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Evaluation of coarse and fine particles in diverse Indian environments

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Evaluation of coarse and fine particles in diverse Indian environments

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Abstract

The estimates of airborne fine particles ($PM_{2.5}$) concentrations are possible through rigorous empirical correlations based on the monitored PM_{10} data. However, such correlations change depending on the nature of sources in diverse ambient environments and, therefore, have to be environment specific. Studies presenting such correlations are limited but needed, especially for those areas, where $PM_{2.5}$ is not routinely monitored. Moreover, there are a number of studies focusing on urban environments but very limited for coal mines and coastal areas. The aim of this study is to comprehensively analyze the concentrations of both PM_{10} and $PM_{2.5}$ and develop empirical correlations between them. Data from 26 different sites spread over three distinct environments, which are a relatively clean coastal area, two coal mining areas, and a highly urbanized area in Delhi were used for the study. Distributions of PM in the 0.43-10 μm size range were measured using eight-stage cascade impactors. Regression analysis was used to estimate the percentage of $PM_{2.5}$ in PM_{10} across distinct environments for source identification. Relatively low percentage of $PM_{2.5}$ concentrations (21, 28 and 32 %) in PM_{10} were found in clean coastal and two mining areas respectively. Percentage of $PM_{2.5}$ concentrations in PM_{10} in the highly urbanized area of Delhi was 51%, indicating a presence of a much higher percentage of fine particles due to vehicular combustion in Delhi. The findings of this work is important in estimating concentrations of much harmful fine particles from coarse particles across distinct environments. The results are also useful in source identification of particulates as differences in the percentage of $PM_{2.5}$ concentrations in PM_{10} can be attributed to characteristics of sources in the diverse ambient environments.

Keywords: PM_{10} ; $PM_{2.5}$; Cascade Impactor; Coal mining; Urban areas; Exposure risks.

1. INTRODUCTION

Exposure to high concentrations of particulate matter (PM) causes respiratory illness, cancer and increase in mortality rates (Dockery and Pope, 1994; Donaldson and MacNee, 1999; Espinosa *et al.*, 2001; Shah *et al.*, 2006a; Heal *et al.*, 2012). A large number of epidemiological studies have extensively assessed the effects due to exposure to PM (ATS, 1996; USEPA, 1999; WHO, 2000; Schneider *et al.*, 2003, Schwartz, 1994; Lipfert and Wyzga, 1995; Vedal, 1997). Recent epidemiological studies associate PM₁₀ and PM_{2.5} with increased lung or cardiopulmonary diseases (Espinosa *et al.*, 2001; Cancio *et al.*, 2008; Leili *et al.*, 2008; Dockery *et al.*, 1993; Schwartz *et al.*, 1996; Kelsall *et al.*, 1997; Pagano *et al.*, 1998). These studies also showed that PM_{2.5} is a better indicator of health exposure effects than PM₁₀ leading to increase in interest on fine fraction of particles (PM_{2.5} and PM_{1.0}) because of their strong correlations with adverse health effects (Begum *et al.*, 2010, Laden *et al.*, 2000). Using such strong indicators, the majority of countries (EU Commission, 1999; USEPA, 1997; CPCB, 2009) included standards for annual or daily PM_{2.5} concentrations. Both the size fractions (PM₁₀ and PM_{2.5}) are usually selected as the monitoring parameters for evaluations of ambient air quality standards (Bešlić *et al.*, 2004; Gehrig, 2007).

More than 3 million people prematurely died in 2010 due to ambient exposure to PM_{2.5}, according to estimates from the Global Burden of Disease Study (Lim *et al.*, 2010). Huang *et al.* (2012) studied seasonal variation of mortality risk in association with PM_{2.5} in Xi'an, China and estimated that each increase of 103 µg/m³ PM_{2.5} exposure increases 2.29% for all-cause mortality and 3.08% for cardiovascular mortality. Atkinson *et al.* (2014) studied associations of PM_{2.5} with the daily mortality and hospital admissions. They reported that for every 10 µg/m³ increment in PM_{2.5} was associated with a 1.04% increase in the risk of death. Yorifuji *et al.* (2015) observed that a reduction in long-term exposure of PM₁₀ and PM_{2.5} to 20 and 10 µg/m³ would have postponed 8% to 9% of all-cause mortality or about 37,000 deaths in 27 cities in Southeast and

East Asian countries (Japan, the Philippines, the Republic of Korea, Singapore, and Vietnam). Hao et al. (2015) studied associations between PM_{2.5} exposure during pregnancy and term low birth weight in the United States and reported that the odds of term low birth rate increased 2% [odds ratio = 1.02; 95% CI: 1.00, 1.03] for every 5µg/m³ increase in PM_{2.5}. Recent work of Kioumourtzoglou et al. (2016) observed significant associations between long-term PM_{2.5} citywide exposure on the first admission for dementia, Alzheimer disease, or Parkinson disease across the north-eastern United States. They estimated a hazard ratio of 1.08 for dementia, 1.15 for Alzheimer disease, and 1.08 for Parkinson disease admissions per 1µg/m³ increase in annual PM_{2.5} concentrations. Likewise, Extensive studies have been carried out worldwide for assessing the levels of PM exposure and its associated health impacts (Crouse et al, 2015; Zanobetti et al ,2015; Green et al, 2015; Chung et al, 2015; Hart et al, 2015; Huang et al,(2015) ; Bell et al, 2015). However, limited studies have been reported in India due to lack of PM_{2.5} data.

In India, Pande et al. (2002) conducted a survey about the visit of patients at All India Institute of Medical Sciences (AIIMS) during 1997-98 and found that visit of patients increased for acute asthma, acute exacerbation of chronic obstructive airway disease, and acute coronary events by 21.3%, 24.9% and 24.3% respectively due to higher pollution levels of CO, NO_x, SO₂. It was concluded that there is a considerable burden of cardiopulmonary diseases in Delhi due to high level of ambient air pollution. Another air pollution and health related study was carried out by CPCB (2008a, 2008b) on adults and children respectively. Odds Ratio (OR) of 2.69 (1.91-3.79) at 95% confidence interval was found to associate PM₁₀ level above 150 µg/m³ for disease related to upper respiratory system (URS). The risk factors were female gender, smoking habit, low SES, high outdoor exposure and elevated PM₁₀ level in ambient air. A similar study for children (CPCB, 2008b) of Delhi revealed odds ratio of 2.6, 2.6 and 2.09 for running nose, sneezing and common cold with PM₁₀ levels above 150 µg/m³.

