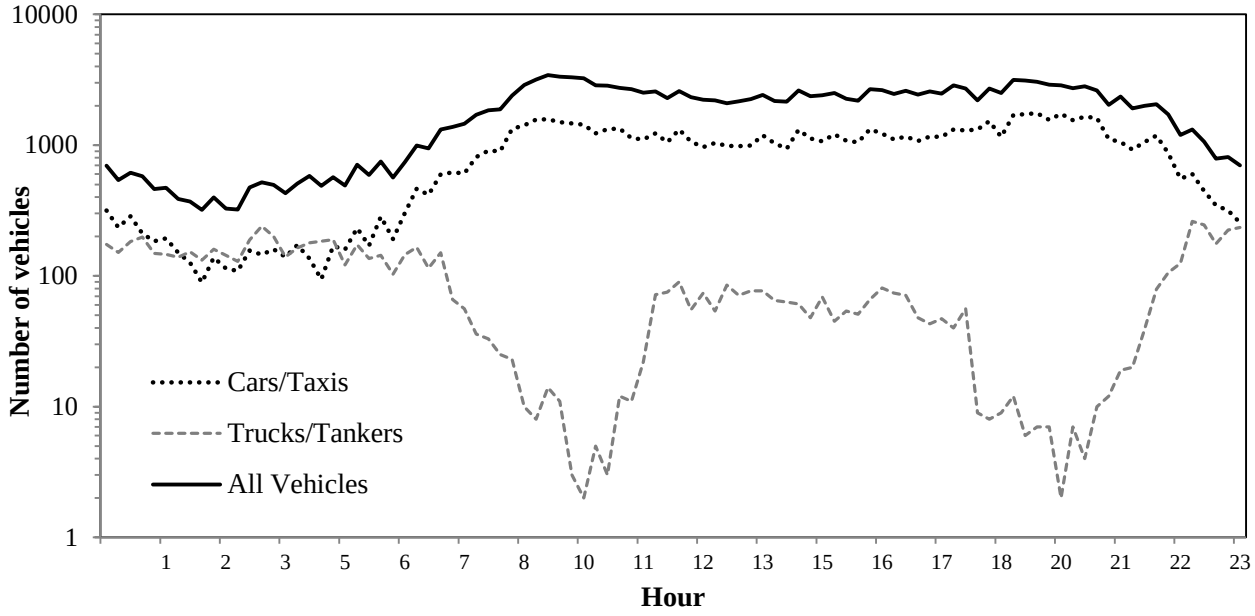
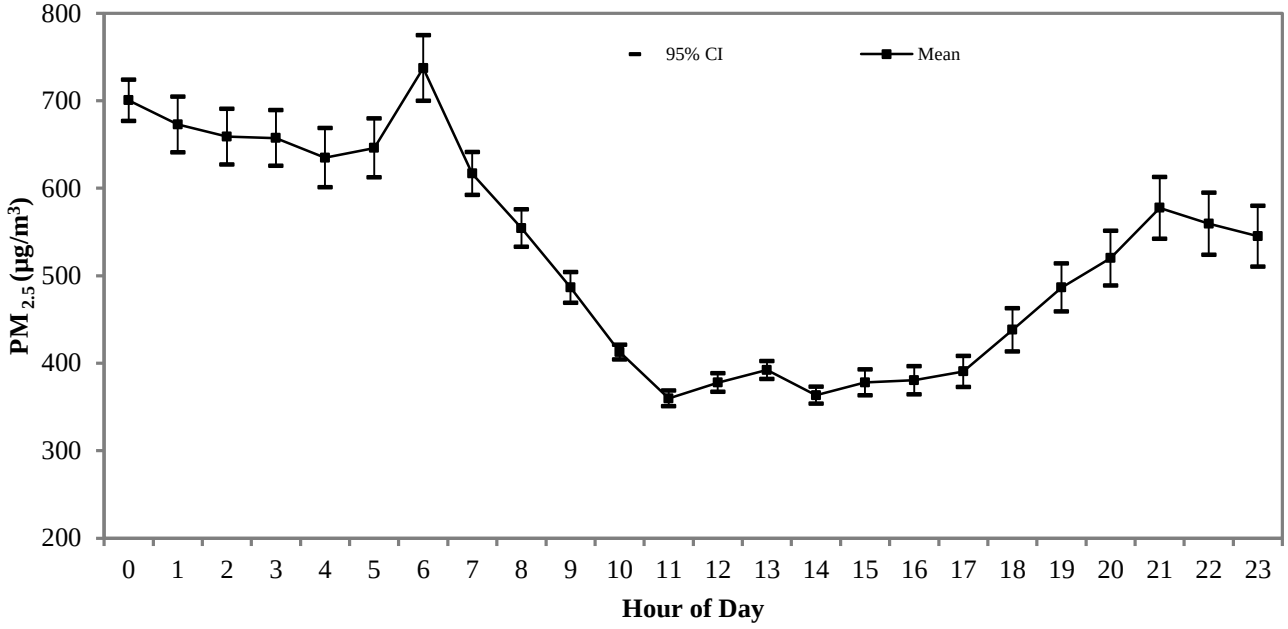


