ANALYSIS OF SURFACE OZONE IN ISTANBUL BY USING CLUSTER ANALYSIS AND HYSPLIT MODEL

by

MELTEM GÜLER

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ABSTRACT

Istanbul is the largest and most populated city of Turkey and one of the biggest megacities in the world. In the framework of the TUBITAK-COST project 105Y005 and TUJJB-TUMEHAP project number 03-06, one urban (Göztepe which is nearby to major traffic), one sub-urban (Kandilli) an one rural (at the crest of Büyükada) stations have been established to investigate surface ozone concentration in Istanbul.

The objectives of this study is to examine the temporal variations, the weekday-weekend and seasonal variations of surface ozone concentrations and their relation with the meteorological parameters as well as to investigation the transport mechanism of surface ozone by using the HYSPLIT model and cluster analysis between 2008 and 2009. Surface ozone profiles were monitored particulary in the ozone season from April 1 to October 1 that is characterized by high ozone levels According to the behaviour of ozone concentration on a diurnal basis, surface ozone trends generally showed maximum concentrations in afternoon hours and minimum concentrations at rush hours due to NO_x titration by traffic emissions. Investigation of O_3 trends during weekdays and weekends demonstrates that weekend ozone concentrations were confirmed to be greater than those of weekdays during early mornings hours especially in Göztepe. Analysis of seasonal variations of surface ozone shows that the maximum surface ozone concentration were observed during summer and while minimum concentrations occured during the colder months. Surface ozone levels had positive correlations with wind speed and temperature. Based on the results of the HYSPLIT model and cluster analysis that were used to understand the transport mechanism of surface ozone, the dominant wind direction was from northwest. Transport to Istanbul was mainly from the Balkans, Europe and Black Sea.

ÖZET

İstanbul, Türkiye'nin en büyük ve kalabalık şehri olmakla beraber dünyadaki en büyük mega kentlerden biridir. 105Y005-TUBITAK COST ve TUJJB-TUMEHAP 03-06 projeleri çerçevesinde, şehir (Göztepe-yogun trafik etkisi altında), yarı-kırsal (Kandilli) ve kırsal alanda (Büyükada) ozon profilini izlemek amacıyla hava kirliliği ölçüm istasyonları kurulmuştur.

Bu çalışmanın amacı yüzey ozon değişimlerinin haftaiçi-haftasonu, mevsimsel olarak farklılıklarını kavramak ve ozon seviyelerindeki değişikliğin meteorolojik şartlar ile ilişkisini anlamak , HYSPLIT model ve kümeleme analizi kullanarak ozon taşınım mekanizmasının 2008 ve 2009 yıllarında incelenmesidir. Ozon seviyelerinin en yüksek olduğu ve "ozon mevsimi" olarak anılan 1 Nisan – 1 Ekim arası dönem öncelikli olmak üzere ozon profili incelenmiştir. Günlük bazda yüzey ozon davranışlarına göre, yüzey ozon trendleri öğleden sonra en yüksek seviyeye ulaştığı, en düşük değerler ise trafik emisyonlarının NO_x titrasyonları ile maksimum seviyeye ulaştığı saatlerde gözlemlendi. Haftaiçi- haftasonu yüzey ozon trendleri incelendiğinde, özellikle Göztepe'de haftasonu-haftaiçi ozon seviyeleri farklılıklarının özellikle sabahın erken saatlerde belirgin olduğu gözlemlenmiştir. Mevsimsel olarak ozon değişimleri inceleğinde, en yüksek konsantrasyonlar beklendiği gibi yaz mevsiminde, en düşük konsantrasyonlar ise kış mevsiminde gözlemlenmiştir. Bu çalışmada, yüzey ozon seviyeleri sıcaklık ve rüzgar hızı ile pozitif ilişki göstermektedir. Yüzey ozonun taşınım mekanizmasını anlamak amacıyla uygulanan HYSPLIT model ve kümeleme analizi sonuçlarına göre, taşınımda kuzey batı yönünün hakimdir ve Avrupa ve Balkanlar'dan gelmektedir.

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LIST OF SYMBOLS/ABBREVIATIONS

GDAS	Global Data Assimilation System
GURME	Gaw Urban Research Meteorology and Environment
HOD	High Ozone Day
HYSPLIT	Hybrid Single-Particle Langrangian Integrated Trajectory
KOERI	Kandilli Observatory and Earthquake Research Institute
LST	Local Sideral Time
WMO	World Meteorology Organization

1. INTRODUCTION

One of the major problems resulting from air pollution is caused by photochemical oxidants. Surface ozone is the most abundant photochemical oxidant in the atmosphere. Increasing surface ozone concentrations have received extensive attention around the world because of their impact on human health (Kley et al., 1999; Stedmand and Kent, 2007) and on the environment (Leeuw, 2000; Cape, 2008). Concerning human health effects, the most important targets of O_3 are on the respiratory system, such as cough, chest, soreness, difficulty in taking a deep breath. Ozone exposure of ecosystems and agricultural crops results in visible foliar injury and in reductions in crop yield and seed production. For vegetation, a long-term, growing season averaged exposure rather than an episodic exposure is generally of concern (Kley et al., 1999; Leeuw, 2000).

Meteorological influences, photochemical mechanisms and ozone precursors emissions can lead to an accumulation of ozone in the lower atmosphere. Surface ozone and related meteorological factors in urban areas have been extensively discussed in the literature (Dueñas et al., 2002; Elminir et al., 2005; Lin et al., 2007; Shan et al., 2009). These studies have analyzed the influences of meteorological parameters and proceses affecting ozone formation and accumulation at the surface. Recent studies have shown that rapid urbanization and transportation in urban areas and industry have caused serious air quality problems in urban areas in the last 30 years. WMO have began a new program on urban atmosphere by the GURME in order to handle meteorological and related aspects of urban pollution.

Surface ozone is the most abundant photochemical oxidant in the troposphere and is used as an indicator of pollution. O_3 is produced by combining an oxygen molecule with an oxygen atom that is provided from the photolysis of nitrogen dioxide (emitted by gasoline vapours, fossil fuel power plants, refineries and other industries) under favorable meteorological conditions. Furthermore, hydrocarbons (HCs) are oxidized to form carbon dioxide and water vapor by the hydroxyl radical, which is produced by the photolysis of O_3 in the presence of water vapor (Pryor, 1998). Increasing number of motor vehicles resulted in increase in emissions of ozone precursors (NO, NO_2, VOC_S, CO) into urban atmopshere under the intense solar radiation which led to high ozone concentrations in urban areas and downwind. Several studies have been reported high ozone levels in urban atmosphere in many cities in the world (Lu Wang et al., 2004; Mazzeo et al., 2005; Teixeira et al., 2009). Furthermore, studies on ozone concentrations in remote areas and unpolluted regions have been extensively discussed in the literature (Nolle et al., 2002; Pires et al., 2008). Surface ozone levels in rural areas as well as mountains have attracted much interest in order to understand the source of ozone and its precursors emission (Debaje et al., 2003; Garcia et al.,2005; Carvalho et al., 2010).

While surface ozone chemistry and the related meteorology have been widely studied around the world, there are only a limited number of reports about the behaviour of surface ozone in Istanbul. Topcu and Incecik (2002) analyzed the preliminary outcomes of the surface ozone measurements in urban area of Istanbul. Furthermore, Topcu et al. (2003) studied the relationships of high ozone concentrations between chemical and meteorological characteristics using the Meteorological Systems Applications International Mesoscale Model (SAIMM) and found that high ozone levels ordinarily observed during low-wind conditions. Topcu et al. (2005) also found that high O_3 episodes were characterized by southwesterly and west–southwest winds. Im et al. (2006) studied the relation of photochemical pollutants with meteorological factors for high ozone days that indicated high concentrations of O_3 can be experienced both during afternoon hours and in the late night due to sharp decreases in mixing heights. Im et al. (2008) studied the interaction patterns of major photochemical pollutant and showed that high levels of surface ozone are observed mostly under relatively anticyclonic conditions with considerably low-wind speeds. High ozone days show a typical diurnal profile with maximum concentrations appearing during afternoon hours and minimum concentrations appearing during rush hours due to NO_x titration from traffic emissions.

In order to control the ozone concentrations, the air quality framework Directive (96/62/EC) and the Final Air Quality Daughter Directive (1999/30/EC) set out limit values for ozone in ambient air of Europe which were due to be met in 2005. According to the EU directive, the threshold value set for protection of vegetation peak ozone concentration in 24 hour is 32.5 ppb (92/72/EEC). Also**,** the population information threshold of 1 hour means the ozone concentration value is 90 ppb while the population warning threshold of 1 hour mean is 120 ppb.

Monitoring studies are of particular importance in order to detect air quality trends, and observe the effectiveness of air quality control regulations. The ozone measurement in Istanbul started in 1998 at the both sides of the (European and Asian) city. Currently, ozone measurements are being conducted in three stations (Aksaray, Alibeykoy and Kadıköy) operated by the Republic of Turkey Ministry of Environment and Forest. However, these are frequently limited to measurements obtained during sampling sites or over a limited period of time. The contiuonus measurements of surface ozone concentrations in Istanbul at three different locations (an urban/traffic area; a semi-urban area; a rural area) was supported by TUBITAK-COST project 105Y005 and by TUJJB-TUMEHAP project 03-06.

In this study, surfce O_3 has been measured at three different stations (Princess' Island or that is called Büyükada, Kandili and Göztepe) on the Asian side of Istanbul. Surface ozone data were selected specifically for high ozone days in ozone season, which met the criteria that at least one hourly ozone concentration equal to or greater than 50 ppb for all stations. The objectives of this study are:

1) To understand the characteristics of ozone and its precursors at three different locations (one rural, one semi-urban, and one urban/traffic site)
2) To examine the characteristics of hourly, diurnal, monthly and sesonal, and ozone levels and to understand high ozone days (HODs) characteristics under different meteorological conditions.
3) To analyze the transport patterns of surface ozone by performing back trajectory analysis (HYSPLIT) and cluster analysis.

2. SITES AND INSTRUMENTATION

2.1.Monitoring Sites

Istanbul is the largest city in Turkey, located at a latitude and longitude of appoximately 40^o 58´ N and 28^o 50´ E, respectively. Istanbul is the second largest metropolitan area in Europe, the 21st largest megacity in the world and one of the top energy consuming cities with a population of 13 million (Turkey Statistical Institute, 2008) within an area of about 5300 km^2. Istanbul is surrounded by Kocaeli to the east, Tekirdağ to the west, Sea of Marmara to the south and the Black Sea to the north. The Bosporus strait, which strecthes from the Black Sea to the Marmara Sea, divides the city into two parts the European Anatolian or Asian parts. The Black Sea to the north and Marmara Sea to the south produce a differential heating of surfaces, leading to different meteorological conditions that may play a role in the transport of O_3. The complex terrain of Istanbul also impact the circulation systems over the city. Meteorology in the region is mainly affected by hot, dry low pressure systems from the Persian located the southeast of Turkey in summer months. The system can be called a “relatively” high-pressure system. During the evening and night, wind shifts to the northerly, northeasterly direction, and this situation lead to the transport of pollutants to the south and southwest (Im et al., 2006). The city experiences a transition climate between Mediterranean and temperate conditions. Strong inversion conditions in the summer causes O_3 levels to reach peak value in the late afternoon (Topcu and Incecik, 2002).

Within the last 40 years, the city has experienced a fast growth in urbanization and industrialization. According to the 2009 statistics, there are 2.7 million automobiles registered in Istanbul. The number of new cars are drastically on the rise which triggered the use of LPG that has been widely used by the taxis from the beginning of 1998. (Ministry of State Institute of Statistics, 2009). Through emissions from the transport sector, a big amount of ozone precursors are emitted to the atmosphere. Traffic rush hours obviously behave as a sink for ozone through the emissions of NO_x (Im et al., 2006).

Table 2.1. Lists the location and period of ozone measurement used in this study.

Station	Location (Lat/Lon)	Site Classification	Monitoring Period
Goztepe	40.990 N, 29.070 E	Urban/Traffic area	July 2007- January 2010
Kandilli	41.060 N, 29.060 E	Semi rural area	September 2007-January 2010
Büyükada	40.510 N, 29.070 E	Rural area	January 2008- January 2010

In this study, surface ozone measurements have been monitored at three different locations (Table 2.1.). Göztepe is a district of Kadıköy, which is a large, populous, and cosmopolitan district of Istanbul. The population of Kadıköy district, according to the 2007 census, is 509.282. The centre of Kadıköy today is the transportation hub for people commuting between the Asian side of the city and the European side across the Bosphorus. There is a large bus and minibus terminal next to the ferry docks. There is a lot of residential property in the centre of Kadıköy. Göztepe air quality station is located in the front of the highway in the garden of State Supply Office (see Appendix A). Hourly continious ozone measurements have been conducted since September, 2007. Due to the heavy traffic load, it would be possible to determine the effects of the nitrogen species on ozone.

The measurements at the Kandilli air quality station have been carried out on the campus of Bogazici University (see Appendix A). The Kandilli Campus is located on the Asian side of the Bosphorus (in Çengelköy) and hosts the Kandilli Observatory and Earthquake Research Institute. The site is located 41 ° 03 ' 48" N. which is located 125 m above sea level.

Büyükada is the largest of the nine islands of Princess' Island located in the Marmara Sea close to İstanbul. Büyükada has an area of 5,42 km^2 with the population of 7320 during winter season based on 2000 data. There is no traffic on the Islands, the only transport being horse and cart. Motorized vehicles except service vehicles are forbidden. Most of the houses are summer houses, therefore, population rises in the summer season. Büyükada has two hills, one of which is in the south (203 meter) and is called Yücetepe. The other one is in the north, with elevation 164 meters and is called Manastır Hill. The measurements of background NO_x and O_3 concentrations at the crest of the island at

Yucetepe started in January 9, 2008 (see Appendix A). The station was established through the TUUJB - TUMEHAP 03-06 project.

2.2.Measurement Techniques

The O_3 measurements at these three sites were made using standard commercial UV photometric O_3 analyzers (Thermo 49i). The same criteria for O_3 monitoring system, instrument calibration, and data handling have been conducted for all these three stations. Regular data checking and instrument maintenance were conducted every week or two weeks to assure the quality of the obtained data.

The analyzer operates based on the principle that ozone (O_3) molecules absorb UV light at a wavelenght of 254 nm. The sample drawn into the UV Photometric O_3 analyzer through the sample bulkhead is split into two gas streams. One gas flows through an ozone scrubber to become the reference gas. The reference gas then flows to the reference solenoid valve. The sample gas flows directly to the sample solenoid valve. The solenoid valves alternate the reference and sample gas streams between cells A and B every 10 seconds. When cell A contains reference gas, cell B contains sample gas and vice versa.

The UV light intensities of each cell are measured by detectors A and B. When the solenoid valves switch the reference and sample gas streams to opposite cells, the light intensities are ignored for several seconds to allow the cells to be flushed. The UV photometric O_3 analyzer calculates the ozone concentration for each cell and outputs the average concentration to the front panel display, the analog outputs, and also makes the data available over the serial or ethernet connection (Thermo Electron Cooperation,2005).

