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Araştırma Makalesi Research Article

EVALUATION OF THE MAJOR AIR POLLUTANTS LEVELS AND ITS INTERACTIONS WITH METEOROLOGICAL PARAMETERS IN ANKARA

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Keywords

Air Quality,
Air Pollutants,
Meteorological Effect,
Temporal Variation,
Statistical Correlation.

Abstract

The aim of this study is to examine levels, temporal changes and interactions of major air pollutants with meteorological variables in Ankara, Turkey. The level of air pollutants namely PM_{10}, $PM_{2.5}$, SO_2, NO, NO_2, NO_X, O_3, CO was evaluated monthly, seasonally, and annually during 2019. The statistical relationship between air pollutants and ambient temperature, relative humidity and air pressure was examined and discussed. The pollutants concentrations started to rise in the morning and evening hours (excluding O_3) when the traffic was at its peak and was at the highest level between 10:00 -14:00 and 22:00-02:00. It was seen at the lowest values (excluding O_3) during daylight hours. A strong positive correlation was reported between PM_{10} and both $PM_{2.5}$ and CO. Also, it was positive between NO and CO and NO_X. On the other hand, negative correlation was reported between O_3 and all other parameters. Moreover, paired comparisons of the selected parameters during the seasons were investigated. A statistically significant difference was found between different paired parameters namely CO/NO_X, SO_2/NO_X and $PM_{2.5}/PM_{10}$. The results revealed that the changes in the meteorological parameters during the mentioned seasons significantly impact the behavior of air pollutant parameters.

ANKARA'DA BAŞLICA HAVA KİRLETİCİ SEVİYELERİNİN VE METEOROLOJİK PARAMETRELERLE ETKİLEŞİMLERİNİN DEĞERLENDİRİLMESİ

Anahtar Kelimeler

Hava Kalitesi,
Hava Kirleticileri,
Meteorolojik Etki,
Zamansal Değişim,
İstatistiksel Korelasyon.

Öz

Bu çalışmanın amacı, Ankara'daki başlıca hava kirleticilerin seviyelerini, zamansal değişimlerini ve meteorolojik değişkenlerle etkileşimlerini incelemektir. Başlıca hava kirleticilerinden olan PM_{10}, $PM_{2.5}$, SO_2, NO, NO_2, NO_X, O_3, CO seviyeleri 2019 yılı boyunca aylık, mevsimsel ve yıllık olarak değerlendirilmiştir. Hava kirleticileri ile ortam sıcaklığı, bağıl nem ve hava basıncı arasındaki istatistiksel ilişki incelenmiş ve tartışılmıştır. Kirletici konsantrasyonları trafiğin en yoğun olduğu sabah ve akşam (O_3 hariç) saatlerinde yükselmeye başlamış ve en yüksek düzeyde 10:00-14:00 ile 22:00-02:00 arasında olmuştur. Gündüz ise en düşük değerler (O_3 hariç) görülmüştür. PM_{10} ile hem $PM_{2.5}$ hem de CO arasında güçlü bir pozitif korelasyon rapor edilmiştir. Ayrıca NO ve CO ve NO_X arasında pozitif korelasyon görülmüştür. Diğer yandan O_3 ile diğer tüm parametreler arasında negatif korelasyon rapor edilmiştir. Ayrıca mevsimlerde seçilen parametrelerin ikili karşılaştırmaları da incelenmiştir. CO/NO_X, SO_2/NO_X ve $PM_{2.5}/PM_{10}$ gibi farklı eşleştirilmiş parametreler arasında istatistiksel olarak anlamlı bir fark bulunmuştur. Sonuçlar, söz konusu mevsimlerde meteorolojik parametrelerdeki değişikliklerin hava kirletici parametrelerin davranışını önemli ölçüde etkilediğini ortaya koymuştur.