Figure 1



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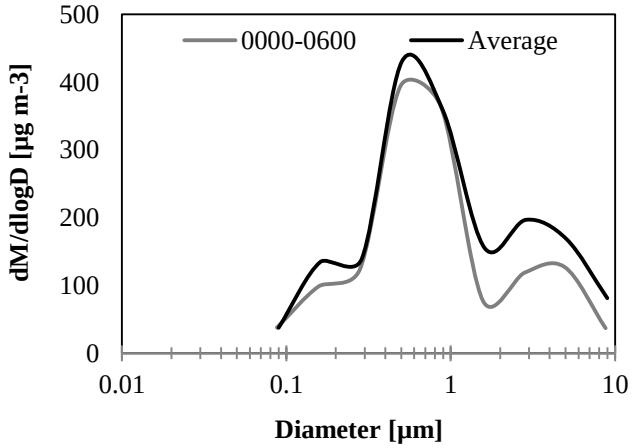
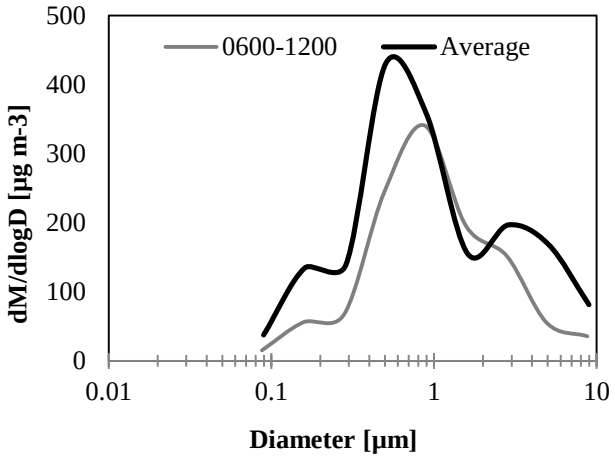
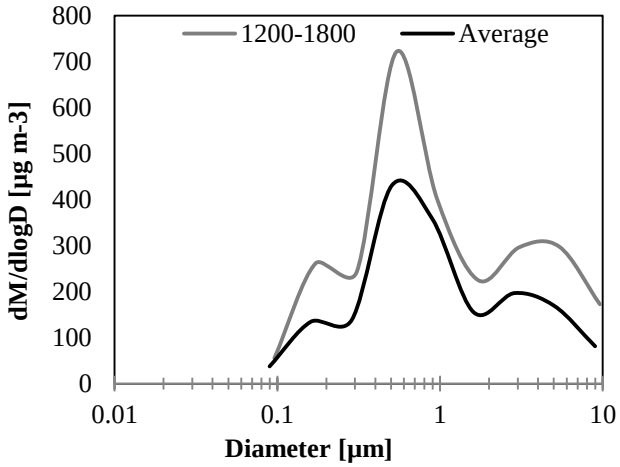

0000-0600
Average
dM/dlogD [µg m-3]
500
400
300
200
100
0
0.01
0.1
1
10
Diameter [µm]


0600-1200
Average
dM/dlogD [µg m-3]
500
400
300
200
100
0
0.01
0.1
1
10
Diameter [µm]


1200-1800
Average
dM/dlogD [µg m-3]
800
700
600
500
400
300
200
100
0
0.01
0.1
1
10
Diameter [µm]

