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Research Article

Linkages between Particulate and Gaseous Pollutants over Two Comparable Environments

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ABSTRACT

The variations and relationship between mass concentrations of PM2.5, PM10, O_3, CO, NO_x, NO_2, NO, NH_3, and C_6H_6 were analysed based upon the data inventory from Central Pollution Control Board (CPCB) monitoring network stations at two neighbouring locations (Dharuhera and IMT-Manesar) with different environmental properties over a period of four years (January 2019-December 2022). The results reveal an uneven pollutant concentration over these two sites, even though both locations are nearer (~28 km) but with different meteorology, environment, and industrial coverage. The daily concentration of air pollutants shows significant increase with time, suggesting the need for an early implementation of air pollution reduction and mitigation techniques at both sites. The results show a strong correlation between the characteristic pollutants such as PM2.5, PM10, NO_x ($NO+NO_2$), O_3, NH_3 and CO. Also, more pollutants exhibit a significant correlation at Industrial Model Township (IMT-Manesar) than at Dharuhera site (quantitatively as well as qualitatively). As a result, the inter-site and intra-site pollutant correlograms indicate the presence of common sources (for example, automobiles, industries etc.) at the study locations. Thus, the above study plays an important role in devising mitigation methods to achieving environmental sustainability *vis-a-vis* minimizing human health hazards at both study locations chosen in the present study or any other elsewhere.

Keywords: Particulate Matter (PM); Precursor gases; Urban locations; Source strength variations; Local meteorology; Physicochemical transport

Abbreviations: CPCB: Central Pollution Control Board; PM: Particulate Matter; LCLU: Land Cover Land Use; VOCs: Volatile Organic Compounds; BTEX: Benzene, Toluene, Ethylbenzene, and Xylenes; CO: Carbon Monoxide; ACOAS: The Amity Centre-of-Excellence in Ocean-Atmospheic Science and Technology; GHG: Gas-to-Particle Conversion

INTRODUCTION

Air pollution a topic that deals with discharge of different gases, fine particulate matter, or finely dispersed liquid aerosols into the atmosphere at rates greater than the environment's capacity to dissipate, dilute, or absorb them. This century has seen air pollution become one of the key environmental concerns, with the consequences becoming more visible over time. It has a tremendous negative impact on human health and quality of life and is regarded as one of the most serious environmental threats to human health [1]. Rapid urbanization is predominantly associated with deteriorating urban air quality [2]. Increased urbanization causes substantial changes in Land Cover Land Use (LCLU) in metropolitan areas. As a result of such rapid land-use changes, the climate in urban regions has been altered from its natural state when contrasted to the surrounding rural and suburban areas [3]. Over the last four decades or so, continuous, and rapid economic expansion and urbanization, as well as a significant increase in vehicle population, have resulted in severe environmental challenges [4-7].

Urban population growth is accompanied by an increase in anthropogenic activities such as burning fossil fuels for transportation, cooking, and building cooling or heating, which in turn raises the levels of air pollutants like Sulphur Dioxide (SO_2), Nitrogen Dioxide (NO_2), Carbon Monoxide (CO), and

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Particulate Matter (PM). Daily deposits and accumulations of primary and secondary particles from many anthropogenic and natural sources are mixed with hazardous compounds from vehicle emissions, and exhausts [8]. Road surface abrasion, road dust resuspension, vehicle component wear and tear, tyre, clutch, and brake wear are all non-exhaust emission sources of PM [9,10]. Non-exhaust emission sources of pollution include factors such as traffic volume and vehicle speed [11]. PTEs (Potential Toxic Elements) and PM with a diameter of less than 10 m are released into the atmosphere because of brake wear, which includes brake lining and disc abrasion brought on by grinding, volatilization, and condensation of brake pad material [12-14]. Particles that have already been deposited may be resuspended due to tyre stress, turbulence from moving vehicles, and other factors like wind and pedestrian activity [15]. The suspension of particles occurs because aerodynamic drag from moving vehicles causes greater turbulent activation than adhesive forces [16,17]. Car speed and particle resuspension have a definite link; as speed increases, so does the rate of resuspension [18-20]. Many atmospheric phenomena are influenced by atmospheric aerosols, including cloud formation, visibility, radiation, and solar radiation transmission; they also play an important part in the acidity of clouds, rain, and fog [21-23]. Gases such as Carbon Monoxide (CO), Nitrogen Oxides (NO_x), Methane (CH_4), and Volatile Organic Compounds (VOCs) are produced because of industrialization, urban development, and transportation, and are chemically involved in the formation of tropospheric ozone. Ozone in the troposphere is also caused by the transfer of air mass from the stratosphere Biomass burning, particularly forest fires, and contributes to ozone levels in tropical regions [24-29]. CO interacts with water vapour to generate the OH radical, which, in the presence of UV radiation, leads to the production of Ozone. The increase in Ozone Gas-to-Particle Conversion (GHG) concentration causes warming of the troposphere, which in turn causes climate change in the long run [30,31]. Ozone at ground level works as a powerful oxidant, harming both people and plants [32]. Ozone in the lower troposphere has roughly doubled due to elevated VOC and NO_X levels during the past couple of centuries, making it the third-most significant human greenhouse gas after CO_2 and CH_4. Ozone generation increases with rising NO_x during the NO_x-limited regime because it is sensitive to variations in NO_x concentrations. In contrast, during the VOC-limited regime, ozone generation increases with rising VOCs and thus decreases with increasing NO_x concentrations. Therefore, any decrease in NO_x under a VOC-limited environment always results in a rise in ambient ozone levels [33]. Ozone exposure has been linked to both acute and chronic respiratory problems in people, with asthmatic patients and children suffering the worst effects. In addition to these effects, ozone also harms plants [34,35].