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1. Introduction

The Global Exposure Mortality Model developed by Burnett et al. (2018) reported that exposure to environmental air pollution was responsible for approximately nine million premature deaths globally in 2015 (Burnett et al., 2018). The principal of human health issues triggered by long-term exposure to air pollutants found are cardiovascular diseases and respiratory disorders. There are adverse effects of heavy metal particulate on respiration, especially on sick and elderly people as well as children living in contaminated areas. Some heavy metal pollutants may also serve as immunotoxins, resulting in increased vulnerability to infection (Sorvari et al., 2017; Kadioglu et al., 2010). Health effects related to urban air pollution have primarily occurred in megacities due to high concentrations of atmospheric air pollutants (Brook et al., 2017; Yurdakul et al., 2019; Tepe and Doğan, 2019). As a result of industrial activities, air pollution has now arisen in developed countries and the quantity of emission sources such as improper vehicles has also increased (Ghorani-Azam et al., 2016). Air quality in Ankara as the capital and high populated city in Turkey relied on varied natural sources, such as man-made pollution (for example traffic, domestic heating, industrial and commercial activities), topographic factors, and meteorological, and atmospheric conditions (Kadioglu et al., 2010; Bari and Kindzierski, 2015; Sari et al., 2019). In the last two decades, Ankara has faced severe ambient air pollution, particularly air pollutants criteria (particulate matter (PM_{10} and $PM_{2.5}$), Carbon monoxide (CO), Nitrogen Dioxide (NO_2), Nitrogen Oxides (NO_X), and sulfur dioxide (SO_2), due to the unsustainable growth of industrialization and urbanization as well as influenced by high traffic activities (Genc et al., 2010; Njoku et al., 2016; Baran 2021). Indeed, Ankara environmental air pollution has become one of the challenging environmental issues for the Ankara municipality government, officials, policy makers, and the people of Ankara. Substantial efforts have been done by the Ankara municipality to reduce the concentration of air pollution (Genc et al., 2010). To date, several studies have been carried out to address the air pollutants levels, temporal changes and their interactions with meteorological variables (Genc et al., 2010; Kadioglu et al., 2010 Chandu and Dasari, 2020; Kalbarczyk and Kalbarczyk, 2017; de Foy, 2018). In Ankara, during 1999 and 2000, Genc et al., (2010) studied the temporal variations of traffic-impacted concentrations of PM_{10}, SO_2, NO_2, NO, and CO using a multiple linear regression model. It was noticed that air quality in residential areas was affected by the traffic activities in the city. In addition, Genc found that meteorology rather than pollution determined the air quality. In 2000, Yatin studied the atmospheric trace elements and factors affecting chemical composition of fine particles. Yatin reported that variations in soil moisture and wind speed determine atmospheric loading and seasonal variations in the intensity of crustal elements. In addition, local meteorology regulates short-term episodes of pollutant concentrations, especially mixing height and wind velocity (Yatin et al., 2000). In 2020, Kadioglu et al., (2010) studied the heavy metal pollutants in road dust levels during the summer season. The road dust collected as a polluted and measurable material for the determination of the pollutants from the abrasion of brake pads, motor vehicle exhaust, and lithology. The outcomes revealed that the toxic trace metals in road dust do not originate from industrial plants and lithology but from brake pad abrasion and motor fuel exhausts. The results showed deleterious effects on ecosystems and human health in Ankara Despite the remarkable studies conducted, a detailed and deep understanding of the temporal volatility of air pollutants as well as the meteorological impacts on their concentrations using a solid approach is still unclear in Ankara to date. Sari et al., (2019) evaluated the levels, temporal changes, interactions, and sources of the major air pollutants during the seasons in Bursa, Turkey. Yousefian et al., (2020) studied the temporal variations of ambient air pollutants and the influences of meteorology on their concentrations in Tehran between 2012 and 2017. Li et al., (2020) discussed the concentrations of some major air Pollutants in ecological functional zones during 22 years in Shenyang, Northeast China. Most of studies are generally evaluated the levels of air pollutants and their relationship to the metrological data are evaluated seasonally and monthly using normal descriptive statistics. However, the hourly behavior of air pollutants has not been well discussed in the literature. Pairwise comparison between air pollutants has not been well reported and evaluated. The use of Kruskal Wallis test, Bonferroni Dunn test and Spearman's Correlation Analysis between air pollutants and meteorological data was not documented. Therefore, this study aimed to analyze the concentrations, temporal changes, and interactions of the main air pollutants with meteorological variables in Ankara, the capital of Turkey. In this work, the hourly concentration levels of the pollutants; PM_{10}, $PM_{2.5}$, SO_2, NO, NO_2, NO_X, O_3, and CO were evaluated. The distribution of meteorological data with selected air quality parameters according to seasons was examined and discussed. The seasonal relationship between meteorological data and concentration of pollutants was presented. The performance of correlation for selected air quality parameters was carried out. Moreover, the pairwise comparisons of the selected parameters during seasons were studied. This study was conducted in Ankara, the capital city of Turkey in 2019.

2. Material and Method

2.1. Study Area

The current study focused on the evaluation of the level of air pollutants and their relationship and interaction with the metrological variables in a capital city of Turkey. Ankara as the capital city of Turkey, which is located in the region of Central Anatolia, has an area of 25,437 km^2, is located at an altitude of 890 m above sea level, and has a total of 25 districts. There are public institutions, ministries, embassies and important commercial and cultural centers which are located within the boundaries of Çankaya district. According to the statistics of Statistical Institute 2019, the total population of the district is 944,609, and the area of the district with the largest population in the province is 46,259 hectares (TSI, 2020; Çankaya Municipality, 2020). The Sıhhiye Air Quality Monitoring Station (SAQMS) is located in the Çankaya district, the center of Ankara, where the population is the highest area and resource type of SAQMS with latitude/longitude 39.92728083/32.85968467 are urban and traffic (Figure 1). SAQMS which is the traffic source is located at Adnan Saygun Street in Çankaya district. SAQMS, which is in the garden of the Ministry of Health, General Directorate of Public Health, is located in the northeast of Ankara and is about 800 m northeast of Kızılay, which we consider as the city center. The station is located in a flat area. SAQMS is mainly surrounded by a residential area with hospitals, workplaces, restaurants and public buildings. There is Adnan Saygun Street about 10 m to the west, Aksu Street about 30 m to the south and east and Celal Bayar Boulevard about 130 m to the north and the D200 highway at a distance of about 4 km to the north of SAQMS. In addition, the Çankaya Municipality's Yenişehir Marketplace, located approximately 50 m southwest of SAQMS, is open every day of the week (NCACACD, 2020).