3. OZONE IN THE ATMOSPHERE

3.1. Production of Surface Ozone

Ozone is a reactive oxidant gas produced naturally in trace amounts in the Earth's atmosphere. Stratospheric ozone is vital for screening of solar ultraviolet radiation while elevated ozone concentrations at ground level can lead to environmental and health problems. The dual role of ozone in the atmosphere leads to the dubbing of stratospheric ozone as "good" ozone. Surface ozone, the most well-known secondary air pollutant (often called "bad ozone") is produced from photochemical reactions involving its precursors such as oxides of nitrogen (NO_x), carbon monoxide (CO), and volatile organic compounds (VOCs) (Pandis, 1997). Surface ozone is formed by reactions of CO, CH_4, and non-methane volatile organic compounds (NMVOC) in the presence of nitrogen oxides and destroyed by the reactions with HO_x radicals. The most important reaction in ozone production in the atmosphere (Figure 3.1) occurs between atomic oxygen and molecular oxygen (Finlayson-Pitts and Pitts, 1997):

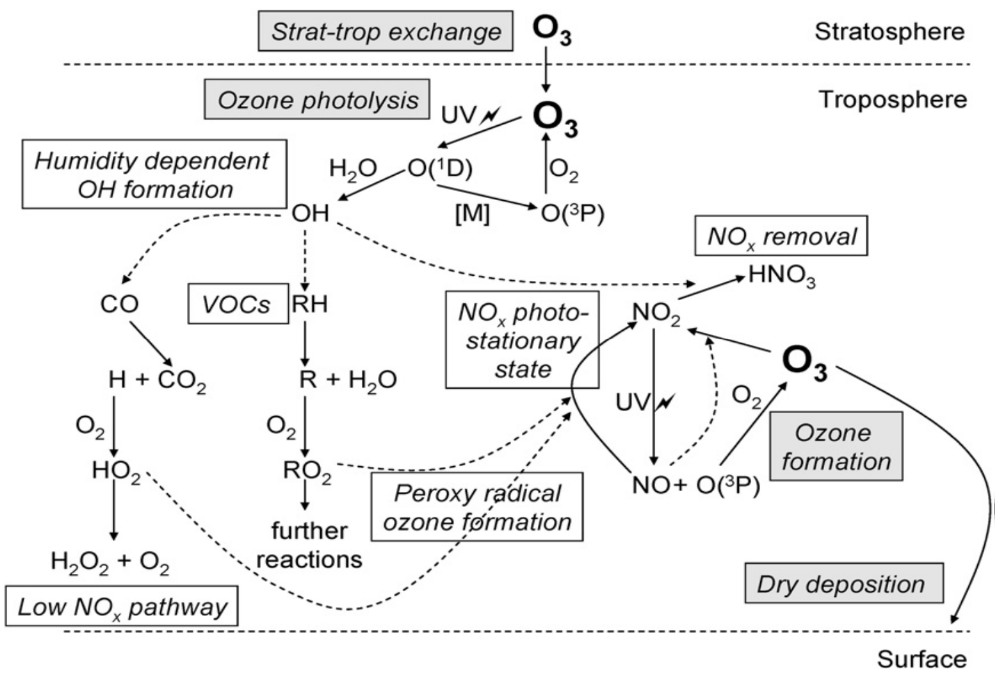

Figure 3.1. Schematic diagram of the major sources and sinks of ozone in the troposphere, showing the key chemical reactions involved.

$$O + O_2 + M \rightarrow O_3 + M \quad (3.1)$$

where M is a third element, such as e.g., N_2 or O_2 or another third molecule which absorbs the excess energy and stabilizes the O_3. Oxygen atoms are produced by photolysis of molecular oxygen by absorption of deep ultraviolet radiation at high altitudes (above 20 km). At lower altitudes, where radiation is longer than 280 nm, the only source of atomic oxygen is the NO_2 photolysis.

$$NO_2 + hv \rightarrow NO + O \quad (3.2)$$

In the presence of NO, O_3 reacts with NO to reproduce NO_2 which is a way of removing ozone through its reaction with nitrogen oxide:

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (3.3)$$

The three main reactions given above occur rapidly and NO, NO_2 and O_3 coexist in an equilibrium (the NO_x photostationary state, Figure 3.1) in the absence of other reactions. However, these reactions do not only accelerate ozone formation in polluted areas.

A reaction that converts NO in NO_2 without consuming an ozone molecule could make ozone collect. This reaction occurs in the presence of hydrocarbons. Peroxy radicals (RO_2*, where R is an alkyl group) produced during the oxidation of hydrocarbon molecules react with NO to form NO_2, resulting in elevated surface ozone production. The ozone formation rate is associated with the production rate of RO_2*. Peroxy organic radicals (RO_2*) are formed by the attack of a hydroxyl radical (OH) on hydrocarbons. The chemical structure of hydrocarbons determines the number and form of peroxy radicals and, therefore, the number of NO to NO_2 conversions occurring while hydrocarbons are oxidized.

$$RO_2^* + NO \rightarrow NO_2 + RO^* \quad (3.4)$$

$$NO_2 + hv \rightarrow NO + O \quad (3.5)$$

$$O + O_2 + M \rightarrow O_3 + M \quad (3.6)$$

Net Reaction: $RO_2^* + O_2 + hv \rightarrow RO^* + O_3$ (3.7)

The photolysis of aldehydes (RCHO) leads to the formation of radicals, which after a series of quick reactions form OH.

$RCHO + hv \rightarrow R + CHO$ (3.8)

$HCO + O_2 \rightarrow HO_2 + CO$ (3.9)

$HO_2 + NO \rightarrow NO_2 + OH$ (3.10)

In the absence of CO or organic compounds, do not produce O_3. In the presence of CO, organic compounds and carbonly compounds (CARB), the reactions involved are:

$CO + OH\ (+O_2) \rightarrow CO_2 + HO_2$ (3.11)

$RH + OH \rightarrow R + H_2O$ (3.12)

$R + O_2 + (M) \rightarrow RO_2 + (M)$ (3.13)

$RO_2 + NO \rightarrow RO + NO_2$ (3.14)

$RO + O_2 \rightarrow HO_2 + CARB$ (3.15)

$HO_2 + NO \rightarrow OH + NO_2$ (3.16)

$NO_2 + hv \rightarrow NO + O$ (3.17)

$O + O_2 + (M) \rightarrow O_3 + (M)$ (3.18)

Net Reaction: $RH + 4O_2 + 2hv \rightarrow RCHO + H_2O + 2O_3$ (3.19)

The photolysis of ozone leads to the formation of oxygen atoms $O(^1D)$, which react with water vapor to form hydroxyl radicals. The destruction of ozone is accomplished by chemical and photochemical degradation, by the oxidative cycle of CO and CH_4, and by dry deposition on the soil (Ferraz, 2006). The overall loss at the earth's surface approximately balances the transfer into the troposphere from the stratosphere (Cape, 2008).The main reactions are the following:

$$O_3 + hv \rightarrow O(^1D) + O_2 \quad (3.20)$$

$$O(^1D) + H_2O \rightarrow 2OH \quad (3.21)$$

$$HO_2 + O_3 \rightarrow OH + 2O_2 \quad (3.22)$$

$$OH + O_3 \rightarrow HO_2 + O_2 \quad (3.23)$$

$$CO + CH_4 + O_3 + hv \rightarrow CO_2 + CH_3OOH \quad (3.24)$$

An important source of OH radicals is nitrous acid (HONO). In polluted urban atmosphere its level reach 1–10 ppb, with highest levels occurring just before sunrise. In sunlight, HONO has a photolysis life of roughly 15 min and its photolysis produces a source of OH in the early morning.

$$HONO + hv \rightarrow OH^{\cdot} + NO \quad (3.25)$$

The OH scavenging process occurs with the reaction with NO to form nitric acid in its gaseous form. The ozone formation and other secondary species is not instantaneous. The elevated ozone level in areas far from the emitting source results from the interaction of transport, turbulent mixing and chemical reactions occurring simultaneously (NO_x removal in Figure 3.1).

$$OH + NO_2 + M \rightarrow HNO_3 + M \quad (3.26)$$

Reactions such as NO_2 with HO_2 and RO_2 radicals and reactions among radicals themselves may also be of importance as “indirect ozone destroyers” since they withdraw radicals from the photochemical reaction system which leads to ozone formation.

Ultimately, the budget of ozone in a given region is governed by transport of ozone into or out of the region and the net rate of ozone formation, that is the difference between ozone production and destruction. From the reactions given it is obvious that the rate of O_3 production depends on the availability of NO_x. In some parts of the troposphere the concentration of NO_x is so small that the ozone destruction exceeds the ozone production. (Guicherit and Romer, 2000).

4. RESULTS and DISCUSSION

4.1. Temporal Variations of Ozone Level

4.1.1. Time Series of Surface Ozone

The temporal and spatial variations of surface ozone concentrations in an urban (Göztepe), a sub-urban (Kandilli) and a background area (Büyükada) were evaluated to understand the ozone pollution potential in Istanbul. The hourly average ozone concentrations as a function of time at the Göztepe air quality station are shown in Figure 4.1. The hourly average O_3 and NO_x levels for Göztepe Station between July 20, 2007 and 31 December, 2009 are presented in Figures 4.1 and 4.2. As shown in these figures, high ozone levels (defined as daily maximum ozone concentration greather than and equal to 50 ppb) were observed in ozone seasons (the period from April 1 to September 31, a total of 364 days) of 2008 and 2009. The mean ozone concentrations during ozone season (2008-2009) are calculated to be 14.28 and 17.26 ppb, respectively.

The statistical results of observed high ozone days (Table 4.1) are presented for all stations during the ozone seasons of 2008 and 2009. There are only four hours in 2 day high ozone levels observed at Göztepe air quality station, with the maximum of 63.5 ppb at 1600 LST (Local Sideral Time) on June 19, 2008. The highest hourly average O_3 concentration is calculated to be 55.4 ppb at 1800 LST on July 19, 2009 at the Göztepe Station. At the same time, NO_x levels are recorded at 1600 LST are 23.2 ppb on June 2008 and of 1900 LST are 35.3 ppb on June 2009 respectively. The one-hour maximum O_3 concentration is exceeded 50 ppb 0.55% of the time at the Göztepe downtown site.

Table 4.1. Statistical results of observed high ozone days in Göztepe, Kandilli and Büyükada during 2008 and 2009 ozone season (1 April- 30 September).

Göztepe	April	May	June	July	August	September
Year	2008					
Episode Hours			3			
Episode Days			1			
Max / ppb			63.5			
Year	2009					
Episode Hours				1		
Episode Days				1		
Max/ ppb				55.4		
Kandilli	April	May	June	July	August	September
Year	2008					
Episode Hours	3	30	52	28	52	0
Episode Days	1	13	11	10	8	0
Max / ppb	56.3	64.8	79.4	57.5	59.1	0
Year	2009					
Episode Hours	17	8	13	5	0	0
Episode Days	6	2	5	2	0	0
Max/ ppb	55.8	78.8	59.3	56.6	0	0
Büyükada	April	May	June	July	August	September
Year	2008					
Episode Hours	43	63	78	55	60	8
Episode Days	9	10	13	12	16	1
Max / ppb	58.6	79.2	84.5	76.8	83.9	61.2
Year	2009					
Episode Hours	8	22	72	57	6	6
Episode Days	3	7	15	13	3	2
Max/ ppb	54	67.7	97.8	92.9	63.7	76

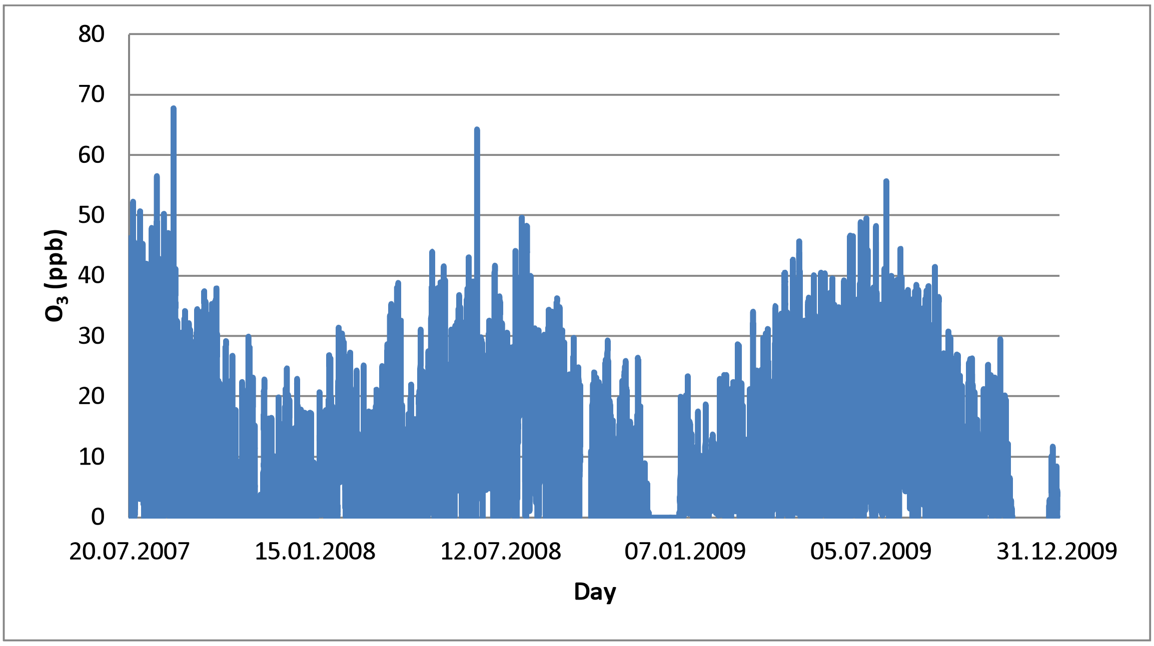

Figure 4.1. Hourly ozone concentration for Göztepe air quality station, from July 20, 2007 to December 31, 2009.

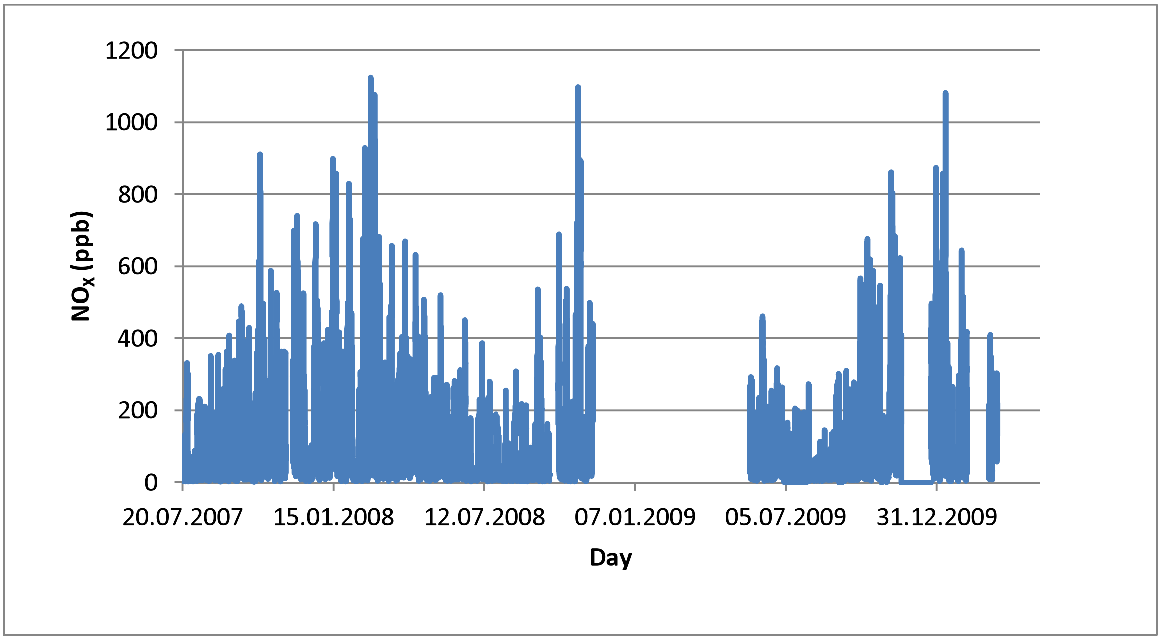

Figure 4.2. Hourly nitrogen concentrations (NO_x) for Göztepe air quality station, from July 20, 2007 to December 31, 2009.

Hourly average surface ozone concentrations at the Kandilli air quality station measured between September 7, 2007 and December 31, 2009 are presented in Figures 4.4 and 4.5. Regarding high ozone levels (above 50 pbb) on hourly basis, there are 208 hours in 58 days within 2 years in Kandilli air quality station with the maximum of 79.4 ppb at 1600 LST on June 19, 2008 and 78.8 ppb 1700 LST on June, 2009 respectively. The percentage of exceedances is calculated as %15.9 within 364 days (the period from April 1 2008 to September 30 2009).