Exposure to CO, SO_2, and NO_2 can lead to decreased work capacity, worsening of pre-existing cardiovascular diseases, unfavorable effects on pulmonary function, respiratory infections, lung irritation, and changes in lung defense systems [36,37]. Emissions from vehicles and industries are substantial contributors to NO_x concentrations in metropolitan areas [38]. And aromatic VOCs such as Benzene, Toluene, Ethylbenzene, and Xylenes (BTEX) account for 60% of non-methane VOCs, furthermore, these VOCs react with nitrates to generate secondary organic aerosols. The presence of VOCs in urban air is primarily due to anthropogenic factors, such as the use of mechanical vehicles powered by petrol or diesel engines [39]. Agriculture is the main source of NH_3 emissions into the atmosphere, and through interactions with water vapour and other air pollutants, such as oxidation products of Sulphur Dioxide (SO_2) or Nitrogen Oxides (NO and NO_2, or NO_X), gaseous NH_3 in the atmosphere leads to the production of airborne fine particulate matter [40,41]. A significant portion of PM2.5 is composed of ammonium compounds, such as Ammonium Sulphates (NH_4HSO_4 and $(NH_4)2SO_4$) and Ammonium Nitrate (NH_4NO_3) [42]. The influence of NH_3 emissions on PM2.5 depends on meteorological factors (such as temperature and relative humidity), the degree of the perturbation to NH_3 emissions, and the amount of Particulate Nitrate (NO^{3-}), Gaseous Nitric Acid (HNO_3), and Particulate Sulphate (SO_4^{2-} and HSO_4-), which are the by-products of the oxidation of SO_2 and NO_x, two combustion by-products [43,44].

NH_3 has a profound impact on the biogeochemical nitrogen cycle and has negative health and environmental consequences [45-47]. NH_3 can also cause eye, nose, and throat irritation, dizziness, and headaches in humans [48-50]. After NH_3 is released into the atmosphere, it can either deposit in the form of rain or dry deposition in the area's water bodies or it can interact with other substances to produce other pollutants and do further damage [45-50]. Ammonia can play a critical role in the nucleation of aerosols [51,52]. These ammoniated particles scatter light, reducing visibility and perhaps cooling the atmosphere. [53] Innovations in science and technology are critical for reducing pollution emissions, increasing resource efficiency, and finding solutions to environmental pollution issues [54]. As in 2016 and 2019, the United Nations Environment Programme issued two assessments recognizing improvements in Beijing's air quality because of efficient control tactics linked to clean fuel, construction dust, transportation dust, and coal- fired boilers [55]. India being a developing country is facing strong air pollution due to large scale urbanization, poor infrastructure and improper implementation of rules and regulation, and other quality measures. Current study checked the air pollutants status of two Indian industrial towns in Haryana state, and their possible interaction among each other. The aim of this study is two-fold, (i) to determine the relationship between particulate and characteristics gaseous pollutants, and to check any possible correlation between different air pollutants during the past four years at the two study sites; (ii) to examine the influence of local meteorological parameters on the concentration of particulate as well as gaseous pollutants, emitted directly and formed in the atmosphere.

MATERIALS AND METHODS

For the present study, two observation sites, Dharuhera and IMT-Manesar (Figure 1A), characterized by small and large industrial activity, respectively, in Haryana State were selected (Figures 1A and 1B) .Depict the sectorial layout and satellite view of the two study sites, respectively. They are well-known industrial hubs of the State. A few of the major industries at these sites include Hero Moto Corp, JTEKT India, Venus Engineers, DELPHI Automotive, Amul, Carlsberg, Lumax industries, ASK automotive, FCC Clutch India, Jaguar, and Company, JNS Instruments. These activities are responsible for the recent increase in urbanization in these towns (having populations of more than 30,000 each). Coupled with high vehicular density and industries these hubs are high on pollution. Dharuhera is a poorly planned place and is surrounded by rural sectors (visible from the satellite view in Figures 1A and 1B, especially the northern part of Dharuhera), while IMT-Manesar is comparatively well planned and with urban background. India's busiest highway NH48 passes through both towns (Figure 2). Which might have dominant hand in air pollution to these sites. Some possible, frequent and distinct air pollutant sources like transport, stubble burning, automotive, chemical industries, road dust resuspension, wood stove burning etc. at both sites are displayed in (Figures 3A and 3B). Some geographical and meteorological features of the study sites are presented in Table 1.

The data for this study was obtained from the real-time Air quality data of monitoring stations of Central Pollution Control Board (CPCB), open archive website, where various air pollutants along with some meteorological parameters are monitored continuously all over the country. For the current study, the datasets of four years (1 January 2019 to 31 December 2022) of particulate matter (PM2.5 and PM10) and gaseous pollutants (NO_x, SO_2, NH_3, CO, O_3, C_6H_6) at two sites were analyzed. Time series for all parameters considered in this study were plotted along with correlograms. Out of the resultant many correlograms, only 18 were chosen, showed correlation coefficient of more than 0.5 and included in this communication. The other correlograms where the correlation coefficients were either very low or negative. We do not mean that they are not important, but they might be showing correlation with lag or lead, and negative correlation indicates inverse relationship. Associated geographical, meteorological, and demographic data was taken from the web (Google maps, census, climate data-org, Metoblue).

RESULTS AND DISCUSSION

The results obtained from the analysis of observations performed are presented and discussed in the following sub-sections.

Time series analysis of particulate matter

This subsection depicts the time series plots of all parameters studied during the study period (from 1 January 2019 to 31 December 2022). The motive of this analysis was to check the trends in the concentrations of pollutants during the last four years. If there is any reduction or increase in pollutants concentrations, exemplify the pollution strategies and mitigation management plans implemented in these regions.