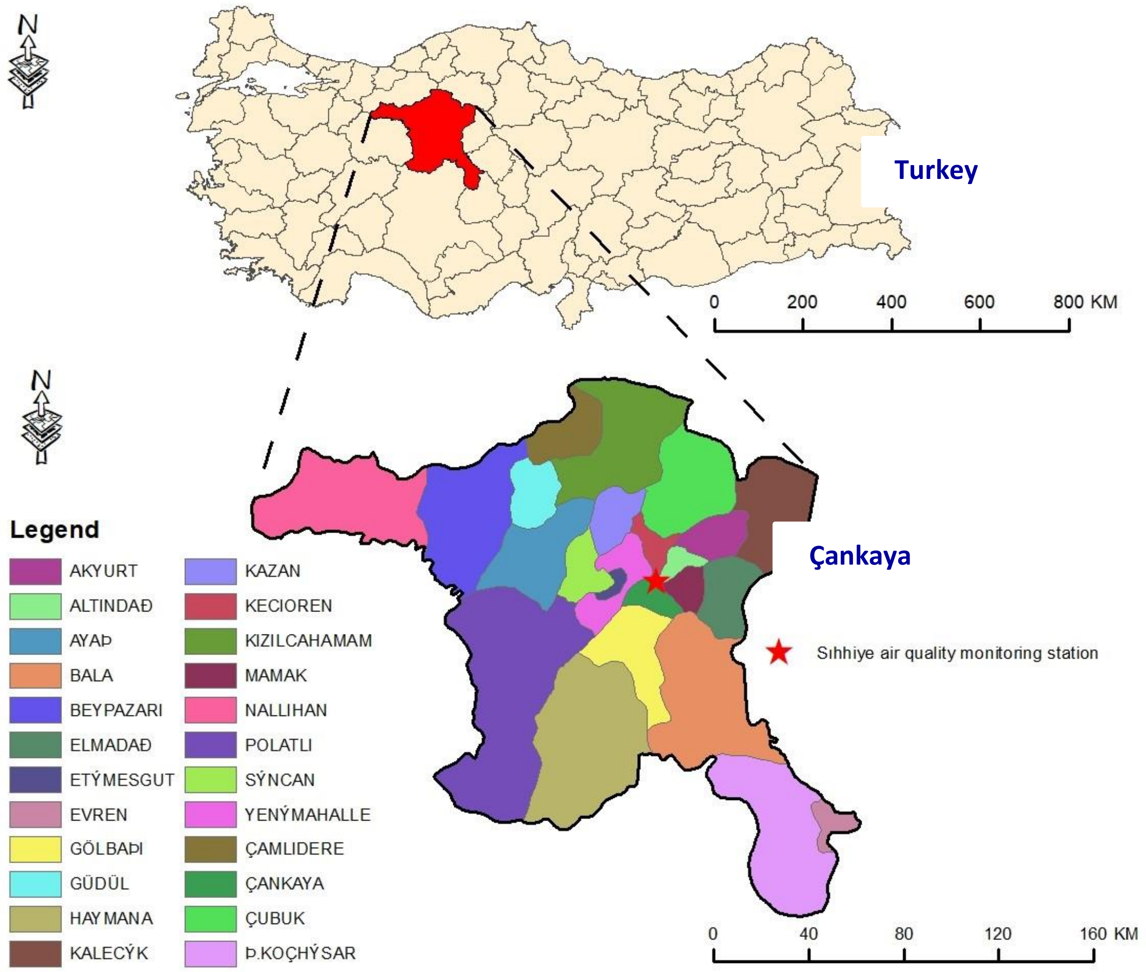

Figure 1. Geographic location of the study area in Sıhhiye Air Quality Monitoring Station in Çankaya district of Turkey

2.2. Data Collection and Statistical Analysis

The data used in this study were obtained from the website of the Ministry of Environment and Urbanization Air Quality Monitoring Network (MEU, 2020). To evaluate the behavior of air quality pollutants, hourly measurements of air pollutants namely PM_{10}, $PM_{2.5}$, SO_2, NO, NO_2, NO_X, O_3, CO were examined with the values of ambient temperature, relative humidity and atmospheric pressure values according to spring, summer, autumn and winter seasons in 2019. Table 2 presents the data about air quality monitoring station. For sulfur dioxide analysis, ISO/FDIS 10498 in outdoor air - determination of sulfur dioxide - UV fluorescence method, for the analysis of nitrogen dioxide and nitrogen oxides ISO 7996:1985 in outdoor air - determination of mass concentrations of nitrogen oxides - chemical radiation (bone-luminescence) method, for PM_{10} sampling and measurement, EN 12341 "Air Quality-Determination of PM_{10} fraction of suspended particulate matter- measurement method, for carbon monoxide measurement, Non-Dispersive Infrared Spectrometry (NDIR) method, for ozone analysis, ISO FDIS 13964 UV photometric method were specified as reference methods by the Regulation of Air Quality Assessment and Management (RAQAM, 2008), Statistical Package for Social Sciences software (version 22.0) was used for the statistical analyses. Descriptive statistical methods (mean, standard deviation, median, minimum, maximum) were used while evaluating the analysis of study data. The suitability of the quantitative data to the normal distribution was tested by Kolmogorov-Smirnov, Shapiro-Wilk test and graphical evaluations. The Kruskal Wallis test was used for comparisons of three and more groups that did not have a normal distribution, and the Bonferroni Dunn test was used for paired comparisons. Spearman's Correlation Analysis was used to evaluate the relationships between variables. Significance was assessed at least at the $p < 0.05$ level. Table 1 presents the data about air quality monitoring station (NCACACD, 2020).

Table 1. Sıhhiye air quality monitoring station

Name	**Ankara-Sıhhiye**	**Air Pollutants (μg/m^3)**		**Meteorological Parameters**
Owner	MEU-NCACACD	PM_{10}	NO_2	AT (°C)
Type	Urban-Traffic	$PM_{2.5}$	NO_x	RH (%)
Province	Ankara	SO_2	O_3	AP (mbar)
District	Çankaya	NO	CO	

AT: Air Temperature, RH: Relative Humidity, AP: Air Pressure, SD: Standard Deviation

3. Result and Discussion

Hourly Concentration Levels of Pollutants

The mean concentrations were calculated for each hour to evaluate hourly fluctuations of the pollutant concentrations based on four seasons (Figure 2). In general, during the first daylight hours between 08:00 and 13:00, the increases of pollutant levels (except O_3) were observed due to the maximum level of residential heating and high traffic in the high populated area such as Ankara. However, the level of these pollutants was reduced after 13:00 pm due to the consumption of the high amount of the pollutants in photochemical reaction (especially for SO_2, NO_2, NO_X and CO) and produce high level of O_3. When residential heating and traffic were at their minimum level at 04:00-07:00 am, the lowest concentrations were observed as seen in Figure 2. However, the highest concentrations of pollutant were seen 1-2 hours later, especially in the winter and autumn seasons. In addition, for the same reasons, the level of pollutants started to rise again in the evening (after 18:00-20:00) and reached their highest level at night due to the lowering of the boundary layer. The level of O_3 started to increase from 8:00 am and started to decrease after 13:00 pm. Its fluctuation is in contrasts with the NO_X due to the photochemical reaction, especially in summer. It was found by US EPA (2020a) that ground-level ozone, also called bad ozone, does not spread directly in the atmosphere and O_3 is formed by photochemical reactions in the presence of NO_X and VOCs. The results obtained are consistent with the EPA's opinion. The concentrations of pollutants (excluding O_3) are highest during the morning and evening hours when traffic is at its peak, and turn into a valley shape in the afternoon. This shows a clear link with the boundary layer height change (Chandu and Dasari, 2020). Despite the absence of industrial facilities and the widespread use of natural gas in the study area, the obviously high pollutant concentrations during the winter months may be evidence of the pollution caused by heating. In addition, it is well known that heavy traffic potential is one of the most important sources of air pollution. It was observed that the highest level of pollutants was reported during peak hours of traffic. In addition, it has been stated by the US EPA and in previous studies that traffic is among the sources of PM, SO_2, CO and NO_X pollutants emitted automobiles, heavy equipment that burn fuel with a high sulfur content, cars, trucks and buses, off-road equipment and other vehicles or machinery by burning fossil fuels (Clarke et al., 2014; Kalbarczyk and Kalbarczyk, 2017; de Foy, 2018; US EPA 2020b, c, d, e).

