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Original Research

Urban Emission Patterns at a Semi-Arid Site in Lahore, Pakistan

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Abstract

The current research is an attempt to find out diurnal and monthly mean patterns of air pollutants, their interrelationships, and their dominant sources through hourly and monthly data analysis. Lahore is a semi-arid region with low rainfall, hot and humid summers, and cold dry winters. Annually, the highest air quality index (AQI) (132 to 185) is observed from November to February due to inversion at low wind speeds (<1.5 m/s monthly average), low temperature (15ºC to 21ºC monthly average), and low solar radiation (104 to 140 W m-2 monthly averages). AQI remained low (74 to 85) from June to August due to relatively heavy rain, relatively high wind speed (1.59 to 1.85 monthly averages), dispersion due to high temperatures, high solar radiation, and summer vacations to schools. With an analogous diurnal trend, the AQI remains stumpy in daytime. The high CO/NOx ratio indicates that mobile sources are dominant contributors to NOx; and the low SO_2/NOx ratio indicates that point sources are dominant contributors to SO_2. CO has a significant positive correlation with NO, NO_2, NOx, CH_4, SO_2, and RH, and a negative correlation with O_3 and temperature. This explains why four-stroke petrol engines are common sources for CO, NO, NO_2, and NOx. $PM_{2.5}$ has a significant positive correlation with SO_2, which explains why diesel engines are a common source for $PM_{2.5}$ and SO_2. O_3 has a significant negative correlation with NO, NO_2, NOx, CH_4, CO, and RH; and has a significant positive correlation with temperature and solar radiation.

Keywords: semi-arid, mobile sources, air pollution, meteorology, air quality index, Pakistan

Introduction

The population of Lahore is 9 million, making it Pakistan's second largest city [1]. There are 2.7 million vehicles along with 1,986 different industrial units in Lahore [1]. The ambient air pollution in the city predominantly originates from vehicular and industrial emissions [2] .

The semi-arid climate of Lahore naturally favors the accumulation of pollutants. Solid aerosols are present in the samples of PM [3].

New housing schemes have not been found to fulfill the needs of sustainable development and transport sustainability. The city district government has failed to achieve its target of ambient air quality improvements under the 2001 devolution plan due to the absence of transport policy, alteration in land use policy, and deprived management and monitoring of air quality [4]. Furthermore, the city has been expanding due to migration from small cities of Punjab. Migration has been observed

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from Karachi and Peshawar as well, due to security reasons.

Diesel-fueled generators have been used extensively in industrial sectors (point sources) as well as in other sectors due to widespread power shortages in the country, which adds a lot to urban ambient air pollution [5]. The use of diesel fuel by mobile sources contributes a lot to particulate matter air pollution [6]. The sulfur contents are very high in diesel (0.5-1%) and furnace oil (1-3.5%) being used in Pakistan, whose fallout comes with higher sulfur dioxide pollution [7].

The environmental damage is associated with health issues. Currently, mobile sources have been found to promote high levels of tropospheric ozone and health concerns in urban areas [8]. The Organosulfatese have been identified and quantified in fine particulate matter ($PM_{2.5}$) collected in Lahore, Pakistan, in 2007-08 [9]. Enhanced diastolic blood pressure has been found to be associated with long-term exposure to NO_2 and $PM_{2.5}$ in those children who used to live at the same place since birth [10]. The $PM_{2.5}$ levels have been exceeding the NEQS in four provincial as well as federal capitals of Pakistan [11]. In the fall season during October and November; burning of crop residues in eastern Pakistan and northwestern India increase the concentrations of $PM_{2.5}$ in the atmosphere [12, 13]. Secondary inorganic PM in the form of sulfates and nitrates is formed by the oxidation of SO_2 and NOx. However, the organic carbon fraction is formed due to oxidation of VOCs [14, 16]. This process is enhanced by ammonia [17]. The black carbon aerosols are present in 90% of $PM_{2.5}$ in winter and contribute about 5-15% to overall $PM_{2.5}$ in the ambient air [18, 19]. Black carbon has been found to be at much higher levels during foggy season. Black carbon has also been found to be trapped in aerosols during the foggy season, resulting in a lessening of solar radiation [20].

Other big cities in Punjab also have high pollution levels. Concentrations of CO, NO_2, and SO_2 have been found above NEQS levels in Faisalabad [21]. The traffic pollution has been found to be the most contributing factor to outdoor air pollution in most urban areas [22].