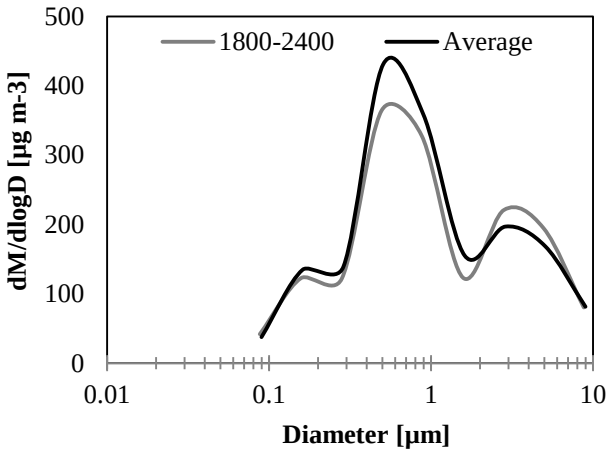

1800-2400
Average
dM/dlogD [µg m-3]
500
400
300
200
100
0
0.01
0.1
1
10
Diameter [µm]

Figure 3

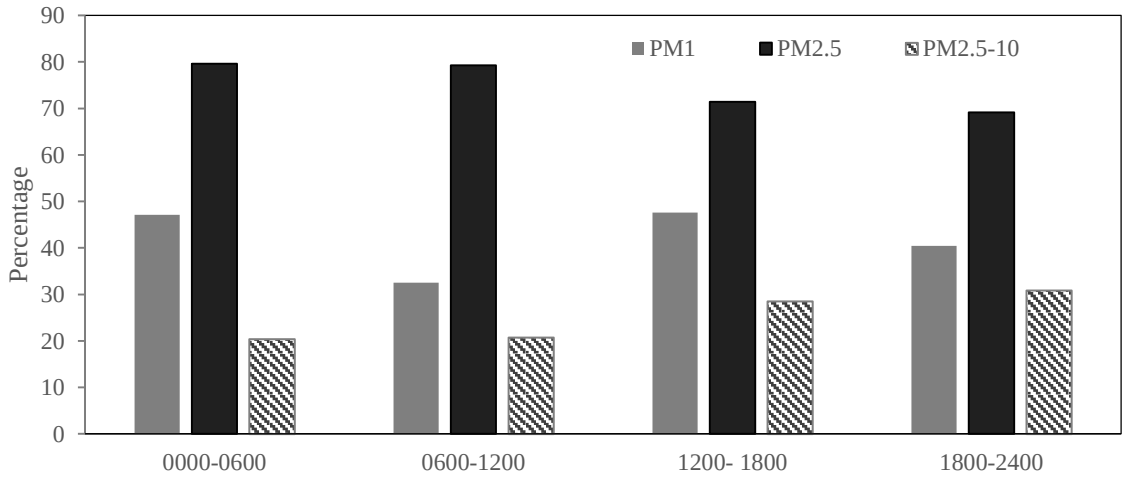

90
80
70
60
50
40
30
20
10
0
Percentage
PM1
PM2.5
PM2.5-10
0000-0600
0600-1200
1200- 1800
1800-2400