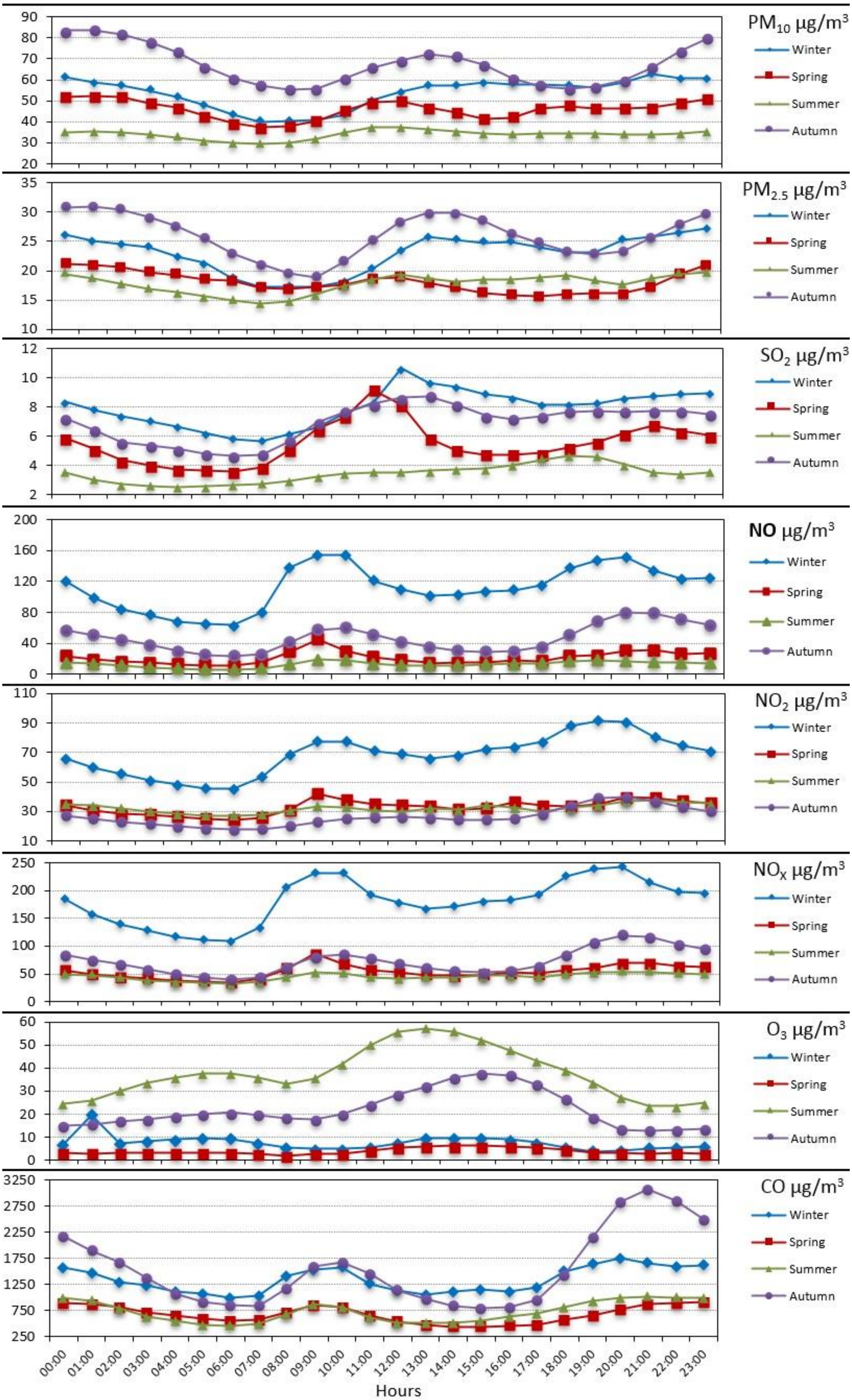

Figure 2. Hourly concentration levels of air quality pollutants

Distribution of Meteorological Data with Selected Air Quality Parameters According to Seasons