Monitoring of suspended particulate matter started in 1984 in India, at the national level under National Ambient Air Quality Monitoring program to meet the regulatory compliance. Subsequently, in 1994 (CPCB, 1995), new ambient air quality regulations requiring monitoring of PM₁₀ were added. Monitoring of PM_{2.5} only started after promulgation of new air quality regulation in 2009 (CPCB, 2009). Therefore, PM monitored in India before 2009 consists of total suspended particles (measured using filtration) and PM₁₀ (measured using cyclonic separator) only (George *et al*, 2012). As a result, data of simultaneously measured PM₁₀ and PM_{2.5} is not available for that period but is important for epidemiological studies. At relatively larger scale, PM_{2.5} monitoring in India was started under six city source apportionment (SA) study. The Dust Emissions Joint Forum (DEJF) of the Western Regional Air Partnership (WRAP) has carried out studies for determining PM_{2.5} and PM₁₀ fraction of fugitive dust emissions (USEPA, 2005; Pace et al 2005). This study has determined that the PM_{2.5} is 10% of PM₁₀ for construction, agricultural operations and windblown dust. These studies were carried out using cyclone fitted high volume samplers and impactors. Subsequently these studies were repeated to improve the estimation of contribution of PM_{2.5} in PM₁₀ using Federal Reference Method (FRM) samplers for different fugitive dust including geological soils (Cowherd et al, 2010). The results shows that in unpaved road fugitive dust, PM_{2.5} is 15 to 26% of PM₁₀; in paved road fugitive dust, PM_{2.5} is 25 to 46% of PM₁₀. In the AP-42 document (2003 revision), the PM_{2.5} fraction in vehicle exhaust and brake and tire wear was found to be 76% of PM₁₀. From these studies, it can be concluded that fugitive dust from unpaved road, geological soils etc. have relatively lower PM_{2.5} component in PM₁₀ compared to vehicular exhaust dominating urban area. Thus a study in coal mine area dominated by geological material would demand PM₁₀ sampling and chemical analysis; and PM_{2.5} for area dominated by fossil fuel combustion like vehicular exhaust emission (Querol *et al*, 2001; Wilson *et al*, 2002; Harrison, 1997). Due to a variety of application of different PM sizes, it is described by different nomenclature (WHO, 2000; CEN 1993; ACGIH 2005; USEPA 1997). Please refer Supplementary Information (SI) Table S1 for details.

To correlate $PM_{2.5}$ and PM_{10} , field monitoring using either two co-located samplers (simultaneous operation), or a single sampler that measures both these fractions are required. If a correlation can be established, the levels of $PM_{2.5}$ can be obtained without its direct measurement (Brook, 1997; Castillejos, 2000; Querol *et al*, 2001; Lee and Hieu, 2011; Marcazzan *et al*, 2001), thereby limiting the number of $PM_{2.5}$ measurements at PM_{10} sites (Gehrig and Buchmann, 2003). Eight stage cascade impactor (8-SCI) is one such sampler that measures PM in nine size fractions, covering 10 to $0.43\ \mu m$, and is an economically feasible option compared with the use of two different samplers for measuring different size fractions. This is particularly important in some areas (e.g. coal mining) where availability of power and space for multiple samples at remote locations are limited and safety and security of personnel are highly important.

In this work, we monitored PM in different size ranges using 8-SCI in three distinct environments (urban, mining and coastal) along with large scale emission sources with the aim to assess and understand the underlining causes of diversity in concentrations in different environments. Monitoring at all sites were carried out during dry (no rain) season. During summer, in the tropical climate, high wind causes dust blow thereby causing apparent higher pollution, particularly in coal mine and urban area. PM size fractionation in natural environment and those generated by anthropogenic activity (vehicular emission) is analysed to identify the sources. The impact of nature like local or regional wind causing long range transport of PM is not studied. We also assessed the spatial variability of PM concentrations in different size ranges in urban, mining and coastal environments. The other aims were to develop correlations for estimating $PM_{2.5}$ from PM_{10} measurements for three distinct environments, which will be useful in determining their sources of pollution from such estimates. The chemical speciation of PM is not included in the study and therefore, source identification is purely based on size fractionation.

2. MATERIALS AND METHODS

2.1 Sites description

For estimating the $PM_{2.5}/PM_{10}$ ratios during different activities, the sites were categorised into three key groups according to their atmospheric environments (Peng et al., 2014). These groups included coastal (5 sites), mining (11 sites), and urban (10 sites) areas, as summarized in Table 1. Field measurement campaigns at these 26 different sites were performed between 2005 and 2011.

The first group (Mithapur town in Okha region) is within a coastal area of western India, which is relatively clean due to high ventilation and low level of anthropogenic activity. The second group (Chandrapur and Ghugus) was represented by a combination of two coal-mining areas where air pollution is mainly of geological origin. The third group (Delhi) is a highly urbanized area, with a large number of vehicles and is likely to have emissions of $PM_{2.5}$. Since the size specific PM data collected is for different sites during short time spans from 2005 to 2011, the data available is not continuous and is not subjected to seasonal variation study.

2.1.1 Coastal sites

Okha is a coastal pilgrimage area in the interiors of coastal border of Gujarat, India. Ambient air quality monitoring was carried out at Mithapur, an Industrial town ($22.41^{\circ}N$, $69.0^{\circ}E$, 7.0 m above the mean sea level, MSL) that is 10 km west of Dwarka towards Okha port. Mithapur is a colony that is supported by Tata Chemicals Ltd. (TCL) covering an area of 22 km^2 with a population of 10,000. The TCL produces Soda Ash and TATA Salt as its core products and uses the waste products to produce construction grade cement. Emission from the chemical plant, sea salt from the ocean, and vehicle plying between Okha and Dwarka for mainly pilgrimage purpose are expected at this site. Meteorological data for three years duration from March 2008 to February 2011 was analyzed, which revealed that the average wind speed during

winter (October) is more than 2.6 m/s and during summer (May) is 3.8 m/s. Such high wind speed (>3 m/s) provides high dilution and ventilation, resulting in relatively clean site. 8-SCI for aerosol measurement is operated at four sites – Padli (PI_c), Devpara (DR_c), Lalpur (LP_c), Surajkaradi (SK_c) and a Cement plant (CP_c) during September to October 2010. These locations were selected for capturing the human exposure.