Brick kilns on the outskirts of Lahore are also a great point source of air pollution. A study of brick kilns in the Wahga and Batapur areas of Lahore revealed that the conventional Bull's Trench Brick Kiln are being used in Lahore, which comprises no control measures to manage the air pollution. Modern brick manufacturing technologies such as vertical shaft brick kiln must be introduced to control the air pollution [23].

It is impossible to monitor the spatial and temporal variations in the atmosphere on the basis of a single monitoring site [24]. In a recent study on some metals in the vehicular exhaust emissions of rickshaws, it has been discovered that a significant boost has been found in Al, P, and Zn in the PM samples of four-stroke Rickshaws [25]. In another study in Beijing, perfluorinated compounds (PFCs) are found in ambient $PM_{2.5}$, PM_{10}, and TSP [26]. The environmental damage costs the country an annual loss of about Rs. 365 billion, of which the urban air pollution loss was approximately Rs. 65 billion in 2006 [27].

Materials and Methods

Hourly air quality monitoring data for 2007-11 and 2014-15 were collected from the Provincial Environmental Protection Agency. The air quality monitoring stations remained almost out of work during 2012 and 2013 due to lack of budget to run them. Fix and mobile air quality monitoring stations had been used to monitor the six major pollutants along with meteorological parameters. The air quality monitoring stations contain an anemometer (KoshinDenkiKogyo Co., Ltd. Model KVS 501) combined wind vane, a solar radiation meter (Koshin Denki Kogyo Co., Ltd. Model SR-010), a thermohygrometer (Koshin Denki Kogyo Co., Ltd. ModelHT-010), and a data logging system (Horiba, Ltd. Model Special).

The six major air pollutants like ozone (O_3), carbon monoxide (CO), sulfur dioxide (SO_2), oxides of nitrogen (NOx, i.e., NO and NO_2), fine particulate matter ($PM_{2.5}$), and hydrocarbons (total hydrocarbons, non-methane hydrocarbons, and methane) were determined through analyzers described in Table 1.

The air quality index (AQI) was calculated according to "Eq.1" [28].

Table 1. Detail of instruments of air quality monitoring station.

Pollutant	Analyzer	Range	Method	Detection Limit
CO	Horiba Ltd; Model APMA-370	0~50 ppm	non-dispersive infrared ray method (ISO4224)	0.1ppm
NO/NO_2 /NOx	Horiba Ltd; Model APNA-370	0~1 ppm	Chemiluminescence (ISO7996) method	0.5 ppb
Sulfur dioxide	Horiba Ltd; Model APSA-370	0~0.5 ppm	U.V. fluorescence method (ISO10498)	1ppb
Ozone	Horiba Ltd; Model APOA-370	0~1ppm	UV photometry method	0.5 ppb
Hydrocarbon	Horiba Ltd; Model APHA-370	0~50 ppmC	Converter oven method	0.1 ppmC
$PM_{2.5}$	Horiba Ltd; Model APDA-370	0~5 mg m^{-3}	β-ray absorption method (ISO6349)	

$$AQI = [(NO_2/80) + (SO_2/120) + (O_3/130) + (CO/5) + (PM_{2.5}/35)]/5 \text{ X } 100 \quad (1)$$

Lahore and its Meteorology

Lahore is located at 31°32′N 74°22′E at 217 m above sea level. The municipal area of Lahore is 332 km^2. Due to rapid urbanization, the area has been extended to 1,000 km^2. Two fixed air quality monitoring stations have been installed in Lahore to monitor air quality. One of the stations is installed on the second floor of the city hall building situated in the northern main commercial area of Lahore with a number of busy roads, markets, and dense population. The second station was installed in Quaid-i-Azam Township area, a southern residential area near Kotlakhpat industrial estate.

The city hall air quality monitoring station was selected for data analysis. The fixed air quality monitoring station installed at city hall on Lower Mall road in Lahore represents the ambient air quality of the main city of Lahore. The monitoring station was located about 8 m from the ground. Most of the main roads of Lahore are within a 1-3 km sphere of the station. The location of the two fixed Air Quality Monitoring Stations can be seen in Fig. 1.

The climate of Lahore can be distributed into five seasons: foggy winter (15 Nov-15 Feb) with low rainfall, low wind speed, and high inversion; spring (16 Feb-5 April) with low rainfall and moderate temperature (T); summer (15 April-June) with high temperature, high rainfall, low relative humidity (RH), and high dispersion effects; rainy monsoon (July-16 September) with high temperature, high relative humidity, and low pollution due to dispersion and washing effect; and dry autumn (16 September-14 November) with low wind speed and low RH [29].

June is the hottest month, with an average temperature of 33.9ºC. The average temperature of January is 12.8ºC, which makes it the coolest month of the year. The average annual temperature of Lahore is 24.3ºC, which is fairly hot as annual average. Average monthly temperature range is 21.1ºC. The average daily temperature variation is 15.5ºC [29].

