

Morphology, elemental composition and source identification of airborne particles in Delhi, India

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ABSTRACT

The present study focused on the morphological and elemental characterisation of PM₁₀ (particulate matter $\leq 10\mu\text{m}$) and total suspended particulate matter present in rainwater (TSP_{RW}) samples at two sites, located in urban background and industrial belt in Delhi region. The scanning electron microscopy, coupled with energy dispersive spectrometer (SEM-EDX), was used to characterise the morphology, elemental composition in PM₁₀ and TSP_{RW} and further link them to the pre-dominant sources. SEM micrographs indicated the predominance of soot aggregates, Fe-rich particles, crystal of sulphate of calcium and potassium (Ca/K) and biological particles in PM₁₀ at Jawaharlal Nehru University site (JNU). Similarly, the Badarpur industrial site (BDP) was found to be predominantly rich in fly ash particles and their aggregates, round/oval aluminosilicate particles, rich in Al, Si and O species. EDX results indicate high carbon contents in the atmosphere at BDP site as compared to the JNU site, suggesting the predominance of the particulates emitted from coal power plants and vehicular emissions in the vicinity of BDP site. Enrichment Factors (EFs) further confirmed the predominance of chlorine and fluorine in the atmosphere at BDP site, which further confirm to the emission from coal based power plants and industries.

Keywords: Atmospheric aerosol, Elemental composition, Morphology, Enrichment factor, Rainwater, Delhi region, Air pollution.

INTRODUCTION

The atmospheric aerosol is one of the important causes of air pollution in Delhi NCR, India. Aerosol plays a significant role in degrading visibility, change in Earth's radiation budget, formation of cloud by scattering and absorption of solar radiation (Ramanathan et al., 2001). These particles also affect human health adversely through various exposure pathways (dermal, ingestion and inhalation). Several authors have reported various health-related issues and mortality due to atmospheric aerosols (Pope and Dockery, 2006; Lelieveld et al., 2015). These aerosols are emitted from the variety of natural and anthropogenic sources such as volcanic eruption, crustal re-suspension sea spray, industrial emission, fossil fuel burning, waste incineration and processing of ores etc (Holman, 1999). Due to the source differences, these particles very much differ in their characteristics such as size, morphologies and chemical compositions (Salma et al., 2009). Such differences, together with the mixing states of aerosol, pose severe effect on climatic and human health (Pöschl, 2005). Further, the trace metals are also one of the important constituents of such aerosols, which are released into the atmosphere after combustion from the variety of natural and anthropogenic activities (Allen et al., 2001). The trace metal level, distribution and chemistry with different size fraction of aerosols, have earlier been discussed by several workers for northwest Indian region (Yadav and Rajamani, 2006; Srivastava and

Jain, 2007). In particular, Srivastava et al., (2009) analysed the possible sources and transport of pollutants from source to sink location in Delhi. Some other studies that also characterised the aerosol and associated elemental concentration in urban areas include Wang et al. (2006) and Campos-Ramos et al. (2009).

Out of various techniques used, Scanning Electron Microscope (SEM), coupled with energy dispersive X-ray microanalyzer (EDX), is considered as a powerful tool to understand aerosol morphology, elemental composition and their particle density that can give us a better insight about the origin of such particles (Pachauri et al., 2013; Singh et al., 2014; Tiwari et al., 2015; Hoffer et al., 2016; Goldstein et al., 2017). The elemental composition of aerosol particles is more useful with a view to establishing their origin and their potential effects on human health. In fact, the studies on elemental composition of aerosol using SEM-EDX analysis are now well established (Pina et al., 2000; Suzuki, 2006; Campos-Ramos et al., 2009; Geng et al., 2010; Agrawal et al., 2011; Alonso-Blanco et al., 2014), but not many studies have been carried out in context to the elemental composition of aerosol in comparison to their level distribution in rainwater TSP_{RW}, especially in north-west India (Chate et al., 2003). Therefore, in the present study, analysis has been carried out on the morphological and elemental composition of aerosols and rainwater particles at an industrial location in comparison to urban background. The study further extends with source apportionment of elements at both the sites in Delhi NCR region.