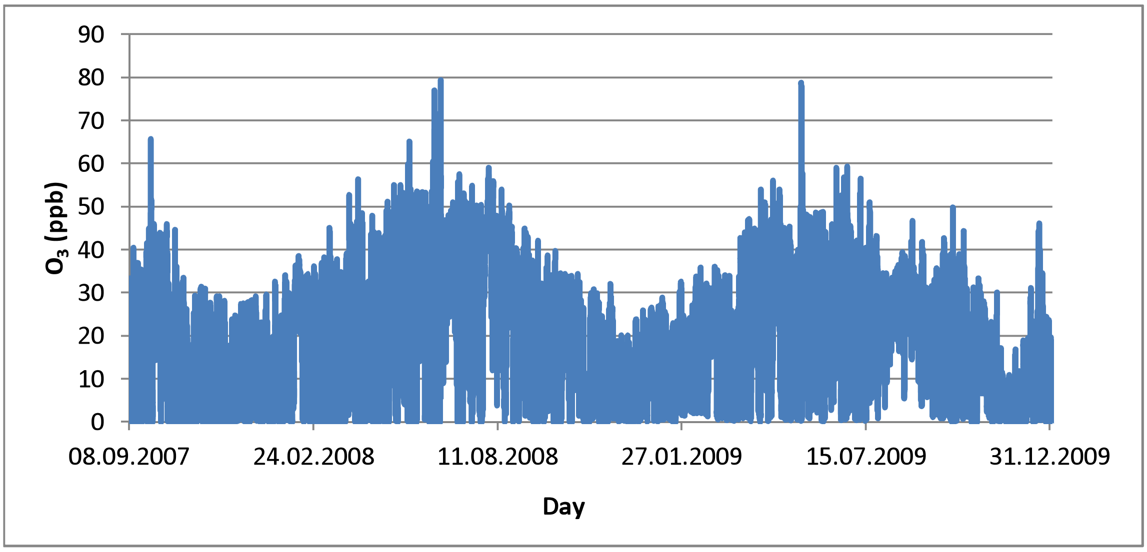

Figure 4.3. Hourly ozone concentrations for Kandilli air quality station, from September 7, 2007 to December 31, 2009.

Surface ozone and nitrogen oxides concentration from on January 9, 2008 to 31 December 2009 in Büyükada are presented in Figures 4.6 and 4.7. The total exceedances (above 50 ppb) between 2008 and 2009 is 478 hours in 104 days at Büyükada station (Table 4.1.). The maximum ozone levels are 84.5 ppb at 2100 LST on June 18, 2008. Further, the highest hourly average O_3 concentration at the Büyükada station is 97.8 ppb at 1900 LST on July 6, 2009 at the Büyükada station.

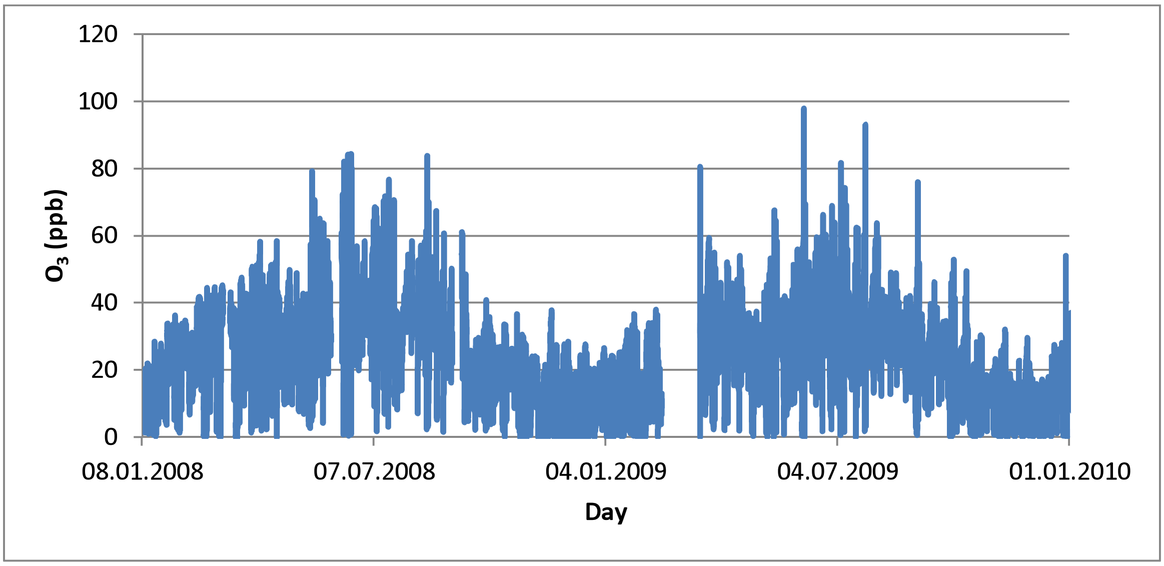

Figure 4.4. Hourly ozone concentration for Büyükada Air Quality Station, from January 9, 2008 to 31 December, 2009.

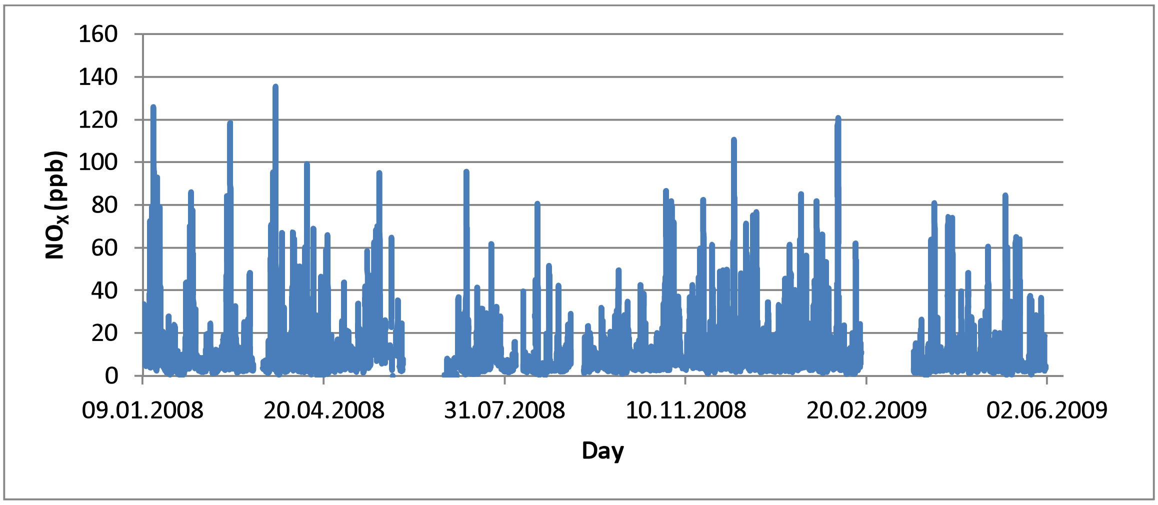

Figure 4.5. Hourly nitrogen oxides (NO_x) concentrations for Büyükada Air Quality Station, from January 9, 2008 to June 2, 2009.

In order to understand variations of surface ozone, the monthly average surface ozone levels are also analyzed. Comparison of the monthly surface ozone levels (Figure 4.6) indicates that ozone concentration start to increase slowly from March to August. In Göztepe and Kandilli station, the peak values are monitored in August with the value of 23 ppb and 31.3 ppb. Furthermore, the highest value at Büyükada (35.4 ppb) is reached in June and the ozone value starts to decrease and droppes to a minimum (11.7 ppb) in

December (Duenas, 2002). O_3 peaks during spring and summer are due to favorable temperature and abundance of solar radiation, thus promoting photochemical reaction. The surface ozone concentration reaches peak during the day between 1400 and 1500 LST.

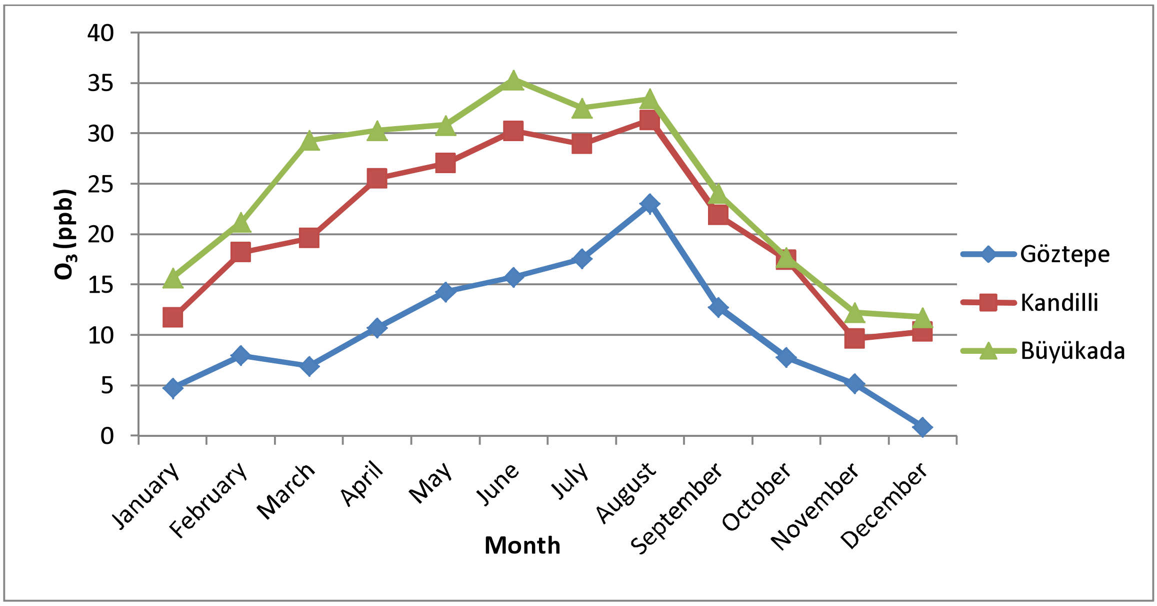

Figure 4.6. Monthly average ozone concentrations in three stations for two consecutive years (2008 and 2009).

The outcomes of time series of surface ozone show that surface ozone measurements play a key role in understanding the pollution in the atmosphere. Similar ozone formation mechanisms were observed for three air quality stations. At Göztepe air quality station, beginning from October, when the NO_x concentrations start rising gradually while the ozone concentrations reach its minimum levels. The reason for this is that the temperature and solar radiation decline leading to the reduction in ozone levels. Besides, the number of vehicles in local traffic increase in parallel with the termination of holiday season and beginning of school which trigger the disintegration of ozone and increase NO_x levels within the winter and autumn. Furthermore, measurements of surface ozone in Kandilli air quality station have shown that the ozone concentrations decreases gradually at the beginning of October similar to Göztepe and Büyükada stations. However, the reduction of the amount of surface ozone in Kandilli station is smaller than Göztepe station. The Kandilli station is characterized as sub-urban and has different emission sources from the Göztepe station. In addition, the biogenic and antropogenic emissions are diluted with the effect of ventilation above sea level 125 m. The lower reduction of ozone is not only related to the ventilation and emission sources but also the location and rare traffic emissions contribute to the increase in ozone levels. The measurements made at Büyükada demonstrates that maximum annual ozone concentrations observed among all three stations. Lower emissions of ozone precursors due to anthropogenic activities and the higher biogenic emissions from the local vegetation at Buy station can be considered as the main reasons for this rise in surface ozone concentration in background station.

Several studies were conducted to analyze the surface ozone concentrations in urban and rural areas all over the world, especially in Europe and the Mediterranean region (Nolle et al., 2002; Garcia et al., 2005, Texeira et al., 2009). Considering the high ozone days (above 50 ppb), on hourly basis, the maximum ozone concentrations reach up to 63.5 ppb at the urban site (Göztepe), and reach up to 98.7 ppb in rural and remote areas (Kandilli and Büyükada) during 2008 and 2009 ozone seasons. Besides, the monthly average ozone concentrations do not exceed 25 ppb at Göztepe station, and 40 ppb at Buyükada and Kandilli stations for 2008-2009. In Spain, by comparison the average ozone concentration increases in summer months with highest values mainly occuring in June and July at an early afternoon up to around 100 ppb in rural location (Garcia et al., 2005) which is a close value to our observations, but it is occasionally higher. Also, studies in Gozo background station indicates that the maximum monthly average seldom exceedes 100 ppbv (Nolle et al., 2002). The maximum monthly surface ozone concentrations in urban varied from 16.5 ppb to 20.5 ppb in warmest months (Texeira et al., 2009). All studies have shown similarites with our study that the peak concentration levels are obtained between 1300 and 1500 LST and the lowest levels at 0400 and 0500 LST. In addition, the maximum ozone concentrations are reached within ozone season while minimum values of the average ozone concentration was monitored in winter months in all sites. However, the ozone fluctuations are different for urban and rural sites. There is less fluctuation in the ozone concentration values throughout the day in the rural area than the urban one.

4.1.2. Diurnal Variations of Surface Ozone in Three Stations

The average diurnal cycles of ozone and nitrogen oxides are presented in Figure 4.7 for Göztepe Station in ozone season 2008 and 2009. From this figure, the minimum ozone concentration appears during morning hours at 0700 and 0900 LST with the value of 7.9 ppb. From then on, ozone concentration starts increasing gradually coinciding with the solar radiation increase, and reaches the peak of 23.4 ppb at the central hours of the day between 1400 and 1900 LST. The diurnal variations of O_3 at Göztepe station are a typical pattern for polluted urban areas, characterized by high concentrations during daytime and low concentrations during late night and early morning. On the other hand, the highest NO_x concentration demonstrates morning peak (around 110 ppb) and a minimum concentration (around 55 ppb) occur at around 1200-1500 LST when ozone reached its maximum.

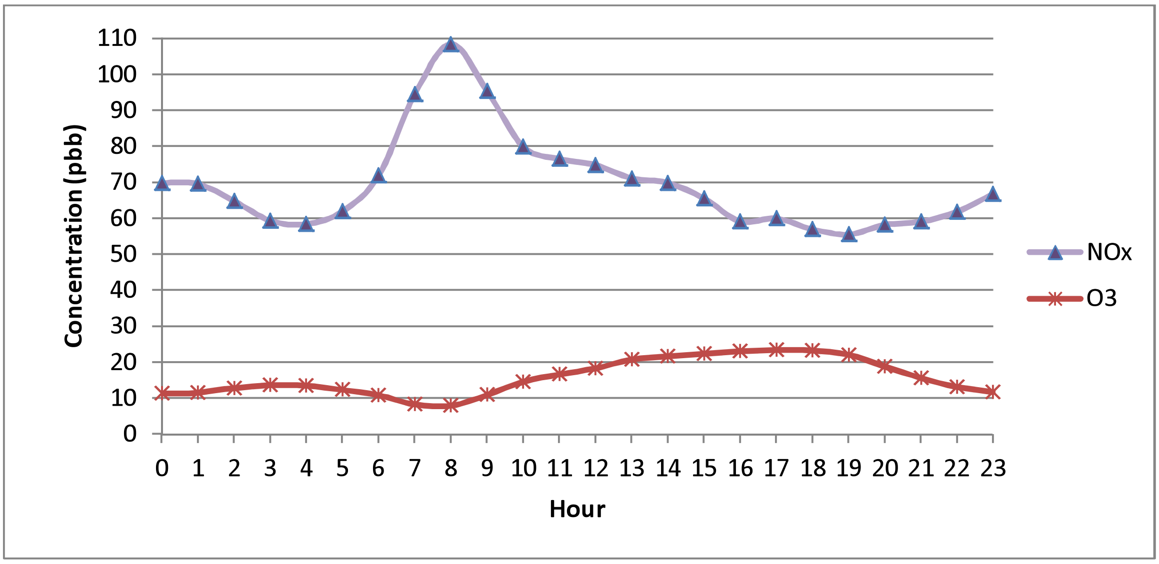

Figure 4.7. Diurnal variations of O_3 and NO_x levels at Göztepe air quality station in 2008 and 2009 ozone season.

Figure 4.8 shows the diurnal patterns of ozone measurements at the Kandilli Station. Some smaller increases in ozone level are observed during early morning hours between 0400 and 0600, average ozone concentration mostly peak between 1200-1700 with the value of 37.6 ppb. This behaviour fits relatively well to what is expected when photochemical ozone formation is involved. The ozone concentrations reach a kind of a saddle around midnight, but begin to drop again in the early morning hours. This may be interpreted as a result of convection still being 'alive' after sunset due the heated land surface, but 'dying' by midnight (Nolle et al., 2002). In addition, ozone exhibits a clear diurnal pattern with a minimum in the morning at about 0900 LST.

