

Chemical and Morphological Characteristics of Particulate Matter Suspended in the Air of the Dhaka University Area of Bangladesh

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Abstract

Total suspended particulate matter (SPM) in the urban atmosphere of Dhaka city was collected using a high volume sampling technique for a period of one month (August 2017-September 2017). Chemical characterization of particulate matter (PM) was investigated, and characterized concerning the size distribution, morphological features such as count, total area, average size, perimeter, circularity, aspect ratio (AR), roundness; equivalent spherical diameter (ESD), surface area and volume of PM. The results of elemental analysis showed that the presence of heavy metal in PM was ten to hundred times higher than the standard value prescribed by WHO and USEPA. Several morphological analysis indicated that particles varying in shape from nearly spherical to various irregular shape, had higher surface energy, higher content of Cl and S bearing particles and had a large surface area which can cause greater damage to lungs. The presence of various organic compounds containing functional groups like alcohols, ketones aldehydes, carboxylic acids as well as unsaturated and saturated carbon bonds was observed by FT-IR analysis. Scanning Electron Microscopy (SEM) was used to characterize the morphology of the PM. Agglomerates and shoots type particles were mostly seen in SPM.

Keywords

Particulate Matter, Fine Particle, Morphology, Heavy Metal, Scanning Electron Microscope

1. Introduction

Air pollution is a pressing issue in Bangladesh which is ranked 169th out of 178

countries in the Environmental Performance Index for Air Quality [1]. The numbers of deaths caused by ambient air, chemical and soil pollution (the forms of pollution associated with modern industrial and urban development) has been increasing rapidly. The number of deaths in the world attributable due to air pollution by only particulate matter (PM) is estimated to have risen from 3.5 million in 1990 to 4.2 million in 2015, *i.e.*, a 20% increase after 25 years. Among the world's 10 most populous countries in 2015, the largest increases in numbers of pollution-related deaths have been reported in India and Bangladesh [2]. The main sources of air pollution include emissions from faulty vehicles, especially diesel-run vehicles, brick kilns, rice and pulse (beans) grinding mill, dust from roads and construction sites, dust from poultry farm and toxic fumes from industries. These sources emit NO_x, SO₂, CO, CO₂, airborne microorganism and PM, which has direct adverse impact on human health and environment.

Heavy metals are severe environmental threat to the world due to rapid industrial growth and urbanization. The problem is driven by the poor environmental management system and lack of strict adherence to environmental protection policies. Airborne PM is a criterion air pollutant that is commonly the most problematic factor in local environments [3]. PM emitted from these sources may contain soot and aerosols like ash particulates, sulfates, metallic abrasion particles, and silicates [4]. The main particulate fraction of these emissions contains fine particles, and due to their modest size these molecules can penetrate deep into the lungs. Since these fine and ultrafine particles have adverse impacts on health, the sizes of molecules emitted from these sources have been brought into consideration. PM typically contains a wide range of chemical species. Chemical composition of PM plays an important role in characteristics of PM and also provides reliable information for identification of different emission sources [5]. Thus, a study on the extent of contamination ambient air by heavy metal in PM and its morphology is necessary to understand its health risk on human body. Several studies have been conducted to analyze the concentration and chemical composition of PM and the content of airborne microorganism at different places of the world [6] [7] [8] [9] [10]. Wide range of techniques such as AAS, XRF, INAA, PIXE and ICP-MS has been employed to characterize PM.

Dhaka, the capital of Bangladesh, is one of the most densely populated cities of the world with a population of 18.89 million and density 29,069/km². The city has been ranked second on a global list of cities with worst air pollution, which claims 122,400 lives a year [11]. Studies on the physical and chemical characterization of PM with respect to the air quality of Bangladesh are scanty. Few reports are found regarding indoor air pollution and its impact on human health from biomass fuel used in Bangladesh [12] [13]. But to the best of our knowledge, there is no report about the characterization of PM concerning chemical composition and morphological characteristics. The aim of the present study is to characterize the chemical and morphological properties of SPM collected in Dhaka University area. Scanning electron microscopy (SEM) analysis has been

employed to identify the source on the basis of their morphological characteristics like perimeter, circulatory, shape, color, size, equivalent spherical diameter (ESD) and aspect ratio of individual particles [14] [15].