Minimum average sunshine has been observed in January with 6.9 hours day^{-1}. Overall annual average sunshine is 8.4 hours day^{-1} [29].

Wind speed remains low almost throughout the year except some windy days in summer. Around 60% of the year remains calm and 33% of days see an average speed of 1-3 knots. Only 6% of the year experiences speeds of 4-6 knots. Wind direction remains mostly northwest during monsoon and summer and southeast during winter [29].

Relative Humidity (RH) remains low throughout the year except during monsoon season. The monthly average of relative humidity exceeds 60% during July, August, and September. Average relative humidity remains around 77% in the morning and 40% in the evening. The average monthly relative humidity ranges around 20% in May to 58% in August. Overall, the annual average relative humidity remains around 37.9%.

The climate of Lahore has observed extreme weather events in the near past. The highest ever recorded temperatures of the city were 48.3ºC on 30 May 1944 and 48ºC on 10 June 2007. The highest recorded rainfall was 221 mm, observed on 13 August 2008, and 4.5 mm hail was observed in Lahore on 26 February 2011 [29].

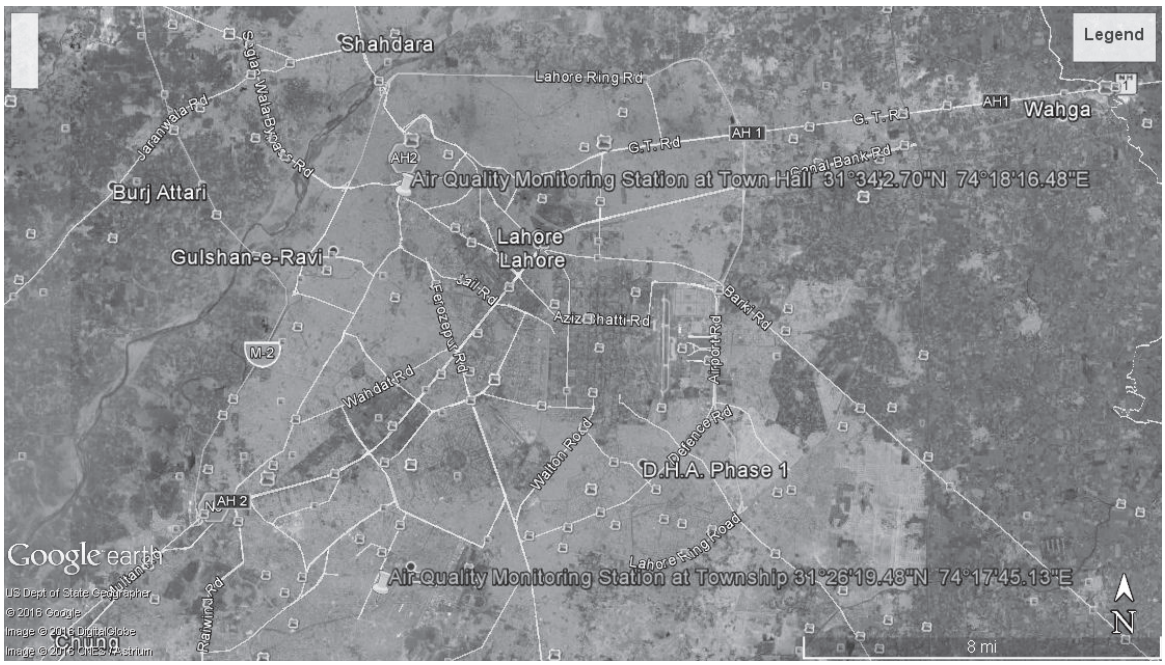

Fig. 1. Locations of automatic fixed air quality monitoring stations in Lahore (based on Google map).

Table 2. Air quality index.

AQI	0-50	50-100	101-150	151-200	201-300	>300
Air Quality	Clean	Moderate	Unhealthy for sensitive	Unhealthy	Very Unhealthy	Hazardous

Results and Discussion

Ambient air quality data of Lahore for 2007-11 and 2014-15 has been analyzed to discern patterns and determine the sources of the six representative air pollutants. The hourly data for each pollutant collected was analyzed for average concentration, monthly mean pattern, and seasonal and diurnal variations.

Air Quality Index

The interpretation of AQI can be elaborated as clean, moderate, unhealthy, and very unhealthy. The Pakistani NEQS for O_3 for 24 hours has yet not been made available. The NEQS for O_3 for one hour have been revised from 180 to 130 and for $PM_{2.5}$ for 24 hours have been revised from 40 to 35 since January 2013 [30]. So before January 2013, the index value would be calculated accordingly. A projected AQI is given in Table 2 [28].

