Particulate Matter as a Giant Fraction of Fossil Fuel in Urbanized Areas

Syed Zafar Ilyas^{1*}, Ather Hassan¹

¹Department of Physics, Allama Iqbal Open University, H-8 Islamabad.

Corresponding Author:

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Abstract

Fossil fuel injects particulate matter into a clean environment which has diverse effects on the biosphere. It is the cry of the masses which stimulates investigation of the local ambient environment for Particulate Matter (PM) and its sources. The purpose has been achieved by using versatile techniques such as Micro-Orifice Uniform Deposit Impactor (MOUDITM) for collection, Fourier Transform Infrared (FTIR) Spectrometry for characterization by Size Mass Concentration, and Atomic Absorption Spectroscopy techniques were utilized to identify and quantify different PM in the study area. The urban territories (different locations of Okara) were found contaminated with coarse, fine, and ultra-fine Particulate matter because of local industries and vehicular emissions. Coarse particles (PM₁₀) of size 3.2 μ m and 10 μ m, fine particles (PM_{2.5}) and Ultra-fine particles (0.056 μ m) were quantified around 8 μ g/m³, 10 μ g/m³ and 25 μ g/m³ respectively. The obtained results could be linked with the widespread use of lowquality fossil fuels and the increased number of vehicles. The ultimate solution to the prevailing scenario can be in hand by switching over to renewable energies such as solar, hydrogen, and wind.

Keywords:

PM, Size distribution, Mass concentration, MOUDI.

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Introduction

Air pollution has been a problem for centuries [1-3]. According to an estimation of the World Health Organization, about 2.4 million people die each year because of air pollution [4]. Ozone depletion, acid rain, greenhouse gases, photochemical smog, and global warming are the known consequences of air pollution.

The ambient air exists with Nitrogen = 78.08%, Oxygen = 20.95%, Argon = 0.93% as major constituents and Carbon Dioxide = 400ppm, Neon = 18.2ppm, Helium = 5.2ppm, Methane = 1.7ppm, Krypton = 1.1ppm, Hydrogen = 0.6ppm and water vapors up to 1% as minor constituents. The air's mean molecular mass is 28.97 g/mol [5].

Air is considered polluted if it exists with the abnormal quantity of any gaseous, liquid, or solid substances that distress the natural life [6] and according to Perkins; air pollution means the existence of dust, gas, fumes, mists, odor, water vapors or smoke in unusual quantities. The Environmental Protection Agency (EPA) has declared 188 toxic air pollutants. These air pollutants comprise particulate matter (PM), the volatile organic compound (VOCs), a halogen compound and more commonly known as Pb, Hg and As, etc [7].

Air pollutants are categorized into two groups i.e., primary air pollutants and Secondary air pollutants. Radioactive compounds, Organic compounds, Carbon monoxide, Halogen compounds, Nitrogen oxides, Sulfur compounds, Coarse particles, and Finer aerosols particles including particles of metals, tar, resins, carbon, bacteria, and pollen are the primary pollutants. Interaction of primary pollutants and photo-activation results in secondary pollutants; like Ozone, Formaldehyde, Photochemical smog, PAN (peroxyacetyl nitrate), and formation of mists (H₂SO₄) by the reaction of dissolved oxygen and sulfur dioxide [8].

An investigation report of the Australian industries revealed that heavy metals and their compounds are mixed into the air by the end-use of fossil fuel. The industries like Textile, leather, steel, paper and pulp, sugar, electroplating, fertilizer, and polyester are introducing numerous metallic and nonmetallic pollutants to the environment. A large group of air toxins is the result of these heavy metals. Industrial smoke, automobile, and aircraft exhaust are the sources of toxic metals.

The main contribution to air pollution is vehicular emission, including the highly damaging emission of fine particulate matter. The major pollutants emitting from the industries and vehicular traffic are SO₂, CO, NO_X, NH₄, Cr, Pb, Zn, and Fe [9].