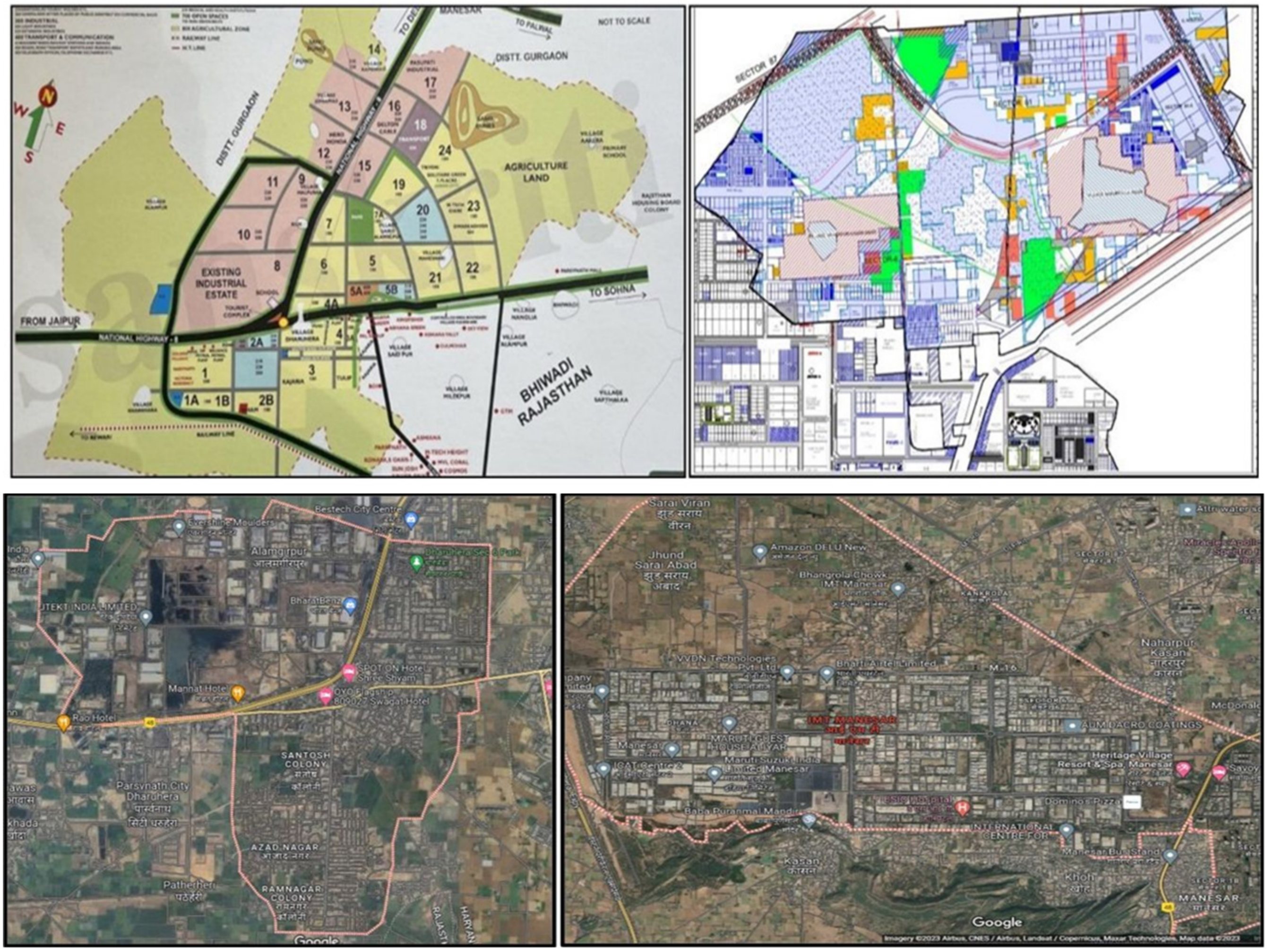


Figure 1: (A) Study sites: Dharuhera (left) and IMT-Manesar (right); (B) Site layouts; Dharuhera (left) and IMT-Manesar (right).

Figure 2: Some characteristic pollution sources prevailing at Dharuhera.

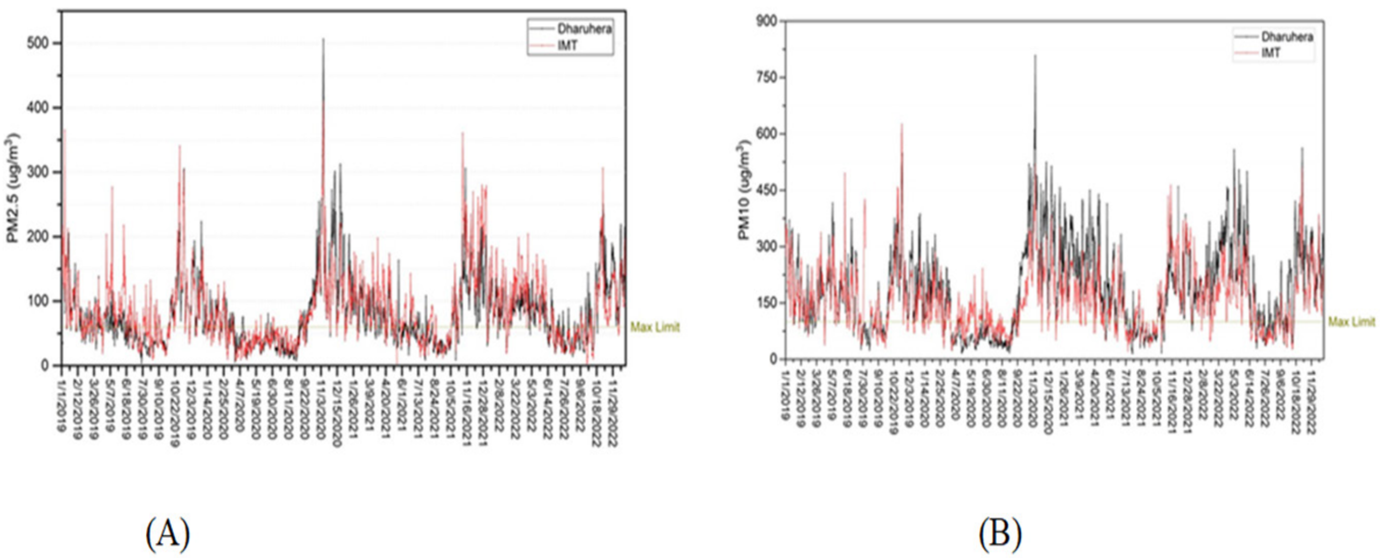


Figure 3: Time series analysis of (A) PM2.5 at study sites; (B) PM10 at study sites.

