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Variation of Ozone, Carbon Monoxide, and Oxides of Nitrogen at Bengaluru, India

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Abstract

The present study analyses the continuous in-situ observations of surface ozone (O_3), carbon monoxide (CO), and nitrogen oxides (NO_X) conducted in an urban location, Bengaluru, India, during the year 2019 (January to December). The seasonal concentration of O_3 fluctuated with the highest concentrations in the summer (39.6 ppbv) and winter (40.4 ppbv) and the lowest concentrations during the monsoon (16.8 ppbv). The seasonal mixing ratio of CO showed the highest value in post-monsoon (1.71 ppmv) and lowest during monsoon (0.79 ppmv). The seasonal trend of NO_X showed highest in winter (56.8 ppbv) and lowest in monsoon (22.5 ppbv). The monthly mixing ratios of O_3, CO, and NO_X showed distinct variability, which may be attributed to changing anthropogenic activities, planetary boundary layer processes, and local meteorology. O_3 was significantly related to temperature but inversely associated with relative humidity and wind speed. The association between CO, NO_X with relative humidity, temperature, wind speed showed discrete results. The (dO_3/dt) in the morning and evening duration were about 5.0 ppbv/h and -4.1 ppbv/h respectively.

Keywords: Ozone; Carbon monoxide; Oxides of nitrogen; Bengaluru.

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1. Introduction

Air pollution triggered by photochemical oxidation is a severe problem affecting air quality in developed and developing countries. Globalization leading to rapid industrial operations has increased emissions of gases and particles into the environment, potentially degrading air quality [1]. According to recent research, fast economic expansion and development in the transportation industry have exacerbated the situation over the last three decades [2]. The emission of gaseous pollutants leads to air quality deterioration in tropical areas [3]. The major gaseous air pollutants are ozone along with its precursors: oxides of nitrogen (NO_X), carbon monoxide (CO), and volatile organic compounds (VOCs) that are emitted into the atmosphere by various sources. Ozone (O_3) is significant

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greenhouse gas leading to climate change [4]. It is a precursor of the highly reactive hydroxyl and nitrate radical that govern the chemical components of the troposphere at different times of night and day [5]. Surface O_3 is a secondary form of air pollutants hazardous to human health and ecosystems at high concentrations [6]. The CO, methane (CH_4), VOCs, and other O_3 precursors are biomass burning products, combustion of fossil fuel. Other anthropogenic sources are oxidized to yield O_3 in a NO_x-rich atmosphere. Ozone is removed from the troposphere through various chemical reactions and surface deposition [7].

The oxidation of organics, biomass burning, soil biological processes, and emission from vegetation and oceans are the natural sources of atmospheric CO. Anthropogenic source of CO is mainly incomplete fossil fuel combustion. The oxidation of methane and VOCs contribute to CO production [8]. CO sinks include hydroxyl radical reactions and soil uptake [9]. The natural sources of NO_X (NO_X=NO+NO_2) in the atmosphere are lightning and microbial activities in the soil. The anthropogenic source is the combustion of fossil fuels [10]. Sinks of NO_X are converted to nitric acid and organic nitrates by photochemical mechanisms, a reaction involving NO_3 radicals and deposition of NO_2 on vegetation.

The O_3 and its precursors have been examined with an in-situ set of data at various locations in India and across the globe [3,11-14]. Seasonal, diurnal and temporal trends of ozone and its precursors have been explored over a period in India and worldwide using in-situ observations [15,16]. The major portion of this research discovered that the ozone levels in metropolitan areas have a significant diurnal change, with high concentrations in the day and low concentrations at night. Further, the ozone precursors have two maxima during the morning and late evening. Seasonal observations have shown that the O_3 concentration is highest during the summer and winter and lowest in the monsoon period [17,18]. Researchers have also examined the variance of O_3 and its predecessors using unique methodologies based on data from festivals, sports, and eclipses [19-21]. The findings demonstrate that values exceed the threshold during these occasions, causing a more significant impact across the regions. Many investigators have also studied the effect of local meteorological variables such as temperature, wind speed, and relative humidity on ozone and its precursors [22,23].

