

# Determination of Urban Dust Signatures through Chemical and Mineralogical Characterization of Atmospheric Dustfall in East Delhi (India)

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## ABSTRACT

The fine road dust particles contribute a dominant fraction of ambient concentration of air particulates in urban areas. The road dust carries toxic pollutants such as heavy metals and polyaromatic hydrocarbons (PAHs) etc. exerting a significant influence on air quality. This study is aimed to analyze the chemical, mineralogical and morphological characteristics of the dustfall deposition during the period from November 2013 to February 2014 in east Delhi. The research findings of this study confirm that the vehicular traffic is a significant cause for high deposition flux of the dustfall resulting in a possible health hazard for roadside population. Average dustfall flux was observed to be 310 mg/m<sup>2</sup>/day and the average pH of aqueous extract of dustfall samples was noticed as 7.7. SEM results showed the dust particles were irregular in shape representing spherical, rectangular, platy and angular shapes. Their diameter ranged from 1.5-151.5 μm. Ca, Si, and Al were the major contributors in dust indicating that the dustfall is weathered material of local rock which consists of calcium aluminum silicates. Other heavy metals such as Zn, Cu contributed primarily from vehicular traffic while Fe, Al, and Mn mainly from suspended road dust. C particles seen in the dustfall samples might be due to interaction of atmospheric dust with industrial and vehicular emissions.

**Key words:** Road dust, vehicular traffic, SEM-EDX, heavy metals, dustfall.

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## INTRODUCTION

Dust is one of the leading aerosol types which plays a very significant role in the modulation of atmosphere and climate (Tegen and Fung, 1995; Kulshrestha, et al., 2003b, Singh et al., 2004). Dust aerosols impact the radiation budget of Earth's atmosphere directly by scattering and absorbing solar and terrestrial thermal radiations, and indirectly by changing cloud optical properties and lifetimes (Lacis, 1995; Liao and Seinfeld, 1998). Due to its large active surface area, mineral dust can also affect gas-phase concentrations of ozone, as well as nitrate, sulfate, and the formation of photochemical smog (Underwood et al., 2001; Dentener et al., 1996; Dickerson et al., 1997).

Fine solid particles on road surfaces are also a significant source of air pollution in urban areas (Thorpe and Harrison, 2008; Amato et al., 2009, 2011). Road dust consists of soil minerals, organic matter (derived from vegetation) and potentially toxic pollutants emitted from various anthropogenic sources (Gunawardana et al., 2012; Rogge et al., 1993). Dust particles function as a carrier of other pollutants which is largely dependent on the chemical composition, shape, size, and their sources (McBride, 1994). Traffic-related pollutants include tire and brake abrasion products, combustion exhaust and pavement wear (Rogge et al., 1993; Kreider et al., 2010; Amato et al., 2011). There is an increasing concern about this nano- and micro-

sized particles because of their possible adverse effects on the human health and environment (Inoue et al., 2006). Therefore, the present study was carried out to determine the influence and contribution of suspended road dust to the free-falling dust particles through their chemical and morphological characterization at site in east Delhi which represents very typical urban characteristics in north India. This study will be helpful in understanding the sources of dust pollution in order to develop the appropriate strategies for the mitigation of dust pollution, further helping in reducing ambient particulate matter levels in the city.

## MATERIAL AND METHODS

### Study area

The samples of atmospheric dust were collected at Babarpur (28°41'N and 77°16'E) region, located near Shahdara Industrial Area of east Delhi. The site represents an Industrial-cum-residential zone. As per census of 2011, the population density of this area is estimated to be 36,155 per km<sup>2</sup>. The area of study around Shahdara has several industries such as plastic, packaging and metal processing. The area has very high traffic density especially the trucks which are the major sources of the nitrogen dioxide (NO<sub>2</sub>) and sulfur dioxide (SO<sub>2</sub>) in the locality. The site has nearly two busy roads nearby (300 m north and south) running