2. Experimental

2.1. Description of the Sampling Area

Dhaka is the largest city and the capital of Bangladesh (Figure 1). It is also one of the largest cities in South Asia, with the population of about 18.89 million people. The latitude of Dhaka, Bangladesh is 23.777176, and the longitude is 90.399452. Dhaka, Bangladesh is located at Bangladesh country in the Cities place category with the gps coordinates of 23°46'37.8336"N and 90°23'58.0272"E. Dhaka, Bangladesh elevation is 22 meters height that is equal to 72 feet. Under the Köppen climate classification, Dhaka has a tropical savanna climate. The city has a distinct monsoonal season, with an annual average temperature of 26°C (79°F) and monthly means varying between 19°C (66°F) in January and 29°C (84°F) in May [16]. The Bangladesh Meteorological Department has categorized the months of January and February as winter season, March-April as summer

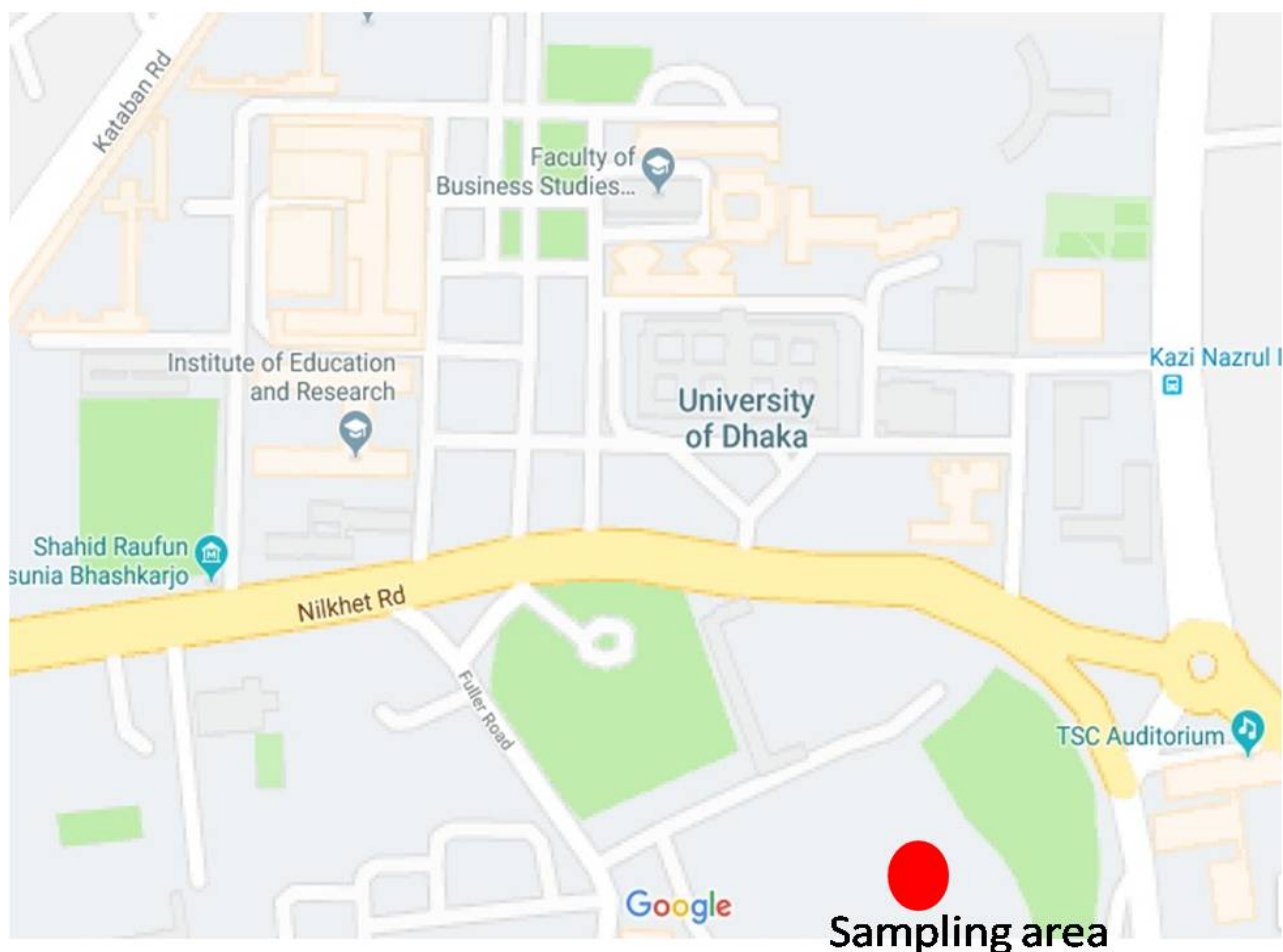


Figure 1. Dhaka city map (red circle marked sampling area).