Table 1: Geographical and meteorological features of the two study sites.

Parameter	Dharuhera	IMT-Manesar
Location	28.22°N 76.78°E	28.35°N 76.93°E
Annual mean temperature	25.06°C	25°C
Annual mean minimum temperature	19.01°C	19.06°C
Annual mean maximum temperature	31.14°C	31.08°C
Annual mean precipitation	570 mm	636 mm
Annual mean relative humidity	51.25%	52.91%
Annual mean wind speed	10.1 kmph	9.83 kmph

Particulate matter

Time series of PM2.5 and PM10 at the Dharuhera and IMT-Manesar sites are depicted in (Figures 4A and 4B). Particulate concentrations are mostly associated with the air quality of any region. Especially PM2.5 concentrations depict health-wise quality of the ambient air of a region. The world's most polluted places are often ranked based upon PM2.5 daily mean emissions. We can deduce that the concentration of PM2.5 at IMT-Manesar (red line) is more than that at Dharuhera (black line) for most of the days in this 4-year period. The concentration is above the daily prescribed limit by the CPCB. The undulations or trends provide an understanding of how much extent these sites are polluted. One common trend that was noticed at both locations was the annual peaking of PM2.5 concentrations during the wintertime (November-December months) and plummeting during the monsoon months (July-August) [56,57]. The increase in concentrations during the wintertime is attributed to the boundary layer height and other meteorological parameters [58]. Further, there is no systematic reduction or increase in their concentrations with time. In the case of PM10 concentration at both sites, as depicted in a similar trend is apparent (Figures 5A and 5B). PM10 pollution remains above (daily) the prescribed limit. The annual trend of peaking and plummeting is like PM2.5 [59]. Dharuhera showed higher PM10 concentrations in comparison to IMT-Manesar for most of the time in these 4 years. The PM10 concentrations signify the presence of more soil dust-driven sources in the Dharuhera region in contrast with the IMT-Manesar but vehicular pollution appears to be more over the IMT-Manesar region. The rural surroundings, open fields, traffic jams etc. in the Dharuhera region contribute more to the PM10 concentrations, which contradicts the IMT-Manesar settings (Figures 6A and 6B). Depicts a considerable proportion of PM2.5 embedded in PM10. As PM2.5 is a part of PM10, the ratio between PM10 to PM2.5 stays always more than one. In the present study, it ranges between 1 and 6, signifying PM10 dominance in these regions (especially in Dharuhera). However, the ratio between two was significantly higher during the summer months than wintertime, usually, during winter, due to low temperatures and hence the possibility for formation of particles is higher than during summertime, lower wintertime ratio could mean significantly high proportion of PM2.5 in PM10 due to higher nucleation possibility [60]. And higher wind speeds aid in the resuspension of coarse dust particles (PM10), and higher vertical mixing of fine particulate matter led to high PM10/PM2.5 ratio during summertime than wintertime. NO_x ($NO+NO_2$) time series of NO_x, NO, and NO_2 are depicted in Figure 7. The overall concentrations of NO_x at these sites throughout the study period were below daily prescribed limits. At Dharuhera site NO_x emissions were below 80 μg/m^3 while at IMT, concentrations occasionally clocked higher during study period. The annual trend of winter peaking and monsoon plummeting was once again apparent like particulate matter, possible influence of BLH and wind (speed and direction) [58,59]. Increased NO_x during winter might have been due to the lowered photolysis of ozone due to temperature plummeting (as NO_X aids in O_3 formation) [61]. IMT-Manesar (Figure 8). Time series of NO_x; (1) Dharuhera; (2) IMT-Manesar. For the NO emissions (Figure 8), at the studied sites, once again, IMT-Manesar had higher NO emissions than that at Dharuhera. Concentration peaks in Dharuhera were close to 100 μg/m^3 while it is above 150 μg/m^3 level at IMT. The winter peaking and monsoon plummeting are like NOX variations (role of planetary boundary layer height and mixing), these findings are consistent with earlier published research works [62,63]. For NO_2 concentrations at both locations (Figures 9A and 9B), the difference between NO_2 concentrations at the two study sites were smaller than NO and the total nitrogen compounds of NO_x, still IMT being the bigger sink (of nitrogen oxides) than Dharuhera. The common peaks of winter were a bit diffused for NO_2 (contrasting to sharp peaks of NO_x and NO) and align with the results reported in the literature [59,62]. The higher concentrations of NO_x ($NO+NO_2$) at IMT sites indicate the presence of stronger NO_x sources, which generally encompasses high temperature combustion processes (industries, vehicles, tobacco etc.). The annual variations in nitrogen oxides can have the meteorological influence (mainly) and seasonal source variability (minor). Although the mean concentration of nitrogen oxide pollutions had been below daily limit by CPCB (80 μg/m^3), indicating low (possible) health issues due to such pollutants at both sites, but the seasonal fluctuations can introduce health problems during wintertime especially to sensitive age group (even though annual mean is into the green zone) [63].

Carbon monoxide (CO)

Time series of CO concentrations of both sites are depicted in (Figures 10A and 10B). The daily averages of CO concentration were below the prescribed limits of CPCB at both sites. Overall CO concentrations were higher in Dharuhera, which might be due to the higher biomass burning processes (rural background/surroundings). In this case the annual trend of concentration was like PM and NO_x pollutants at the IMT site only, while at Dharuhera, it's quite irregular, which might mean the presence of some (constant) local source, like some industry, fireplace, furnace, biomass burning activities, which overcompensate the effects of meteorology [64,65].