An effort is made to study the variation of O_3. Its precursor's chemistry at Bengaluru, a tropical location in India, as part of the Modelling Atmospheric Pollution and Networking (MAPAN) program of the Indian Institute of Tropical Meteorology was funded by the Ministry of Earth Sciences. The objective of the present study is to identify the tropospheric amounts of O_3, CO, and NO_X in Bengaluru's ambient atmosphere, which were measured as part of the project from January to December 2019. We present the monthly and seasonal variability of O_3, CO, and NO_X, the effect of local meteorology on their concentrations, and the rate of change in the creation and loss of O_3.

2. Study Domain

Bengaluru, sometimes referred to as Asia's Silicon Valley, is located in the southern portion of the Indian peninsula and is well known for its information technology (IT) businesses. The measurement station is located on the campus of BMS College of Engineering. The continuous in-situ data used in the present study was collected using an Air Quality Monitoring Station (AQMS) and an Automatic Weather Station (AWS) installed in the BMS campus as part of the MAPAN program. Bangalore is an example of a rapidly rising inland megacity in India in economics and urbanization. Bengaluru's rapid development has resulted in dwindling reservoirs, increased traffic congestion, high levels of air pollution, flood events during heavy rains, and, to some extent, a rise in summer temperatures [24]. As the population grows and there is an economic shift, this growth has put much strain on infrastructure and resources. The city's exponential development and changing morphology have reduced the amount of public open spaces over time. Increased vehicular activity has resulted in higher levels of suspended particulate matter and oxides of carbon, nitrogen, and sulfur oxides in the atmosphere.

3. Measurement Technique

The O_3 concentration was determined using a Serinus 10 ozone analyzer with an auto-range of 0-20 ppm and a detection limit of 0.5 ppb. Ozone analyzers operate on the concept that O_3 molecules absorb entirely UV light at a specific wavelength of 254 nm in the solar spectrum. According to Beer-Lambert's rule, the amount of UV radiation absorbed is proportional to the concentration of O_3. CO was monitored using a Serinus 30 model with an auto-range from 0 to 200 ppm and a detection threshold of 40 ppb. CO measurements used the non-dispersive infrared (NDIR) absorption method with correlation wheel technology. The CO analyzer has a processing time of around 60 seconds and a detection threshold of 0.04 ppm. NO_X measurement was done using Serinus 40 NO_X analyzer based on chemiluminescence technique with an auto-range from 0 to 20 ppm with a sensitivity of 0.4 ppb. The combination of nitric oxide (NO) and nitrogen dioxide (NO_2) is provided by this analyzer. A pneumatic device, a NO_2-to-NO molybdenum converter, a reaction cell, a PMT detector, and processing electronics make up the instrument. Yadav *et al*. [18] provided a complete overview of these analyzers. An automated weather station (AWS) mounted in the observational site monitors meteorological variables such as relative humidity, temperature, wind direction, and wind speed.

4. Results and Discussion

4.1. *Seasonal variability of ozone, CO and NO_X*

Fig. 1 depicts the seasonal change of O_3, CO, and NO_X concentrations in Bengaluru over the observations. The winter and summer seasons had the highest ozone levels. In