AQI remains low (~74 to ~85) from June to August due to heavy rain, relatively high wind speed (~1.59 to ~1.85 monthly average), and dispersion due to high temperatures and high solar radiation. In summer, an improved air quality index also has been observed in northern China. [31].

The highest AQI (~132 to ~185) was observed from November to February due to inversion at low wind speed (< 1.5 m/s monthly average), low temperature (~ 15-21ºC monthly average), and low solar radiation (~104-140 W m^{-2} monthly averages) due to heavy fog during December and January**.** Another reason for the high AQI during fall can be due to burning crop residue in southwestern India and eastern Pakistan. The wind direction during winter remains mostly southeast, which can also be a reason for contributing to pollution in Lahore from a number of polluted steel industries in the northern part of Lahore and industrial clusters in Sheikhupura and Gujranwala. The steel industries are mostly located in Badami Bagh, Misry Shah, Daroghay Wala, and around the Band Road area in northern Lahore. Fig. 1 shows a map of Lahore.

Data Analysis

For data analysis, the data of daytime (07:00-15:00) has been taken for analysis of ozone and its precursors. The data of a sunny and clear day has been taken. The mean concentration of the ozone, other pollutants, and meteorological parameters are given in Table 3.

The day is dry and hot with low mean RH (30.66), high solar radiation (about 680 W m^{-2}), and high mean temperature (around 38ºC). Wind speed remained low (mean value = 1.72 m/sec) as a routine matter in semi-arid regions. NO remained almost nil (mean value = 1.93 µg m^{-3}) during sunny hot days due to its conversion to NO_2 (mean value = 26.8 µg m-3) in the presence of high concentrations of O_3 (mean value = 122.50 µg m^{-3}). Concentrations of CH_4 remained below (mean value = 2,210.61 ppb) its natural level (around 3,000 ppb) due to its consumption as a precursor of ozone. The mean value of $PM_{2.5}$ (155.07mg m^{-3}) remained high due to a high amount of un-burnt carbon from vehicular exhaust emissions in the atmosphere.

Correlation Analysis

Table 4 shows the correlation of different air quality parameters. The following results are made according to statistical analysis of data in Table 4.

O_3 has a significant negative correlation with NO, NO_2, NOx, CH_4, CO, and RH (r-value> -0.5); and has significant positive correlation with T and solar radiation (r-value> 0.5). The level of tropospheric ozone is highly dependent on solar radiation and atmospheric temperature [32], while NO has significant positive correlation with NO_2, NOx, CH_4, CO, and RH (r-value> 0.5 for each); and has negative correlation with O_3, T, and solar radiation (r-value> -0.5 for each). NO concentration is almost negligible from 07:00-15:00 in the summers due to its conversion into NO_2 by reacting with abundant O_3 produced by different sources such as CO, NO_2, VOCs, and NMHCs in the presence of sunlight.

Table 3. Mean values of different pollutants and meteorological parameters (07:00-17:00).

Variable	NO	NO_2	NOx	CH_4	NMHC	CO	SO_2	O_3	$PM_{2.5}$	Wind Speed	T	RH	Solar radiation
Unit	µg m^{-3}	µg m^{-3}	Ppb	ppb	ppb	mg m^{-3}	µg m^{-3}	µg m^{-3}	µg m^{-3}	m/s	ºC	%	W m^{-2}
Mean Value	1.93	28.52	16.14	2210.61	735.85	0.68	42.64	122.50	155.07	1.72	37.68	30.66	539.35

Table 4. Correlation analysis of ambient air variables of semi-arid region, Lahore.

