DOKUZ EYLUL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

STUDY ON ATMOSPHERIC OZONE LEVELS IN IZMIR

by
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İZMİR

STUDY ON ATMOSPHERIC OZONE LEVELS IN IZMIR

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by
Yetkin DUMANOĞLU

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İZMİR

Ph. D. THESIS EXAMINATION RESULTS FORM

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Yetkin DUMANOĞLU

STUDY ON ATMOSPHERIC OZONE LEVELS IN IZMIR

ABSTRACT

The objectives of this study were to measure ozone concentrations in air and investigate ozone formation and degradation mechanisms in urban and suburban atmospheres in the city of Izmir. Ozone concentrations were measured at two urban and suburban sites in Izmir, Turkey. In addition to ozone, nitrogen oxides (NO, NO_2, NO_x) were also measured continuously at the suburban station. It was observed that O_3 concentrations were at the lowest levels during rush hours of 07:00-09:00 based on the hourly results of continuous measurement devices. NO_2, resultant of a reaction between traffic based NO and O_3, showed high concentration levels during rush hours (morning time 07:00-09:00 and evening time 19:00-21:00). Highest O_3 concentration levels were observed between May and August during the sampling period. The highest maximum level of European Union standard (180 $\mu g\ m^{-3}$) was exceeded only during that timeframe. Whereas NO_2 concentrations were measured at well below the limit value of 200 $\mu g\ m^{-3}$.

Ozone, NO_2, and volatile organic compounds (VOCs) were also measured by diffusive sampling technique at 16 additional sites representing urban, industrial, and suburban areas in the study area of Izmir. As a result of these measurements, concentration changes due to area and time were noted for pollutants within the scope this study. NO_2, and VOC concentrations were relatively high at urban sites and industrial areas while ozone concentrations were higher at suburban sites. O_3 concentrations were higher at semi-suburban sites compared to other sites. The highest average weekly ozone concentrations were measured at two suburban sites.

Keyword: Air pollution, ozone, nitrogen oxides, volatile organic compound (VOC)

İZMİR’DE ATMOSFERİK OZON SEVİYELERİNİN İNCELENMESİ

ÖZ

İzmir Bölgesinde, kentsel ve yarı kırsal bölgelerde atmosferdeki ozonun seviyeleri ile oluşum ve giderim mekanizmalarının incelenmesi amaçlanmıştır. Kent merkezinde ve yarı kırsal bölgede seçilen iki istasyonda atmosferdeki ozon (O_3) konsantrasyonları ölçülmüştür. Yarı kırsal istasyonda O_3’a ek olarak azot oksitler de (NO, NO_2, NO_x) sürekli ölçüm cihazları ile izlenmiştir. Sürekli ölçüm cihazlarında elde edilen saatlik veriler incelenmiş ve O_3 konsantrasyonlarının trafiğin yoğun olduğu sabah 07:00-09:00 saatleri arasında en alt seviyeleri indiği görülmüştür. Trafik kaynaklı bir kirletici olan NO’nun O_3 ile reaksiyone girmesi sonusunda oluşan NO_2 ise trafiğin yoğun olduğu saatlerde (sabah 07:00-09:00, akşam 19:00-21:00) yüksek konsantrasyonlara sahip olmuştur. Örnekleme dönemi boyunca en yüksek O_3 konsantrasyonları Mayıs ve Ağustos ayları arasında görülmüştür. Avrupa Birliği tarafından belirlenmiş olan 180 $\mu g\ m^{-3}$ saatlik ortalama sınır değeri sadece bu dönemde aşılmıştır. NO_2 konsantasyonları ise limit değer olan 200 $\mu g\ m^{-3}$ ‘ün oldukça altında ölçülmüştür.

Sürekli ölçümlerin yapıldığı iki istasyona ek olarak İzmir ve çevresinde kent merkezleri, sanayi bölgeleri ve yarı kırsal alanları temsil edecek şekilde seçilmiş toplam 16 noktada pasif örnekleme yöntemi ile O_3, NO_2 ve uçucu organik bileşiklerin (VOC) ölçümleri yapılmıştır. Ölçümler sonucunda bu çalışmada incelenen kirleticilerin atmosferdeki konsantrasyonlarının bölgesel ve zamana bağlı değişimleri belirlenmiştir. NO_2 ve VOC gibi kirleticilerin konsantrasyonlarının kent içinde ve sanayi bölgelerinde daha yüksek olduğu görülürken O_3 konsantrasyonları bu bölgelerden uzaklaştıkça yükselmiştir. Yarı kırsal bölge niteliğinde olan istasyonlarda O_3 seviyeleri diğer noktalara göre daha yüksektir.