contrast, the monsoon and post-monsoon seasons had the lowest levels. In winter, the maximum ozone concentration can be attributed to lower mixing layer height and the temperature inversions observed during these seasons, causing the pollutants to be trapped near the ground [25]. Elevated concentrations in the summer were related to higher temperatures and strong solar radiation, both of which favor photochemical O_3 development. Minimum concentrations during the other two seasons may be linked to the fact that these two seasons are cloudy, leading to reduced sunlight resulting in lower production of O_3. The daytime 8 h (10:00-17:00 LT) average ozone values during winter, summer, monsoon, and post-monsoon season are 55.33, 62.39, 21.14, and 16.82 ppbv, respectively. Verma *et al*. [26] found a similar pattern in Agra, with greater concentrations in the summer and decreased concentrations during the monsoon season. The high summer trend is attributable to the high temperature, solar radiation, and planetary boundary layer's role, whereas the lowest amount in monsoon is attributed to the washout of precursors. A seasonal pattern of ozone was found with winter high and monsoon low at Kannur [27]. Lower concentrations were attributed to the scavenging, while higher concentrations were attributed to shallow boundary layers and clear blue sky. Kanchana *et al*. [22] reported similar seasonal fluctuations in Shadnagar, with higher ozone concentrations in the winter and lower concentrations in the monsoon. Verma *et al.* [26] made a similar observation, reporting higher concentrations in the summer and lower concentrations during the monsoon season. The combined influence of high temperature, solar radiation, and the involvement of the planetary boundary layer is assigned to the high summer trend. At the same time, the washout of precursors is linked to the low monsoon trend.

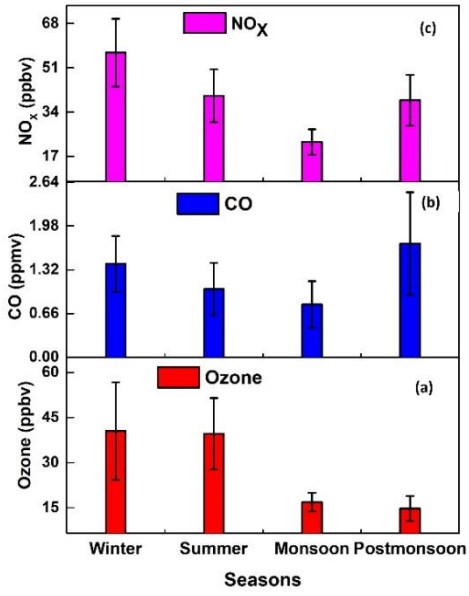

Fig. 1. Seasonal variation of O_3, CO, NO_X.

The seasonal variation of CO is shown in Fig. 1(b). The seasonal pattern of CO is influenced by the variability in CO transport, hydroxyl radical (OH) mixing proportion, boundary layer height, and meteorological factors. CO showed the highest concentration in the post-monsoon season on the seasonal scale, whereas the lowest was observed in the monsoon season. The high level in post-monsoon could be due to the increased pollution from local sources and long-range transport from polluted places. The lowest CO levels found during the monsoon season can be attributed to the dilution and dispersion of pollutants under prevailing strong south-westerly wind regimes. For the winter, summer, monsoon, and post-monsoon seasons, the highest average CO concentration during day time (10:00 LT) is 1.31 ppmv, 0.77 ppmv, 0.84 ppmv, 1.42 ppmv, while at night (21:00 LT) is 2.69 ppmv, 2.36 ppmv, 1.23 ppmv, and 3.60 ppmv. The planetary boundary layer height and chemical removal processes are responsible for the variance between night-time and daytime averages. Kanchana *et al.* [22] found a similar seasonal variation of CO in Shadnagar, with a highest in the post-monsoon season and a lowest in the monsoon. They concluded that the high CO levels during the season were ascribed to long-range air masses carrying additional CO loading from biomass burning. A study by Dumka *et al.* [28] in Guwahati on the variation of CO showed maximum and minimum concentrations in monsoon and winter seasons, respectively.

