Carbonaceous Analysis of Fine Particulate Matter in Proximity to the Historical Monument Itimad-ud-Daulah, Agra

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KEYWORDS

"$PM_{2.5}$", "OC", "EC", "WHO", "NAAQS"

ABSTRACT

$PM_{2.5}$ which is also known as Fine Particulate Matter (having aerodynamic diameter of less than equal to 2.5µm) is a designated criteria pollutant by USEPA, is directly emitted into the atmosphere or results from the transformation of gaseous pollutant. $PM_{2.5}$ is found to be associated with various health hazards such as chronic lung disease and asthma, lung cancer, heart attack, exacerbation of COPD and premature death. One of the carbonaceous content of $PM_{2.5}$ elemental carbon is found to be associated with climate change. The present study aims to investigate the concentration and carbonaceous characterization of fine particulate matter. The study was carried out near a historical monument Itimad –Ud –Daulah during the winter period (January 2022), samples of $PM_{2.5}$ were collected at the sampling site via Fine Particulate sampler APM 550 on Quatrz Fiber Filter paper and analyzed for organic carbon and elemental carbon. The average mass concentration of $PM_{2.5}$, OC and EC were 231.60 µg/m^3, 29.74 µg/m^3 and 11.98 µg/m^3 respectively. The % contribution of OC and EC to the mass $PM_{2.5}$ is found to be 12.84 % and 5.17 % respectively which indicates that OC and EC contribute a significant portion in $PM_{2.5}$.

The concentrations of $PM_{2.5}$ were also found to be 6 and 46 times higher than the annual average standards provided by NAAQS and WHO. The results of the study indicate that the burning of carbon-containing fuel for residential heating and unfavourable meteorological conditions during the winter period combined contribute to the increased concentration of OC, EC and $PM_{2.5}$. OC and EC were also found to be positively correlated to each other, indicating their emission from common sources.

1. Introduction:

Air pollution, driven largely by particulate matter, is now widely recognized as one of the most significant environmental concern, particularly in developing nations like India. Rapid industrialization and urbanization in these regions have rendered industrialized cities highly vulnerable to deteriorating air quality. Aerodynamic particle diameter of less than equal to 2.5 µm is of more concern due to its detrimental impact on human health, environment and climate [1-2]. The small diameter and extensive surface area of $PM_{2.5}$ make it potentially capable of transferring many hazardous substances through diffusion, causing harm to different parts of the body through lung air exchange [3]. Major sources of fine particulate pollution include automobile emissions, soil-derived aerosols, industrial processes, biomass and coal burning [4]. In addition to emission sources, meteorological parameter plays a very important role in the dispersing and diffusing the pollution. $PM_{2.5}$ pollution also shows seasonal variation with it being high during the time of winter followed by summer and monsoon. During wintertime, fine particulate pollution is found to be at its peak because of adverse meteorological conditions that restrict the dispersion and increase the concentration of $PM_{2.5}$ pollution close to the earth's surface.

$PM_{2.5}$ is majorly composed of carbonaceous fractions, inorganic ions, and trace elements, which can be emitted directly into the atmosphere from various primary emission sources and can be formed through chemical reactions of precursor gases in the atmosphere [5-6]. The carbonaceous fraction of $PM_{2.5}$ usually comprises EC and OC, OC consists of a large variety of aliphatic and aromatic organic compounds and a significant fraction of these compounds contain potential mutagens or carcinogens [7]. OC can be generated by atmospheric reactions involving gaseous organic precursors or it can be directly released from emission sources such as power generation, transportation, heating, industrial processes, bio-fuels, and biomass burning [8], however, incomplete combustion of biomass, biofuel, and fossil fuels results in the emission of elemental carbon and because of its warming influence on the climate, EC is thought to be the second most significant direct forcing factor contributing to global warming after CO_2 [9]. EC may also interfere in several significant chemical reactions involving ambient sulfur dioxide (SO_2), nitrogen oxides (NOx), ozone (O_3), and other gaseous substances because it has many adsorption sites that can improve catalytic processes [10-12] alongside being detrimental for the environment. EC can also serve as a carrier for toxic substances, including heavy metals, benzopyrene, and polychlorinated biphenyls causing harm to human health [13].

Carbonaceous particles have a substantial impact on the environment, although little is known about their sources and concentrations in various locations. Therefore, the main objective of this research is to report the concentration of EC and OC and to comprehend how meteorology affects their concentration, as this will further help policymakers in making strategies to control pollution.