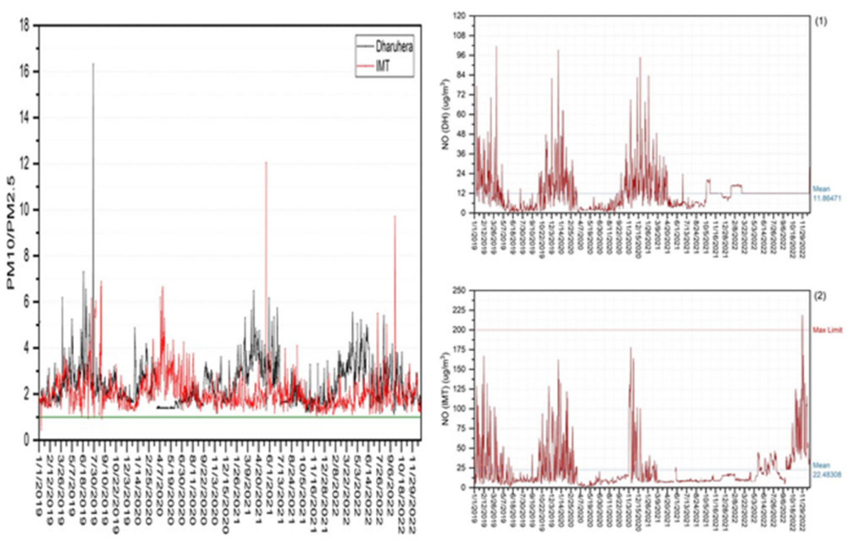
Ammonia (NH_3)

Time series of ammonia at both sites are depicted in Figure 11. The ammonia concentrations at both sites were well into safe zone. IMT-Manesar emitted considerably higher ammonia than Dharuhera into the atmosphere. Ammonia emissions might have been general agriculture (fertilizer and livestock) and waste (anaerobic digestion) based material in Dharuhera, while industrial (coal-based boilers, fertilizer plants) and waste at the IMT-Manesar. NH_3 concentrations at this place follow winter peaking and summer plummeting trend which was peaking during summertime absent at the Dharuhera site [66]. The significantly higher concentrations at IMT-Manesar showed the dominance of non-agricultural based sources and role of meteorology over seasonal fluctuations [67]. Time series of ozone of the studied sites are depicted in the ozone is also a by-product of photochemical reaction between VOCs and NO_X in the presence of UV. Its direct emitters are airplane, smokestacks, and heating systems. At study sites ozone concentrations were below prescribed limits of 8 hour-100 μg/m^3 by CPCB. Ozone concentrations peaked during summertime and plummeted during wintertime, showing its temperature dependencies [62]. The reason of NO_X plummeting and ozone could be due to the increased formation of ozone from NO_X through photochemical oxidation, although it would have been clearer with VOC's trend. The mean and maximum emission levels are depicted in the figure with blue and red lines, respectively [68,69].

Intra-site correlograms

To check direct interactions among air pollutants, all parameters (particulate matter, gaseous pollutants, relative humidity, and wind speed) were correlated with each other. In the following subsection, correlation plots with Pearson's coefficient are depicted for each site.

Correlograms pf pollutants at dharuhera site: Out of 65 correlograms between variables, only 6 exhibited significant correlations (better than ± 0.5) at the Dharuhera site may be partly due to relative strength of sources also and due to lack of synchronization between the variations in concentration of pollutants under study. The significant six correlation plots are shown in and explained in the paragraphs to follow. PM2.5 *versus* PM10 showed a strong positive correlation (0.81), which signifies a constant proportion of PM2.5 in the PM10 concentration at Dharuhera site throughout these four years. As PM2.5 (particles with less than 2.5 micrometer aerodynamic diameter) is a subpart of PM10 (diameter of less than 10 micrometer), so this kind of correlation is inherent. PM2.5 *versus* NO_x showed a moderate positive correlation (0.5), which simply directs towards any possible interaction between these two (without complete surety). Usually, NO_x particles aid in secondary particulate formation in the atmosphere, so a moderate correlation shows possible formation of secondary PM2.5 particles through GPC (Gas-To-Particle Conversion) phenomenon in the atmosphere. PM10 *versus* NO_x showed a moderate positive correlation coefficient (0.52), as in the case of PM2.5 and NO_x. Formation of secondary PM10 particles is unlikely (because it requires ambient environmental conditions favorable to GPC conditions), so there might have been some common sources of PM and NO_x ((like vehicles). Multiple studies have showed similar findings. The Nitrogen family (NO_x, NO, NO_2) showed significant positive correlation among the three, with highest correlation between NO and NO_X (0.87), followed by NO_2 and NO_x (0.83), and NO and NO_2 (0.58). Possible reasons for their high correlation are common emitters or sources like vehicles and industries, and their interaction in the atmosphere (NO_X is made up of NO and NO_2), and other NO-NO_2-O_3 quasi- equilibrium. Such relationships and interactions were found in related works and they need further study [70-75].



(A) (B)

Figure 4: Time series analysis. **Note:** (a) PM10/PM2.5 at study sites; (b) Time series analysis NO: (1) Dharuhera, (2) IMT-Manesar.

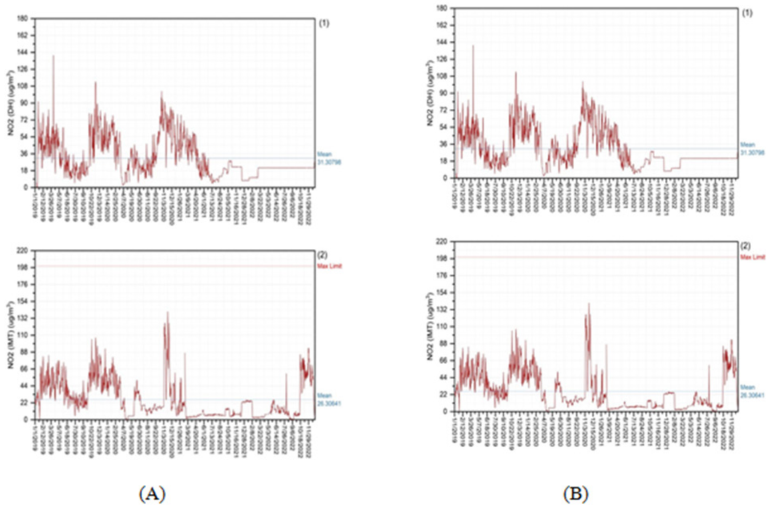


Figure 5: Time series. **Note:** (A) NOx; (1) Dharuhera, (2) IMT-Manesar; (B) NO_2: (1) Dharuhera, (2) IMT-Manesar.