The rapid growth in population and the standard of living may be considered the stimulating factors of pollution [10]. South Asia is densely polluted, due to its high population and many industries. Pakistan is an important country on the South Asian map and is suffering from severe environmental problems. According to the World Health Organization (WHO) report, South Asia has been declared the most polluted region of the world.

Air pollution is a major problem in Pakistan. Incomplete burning of fossil fuels, burning of solid waste and toxic plastics, many industries and vehicles are the factors involved in contaminating the environment [9].

Some cities of our neighboring countries such as (India) has been found contaminated with (106 ±62) μ gm⁻³ of benzene soluble organic fraction (BSOF) of PM₁₀ [11] and Shanghai (China) is reported with 50% fine (< 1.6 μ m) particulate of mercury [12]. W.

Yue et al attributed $PM_{2.5}$ (0.2 to 1.4 µm) to metallurgical industries, coal combustion, and automobile exhaust in the city of Shanghai [13]. Aluminum manufacturing dust, silicomanganese, fly ash, burning coal, sulfur-rich, zinc-rich particles, soil, quartz, lead sulfate, syngenite, iron, dolomite, s-bearing iron, dolomite, sphalerite, calcium-rich and gypsum have been reported in the environment of Guiyang (China), which are anthropogenic particles [14]. In China, Kristin Aunan and Xiao-Chuan Pan studied the health exposure-response coefficient against surrounding air pollution, and calculated 0.04% (S.E. 0.01), 0.06% (S.E. 0.02) and 0.10% (S.E. 0.02), 0.03% (S.E. 0.01) and 0.04% (S.E. 0.01) raise in mortality due to cardiovascular, respiratory, and other diseases respectively for an increase of one µg/m³ of SO₂ and PM₁₀. The exposure-response coefficient for China has been confirmed less as compared to the USA and Europe [15].

Q. Wang et al studied the refractory black carbon (RBC) in the Qinghai Lake situated in the North-Eastern Tibetan Plateau of China. The average RBC's mass concentration during the two-week campaign period was recorded at about $0.36 \,\mu g \, \text{STP/m}^3 \, [16]$.

Some urban areas of Western Europe are reported contaminated with PM_{10} and black smoke (BS) more than rural areas [17].

Karin N. Jallad reported Kuwait with a high concentration of non-methane hydrocarbons (NMHC), ozone (O_3) , and nitrogen dioxide (NO_2) [18].

Hui Hu connected the risk of preeclampsia and hypertensive disorders of pregnancy (HDP) with air pollutants [19].

G. Mazzarella and F. Ferraraccio observed diverse effects of diesel engine exhaust on human respiratory system [20] and Lkenna C. Eze et al, suggested that long-term exposure to air pollution may be linked to diabetes mellitus [21].

J. Anne E. et al. found cytotoxic water-soluble particulate matter in the cities of Auckland and Christchurch [22].

A. Valavanidis et al. analyzed the atmosphere of Athens and attributed the metal particles of Cd, Fe, V, Pb, Zn, Cr, and Cu in PM fraction to local anthropogenic and vehicular traffic emission [23].

H. Shan Tai et al. studied the nature of particles that were accumulated on surfaces of the existing objects in that locality [24]. The average size, for the urban and non-urban locations, was reported in the range of 33 and 27 μ m.

Laser-Induced-Fluorescence (LIF) was used to characterize the biological and organiccarbon (OC) atmospheric aerosol particles [25].

It has been realized that the instrumentation and sampling technique plays an important role to characterize particulate emissions [26].

The current research was carried out in Okara (Pakistan). Okara District is a district of Sahiwal Division in Punjab, Pakistan situated at 30.6842° N, 73.7478° E, with a total area of 4,377 km² that accommodates 3.039 million people. District Okara is bounded on the East by Kasur district, Sahiwal and Pakpattan districts on the West, Sheikhupura and Faisalabad districts on the North, and Bahawalnagar district on the South. The Indian border also lies on the South-Eastern side of the district [27].