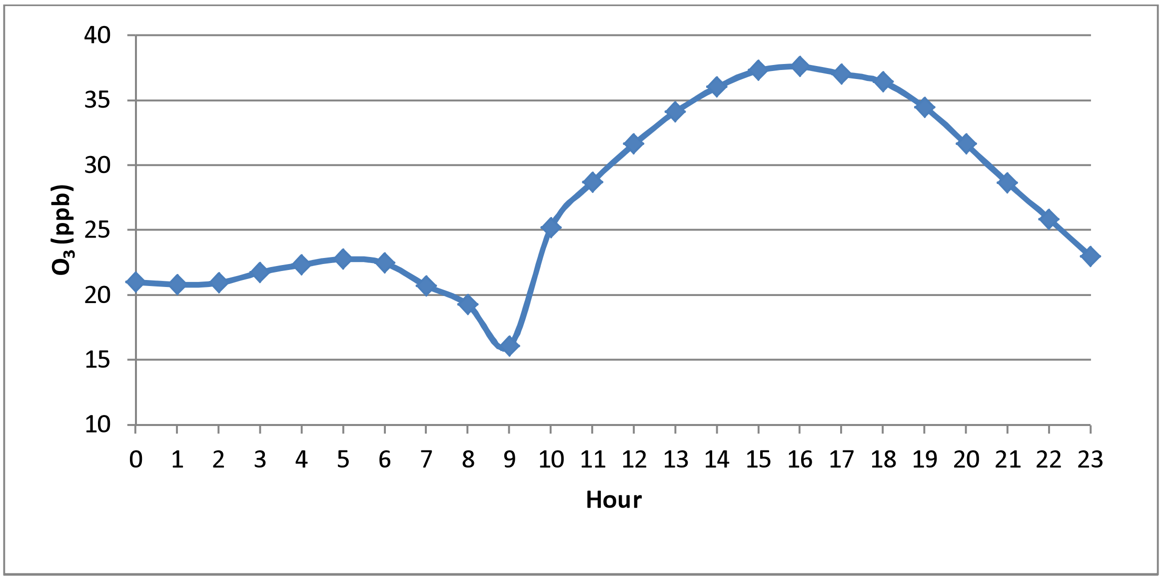

Figure 4.8. Diurnal profile of O_3 levels at Kandilli air quality station in 2008 and 2009 ozone season.

At Büyükada station, the minimum ozone concentration appears during morning hours at 0700 and 0900 LST (Figure 4.9). From then on, ozone concentration starts increasing gradually coinciding with the solar radiation increasing, and reaches the highest concentration at the central hours of the day between 1400 and 1700 with the value of 40.5 ppb. Anteplioglu, (2000) showed that surface ozone deposites in the morning hours over Marmara Sea which is triggered by Kocaeli and Istanbul emissions and ozone precursors. The outcomes of measurement have shown that the highest ozone value surface levels were monitored in Büyükada. It is known that the sea wind can have an important contribution towards the increase in the O_3 concentration (Pires et al., 2008). In contrast to Göztepe Station, NO_x level is relatively small owing to absence of industrial activities.

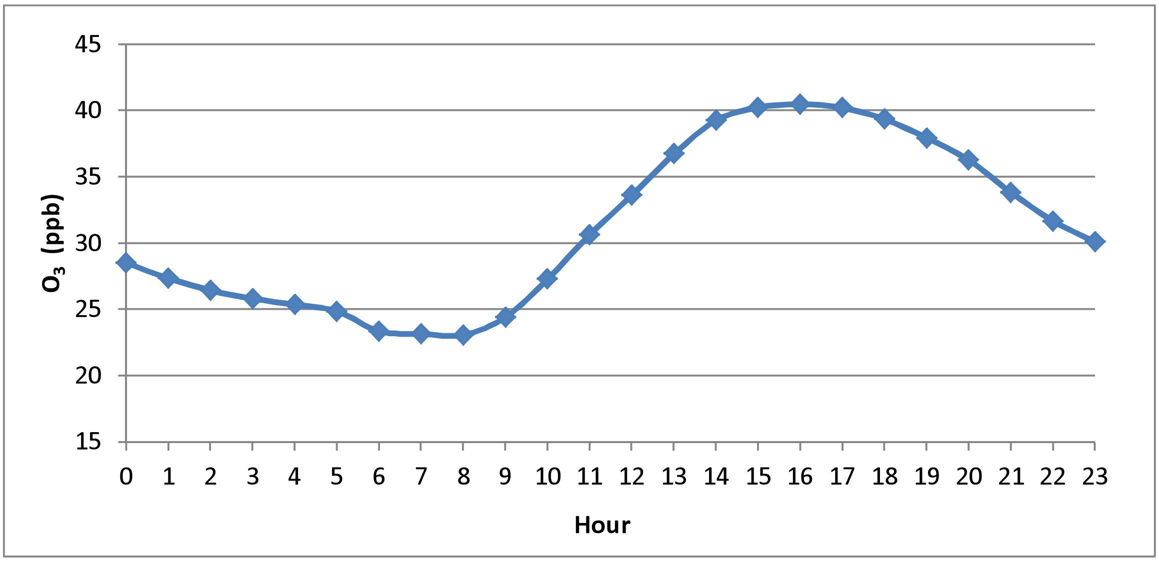

Figure 4.9. Diurnal variations of O_3 levels at Büyükada air quality station in 2008 and 2009 ozone season.

The similar diurnal variation pattern in O_3 levels were observed in numerous urban areas and (Lu Wang et al., 2004; Mazzeo et al., 2005; Im et al., 2006; Im et al., 2008). Studies conducted by Lu Wang et al. (2004) and Mazzeo et al (2005) examined the general profiles of diurnal variations of surface ozone and nitrogen oxides in urban areas. Im et al. (2006 and 2008) found that the minimum ozone concentrations were monitored during the rush hours around 0600–0800 Local Standard Time (LST) below 25 ppb in urban areas in Istanbul. On the other hand, the maximum ozone concentrations in Istanbul were below the 60 ppb between 1400-1700 LST in urban areas. The diurnal variations of surface ozone concentration in rural areas has already been detected by other authors in different parts of the world (Kalabakos et al., 2000; Debaje et al., 2003; Klumpp et al., 2006; Carvalho et al., 2010). Kalabakos et al (2000), Klumpp et al (2006) and Carvalho et al (2010) focused on the general trends of the hourly surface ozone concentration. Likewise, Debaje et al (2003) has given detail information about the diurnal profiles of surface ozone and found that the maximum O_3 concentrations varies between 29 and 40 ppbv, and the minimum ozone concentration ranging from 9 ppb to 13 ppb during the period from May 1997 to October 2000. The maximum and minimum ozone concentrations in India show similar trends with our study. These studies showed that NO_x levels reach the maximum values when the human activities and traffic flow peaks and higher ozone concentrations correspond to lower NO_x concentration levels, and vice-versa during the 24-hour period. The morning and evening peaks of NO and NO_2 correspond to morning and evening commute periods, predominantly emitted by mobile sources as the day advances and the sunlight intensity increases the NO oxidation rate. The precursors NO_x show and almost opposite diurnal variation pattern to ozone for Göztepe, characterized by high concentrations during morning and low concentration during nighttime day time, particularly noon and afternoon. As the solar intensity increased the rate of photolysis of NO_2 increased, and thus NO_2 dropped while O_3 increased (Pudasainee et al., 2010). Ozone variations tend to follow the general behaviour usually reported, namely an increase in ozone levels during the day attributed to photochemical processes of ozone production in the mixing layer and transport from the upper layer, both favoured by solar radiation, and lower values at night due to in situ destruction of ozone by deposition and/or the reaction between O_3 and NO (Duenas et al., 2002).

4.1.3. Ozone Variations with Nitrogen Oxides

In this part of the thesis, O_3- NO_x ratios were calculated for Göztepe and Büyükada (remote-rural area) to get a clearer understanding of the relationship between production and destruction of surface ozone with NO_x at urban and rural locations. To investigate the relationship among the hourly mean values of O_3 and NO_x during 2008 and 2009 ozone season, ozone data from three air quality stations have been used and compared in the diagrams. Hourly ozone concentrations in Büyükada and Göztepe air quality stations have been plotted against ozone precursors (NO_x) concentrations. Due to the technical problems in Kandilli air quality station, it was not possible to monitor the NO_x concentrations. In addition, nitrogen oxides measurements the period from April 1, 2008 to May 31, 2009 were used because of the technical problems with nitrogen oxides analyzer in Büyükada air quality station.

Scatter diagrams are plotted (Figures 4.10 and 4.11) and the correlation factors and their significance levels have been calculated using SPSS 11.5. The results are presented in Table 4.2 for 2008 and 2009 ozone seasons. The correlations between NO_x and O_3 at Göztepe station is calculated to be -0.637 (p value= 0.000). For the Büyükada station, the correlation factor is found to be -0.543 and p value is 0.000. These results clearly demonstrate that negative correlation between NO_x and O_3 and the correlations are significant for both Göztepe and Büyükada stations. That means NO_x reduces ozone by titration ($NO + O_3 \rightarrow NO_2 + O$)

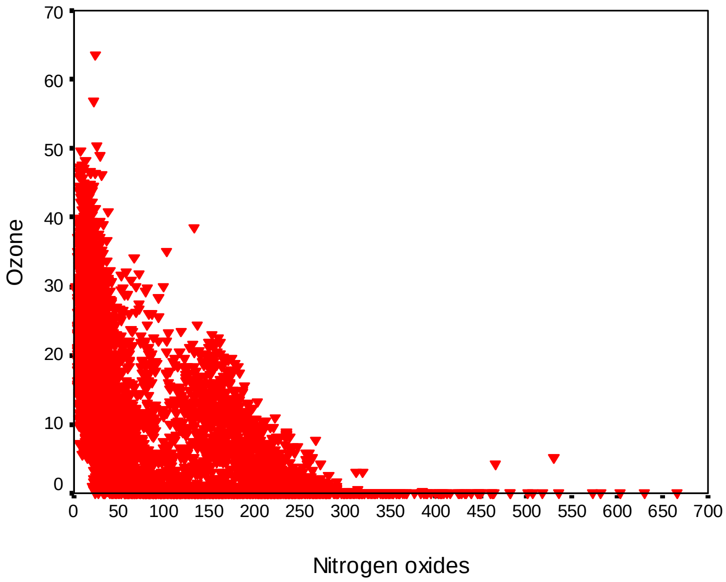

Figure 4.10. Scatter diagram of hourly ozone and nitrogen oxides for Göztepe air quality station for two ozone season from April 1 2008 to September 30 2009.

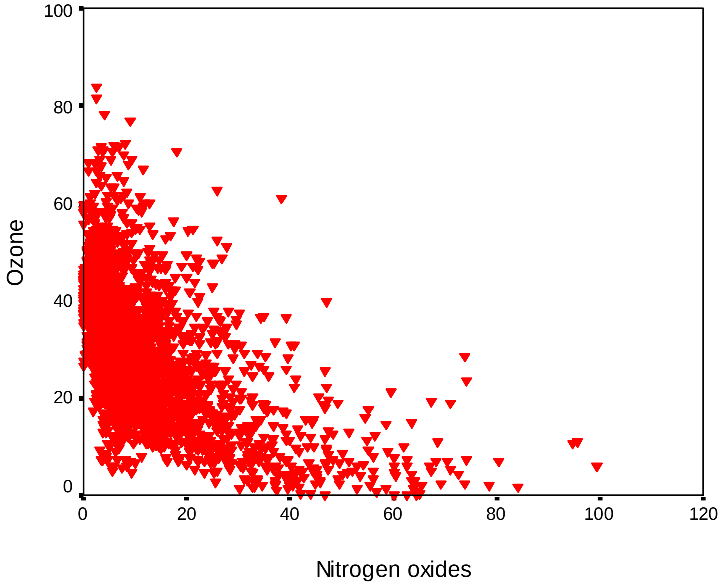

Figure 4.11. Scatter diagram of hourly ozone and nitrogen oxides for Büyükada air quality station for ozone season from April 1 2008 to 31 May 2009.

There are some earlier studies resporting the correlation coefficent between NO_x and O_3 for Istanbul. Topcu et al. (2002) reports correlation coefficients varying from -0.54 to -0.84 for the ozone months -in years 1998 and 1999. Furthermore, Im et al. (2008) indicates that the correlation factor between ozone and NO_x reaches up to -0.84 the period from 2001 to 2005. The correlations in our study are calculated to be lower. Teixeira et al (2009), reports correlation coefficients of ozone and NO_x species ranging from −0.282 to −0.503 in Brazil during 2006 which implies the correlation coefficent near our study.

Table 4.2. Pearson correlations of O_3 with NO_x, and respective level of significance in Büyükada and Göztepe air quality stations.

Location	Pearson Correlation	Significance	Number of variables
Göztepe	-0.637	0.000	6672
Büyükada	-0.543	0.000	4299

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

4.1.4. Comparison of Weekday-Weekend Surface Ozone Concentrations

In order to understand the mechanism of surface ozone levels at the three stations, ozone profiles were analyzed during weekdays and weekends (that is defined as Saturday and Sunday) individually. The time periods studied were from 2008 and 2009 ozone season with the total of 364 days.

Figure 4.12 shows that the morning ozone peak occurs between 0300 and 0500 LST in Göztepe during weekend and weekdays. Since Göztepe air quality station is characterized as urban that is impacted mostly by traffic emissions and domestic heating, the minimum values are monitored at this station. The diurnal peak value of 23.2 ppb is reached at 1800 LST in weekends, and of 23.6 ppb at 1700 LST in weekdays. Meanwhile, the ozone concentrations have a minimum value between 0700 and 0900 LST for both weekends and weekdays.

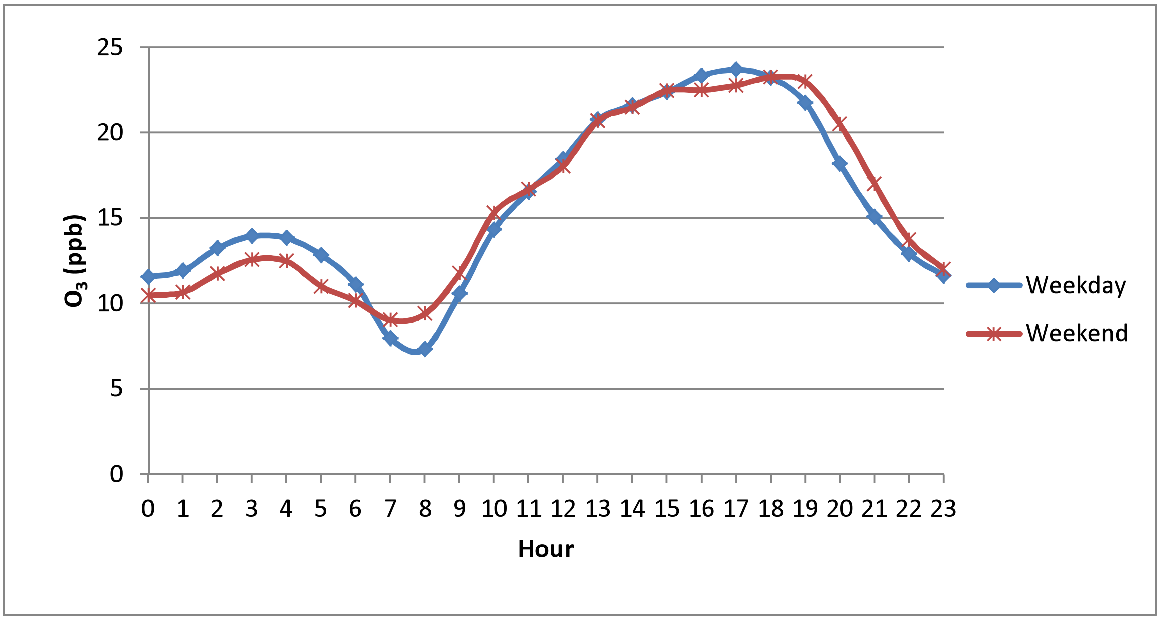

Figure 4.12. Diurnal variation of O_3 concentrations during weekdays and weekends at the Göztepe air quality station for 2008 and 2009 ozone season.

At Kandilli station, the morning ozone peak concentrations are observed between 0300 and 0600 during weekdays, and between 0600 and 0700 LST during weekends (Figure 4.13). Ozone levels increase gradually with the effect of enhanced solar radiation and temperature, and reach the maximum value of 37.8 ppb in weekdays and 37.0 ppb in weekends; minimum value is observed at 0700 and 0900 LST with the value of 7.6 ppb in weekdays and 9.5 ppb in weekends. The results show higher ozone concentration are observed in Kandilli station both on weekdays and weekends compared to Göztepe station. That is because Kandilli air quality station is located 125 m above sea level and covered with large vegetation. In this area, ventilation is very effective that leads to the transport and dilution of the pollutants.