season, May-June as rainy season, July-August as autumn, September-October as the late autumn and November-December as monsoon. Most of the rainfall occurs during northeast monsoon and less rainfall during the southwest monsoon. Typical meteorological conditions in winter with low wind speed and low mixing height restrict diffusion, dilution and transport of air pollutant resulting in high levels of particulate matter.

2.2. Sampling

The sample was collected from a continuous air quality monitoring station (CAMS) that was installed in the Centre for Advanced Research in Sciences (CARS), University of Dhaka, Bangladesh. The CAMS was installed by a joint collaboration of Wuppertal University, Germany and the University of Dhaka, Bangladesh that can suck air at a rate of 16 m³/min for PM₁₀ and 15.2 m³/min for PM_{2.5} at 24 hours. The sample was taken in the period of 16th August to 17th September. The sample was collected on 25-mm diameter PTFE filters of pore size 0.3 mm (Whatman International Limited, USA).

2.3. SEM-EDS Instrumentation

Morphological and elemental characterization of airborne particulates were performed by SEM (JEOL, JSM 6490LA). Dry and particle loaded filters were cut in to approximately 1 mm² size and mounted on aluminum stubs with double sided sticky carbon tape. Samples were observed and photographs were taken by changing different magnification by stereo SEM at 30 tilt and 10 KV. Three images of every sample were taken at different magnifications to feature the morphological characteristics.

2.4. FTIR Instrumentation

Particulate matter collected on the filter paper was scrapped with the brush and mixed with potassium bromide. The KBr based pellets were compressed into a thin disk using hydraulic pressure of ten ton (CAP-15T). The absorbance spectrum was measured between 400 - 4000 cm⁻¹ at a resolution of 0.09 cm⁻¹ using (IRPrestige 21, Shimadzu, Japan)). Final sample spectra were obtained by subtracting the spectra of field blank from the spectra of corresponding sample.

2.5. Elemental Analysis of PM

Dust sample was collected for the analysis of Calcium, Cadmium, Cobalt Iron, Magnesium, Manganese, Nickel, Lead and Zinc content. Calcium (wavelength 422.7 nm), Cadmium (wavelength 228.8 nm), Cobalt (wavelength 240.7 nm), Iron (wavelength 248.3 nm), Magnesium (wavelength 285.2 nm), Manganese (wavelength 279.5 nm), Nickel (wavelength 232.0 nm), Lead (Wavelength 283.3 nm) and Zinc (wavelength 213.9 nm) specific hollow cathode lamps were used to analyze the samples. The instrument (Perkin Elmer, Analyst 200) has minimum detection limit of 0.06 mg/L for Ca, 0.01 mg/L for Cd, 0.03 mg/L for Co,

0.05 mg/L for Pb, 0.04 mg/L for Fe, 0.01 mg/L for Mg, 0.02 mg/L for Mn, 0.06 mg/L for Ni and 0.01 mg/L for Zn in the flame method. Samples were aspirated through nebulizer and the absorbance was measured. Calibration curve was obtained using standard samples (containing 1.0, 2.0, 3.0, 4.0 and 5.0 mg/L for Ca, 0.2, 0.4, 0.6, 0.8 and 1.0 mg/L for Cd, 0.2, 0.4, 0.6, 0.8, 1.0 mg/L for Co, 0.5, 1.0, 1.5, 2.0 and 3.0 mg/L for Fe, 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 mg/L for Mg, 0.2, 0.4, 0.6, 0.8 and 1.0 mg/L for Mn, 0.2, 0.4, 0.6, 0.8 and 1.0 mg/L for Ni, 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 mg/L for Pb, 0.2, 0.4, 0.6, 0.8 and 1.0 mg/L for Zn. The correlation coefficient was found for Ca 0.999, for Cd 0.998, for Co 0.998, for Fe 0.996, for Mg 0.999, for Mn 0.998, for Ni 0.997, for Pb 0.999 and for Zn 0.996 respectively. The sample had to be diluted many folds to keep the results in the analytical range.