2. Material And Methods:

Study Area/Sampling Site

Agra ($27^{\circ}10'$ N latitude $78^{\circ}20'$ E longitude) is located in the north-central part of India, it is about 204 km of south of Delhi. Agra is the most famous tourist place in India due to the presence of the Taj Mahal. Soil found in the city is sandy, calcareous and dusty. The climate of the city is semi-arid type with a hot and dry summer, a wet monsoon and a chilly winter.

Sampling was carried out in Nunhai near historical monument Itimad-ud-Daulah which was constructed by the Mughal queen Nur Jahan the wife of Jahangir. It was constructed between 1622 and 1628. She built this mausoleum as a tribute to his father Ghiyas Beg. The tomb is made up of pure marble. In the east of the monument, Nunhai which is the major industrial area of Agra and it mainly comprises industrial establishment and slum localities, industries located in this area include ferrous and non-ferrous metal and alloy processing, iron casting, lime oxidation, rubber processing, pulverization and engineering works. The dense slum population extensively burns traditional fuels such as wood, agricultural material and animal dung for domestic purposes arise air pollution in this area.

Fig. 1 Location of sampling site [14]

Methodology:

$PM_{2.5}$ samples were collected in January 2022 periodically in Nunhai near Itimad – ud – Daulah. The $PM_{2.5}$ mass was collected for 24 hrs each day on 47 mm Quartz fiber filter paper (Whatman Inc.) using a Fine particulate sampler (Model: APM 550, Envirotech, New Delhi) having a flow rate of 16.67 lpm. The sampler was placed on the rooftop of a residential block having a height of 10 meters from the ground level. Before exposure, the filter papers were pre-heated in a muffle furnace (Biocraft Pvt. Ltd. India) at $900^{0}C$ for 3 hrs to remove organic impurities. Pre and post-monitoring filter paper were desiccated in desiccators containing silica gel in a humidity-controlled room for 24 hrs and then weighed by the electronic microbalance (SHIMADZU, Model: AUX220) to determine the mass concentration of $PM_{2.5}$. Each filter paper was weighed thrice before and after sampling to get the mean weight. After pre–weighing before the collection of particles, the filter papers were stored in a filter cassette and taken to the sampling site and after post-weighing, after the collection of particles filter papers were sealed in the same filter cassette and wrapped in aluminium foil and stored in a deep freezer at -4^{0}C until the time of chemical analysis to prevent the evaporation of volatile components. Each filter was used to OC and EC analysis using OC/EC carbon analyzer (DRI 2001 A, Atmoslytic Inc., Calabasas, CA, USA).

3. Result And Discussion:

Mass Concentration of $PM_{2.5}$

Table I. Concentration of $PM_{2.5}$, OC and EC in µg/m^3

Date	$PM_{2.5}$	EC	OC
10/01/2022	183.29	7.12	16.74
16/01/2022	208.29	10.17	24.63
17/01/2022	291.61	13.67	32.83
23/01/2022	237.45	14.89	33.81
24/01/2022	217.35	13.05	33.81
30/01/2022	229.18	15.02	43.99
31/01/2022	254.11	9.94	22.41
Average	231.60	11.98	29.74
Standard Deviation	34.71	2.75	8.41

Table I presents the daily mass concentration of $PM_{2.5}$ measured during the study period at the monitoring site. The average $PM_{2.5}$ concentration during the period was 231.60± 34.71 µg/m^3 which ranges from 291.61 to 183.29 µg/m^3. Daily mass concentration at the sampling site is significantly higher than the daily standard stipulated by Central Pollution Control Board called National Ambient Air Quality Standards (NAAQS) (60 µg/m^3) and by the World Health Organization (15 µg/m^3) as shown in fig 1. The result was similar with the earlier reported values of fine particulate matter over different region of India such as 122 ± 94.1 µg/m^3 at Delhi by [15]; 158 ± 64 µg/m^3 at Delhi by [16] 116 ± 88 µg/m^3 at Agra by [17].