2.1.2 Coal mining sites

Chandrapur (19.93°N, 79.13°E, 189 m above MSL), which is also known as City of Black Gold, is one of the oldest coal mines in the state of Maharashtra in India. This covers an area of 77 km² with a population of 3,20,379. The Chandrapur Super Thermal Power Station (2340 MW) is located on the edge of Chandrapur City. Coal from mines is transported through a road network around the city. As coal is easily available, most of the lower income groups prefer to use it for cooking. The city is therefore polluted due to emission from a thermal power plant and coal trading and burning activity within the city. Aerosol measurements were carried out using 8-SCI at six different sites, namely Chota Nagpur village (CH_m), and Ambhora village (AM_m), Ghutkala (GK_m), Chatrapati Nagar (CN_m), Hanuman Nagar (HN_m) and Western Coalfields Limited (WCL) Office (WO_m).

The second coal mine Ghugus is 20 km towards southwest from Chandrapur. Several coal washeries, cement plant (Associated Cement Company), Sponge Iron plant (Lloyds Metals and Engineers Limited) makes use of the available local natural resources. The town has a population of 32,654 that live in 7,438 households. Easy availability of coal has made it popular to be used at domestic level by the low-income group for cooking. Aerosol measurements were carried out using 8-SCI at five sites namely Ghugus Open Cast Office (OC_m), WCL Hospital (WH_m), VIP Guesthouse (VG_m), 11KV Substation office (SO_m) and Old View Point (OV_m).

2.1.3 Urban sites

National Capital Region (NCR, 28.61°N, 77.23°E, 293.0 m above MSL) is India's largest and the world's second largest agglomeration with a population of about 22.2 million in 2011 (Beig, 2013; Kumar et al., 2015). It is known to be highly polluted due to emission from a large number of vehicles. Nearly half of the PM₁₀ particles originate primarily from road dust (53%) while vehicular exhaust being the largest contributor to PM_{2.5} (Auto Fuel Vision and Policy 2025, 2014).

About 63,000 tons of PM_{2.5}, 114,000 tons of PM₁₀, 37,000 tons of sulfur dioxide, 376,000 tons of nitrogen oxides, 1.42 million tons of carbon monoxide, and 261,000 tons of volatile organic compounds are emitted in 2010 in Delhi (Guttikonda and Calori, 2013). There are currently 8.83 million registered vehicles compared with 4.17 million in 2004 (Transport Department, 2015).

PM measurements were carried out using 8-SCI from September to December 2005 at 10 different *urban* sites, Ashram Chowk (AC_u), Small Scale Industry (SI_u), Loni Road (LR_u), Road No. 56 (RN_u), Prahladpur (PD_u), Mayapuri (MP_u), Pitampura (PR_u), Hauz Khas (HK_u), ISBT (IT_u) and Dhaula Kuan (DK_u). During the monitoring period, construction of the flyover, underpass, metro rail, games village and bus corridor for 19th commonwealth games were underway. All the work consisted of digging of earth's surface, removal and dumping of soil, and movement of heavy machinery. All the 10 sampling locations and periods were divided into two sub-groups: (i) close to construction activity; referred hereafter as 'Delhi (road-dust)' sites (i.e., AC_u, SI_u, LR_u, RN_u, PD_u, MP_u and PR_u), and (ii) the sites influenced by vehicular emission; referred hereafter as 'Delhi (vehicle)' sites.

2.2 Cascade impactor and PM sampling

Ambient air PM sampling was carried out using one actual cubic (ACFM) Non-Viable 8-SCI (model: Thermo Andersen, GA-USA). It is a multi-orifice cascade impactor and is normally used to measure the size distribution and total concentration levels of PM gravimetrically. The

sampling instrument classifies the particles collected according to the aerodynamic diameter, which is a true measure of lung penetrability. 8-SCI used in the monitoring comprised of a pre-separator and nine aluminum stages (including a backup filter holder) that are held together by three spring clamps and gasket with O-ring seals.

Eight orifice cascades provide enough velocity for larger size particles to escape the main air flow by mass inertia. The PM laden air is then impacted upon a glass fiber substrate. Each stage in the 8-SCI is designed for eight different size fractions (10, 9.0, 5.8, 4.7, 3.3, 2.1, 1.1, and 0.7 μm). PM smaller than 0.43 μm is collected by filtration in the last stage. The final filter can be quartz, glass fiber or Teflon, depending on the type of chemical analysis required. The flow rate was maintained constant ($28.3 \pm 1\%$ lpm) throughout the sampling period of 24 hours.

The samplers were placed at a height of 2 to 3 m above the ground level. Filters were conditioned at 25 °C (45% relative humidity, RH) before and after the sampling for 24 hours. Gravimetric analysis was performed to determine different fractions of PM mass using an electronic balance with a resolution of 0.001 mg (Citizen Scaltec, SBC 22). Total PM₁₀ mass was estimated by summing up the PM mass collected in all stages. The concentration of PM₁₀ in the ambient air was estimated using the air flow rate and total time of sampling.

2.3 Statistical analysis

Inter-comparison of PM size fractions across three cities was analysed by collecting and arranging data from 8 SCI in nine different size (μm) fractions (9-10 , 5.8-9, 4.7-5.8, 3.3-4.7, 2.1-3.3, 1.1-2.1, 0.65-1.1, 0.43-0.65 and <0.43). Variability of concentrations in these size fractions across three cities and variability of concentrations within the size fractions of each city was analyzed. Statistical estimates such as mean and median, 25th percentile, 75th percentile, minimum, maximum, and ANOVA were determined using open source package, R (R Core Team, 2013).