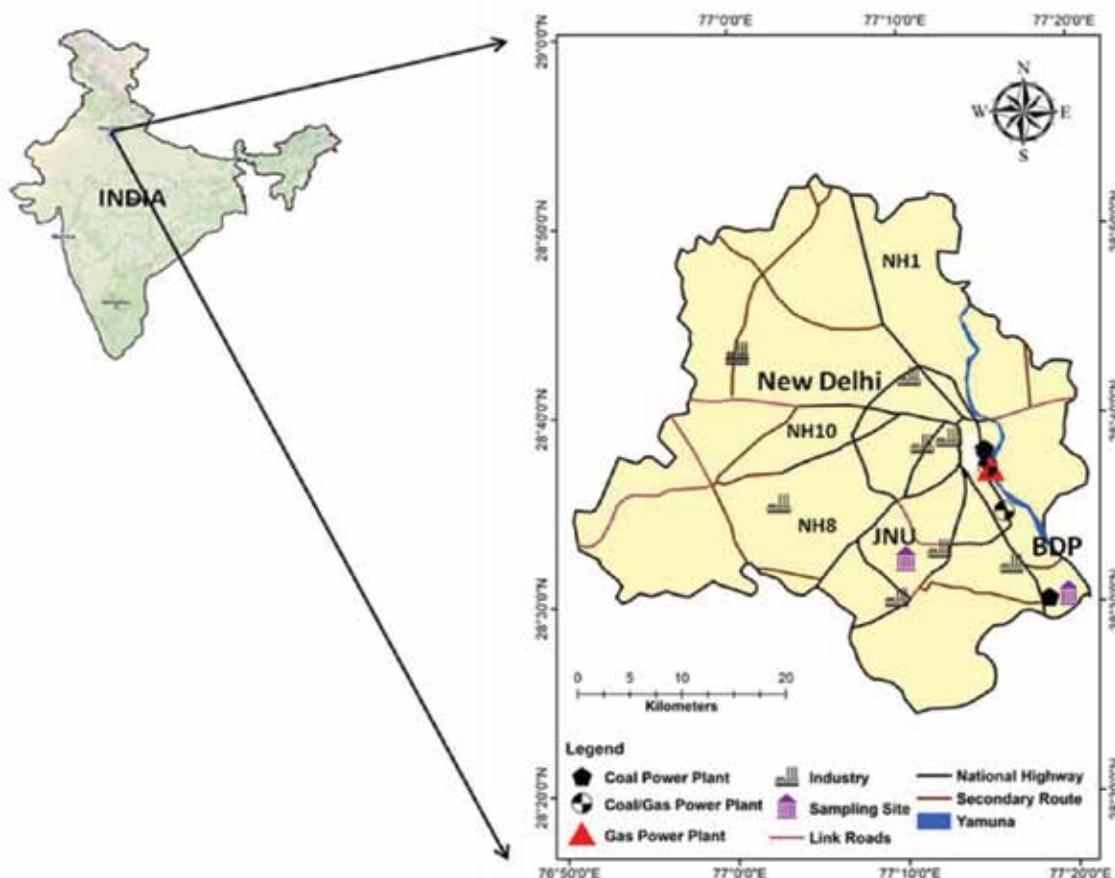


Figure 1. Map showing the study area in New Delhi region.

STUDY AREA

Delhi, the capital of India, is located between latitudes of 28°24' to 28° 53' and longitudes 76°20' to 77°20', with an average elevation of approximately 216 m above mean sea level. This city is bounded by western Indo-Gangetic alluvial plains in the north and east, by The Thar desert in the west and Aravalli hill ranges in the south. In general, the terrain in Delhi is flat, except for a low NNE-SSW trending ridge, which is considered an extension of the Aravalli hills of Rajasthan. According to the census, Delhi has 16.7 million peoples residing in the area of about 1483 km² (Census, 2011). The Delhi region has a semi-arid climate, with extremely hot summers (avg. Temp.: 32–34 °C in May–June) and cold winters (avg. temp.: 12–14 °C in December–January). Delhi area is under the influence of monsoon winds, ranging from NE to NW in winter and SE to SW in the summer (Varshney and Padhy, 1998), with an average annual rainfall of about 715 mm, three-fourths of which falls in July, August and September (Rana et al., 2012). The annual relative humidity (RH) is in the range of 60-70 %, with a maximum (90%) RH in

the month of August and September (Jain et al., 2005). During the summer months of April-June, temperatures can rise to 40-45 degrees Celsius, while winters are typically cold with temperatures during December and January falling to about 4 to 5 degree Celsius. The forest cover has increased from 0.76% of the total area in 1980-81 to 1.75% in 1994-95 and 5.93% in 2000-01. Delhi's mineral resources are primarily sand and stone, which are useful for construction activities. However, the stone quarries in the ridge area have been shut down since 1984 on account of environmental considerations. The vehicular population of Delhi (6.6 million) is the highest in India and increased at an exponential rate of 85.5 % between 1997-1998 and 2007-2008 (Planning Department, 2009). The traffic volume count was conducted by the Central Road Research Institute, Delhi (CRRI) in the year 2002. The traffic volumes recorded at 51 locations of Delhi was found very high varying in the range between 166175 and 19056 (CRRI, 2002). Delhi region is also characterized by 28 industrial estates. In addition, there are two coal power plants and one gas power plants located within the city area (Sarkar and Khillare, 2013). Fuel wood, charcoal,

LPG, coal, biogas and kerosene are the potential sources of air pollution, especially in the residential areas, containing rural and low-income urban categories (Kadian et al., 2007).

SAMPLE COLLECTION AND SEM MEASUREMENTS

Sampling sites

Map of the sampling sites used in the present study is shown in Figure 1. The selected site of Jawaharlal Nehru University area (JNU) is located in south Delhi at latitude of 28°54'02" and longitudes of 77°16'62". JNU is a green university campus, which comes under the range of Aravali hills and considered as an urban background area due to the relative absence of fresh emission sources of pollutants. In comparison, the Badarpur industrial area (BDP) is situated in the south-east region of Delhi, around latitudes 28°50'42" and longitudes 77°30'22". This site is characterised by the presence of the coal-based thermal power plant and industries. The high volume of traffic also affects the air quality of this area. The JNU site has downwind location with a very dense green vegetative cover, whereas the BDP site is on the upwind location and characterised by nearby industrial area.

Sample Collection

Particulate (PM₁₀) samples were collected on quartz fiber filter (8"x10" size) respirable dust sampler (RDS) at a particular flow rate of 1.0 m³ min⁻¹ flow rate. The rainwater samples were collected on an event basis. The collected samples (N=32; 19 for PM₁₀ and 13 for TSP_{RW}) were filtered through the quartz filter (diameter of 47mm). Both types of sample filters were used for the analysis of surface morphology, and elemental analysis was carried out through Scanning Electron Microscope (SEM) with Energy Dispersive Spectroscopy (EDS) (Carl Zeiss AG-EVO® 40 Series Model).

SEM and EDX analysis

Samples were analyzed by SEM-EDX at Advanced Instrumentation Research Facility (AIRF), Jawaharlal Nehru University, New Delhi. The PM₁₀ and TSP_{RW} samples collected from the respirable dust sampler and filtration of rain samples respectively. The samples were analyzed for their elemental characterisation using energy dispersive spectrometer (EDX). For EDX analysis, the X-ray beam was shot at a particular point from the bulk sample kept on the carbon tape. A graph is obtained between numbers of counts per channel versus energy in keV. Each peak in the graph represents an element. The elemental analysis was done in the auto mode and the data are presented in

terms of atomic weight percent. The elements taken into consideration are Be, C, N, O, F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ba, and Pb. The samples were cut through a punch of 0.5 mm diameter size (N=32; 19 for PM₁₀ and 13 for TSP_{RW}) out of the main quartz filter and was attached to an aluminium stub, using a carbon sticky tab for the EDX analysis. The EDX analysis was carried out both qualitatively and quantitatively. The atomic weight percentage of each element present in the spectrum was identified. On normalization to 100% for Si and O, the atomic weight percentage of different elements was also identified. The EDX spectra of blank quartz fibre filter were also obtained and its composition was manually subtracted during the evaluation of the EDX spectra of individual aerosol particles. However, it may have implications for the accurate measurement of particles such as silicon, as the penetration depth of the electron beam in SEM due to which any corrections in this regard may lead to underestimation of Si, and O in the PM₁₀ aerosol (Brunner et al. 2001; Sellaro et al. 2015).