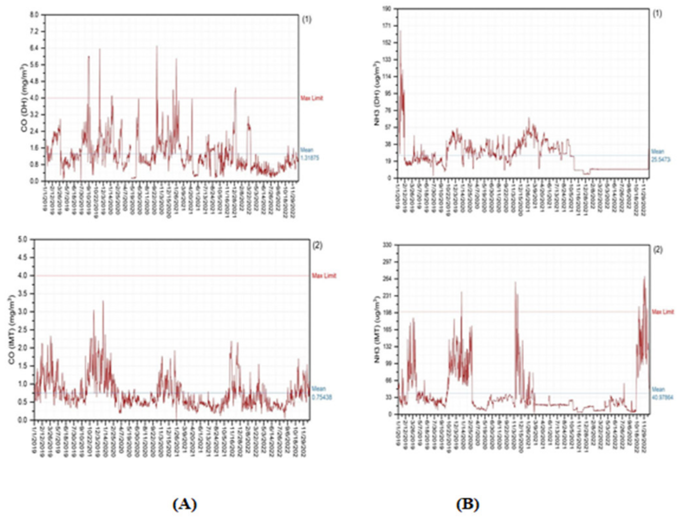


Figure 6: Time series. **Note:** (A) CO at (1) Dharuhera, (2) IMT-Manesar; (B) NH3: (1) Dharuhera, (2) IMT-Manesar.

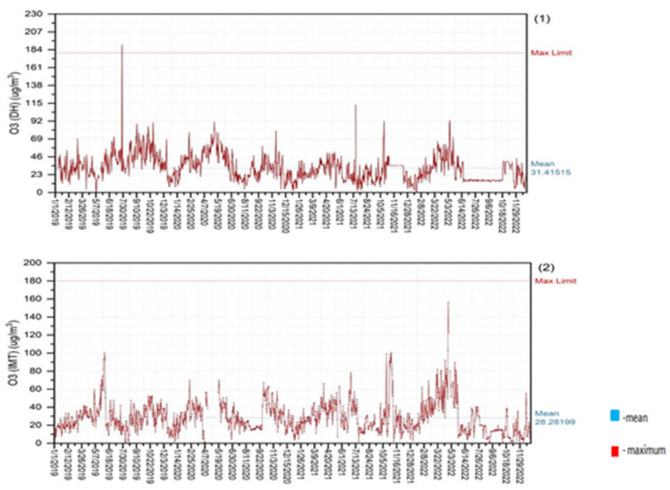


Figure 7: Time series of ozone: (1) Dharuhera, (2) IMT-Manesar.

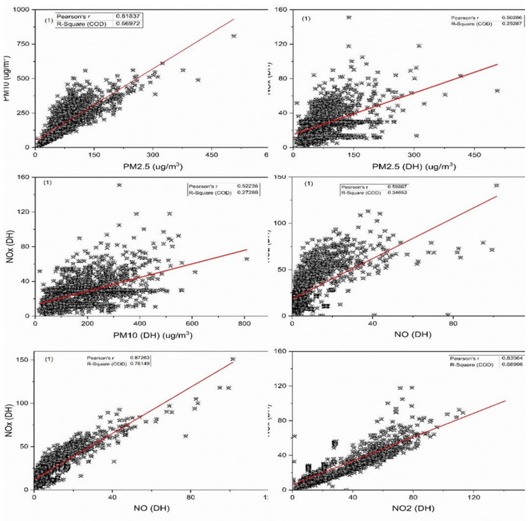


Figure 8: Correlation between various pollutants at the Dharuhera site.

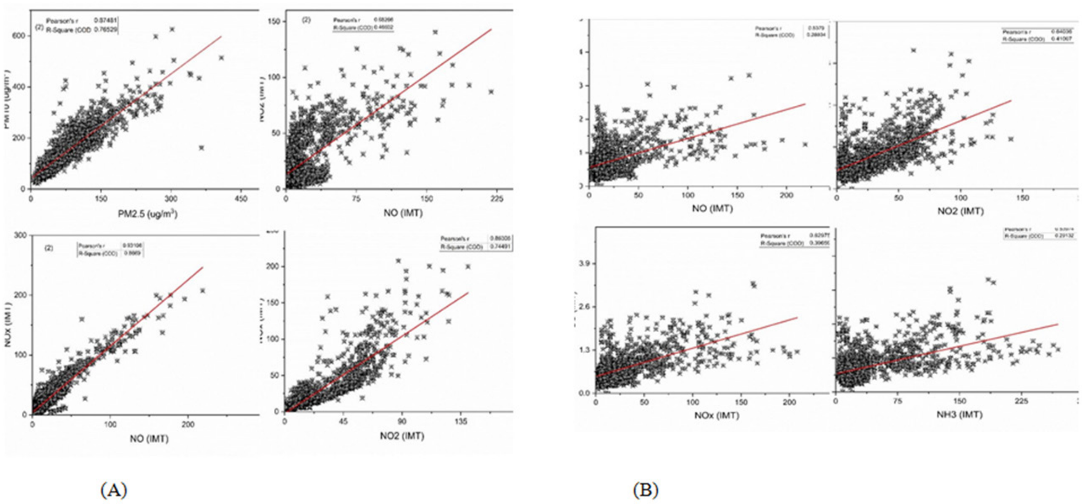


Figure 9: (A) Correlation between various pollution parameters; (B) Co-relationship between various pollutants at IMT-Manesar.