Anahtar sözcükler: Hava kirliliği, ozon, azot oksitler, uçucu organic bileşikler (VOC)

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CHAPTER ONE
INTRODUCTION

Apart from primary pollutants emitted directly from their sources, a major part of the air pollution in the cities is caused by reaction of these pollutants in the atmosphere leading into the formation of secondary pollutants. Tropospheric ozone is generally considered as one of the most important secondary pollutant which is formed through photochemical reactions.

Tropospheric ozone (O_3) is the predominant pollutant of a group of chemicals called photochemical oxidants, commonly referred to as photochemical smog. Formaldehyde, other aldehydes, and peroxyacetyl nitrate are also present in photochemical smog. All of them are secondary pollutants formed in the atmosphere under conditions of sunlight and high temperature as a result of photochemical reactions involving nitrogen oxides (NO_x), carbon monoxide (CO) and volatile organic compounds (VOCs) as primary pollutant precursors. Sources of these primary pollutants rise mainly from motor-vehicle emissions, stationary combustion sources, and industrial and domestic use of solvents and coatings (Gao, 2007).

Meteorological conditions play an important role in O_3 formation, transfer and dispersion. Variations of local meteorological conditions, such as solar radiation, temperature, wind direction, wind speed, rainfall and relative humidity, can greatly affect the temporal variations of O_3 (Shan, Yin, Zhang & Ding, 2008.

In the Mediterranean basin, high levels of solar irradiation in combination with existing anthropogenic and biogenic O_3 precursors favor photochemical O_3 production. Previous measurements have shown high O_3 concentrations in this region (Ribas & Penuelas, 2004), although such studies are still few and need more detailed temporal and spatial coverage. In line with the Mediterranean regional aspect, identification of O_3 concentration was aimed also in Izmir atmosphere located in Aegean Sea coast.

Human health is negatively affected from O_3 formed by atmospheric reactions. O_3 is a parameter that needs to be closely monitored as it has not only serious human health impact but also damage on agricultural products, forests and toxic effects in the cities (Sather, Varns, Mulik, Glen, Smith & Stallings, 2001).

Legislation regulates the standard levels of tropospheric ozone (O_3), and also recommends that whole list of VOC and NO_x, O_3 precursors be measured so that trends can be analyzed, the efficiency of emission reduction strategies checked, and sources of emission determined (Yang, Ting, Wang, Wingenter & Chan, 2005). When the U.S. Clean Air Act was amended in 1990 it required enhanced monitoring for O_3 and O_3 precursors in areas with serious, severe and extreme 1 hour ozone problems (Sather & Cavender, 2007). Accurate characterization of O_3 precursors is extremely important for understanding tropospheric ozone formation and crafting effective control strategies to better address ozone air quality management issues.

Accordingly, environmental agencies have placed considerable emphasis on O_3 reduction policies involving a reduction in vehicle emissions, which are the main anthropogenic sources of O_3 precursors. However, O_3 has proven difficult to measured and control. Not only is the amount of O_3 measured at any given location the result of global background, regional transport, and local photochemistry, but the chemistry of O_3 formation is complex and, in some cases, non-linear (Heuss, Kahlbaum & Wolff, 2003; Stedman, 2004).

All previous studies in the city of Izmir were performed with an active sampling method. During these studies air samples were collected for short time periods and at limited number of sampling points. While active samplers have the advantage of being able to collect a precise volume of air in a short time, it is difficult to survey the several points simultaneously because they are expensive and require electricity. During this study it was aimed to include several sampling sites to represent the city of Izmir sites.