Seasonal variation of NO_X showed highest in winter (56.80 ppbv), following that is the summer concentration (40.30 ppbv), post-monsoon (38.60 ppbv), and lowest in monsoon (22.54 ppbv), respectively. During the winter, the lower boundary layer causes pollutants to become entrapped in the shallow surface layer, leading to higher levels. During the summer, the polluted air could be mixed with the tropospheric air that causes pollutant dispersion and photochemical loss due to strong solar radiation. Overcast cloud conditions and rainfall events over the measuring location in the monsoon and post-monsoon seasons cause pollutant washout. The highest NO_X concentration during daytime is 52.79 ppbv, 31.98 ppbv, 22.99 ppbv, 34.77 ppbv, and the nigh-time average is 98.91 ppbv, 72.58 ppbv, 28.53 ppbv and 62.56 ppbv for winter, summer, monsoon, and post-monsoon season. Night-time levels are higher than daytime during all seasons, attributable to the decreased Planetary Boundary Layer (PBL) height. Pollutants become trapped at night as the PBL dips, resulting in less dispersion. The PBL stretches during the day, resulting in effective pollutant dispersion. Similar observations for NO_X levels with maximum concentration in winter and minimum in monsoon are reported for Anantapur, Udaipur, and Pune [3,18,29].

4.2. *Monthly variation of ozone, CO and NO_X*

Fig. 2 displays the monthly variability of O_3 at the observational site. The monthly ozone mixing ratio was high in the first half of the year and gradually decreased in the second half. The maximum and minimum ozone concentration was seen in March (58.3 29.6 ppbv) and October (14.3 3.1 ppbv), respectively. We can see that the ozone concentrations are high in the summer months (March, April and May) and lower in the monsoon months

(June, July, August and September). Higher concentrations can be due to high solar radiation and its precursors being prevalent during the summer months, allowing for the higher photochemical formation of O_3. Lower concentrations in monsoon months can be due to cloudy weather, scavenging of O_3 precursor gases, and rainfall episodes, thus indicating decreased photochemical activity for O_3 generation. The maximum and minimum in the winter, summer, monsoon, and post-monsoon months are 15.10 – 70.65 ppbv, 16.98-73.97 ppbv, 11.90 – 27.22 ppbv, and 11.54-26.55 ppbv. The annual average of O_3 for 2019 is 26.45 ppbv with a minimum and maximum varying from 10.14 to 73.97 ppbv. However, ozone followed different monthly average variations at other sites in India. At the Udaipur site, the concentration of O_3 displays evident seasonality with a maximum of 28.9 ppbv in April and a minimum of 16.4 ppbv in September. Elevated concentrations of CO and NO_X were associated with higher O_3 values, while lower values of O_3 were associated with lower levels of both CO and NO_X [18]. The O_3 was higher at the coastal location, Kannur, in February (29.7 ppbv), while the lower (13.1 ppbv) mixing proportion was noticed in August. The high value during February is caused due to long-range transport of air masses, while the prevailing southwest monsoon resulted in reduced O_3 concentrations during August. The monthly average highest and lowest of O_3 at Hyderabad were observed in December (47.88 ppbv) and July (17.83 ppbv), respectively. Allu *et al*. [30] found that the high value could be due to high solar radiation and boundary layer height, favoring the photochemical formation of O_3, while the low value could be related to the washout effect, which removes contaminants from the air. The differences in the variations observed are due to differences in pollution sources, observation site topography, and meteorological conditions.

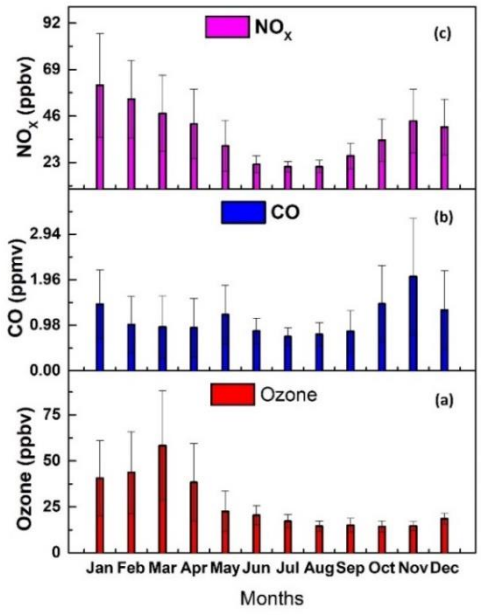

Fig. 2. Monthly variation of O_3, CO, NO_X.