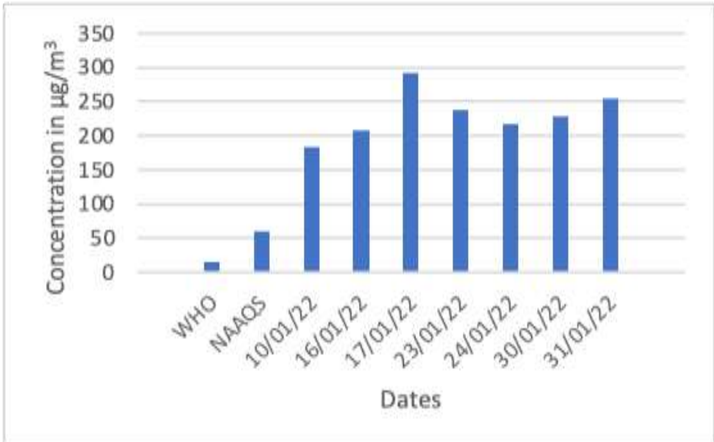

Fig. 1 Comparison of daily concentration of $PM_{2.5}$ with NAAQS and WHO

Throughout the entire study period, variation in the concentration of $PM_{2.5}$ could be attributed to the thermodynamic condition in the planetary boundary layer, which either facilitates or hinders the pollutant's dispersion. Consistently elevated concentration of $PM_{2.5}$ at the sampling site may be mainly due to the collective effect of meteorological conditions and anthropogenic emission such as vehicular and fossil fuel emissions, biomass burning, road dust and industrial effects. During winter, very frequent and persistent thermal inversion, foggy conditions, low wind speed, low mixing height and low temperature at ground level cause a considerable amount of aerosol to accumulate at the ground level worsening the air pollution. Source apportionment studies of $PM_{2.5}$ conducted at the Taj Mahal reveal that approximately 40% of the organic matter—a component of $PM_{2.5}$ deposited on the monument—is linked to biomass burning [18].

As the Itimad-ud-Daulah is also constructed from pure marble, the high concentration of pollutants in its vicinity could lead to the soiling of the monument. This not only tarnishes its pristine appearance but also detracts from its historical and architectural beauty, highlighting the detrimental impact of air pollution on cultural heritage.

Mass Concentration of EC and OC

As presented in table I average concentrations of EC and OC during the study period were found to be 11.98 and 29.74 µg/m^3, concentrations of EC were found ranging from 7.12 to 15.02 µg/m^3 and OC concentrations were found ranging from 16.74 to 43.99 µg/m^3. Results were similar to the earlier reported values of EC and OC such as 10.2 ± 7.54 &17.6 ± 14.1by [19] at Delhi, 7.31 ± 6.17 & 15.7 ± 12.7 by [20] at Delhi.

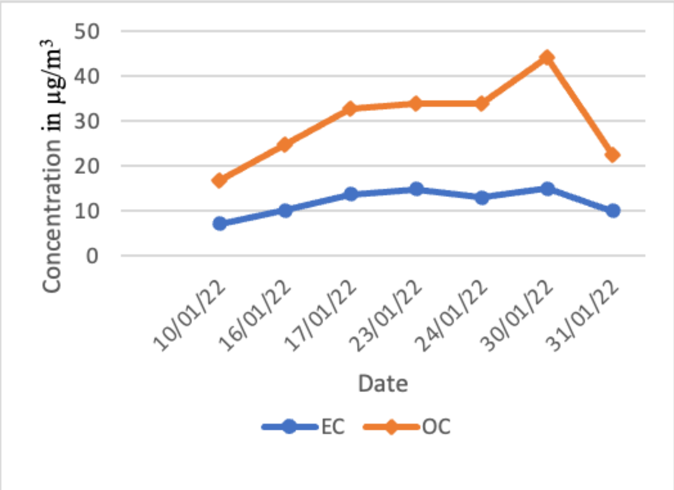

Fig. 2 Concentration of OC and EC in µg/m^3

A significant variation in the concentration of OC and EC can be seen during the study period as shown in fig 2, which may be due to the variation in the meteorological parameter as dispersion and dilution of the pollutant in the atmosphere is governed by them. During the whole study period concentration of carbonaceous aerosols is dominated by OC, this is due to the burning of biomass and coal by locals during the winter period to recover from near zero degree temperature conditions and also due to the meteorological parameters that restrict the dispersion of pollutants. The % contribution of OC and EC to the mass concentration of $PM_{2.5}$ is found to be 12.84 % and 5.17 % respectively which indicates that OC and EC contribute a significant portion in $PM_{2.5}$.

Correlation between PM2.5, OC, EC and Meteorological Parameters

Strong positive correlation between OC and EC is usually indicative of similar sources like vehicular emissions or biomass burning [21]. However weakly correlated values of OC and EC point to the existence of secondary aerosols and suggest ideal circumstances for gas-to-particle conversion of VOCs via photochemical atmospheric reactions [22]. In the present study correlation among OC and EC is found to be strongly positive (R^2 = 0.94) indicating common emission sources.