Figure 4

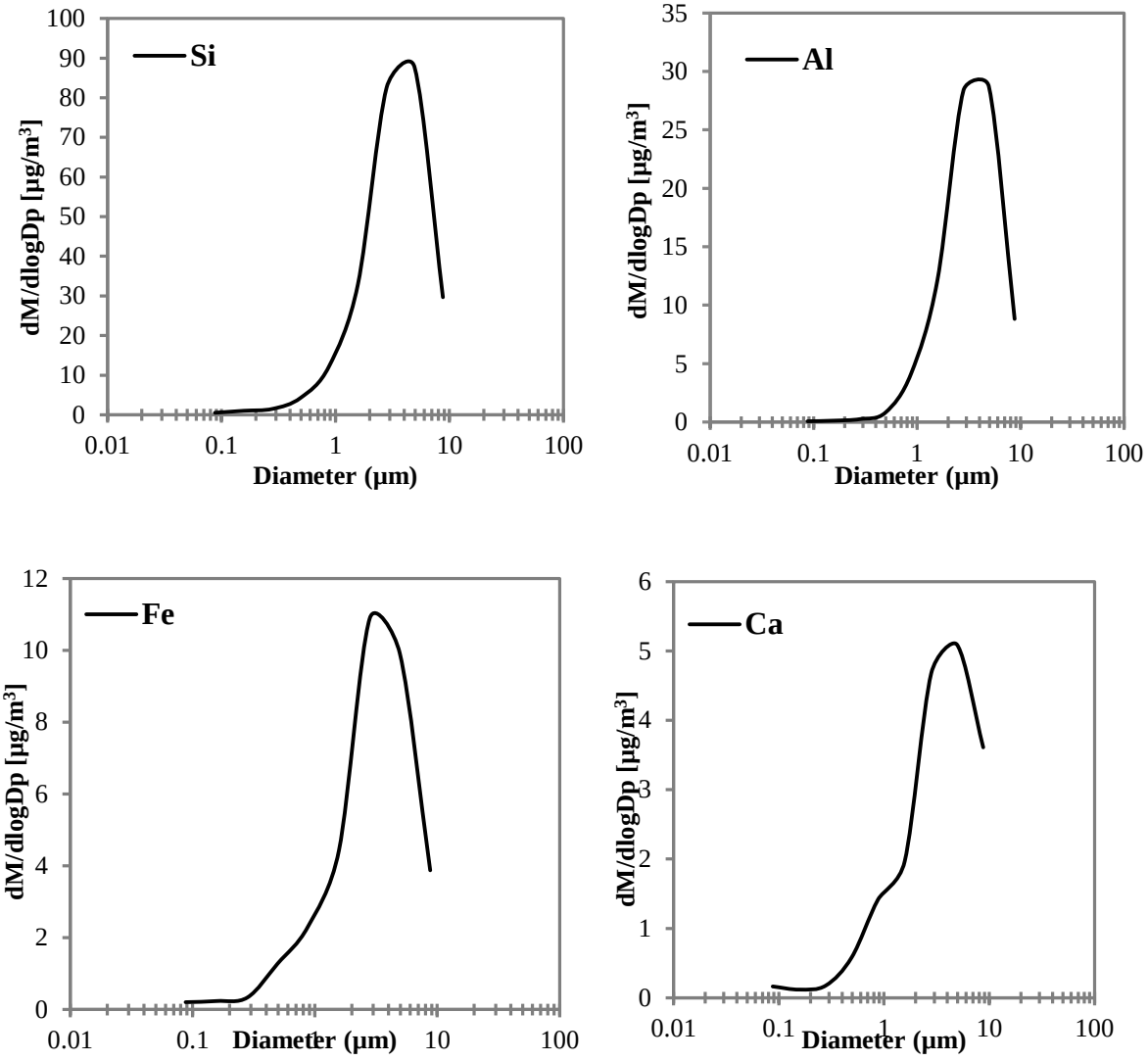
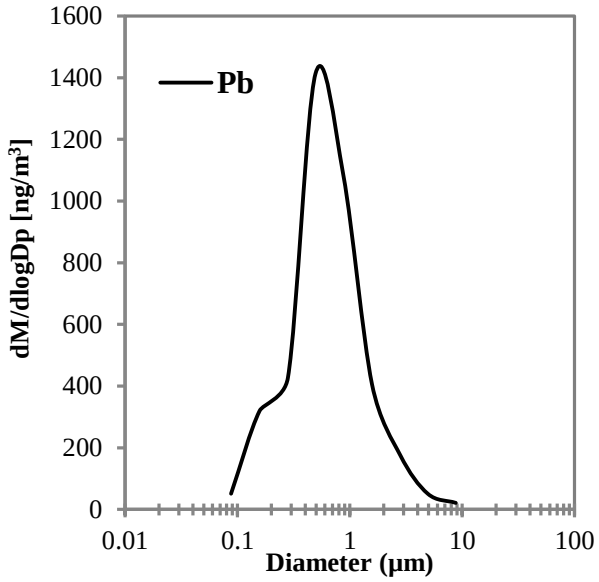