**Table 1.** Comparison of dustfall fluxes at worldwide.

Sampling site	Country	Deposition flux (mg/m <sup>2</sup> /day)	References
Delhi	India	310.3	Present study
Delhi	India	96.6	Kumar et al., (2014)
Jharia coal mining (Commercial)	India	461.8	Rout et al., (2014)
Jharia coal mining (Residential)	India	318.8	Rout et al., (2014)
Miami, Florida	USA	0.7	Prospero et al., (1987)
French Alp	France	5.7	Angelis and Gaudichet, (1991)
Coast Mountain, BC	Canada	29.8	Owens and Slaymaker, (1997)
Namoi Valley	Australia	85.9	Cattle et al., (2002)
Northern Nigeria	Africa	435.2	McTainsh and Walker, (1982)
Guagzhou	China	124.2	Zhao et al., (2010)

east westerly. The sampling was carried out at a residential building located 2km away from Shahdara and about 300 m away from Babarpur bus terminal, which is considered as very busy terminal.

### Sample collection and analysis

#### *Dustfall Sample collection:*

Dustfall samples were collected in a plastic tray (500 cm<sup>2</sup>, polypropylene) which placed on the terrace of the building (about 10 meters from the ground surface) on the basis of 7 days ambient exposure. The sampling was carried out from November, 2013 to February, 2014 (Kumar et al., 2014). The tray was carefully weighted before and after the collection for obtaining the amount of deposited dust. The tray was thoroughly cleaned with high quality deionized water and dried before the collection of next sample. Total four samples were collected during this period, representative of each month. The collected amount of dust samples were wrapped in aluminum foil and stored in refrigerator at 4°C till further analysis.

The total dustfall weight was calculated by the difference of  $m_1$  and  $m_2$ , and the dustfall fluxes were calculated by using the following formula (Gupta et al., 2015a):

$$DF = (m_2 - m_1) / A \times d$$

Where DF is the total dustfall flux (mg/m<sup>2</sup>/day),  $m_1$  is the initial weight of tray,  $m_2$  is the final weight of the tray in mg, A is the surface area of plastic tray (m<sup>2</sup>) and d is the number of days for which tray was exposed in the open air.

#### *Chemical Analysis:*

0.2g of the sample was transferred to a centrifuge tubes following adding 10ml ultrapure water. The sample was then sonicated for half an hour at 1 Hz in an ultrasonicator in order to extract water soluble components. Finally, the

sample was filtered with Whatman 41 filter. Major anions (F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) and cations (Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>) were determined in the aqueous extract of dustfall by Ion Chromatography (Metrohm 883 Basic IC Plus). Details of ionic analysis are given elsewhere (Singh et al., 2014).

#### *Morphological and elemental Analysis:*

Surface morphology and elemental analysis of the dust samples were carried out using SEM-EDX (Carl Zeiss AG-EVO 40 Series model). SEM images were taken for identifying the shape and size of dust particles in the sample at different magnifications. More details about the SEM analysis are given in Gupta et al., (2015c).

#### *Quality Assurance and Quality Control (QA/QC)*

The quality of sampling and analysis was ascertained by analyzing blank of tray. All the cationic and anionic species had area below the detection limit in the blank. Calibration of methods and quantification of components were carried out using MERCK reference standards (CertiPUR).

## RESULTS AND DISCUSSION

### **Dustfall fluxes at Trans-Yamuna region**

Dustfall fluxes varied from 185 to 447 mg/m<sup>2</sup>/day with an average flux value 310 mg/m<sup>2</sup>/day. Kumar and coworkers (2014) have reported an average dustfall flux 95.82 mg/m<sup>2</sup>/day at different sites of Delhi. Therefore, these fluxes are considered higher at this site. Such higher fluxes can be attributed to the suspended soil dust, road dust and increasing construction activities (Kumar et al., 2014). In addition, changing land use pattern in urban regions is also a significant source of global atmospheric dust (Tegen and Fung, 1995). Table 1 gives the comparison of dustfall

**Table 2.** Dustfall flux and pH of aqueous extract.

Sample No.	Sampling duration	Dust Flux (mg/m <sup>2</sup> /day)	pH
1	01/11/2013-07/11/2013	185	7.9
2	29/11/2013-05/12/2013	446.7	7.6
3	03/01/2014-10/01/2014	182.2	7.7
4	09/02/2014-16/02/2014	427.5	7.6
Average		310.3	7.7

fluxes at different sites worldwide. It is indicated that the dustfall deposition fluxes are very high at the tropical sites as compared to temperate sites.