3. Results and Discussion

3.1. SEM Image Analysis

More than 5300 individual particles were analyzed with Image J software that was developed by National Institute of health, Maryland [17]. Thereafter, morphological features such as count, total area, average size, perimeter, circularity, aspect ratio, roundness, ESD, surface area and volume of PM have been calculated (Table 1). Primary feature such as aspect ratio is an image projection attribute that describes the proportional relationship between the width (W_{max}) of an image and its height (L_{max}). The nano-particle shows a higher aspect ratio. This implies the higher surface energy or higher activity of the nano-particle. So the aspect ratio of nano-particle has a significant role in its cellular uptake. Average AR was found 1.626 which is recorded for Cl and S bearing particle [18]. Circularity (Equation (2)) affected the fractal particles in the transition regime; average circularity was 0.913 (less than one) which indicates that most of the particles are not perfectly spherical [19]. The factors roundness is very important in characterizing the particles, regardless of their sizes. Roundness (Equation (3)) of the particle was ranged from 0.51 to 0.90 (mean 0.713), indicates that the particles vary in shape from nearly spherical to irregular. According to the IUPAC definition, the ESD of a non-spherical particle is equal to a diameter of a spherical particle that exhibits identical properties (e.g., aerodynamic, hydrodynamic, optical, electrical) to that of the investigated non-spherical particle. For particles in non-turbulent motion, the equivalent diameter is identical to the diameter encountered in the Stokes' law [20]. A value of ESD of PM greater than 0.93 is known as a respiratory fraction. A mean value of ESD was found 11.01 in

Table 1. Morphological characteristics of PM (dimensional parameters were measured in calibrated units microns).

Count	ESD	Circularity	Aspect Ratio	Roundness	Solidity	Surface area (μm^2)
5229	11.103	0.913	1.626	0.713	0.917	182

the current study that gives an alarming message regarding air quality of the sampling area. Nanoparticles are characterized by having a high surface area per mass. Mass of particles or particulate surface area plays an important role in determining the biological activity of nanoparticles. Large surface area (Equation (5)) of the ultrafine particle increases their interaction with lung tissue and can cause greater damage to lungs.

$$\text{Aspect Ratio} = L_{\max}/W_{\max} \quad (1)$$

$$\text{Circulatory} = 4\pi \times A/P^2 \quad (2)$$

$$\text{Roundness} = P^2/4\pi \quad (3)$$

$$\text{Equivalent Spherical Diameter} = \frac{2\sqrt{A}}{\pi} \quad (4)$$

$$\text{Surface Area} = 4\pi \times (ESD/2)^2 \quad (5)$$

3.2. Elemental Analysis

The average concentrations of Zn, Mg, Mn, Pb, Ca, Cd, Co and Fe in PM sample are presented in **Table 2**. Lead had the highest average concentrations of 1.89 mg/L. Lead had been reported to be one of the major constituents of industrial emissions [21]. Zinc had a second highest concentration of 1 mg/L. Querol *et al.* reported that from Fe and steel metallurgical emission, the concentration of Zn is higher compared to other materials [22]. The major industrial sources of zinc include electroplating, smelting and ore processing, and drainage from both active and inactive mining operations. The average concentrations for Fe was found 0.75 mg/L. Fe is of particular interest as it is the most abundant transition metal in the atmosphere and the fourth most abundant element in the Earth's crust. Fe has also been identified as a component of PM that leads to the formation of reactive oxygen species through Fenton chemistry [23]. **Table 3** shows the comparison of the average metal concentrations in airborne particles with the safe limits proposed by international World Health organization (WHO) and United State Environmental Protection Agency (USEPA). The average values of all the metals obtained in this study were higher than the recommended safe limit [24].

3.3. Composition of Inorganic Mass

The FT-IR spectra of the particle (**Figure 2**) display numerous peaks, assigned to a large number of functional groups. The peak for sulphate and bisulphate was found integrated at 1090 cm^{-1} and 480 cm^{-1} respectively (**Table 4** and **Figure 2**). In the atmosphere, sulphate is formed from photo-oxidation of sulphur dioxide [25]. Particle water firmly bound to aerosol salts which absorb wavelength at 1600 - 1700 cm^{-1} , but if water comes from salt hydrates it absorbs the radiation in the range of 3350 - 3450 cm^{-1} [17]. The absorbance peak at around 1425 cm^{-1} indicates the presence ammonium ion [26]. Presence of quartz and kaolinite in the particulates were confirmed from the absorption at 730 - 1090 cm^{-1} [27]. The intensity and the position of peaks between 461 - 467 cm^{-1} assigned to some

Table 2. Average elemental concentration of the heavy metals in PM sample.