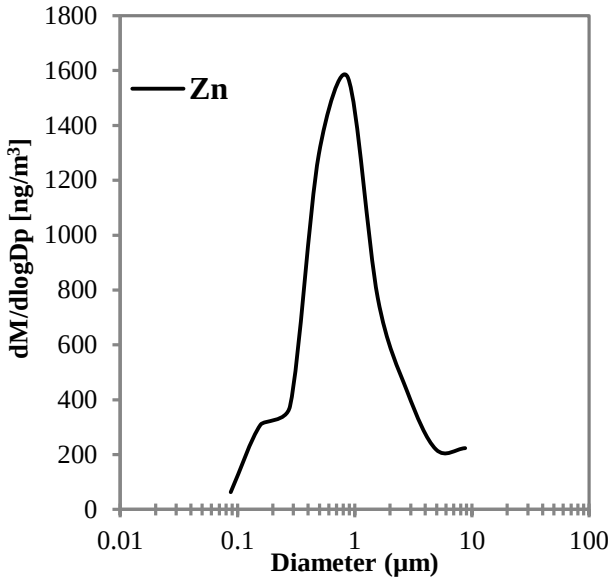
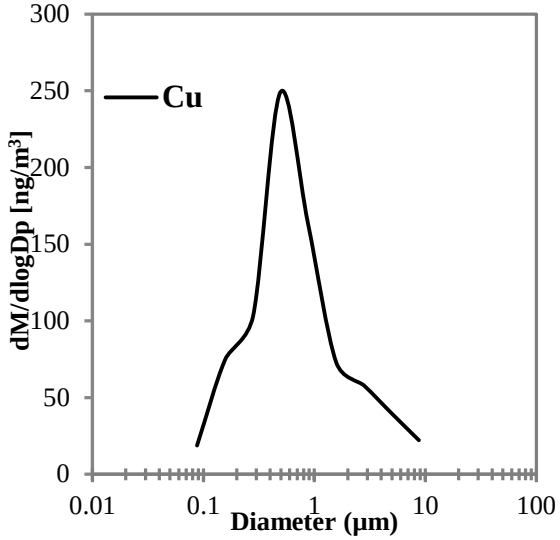
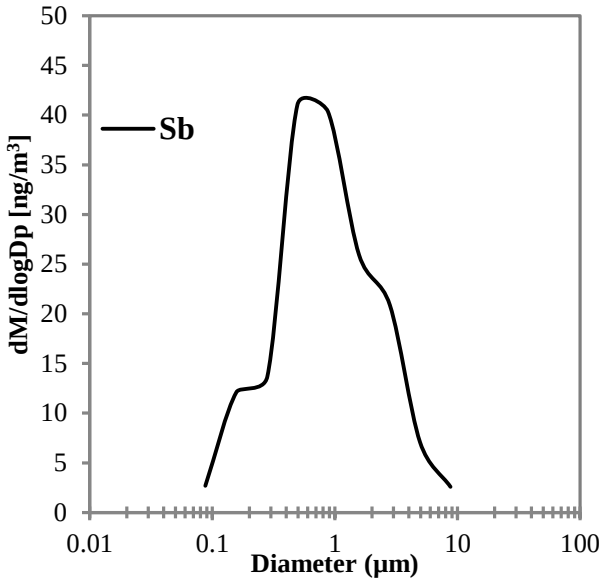