The monthly variation of CO is shown in Fig. 2b. The monthly variability of CO showed highest in November (2.02 ppmv) and lowest in July (0.73 ppmv). The variation of CO shows higher levels in the post-monsoon and winter months and lower levels in the monsoon months. Higher levels during November might be due to the increased contamination from local areas and the long-range transport. Lower levels in July could be ascribed to the active southwest monsoon, which induces extensive mixing and transport of air across the region. The lowest and the highest concentrations for winter, summer, monsoon, and post-monsoon are in the range 0.15 to 2.97 ppmv, 0.24 to 2.40 ppmv, 0.32 to 2.37 ppmv, and 0.58 to 2.97 ppmv. The annual average of CO during the year 2019 is 1.12 ppmv. Different monthly average trends for CO from various locations in India have been reported. Tiwari *et al*. [31] reported that monthly CO concentrations were highest in December (22 ppmv) and lowest in July (0.99 ppmv) in the city of Patna. In December, the highest concentrations were found during December due to crop waste burning in the IGB region, whereas the lowest concentrations were found in July due to pollution washout caused by effective rain scavenging. Yadav *et al*. [32] measured the total monthly maximum and minimum CO in the city of Udaipur in January (0.57 ppmv) and July (0.21 ppmv). Higher amounts were attributable to emissions from local sources and long-distance transport. An observation by Allu *et al*. [30] in the city of Hyderabad on the monthly mixing ratio for CO shows the lowest values in November (0.59 ppmv) and high values in October (0.33 ppmv). The variations in CO concentrations over the year could be attributed to different emission sources and varying meteorological conditions.

Fig. 2c depicts the monthly variability in NO_X over the study period. The monthly average of NO_X showed a maximum value of 61.20 ppbv in January and a minimum of 20.95 ppbv during July. The higher concentrations in January are attributable to a lower mixing height, which causes contaminants to be trapped near the surface due to temperature inversion. Lower concentration might be due to meteorological variables and the lower mixed layer height. During winter, summer, monsoon, and post-monsoon months, the monthly NO_X concentration for 2019 varied from 26.18,23.9,17.65,18.01 ppbv to 83.05, 62.3,38.17 and 54.49 ppbv, respectively. The yearly average of NO_X during the study period is 37.08 ppbv, and it varied from minimum to maximum in the range of 17.65 to 80.68 ppbv. NO_X has a variety of monthly average patterns in diverse places of India. The monthly variation in the city of Udaipur showed a maximum in December (19 ppbv) and a minimum in July (6.4 ppbv) [32]. The monthly variations were attributed to long-range mobility, anthropogenic emission and boundary layer height. The observations of NOx by Allu *et al*. [30] in the city of Hyderabad at Tata Institute of Fundamental Research-National Balloon Facility showed the highest variation in November (21.33 ppbv) and lowest in July (6.26 ppbv). The differences they found were related to meteorological parameters. Variances in measured values of NO_X in different places could be due to differences in site location, sources of pollution, and local meteorological parameters.

4.3. *Influence of meteorological parameters*

Fig. 3 is a correlation plot of ozone with temperature, relative humidity (RH), wind speed (WS). The correlation coefficient for ozone with temperature, RH and WS are (r=0.53, p < 299 0.000), (r=-0.68, p<0.000) and (r=-0.25, p<0.011), respectively. A strong correlation of ozone with temperature can be observed during the entire study period. We can observe from the correlation that as the temperature rises, so does the ozone concentration. The positive relation shows that photochemical reactions are key in ozone production in the observation site. Earlier research has shown that ozone has a significant association with temperature [23,33]. O_3 and RH have a significant negative association.