The climate of the district is hot in summer and cold in winter. May and June are the hottest months with the maximum temperature reaching $44C^{\circ}$. January is the coldest

month with a minimum temperature falling to $2C^{\circ}$. The average annual rainfall is 200 mm.

Materials and Methods

Samples from different sites (WAPDA Grid Station, Purani Choungi Depalpur, Depalpur Chowk, Madina Chowk, Ketchehri Chowk Depalpur) of Okara (Pakistan) were collected using 10-stages Micro-Orifice Uniform Deposit Impactor (MOUDITM), with cut points of "10-µm, 5.6-µm, 3.2-µm, 1.8-µm, 1.0-µm, 0.56-µm, 0.32-µm, 0.18-µm, 0.10-µm, and 0.056-µm". The MOUDITM was run for eight hours to collect air samples.

The working principle of MOUDITM is based on the inertial impaction in series using multiple-nozzle stages. The nozzles comprise jets with particle-loaded air at each stage imposed on an impaction plate. Particles larger than the cut-size cross the airflow streamline of that stage and collect on the impaction plate. Smaller particles don't cross the streamlines due to less inertia and keep on to the next stage with the smaller nozzles size, the velocity of air from first to last increases and finer particles are collected.

The nominal cut size, the number, and the diameter of each impactor stage of the corresponding nozzles are shown in Table 1. The particle collection efficiency curves experimentally obtained are shown in Figure 1. The calibrations were performed with the Berglund- Liu Vibrating Orifice Monodisperse Aerosol Generator for particle sizes larger than $1.0-\mu m$ and with the electrostatic classifier technique for sub-micrometer particles [10,28].







Sample preparation for Atomic Absorption Spectroscopy (AAS)

We took 1 g of each collected sample and prepared a 100 ml solution in distilled water. For detection of nickel, copper, and lead elemental percentages, appropriate amounts of Ni (CH₃COO)₂. 4H₂O, CuCl₂, and Pb (NO₃)₂ were dissolved in distilled water to

make the samples of 1ppm, 2ppm, 3ppm, and 4ppm respectively. And then these samples were analyzed by AAS.

Results and Discussion

Samples were characterized by Size Mass Concentration, Fourier Transform Infrared (FTIR) Spectrometry, and Atomic Absorption Spectroscopy.

The samples collected through MOUDI were analyzed to find out the parameters that describe the particulate matter (PM). The relation of particle size and mass concentration was used to calculate the size of the particulates. Particle size and mass concentration are evaluated in table 2 and figure 2.

Table 2 Particles Size and Concentration at Different Sites

	Particle size(µm)	Mass (g)	Area of deposition (cm ²)	Thickness of deposited layer (cm)	Volume (cm ³)	Concentration (g/cm ³)	
5	0.32	0.077	6.154	0.001	0.003	25.06	WAPDA Grid Station
6	0.056	0.078	6.154	0.001	0.004	20.99	Purani Choungi
6	0.056	0.096	6.154	0.0004	0.002	39.04	Depalpur Chowk
3	1	0.080	6.154	0.001	0.003	25.93	Madina Chowk
6	0.056	0.083	6.154	0.001	0.005	16.84	Ketchehri Chowk

All sites have been observed with a high concentration of coarse particles (PM_{10}) of size 3.2 µm and 10 µm, fine particles ($PM_{2.5}$), and Ultra-fine particles of size 0.056 µm.

The Depalpur Chowk Okara, which is choked with more automobile workshops, has been reported with a high concentration of ultra-fine particles. The people living around are at high risk of lung disease. Exposure to particulate matter leads to more visits to the doctors or emergency room.



Figure 2 Particle size and mass concentration

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Figure 3 Comparison of different PM concentrations at different sites

Locality vise analysis is given in Figure 3 which depicts the remarkable concentration of coarse particles at Madina Chowk as compared to other sites. A high concentration of fine particles has been observed at Madina Chowk and the WAPDA grid station. A significant amount of ultra-fine particles are reported at Depalpur Chowk.





The time-span effect of particle concentration in District Okara was also focused.