The monthly and seasonal distribution of the selected air quality parameters including PM_{10}, $PM_{2.5}$, SO_2, NO, NO_2, NOx, O_3, and CO, and meteorological data including air temperature, relative humidity and air pressure were presented in Table 2. The highest concentration of PM_{10} (87.99±29.02 μg/m^3), $PM_{2.5}$ (36.15±12.13 μg/m^3), SO_2 (11.31±4.39 μg/m^3), NO (149.48±98.90 μg/m^3), NO_2 (76.14±12.64 μg/m^3), NO_x (207.05±117.65 μg/m^3), O_3 (48.00±10.06 μg/m^3) and CO (2102.83±628.05 μg/m^3) were obtained in November, November, February, December, February, December, July and November, respectively. In addition, the maximum temperature (27.04±2.64 °C), relative humidity (81.46±8.62 %) and air pressure (909.72±3.77 mbar) were obtained in August, December and November, respectively. These results for the selected pollutants are consistent with the pollutants in the studies carried out by Dogruparmak and Ozbay (2011) and Ulutas (2020). The difference between PM_{10}, $PM_{2.5}$, SO_2, NO, NO_2, NO_X, O_3, and CO measurements according to the seasons was found statistically significant (p = 0.001; p <0.01) and the difference between the level of pollutants according to the seasons was presented in Table 3. PM_{10} in autumn were higher than in winter, spring, and summer (p = 0.001; p <0.01), while the level of $PM_{2.5}$ in autumn is higher than that in winter, spring and summer (p = 0.006; p = 0.001; p = 0.001; p <0.01, respectively). The concentration of SO_2 in autumn is reported higher than that in spring and summer seasons (p = 0.004; p = 0.001; p <0.01, respectively). SO_2 measurements in the winter season are also higher than in the spring and summer seasons (p = 0.001; p <0.01). Moreover, the levels of NO, NO_X and NO_2 in winter are reported higher than in spring, summer and autumn seasons (p = 0.001; p <0.01). For O_3, The higher level was found in summer (p = 0.001; p <0.01), which may due to the activation of photochemical reaction with exist of high sunlight. In addition, as a result of the photochemical reaction, O_3 concentrations increase while NO_X concentrations decrease in summer. Moreover, depending on seasonal conditions, O_3 concentrations indirectly affect the CO level. O_3 acts as the photochemical precursor of hydroxyl radicals (OH) in the lower troposphere. The OH reaction is an effective mechanism for removing CO from the atmosphere. If there is sufficient NO presence, a significant amount of O_3 is produced as a result of the troposphere oxidation reactions of CO (Dogruparmak and Ozbay, 2011; Riga-Karandinos and Saitanis, 2005). Chandu and Dasari (2020) reported the highest level of $PM_{2.5}$ and PM_{10} in winter, while Bozkurt et al. (2018) found that the highest NO_2 and SO_2 levels were observed in the winter due to changes in some meteorological conditions and pollutant sources, such as the increased use of fossil fuels for heating, as well as the high traffic density. According to the Regulation of Air Quality Assessment and Management (RAQAM, 2008) and European Union (EU, 2008) daily and annual limit values for PM_{10} is 50 and 40 μg/m^3 respectively. In addition, daily limit values cannot be exceeded more than 35 times in any calendar year. The annual average concentration (50.1±29.77 μg/m^3) is determined above the limit. In addition, the daily limit value has been exceeded 127 times. The annual average concentration of $PM_{2.5}$ in this study is 21.3±11.96 μg/m^3. however, there is no limit value for PM2.5 pm3 in RAQAM. The limit value (35 μg/m^3) set by the US EPA (2012) for 24 hours was exceeded 32 times. The annual SO2 concentration was determined as 5.94±3.63 μg/m^3. According to RAQAM (2008) and EU (2008) hourly and daily limit values for SO_2 are 350 and 125 μg/m^3 respectively and these values were not exceeded. The annual average NO, NO_2 and NO_X concentrations were determined as 45.29±56.9, 38.37±22.16, 83.67±74.13 μg/m^3, respectively. Hourly and annual limit values of NO_2 are set as 200 and 40 μg/m^3 for the protection of human health by RAQAM (2008) and EU (2008). According to the results, the hourly limit value was exceeded 170 times, but the annual limit value was not exceeded. The annual limit value of NO_X is set at 30 μg/m^3 for the protection of vegetation. However, it is seen that this value was exceeded. The annual average concentrations of O_3 and CO are 21.84±18.69 and 1074.58±714.12 μg/m^3 respectively. The limit values of O_3 and CO are set as 120 and 10.000 μg/m^3 for 8 hours by RAQAM (2008) and EU (2008) and both parameters have not exceeded these limit values.

Table 2. Monthly and seasonal distribution of pollutant concentrations and meteorological data for 2019

Months Seasons		Concentration (μg/m³)								Meteorological parameters		
		PM_{10}	$PM_{2.5}$	SO_2	NO	NO_2	NO_x	O_3	CO	AT(°C)	RH(%)	AP(mbar)
January	Mean	40.75	20.27	7.18	83.37	74.58	157.95	8.89	982.69	5.92	78.25	902.19
	SD	14.82	10.14	3.48	27.32	14.08	40.36	3.00	332.42	2.42	8.00	6.27
February	Mean	46.49	16.50	11.31	88.59	76.14	164.73	5.27	1027.33	7.40	68.66	907.62
	SD	17.35	5.63	4.39	27.06	12.64	38.32	1.75	295.81	1.53	9.61	4.47
March	Mean	38.04	14.79	5.60	27.88	26.83	54.71	4.44	836.19	10.17	53.25	905.51
	SD	13.72	3.07	2.93	23.35	19.61	42.71	1.52	256.32	2.59	11.93	5.35
April	Mean	43.34	16.75	5.05	17.42	21.86	39.28	5.13	689.63	13.70	53.61	904.87
	SD	20.65	6.89	3.86	4.56	4.56	7.59	1.15	180.39	3.83	12.61	4.90
May	Mean	56.28	22.64	5.89	14.13	42.82	56.95	3.92	510.55	20.71	49.55	904.43
	SD	43.75	6.88	4.02	4.50	6.18	9.40	0.87	136.41	4.41	11.35	3.55
June	Mean	25.44	20.59	3.13	11.56	43.20	54.76	19.71	719.76	25.12	53.04	904.12
	SD	18.24	4.96	0.91	2.91	8.85	10.33	12.53	226.02	2.77	9.64	2.30
July	Mean	38.96	17.86	3.55	12.69	34.94	47.63	48.00	715.67	26.18	41.66	902.65
	SD	9.63	4.76	1.35	2.51	8.29	8.98	10.06	170.42	2.82	11.09	3.71
August	Mean	37.03	15.13	3.59	14.11	19.04	33.15	41.40	757.68	27.04	41.31	904.74
	SD	10.31	5.23	1.32	3.91	6.13	8.15	15.10	262.94	2.64	11.39	3.06
September	Mean	46.61	15.48	4.41	20.71	19.14	39.85	39.49	994.66	22.76	40.46	906.48
	SD	17.20	6.62	2.79	9.93	3.86	13.32	7.18	467.65	3.13	6.54	2.74
October	Mean	67.76	26.23	8.53	34.56	21.44	56.00	22.67	1533.65	18.16	52.29	908.92
	SD	19.53	7.09	3.18	12.74	3.40	15.87	11.07	531.69	2.30	10.34	3.90
November	Mean	87.99	36.15	7.76	85.90	39.02	124.92	6.40	2102.83	12.12	62.09	909.72
	SD	29.02	12.13	1.98	62.30	22.98	84.35	2.66	628.05	2.57	11.23	3.77
December	Mean	73.08	33.30	5.64	149.48	57.57	207.05	7.91	1980.19	6.53	81.46	906.99
	SD	46.97	26.11	2.10	98.90	20.18	117.65	5.41	1332.13	2.37	8.62	8.54
Winter	Mean	53.67	23.19	7.94	112.16	67.99	180.14	7.90	1340.16	6.65	76.37	905.54
	SD	33.39	17.64	4.13	73.37	18.57	83.77	4.35	938.05	2.19	10.18	7.06
Spring	Mean	45.92	18.11	5.52	18.63	31.16	49.79	4.48	678.68	14.79	52.18	904.95
	SD	29.81	6.74	3.60	12.99	14.16	23.20	1.27	237.24	5.69	11.99	4.65
Summer	Mean	33.84	17.76	3.43	12.80	32.27	45.07	37.72	731.86	26.26	44.23	903.81
	SD	14.43	5.44	1.22	3.30	12.71	12.81	17.14	223.42	2.81	11.84	3.27
Autumn	Mean	67.23	25.95	6.92	46.49	26.34	72.82	22.89	1543.60	17.74	51.51	908.36
	SD	27.82	12.27	3.22	45.69	15.91	61.08	16.26	704.65	5.09	12.94	3.74
Annual	Mean	50.1	21.3	5.94	45.29	38.37	83.67	21.84	1074.58	16.33	56.41	905.72
	SD	29.77	11.96	3.63	56.9	22.16	74.13	18.69	714.12	8.06	16.88	5.2