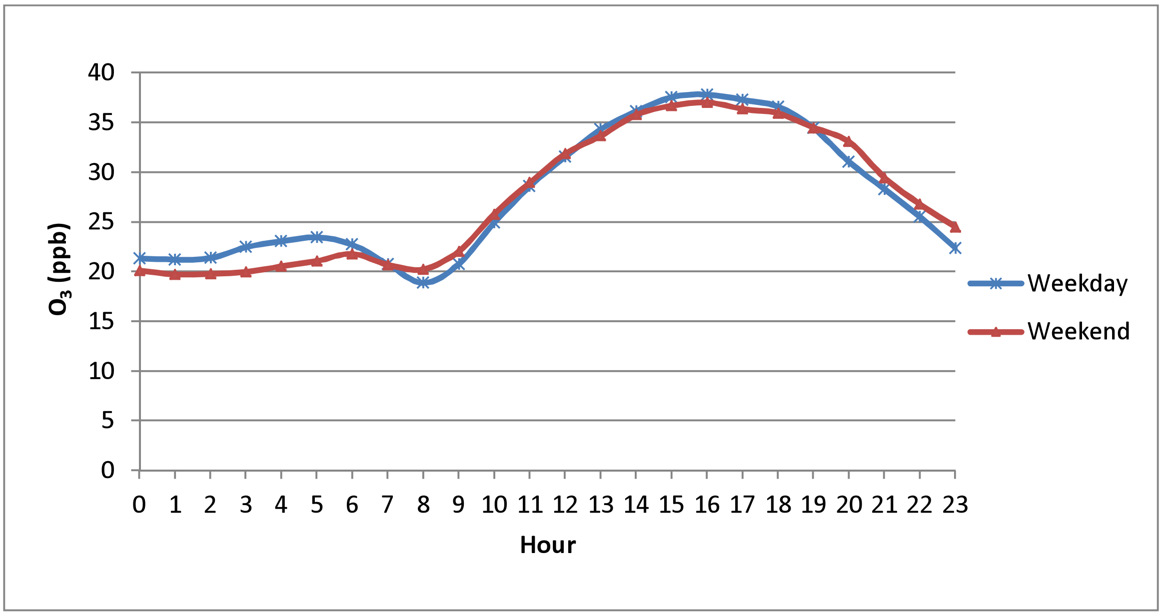

Figure 4.13. Diurnal variation of O_3 concentrations during weekdays and weekends at the Kandilli air quality station for 2008 and 2009 ozone season.

Büyükada Station is classified as a background station and the peak concentrations are observed between 1400-1700 LST on the weekend, and the 1400-1800 LST on the weekday (Figure 4.14) which decreases slowly paralel with the temperature and solar radiation (Pudasainee et al., 2010). The maximum diurnal ozone concentration is calculated to be 40.2 ppb around 1500 LST for weekdays and 40.0 ppb around 1700 LST for weekends, respectively. The ozone concentrations have a minimum value between 0700 and 0900 LST similar to Göztepe and Kandilli. The ozone concentrations at the background station is higher than urban areas since both local and transported ozone are not disintegrated by the nitrogen oxides. Besides, precursors from both Istanbul and Kocaeli sources combine above the Marmara Sea. As a result, decomposition of ozone by nitrogen oxides is less than the other stations and higher ozone concentration are observed.

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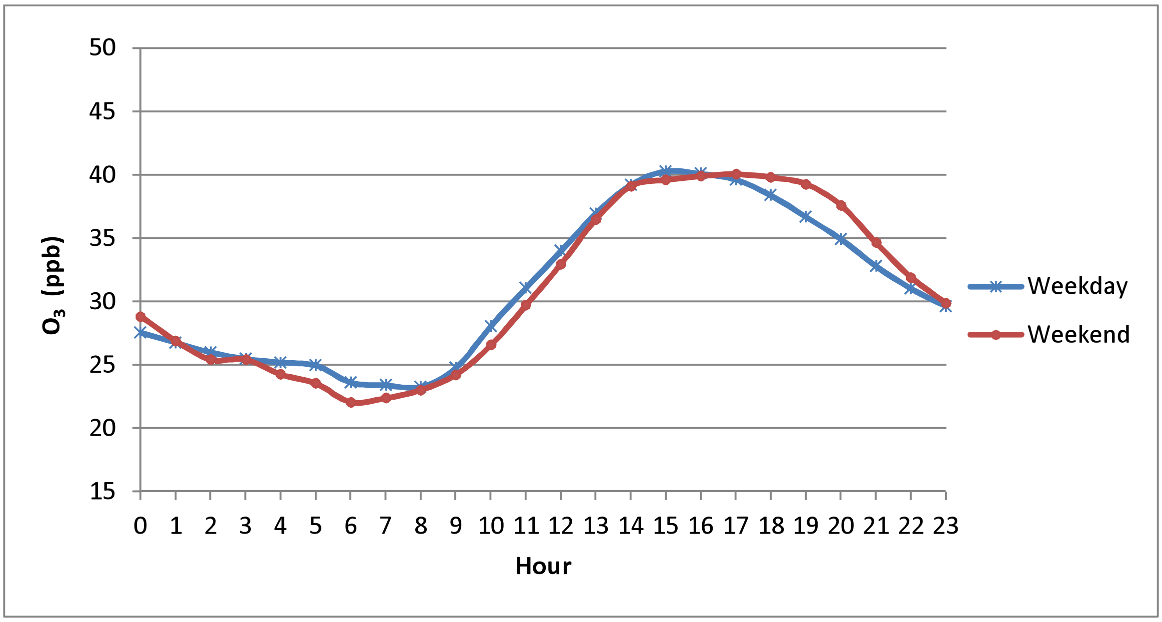


Figure 4.14. Diurnal variations of O_3 concentrations during weekdays and weekends in Büyükada air quality station for 2008 and 2009 ozone season.

The ozone ‘‘weekend effect’’is a common phenomenon of ozone behavior in the urban atmosphere: ozone concentrations on weekends are higher than those on weekdays despite lower concentrations of ozone precursors. The ‘‘weekend effect’’ on ozone formation whereby ozone concentrations observed at weekend are higher than that on weekday though relatively low concentrations for ozone precursors such as nitrogen oxide (NO_x =NO+ NO_2) and volatile organic compounds (VOCs) occur at weekends has been studied by Blanchard and Fairley (2001), Qin et al. (2004) and Sadanaga et al. (2008) and Pudasainee et al. (2010). However, the outcomes of the study indicate that the differences of surface ozone concentrations are slightly different in late afternoon. The main reason is that Istanbul is the megacity where reduction of NO_x emissions is minor on weekend because of heavy traffic in urban area. The weekday/weekend differences are shown clearly when the minimum values observe between 0700 and 0900 LST. Morning O_3 levels are higher on weekends especially in urban area that are affected by fresh NO_x emissions.

4.1.5. Seasonal Variations of Ozone Concentrations over Istanbul

The ozone concentrations near the surface (0-2 km) can be affected by large local or regional emissions of hydrocarbons and nitric oxides in the presence of sunlight and the resulting photochemical reactions. Due to the specific meteorological conditions at these altitudes and the pollutant emission situation in the area, the ozone-mixing ratio below 2 km may have a very different seasonal behavior from that above (Chan et al, 1998).

The diurnal variations of O_3 observed at Göztepe, Kandilli and Büyükada air quality stations are highly influenced by the seasonal changes. The seasonal differences in ozone concentrations among these sites depend on the site characteristics and meteorological variables. As mentioned in section 2, Büyükada and Kandilli stations are situated at higher altitudes compared to the Göztepe station. Thus, higher ozone levels are obtained at these stations. On seasonal basis, the diurnal variations of surface ozone concentrations at the three stations are depicted in Figures 15,16,17 and 18. These figures indicate that ozone measurements in Göztepe are higher in summer months (26.5 ppb at 1700 LST) and lower in the winter (3.8 ppb at 0800 LST). The reduction of O_3 concentrations in the area of study during the first hours of the day 0700–1000 LST is mainly due to the increase in traffic flow (rush hours) in all seasons. On the other hand, high ozone concentrations are observed during midday or afternoon hours.

Observations at the sub-urban and background sites of Kandilli and Büyükada are different from those at the urban/traffic Göztepe station. A similar seasonal trend has been observed for both Kandilli and Büyükada stations. Higher daily average ozone levels are identified during the warmest months (June-August) at Kandilli and Büyükada stations. Ozone reaches peaks of 44.8 ppb at 1500 LST and 39.7 ppb at 1600 LST in Princes' Island and Kandilli stations, respectively. The maximum occurs in summer during afternoon hours when the photochemical production is fastest. Seasonal ozone peaked during summer months as expected even in the rural background station. On the other hand, lower ozone levels were observed in colder season with the value of 14.5 ppb and 10.2 ppb at Büyükada and Kandilli stations, respectively.

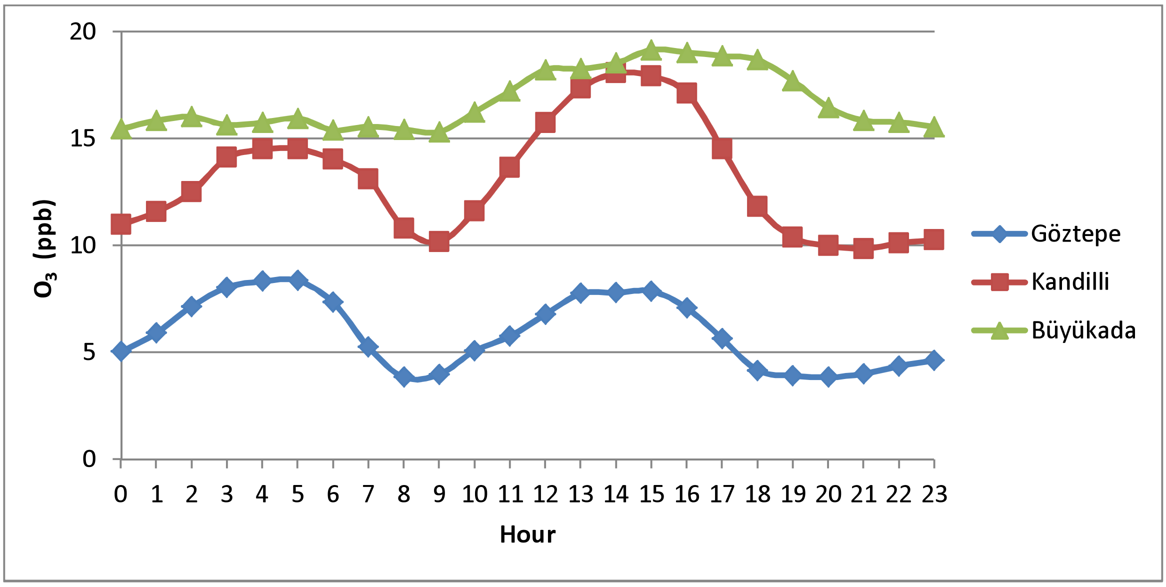


Figure 4.15. Diurnal variations of averaged ozone concentrations at Göztepe, Kandilli and Büyükada air quality stations in Istanbul in winter of 2008 and 2009.

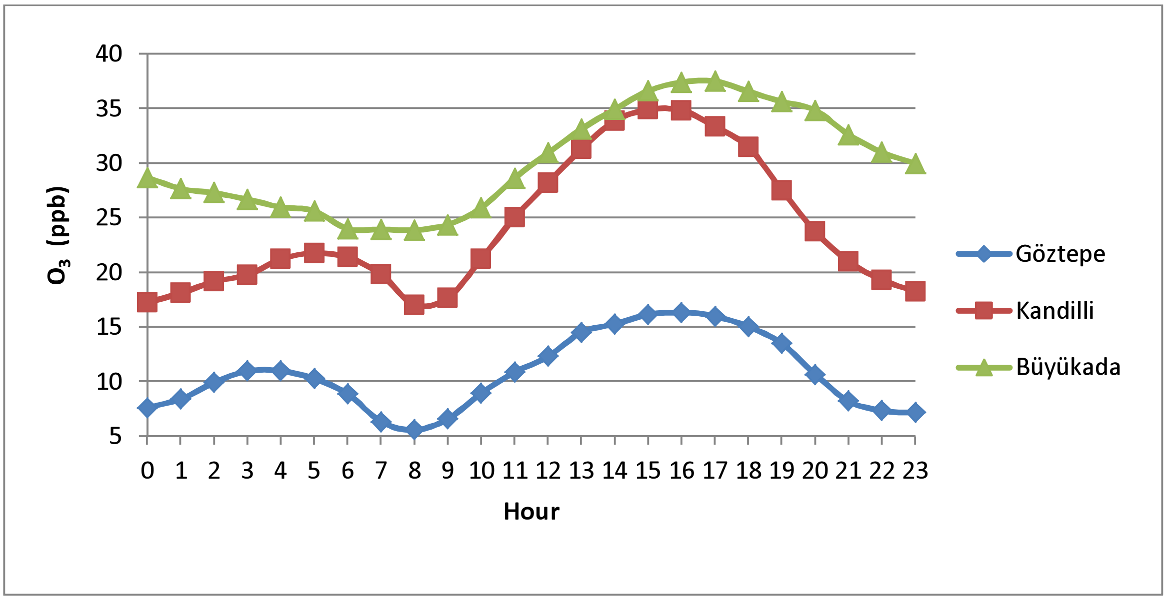


Figure 4.16. Diurnal variations of averaged ozone concentrations at Göztepe, Kandilli and Büyükada air quality stations in Istanbul in spring of 2008 and 2009.

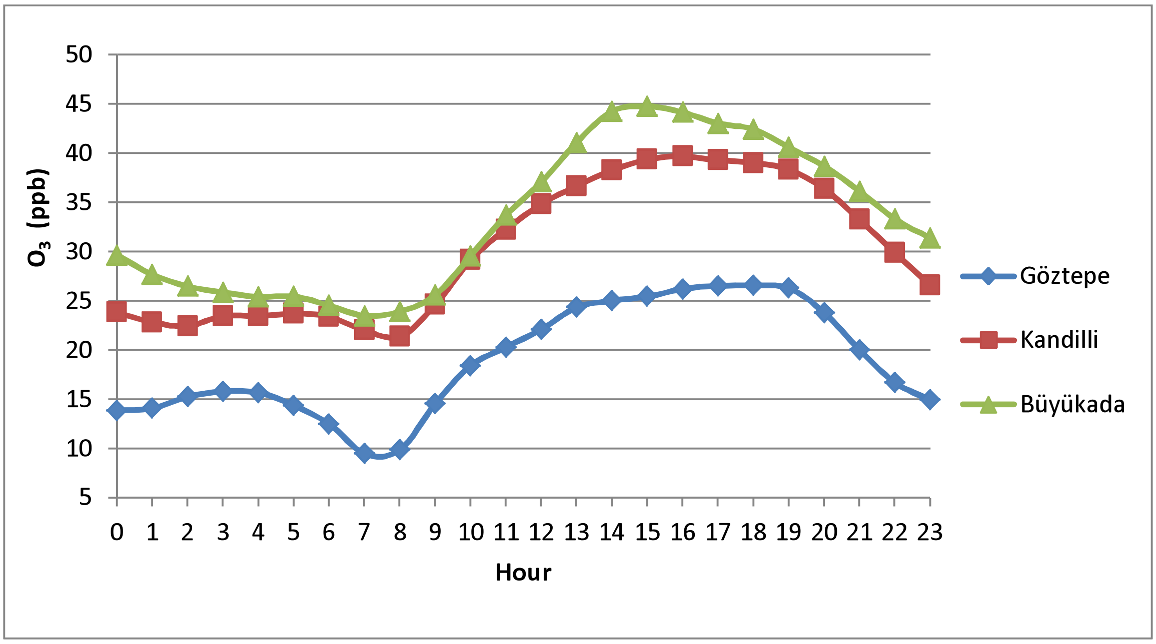


Figure 4.17. Diurnal variations of averaged ozone concentrations at Göztepe, Kandilli and Büyükada air quality stations in Istanbul in summer of 2008 and 2009.