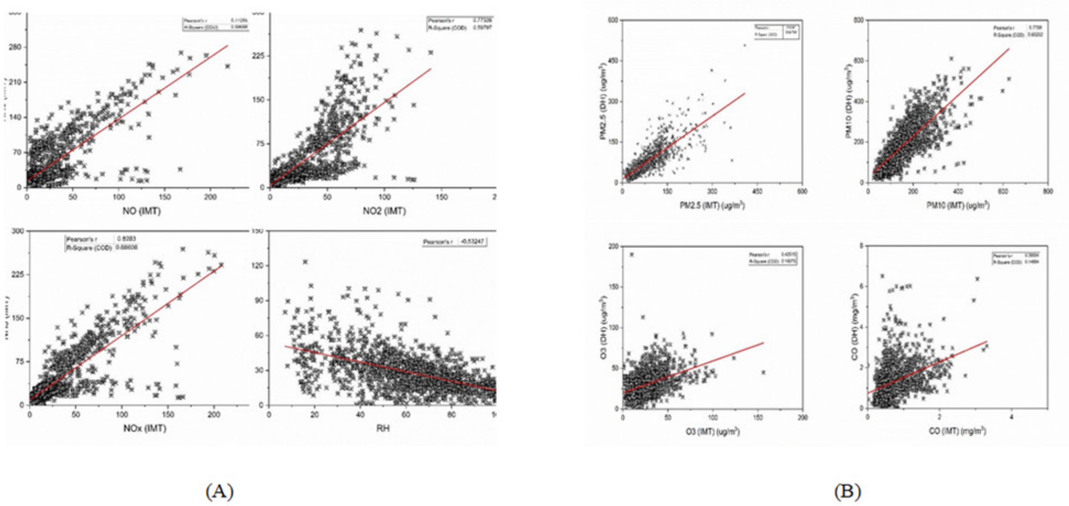


Figure 10: (A) Co-relationship between various pollutants at IMT-Manesar; (B) Inter-site linear regression analysis plots.

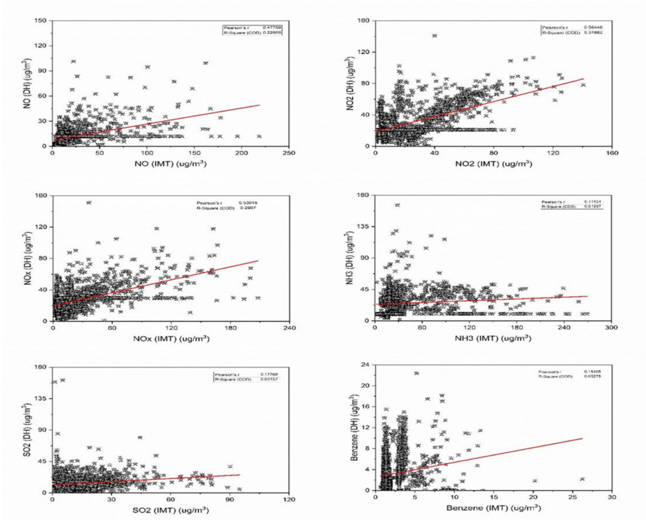


Figure 11: Inter-site trend analysis plots.

Correlograms of pollutants at IMT (Manesar Site): At IMT site more parameters showed meaningful correlation than the first site. Twelve out of 65 had better than ± 0.5 correlation coefficient during the study period, which are depicted in only PM2.5 to PM10, Nitrogen family correlations were common between two sites, even though the meteorology of both sites is quite similar. So, the obtained correlations might be due to the common sources (majorly) and atmospheric interaction. It is clear from the figure that PM2.5 and PM10 show a strong positive correlation (0.87), little higher than of Dharuhera site. The reason will be like the first case (at Dharuhera site) [75,76]. Nitrogen family (NO_X, NO, NO_2)-showed strong positive correlation. With highest correlation between NO and NO_X (0.93), followed by NO_2 and NO_X (0.86), and NO and NO2 (0.68). These correlations were higher than the previous site (like particulate matter) [73,75,77]. Ammonia has a significant positive correlation between NH_3, NO_x, NO, and NO_2 were seen at IMT (only). With a correlation of 0.82 between NH_3 and NO_X, 0.77 for NH_3 and NO as well as NO_2. Strong positive correlation might showcase the presence of NO_X and NH_3 interaction in the N_2 formation in the air [75,78]. Carbon Monoxide showed a positive correlation with ammonia and N family pollutants. A correlation coefficient of 0.64 between CO and NO_2, 0.62 between CO and NO_X, and 0.53 for CO and NO and same with NH_3 also. Common sources among these three are most apparent reason for positive correlation (industries with poor combustion and ventilation processes) [79]. Ozone showed correlation with relative humidity at IMT site only. The correlation coefficient was negative and moderate (-0.53). The inhibition of ozonolysis due to increased humidity results in negative correlation. Only temperature shows a positive correlation with ozone among meteorological parameters, which aids in the photochemical process of ozone formation. Other parameters were not included here because of their weak relationship. For most interactions, the correlation coefficient was in-between ± 0.15 and ± 0.45. It may be noted here that the poor correlation coefficient doesn't always mean absence of any kind of interaction between two, as explained above portray the regression analysis plots together with derived correlation coefficients between air pollutant concentrations, recorded at the IMT-Manesar site. It is clear from the figure that PM2.5 and PM10 show a strong positive correlation (0.87), little higher than of Dharuhera site. The reason will be like the first case (at Dharuhera site). Nitrogen family (NO_X, NO, NO_2)-showed strong positive correlation. With highest correlation between NO and NO_X (0.93), followed by NO_2 and NO_X (0.86), and NO and NO_2 (0.68). These correlations were higher than the previous site (like particulate matter). Ammonia has a significant positive correlation between NH_3, NO_X, NO, and NO_2 were seen at IMT (only). With a correlation of 0.82 between NH_3 and NO_X, 0.77 for NH_3 and NO as well as NO_2. Strong positive correlation might showcase the presence of NO_X and NH_3 interaction in the N_2 formation in the air. Carbon Monoxide showed a positive correlation with ammonia and N family pollutants. A correlation coefficient of 0.64 between CO and NO_2, 0.62 between CO and NO_X, and 0.53 for CO and NO and same with NH_3 also. Common sources among these three is most apparent reason for positive correlation (industries with poor combustion and ventilation processes). Ozone showed correlation with relative humidity at IMT site only. The correlation coefficient was moderate (-0.53). The inhibition of ozonolysis due to increased humidity results in negative correlation. Only temperature shows a positive correlation with ozone among meteorological parameters, which aids in the photochemical process of ozone formation. Other parameters were not included here because of their weak relationship. For most interactions, the correlation coefficient was in-between ± 0.15 and ± 0.45. It may be noted here that the poor correlation coefficient doesn't always mean absence of any kind of interaction between two, as explained above pollutants at IMT-Manesar (Tables 2 and 3).