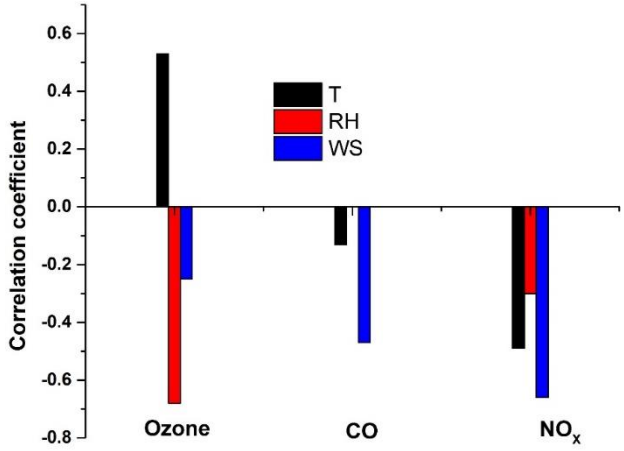

Fig. 3. Correlation analysis of O_3, CO, NO_X with temp, RH, WS.

The decrease of O_3 due to interactions with OH radicals, for which water vapor serves as a source, might be attributed to this inverse correlation [7,29]. The current findings of a negative relationship between O_3 and RH are close to Gaur *et al*. [33] and Pudasainee *et al*. [34]. A significant negative association exists between O_3 and WS during observation. The decrease in O_3 with wind speed may be attributed to lesser O_3 concentrations in Bengaluru's surrounding urban spaces. The correlation coefficient of CO with temperature and RH was less significant and is attributed to the dilution of pollutants.

Similar findings were made at Kanpur, where the minimal CO-with temperature and RH correlation [33]. In Belgrade, Markovi *et al*. [35] found a limited or insignificant association between CO and meteorological factors (temperature and relative humidity). The correlation coefficient of CO with WS showed a significant negative correlation with a correlation coefficient of (r=-0.47, p < 0.000), and is due to the dispersion and mixing of pollutants when the WS increases. Correlation analysis of CO with WS revealed a value of -0.3 in Udaipur city, where CO emissions are attributed to mainly local sources and regulated by anthropogenic activities [18]. The correlation coefficient of NO_X with temperature, RH and WS are (r=-0.049, p < 0.638), (r=-0.30, p<0.003) and (r=-0.66,

p<0.000), respectively. The correlation of NO_X with temperature was not significant during the study period. A negative correlation between NO_X and RH may be attributed to the fact that RH influences chemical interactions of gases in the atmosphere by regulating chain termination reactions, reducing pollutants. NO_X was negatively correlated with WS. It could occur as a result of pollutants being carried by the wind. Similar findings are reported by Gasmi *et al.* [36] in Dhahran, Saudi Arabia, where they attribute to high wind speed, promoting the distribution and mixing of these air pollutants, reducing their cumulative levels. The importance of meteorological variables is critical since it determines the potential for either pollutant dilution or build-up in the region.

4.4. *Variations in O_3 formation and destruction rates*

Fig. 4 depicts the diurnal variability in the seasonally averaged rate of change of O_3 concentrations (dO_3/dt) in Bengaluru. The rate of change of O_3 can be utilized as a chemical environment indicator in both rural and urban areas. The morning and evening rates of change in O_3 are frequently similar in urban places, although rural areas have higher during morning and lower loss levels in the evening [37]. The rate of change in O_3, especially in the morning and evening hours, exhibits significant seasonal variation. The highest seasonal positive and negative rate of change of O_3 was observed in summer, followed by winter, monsoon and lowest during post-monsoon season.