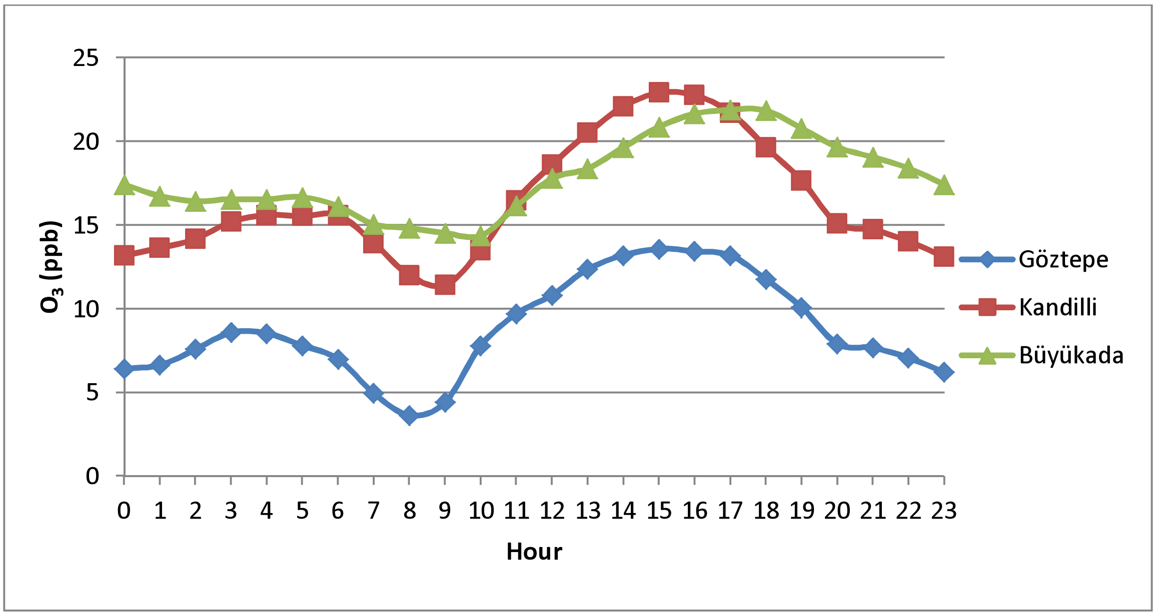


Figure 4.18. Diurnal variations of averaged ozone concentrations at Göztepe, Kandilli and Büyükada air quality stations in Istanbul in autumn of 2008 and 2009.

The comparison of seasonal variations in surface ozone observed at both urban and rural sites in general shows a similar pattern in monthly variation of O_3 at all locations (Figure 4.1.1.). While a minimum values appear in the early hours of the morning, ozone concentrations reach a maximum at 1500 LST in agreement with the maximum activity for 2008-2009 in all seasons. The maximum winter ozone concentrations (above 7 ppb) at Göztepe were determined at 1200-1700 LST. The highest summer O_3 is observed at the Büyükada air quality station (about 40–45 ppb) compared to all other stations. This is due to the availability of intense solar radiation with a possible increase in precursors, which provokes the production of O_3 by photoxidation processes and the limited atmospheric diffusion that favors the accumulation of ozone in the layers close to ground. These results are comparable with several studies, amongst which, Kley et al. (1999), Salisbury et al. (2002) and Bloomer et al. (2010) reported lower ozone concentrations during the cold months compared to the warmer months. Besides, these results are in agreement with recent studies in urban and rural sites (Duenas et al., 2004; Cristofanelli et al., 2009; Reddy et al., 2010). Seasonal cycle of surface ozone concentrations in urban and rural sites were investigated by Duenas et al. (2004) where the average ozone concentrations in all the four seasons were higher at the rural site than at the urban. The highest ozone concentrations were above 50 ppb during the afternoon 1200-1700 LST in summer months in urban and rural areas. These stations had minor differences in ozone levels. The winter ozone concentrations were monitored at an urban site and were above 40 ppb during afternoon. In general, they found that the average in all four seasons are higher at the rural site than at a urban one.

4.2. Meteorological Effects on Ozone Levels

Meteorological parameters play an important role on the formation, dispersion, transportation and dilution of air pollutants. The variations in local meteorological conditions, such as wind direction, wind speed, temperature, can affect the temporal variations in O_3 and its precursors (Dueñas et al., 2002; Elminir, 2005; Satsangi et al., 2004). Shan et al. (2009) were also analyzed monthly variation of surface ozone concentrations that are reported that ozone levels are correlated with temperature (r=0.66 during 2004). High ozone concentrations are mainly associated with the wind from 180 to 247.5°. An analysis of the influences of meteorological parameters on O_3 and its precursors at a specific site can contribute to a better understanding of the local and regional causes of O_3 pollution (Jun Tu et al., 2007) . In addition, similar pattern was also observed in recent study by Im et al. (2008).

In this part of thesis, the relationship between monthly averaged ozone levels and meteorological parameters such as average temperature and wind speed were evaluated. Meteorological variables such as temperature, wind speed were taken from the Maltepe Meteorology Station for Göztepe and Büyükada stations. Additionally, meteorological parameters used for evaluating Kandilli measurements were obtained from Kandilli Observatory and Earthquake Research Institute (KOERI). The variation of monthly ozone concentrations at three different locations in Istanbul are shown in Figure 4.6. The relationships of ozone variation with temperature, wind speed and direction are examined for three different locations. At the Göztepe Station, the highest monthly average ozone concentration is calculated to be 23.1 ppb in August. Meanwhile, the temperature is recorded about 25.4 ^{o} C and the average wind speed was recorded as 2.6 m/s. As shown in Table 4.3, monthly average ozone concentrations show strong positive correlation with the monthly average ozone temperature (r= 0.862, p= 0.000) and wind speed (r= 0.814, p=0.000) in 2008 and 2009. At the Büyükada station, a maximum ozone concentration of 35.4 ppb is reached in June. The differences in the occurrence of peak of O_3 in the urban and in rural sites appear to be related to the maximum emission of NO_x and hydrocarbons (Debaje et al.2009). In the Göztepe, large emissions of NO_x concentration in the morning hours from commuter vehicular traffic. The temperature is observed to be roughly 23.6 ^{o} C and wind speed is monitored to be 2.1 m/s. Ozone shows strong positive correlation with the temperature (r= 0.717, p= 0.009) and wind speed (r= 0.666, p=0.018). This significant correlation between temperature and ozone could be explained by the well known ozone production processes. Furthermore, high wind speeds often imply rapid transport of air massesto or from a particular region, which may lead to dilution of primary pollutant.

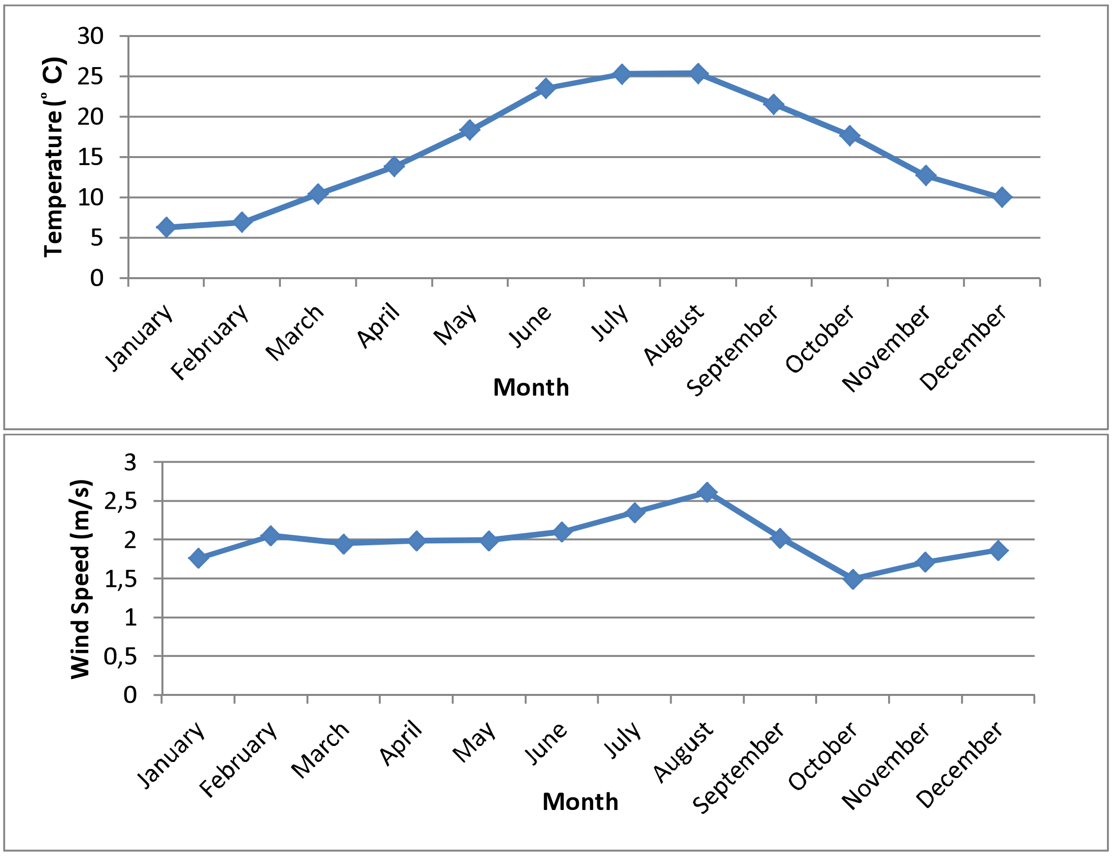


Figure 4.19. Monthly average temperatures and wind speed for Göztepe and Büyükada stations the period from 2008 to 2009.

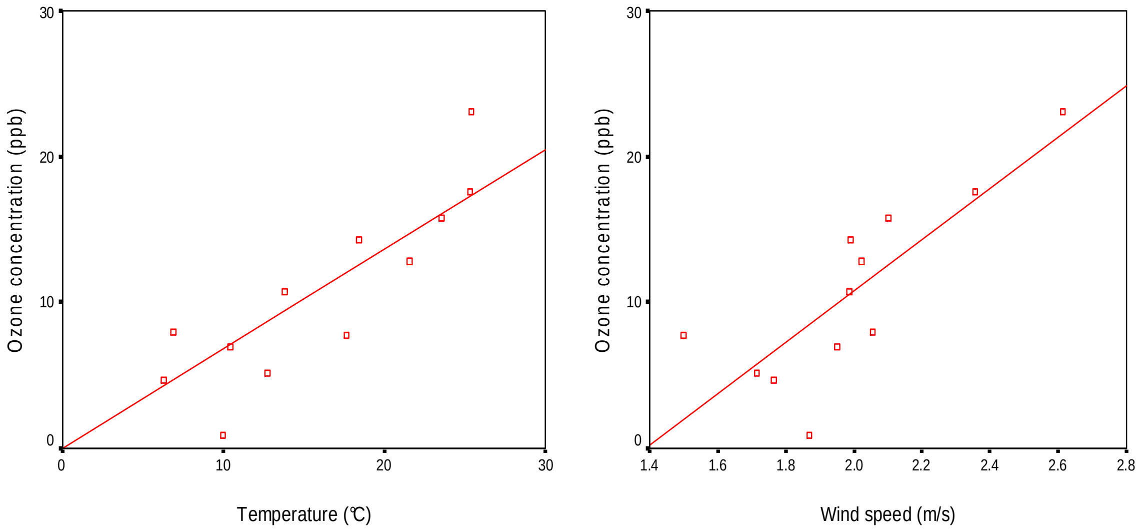


Figure 4.20. Regression analysis of monthly average ozone concentration for Göztepe air quality station from 2008 and 2009.

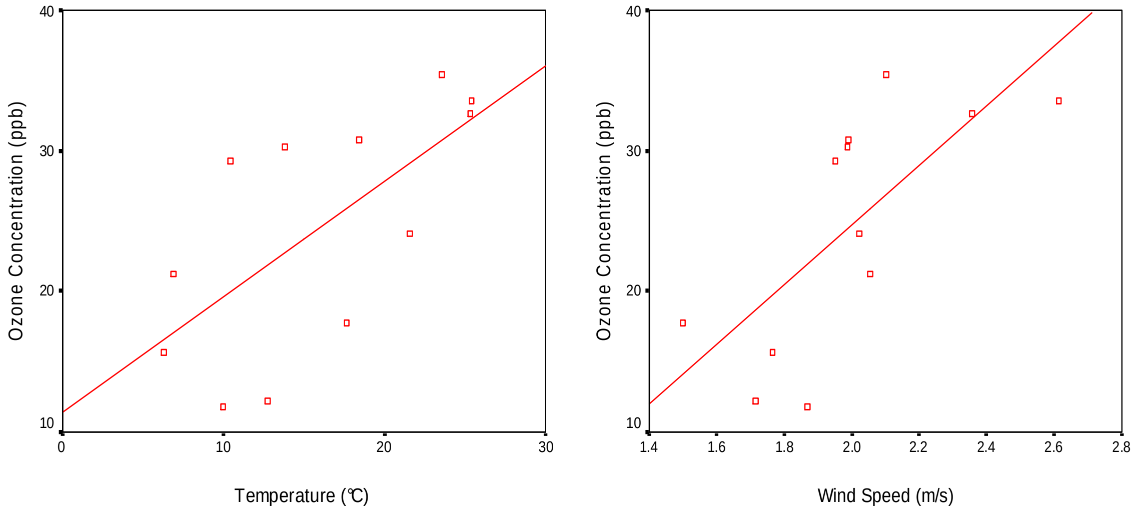


Figure 4.21. Regression analysis of monthly average ozone concentration for Büyükada air quality station from 2008 and 2009.

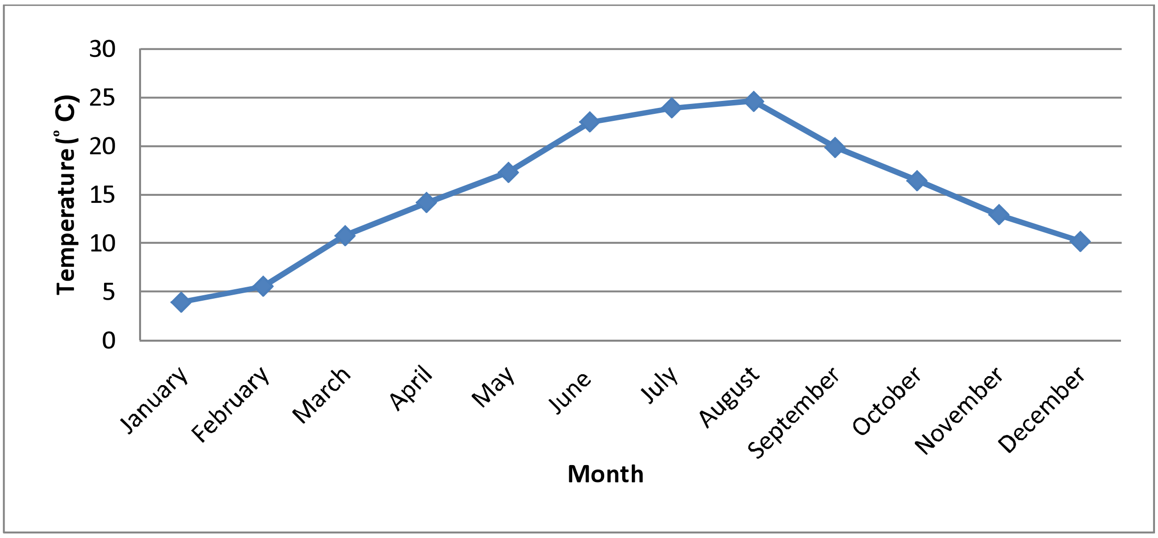
Table 4.3. Correlation factors and significance level of ozone with temperature and wind speed at three stations.

Meteorological variables	Correlation	Significance
	Göztepe	
Temperature	0.862*	0.000
Wind Speed	0.814**	0.001
	Büyükada	
Temperature	0.666*	0.018
Wind Speed	0.717**	0.009
	Kandilli	
Temperature	0.763**	0.004
Wind Speed	0.695*	0.012

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

To investigate whether temperature changes can explain the O_3 trend, ozone concentration in Kandilli station were examined. The monthly average ozone concentrations at the Kandilli station reached up to 31.3 ppb in August. The temperature and wind speed were around 24 ^{o} C and 3.82 m/s, respectively, during this period. As Figure 4.20 depicts, highest ozone concentrations are measured when temperature is high.

Surface ozone concentration are related to high temperature (R= 0.763, p=0.004) and low wind speed (R=0.695 p=0.012) .