AT: Air Temperature, RH: Relative Humidity, AP: Air Pressure, SD: Standard Deviation

Table 3. Evaluation of concentrations of pollutants according to the seasons

Conc. (μg/m³)		Winter¹	Spring²	Summer³	Autumun⁴	ᵃp	Post Hoc; ᵇp
PM_{10}	Min-Max	16.6-194.6	3.1-231.4	1.9-72.6	17.1-135.7	0.001**	4 > 1. 2. 3 1. 2> 3
	(Median)	(46.5)	(42.4)	(38.5)	(67.1)		
	Mean±SD	53.67±33.39	45.92±29.81	33.84±14.43	67.23±27.82		
$PM_{2.5}$	Min-Max	4.9-102.2	5.5-39.7	6.3-33.3	4.2-59.5	0.001**	4 > 1. 2. 3
	(Median)	(17.5)	(16.8)	(17.9)	(25.8)		
	Mean±SD	23.19±17.64	18.11±6.74	17.76±5.44	25.95±12.27		
SO_2	Min-Max	2-24.5	1.5-19.5	1.6-8.9	1.8-18.4	0.001**	1. 4 > 2. 3 2 > 3
	(Median)	(6.7)	(4.4)	(3.1)	(6.9)		
	Mean±SD	7.94±4.13	5.52±3.60	3.43±1.22	6.92±3.22		
NO	Min-Max	22.8-461.8	6-103.6	6.7-22.5	10-214.1	0.001**	1 > 2. 3. 4 4 > 2. 3 2 > 3
	(Median)	(95.4)	(15.8)	(12.5)	(34.7)		
	Mean±SD	112.16±73.37	18.63±12.99	12.80±3.30	46.49±45.69		
NO_2	Min-Max	32.6-137.4	13.2-82.9	10.1-82.2	12.4-80.9	0.001**	1 > 2. 3. 4 3 > 4
	(Median)	(66.4)	(23.8)	(33.2)	(21.8)		
	Mean±SD	67.99±18.57	31.16±14.16	32.27±12.71	26.34±15.91		
NO_x	Min-Max	66.8-599.3	23.1-186.5	17.1-96.4	23.2-287.4	0.001**	1 > 2. 3. 4 4 > 3
	(Median)	(162.3)	(46.4)	(44.7)	(57.3)		
	Mean±SD	180.14±83.77	49.79±23.20	45.07±12.81	72.82±61.08		
O_3	Min-Max	2.4-25.4	2.4-7	5.6-73.7	2.7-58.8	0.001**	3 > 1. 2. 4
	(Median)	(6.5)	(4.2)	(38.7)	(20.7)		
	Mean±SD	7.90±4.35	4.48±1.27	37.72±17.14	22.89±16.26		
CO	Min-Max	316.5-5903.8	283.8-1343.8	236.9-1365.6	398.2-3715.9	0.001**	
	(Median)	(1122.7)	(636.3)	(740.1)	(1582.5)		
	Mean±SD	1340.16±938.05	678.68±237.24	731.86±223.42	1543.60±704.65		

ᵃKruskal Wallis Test; ᵇBonferroni Dunn Test; **p<0,01

The Correlation Between Selected Air Quality Parameters

The scope and nature of the relationship between O_3, NO_X, CO and $PM_{2.5}$ variables were measured with the correlation method (Chandu and Dasari 2020). Table 4 presents the correlation between selected air quality parameters annually. A strong positive correlation was reported between PM_{10} and both $PM_{2.5}$ and CO, and between NO and CO and NO_X. The strong positive correlation between these parameters may attribute to the same source of these parameters. The negative correlation was reported between O_3 and all other parameters. Since the PM may be various sizes and shapes depending on its source, a correlation may be observed between them if the source is the same. Therefore, in this study, it is an expected result to see a correlation between PM_{10} and $PM_{2.5}$, as natural process, such as re-suspension of local soil, and primary and secondary anthropogenic combustion products resulted from traffic affect their concentration. In addition, there may be a strong correlation between NOX and NO, since there is a conversion between NOX and NO as a result of photochemical reaction in summer, especially in sunny and stable weather conditions. As stated in US EPA and previous studies, one of the most important emission sources of PM, SO_2, CO and NOX pollutants is cars, trucks and buses, off-road equipment and other vehicles s using fossil fuels (US EPA 2020a). Therefore, a strong correlation may be seen between these pollutants. Pollutants except O_3 are directly associated with traffic pollution. Tropospheric O_3 is known as a secondary pollutant due to the increasing of ozone formation by other pollutants in the atmosphere (Mohan et al., 2019). Combustion of fossil fuels, vehicle exhausts and industry cause emission of NOX, CO, SO_2 and VOCs as a primary air pollutant. The photochemical reaction reacts with the primary pollutants such as SO_2 and NOx in the environment and provides the formation of secondary pollutants such as O_3. The photochemical reaction causes a decrease in the concentration of primary pollutants in the environment while increasing the O_3 concentration (Jenkin and Clemitshaw 2000; Rani et al., 2011). In the troposphere O_3 is formed or its concentration increases at the end of photochemical reactions (Bozkurt et al., 2018). The concentration of NO_X and intensity of solar radiation extremely affect the formation and concentration of O_3 (US EPA 2020a; Bozkurt et al., 2018; Mohan et al., 2019). As a result, the highest levels of ozone pollution occur during periods of sunny weather (WHO, 2000). Therefore, a negative correlation was observed between O_3 and other pollutants as expected.