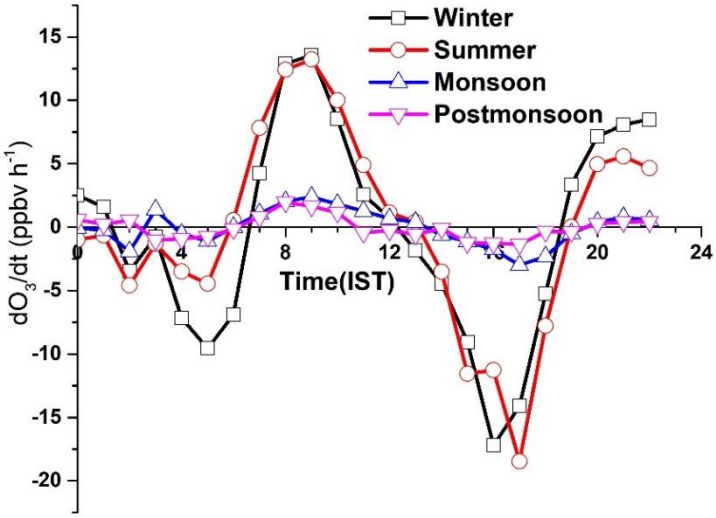

Fig. 4. Seasonally averaged diurnal variation of (dO_3/dt) at Bengaluru.

The highest production rate occurs in the summer due to favorable photochemical conditions for O_3 production. The minimum production rate in post-monsoon can be attributed to mixing layer heights and reduced photochemical activity. The positive morning (8:00 -11:00 LT) rate of change of ozone is 9.3, 10.1, 1.8, 1.0 ppbv/h while the

negative evening (19:00-21:00 LT) rate of change of ozone is -5.7, -8.7, -1.9, -0.6 ppbv/h for winter, summer, monsoon and post-monsoon, respectively.

Table 1. The mean rates of change of O_3 at Bengaluru and other urban sites of India.

Location	Type of Site	Rate of change dO_3/dt		References
		(08:00-11:00 LT)	(17:00-19:00 LT)	
Bengaluru	Urban	5.0	-4.1	Present Study
Shadnagar	Sub-Urban	3.6	-3.9	[22]
Agra	Urban	7.9	-6.9	[26]
Kannur	Coastal Rural	4.9	-6.4	[27]
Patna	Rural	1.6	-1.9	[31]
Udaipur	Sub-Urban	3.7	-4.5	[32]
Anantapur	Rural	4.6	-2.5	[38]
Delhi	Urban	4.5	-5.3	[39]

Table 1 compares the rate of change of O_3 at the current location to that at several sites across India. The average rate of change of O_3 (5.0 ppbv/h) was higher in the morning period than the loss rate (-4.1 ppb/h) in the evening period. Morning time variations in the boundary layer height, along with solar radiation, are relatively quick, and hence the highest variation in ozone is recorded at this time. Bengaluru's rate of change of O_3 is comparable to that of Kannur and Delhi, but it is lower than that of Agra's urban areas and higher than that of Shadnagar and Patna. The rates of change in O_3 concentrations during morning and evening were comparable in urban environments; however, this was not the case in rural locations. The rate of O_3 creation in the morning is mainly determined by the number of precursors present, whereas the rate of O_3 loss in the evening is mainly determined by the concentration of nitrogen oxide (NO), which is involved in O_3 titration.

5. Conclusion

We reported the analysis of a continuous dataset of O_3, CO, and NO_X from an urban location in Bengaluru, India, from January 2019 to December 2019. The levels of O_3 changed between season-to-season, with a maximum in summer and winter season while minimum in monsoon season. High levels in the winter could be associated with a decrease in mixing height, allowing contaminants to be trapped caused by temperature inversions. In contrast, high temperatures in the summer can be related to higher temperatures and strong solar radiation, favoring photochemical O_3 generation. The highest seasonal variation of CO and NO_X was seen in the post-monsoon and winter season. CO and NO_X pollution levels were lowest in the monsoon season. The monthly variation of O_3, CO, and NO_X showed unique variability in anthropogenic emission sources, PBL processes, and meteorological variables. The relationship of pollutant behavior with meteorological variables was also studied. Our findings showed that O_3 was positively associated with temperature but negatively correlated to relative humidity and

wind speed. The association between CO with temperature, RH showed a poor correlation while wind speed showed a significant negative value. NO_X showed a negative correlation with meteorological factors. The mean dO_3/dt in morning and evening periods at the observational location was 5 ppbv/h and -4.1 ppbv/h, respectively, typical of an urban location.

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