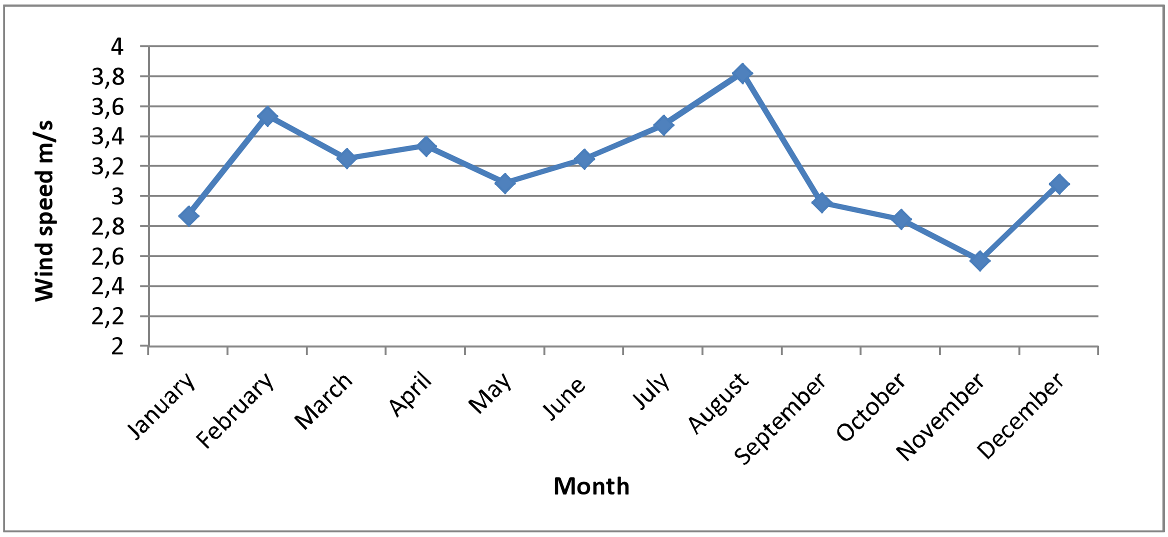


Figure 4.22. Monthly average temperatures and wind speed for Kandilli air quality station the period from 2008 to 2009.

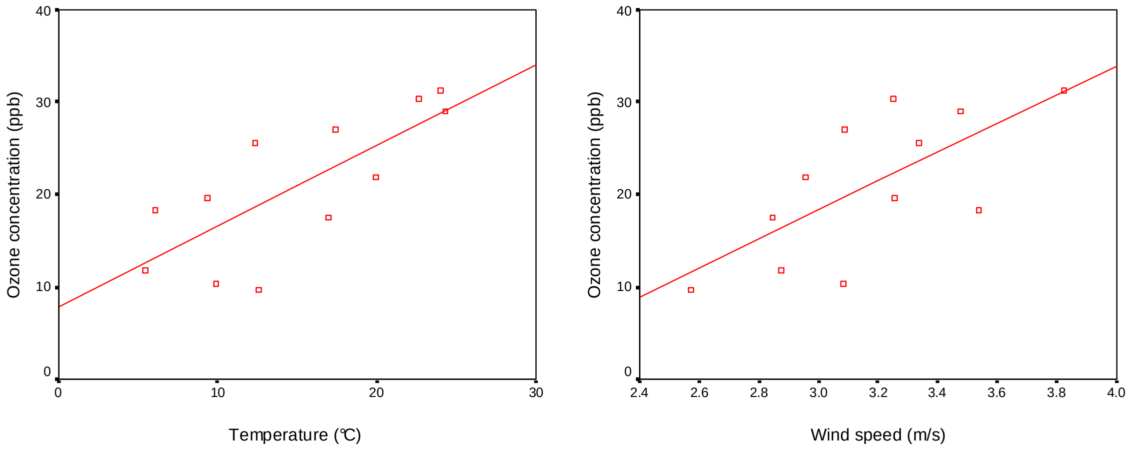


Figure 4.23. Regression analysis of monthly average ozone concentration for Kandilli air quality station from 2008 and 2009.

Results clearly demosnstrate that elevated ozone concentrations are associated with warm temperatures. Emission of biogenic hydrocarbons increase with temperature as do evaporative emissions of anthropogenic volatile organic compounds, and these increases in emissions can be associated with increased ozone (Im et al., 2011).

4.3. Backward Trajectory Analysis: Case Study of High Ozone Days in Kandilli Station

4.3.1. Scope of Analysis

Air quality models are mostly used for studying source-receptor relationship (Collet and Dyuyemi, 1997; Zanetti and Puckett, 2004). The Hybrid Single – Particle Lagrangian Integrated Trajectory (HYSPLIT, Draxler and Hess 1997,1998) is an well known model which compute both simple air parcel trajectories and complex dispersion and deposition simulations. HYSPLIT model is mostly used to determine the paths of air mass from one region to another and thereby demonstrate whether the vector for air pollution transport is present (e.g. Perkauskas, 2000; Im, 2008). Global Data Assimilation System (GDAS) analyses were used as input to the HYSPLIT model. The back trajectory simulations were initialized and run 72 hour before the first days of the episodic periods. The runs continued throughout This 3-day time period is well suited for capturing potential long range transport of air pollutants, particularly considering that most pollutants will be deposited within couple of days (Im et al., 2008).

Table 4.4. HYSPLIT Model parameters used for run

Model Parameter	Setting
Meteorological dataset	2
Trajectory direction	Backward
Total run time (trajectory duration)	72 hour
Start Point	Kandilli
Start time	12:00
Start Height	1000 m AGL and 3000 m AGL

In this study, HYSPLIT model was employed backward for three long episodes so as to visualize pollutant transport to Istanbul during episodic day. High ozone days in Kandilli (4-6 August 2008; 15-17 May, 2009) was modeled so that the effects of ozone levels on air quality was determined more effectively.

4.3.2. Episodic Analysis and HYSPLIT Trajectories

HYSPLIT model is widely applied in many studies of long-range transport assessing its influence on high ambient pollutant concentrations (Collet and Dyuyemi, 1997; Zanetti and Puckett, 2004; Garcia et al., 2005. In this thesis, in order to understand transport patterns, the suburban site of Kandilli in the center of the Beykoz was chosen as a target site. Episodic days were observed on 4-6 August 2008 and on 15-17 May 2009. Monthly average ozone concentrations (Figure 4.6) analyzed in previous section suggested that episodic days should be choosen from the period April to September. The episodes were selected such that there were no missing data so that the Pearson's correlation coefficients were accurately calculated together with the significance levels of these correlations. Selected episodes with maximum O_3 concentrations and meteorological factors, such as, temperature and average wind speed are summarized in Table 4.5.

Table 4.5. Maximum/minimum ozone concentrations in the selected episodes and the corresponding temperatures and wind speeds.

Date	Station	Max./Min. Ozone Concentration(ppb)	Max./Min Temperature □ C	Max./Min Wind Speed m/s
04.08.2008	Kandilli	55.5 / 31.1	27/20.4	5.4 / 2.7
05.08.2008	Kandilli	53.3 / 24.4	29.3 /19.3	5.0 / 1.4
06.08.2008	Kandilli	55.9 / 12.1	29.3/18.7	4.4 / 1.6
15.05.2009	Kandilli	49.9 / 0.5	29.8 /15.4	0.9 / 1.3
16.05.2009	Kandilli	78.8 / 0.2	27.6 /17	1.0 / 2.3
17.05.2009	Kandilli	57.8 / 0.7	23.7 /19.8	4.3 /1.9

The episode analysis shows that ozone concentrations started increasing at 1200 LST when solar radiation and temperature are at the maximum and maintained high levels until the end of the episodic days. During the episodic days, daily maximum O_3 concentrations were above 50 ppb. Wind directions were characterized by westerly and northwesterly in 2008 and northeasterly in 2009 episodes, respectively. Between these periods, temperatures were above 23 ^oC. Wind speeds were mostly above 4m/s. On the other hand, minimum concentrations are recorded during rush hours when NO_x emissions are at their maximum, leading to NO_x titration of O_3. Between these periods, temperatures were above 23 ^{o} C and moderate wind speed were determined which are mostly above 4 m/s. The relation between the average ozone levels and wind speeds, temperature, and solar radiation are evaluated using Pearson's correlation. Correlation factors and their significance levels are calculated and are presented in Table 4.7 and 4.8. During these episodes, ozone showed strong correlation with temperature and wind speed similar to 2008-2009 ozone seasons in Kandilli (Table 4.6 and 4.7).

Table 4.6. Correlation factors and significance levels between ozone and temperature and wind speeds for 4-6 August,2008.

Kandilli	Correlation	Significance
Temperature	0.641	0.000
Wind speed	0.811	0.000

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

Table 4.7. Correlation factors and significance levels between ozone and temperature and wind speeds for 15-17 May,2009.

Kandilli	Correlation	Significance
Temperature	0.525	0.000
Wind speed	0.470	0.000

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

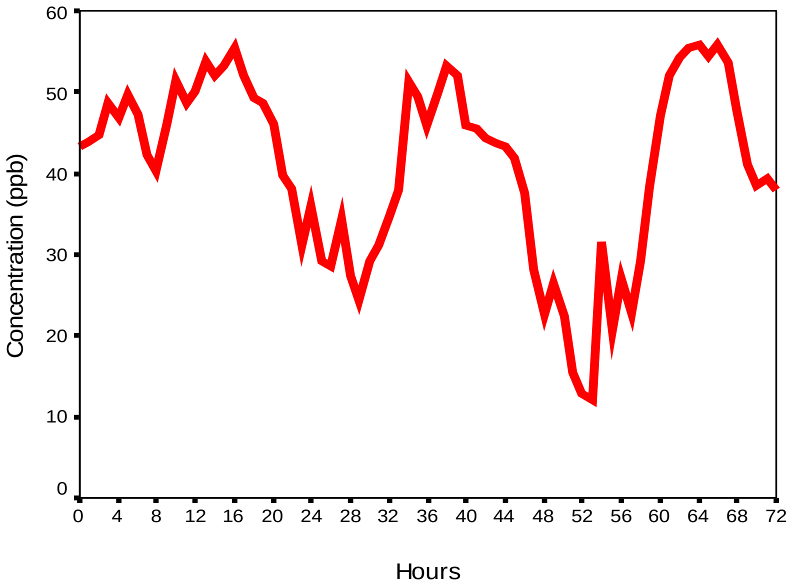


Figure 4.24. Ozone, profiles for the episode; August 4-6, 2008.

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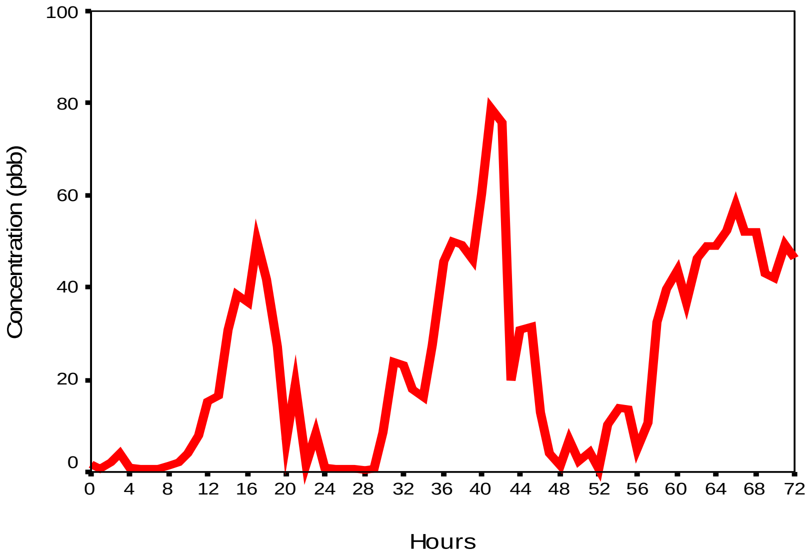


Figure 4.25. Ozone, profiles for the episode; May 15–17, 2009.

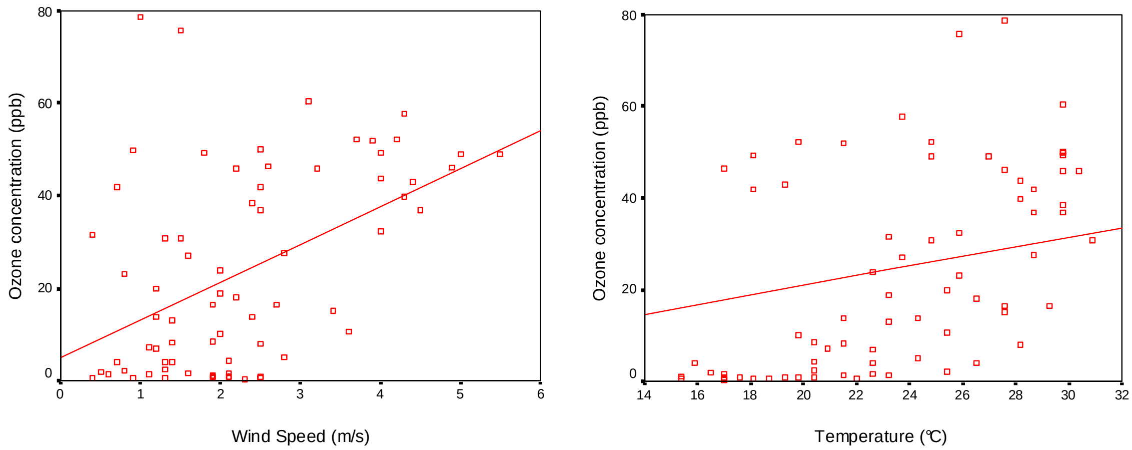


Figure 4.26. Relations ozone / temperature and ozone/wind speed 15-17 May, 2009

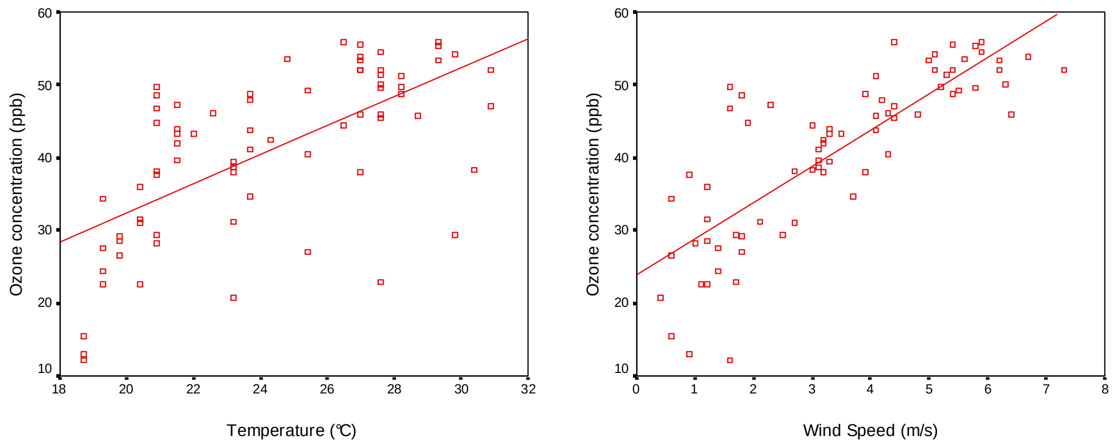
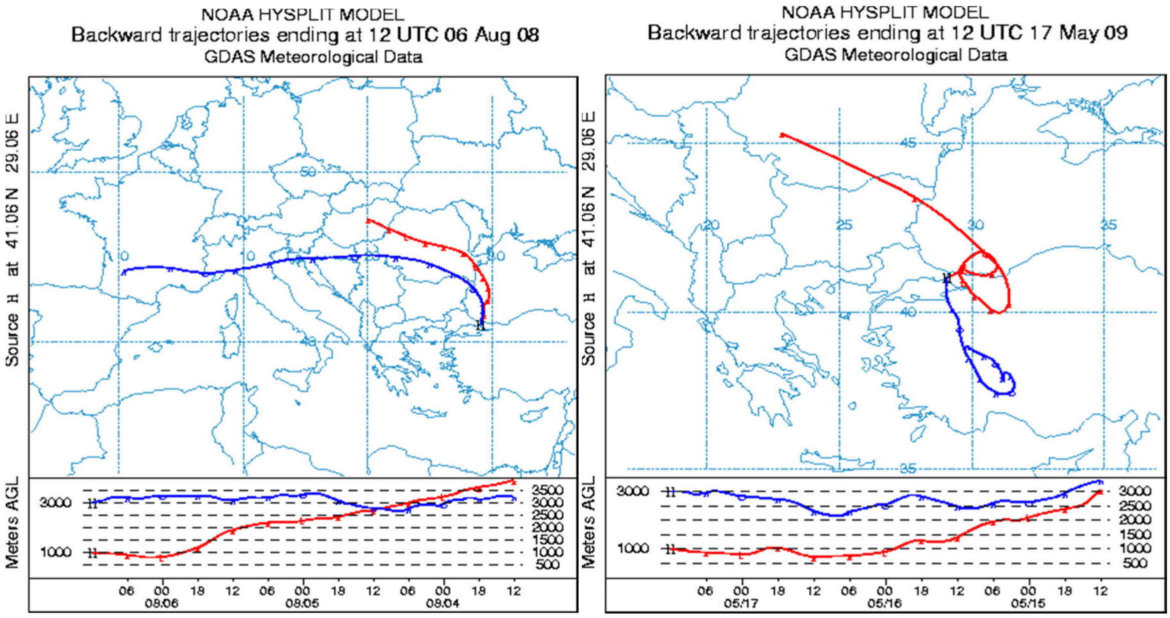


Figure 4.27. Relations ozone / temperature and ozone/wind speed 4- 6 August, 2008

To analyze the source origins and transport characteristics of surface ozone and calculate air-mass paths from the surrounding regions to Istanbul, the air-mass trajectories arriving to the Kandilli Station was investigated with the use of the HYSPLIT model. 72 h backward trajectories reaching the target site Kandilli at 125 meter and the boundary layer heights were calculated using GDAS data for all days, and mid-afternoon LST was chosen as the start time (Turkey local time 12:00). HYSPLIT backward trajectory results for 2008 and 2009 episodes are presented in Figure 4.28. Trajectories showed that west, northwest, and south are the main transport pathways for 2008 and 2009 episodes, respectively. Figure 4.28 also shows that on August 6, 2008, at 1000 m and 3000 m altitudes, northwesterly and westerly winds are dominant. During the 2009 episode, nortwesterly and westerly winds are clearly dominant both at 1000m and 3000 m altitudes. Results show that transport to Istanbul occurs especially in summer, originating from Europe, Balkans and Black Sea. The results of the HYPSLIT model clearly shows the strong influence of the Balkan regions on Kandilli.