Diffusive sampling methodology was employed to assess the pollutant levels in the study area instead of conventional on-line monitoring in order to cover a wide study area with a low cost as well as to avoid the necessity of using electric power on the selected sites. The diffusive sampling technique is an alternative monitoring method regarded as a viable option for measuring ambient pollutant concentrations for the purposes of atmospheric chemistry and ecological assessment. This methodology has been successfully used for assessing exposure to ambient pollutant levels.

Ozone measurements were performed in two sampling sites one in the city center and the other in a suburban site. Additional measurements of nitrogen oxides (NO, NO_2 and NO_x) were also performed continuously in the suburban site. Ozone, NO_2 and VOCs were measured through diffusive sampling method in 14 addition sampling sites.

The overall objective of this study is investigation of ozone levels in both urban and suburban atmospheres which is formed by photochemical reactions during sunny hours involving volatile organic compounds (VOCs) and NO_x.

The specific objectives of this study were: (1) measurement of spatial and temporal variations of ozone and its precursors (VOCs and NO_x) via diffusive and on-line sampling. (2) investigating the effect of meteorological parameters and other pollutant concentrations (VOCs and NO_x) on the measured ozone levels.

This study consists of five chapters. An overview and objectives of the study were presented in Chapter1. Chapter 2 reviews the concepts and previous studies related to this work. Experimental work is summarized in Chapter 3. Results and discussions are presented in Chapter 4. Chapter 5 includes the conclusions drawn from this study.

CHAPTER TWO
LITARETURE REVIEW

This chapter presents information on general properties of troposheric O_3 and precursor, health and environmental effects of ozone, and previous studies on O_3 measurements via diffusive sampling methods.

2.1 General Properties of Troposheric Ozone

In the presence of volatile organic compounds (VOCs) and nitrogen oxides (NO_x=NO+NO_2), troposheric O_3 is photo chemically produced and can accumulate to hazardous levels in certain weather conditions (Davidson, 1993).

It is well known that O_3 is an important secondary pollutant in the boundary layer and comes from transport from stratospheric across the troposphere into the boundary layer, or from influx from the free troposphere, or itself. Observational and modeling studies show that elevated rural O_3 levels in summer is the product of long-range transport of O_3 precursors and multi-day photochemical production and accumulation of O_3. The O_3 concentration near the ground (0-2 km) can be affected by large local or regional emissions of precursors 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 local area, the O_3 -mixing ratio below 2 km may have a very different seasonal behavior from that above (Chan, Liu, Lam & Wang, 1998).

Chemistry transport model simulations suggested that in the free troposphere, on average, 20%-40% of the O_3 originates from the stratosphere (Alvim-Ferraz, Sousa, Pereira & Martins, 2006). The rest is photochemically produced within the troposphere, and about half of this latter O_3 is anthropogenic. In the boundary layer in the Mediterranean region during summer, about 90% of the O_3 is formed in situ, with an anthropogenic fraction of about 75% (Ribas et.al, 2004). The photochemical origin and the reactive nature of O_3 produce large temporal and spatial variations in its ambient concentrations. In parallel low O_3 concentrations were noted in areas with dense traffic, possibly the result of O_3 being trapped by NO. O_3 concentrations were low in the city center in both seasons: 20.1 μg m^{-3} in winter and 26.5 μg m^{-3} in summer (Bernard, Gerber, Astre & Saintot, 1999). Concentrations therefore increased with distance from the city center and were highest in suburban areas.

O_3 concentrations depend on a multitude of factors, such as proximity to large source areas of O_3 precursors, geographical location and meteorology (Logan, 1985; Yang et.al., 2005; Wang, Ogden & Chang, 2007,). In evaluating the O_3 production in the rural areas of industrialized countries it was realized that the relationship between O_3 and its precursors is highly nonlinear. Lesser degree of nonlinearity exists at urban levels of O_3 precursors. The photochemical lifetime of O_3 in mid-latitudes in winter is of the order of a few months. Also the lifetimes of O_3 precursors will be considerably greater than the summer values. Therefore, a significant accumulation of O_3 may occur in winter even with slow O_3 production, building up higher O_3 concentrations than those in summer. However, the stratosphere–troposphere exchange (most effective during the late winter and early spring) was the conventional view for the O_3 spring maximum (Varotsos, Kondratyev & Efstathiou, 2001).