### ***pH of dustfall extract***

The pH of aqueous extract of dustfall was found to be in the range of 7.55 - 7.96, (Table 2) clearly showing the alkaline nature of atmospheric dust. Such high pH of alkaline atmospheric dustfall extract suggests the dominance of crustal components particularly, the presence of carbonates and bicarbonates of Ca (Kulshrestha et al., 2003a). CaCO<sub>3</sub> rich soil of this region contributes to a major fraction of atmospheric dust in Indian region (Kulshrestha et al., 1999; Jain et al., 2000). Very similar range of pH was found at different sites of Delhi (Kulshrestha et al., 2003b).

### ***Chemical characterization of dustfall***

Figure 1 shows the variation of dustfall flux and dustfall fluxes of major ions in the samples. Dustfall deposition fluxes mainly depend upon the particle density and the size (Hicks et al., 1986). Higher the mass mean diameter of particles, greater will be their dustfall deposition flux. SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> particles, which are mainly originated from anthropogenic activities, showed almost rates to those of the soil-derived elements. This suggests the possibility of association with such particles. Variation of Ca<sup>2+</sup> and Na<sup>+</sup> fluxes is in accordance with dustfall fluxes suggesting that these are originated from soil. According to earlier studies origin of Ca<sup>2+</sup> has been reported from soil (Kulshrestha et al., 2003b; Kumar et al., 2014). Generally, Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup> are considered as initial components which are found abundant in the atmosphere (Rahn, 1976; Kulshrestha et al., 1998). However, biomass burning and other combustion sources have also been responsible for K<sup>+</sup> emissions (Andrae et al., 1990; Simoneit, 2002). The Na<sup>+</sup> and Cl<sup>-</sup> ions are contributed by sea salts as major fraction. However, Na<sup>+</sup> is also contributed by local soils in this region (Lakhani et al., 2007) while Cl<sup>-</sup> is also contributed by some industrial units such as combustion of municipal waste, waste incineration, vehicles exhaust etc. (Singh et al., 2014; Moffet et al., 2008).

The fluxes of the major ions decreased in the following order Ca<sup>2+</sup> > K<sup>+</sup> > Na<sup>+</sup> > Mg<sup>2+</sup> > NH<sub>4</sub><sup>+</sup> > SO<sub>4</sub><sup>2-</sup> > NO<sub>3</sub><sup>-</sup> > Cl<sup>-</sup> > F<sup>-</sup> (Figure 2). Among cations, the fluxes of Ca<sup>2+</sup> were observed to be highest with mean value 3.56 ± 1.16 mg/m<sup>2</sup>/day followed by K<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup> and NH<sub>4</sub><sup>+</sup>. Relative percentage of Ca<sup>2+</sup> among major ions is about 59%, which shows the dominance of crustal components, i.e. CaCO<sub>3</sub> in dustfall, rich in soil of India region (Kulshrestha et al., 1996; 1998). Fluxes of K<sup>+</sup> and Na<sup>+</sup> were found to be 0.58±0.05 and 0.45±0.13 mg/m<sup>2</sup>/day, contributing 9% and 7%, respectively. This may be due to their common origin as a crustal component. In coarse mode, K<sup>+</sup> origin is mostly considered from soil dust (Li et al., 2008; Shen et al., 2009) while in fine mode it is contributed by biomass burning (Andrae et al., 1990). Among cations, Mg<sup>2+</sup> and NH<sub>4</sub><sup>+</sup> have recorded lower fluxes with average mean value 0.23±0.04 (4%) and 0.1±0.07 (2%) mg/m<sup>2</sup>/day respectively.