In order to understand the cumulative distribution of the different size of PM, the size specific PM concentration data were transformed into cumulative fraction (percentage) in the respective mean size. The data of site VG_m, Ghugus is demonstrated as an example in **Table 2**. The logarithm of mean particle size on the x -axis and the cumulative fraction (percentage) of particles in that size bin on the y -axis is plotted for graphical visualization to assist in selecting appropriate tools for subsequent analysis. Regression curve using Power law model [$y = a(x)^b$] was drawn on the scatter plot and the model equations and coefficient of determination (R^2) were determined for each of the same sites. Statistical estimates such as standard error, t -value, and a p -value of model parameters (a , b) were also determined. For all the study areas, data transformation, scatter plots, regression curves, model equations and statistical analyses were performed. Estimate of percentage fraction of PM_{2.5} in PM₁₀ along with the uncertainty was determined using the model equations generated through the regression analysis.

3. RESULTS AND DISCUSSION

3.1 Spatial variability of PM size fractions

Fig. 1 illustrates the spatial variability of the PM size fractions in the three distinct environments at five different locations. From the results presented in Fig. 1, two groups of sites (i.e. Okha, Chandrapur and Ghugus as Group 1, and Delhi (road-dust) and Delhi (vehicle) as Group 2), each with different concentrations of different size fractions, can be distinguished. Group 1 shows decrease in concentrations from 9-10 μm to <0.43 μm size range whereas concentrations across size fractions among the sites in Group 2 are homogeneous.

Table 3 provides the mean and median concentrations of PM size fractions observed at the three distinct environments. Fig. 1 and Table 3 suggest that variability of concentrations of fine PM in an urban area and coal mine area, which are important in identifying the source of pollution. Further, to analyze variability within the size fractions from the Groups 1 and 2, ANOVA was run by selecting Chandrapur from Group 1 and Delhi (vehicle) from Group 2. Statistically

significant difference was observed between PM concentrations in Chandrapur at the $p < 0.05$ level for the nine different size fractions [$F(8, 171) = 39.96, p = 2.27 \times 10^{-35}$]. In the case of Delhi, PM concentrations across nine size fractions were not statistically significant as there is no statistical difference in observed PM concentrations [$F(8, 171) = 1.05, p = 0.4$]. These results from ANOVA clearly illustrate that the variability in concentrations across various PM size fractions can be used to identify the potential source contributions in different cities. Similar studies on spatial variability of particle number concentrations of aerosols across different size fractions were used to differentiate between sources (Hofman et al., 2016; Azarmi et al., 2016; Birmili et al., 2013).

3.2 PM_{2.5} estimations from PM₁₀

Fig. 2 shows the cumulative distribution of PM at different locations (Okha, Chandrapur, Ghugus, Delhi (road-dust) and Delhi (vehicle)). The x -axis shows the logarithm of particle size and the y -axis shows the cumulative amount (percentage) of PM below that size. For example, each figure shows that 100% of the collected mass in different size bin is less than 10 μm . The regression analysis using power law is found to be the best fit with R^2 values above 0.80. Table 4 shows the model parameters and statistical test result for all the sites. If the t -value is high, and p -value (probability) is very low for the model parameters 'a' and 'b', the model is said to have a good fit. Table 4 shows that the ' t ' and ' p ' values of the two parameters 'a' and 'b' suggest good model fit for all the sites. The amount of PM_{2.5} present in the PM₁₀ can be estimated using the regression equation shown in Figure 2. For example, at coastal sites, the fraction of PM_{2.5} in PM₁₀ is 21% ($R^2=0.87$) as estimated from $[PM_{2.5} = 6.84(2.5)^{1.22} \times PM_{10}]$. It is concluded that in a relatively clean coastal area, PM_{2.5} can be estimated as 21% of monitored PM₁₀ with $\pm 5\%$ standard deviation.

3.3 Source identification using PM_{2.5} fraction

An attempt has been made to identify the sources of PM from the estimated fraction of $PM_{2.5}$. Keuken et al. (2013) identified sources of $PM_{2.5}$ and $PM_{2.5-10}$ for the city of Rotterdam, the Netherlands, using PM speciation. It is concluded that finer fraction are primary and secondary PM from vehicular emissions and the coarse fraction usually from re-suspension of road dust and geological material. Table 5 presents the summary of the analysis consisting of percentage fraction of $PM_{2.5}$ in measured PM_{10} with predominant local activities at different sites (Fig. 3). If the $PM_{2.5}$ fraction at any site is low ($\leq 21\%$), as in Okha, it can be interpreted that the site is not dominated by anthropogenic combustion activity such as emissions from road vehicles. On the contrary, if the $PM_{2.5}$ fraction at any site is relatively high ($\geq 50\%$), such as on the Delhi (vehicle), the data at such sites can be interpreted as dominated by anthropogenic combustion activity.

Source identification using particle size distribution has been attempted in the past. For example, Kikas and Tamm (1996) correlated shape of the distribution of geometric standard deviation (GSD) of PM concentration in each size range with the ‘urban’ and ‘rural’ sources. Different shapes of GSD distributions indicated the presence of different emission processes that control the size distribution of particles. This study also identified the concave shape of the GSD distribution for urban emissions and convex shape for rural emissions. Later, Chelani *et al* (2010) applied the same approach and concluded that the distribution of GSD for a curb site is concave and that for the industrial and residential site is convex. While this approach does not reveal the nature of rural and urban emission, it provides some lead on source identification technique. Site-specific source identification using the particle size ratio ($PM_{2.5}/PM_{10}$) derived from particle size distribution is presented in each site type separately in the following sections.

Coastal sites: $PM_{2.5}$ was 21% of PM_{10} in the studied coastal area, Okha (Tables 4 and 5; Fig. 3). These fine particles in the coastal area are likely to be formed by both natural (sea salt spray) and local anthropogenic (vehicular emission, biomass burning) activities. Since the Mithapur town is an extension of a chemical plant, having some minor commercial establishments to support the

residents of the township, there is no significant source of pollution in the town. Therefore, at any site, if the ratio of the concentration of $PM_{2.5}$ and PM_{10} is near 0.21, it can be interpreted that the site is less polluted by anthropogenic activity and is the relatively clean area.