Table II. Correlation Between $PM_{2.5}$, Temperature and Wind Speed

	$PM_{2.5}$	Temperature	Wind Speed
$PM_{2.5}$	1		
Temperature	- 0.33	1	
Wind Speed	- 0.34	.81	1

The dispersion of pollutants in the atmosphere is greatly affected by meteorological factors. To understand the influence of meteorology on particulate pollution, the Pearson correlation coefficient is applied to the data set for $PM_{2.5}$ and meteorological parameters viz temperature and wind speed.

Temperature shows a negative correlation with $PM_{2.5}$ and a positive correlation with wind speed suggesting that low temperatures result lower wind speeds which will lead to a stagnant and static atmosphere which favour accumulation by limiting dilutions and dispersion and enhancing longer residence time of particulate aerosols in the atmosphere. $PM_{2.5}$ shows a negative correlation with wind speed suggesting that low wind can enhance the concentration of pollutant by limiting vertical distribution of $PM_{2.5.}$

4. Conclusion:

Deteriorating air quality is a major problem faced by millions of urban Indians because most of the Indian cities are highly polluted with particulate concentrations well above the recommended limit of WHO and NAAQS and combustion of fossil fuels to meet growing energy demand for alarming population and vehicular growth, combustion of conventional fuel such as coal, firewood, biomass material, agriculture residue has resulted in significant rise of particulate pollution in the city.

During the study period daily 24-hour mass concentrations of $PM_{2.5}$ are found to be considerably higher than the NAAQS and WHO standards limit by a factor of 3.8 and 15.4 respectively. These higher mass concentrations during winter can be attributed to enhanced human activities such as the combustion of fossil fuels like oil, coke and coal, the burning of biomass and other traditional fuels for domestic, and commercial cooking purposes and space heating plus higher exhaust emission from automobiles and engine sets due to cold condition. In winter time meteorological factors also play an important role, cold and calm condition results in stagnant or static atmospheres which limit the dispersion and dilution of pollutants and favour accumulation & ultimately enhance the longer residence time of pollutants near the ground making the pollution condition worse. Mean concentrations of OC and EC were found 29.74 μg/m^3 and 11.98 μg/m^3 respectively, which account for 12.84 % and 5.17 % of $PM_{2.5.}$ Given the high concentration of fine particles and carbonaceous aerosol in the city, it is advised to take the appropriate action right once to reduce carbonaceous aerosol emissions. The result of the present study can be utilized to evaluate existing and devise more efficient emission reduction strategies. To comprehend the kind and intensity of the emission source and to devise and implement an appropriate air pollution control mechanism, a thorough physiochemical investigation and source apportionment are necessary.

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Reference

[1] J. Schwartz, and D. W. Dockery, "Increased mortality in Philadelphia associated with daily air pollution concentrations," *American Review of Respiratory Disease*, vol. 145, no. 3, pp. 600-604, July 1992.

[2] P. R. Buseck, and M. Pósfai, "Airborne minerals and related aerosol particles: Effects on climate and the environment," *Proceedings of the National Academy of Sciences*, vol. 96, no. 7, pp. 3372-3379, March 1999.

[3] J. S. Rajput, and M. K. Trivedi, "Determination and assessment of elemental concentration in the atmospheric particulate matter: a comprehensive review," *Environmental Monitoring and Assessment*, vol. 194, no. 4, pp. 243, March 2022.

[4] P. Kothai, P. Prathibha, I. V. Saradhi, G. G. Pandit, & V. D. Puranik, (2009). "Characterization of atmospheric particulate matter using pixe technique," *International Journal of Environmental and Ecological Engineering*, vol. 3 no.3, pp. 39-42, 2009.

[5] S. Hama, P. Kumar, M. S. Alam, D. J. Rooney, W. J. Bloss, Z. Shi, ... and S. K. Gupta, "Chemical source profiles of fine particles for five different sources in Delhi," *Chemosphere*, vol. *274*, pp.129913, July 2021.

[6] J. L. Matawle, S. Pervez, S. Dewangan, A. Shrivastava, S. Tiwari, P. Pant, ... and Y. Pervez, "Characterization of PM2. 5 source profiles for traffic and dust sources in Raipur India," *Aerosol and Air Quality Research*, vol. 15, no. 7, pp. 2537-2548, December 2015.