Among the anions, SO<sub>4</sub><sup>2-</sup> had the maximum fluxes with mean value 0.50±0.32 mg/m<sup>2</sup>/day followed by NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, and F<sup>-</sup>. The largest source of sulfate could be the oxidation of sulfur dioxide (SO<sub>2</sub>) emitted from the burning of fossil fuels, biomass, coal in thermal power plants and vehicular exhaust (Jain et al., 2000; Gupta et al., 2015b). High levels of NO<sub>3</sub><sup>-</sup> (0.42±0.33 mg/m<sup>2</sup>/day) may be contributed by vehicular emission, as the site was surrounded by two major roads. Cl<sup>-</sup> (0.22±0.16 mg/m<sup>2</sup>/day) may be due to complicated sources such as sea salts, vehicles exhaust, waste disposal or wood burning, etc., (Perrino et al., 2011; Andrea et al., 1990). SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> contribute about 8%, 7% and 4% respectively of total ions. The alkaline nature of dust in Indian region promotes SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> scavenging through dry deposition forming secondary aerosols such as CaSO<sub>4</sub> and Ca(NO<sub>3</sub>)<sub>2</sub> (Kulshrestha, 2013; Kulshrestha et al., 2003b).

### ***Morphological observations of Dust***

Morphological analysis of the dustfall was carried out using SEM-EDX technique. SEM images revealed that the particles were fine to coarse in size diameter ranging from 1.5 μm -151.5 μm. The dustfall was dominated by spherical, irregular, long, tubular, grapes like structure, aggregated and rhombic shape of particles. Images of dust particles with

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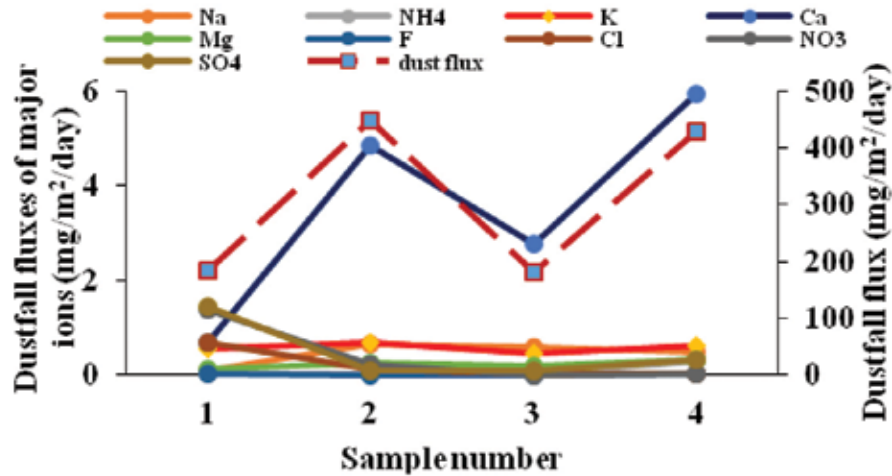


Figure 1. Variation of dust fall flux and major ion fluxes from Nov.2013 to Feb. 2014.

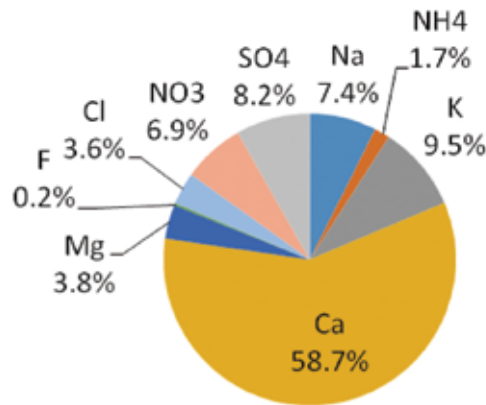


Figure 2. Relative percentage contribution of major ions in dustfall.

different magnifications are shown in Figure 3 (A to I). Almost similar morphological features have been reported in dustfall in this region (Mishra et al., 2015; Kumar et al., 2014; Pachauri et al., 2013). The various shapes of dust particles might be due to their emission from different sources, geological characteristics, and meteorological parameters. Elemental and morphology of dust particles are controlled by wind direction and geology of that area (Zarasvandi et al., 2011).