For SEM analysis, a very thin gold-palladium (Au-Pd) film was coated on the sample's surface to make it electrically conductive. This extremely fine coating was done through evaporation of Au-Pd plate under inert argon atmosphere. The atomic percentage of each element present in the spectrum was identified. The EDX spectra of blank quartz fibre filter were also obtained and its composition was manually subtracted during the evaluation of the EDX spectra of individual aerosol particles. SEM images for each sample were taken at four magnifications namely 1500x, 5000x, 10000x, 35000x and 50000x. At 1500x, the dimensions of the largest and smallest particles were taken.

Enrichment factor analysis

For the identification of the different pollution sources at the selected locations, the enrichment factors have been calculated (Caridi et al., 1992; Yatin et al., 2000; Rastogi and Sarin, 2009; Khillare and Sarkar, 2012; Sarkar, and Khillare, 2011). The enrichment factor (EFs) method, analyses the elemental content with respect to the sample reference element such as Al or Fe (Ravichandran et al., 1995). In this method, the reference element is considered to act as a "proxy" for the clay content (Windom et al., 1989; Din, 1992). In continuation of this approach, Stewart (1989) used Mn for EFs calculations in a study of marine sediment. Deely and Fergusson (1994) proposed Fe as an acceptable normalisation element to be used in the calculation of EFs. The enrichment factors of detected elements were calculated with reference to the seawater, as defined by:

$$EF_x = (X_{\text{aerosol}}/Ref_{\text{aerosol}})/(X_{\text{UCC}}/Ref_{\text{UCC}})$$

Where, X is the element under consideration both in aerosol and the upper continental crust (UCC), and Ref is

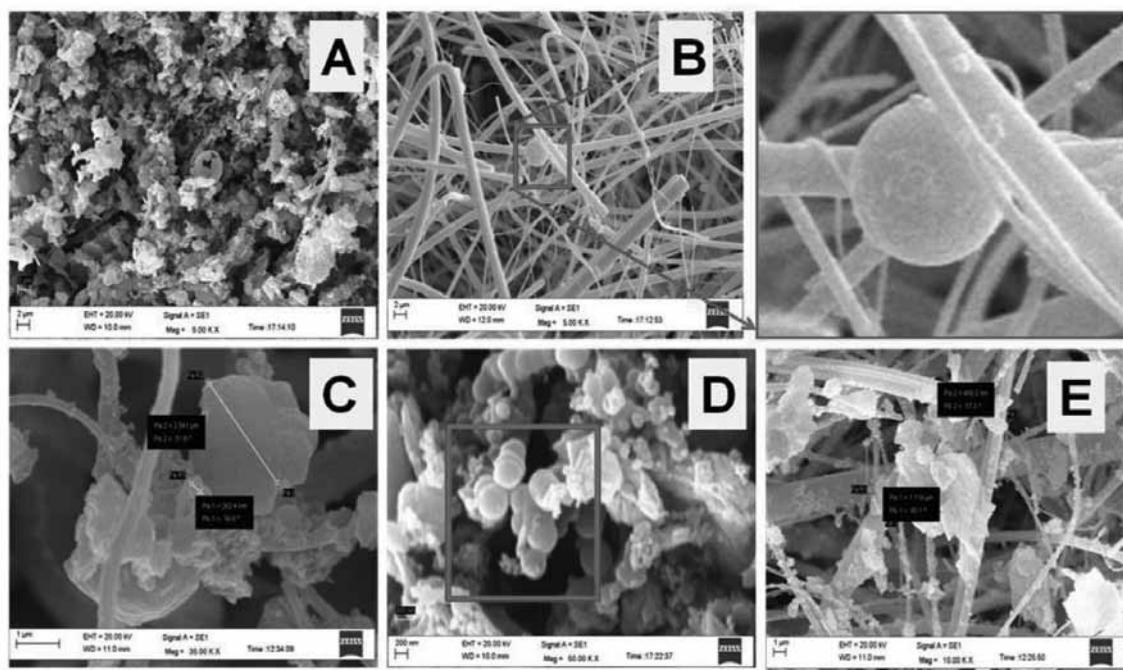


Figure 2. Scanning electron microscopy images in PM_{10} at JNU site.

a reference element that is typically crustal such as Al, Fe, Li, Ti etc. Metal abundances in UCC, as given in Wedepohl (1995), were used and Fe was chosen as the reference metal. EF_x is the enrichment factor of X, X_{UCC} is the concentration of X in upper continental crust and Ref_{UCC} is the concentration of a reference element that is typically crustal such as Al, Fe, Li, and Ti etc. According to this expression, elements with EF values close to unity would indicate a strong crustal origin, while high EF values could indicate a non-crustal (including anthropogenic) origin. In this study, because Al is abundant in crustal materials and is not involved in anthropogenic particles, it was used as the reference element and, consequently, EF_{Al} will be 1.

RESULT AND DISCUSSIONS

Morphological characteristics of PM_{10} and TSP_{RW}

Figures 2 and 3 show the SEM micrographs of PM_{10} collected at both JNU and BDP sites respectively. Essentially, particle micrographs at urban background site (JNU) were found different from the industrial site (BDP) by having high particulate deposition with irregular, flaky, crystal and more roundish particles.