		NO	NO_2	NOx	CH_4	NHMC	CO	SO_2	O_3	$PM_{2.5}$	WS	T	RH	Solar radiation
NO	Pearson Correlation	1	.946**	.741**	.953**	.416	.917**	.556	-.825**	.163	.058	-.725*	.616*	-.614*
NO_2	Pearson Correlation	.946**	1	.871**	.978**	.254	.912**	.571	-.675*	.200	-.084	-.634*	.496	-.660*
NOx	Pearson Correlation	.741**	.871**	1	.797**	.039	.734*	.363	-.520	.072	-.138	-.401	.249	-.635*
CH_4	Pearson Correlation	.953**	.978**	.797**	1	.214	.892**	.576	-.714*	.094	-.003	-.710*	.571	-.717*
NHMC	Pearson Correlation	.416	.254	.039	.214	1	.336	.185	-.238	.497	-.157	-.135	.184	.245
CO	Pearson Correlation	.917**	.912**	.734*	.892**	.336	1	.809**	-.758**	.443	.224	-.805**	.737**	-.466
SO_2	Pearson Correlation	.556	.571	.363	.576	.185	.809**	1	-.516	.654*	.519	-.820**	.841**	-.160
O_3	Pearson Correlation	-.825**	-.675*	-.520	-.714*	-.238	-.758**	-.516	1	-.004	-.491	.824**	-.763**	.525
$PM_{2.5}$	Pearson Correlation	.163	.200	.072	.094	.497	.443	.654*	-.004	1	.045	-.189	.282	.487
WS	Pearson Correlation	.058	-.084	-.138	-.003	-.157	.224	.519	-.491	.045	1	-.678*	.769**	-.088
T	Pearson Correlation	-.725*	-.634*	-.401	-.710*	-.135	-.805**	-.820**	.824**	-.189	-.678*	1	-.978**	.523
RH	Pearson Correlation	.616*	.496	.249	.571	.184	.737**	.841**	-.763**	.282	.769**	-.978**	1	-.364
Radiation	Pearson Correlation	-.614*	-.660*	-.635*	-.717*	.245	-.466	-.160	.525	.487	-.088	.523	-.364	1

**Correlation is significant at the 0.01 level (2-tailed). * Correlation is significant at the 0.05 level (2-tailed)

NO_2 has significant positive correlation with NO, NOx, CH_4, CO, and SO_2 (r-value> 0.5 for each), and has significant negative correlation with O_3, T, and solar radiation (r-value> -0.5). In daytime almost all the NO has been converted to NO_2 by reacting with O_3 in the presence of sunlight. The dominant sources of nitrogen oxides as far as vehicles are concerned are diesel and four-stroke engines [33].

NOx has a significant positive correlation with NO, NO_2, CH_4, CO, and SO_2 (r-value> 0.5 for each), and has a significant negative correlation with O_3 and solar radiation (r-value> -0.5).

CH_4 has significant correlation with NO, NO_2, NOx, SO_2, and RH (r-value> 0.5 for each), and significant negative correlation with O_3, T, and solar radiation (r-value> -0.5).

NMHC has no significant correlation with any of the parameters.

CO has a significant positive correlation with NO, NO_2, NOx, CH_4, SO_2, and RH,(r-value>0.5 for each), and has significant negative relation with O_3 and T (r-value>-0.5). The correlation studies among NO, NO_2, NOx, CH_4, CO, and SO_2 suggest that the dominant sources of air pollution are direct or primary in nature. The major sources of CO are CNG, LPG, and petrol engines. Diesel engines generate a relatively very low amount of CO. Ambient CO emissions always remain within the permissible limit of 5 mg m^{-3} = 5000 µg m^{-3}. Therefore, CO emissions may not be considered low in terms of µg m^{-3} units. The significant positive correlation between CO and NO ($r = 0.72$; p-value < 0.01) shows a common source for both. CNG engines are a main common source for the emission of CO and NO [33]. Pakistan has the highest number of vehicles using CNG fuel [33]. CO produces O_3 through a number of chemical reactions with hydroxyl radicals, and NO in the polluted environment in the presence of sunlight. The dominant sources of CO emissions are two- and four-stroke petrol, CNG, and LPG vehicles. Diesel engines produce only a minute amount of CO emissions [33].

The major source of SO_2 emissions are diesel engines and two-stroke LPG vehicles [33]. SO_2 has a significant positive correlation with NO, NO_2, CH_4, CO, $PM_{2.5}$, WS, and RH (r-value > 0.5 for each), and has significant negative correlation with O_3 and T. The correlation of SO_2 with WS suggests that point sources can be a dominant source for SO_2 emissions. The common source for CO and SO_2 are LPG engines.

$PM_{2.5}$ has significant positive correlation only with SO_2 (r-value > 0.5). The correlation of $PM_{2.5}$ with SO_2 suggests that most of these pollutants originates with fresh emissions from mobile and point sources. Some amount of $PM_{2.5}$ may be produced by chemical conversion of SO_2 into particles. A negative correlation of $PM_{2.5}$ with T has already been reported [34]. Some researchers have reported the conversion of semi-volatile components from particle phase to gas phase at high temperatures [35-38].

Yasar has reported high smoke opacity for most diesel engines, which are a dominant source for $PM_{2.5}$ [33]. Diesel engines are a dominant source for SO_2 and $PM_{2.5}$ emissions, which explains the high correlation between $PM_{2.5}$ and SO_2.