Coal mining sites: In coal mining areas of Chandrapur and Ghugus, the fraction of $PM_{2.5}$ was 28 and 32% of PM_{10} , respectively. In Chandrapur, coal mines are on the eastern side at the outer periphery of the city while in Ghugus, which is a relatively small town is at the edge of a coal mine and permits coal transport and related ancillary activity (Sections 2.1.2). An increase in the $PM_{2.5}$ fraction indicates increased anthropogenic activity resulting in the formation of fine particles compared with those in the clean coastal area. Anthropogenic activities in coal mining areas include blasting for loosening the topsoil, removal of overburden, loading and unloading, coal transportation by road and rail, coal trading, domestic combustion, and small-scale commercial activity (Gautam *et al.*, 2014; Patra *et al.*, 2015). Mining also leaves large tracts of land with loose soil that gets lifted up during high wind or under the vehicle wake on the haul road. Except for coal combustion, all the other activities in the mining area release dust of geological origin, mostly coarse particles, accompanied with a small fraction of fine particles. Coal combustion releases primary coarse and fine particles, together with gaseous pollutants, which undergo chemical transformation to form secondary fine particles. The fraction of $PM_{2.5}$ in the mining area suggests that even though the overall concentration of PM_{10} in mining area is high, the fraction of $PM_{2.5}$ remains the same as that of a clean area. Concentrations of $PM_{2.5}$ in PM_{10} can be visualized using a paired box plot of concentration of PM_{10} and $PM_{2.5}$ (Fig. 4).

Urban sites: Monitoring at Delhi was carried out at two types of sites: Delhi (road-dust) and Delhi (vehicles), as explained in Section 2.1.3. The fraction of $PM_{2.5}$ in PM_{10} at the site dominated by vehicular emission had a very high fraction (51%) compared to only 34% at the Delhi (road-dust). This primarily indicates that the emission from combustion of gasoline, diesel, and CNG (liquid and gaseous fuel) consists of a relatively large fraction of $PM_{2.5}$. Conversely, it

can be stated that if $PM_{2.5}$ fraction of PM_{10} is high, the possible source could be fuel combustion in road vehicles. On the other hand, if $PM_{2.5}$ fraction is low, the possible source of emission is geological material in the absence of any other anthropogenic sources. Venkataraman *et al.* (2005) reported that fine particles are emitted from sources like biomass burning, domestic fuel, thermal power plants, brick kilns, and fossil fuel burning and vehicular exhausts. Combined emission from vehicular exhaust and road dust re-suspension in Delhi may cause relatively higher PM levels compared to coal mine area having emissions, mostly consisting geological material (George *et al.*, 2010).

Comparison of our results with literature show similar conclusions. For example, Nguyen *et al* (2010) used an 8-SCI at an urban site in Nam-Gu (Ulsan, Korea) during April to August 2008. They found $PM_{2.5}$ fraction in PM_{10} as 55%, which is fairly close to the observation made in our study at Delhi. Similar studies were carried out using Beta Attenuation Monitor (BAM) at 11 different places in Delhi. These sites were part of SAFAR Monitoring Network in Delhi during 19th Commonwealth Games. The $PM_{2.5}$ fractions in PM_{10} from these studies are summarized in Table 6. It can be observed from Table 6 that for an urban site more than 40% of PM_{10} is $PM_{2.5}$, which is fairly close to our observation (51% and 34%) at Delhi.

4. SUMMARY AND CONCLUSIONS

Size-resolved PM in ambient air at 26 sites spread over three groups of the coastal area, coal mining, and urban areas were monitored. Spatial variability of PM concentrations in different size fractions was analyzed. The concentrations were homogeneous at the two urban locations of Delhi. A decreasing variability of particle size was observed in the two coal mining areas and coastal area (pl. refer Fig. 1). These observations can help in identifying the regional background and local sources from particle size fractions variability. Regression analysis was applied to the data collected in eight different size ranges to estimate the fraction of $PM_{2.5}$ present

1 in PM₁₀. In clean coastal areas, PM_{2.5} was 21% of PM₁₀, which increased to 28 and 32% in two
2 different mining areas. The urban area dominated by the excavated geological material showed
3 similar PM_{2.5} fraction to those observed in the mining areas. It is concluded that PM_{2.5}
4 contributed approximately half (~51%) of the PM₁₀ in vehicular emissions dominated urban
5 areas. Having information on aerosol size distribution is crucial for assessing the respiratory
6 deposition, and hence the health outcomes, which could differ from diverse environmental
7 conditions. For example, at times, PM₁₀ concentration in mining area may be high, but with the
8 lower PM_{2.5} fraction, it may not be as detrimental to health as in an urban area dominated by
9 vehicular emission with a relatively higher fraction of PM_{2.5}.

10 The findings from the data analysis of PM fractions is acceptable within the boundary of
11 uncertainty involved in the monitoring technique. This uncertainty is due to fluctuation in
12 sampling flow rate, filter paper conditioning, weighing, and efficiency of sample collection added
13 with relatively smaller sample size. PM_{2.5}/PM₁₀ ratio can be included in the data analysis for
14 monitoring stations that uses BAM or Thermo-Electrical Oscillating Microbalance (TEOM),
15 which generates data at higher frequency and accuracy with relatively lesser uncertainty. Based
16 on the PM_{2.5}/PM₁₀ ratio, the nature of source can be assessed. If the ratio is high, increased
17 anthropogenic emission can be suspected and accordingly, sources can be identified.

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List of Tables

Table 1. Summary of information providing a description of measurement sites in three distinct environments. Please note that the words in parenthesis against each site represent a short name of each site, and subscripts u, m and c indicate urban, mining and background/coastal, respectively.