Si
dM/dlogDp [µg/m³]
Diameter (µm)
Al
dM/dlogDp [µg/m³]
Diameter (µm)
Fe
dM/dlogDp [µg/m³]
Diameter (µm)
Ca
dM/dlogDp [µg/m³]
Diameter (µm)

Figure 5


Pb
dM/dlogDp [ng/m³]
Diameter (µm)
0
200
400
600
800
1000
1200
1400
1600
0.01
0.1
1
10
100


Zn
dM/dlogDp [ng/m³]
Diameter (µm)
0
200
400
600
800
1000
1200
1400
1600
1800
0.01
0.1
1
10
100


Cu
dM/dlogDp [ng/m³]
Diameter (µm)
0
50
100
150
200
250
300
0.01
0.1
1
10
100


Sb
dM/dlogDp [ng/m³]
Diameter (µm)
0
5
10
15
20
25
30
35
40
45
50
0.01
0.1
1
10
100

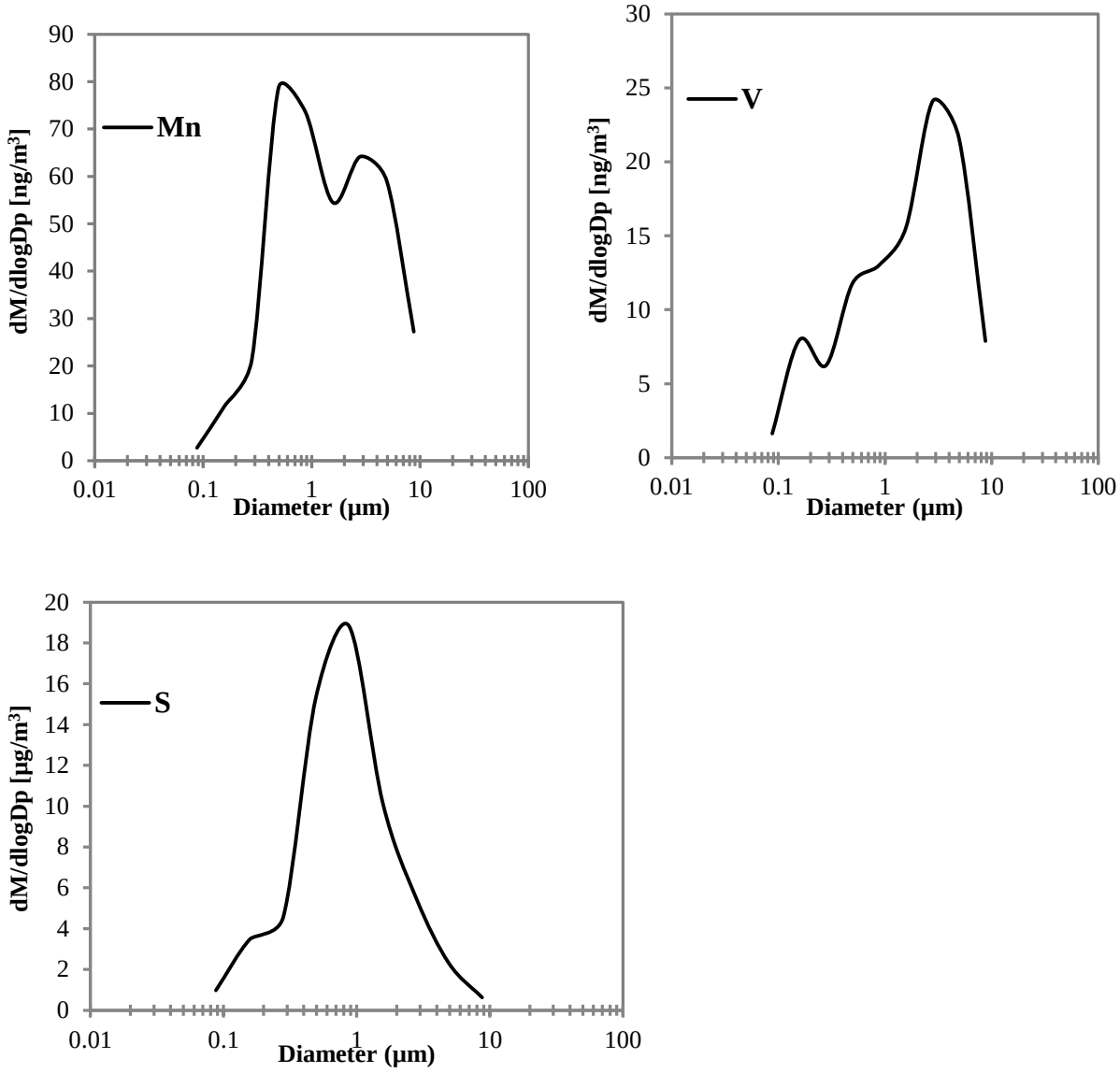

Mn
dM/dlogDp [ng/m3]
Diameter (µm)
V
dM/dlogDp [ng/m3]
Diameter (µm)
S
dM/dlogDp [µg/m3]
Diameter (µm)