RH has significant positive correlation with NO, CO, SO_2, and WS (r-value> 0.5), and significant negative correlation with O_3 and T (r-value> -0.5). In fact, RH has significant negative correlation with T and has very little correlation with other pollutants. The pollutants may have very minute correlations with WS and RH. In other words, it is difficult to explain the correlation of pollutants with WS and RH in the presence of many other factors as well.

In the winter, the excess amount of ammonia at low temperatures and high relative humidity upturns PM by producing nitrate particles [39, 40]. Temperature has a significant negative correlation with NO, NO_2, CH_4, SO_2, WS, and RH (r-value> -0.5), and has significant positive correlation with solar radiation and O_3 (r-value> 0.5). This explains the production of ozone in the presence of solar radiation at the cost of the precursors of O_3.

Table 5. Ratio analysis based on average emissions and/or ambient data.

Region		CO/NOx	SO_2/NOx
Eastern US	Ambient	4.3	0.94
	Mobiles	8.4	0.05
	Point Sources	0.95	1.8
Pennsylvania Area	Ambient	2.6	1.7
	Mobiles	7.8	0.05
	Point Sources	0.8	2.3
Western US	Ambient	7.3	0.19
	Mobiles	10.5	0.05
	Point Sources	0.18	0.44
Denver Metropolitan area	Ambient	7.3	0.19
	Mobiles	10.5	0.05
	Point Sources	0.18	0.44
Raleigh, NC	Ambient	16.3	0.73
New Delhi, India	Ambient	50	0.58
Lahore (Current Study)	Ambient	16	0.52
	Mobiles	9.71831	0.070423
	Point Sources	0.789474	0.131579

Ratio Analysis

High ratios of CO/NO and low ratios of SO_2/NO indicate that mobile sources are the major source of NO, and point sources are the major source for SO_2 emissions. The production of NOx is associated with high temperatures during fossil fuel burning. Therefore, NOx is usually produced at high temperatures in four-stroke petrol and diesel engines. However, SO_2 is dominantly produced due to high sulfur content in fuel. High sulfur content (0.25-1%) is present in diesel available in Pakistan. Therefore, diesel engines are the major anthropogenic source of SO_2 emissions in Lahore [33]. As NOx is abundantly produced by both 4-stroke petrol engines as well as diesel engines at high temperature, the concentration of NOx usually remains high in Lahore city.

An emission inventory has been provided by [41, 42] for CO, SO_2, and NOx. The data of ratio of CO/NO and CO/SO_2 is given in Table 5, which also provides the ratio analysis of CO by NOx and SO_2 by NOx provided by different studies, such as one in Denver, CO, US [43]; Boulder, CO, US [44]; Raleigh, NC, US [45]; and New Delhi, India [46]. The above studies show a similar trend of ratios of CO/NO and SO_2/NO as do in the current study.

Analysis of Ozone Formation

Ozone is a secondary pollutant. The primary sources for ozone are CO, VOCs, CH_4, NO_2, and solar radiation. A large amount of O_3 has also been produced around high-voltage electric lines. Some countries also claim a high amount of O_3 due to trans-boundary movements. It has been observed that during summers, almost all the NO has been converted to NO_2 by reacting with O_3, being produced by different chemical reactions of CO, CH_4, VOCs, and NO_2 in the presence of sunlight. Therefore, NO concentrations remain almost nil in the presence of high solar radiation during the day in summers. A possible dynamic equilibrium between NO and NO_2 is given in "Eq. 2" [47]:

$$NO + O_3 \leftrightarrow NO_2 + O_2 \quad (2)$$

NO_2 reacts with oxygen in the presence of sunlight to produce O_3 and NO. As the NO concentration is almost nil in day-time in summers, it may be assumed that O_3 has been produced in abundant amounts by different primary sources to keep the reaction forward according to the Le Chatlier principle, i.e., almost all the NO has been converted to NO_2 due to an abundant amount of O_3 being produced by a number of primary sources in the presence of sunlight. Therefore, it can be assumed that O_3 concentration measured at day-time in summers (high solar radiations) is the O_3 that has been produced by sources other than NO_2 or NOx (as the amount of O_3

Table 6. Comparison of dependents through paired sample T-test.

		t	p
Pair 1	NO - O_3	-4.872	.005
Pair 2	NO_2 - O_3	-3.923	.011
Pair 3	NOx - O_3	-4.354	.007
Pair 4	CH_4 - O_3	16.787	.000
Pair 5	$PM_{2.5}$ - O_3	1.811	.130
Pair 6	WS - O_3	-4.977	.004
Pair 7	T - O_3	-3.713	.014
Pair 8	RH - O_3	-3.668	.014
Pair 9	Solar radiation - O_3	15.505	.000

produced by NO_2 has been consumed by NO). Or it may be assumed that whenever the value of NO is negligible, the amount of O_3 produced would be that amount of O_3 that is produced by sources other than NO_2 or NOx.