The rounded shaped particle with smooth surface (Figure 3B) are considered as soot particles and fly ash. The presence of soot particles may be due to emissions from vehicular traffic, thermal power plants, and other industrial units located in and around Delhi. Soot particles at residential and commercial site is indicating of domestic coal burning and biomass burning (Rout et al., 2014). Some rounded shaped particles was found with specific shape pattern having with rough surface (Figure 3C). These particles showed the presence of pollens. Figure 3D shows grossular structure of the particles. In the earth's crust the

major type of chemical compound is composed of about 72% of aluminosilicate group in terms of weight (Cong et al., 2010; Van Malderen et al., 1996). Aluminosilicate particles are mainly composed of Si and Al oxides with varying amount of K, Mg, Ca, and Fe. Similar results were observed by other coworkers in this region (Kumar et al., 2014; Pachauri et al., 2013). Some grape like structure of the particles (Figure 3E) are similar to the structure of a big aged carbon fractal comprising of carbon monomers (Mishra et al., 2015). Due to vehicular emission or combustion activities including tire abrasion and fly ash from asphalt, fresh carbon fractals (open long chain fractals) are released in the atmosphere which reside in the atmosphere for long time and form close fractals (closed chain compact fractal) due to surface tension and particle dynamics. In our study, we found some triangular structures (termed as triangular flaky structure) (Figure 3F) and flattened crust like particles (Figure 3I). The flattened structures are of oblate shape and thicker than the flakes. Mishra and coworkers (2015) suggested that the layered structure particles inferred to be

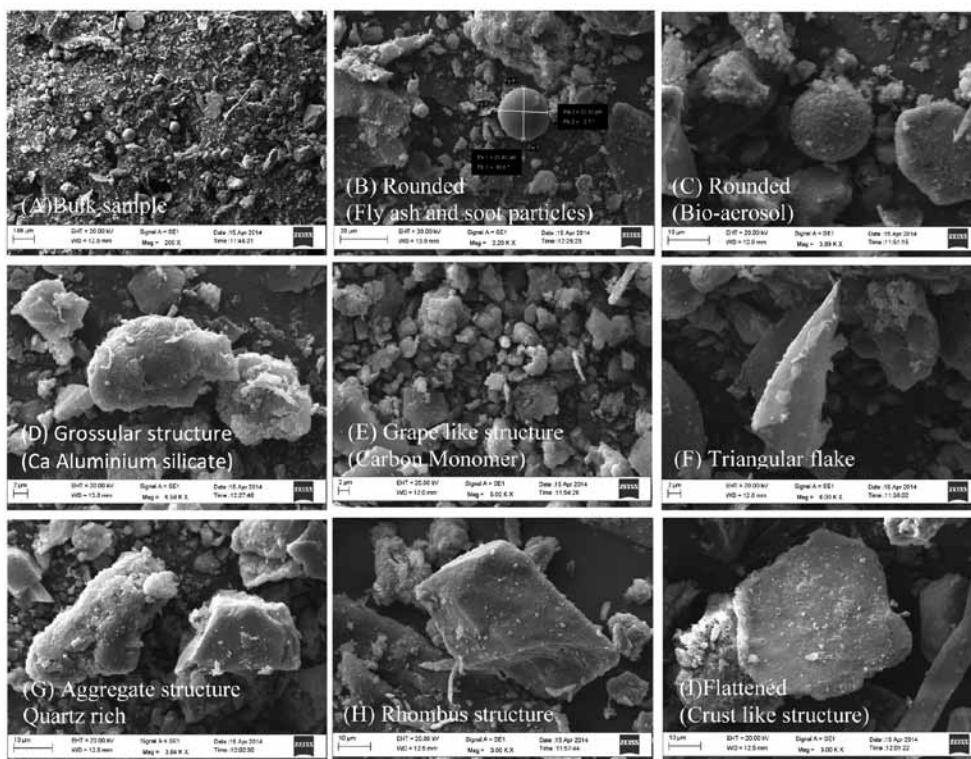


Figure 3. (A to I) SEM Images of dust particles with different magnifications.