In contrast, industrial site PM_{10} micrograph shows the most notable deposition of combustion-derived aggregates, irregular, sharp-edged, crystal shape and fluffy, amorphous shaped aggregates. Fly ash particles were noticed at the JNU site (Figure 2A). Freshly emitted soot particles are mentioned in the Figure 2b and 2d within

the frame. Fe-rich particles are seen brighter than others; Calcium sulphate crystal. The sulphate of Ca and K are shown in the Figure 2E. On the basis of ageing of the particles present in the ambient atmosphere, soot can be classified into the two major categories: freshly emitted soot (Figure 2B) and aged soot particles (Figure 2D). Soot is also an important category emitted from different sources into the atmosphere. Basically, soot is emitted from the incomplete combustion of the fossil fuels and biomass burning and contains several PAHs and toxic metals. Morphologically, soot particles can be generally classified into three categories: oval/spherical, rod-like, and flocculent amorphous bodies (Wu et al., 2015). Soot is a visible black smoke and also known as Black Carbon (BC), emitted mainly from engine exhaust and campfire and thermal power plants. Figure 2C shows the presence of the clay particles in the atmosphere of JNU campus. According to reports, a significant proportion of aerosol mass is composed of carbonaceous species, predominantly originated from fossil fuel combustion, as implied by the close association of C, O with S-rich (3.4 %) particles (Paoletti et al. 2002; Cong et al. 2010). Figure 3 shows the combustion-related soot aggregates (Figure 3A and 3B with an amplified image in rectangle). The cluster of iron oxides is shown in Figure 3D, while the cluster of calcium sulphates have been shown as a rose-like structure in Figure 3E at BDP site. Apart from the PM_{10} , TSP_{RW} was also collected through rain and analysed through SEM for the identification of different suspended particulates originated from different sources. The Figures 4 and 5 showed the

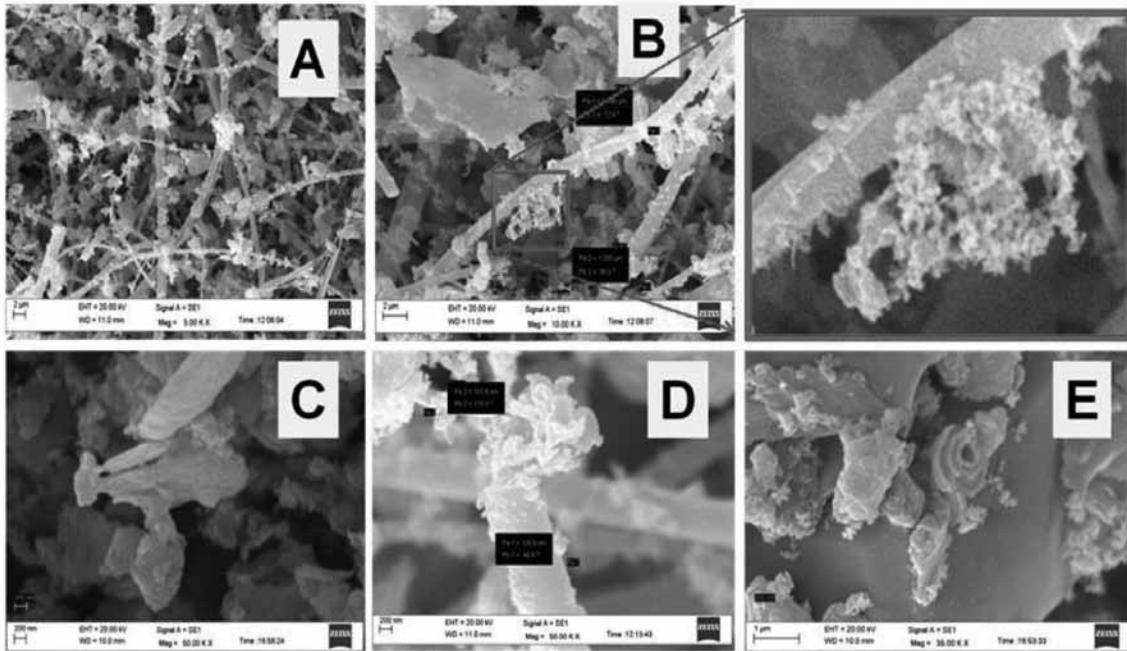


Figure 3. Scanning electron microscopy images in PM_{10} at BDP site

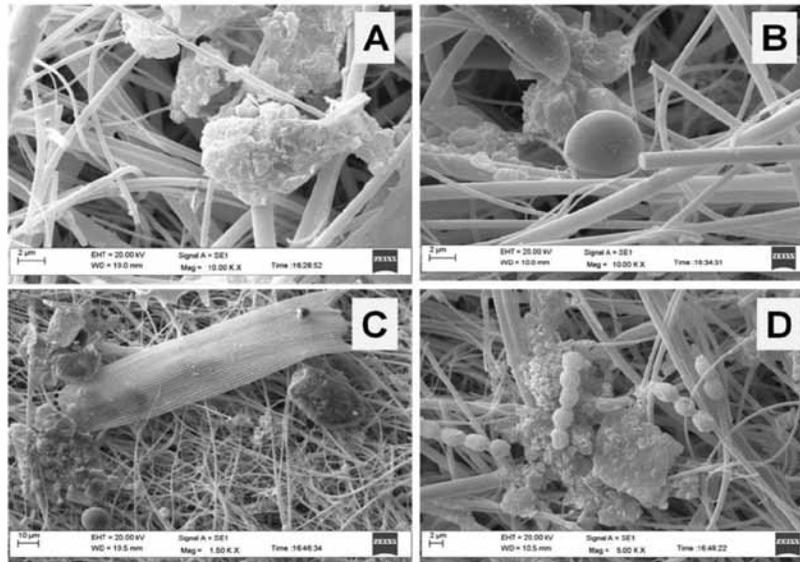


Figure 4. Scanning electron microscopy images in TSP_{RW} at JNU site

SEM images of atmospheric suspended particulate at JNU and BDP both the sites.

Figure 4 shows the different morphology, ultimately indicating towards their different source origin of atmospheric TSP. The cluster of aged particles, soot, biochar and biological particles are the main compositions of the TSP collected through the rain at the JNU site. The formation of the aged particles is a result of the presence of these particles into the atmosphere for the longer duration, transport and the physical and chemical

process involved in the atmospheric particulates ageing and formation of particles aggregates. Condensation of different acids (sulphuric acids and nitric acids) onto aerosols and coagulation with soluble aerosols such as sulphate and nitrates are the most important physical process involved in the formation of the aged particles. Chemical processes that make the ageing of the carbonaceous aerosol include the oxidation of organic coatings by ozone (Croft et al., 2005).