Type	City/ Town	Sites	Sampling period
Urban	Delhi	Ashram Chowk (AC _u)	September – October 2005
		Small Scale Industry (SI _u)	September – December 2005
		Loni Road (LR _u)	September – October 2005
		Road No. 56 (RN _u)	September – December 2005
		Prahladpur (PD _u)	November – December 2005
		Mayapuri (MP _u)	September 2005
		Pitampura (PR _u)	October – December 2005
		HauzKhas (HK _u)	November 2005
		ISBT (IT _u)	October – November 2005
Mining	Chandrapur	DhauraKuan (DK _u)	September 2005
		WCL Office (WO _m)	May 2010; February 2011
		Ghutkala (GK _m)	May 2010; February 2011
		Chatrapati Nagar (CN _m)	May 2010; March 2011
		Hanuman Nagar (HN _m)	May 2010; March 2011
		Chota Nagpur (CH _m)	May 2010; February 2011
		Ambhora (AM _m)	May 2010; February 2011
	Ghugus	Substation office (SO _m)	May 2011; February 2012
		Old View Point (OV _m)	May 2011; February 2012
		Open Cast Office (OC _m)	May 2011; February 2012
		WCL Hospital (WH _m)	May 2011; February 2012
		VIP Guesthouse (VG _m)	May 2011; February 2012
Coastal/ Background	Okha/ Mithapur	Padli (PI _c)	September to October 2010
		Devpara (DR _c)	
		Surajkaradi (SK _c)	
		Cement plant (CP _c)	
		Lalpur (LP _c)	

Table 2. Transformation of size specific PM concentrations to cumulative fraction (%) at VG_m, Ghugus.

Cascade Stage	Size Range (μm)	Mean Size (μm)	Concentration (μg/m³)	Frequency (%)	Cumulative fraction (%)
0	9 to 10	9.5	68.95	25.35	100.00
1	5.8 to 9	7.4	65.86	24.22	74.65
2	4.7 to 5.8	5.25	27.10	09.96	50.43
3	3.3 to 4.7	4.0	42.72	15.71	40.47
4	2.1 to 3.3	2.7	20.99	07.72	24.76
5	1.1 to 2.1	1.6	12.17	04.47	17.04
6	0.65 to 1.1	0.9	05.50	02.02	12.57
7	0.43 to 0.65	0.55	13.59	05.00	10.55
Backup Filter	<0.43	0.4	15.09	05.55	05.55

Table 3: Statistical analysis of the PM size fractions.

Chandrapur									
PM Size range (μm)	9-10	5.8-9	4.7-5.8	3.3-4.7	2.1-3.3	1.1-2.1	0.65-1.1	0.43-0.65	<0.43
Minimum	24.62	23.07	11.57	15.28	6.94	8.08	0.56	0.28	0.50
Mean	63.72	50.47	29.18	31.46	19.72	16.48	15.78	9.89	12.72
Maximum	130.89	86.67	53.33	43.51	28.89	29.64	40.49	27.77	26.10
1 st Quartile	48.38	35.64	20.13	25.53	13.71	12.58	7.42	2.01	6.72
2 nd Quartile	59.26	53.37	30.00	31.69	20.41	16.29	15.08	10.26	13.37
3 rd Quartile	79.51	53.37	37.87	39.79	25.98	21.01	20.93	15.06	19.08
Ghugus									
Minimum	17.23	26.55	12.00	14.02	19.07	4.76	5.50	8.05	11.24
Mean	79.78	75.80	49.40	50.68	36.59	22.92	16.08	15.55	24.95
Maximum	135.25	127.89	115.58	89.21	52.58	43.68	30.39	24.35	42.45
1 st Quartile	47.73	43.32	25.65	39.61	23.51	11.73	6.89	11.92	18.24
2 nd Quartile	75.01	75.45	44.61	51.74	40.88	22.97	18.36	15.18	21.32
3 rd Quartile	125.23	111.47	63.65	60.12	49.20	32.62	21.63	19.01	35.05
Okha									
Minimum	6.70	8.01	6.68	13.35	12.00	2.67	2.67	0.00	0.00
Mean	84.98	68.68	28.88	38.67	20.34	13.46	9.23	3.83	3.94
Maximum	355.2	288.46	82.80	85.47	34.70	24.04	18.70	16.00	9.00
1 st Quartile	31.62	35.52	15.35	22.03	13.65	6.46	3.09	1.67	1.67
2 nd Quartile	48.41	38.72	22.13	34.72	19.46	14.02	9.710	2.67	4.13
3 rd Quartile	79.46	55.22	32.38	46.29	24.83	19.69	13.23	2.85	5.34
Delhi (road-dust)									
Minimum	1.51	6.17	2.78	7.10	9.61	10.87	9.36	3.03	4.00
Mean	84.58	73.79	42.94	55.37	43.35	65.83	54.24	19.57	14.92
Maximum	376.02	305.35	120.21	151.31	86.98	172.15	195.41	63.73	48.00
1 st Quartile	15.04	20.92	15.77	31.52	25.52	20.87	12.63	5.86	5.79
2 nd Quartile	28.82	43.43	32.64	38.97	35.88	42.10	42.82	11.56	11.57
3 rd Quartile	131.33	86.53	63.39	76.96	63.90	115.55	71.02	29.01	20.00
Delhi (vehicle)									
Minimum	2.92	4.30	3.07	0.28	1.03	4.07	4.83	3.60	5.92
Mean	52.53	39.81	29.52	33.21	32.65	48.15	39.80	33.35	38.92
Maximum	321.14	190.60	171.38	186.33	189.27	180.46	171.65	147.09	134.01
1 st Quartile	7.97	6.13	6.36	1.80	5.29	13.12	7.25	8.14	8.65
2 nd Quartile	15.52	15.26	17.17	20.44	15.52	27.97	30.69	14.44	17.09
3 rd Quartile	58.34	47.40	22.83	35.28	36.27	75.27	46.82	54.67	51.51

Concentration in $\mu\text{g}/\text{m}^3$

Table 4. Model parameters and statistical test values for different sites.