In March, the concentration of PM is significant, as depicted in Figure 4. The possible reason is the increase of pollens in the spring season.



Elemental confirmation through FTIR absorption spectrum

Figure 5-a stage S1 (10 μ m), 5-b stage S3 (3.2 μ m), 5-c stage S7 (0.32 μ m), 5-d stage S8 (0.18 μ m), 5-e stage S10 (0.056 μ m) at Ketchehri Chowk Depalpur (Okara)



Figure 5-f stage S2 (5.6 μ m), 5-g stage S5 (1.0 μ m), 5-h stage S6 (0.56 μ m), 5-i stage S7 (0.32 μ m), 5-j stage S8 (0.18 μ m) at Purani Chowngi Depalpur (Okara)

Ammonium Bicarbonate (NH₄HCO₃) Lead Carbonate (PbCO₃), Ammonium Sulphate $[(NH_4)_2 S_2O_3]$, Nickel, Zinc and Cobalt bi-pyridine compounds, Potassium Bicarbonate and Sodium Carbonate [fig 5(a-j)], has been confirmed in Ketchehri Chowk Depalpur

(Okara) and Purani Chowngi Depalpur (Okara), that verify the presence of toxic elements flying in the atmosphere of the local environment.

Quantification of Metals through Atomic Absorption Spectroscopy (AAS)

Different trace metals and their percentage has been found with AAS (model A. Analyst 100). As per prerequisites of the procedure a 100 ml solution was prepared for 1 gram of each collected sample. Then 1ppm, 2ppm, 3ppm and 4ppm solutions of Ni (CH₃COO)₂ .4H₂O, Pb(NO₃)₂, CuCl₂ and ZnCl₂ were prepared for % age calculation.

Table 3 WHO standards

Sr.	Elements	Concentration in living areas	Concentration in Polluted areas
1	Zn	0.09 µg/m ³ or 0.01%	1 μg/m ³ or 0.05%
2	Cu	0.1 µg/m ³ or 0.001%	0.1 µg/m ³ or 0.001%
3	Ni	0.2 µg/m ³ or 0.0001%	0.2 µg/m ³ or 0.0001%
4	Pb	1.55 μg/m ³ or 0.0053%	1.55 µg/m ³ or 0.0053%





Figure 6-a Nickel



Figure 6-b Lead



Figure 6-c Copper

Figure 6-d Zin

The figure 6(a-d) confirmed the values of nickel particles about 0.047% and 0.001%, lead particles about 0.111% and 0.05%, copper particles around 0.0072% and 0.022% and zinc particles about 0.024% and 0.039% at industrial and traffic zones, and residential areas respectively. All the calculated values exceeded the recommended values of WHO, which are tabulated in table-2 for comparison purposes.

These abnormal quantities of the pollutants are the result of used motor oils. As in some cases, fractions of copper particles have been reported in aerosols [29]. Similarly in industries, where coal is used as a fuel, copper traces have been reported in the plumes of fly ash [30]. Other sources of such pollutants are the brake pads of modern cars which contain copper. As time goes on, these pads wear away which contaminates the ambient atmosphere of that locality [31]. In some areas where sanitary pipes are used for water distribution, traces of copper have been reported in the environment [32].

It is observed that increase in emissions from vehicular traffic, industries, cooking, open solid waste burning and use of low-quality fuel in many bricks kiln pose a potential risk to the air quality of district Okara.

Conclusions

The findings of the current study confirm the unfavorable living conditions for the residents of Okara (Pakistan). The major interventions to the environment of Okara are vehicular emission and industrial exhausts. The vehicular emissions, including highly damaging fine PM emission, is often among the major contributors to air pollution. The widespread use of low-quality fuel along with a dramatic increase in the number of vehicles particularly in urban areas increases air pollution.

The ultimate solution to the prevailing scenario could be achieved by switching over to renewable energies such as solar, hydrogen, and wind. Although it will cost more to replace the existing energy with renewable energies, the results will be acceptable to all societies.

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