Zn (mg/L)	Ca (mg/L)	Mg (mg/L)	Cd (mg/L)	Mn (mg/L)	Co (mg/L)	Pb (mg/L)	Fe (mg/L)
1	0.69	0.16	0.06	0.57	BDL	1.89	0.75

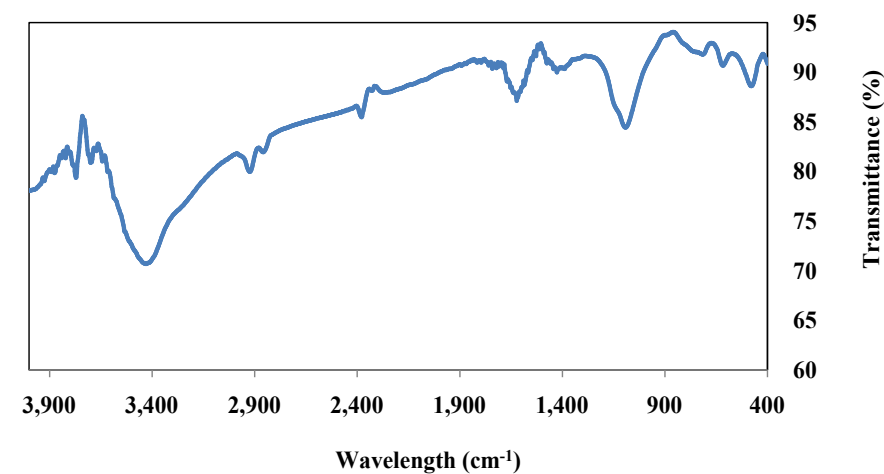
*BDL: below detection level.

Table 3. Comparison of the concentration of some heavy metals with WHO and USEPA Guidelines (mg/L).

Elements	WHO	USEPA	This study
Cd	0.005	0.0006	0.06
Mn	0.15	0.50	0.57
Pb	0.50	1.15	1.89
Fe	0.005		0.75

Table 4. Relative abundance of organic and with inorganic inclusions found at the sampling area.

S/N	Wave number (cm ⁻¹)	Functional group
1	480.28	SO ₄ ⁻ (silicate))
2	617.22	SO ₃ ²⁻ (sulfite ions), 1-nitropyrene
3	1091.7	SO ₄ ²⁻ HSO ₄ ⁻ (sulphate, bisulphate)
4	1425.4	NH ₄ ⁺ (ammonium)
5	1616.35	Aerosol salt
6	2858.51	CH ₃ , CH ₂ and CH alkanes
7	2924.09	Aliphatic hydrocarbon
8	3429.43	Alcohol, phenol
9	3699.47	OH ⁻
10	3770.84	C=O, OH ⁻

**Figure 2.** FTIR spectra of particulate matter collected from Dhaka University area of Bangladesh.

characteristic functional groups indicate the presence of silicate ions in PM, whereas, the transmittance spectrum of PM in the 600 - 900 cm^{-1} spectral range showed a peak at 617 cm^{-1} that was identified in the spectrum of 1-nitropyrene. However, at this frequency (617 cm^{-1}) molecular vibration from sulfite ions (SO_3^{2-}) present in the particulate matter can also be observed [28].

3.4. Composition of Organic Mass

Various functional groups present in particulates are analyzed using FTIR and the results presented in **Table 4**. Presence of aliphatic hydrocarbons, alcohols and carbonyl compound was seen in all the particle size fractions. The peaks in range of 3300 - 3600 cm^{-1} are attributed to alcohols, phenols (both monomeric and hydrogen bonded), carboxylic acids etc. [29]. The peaks lying in the range of 2850 - 3000 cm^{-1} characterize the aliphatic hydrocarbons due to asymmetric and symmetric C-H stretching vibration of aliphatic CH_2 group, whereas, higher intensity of the band at 1384 cm^{-1} may be attributed to symmetrical C-H bending vibrations from aliphatic CH_3 [30] [31]. These aliphatic carbon groups are mainly formed in the fine particle fraction of respirable dust [32]. Peaks in the range of 3600 - 3870 cm^{-1} and 1650 - 1750 cm^{-1} are attributed to C=O bond of aldehydes, ketones and carboxylic acids. It is considered that the compounds containing the -C=O and -OH groups are the important components of secondary organic aerosol [33]. The prominent band near 1616 cm^{-1} confirms the presence of organic nitrate in the aerosol which may be conjugated by secondary particles emitted by fossil fuels, natural gas and residential heating [32] [33].