[7] K. Ali, A. S. Panicker, G. Beig, R. Srinivas, and P. Acharja, "Carbonaceous aerosols over Pune and Hyderabad (India) and influence of meteorological factors," *Journal of Atmospheric Chemistry*, vol. 73, pp. 1-27, July 2016.

[8] B.J. Turpin, and J.J. Huntzicker, "Identification of secondary aerosol episodes and quantification of primary and secondary organic aerosol concentrations during CAQS," *Atmospheric Environment*, vol. 29, pp. 3527–3544, 1995.

[9] M.G. Zhang, Y.Y. Xu, and R.J. Zhang, "Emission and concentration distributions of black carbon aerosol in East Asia during the spring time," *Chinese Journal of Geophysics*, vol. 48, no. 1, pp. 55–61, May 2005.

[10] T. Lin, W. Zhou, S. Zhao, M. Li and Z. Guo, "Source contribution of PCBs and OC/EC at a background site in the Yangtze River Estuary: insight from inter-comparison by Positive Matrix Factorization (PMF)," *Carbon Research*, vol. 2, no. 15, pp. 1-13, April 2023

[11] L. Dawidowski, J. G. Constantin, J.H. Murillo, M. Gómez-Marín, T. Noueria, S.B. Jiménez, …. and M.I. Manousakas, "Carbonaceous fraction in PM2. 5 of six Latin American cities: Seasonal variations, sources and secondary organic carbon contribution," *Science of The Total Environment*, vol. *948*, 174630, October 2024.

[12] L.A. Gundel, N.S. Guyot-Sionnest, and T. Novakov, "A study of the interaction of NO_2 with carbon particles," *Aerosol Science and Technology*, vol.10, pp.343–351, 1989

[13] J. L. Mauderly, and J. C. Chow, "Health effects of organic aerosols," *Inhalation Toxicology*, vol. 20, no. 3, pp 257-288, May 2008.

[14] https://www.mapsofindia.com/maps/uttarpradesh/agra.html accessed on 16/11/2024.

[15] S. K. Shrama, T. K. Mandal, S Jain, Saraswati, A. Sharma and M. Saxena, "Source apportionment of PM 2.5 in Delhi, India using PMF model, "*Bulletin of Environmental Contamination and Toxicology*, vol. 97, pp 286 – 293, May 2016.

[16] S. K. Sharma, T. K. Mandal, R. Banoo, A. Rai, and M. Rani, "Long-Term Variation in Carbonaceous Components of $PM_{2.5}$ from 2012 to 2021 in Delhi," *Bulletin of Environmental Contamination and Toxicology*, vol. 109, pp. 1-9, March 2022.

[17] P. Gupta, A. Jangid, and R. Kumar, "Measurement of PM_{10}, $PM_{2.5}$ and Black Carbon and Assessment of Their Health Effects in Agra, A Semiarid Region of India," *Indian National Science Academy*, vol. 85, no. 3, pp. 667-679, August 2019.

[18] M. H. Bergin, S. N. Tripathi, J. Devi, T. Gupta, M. McKenzie, K. S Rana, …. and J. J. Schauer, "The discoloration of the Taj Mahal due to particulate carbon and dust deposition," *Environmental Science & Technology*, vol. 49 no. 2, 8 pp. 08-812, December 2013.

[19] S. Jain, S. K. Sharma, N. Choudhary, R. Masiwal, M. Saxena, A. Sharma,... and C. Sharma, "Chemical characteristics and source apportionment of PM $_{2.5}$ using PCA/APCS, UNMIX, and PMF at an urban site of Delhi, India," *Environmental Science and Pollution Research*, vol. 24, no. 17, pp. 14637-14656, April 2017.

[20] S. Jain, S. K. Sharma, N. Vijayan, and T. K. Mandal, "Seasonal characteristics of aerosols ($PM_{2.5}$ and PM_{10}) and their source apportionment using PMF: a four-year study over Delhi, India," *Environmental Pollution*, vol. 262, pp.114337, July 2020.

[21] I. Salma, X. Chi, and W. Maenhaut, "Elemental and organic carbon in urban canyon and background environments in Budapest, Hungary," *Atmospheric Environment*, vol. 38, no.1, pp. 27-36, January 2004.

[22] B. A. Begum, E. Kim, S.K. Biswas and P. K. Hopke, "Investigation of sources of atmospheric aerosol at urban and semi urban areas in Bangladesh," *Atmospheric Environment*, vol. 38, no. 19, pp. 3025-3038, June 2004.