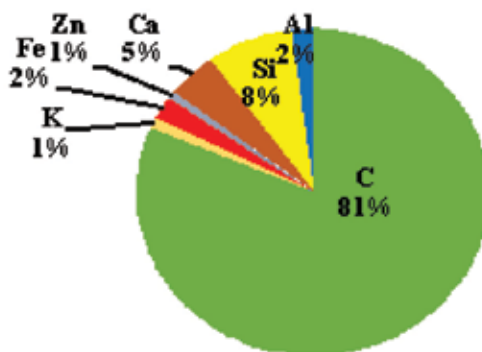


Figure 4. Average elemental composition of dust sample (excluding oxygen %).

rich in calcite and quartz. Figure 3G shows some irregular aggregate structure. Zhao and coworkers (2010) found that the irregular granular aggregates are the marker of construction dust and normal granular were markers of road dust. Angular crust like particles was found to be rich in quartz while some angular particles were found to be rich in C, N, O and Si (Mishra et al., 2015).

**Elemental composition of Dustfall particles**

Figure 4 illustrates the elemental composition of dust samples as determined by SEM-EDX. It shows the relative contribution of various elements which are present in the

dust in major quantity. Oxygen was excluded due its very high contribution about 75% of the mass. As the figure clearly shows carbon, silicon and calcium has the highest percentage among all the elements contributing 81%, 8% and 5%, respectively. Similar results have also been observed by Kumar et al., (2014) in south Delhi area. It has been found that dust particles over urban areas have been multifold enriched with carbon as compared with local soil (Mishra and Kulshrestha, 2016; Kulshrestha et al., 2012). Dust particles due to their suspension in air have greater possibility to interact with various air pollutants allowing the adsorption of gases and other particulates including carbonaceous aerosols (Kumar et al., 2014).

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In addition, copper and sulfur were also present in trace amount. The dust consisted of oxides of carbon, calcium, silicon, iron, aluminum, potassium, zinc, copper and sulfur. Such contribution indicated that the dustfall is a mixture of natural as well as anthropogenic emissions. Presence of metals such as zinc and copper indicated an influx of industries while contribution of zinc and sulfur indicates the influx of diesel combustion particularly from heavy duty vehicles. Presence of oxides of aluminum, silicon, calcium, iron, and potassium suggested that the dust is primarily of crustal origin.

### CONCLUSIONS

The present study mainly carried out around Shahdara Industrial Area reveal that the road dust suspension and industrial emissions have significant effect on the chemical characteristics of atmospheric dust in East Delhi. The pH of dustfall suggest that the atmospheric dust is alkaline in nature. High rate of dustfall indicate the effect of increasing urbanization and decreasing forest cover. Deforestation and construction activities due to rapid urbanisation are significant factors resulting in increase in the atmospheric dust. The alkaline nature of dust in Indian region promotes  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  scavenging through dry deposition forming secondary aerosols such as  $\text{CaSO}_4$  and  $\text{Ca}(\text{NO}_3)_2$ . High correlation between of  $\text{Cl}^-$  with  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  suggested their emissions from biomass burning and waste incinerations. Morphologies of dust indicated that the major constituents of the urban dust are derived from industrial and vehicular activities including tire abrasion, fly ash from asphalt and combustion byproducts. The elemental analysis further indicated that C, Si and Ca as the major elements of dustfall, while traces of Cu and Zn were also recorded.

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### Compliance with Ethical Standards

The authors declare that they have no conflict of interest and adhere to copyright norms.

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### How do you find an Exoplanet?—Recent publication

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