Figure 4 shows an amorphous particles aggregates (formed after atmospheric transformations), Soot particles

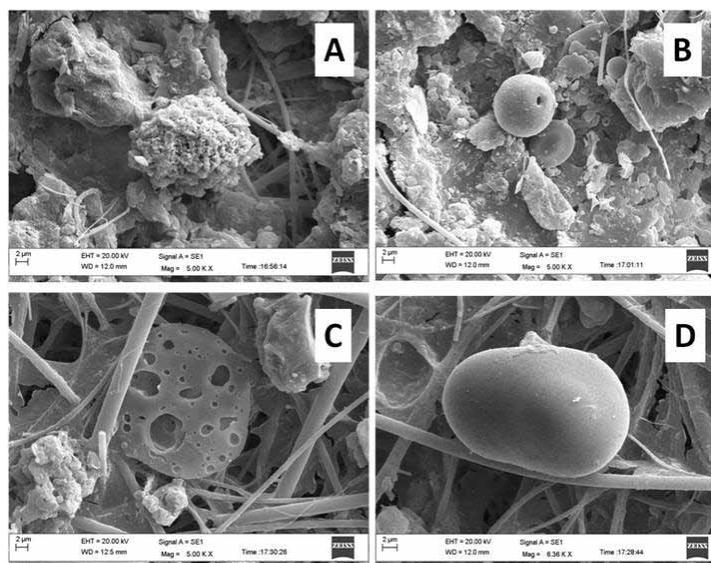


Figure 5. Scanning electron microscopy images in TSP_{RW} at BDP site

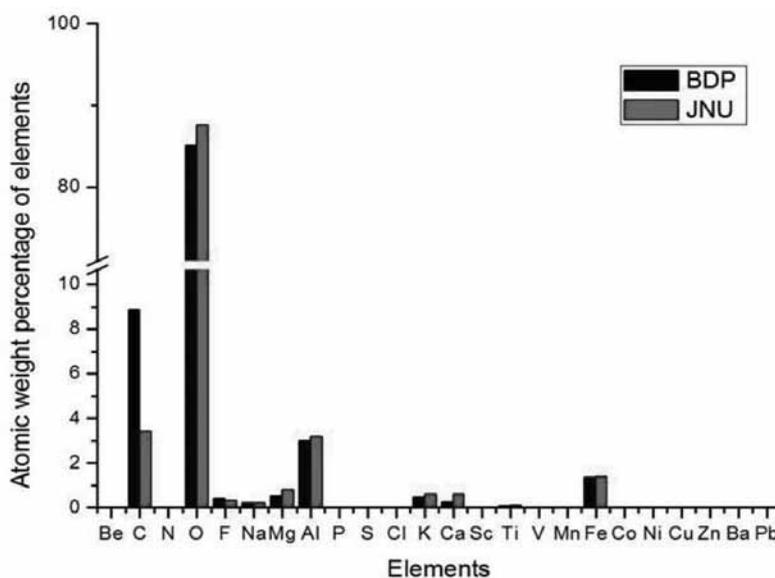


Figure 6. Percentage distribution of elements in PM10 at JNU and BDP site.

(emitted from vehicular exhaust, biomass burning and smelters), biochar (emitted from the combustion of plant materials), and bioaerosol or colony of pollen, fungi, air-borne pathogens etc. the presence of the bioaerosol in the campus area may be due to its high vegetation cover (Sharma et al., 2017; Kumar et al., 2014). Detailed inspection of Figure 5 denoted the predominance of combustion related aggregates such as fly ash, soot aggregates, iron particles and aluminosilicates minerals from TSP collected from rain samples at BDP site.

It represents clusters of soot (Figure 5A), ceramic particle or particles from pharmaceutical industries (Figure 5B) (Effting et al., 2010; Ibraheem et al., 2014), flocculent amorphous body (Figure 5C) and near-spherical fly ash of

aluminosilicate in nature having Al, Si and O rich species were ubiquitous in the coarser particulates (Figure 5D) at BDP site (Pachauri et al. 2013).

Elemental composition in PM₁₀ and TSP_{RW}

The descriptive statistics of elements in PM₁₀ and TSP_{RW} in total, monsoon season and non-monsoon season have been shown in the Table 1.

Elemental composition of PM₁₀

Figure 6 shows the atomic weight percentage of the different elements found in the JNU and BDP sites. Oxygen fraction

Table 1. Descriptive statistics of elements in PM₁₀ and TSP_{RW} in Total, Monsoon season (M) and Non-monsoon season (NM)

PM ₁₀ Elements	C	N	O	F	Na	Mg	Al	S	Cl	K	Ca	Ti	Fe	Ba	Pb
JNU Total (Mean ± SD)	9.34±6.73	0.50±1.10	89.10±5.55	2.81±4.26	0.003±0.01	0.04±0.09	0.40±0.37	0.26±0.35	0.02±0.05	0.13±0.14	0.33±.27	ND	0.28±0.23	ND	0.002±0.01
M (Mean ± SD)	6.67±3.93	0.52±1.13	90.63±6.71	3.03±5.15	0.005±0.01	0.05±0.11	0.38±0.45	0.09±.13	ND	0.05±0.07	0.22±0.23	ND	0.15±0.20	ND	0.002±0.01
NM (Mean ± SD)	13.81±8.94	ND	86±4.05	ND	ND	0.02±0.03	0.44±0.24	0.54±0.46	0.05±0.07	0.28±0.12	0.52±0.25	ND	0.48±0.03	ND	ND
BDP Total (Mean ±SD)	19.59±8.85	ND	88.80±10.13	ND	ND	0.003±0.01	0.23±0.17	0.25±0.22	1.22±1.41	0.14±0.12	0.29±0.24	0.03±0.06	0.20±0.19	ND	ND
M (Mean ± SD)	12.77±3.58	ND	97.15±5.35	ND	ND	0.003±0.01	0.20±0.28	0.08±0.11	ND	0.04±0.06	0.29±0.41	0	0.22±0.31	ND	ND
NM (Mean ± SD)	26.41±6.03	ND	80.44±0.15	ND	ND	ND	0.27±0.01	0.43±0.11	2.45±0.09	0.24±0.02	0.28±0.01	0.06±0.08	0.18±0.08	ND	ND