Another assumption is that sources like VOCs, CO, and CH_4 convert NO to NO_2 and higher oxides of nitrogen. The NO_2 is further photo-lysed to produce O_3. In daytime the value of NO is negligible due to its conversion to NO_2. The value of NO_2 or NOx has been found to be as high as the O_3 value. Therefore, a significant positive correlation is observed between NO_2 and O_3 or between NOx and O_3 in daytime.

To assess the extent of dependence of Ozone on other variables, paired sample t test has been applied on data. The results of paired sample t test are given in Table 6.

The t value of all the precursors of ozone like NOx, CH_4, temperature, and solar radiation is non-zero. The p value of NO, NO_2, NOx, T, and solar radiation are less than or very close to 0.01 (99% confidence level), indicating their significant effect on ozone. For $PM_{2.5}$ p-value is 0.13, indicating no significant dependence of Ozone on $PM_{2.5}$. Although p values for wind speed and RH are close to 0.01, practically RH has no significant relation for ozone, and the dependence of ozone on wind speed depends on wind direction.

Diurnal and Monthly Mean Pattern of Air Quality Parameters

It has been observed that all the primary pollutants like CH_4, NMHC, CO, NO, NO_2, NOx, SO_2, and $PM_{2.5}$ have positive correlations with each other and negative correlations with O_3. The peak value of O_3 has been observed in the daytime due to the presence of high solar radiation, especially in summers. In the absence or reduction of light at night, almost nil or minimum values of O_3 have been observed. The diurnal variations remain the same in every season and all months of the calendar. The value of O_3 has been observed as very high during the summer noon due to high solar radiation. Maximum pollution of primary pollutants has been observed from

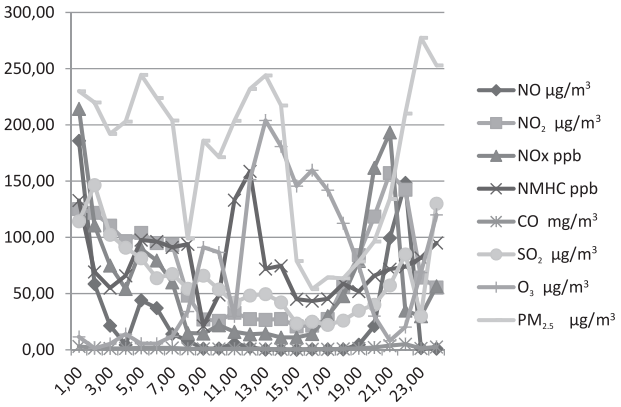

Fig. 2. Diurnal trends of air quality pollutants in the semi-arid region of Lahore.

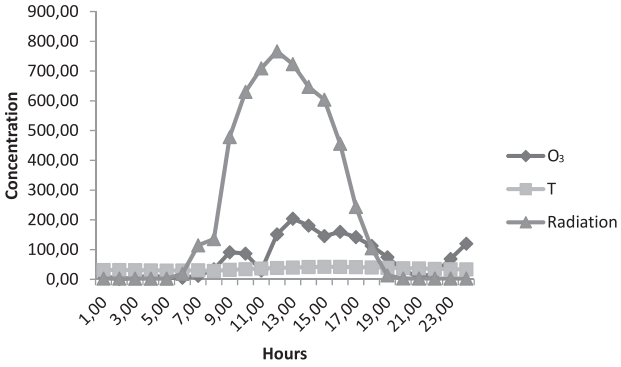

Fig. 3. Diurnal trends of ozone, temperature (T), and solar radiation.

November to February due to low solar radiation and low photochemical reactions to produce O_3. Fig. 2 shows the diurnal variation of O_3 and other pollutants, while Fig. 3 shows the significant correlation of O_3 with temperature and solar radiation. In Fig. 3, CH_4 levels are divided by 100, NMHC are divided by 10, and CO levels are multiplied by 10 to better elaborate upon their monthly patterns.

Seasonal Pattern of Ozone and other Air Quality Parameters

There are five different seasons in Lahore. The two main seasons are winter and summer with extreme climatic conditions. As already discussed, O_3 has a significant correlation with temperature (r = 0.7; Table 3). The value of O_3 remains high during summers due to high solar radiation. The concentration of precursors of O_3 remains high during winter mainly due to low solar radians.