The Correlation Between Selected Air Quality Parameters

The variations of air temperature, relative humidity, and atmospheric pressure and their influences on pollutant concentrations of in the ambient air were analyzed using Spearman correlation annually. There was no statistically significant correlation between air temperature and PM_{10} and $PM_{2.5}$ ($p> 0.05$). SO_2, NO_2 and CO had weak and negative significant correlation with temperature ($r=-0.399$; $r=-0.384$; $r=-0.300$; $p<0.05$), while NO_X had moderate and negative significant correlation with temperature ($r=-0.538$; $p<0.05$). Temperature had a moderate significant correlation negatively with NOX and positively with O_3. Temperature had a good significant correlation with NO negative and with O_3 positive ($r=-0.693$; $r=0.752$; $p<0.05$). As with temperature, there was no statistically significant relationship between relative humidity and PM_{10} and $PM_{2.5}$ ($p> 0.05$). While there was a statistically positive, very weak / weakly significant relationship between relative humidity and SO_2, NO_2 and CO ($r=0.240$; $r=0.488$; $r=0.342$; $p<0.05$), there was a statistically positive and moderately significant relationship of relative humidity with NO and NO_X ($r=-0.611$; $p<0.05$). A negative, statistically significant and moderate correlation was found between relative humidity and O_3 ($r=-0.611$; $p <0.05$). There was no statistically significant correlation between air pressure and NO_X ($p> 0.05$). While a very weak / weak, positive significant relationship was found between pressure and PM_{10} and $PM_{2.5}$, SO_2, NO and CO ($r=0.342$; $r=0.219$; $r=0.280$; $r=0.213$; $p<0,05$), a negative, very weak statistically significant relationship was found between pressure and NO_2 and O_3 ($r=-0.177$; $r=-0.202$; $p<0.05$). The increase in temperature causes the evaporation that provides moisture to increase as well (Shaman and Kohn 2009). Since moisture has a direct effect on the felt temperature, it affects each other and causes the opposite effect to each other, as is the case with the results obtained on contaminants. The air is dry and calm under high pressure. Especially in big cities, if high pressure is effective for a long time, a dirty, foggy and misty air will be created. Therefore, the impact of pollutants on the environment will increase. This situation indicates that there will be an increase in the primary pollutant concentration during the periods when the pressure increases. As in this study, it is stated that the primary pollutant concentration increases with high pressure (Avdakovic et al., 2016).

Table 4. Annual correlation between selected air quality parameters

Parameters		PM_{10}	$PM_{2.5}$	SO_2	NO	NO_2	NO_X	O_3	CO
PM_{10}	r	1.000	0.759	0.525	0.492	0.153	0.420	-0.207	0.661
	p	-	0.001**	0.001**	0.001**	0.005**	0.001**	0.001**	0.001**
$PM_{2.5}$	r	-	1.000	0.430	0.367	0.293	0.462	-0.346	0.529
	p	-		0.001**	0.001**	0.001**	0.001**	0.001**	0.001**
SO_2	r	-	-	1.000	0.566	0.277	0.499	-0.417	0.521
	p	-	-	-	0.001**	0.001**	0.001**	0.001**	0.001**
NO	r	-	-	-	1.000	0.490	0.780	-0.528	0.769
	p	-	-	-	-	0.001**	0.001**	0.001**	0.001**
NO_2	r	-	-	-	-	1.000	0.875	-0.416	0.248
	p	-	-	-	-	-	0.001**	0.001**	0.001**
NO_X	r	-	-	-	-	-	1.000	-0.530	0.580
	p	-	-	-	-	-	-	0.001**	0.001**
O_3	r	-	-	-	-	-	-	1.000	-0.250
	p	-	-	-	-	-	-	-	0.001**
CO	r	-	-	-	-	-	-	-	1.000
	p	-	-	-	-	-	-	-	-