(a) (b)

Figure 4.28. HYSPLIT trajectory for (a) August 4–6, 2008, episode; (b) May 15–17, 2009, episode.

In this study, clustering methodology was applied to back trajectories arriving in Kandilli. These trajectories were clustered using a non-hierarchical clustering analysis (Ward's Method) (Timm, 2002). Distances are calculated over a sphere by using the latitude and longitudes of the locations at each trajectory for the same hour. After that, Euclidean distance matrix is formed. Clusters are indentified by the assessment of relative distance between points and the relative homogeneity of each cluster and the degree of their seperation makes the task relatively simple. The aim of cluster analysis is to discover the types and reduce the number of cases by enabling consideration of several types instead of numerous records. Similarities are a set of rules that serve as criteria for grouping or separating items. The most straightforward way of computing distances between objects in a multi-dimensional space is to compute Euclidean distances. Euclidean distance is probably the most commonly chosen type of distance that is appropriate for variables that are uncorrelated and have equal variances. Note that Euclidean (and squared Euclidean) distances are usually computed from raw data, and not from standardized data. This method has certain advantages (e.g., the distance between any two objects is not affected by the addition of new objects to the analysis, which may be outliers).

Table 4.8. The direction of trajectories

Number of cluster	Direction	
	1000 m	3000m
1	W	NW
2	W	NW
3	NE	NW
4	NE	NE
5	NW	N
6	NE	NE
7	NW	SW
8	NW	W
9	NW	N
10	NW	W
11	NW	NW
12	N	N

In this study, 805 trajectories were obtained from Backward Trajectory Analysis at two different heights between September 2007 and December 2009. The cluster analysis yields an optimal number of 12 clusters for 1000 m height, and 12 for 3000 m height. These groups are then further combined to represent four main directions or sectors. Red lines in figures 4.27 and 4.28 represent cluster centroides cluster 1000 m and 3000 m respectively. Direction for each cluster (Table 4.8) is demonstrated for two different heights. At 1000 m, the clusters 1 and 2 mainly composed of trajectories that comes from west direction. The dominated direction is northwest in cluster 5, 7, 8, 9, 10, 11. The trajectories grouped into cluster 3,4 and 6 comes from northeast. Trajectories grouped into cluster 12 comes from north. At 3000 m, cluster 8 and 10 are originated from west direction. The clusters 1, 2, 3, 11 and 12 are composed of trajectories that direction is northwest. Cluster 4, 5, 6 and 9 comes from north and northwest. Trajectories grouped into cluster 7 mainly originated from southwest. It is noteworthy that westerly flow reaching Kandilli comprises faster wind speeds at 1000 m, therefore it may support the very long range transport of pollutants. Dominated direction is northwest in two different heights that are associated with maximum hourly average ozone concentration 79.9 ppb.

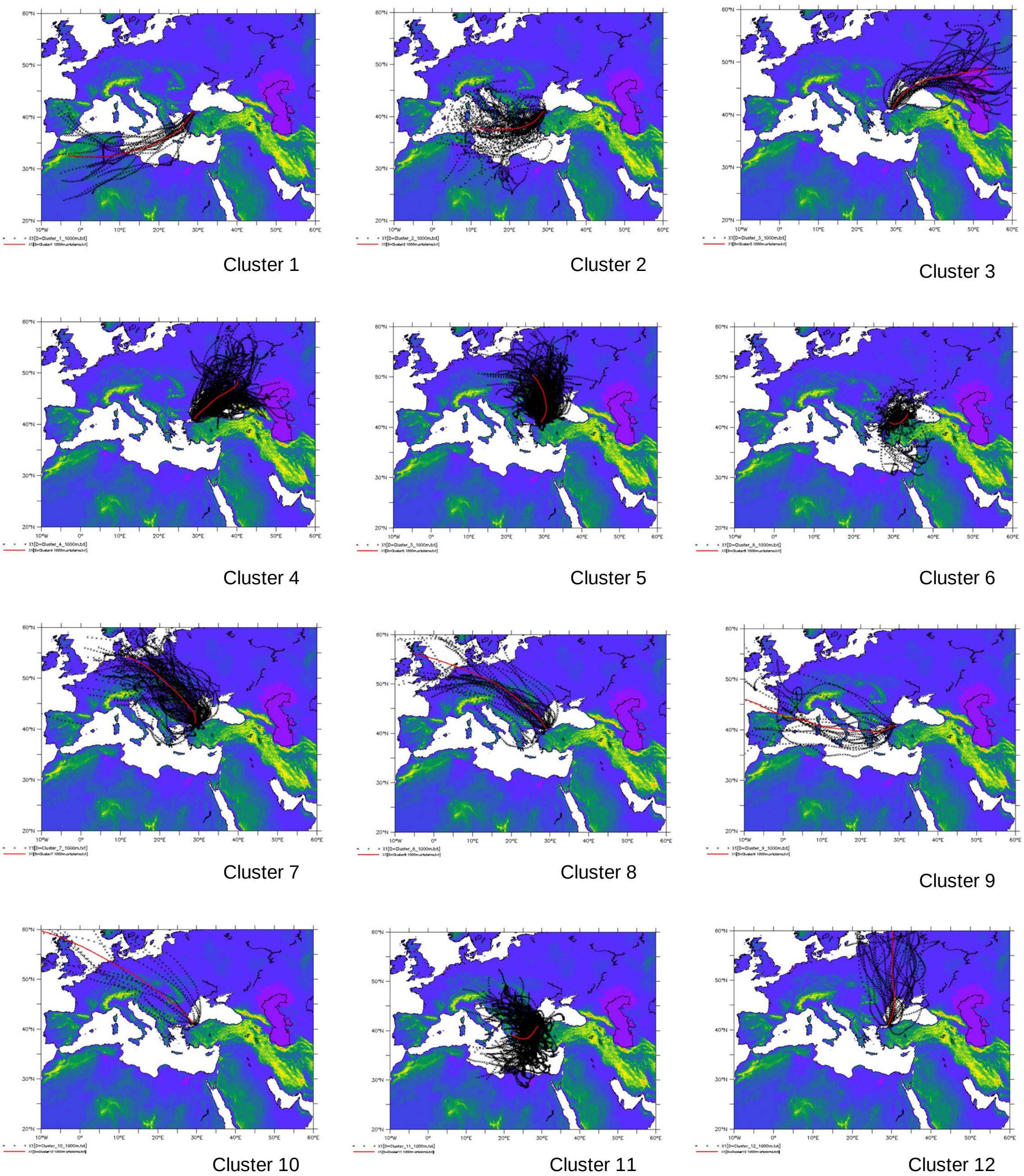


Figure 4.29. Back trajectory clusters at 1000m for Kandilli (2008-2009).

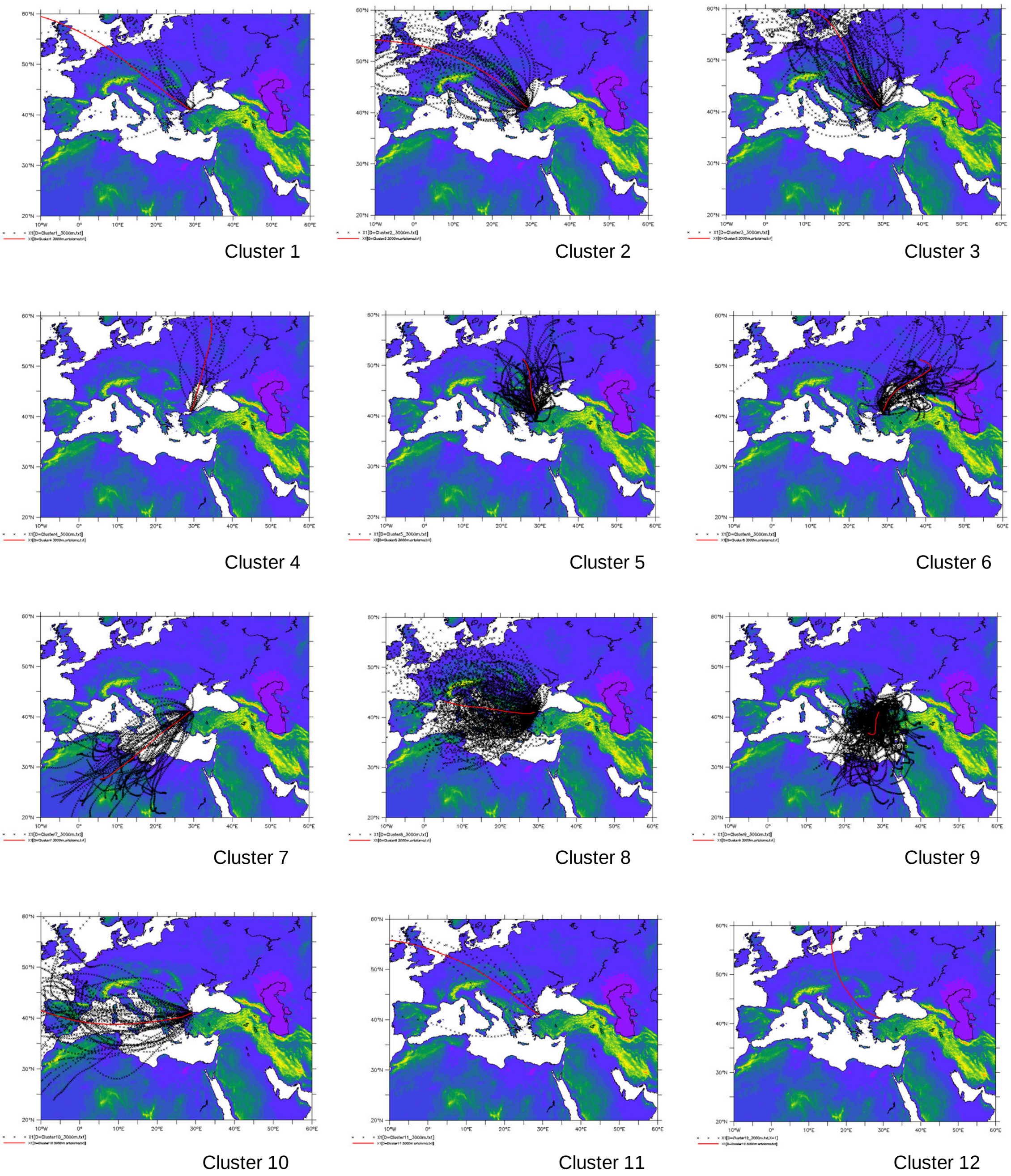


Figure 4.30. Back trajectory clusters at 3000m for Kandilli (2008-2009).

5. SUMMARY and CONCLUSIONS

Although Istanbul has not yet experienced critical levels of surface ozone, a potential ozone problem is in paralel with the uncontrolled urbanization, industralization, transportation and global warming. Air quality data from continuous measurement of O_3 and its main precursors at three different locations were analyzed in terms of diurnal, weekly, seasonal and annual variations. Also, meteorological impacts on surface ozone concentrations in rural and urban areas in Istanbul were evaluated during this study.

In this study, high ozone days are characterized with hourly O_3 concentrations larger than 50 ppb. High ozone days demonstrated a typical diurnal profile with maximum concentrations appearing during afternoon hours and minimum concentrations appearing during rush hours due to NO_x titration from traffic emissions. 24-hour maximum O_3 concentrations were around 23.4 ppb at Göztepe, 37.6 ppb at Kandilli and 40.5 ppb at Büyükada stations. Day time ozone formation presented the “weekend effect” where ozone concentrations for weekend are higher than that on weekday between 0700 and 0900 LST. The probable cause of the weekend ozone effect in early morning particularly in Göztepe Station is related to changes in VOC sensitivity and fresh NO_x emissions. Ozone concentrations are negatively correlated with nitrogen oxides in measurement sites. This result is expected since these pollutants are known precursors of ozone. The presence of maximum occurs in June-July, temperature being a significant controlling factor, whereas the secondary maximum occurs in spring during April-May. Typically, the highest ozone levels in Istanbul are observed at the remote site (Büyükada) which is attributed to the different site characteristics influencing the nocturnal ozone destruction close to the ground. The differentiated temporal ozone variations of at Göztepe station may be ascribed to the great number of vehicles circulating in the area. The NO_x have been measured at this site with the purpose of supporting this hypothesis. These differences in O_3 at rural and urban locations are due to differences in the concentrations of precursor gases, chemical processes and meteorological parameters as observed earlier. It can be seen that the concentrations of O_3 precursors are higher at Kandilli and Büyükada and lower at Göztepe. Both monthly and daily evolutions indicate that the highest ozone concentrations are obtained during spring and summer months in which the optimum conditions for the formation and transport of ozone occur.

The assesment of meteorological variables has shown that the production and destruction of surface ozone are highly related to temperature and wind speeds. In urban and rural areas, emissions of NO decrease ozone concentrations in the absence of solar radiation due to the reaction O_3, NO, NO_2 and NO_x. Conversely, O_3 concentrations show comparatively less diurnal variability in rural areas due to the absence of high NO_x emission sources. Ozone can be produced or destroyed due to VOC/ NO_x ratios (NO_x availability) as well. Here we can not see this ratio since VOC observations are not conducted in rural areas.

According to European Ozone Directive, 90 ppb for 1 h average is set as an information threshold while 120 ppb for 1 h average is set as alert thresholds. The ozone dynamics at three different locations indicate that high ozone concentrations are measured mainly during the summer months at the urban, rural and background stations of Göztepe, Kandilli and Büyükada, with levels that do not exceed the threshold of 120 ppb established in the European Ozone Directive.

To better characterization the transport dynamics that bring polluted air into Kandilli, the HYSPLIT model and cluster analysis were used to perform a series of back-trajectory calculations. Trajectories and cluster analysis clearly show that the dominant wind direction is northwest which proved the air masses are mainly transported from Europa and Balkans to Istanbul.

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APPENDIX A MEASUREMENT SITES

Figure A.1. Göztepe air quality station.

Figure A.2. Büyükada air quality station.

Figure A.3. Kandilli air quality station.