TSP _{RW}	C	N	O	F	Na	Mg	Al	S	Cl	K	Ca	Ti	Fe	Ba	Pb
JNU Total (Mean ±SD)	3.89±2.0	ND	89.54±5.34	0.25±0.57	0.22±0.28	0.70±0.95	3.13±2.82	ND	ND	0.70±0.48	0.68±0.56	0.08±0.08	1.75±0.85	0.03±0.10	ND
M (Mean ± SD)	3.23±0.85	ND	89.1±6.57	0.28±0.68	0.32±0.29	0.92±1.10	3.87±3.26	ND	ND	0.77±0.56	0.72±0.64	0.10±0.08	1.96±0.92	0.05±0.12	ND
NM	5.21±3.20	ND	90.42±2.07	0.19±0.33	0.02±0.03	0.26±0.36	1.67±0.73	ND	ND	0.56±0.31	0.59±0.46	0.04±0.07	1.32±0.63	0.02±0.005	ND
BDP Total (Mean ±SD)	13.82±8.75	ND	82.2±18.5	ND	0.09±0.20	0.25±0.54	1.28±2.43	0.17±0.19	0.82±1.12	0.29±0.40	0.26±0.182	0.04±0.06	0.53±0.82	0.012±0.023	ND
M (Mean ± SD)	8.23±4.83	ND	87.7±12.56	ND	0.15±0.25	0.41±0.70	1.99±3.15	0.04±0.08	ND	0.35±0.55	0.29±0.25	0.04±0.06	0.78±1.05	0.02±0.03	ND
NM (Mean ± SD)	22.19±5.06	ND	74.52±20.81	ND	ND	ND	0.230±0.01	0.37±0.09	2.05±0.08	0.20±0.01	0.24±0.01	0.05±0.07	0.15±0.07	0.01±0.001	ND

*Elements not detected in any of the season had excluded from the list of the descriptive table; TSP_{RW}: total suspended particulate in rainwater; PM10: particulate matters ≤ μm in diameters; M: Monsoon season; NM: Non-monsoon season

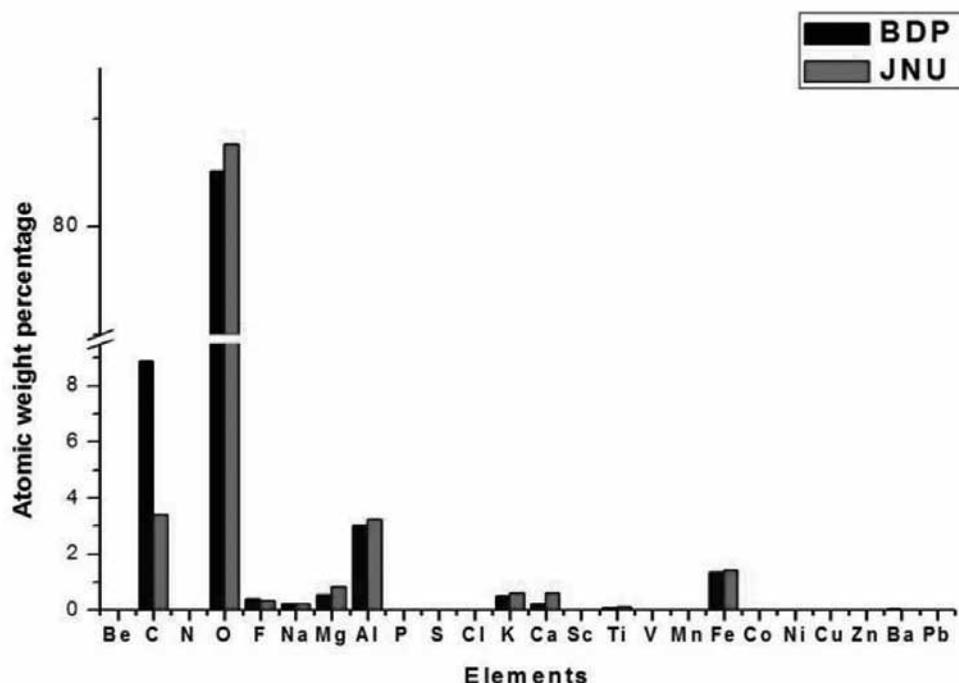


Figure 7. Percentage distribution of elements in TSP_{RW} at JNU and BDP site.

was found on the peak at both the sites, which might be due to the presence of the oxides of different metals emitted from fossil fuel burning, various industrial sectors and also from the vehicular exhaust. Apart from the oxygen, carbon was the most predominant element among all. The atomic carbon fraction was found significantly high at BDP site as compared to the JNU site, and it might be due to the difference of the nature of both the sites. As mentioned before, BDP site is characterised by the presence of a large number of coal thermal power plants and different industries such as electroplating, iron and steel, pharmaceutical industries. The high fraction of the carbon content at the BDP site represents its emission from coal power plants, whereas the presence of iron also pointed towards emission of fly ash from coal power plants.

A large fraction of aluminium represents its emission from different industrial activities at BDP site. The small fraction of the sodium, and soil-based elements (magnesium, calcium and potassium) indicating towards their natural origins such as sea salts, mineral dust and crustal dust (Kulshreshtha et al., 2003, 2009; Tiwari et al., 2007).

Elemental composition of TSP in rain

Figure 7 showed the elemental composition of TSP_{RW} at both the sites and follows a similar pattern of percentage distribution of elemental in PM₁₀. Oxygen was observed with the highest fraction among all elements, which played a significant role in the formation of different oxides with

different elements. Secondary carbon fraction was found on the peak after oxygen at both the sites and it is the clear-cut marker of the different emission sources such as emission from coal power plants, vehicles, biomass burning and emission from fossil fuel combustion. Comparatively high carbon fraction at BDP site, as compared to JNU site might be due to its location, which is in the vicinity of coal power plants and very busy traffic area. Iron and aluminium represent the emission from industries in case of anthropogenic source and natural sources such as mineral dust. The presence of calcium, potassium and magnesium refer to their natural sources such as crustal resuspension, mineral dust, and sea salts. Further, confirmation of the sources (Natural and Anthropogenic) of different elements at both the sites will be discussed with the help of the Enrichment Factor analysis.