r: Spearman's corelation coefficient; *p<0.05; **p<0.01

Identification of Pollutant Sources and Correlations of Some Pollutants

CO/NO_X, SO_2/NO_X, and $PM_{2.5}/PM_{10}$ ratios can be used to determine the emission sources. The high CO/NO_X and low SO_2/NO_X ratios is related to mobile source of pollutants, while low CO/NO_X and high SO_2/NO_X ratios classified the point source. In addition, the $PM_{2.5}/PM_{10}$ ratio is used to describe anthropogenic (high ratio) or natural (low ratio) resources (Sari et al., 2019; Dogruparmak and Ozbay, 2011; Xu et al., 2017). Sari et al. (2019) used the ratios such as CO/NO_X, SO_2/NO_X, and $PM_{2.5}/PM_{10}$ to characterize the sources of emission. In the study, it was stated that the CO/NO_X ratio obtained in the winter and autumn seasons in 2016 and 2017 was low due to the effect of anthropogenic sources. While SO_2/NO_X ratio (0.09 and 0.16) indicates that mobile resources are effective, the increase in $PM_{2.5}/PM_{10}$ ratio was affected by very high combustion sources in winter and industrial activities in summer (Sari et al., 2019). The pollutant ratios are presented in Table 5. A statistically significant difference was found between the seasonal CO/NO_X measurements ($p = 0.001$; $p < 0.01$). As a result of the paired comparisons; CO/NO_X measurements in autumn season are higher than in winter, spring and summer seasons ($p = 0.001$; $p < 0.01$). CO/NO_X measurements in summer and spring are also higher than in winter ($p = 0.001$; $p < 0.01$). No statistically significant difference was found between the CO/NO_X measurements of summer and spring seasons ($p > 0.05$). A statistically significant difference was found between SO_2/NO_X measurements according to the seasons ($p = 0.001$; $p < 0.01$). Moreover, SO_2/NO_X measurements in autumn season are higher than in winter and summer seasons ($p = 0.001$; $p < 0.01$). SO_2/NO_X measurements in the spring season are also higher than in the winter and summer seasons ($p = 0.001$; $p = 0.025$; $p < 0.05$, respectively). SO_2/NO_X measurements in summer are also higher than in winter ($p = 0.001$; $p < 0.01$). No statistically significant difference was found between SO_2/NO_X measurements of autumn and spring seasons ($p > 0.05$). A statistically significant difference was found between $PM_{2.5}/PM_{10}$ measurements according to the seasons ($p = 0.001$; $p < 0.01$). As a result of pollutant ratios; $PM_{2.5}/PM_{10}$ measurements in summer are higher than in winter, spring and autumn seasons ($p = 0.032$; $p = 0.010$; $p = 0.001$; $p < 0.05$, respectively). No statistically significant difference was found between $PM_{2.5}/PM_{10}$ measurements of other seasons ($p > 0.05$). In this study the lowest and the highest ratios of CO/NO_X and SO_2/NO_X were determined in winter (the low ratio in winter indicates anthropogenic sources) and autumn seasons, respectively while $PM_{2.5}/PM_{10}$ ratio was the highest level in summer season. According to these results, it can be thought that mobile-borne anthropogenic pollutants are effective in this study area.

Table 5. Evaluation of CO/NO_X, SO_2/NO_X, $PM_{2.5}/PM_{10}$ ratios according to the seasons

Seasons	**Statistics**	**CO/NO_x**	**SO_2/NO_X**	**$PM_{2.5}/PM_{10}$**
Winter	Min-Max (Median)	4.7-12.8 (6.7)	0.01-0.11 (0.04)	0.2-0.8 (0.4)
	Mean±SD	7.28±1.98	0.04±0.02	0.44±0.15
Spring	Min-Max (Median)	4.1-22.6 (14.6)	0.02-0.43 (0.1)	0.1-9.5 (0.4)
	Mean±SD	13.90±5.25	0.12±0.08	0.51±0.97
Summer	Min-Max (Median)	5.7-31.7 (16.1)	0.03-0.26 (0.07)	0.2-14 (0.5)
	Mean±SD	17.16±5.82	0.08±0.04	1.38±2.83
Autumn	Min-Max (Median)	7.9-44.8 (25.8)	0.02-0.36 (0.11)	0.2-1 (0.4)
	Mean±SD	24.93±7.62	0.12±0.06	0.10
	[a]p	0.001**	0.001**	0.001**
	Post Hoc; [b]p	4 > 1, 2, 3 2, 3 > 1	2, 4 > 1, 3 3 > 1	3 > 1, 2, 4

*[a]Kruskal Wallis Test; [b]Bonferroni Dunn Test; **p<0.01*

4. Conclusion

The measurements of PM_{10}, $PM_{2.5}$, SO_2, NO, NO_2, NO_X, O_3 and CO pollutants and meteorological parameters (air temperature, relative humidity and air pressure) were carried out in Ankara during the year 2019. The annual average concentrations were 50.15, 21.31, 5.97, 46.7,39.715, 86.42, 17.77, 12 and 1070.91 μg/m^3, respectively. All data were collected hourly and determined the concentration of all parameters at each hour to see the fluctuation so that when the pollution peaked, it was observed. The pollutant concentrations (excluding O_3) started to rise in the morning and evening hours when the traffic was at its peak and was the highest level between 10:00 -14:00 and 22:00-02:00. It was seen at the lowest values during daylight hours. In addition, the lowering of the boundary layer can be shown as the reason for the concentration increase in the evening, especially after 19:00. On the contrary, the ozone concentration started to increase after 10:00 and was observed at the highest level between 12:00-14:00, when the sunlight was at its peak. The increase in ozone concentration, which is a type of secondary pollutant, can be clearly explained by a photochemical reaction. The selected parameters was distributed seasonally and the highest level of PM_{10}, $PM_{2.5}$ and CO was reported in autumn, the highest level of SO_2, NO, NO_2 and NO_X was reported in winter, while O_3 was reported in summer. In this study the lowest and the highest ratios of CO/NOX and SO_2/NOX were determined in winter (the low ratio in winter indicates anthropogenic sources) and autumn seasons, respectively while $PM_{2.5}/PM_{10}$ ratio was the highest level in summer season. According to these results, it can be thought that mobile-borne anthropogenic pollutants are effective in this study area. A strong positive correlation was reported between PM_{10} and both $PM_{2.5}$ and CO, and between NO and both CO and NO_X. The strong correlation between these pollutants indicates that they can be affected by the same pollution source. The correlation method was applied to evaluate the relationship between selected air pollutants and meteorological factors. There was statistically significant correlation between air temperature and humidity with air pollutants except PM_{10} and $PM_{2.5}$ as well as pressure with air pollutants except NO. The paired comparisons for the selected air quality parameters during the different seasons was investigated. A statistically significant difference was found between the seasonal CO/NOx measurements ($p = 0.001$; $p < 0.01$). Although the relation between air pollutants and metrological parameters based on seasonal variation provide a significant difference. The statistical relationship between air quality parameters on a monthly, daily, and hourly basis in future work will provide more understanding about the behavior of air pollutants which will be useful for direct and immediate evaluation and action.

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Conflict of Interest

No conflict of interest was declared by the authors.

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