The main features of winter in Lahore are:

- Low wind speed,
- Low solar radiation/temperature
- Less precipitation

This favors accumulation and inversion of air pollutants. Therefore, the highest air pollution has been

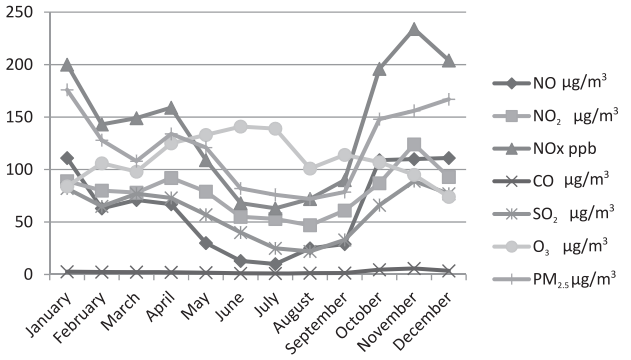

Fig. 4. Seasonal/Monthly patterns of air quality pollutants in the semi-arid region of Lahore.

found from November to February in Lahore as a semi-arid region. But concentrations of secondary O_3 pollutants remain low in winter due to low solar radiation.

Summer is composed of:

- Relatively high wind speed
- High solar radiation/temperature
- Monsoon rains during July and August

All these factors results in the dispersion and washout of air pollutants. But O_3 concentrations remain high during summers due to high solar radiation. Fig. 4 elaborates upon the monthly pattern of O_3 and other pollutants.

Conclusions

We have characterized the ambient air quality for criteria pollutants for Lahore, Pakistan. The annual average concentrations of $PM_{2.5}$ and NO are exceeding the Pak-NEQS. The NEQS for $PM_{2.5}$ needs to be relaxed for a semi-arid region as $PM_{2.5}$ levels are exceeding strict NEQS of 35 µg m-3, even in rural areas around the city.

24 hours and annual Pak-NEQS have not been established for ozone, although its concentration remains too high during summers. Mobile sources are a major source of such high concentrations of NO. The hourly average concentrations of ozone exceed the Pak-NEQS primarily during summer. Carbon monoxide and sulfur dioxide are found to remain in compliance with the Pak-NEQS for the entire calendar year.

The monthly pattern of pollutants show that AQI remains high during winter due to relatively low washing effect (low rain), low wind speed, and high inversion. Moreover, the dominant wind direction from the southeast enables the polluting steel industry to contribute to pollution of Lahore in winter. But ozone levels remain low during winter due to low solar radiation. The diurnal trend of pollutants is similar to the monthly pattern, i.e., AQI remains low in the daytime at high T and solar radiation. The concentration of primary pollutants like NO, NO_2, NOx, CO, SO_2, CH_4, NMHC, and $PM_{2.5}$ remains low in the daytime due to their use as a precursor of O_3 , dispersion effect, and many other factors. The ozone level remains high in the daytime (like in summers) due to high solar radiation and the presence of high concentrations of its precursors.

Ozone has positive correlation with T and solar radiation, and negative correlation with most pollutants like NO, NO_2, NOx, CO, and CH_4. Wind speed, T, and solar radiation have negative correlations with primary pollutants. A wide range of fluctuation in NO concentration has been observed in the presence and absence of solar radiation. Ozone in the presence of solar radiation has a reduction effect for most pollutants other than $PM_{2.5}$ and NMHC.

Correlation studies suggest that the dominant sources of the primary pollutants are fossil fuels, either from mobile sources or point sources. Four-stroke petrol engines are a common source for CO, NO, NO_2, and NOx, which are precursors of O_3. Diesel engines are a major common source for NOx, SO_2, and $PM_{2.5}$. There is a need to reduce sulfur contents in diesel being used in Pakistan. SO_2 emissions mostly remain in compliance with NEQS in Lahore, as most of the vehicles use petrol as fuel. As NOx are abundantly produced by diesel and four-stroke petrol engines, the concentration of NOx mostly remains high in Lahore. Ratio analysis showed that mobile sources are the major sources for NO and point sources are the major source for SO_2 emissions in the city hall area of Lahore.

Ozone is a dreadful pollutant for road traffic for arid and semi-arid areas in summer. There is a need to collect more data of its other primary precursors like VOCs as well.

The population of Lahore has been increasing at a very fast pace. There is a need to stop migration through the provision of health, education, employment, industrial, and fast transport facilities in other cities and remote areas as well.

There is also a need to provide better and more accessible public transport for all the housing societies of Lahore, to promote the use of public transport, and to lessen the use of private vehicles – especially cars.

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