Seasonal distribution of elements

JNU site

Figure 8 shows the percentage fraction of different elements during monsoon and non-monsoon season at JNU site. Elements such as sulphur, aluminium, calcium, and potassium were found with their relatively higher contribution in the non-monsoon season as compared to the monsoon season at JNU site. It may be due to the low temperature which leads to low dispersion conditions of the pollutants such as oxides of sulphur and aluminium. While the presence of higher potassium and calcium pointing towards their emission from biomass burning and crustal

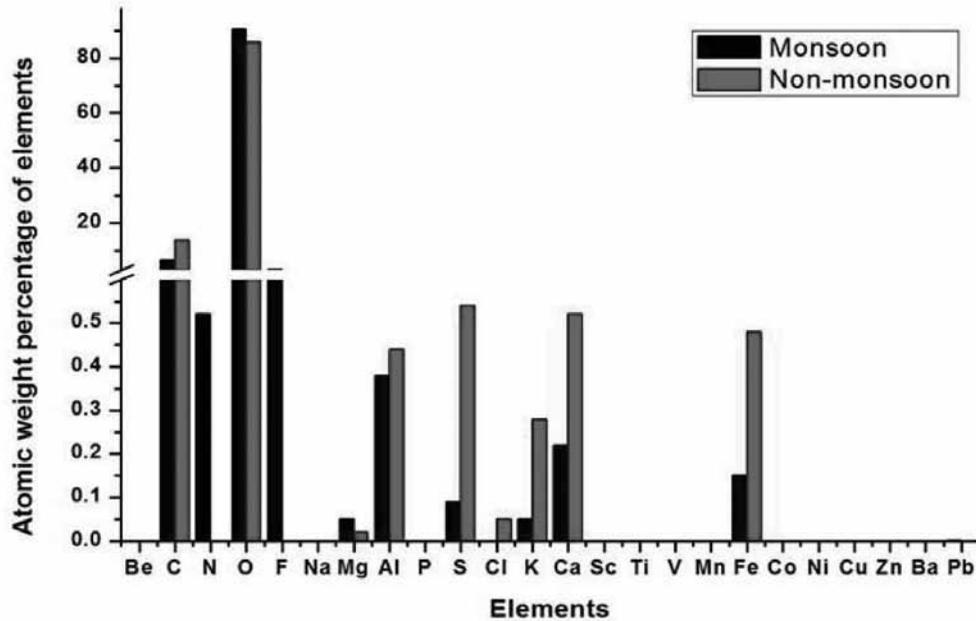


Figure 8. Elemental composition of PM₁₀ at JNU site.

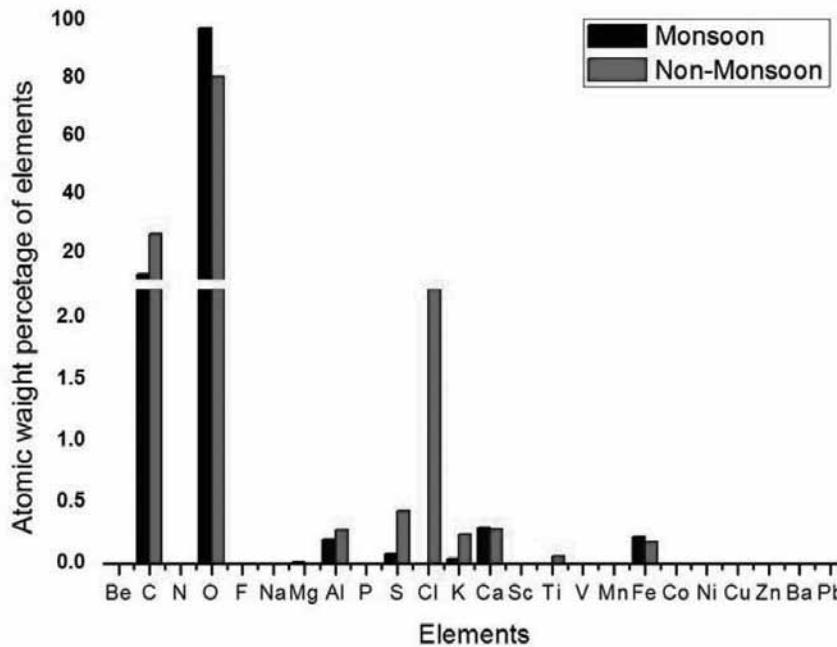


Figure 9. Elemental composition of PM₁₀ at BDP site.

dust during early summer season (Sardans and Peñuelas, 2007; Kumar et al., 2014).

BDP site

Figure 9 shows the percentage contribution of the elements during monsoon and non-monsoon season at BDP site. The carbon content was found significantly high in the non-monsoon season as compared to the monsoon season and it may be due to the high scavenging/washout of

the carbonaceous content from the atmosphere during monsoon season.

The traffic congestion, cold start of the vehicle, idling of motor vehicles and low atmospheric dispersion condition in non-monsoon season leads to higher accumulation of carbonaceous contents. Presence of higher chlorine, sulphur, potassium and titanium during the non-monsoon season may be due to their emission from the anthropogenic sources such as industries, brick kilns and seas salts

Table 2. Enrichment Factors (EFs) of Different Elements at Both the Sites

Elements	JNU	BDP
C	554.28	2018.27
N	757.49	0.00
F	654.82	71.01
Na	0.02	0.00
Mg	0.53	0.07
Al	1.00	1.00
S	52.48	89.60
Cl	5.36	637.62
K	0.90	1.63
Ca	2.17	3.24
Ti	0.00	3.19
Fe	1.73	2.15
Pb	16.81	0.00

JNU= Jawaharlal Nehru University, New Delhi, BDP= Badarpur Industrial area, New Delhi; C: Carbon, N: Nitrogen, F: fluorine, Na: Sodium, Mg: Magnesium, Al: Aluminium, S: Sulphur, Cl: Chlorine, K: Potassium, Ca: Calcium, Ti: Titanium, Fe: Iron, Pb: Lead

(Kulshrestha et al., 2009; 2003; Rastogi and Sarin, 2005). The high oxide of sulphur further accumulated in the atmosphere due to low-temperature conditions after their emission from industries and diesel driven vehicles.