No.	Statistical parameters	Okha	Chandrapur	Ghugus	Delhi (road-dust)	Delhi (vehicle)
1	‘a’	6.85	12.12	15.52	14.06	29.39
2	Std. Error of ‘a’	0.51	0.55	0.60	0.67	1.15
3	<i>t</i> - value for ‘a’	13.36	21.94	25.60	20.82	25.57
4	<i>p</i> - value of ‘a’	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
5	‘b’	1.22	0.93	0.81	0.98	0.60
6	Std. Error of ‘b’	0.05	0.55	0.03	0.03	0.03
7	<i>t</i> -value for ‘b’	21.86	21.94	27.65	27.24	20.60
8	<i>p</i> - value of ‘b’	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
9	Beta	0.93	0.89	0.95	0.95	0.90
10	PM _{2.5} /PM ₁₀	6.84(2.5) ^{1.22}	12.11(2.5) ^{0.92}	15.51(2.5) ^{0.8}	14.06(2.5) ^{0.976}	29.39(2.5) ^{0.60}
11	Range (%)	21±5	28±4	32±4	34±6	51±7

Table 5. The fraction of PM_{2.5} in measured PM₁₀ with predominant local activities at different sites.

No.	Place	PM _{2.5} = % of PM ₁₀	Predominant Activity
1.	Okha	21±5	Coastal area
2.	Chandrapur	28±4	Coal Transportation, Power Plant
3.	Ghugus	32±4	Coal Mining, Coal Transportation
4.	Delhi (road-dust)	34±6	Construction, Vehicular Emission, Gas based Power Plant
5.	Delhi (vehicle)	51±7	Vehicular Emission, Gas based PP

Table 6. Summary of results on PM_{2.5}/PM₁₀ obtained from studies during CWG.

Author	PM _{2.5} /PM ₁₀	Equipment	Sites
Beig et al. (2013)	DU> 50 % MDNS> 30 % IITM> 50 %	BAM	Delhi University (DU), Major Dhyanchand National Stadium (MDNS) and Indian Institute of Tropical Meteorology (IITM), Delhi.
Kaushar et al. (2013)	Overall> 40 %	BAM	11 sites from SAFAR Monitoring Network.
Marrapu et al. (2014)	Overall> 45%	BAM	11 sites from SAFAR Monitoring Network.
Bist et al. (2013)	Overall> 45 %	BAM	11 sites from SAFAR Monitoring Network.
This work	Vehicle> 50% Road Dust > 30%	8 SCI	Please see Table 1 of this paper.

Figures

Fig. 1: PM concentrations variability across nine size fractions at different sites.

Fig. 2: Cumulative particle size distribution at (a) Coastal site, Okha, (b) Coal mining site-1, Chandrapur, (c) Coal mining site-2, Ghugus, (d) Urban site-1, Delhi (road-dust), and (e) Urban site-2, Delhi (vehicle).

Fig. 3: Fraction (%) of $PM_{2.5}$ in measured PM_{10} in distinct environments.

Fig. 4: Comparison of PM₁₀ and PM_{2.5} concentration in distinct environments.

Supplementary Information

Table S1. Criteria for defining ambient air particulate matter.

No.	Definition	Criteria	Agency
1.	Suspended Particulate Matter (SPM) Total Suspended Particulates (TSP) Black Smoke	Sampling and / or Analytical Methods	(USEPA, 1986)
2.	Alveolar (PM _{2.5}) Tracheobronchial (PM _{2.5-10}) Nasopharyngeal (PM ₁₀)	Site of Deposition in Respiratory Tract	(CEN, 1991, 1993), (ISO, 1991), (ACGIH, 1994, 2005)
3.	PM ₁₀ PM _{2.5} PM _{1.0}	Aerodynamic Diameter (μm)	(USEPA, 1997)
4.	Thoracic fractions (D ₅₀ =10μm) Respirable fractions (D ₅₀ =4μm) Inhalable fractions (D ₅₀ =100μm) Extrathoracic fractions (Inhalable minus Thoracic) Tracheobronchial fractions (Thoracic minus Respirable)	Penetration into Respiratory Tract	(CEN, 1991, 1993), (ISO, 1991), (ACGIH, 1994, 2005)

Evaluation of coarse and fine particles in diverse Indian environments

Ref.: Ms. No. ESPR-D-16-03056; Environmental Science and Pollution Research journal.

Reviewer #2:

The manuscript analyses mainly PM10 and PM2.5 in three environments and computes the ratio of two to identify the possible source signature of these environments. The statistical techniques are used very meticulously to get the required information which is much needed in the present scenario of India. The paper merits publication in the journal with few minor revisions. Author needs to be careful of writing style with appropriate use of tenses. The manuscript should be written either in present or past tense.

- 1) Pg. 1, L32: Developing - replace with develop

Suggested change incorporated.

- 2) Pg. 1, L27-37: break the text into two sentences

Suggested change incorporated.

- 3) Pg. 2, L24-33: repetitive text may be avoided

Repetitive text removed.

- 4) Pg. 3 L57: replace bins with fractions

Suggested change incorporated.

- 5) Pg. 9, L15: there is no need to again mention the software package R

Needful done.

- 6) Pg. 9, L48-49: changed only - pl. elaborate it

Sentence rewritten for better understanding.

- 7) Pg. 10, L57-replace uncertainty with standard deviation

Replaced as suggested.

Evaluation of coarse and fine particles in diverse Indian environments

Ref.: Ms. No. ESPR-D-16-03056; Environmental Science and Pollution Research journal.

Reviewer #3:

This manuscript is trying to present a possible route for PM_{2.5} estimation out of the PM₁₀ data measured at various sites in the Delhi area. At a first glance the manuscript seems to impress by the number of the monitored sites but (26 sites), however, it lacks details which might increase the confidence into the data analysis session. The performed study has generated to some extent interesting results although the redundancy of the monitored sites does not significantly increase the quality of the manuscript.

Although in a more critical debate I would have many scientific issues to rise up with regard of the manuscript content, considering the importance of the subject at a wider scale, I would recommend this work for publication in the Environmental Science and Pollution research journal only after the author would undertake major revision of the manuscript.

To my opinion the author must take into account for the revised version also the following comments:

- 1) Considering the content of the manuscript the title does not reflect the main idea since "urban roadsides, coastal and coal-mine environments" might let the possible reader to think of any world-wide location. Even in the title the authors should be more specific.