Inter-site correlograms

This section deals with the relationship between similar parameters of both sites. Due to the short distance between two sites, there can be some common sources of pollutants. This can include the contribution of mobile sources (vehicles) and dispersion by the wind. The resultant regression analysis plots of similar pollutants at both the study sites are presented in during January 2019-December 2022. Some pollutants like PM2.5 (0.84) and PM10 (0.77) exhibited strong positive correlation, while other exhibited moderate to insignificant positive correlation, NO_2 (0.56), NO_x (0.53), NO (0.47), Ozone (0.42), CO (0.38), Benzene (0.18), SO2 (0.17), and NH3 (0.11). The strong positive correlation between particulate matter of two sites might be due to the common source of traffic, as National Highway 48 [NH 48]passes through both sites and both sites are close to each other, so this might be the contribution of long-range commute and heavy transport vehicles (diesel) plying on the national highway. For NO_x, the moderate correlation signifies poor overlapping of sources, as vehicles also emit these pollutants, so the moderate positive correlation is possibly due to the common vehicles plying on the NH 48, and interaction between PM and NO_x (nucleation). Like the contribution of agriculturally based sources in Dharuhera while non-agricultural based sources at IMT for NH_3 emissions. Moreover, the sites are around 28 km apart, so contribution from any stationary source in-between or away from both sites could be solely due to the wind transport and dispersion. While for the mobile sources, NH 48 played a significant role in pollutant concentrations. Such features, depicting higher concentrations due to transport phenomenon have been reported, over a pristine station (Panchgaon), lying in between the experimental sites considered in the present study. Table 4, presents a composite picture of particulate and gaseous pollutant concentrations (average and maximum values) at both the study sites, together with their inter-site correlation coefficients, computed between two sites during the study period of four years (2019-2022) [80].

Table 2: Correlation between pollutants at Dharuhera site.

Parameter 1	Parameter 2	Correlation(r)
PM2.5	PM10	0.81
PM2.5	NO_X	0.5
PM10	NO_X	0.52
NO	NO_2	0.58
NO	NO_X	0.87
NO_2	NO_X	0.83

Table 3: Correlation between pollutants at IMT-Manesar site.

Parameter 1	Parameter 2	Correlation
PM2.5	PM10	0.87
NO	NO_2	0.68
NO	NO_X	0.93
NO	NH_3	0.77
NO	CO	0.53
NO_2	NO_X	0.86
NO_2	NH_3	0.77
NO_2	CO	0.64
NO_X	NH_3	0.82
NO_X	CO	0.62
NH_3	CO	0.53
O_3	RH	-0.53

Table 4: Mass concentrations and correlation of various pollutants at two sites.

Pollutant	Correlation	Concentration at Dharuhera	Concentration at IMT-Manesar	CO	CO
(r)		Average	Maximum	Average	Maximum
PM2.5	0.8	79 ± 52	506	85 ± 54	408
PM10	0.77	185 ± 112	808	159 ± 85	626
O_3	0.42	31 ± 16	190	28 ± 17	156
NO	0.47	12 ± 10	101	22 ± 20	218
NO_2	0.56	31 ± 20	140	26 ± 22	140

NO_x	0.53	27 ± 16	151	28 ± 25	208
NH_3	0.11	25 ± 16	165	41 ± 38	269
SO_2	0.17	13 ± 11	161	13 ± 11	94
CO	0.38	1.31 ± 0.88	6.51	0.75 ± 0.44	3.31
C_6H_6	0.18	3.26 ± 3.18	22.38	2.49 ± 2.1	26.22

CONCLUSION

The motivation behind this study was to understand the trend of various pollutants at the study sites (Dharuhera and IMT-Manesar), associated with different industrial complexes in the last four years, and their interactions with local meteorology. Following are the salient results obtained from the study:

No significant reduction in pollutant emissions was observed in the study period (except slight reduction in CO concentration) over both study regions. Except for PM2.5 and PM10, all pollutant emission levels were below prescribed limits throughout the study period. Daily concentrations of Particulate Matter (PM) were found to be higher than the prescribed values by the CPCB at both locations, with a leading hand of Dharuhera in PM10 (coarse-mode) and IMT-Manesar in PM2.5 (fine-mode).Both Particulate Matter (PM2.5 and PM10) and NO_x (NO and NO_2) peaked during winter season and plummeted during rainy season. Both Particulate Matter (PM2.5 and PM10) and NO_x (NO and NO_2) peaked during winter season and plummeted during rainy season. Both Particulate Matter (PM2.5 and PM10) and NOx (NO and NO_2) peaked during winter season and plummeted during rainy season. Concentrations of NOx were higher over IMT-Manesar region than over Dharuhera. Annual variation in CO concentration was not clear over Dharuhera while it is prominently seen with winter peaking and summer (rainy) plummeting over IMT-Manesar. O_3 concentration was found peaking during summer and dropping during winter over both study sites. More pollutants showed significant correlation over IMT-Manesar than over Dharuhera region. A significant positive correlation was seen between NO_x, PM2.5 and PM10, CO and NH_3.Relative humidity showed negative while temperature and wind speed showed positive correlation with O_3. For inter-site correlation analysis, only particulate matter exhibited strong positive correlation, indicating the role of NH 48 for particulate pollution at both sites.

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