Source identification through Enrichment Factors (EFs)

JNU site

The results of the various methods for calculating heavy metal enrichment at JNU and BDP aerosol in ambient atmosphere are summarised in Table 2. The EFs values more than unity pointed towards their origin from anthropogenic sources. Three distinct groups can be classified on the basis of results obtained among the elements on the basis of their Enrichment Factors (EFs). Carbon (C), nitrogen (N) and fluorine (F) come under the extremely high EF value ranging between 100-1000 with the average 554.3 ± 29.0 and 757.5 ± 37.21 , and 654.8 ± 41.6 respectively. It was followed by high enriched elements (EFs between 10-100) such as sulphur (S) and lead (Pb) with average EFs of 52.50 ± 17.5 , and 16.8 ± 5.9 respectively. The third group was identified as non-enriched elements (EFs between: 1-10) such as chlorine (Cl), calcium (Ca) and iron (Fe) with an average EF of 5.4 ± 1.82 , 2.2 ± 0.2 , and 1.7 ± 1.52 respectively. The last category was also noticed with the EFs below 1, such as sodium (Na), magnesium (Mg) and potassium (K) with an average value of EFs was 0.02 ± 0.1 , 0.5 ± 0.05 , and 0.9 ± 0.1 respectively. Low enrichment factor for sodium (Na), magnesium (Mg) and Potassium (K) indicates towards their natural sources such as their origin from the sea, as all are the important constituents of seas salt. These elements with an extremely low value of the EFs basically originated from the natural sources such as sea salts, crustal/geogenic origin, and

biogenic origin. The presence of these seas salts in the Delhi may be the result of air mass movement through long-range transport (Kumar et al., 2016; Kulshrestha et al., 2009; 2003). A wide range of EFs values usually point out towards the mixed sources which are dominated by the anthropogenic emission sources (Khillare and Sarkar, 2012; Caridi et al., 1992; Srivastava et al., 2009). Similarly, EFs for the Sulphur and Lead point towards the automobile exhaust as JNU campus surrounded by ring road caring high volume of traffic, fossil fuels combustion, metal smelting, and waste incineration which may come to the JNU campus through atmospheric transport. Non-enriched Calcium pointed towards the natural sources of Ca at JNU, such as dust storm events and crustal resuspension due to the vehicular activities in university campus area (Guerzoni et al., 1997; Cheng et al., 2005). Chlorine showed the presence of the organic or inorganic chlorine (hydrogen chloride) into the atmosphere which may form through atmospheric chlorine cycles. Hydrogen Chloride is a principal source of acidification of salt spray-reaction of atmospheric sulfuric and nitric acids with chloride ions in aerosols (Harris et al, 1992; Vierkorn-Rudolf et al. 1984). It may also released from the anthropogenic sources such as Chloro Fluoro Carbons CF_2Cl_2 (CFC-12), CFCl_3 (CFC-11), and $\text{CF}_2\text{ClCFCl}_2$ (CFC-113), Carbon Tetra Chloride (CCl_4) and sea salts (Vierkorn-Rudolph et al., 1984). In extremely humid condition, ultrafine particles having Cl and S possibly form agglomerates through gas-to-particle conversion of gaseous Cl with CaO and CaSO_4 .

BDP site

The second site was also identified with a range of extremely high, high, moderate and non-enriched range of enrichment factors. Carbon fall in the extremely high EFs category with an average value of 2018.3 ± 76.2 , which can be ascribed

towards the emission from the coal thermal power plants situated in the vicinity of the sampling location. Vehicular emissions were also a significant source of Carbon in BDP site. Similarly, Chlorine (EFs: 637.6 ± 28.5) can also be released from various industries located at BDP site and can also participate in the atmospheric transformations reaction during acid deposition. Fluorine and Sulphur fall into the second category with the average EFs of 71 ± 26.4 , and 89.6 ± 12.5 respectively. Such high level of EFs of Sulphur indicate emissions from the automobiles, as the sampling area is located very near to the crossroad area having a large number of vehicles all day. Fossil fuels combustion, metal smelting, and waste incineration are the other sectors releasing sulphur into the atmosphere. The source of the Fluorine in the atmosphere near BDP may be related to emissions from the coal power plant and industries (Caridi et al., 1992; Pipal and Satsangi, 2015). Some other anthropogenic fluoride emissions will include hydrogen fluoride and particulate fluorides (Kirk and Lester 1986). Low EFs category of elements was also identified and found in the range of 1 to 10. Potassium, calcium, titanium and iron fall into this category with average EFs of 1.6 ± 1.2 , 3.2 ± 2.1 , 3.2 ± 0.8 , and 2.2 ± 1.5 respectively. The source of calcium may be from the crustal origin, whereas Iron, Titanium and Potassium may come from rock and mineral dust and Sea-water dissolved iron (Wang et al., 2015; Reynolds and Goldhaber 1978; Belousova et al., 2002). Magnesium was the only element falls into the non-enriched elements category indicating towards the mineral and sea salt related sources. Thus the potential elemental sources are coal power plants and vehicular emission among the anthropogenic sources, apart from mineral and crustal re-suspension of dusts from the natural sources of Delhi region.

CONCLUSIONS

The present study describes the morphology and elemental composition of the collected atmospheric PM_{10} samples and TSP present in rain samples. Using Enrichment Factor analysis, it has been identified that several natural and anthropogenic sources are responsible for the elemental contribution in ambient atmosphere. Morphological analysis of PM_{10} and

TSP_{RW} through SEM imaging showed that the freshly emitted soot particles, cluster aggregates of soot, Fe-rich particles, the crystal of sulphate of Ca/K and biological particles such as pollen, fungi and plant materials predominated at the JNU site. On the other hand at BDP site, fly ash particles and their aggregates, and aluminosilicate particles rich in Al, Si and O species and ceramic materials appears to have predominated. Elemental composition showed the high carbon contents at BDP site as compared to the JNU site, indicating the

predominance of the particulates emitted from coal power plants, vehicular emissions in the vicinity of sampling site at the industrial location.

Enrichment Factor (EFs) analysis further confirm the major source contributor of different elements at both the sites. Extremely enrichment in Carbon, Nitrogen and Fluorine, followed by Sulphur and Lead indicate mixed source contribution at JNU. Results showed that they are emitted from several anthropogenic sources such as fossil fuels combustion, metal smelting, and waste incineration and atmospheric long-range transport. On the other hand, Carbon, Chlorine and Fluorine were identified as the major contributor of the atmosphere at BDP site and point to their emission from coal power plants, smelters, steel and electroplating industries and atmospheric organic and inorganic chlorine released from various anthropogenic sources. Thus present study successfully determined the contribution of different elements from Natural as well as Anthropogenic sources at an Industrial location in comparison to JNU at Delhi.

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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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