We have changed the Title to:

"Evaluation of coarse and fine particles in diverse Indian environments"

- 2) The abstract needs improvements as well. Information like "PM_{2.5} found to be 21, 28, 32 and 51% of PM₁₀ in clean coastal, mining, and highly urbanized areas, respectively" makes the reader ask him/her-self what would be the way these number and environments are associated. Even the next sentence is confusing. The last sentence from the abstract should be removed or rewarded since within the manuscript are not given data to sustain how much is the harm and risks induced by the particulate matter fraction (within the manuscript there are no epidemiological data).

As suggested, we have now updated the abstract and the last line on health problem deleted

- 3) The introduction is focusing too much on information related to health aspects (from epidemiological or mortality risk assessment studies in other regions of the world) while the author is not giving enough attention to what could be measured in Delhi' area or in India up to this moment (especially in terms of the particles mass concentration atmospheric burden).

Air pollution and health related studies carried out for Delhi is now incorporated in the introduction.

- 4) Also in the Introduction section the assessment related to "besides determining their sources of pollution from such estimates" is disregarded since the manuscript is not presenting any details related to the chemical composition of the collected particulate matter samples there are only suppositions).

Appropriate changes made.

- 5) Problems occur also due to the lack of consistency in using the same terminology within the text. See for example "Delhi (road dust)", "Delhi (vehicle)" or "Delhi vehicular", "Delhi geological". What's the role of a,b, c,...in the Figure 1 captions?

All terms made consistent by appropriate replacements in text and figures.

- 6) The author describe the cascade impactor but since the estimation of the PM mass concentration is a gravimetrically based procedure a short paragraph should be dedicated to particles mass measurements.

Section 2.2 provides PM concentration determination.

- 7) For the "open source package, R (R, 2008)" clear indication should be given for the reference.

Citation updated

- 8) Moreover, the author refers to Figure 2 prior using Figure 1 in the text.

Material and Methods section describes the statistical analysis and regression curve proposed for power law, which is applied on this data and presented in Fig. 2.

Fig. 1 is referred on page 9 followed by Fig. 2 on page 10.

- 9) The example given in Table 2 shows that particle larger than $2.1\ \mu\text{m}$ are dominating but what about other sites? Are the behaviours at the investigated sites clearly reflected by the details in Fig. 1?

Fig. 1 reflects the behaviours at each site and has been discussed in section 3.1

- 10) The information in Table 3 would become more relevant if graphically presented.

Fig. 1 shows the same using box-whisker plot.

- 11) The assertion "In case of Delhi, PM concentrations across nine size fractions were not statistically significant" sounds unclearly.

Elaborated in the same paragraph.

- 12) The author should revisit also the "PM_{2.5} estimations from PM₁₀" section and check for the used fitting equation.

Fitting equation given in the referred section is correct. However, this has helped identifying another error in Fig. 2, which is now changed with appropriate description of x and y. Thank you for pointing out.

- 13) Although for the "Source identification using PM_{2.5} fraction" section an important fraction of the work is given, the opinion is that the interpretation is poor, redundant in assumptions with no clear evidences in order to sustain author's point of view.

Source apportionment study involving detailed chemical speciation of PM would yield better evidence to sustain the view that fine fraction of PM is from anthropogenic emission (combustion, vehicular) and coarse fraction of geological origin. Reference to this is now

included in the revised manuscript. In this study, source identification is attempted using size fraction of PM only.

- 14) For the mechanism proposed to be used for "Source identification using particle size distribution" there are two references given which to some extent might explain the possible correlation between "shape of the distribution of geometric standard deviation (GSD) of PM concentration in each size range with the 'urban' and 'rural' sources", but the chemical analysis could do much more.

Authors agree that the chemical analysis is useful for source determination. However, the size distribution and size fraction approaches are used by past studies where detailed chemical analysis of PM is not available. The chemical characterisation is not available in our case also and therefore adopted this approach.

Evaluation of coarse and fine particles in diverse Indian environments

Ref.: Ms. No. ESPR-D-16-03056; Environmental Science and Pollution Research journal (ESPR).

Reviewer #4:

The aim of the manuscript is to establish empirical correlations to estimate PM_{2.5} concentrations from measured PM₁₀ concentrations. To this purpose the author measured PM concentration over eight size fractions (10 µm - 0.43 µm) by means of an eight stage cascade impactor. Overall, 26 sites classified as coastal, coal mining and traffic sites were considered. For each kind of site a relationship of the kind $Y = aX^b$ (where X is the logarithm of the particle size and Y is the relevant cumulative fraction) was determined. The proposed manuscript fail to address some major points and cannot be accepted for publication in its present form.

Major revisions addressing the following points are needed:

1. No consideration has been taken on the influence of meteorological variables on the shape of the size distributions measured, and hence on the relationships proposed. E.g. rain, wind that can influence the contribution of coarse fraction (dust resuspension) and the sea salt aerosol contribution, atmospheric stability that may hinder the dispersion of anthropogenic fine fraction.

The study intends to correlate the different size fraction of monitored ambient air PM. We have now made this point clearer in Section 1.0.

2. No seasonal variation of the proposed data (spanning a long period of time from 2005 to 2011) has been discussed.

The study at different sites were carried out during different months from 2005 to 2011. For each location, data is available for a short duration. This was not a continuous monitoring program where data gathered can be subjected to seasonal variation. We have now made this point clearer in Section 2.1.

3. The analysis performed relies on local sources only. For instance, the possible influence of dust transport from desert areas has not been considered (Kumar et al. Tracing dust transport from Middle-East over Delhi in March 2012 using metal and lead isotope composition. 2016, Atmospheric Environment 132, 179-187).

This study is about attributing emission sources based on size of particulate matter. Tracing the distant sources such as dust storm of middle-east, would require chemical speciation besides long range transport model, which is not in the scope of the present study. We have now made this point clearer in last paragraph of introduction.

Minor comments:

1. Page 8, line 32: please report the resolution of the balance used

Resolution of balance added.

2. Page 14, line 13: it is aerosol size distribution rather than PM_{2.5} crucial to assess particle respiratory deposition.

Correction incorporated.