3.5. Particulate Morphology

Using secondary electron imaging individual, three different kinds of particles were identified: a) a nearly-spherical HCs droplets, b) large agglomerates composed of small primary particles, and c) mineral dust and other unidentified particles (**Figure 3**). Morphologies of different types of particles found in the particle are in agreement with the work presented in [34]. Spherical structure of the particles and resistance to electron beam make it easily attributable. Agglomerates and shoots type particles are mostly seen in slightly age smoke of biomass burning. The particle of around 6 nm that are spherical in size is also found according to the work described in elsewhere [35]. Particle size and shape vary depending on their mode of formation and distance from the sources. For example, absolute spherical particles can usually be assigned to smelters and larger particles tend to fallout closer to the source. The elemental compositions of individual particles provide a lot of information about the origin of particle sample but this information is implied during sample analysis due to the presence of chemically complex mixtures of particles from multiple sources [36].

4. Conclusion

Dhaka University area is considered comparatively cleaner than another part of the Dhaka city. Our study showed a general view of the quality of the air of this

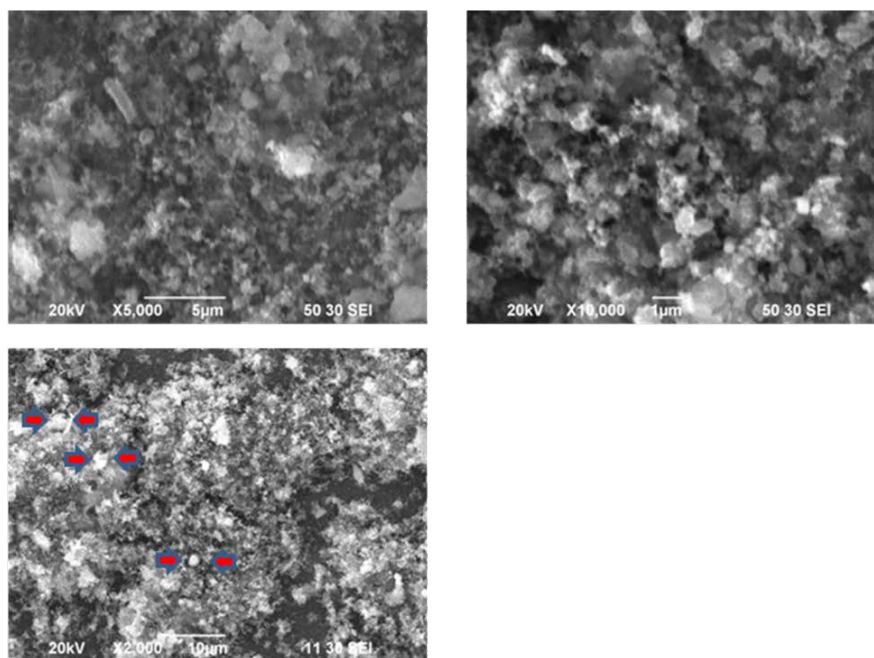


Figure 3. SEM images of suspended PM with organic and inorganic inclusions.

area by characterization of PM. The sources of PM in this area are mainly emission from vehicle and road dust. The result showed that heavy metals content in the air is 10 to 100 times higher than the standard value of WHO and USEPA. Morphological analysis showed that the specific types of amorphous, spherical and carbonaceous particles were dominant, namely, soot, tar balls, aluminosilicates and sulfur-rich particles. Moreover, the physiochemical characteristics of particle like. Aspect ratio, circulatory, ESD and surface area provide an alarming message regarding the enhancement of the pathogenicity of respiratory disease as well as silicosis. The elemental compositions of individual particles provide a lot of information about the origin of particle sample.

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Conflict of Interest

The authors declare no conflict of interest.

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