Figure 6

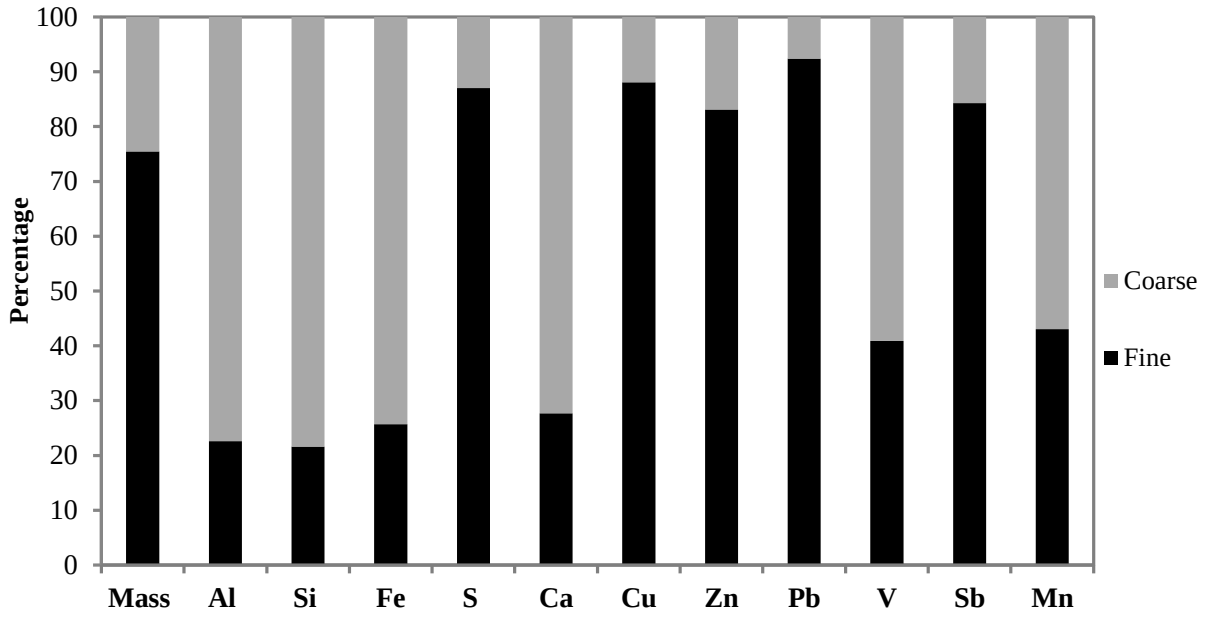


Figure 7

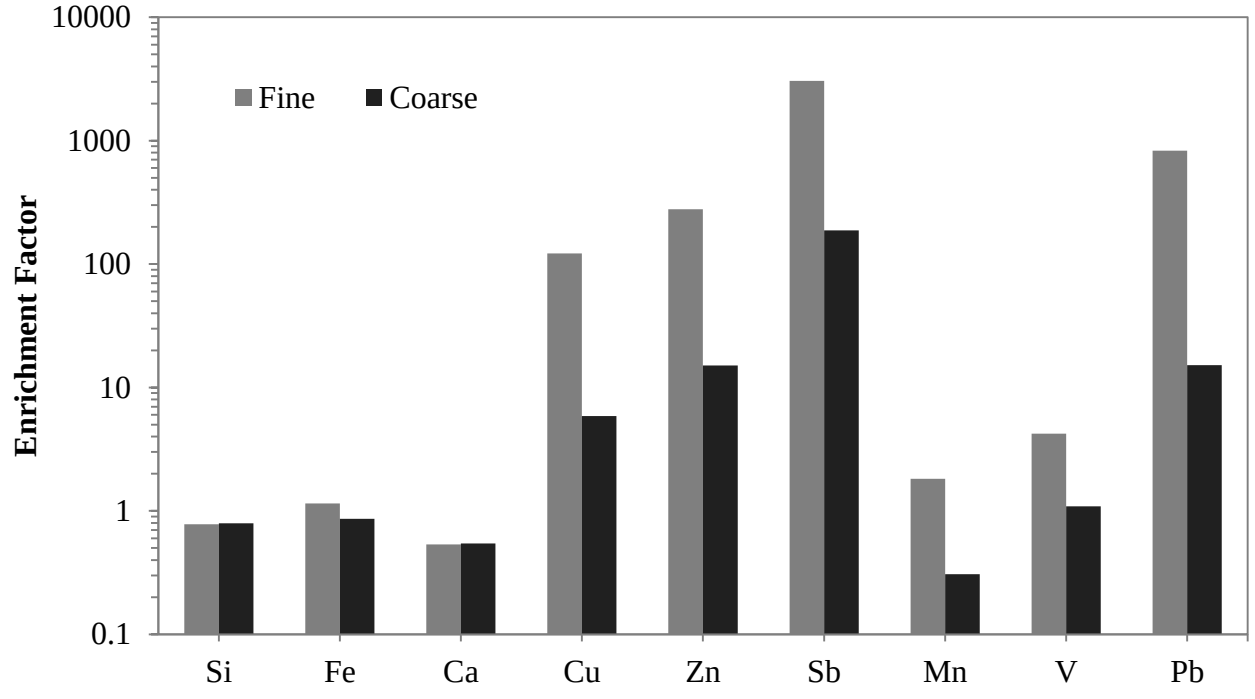


Figure 8