Observations in the earth’s surface at different sites in Europe suggest that tropospheric O_3 has increased during the last century (WHO, 2000). Increases in O_3 concentrations since the pre-industrial period are evident in Europe and East Asia, and appear to be associated with large increases in gaseous precursors, which react with solar radiation to produce O_3. There are many rural air pollution-monitoring stations in Europe providing a satisfactory picture of the spatial distribution of surface O_3 concentrations, but there are fewer regular measurements for the Mediterranean region (Millan, Artinano, Alosnso, Navazo & Castro, 1991; Kalabokas, Viras, Bartzis & Repapis, 2000; Ribas et. al., 2004).

O_3 in the troposphere is also of relevance to the climate change issue, as O_3 is a greenhouse gas and by interaction with tropospheric photochemistry O_3 may also influence the atmospheric residence time of other greenhouse gases. The global average radiative forcing due to the increases in tropospheric O_3 since pre-industrial times is estimated to be about 0.35 W m^{-2}. As the forcing due to the increases in concentrations of long-living greenhouse gases since pre-industrial times is about 2.5 W m^{-2}, O_3 contributes about 10-20 % (Leeuw, 2000).

2.2 General Properties of Ozone Precursors

2.2.1 Nitrogen Oxides

Nitrogen oxides are important gaseous air pollutants consisting of the sum of nitric oxide (NO) and nitrogen dioxide (NO_2). They play a major role in atmospheric chemistry, particularly in the formation of secondary air pollutants such as O_3, peroxyacetyl nitrate (PAN), nitrate aerosols, and contributes to environmental acidification.

Nitrogen dioxide (NO_2) is a common secondary pollutant of the urban atmosphere, arising mainly as a by-product of combustion processes, particularly traffic-related. As a supporting study high values of NO and NO_2 were monitored at late nights and early mornings, and showed good correlation with each other. This was linked to rush times in the morning and night. The highest 1h average concentration of NO_x was of 156 μg m^{-3} exceeded the China Ambient Air Quality Standard of 150 μg m^{-3} (Duan, Tan, Yang, Wu & Hao, 2008).

A number of studies have indicated that personal exposure to NO_2 is associated with both chronic and acute adverse health effects on lung function, especially in high-risk populations such as children, the elderly and asthmatics. As a consequence, permitted outdoor concentrations of NO_2 are subject to statutory regulation.

In recent years, NO_2 pollution has become a cause of increasing concern because emission of nitrogen oxides is steadily increasing, especially in urban and industrial areas, despite the growing appreciation by industries and public utilities for reducing

NO_2 emission. Ambient concentrations of NO_2 can vary widely, and rapidly, ranging from 27~30 µg m^{-3} to peaks of 300 µg m^{-3} during particular episodes of high pollution (Heal, Donoghue & Cape, 1999). In order to assess the potential effect of NO_2 on ecosystems, as well as developing strategies for effective control of O_3 and NO_2 pollution, spatial monitoring of NO_2 in the ambient environment is critically important (Sather, Slonecker, Kronmiller, Williams, Daughtrey & Mathew, 2006). Generally NO_x monitoring is carried out using chemiluminescence analyzer.

2.2.2 Volatile Organic Compounds

Volatile organic compounds (VOCs) are a major group of pollutants significantly affecting the chemistry of atmosphere and human health (WHO, 2000). They play an important role in the stratospheric O_3 depletion, formation of highly toxic secondary pollutants (i.e., tropospheric ozone and peroxyacetylnitrate), and enhance the global greenhouse effect (Filella & Penuelas, 2006; Hung-Lung, Jiun-Horng, Shih-Yu, Huo-Hsiung, Sen-Yi & Hung-Lung, 2007). Individual compounds of VOCs have different effects on O_3 formation due to their reaction rate and reaction pathway (Carter & Atkinson, 1987). In order to develop air pollution abatement strategies, it is important to know the sources of VOCs, especially in the Mediterranean area covered in this study is located and high levels of solar radiation in combination with anthropogenic/biogenic O_3 precursors favor photochemical O_3 production (Hung-Lung et al., 2007; Kansal, 2009; Roukos, Riffault, Locoge & Plaisance, 2009). One O_3 measurement study was conducted in the city of Athens like most large European cities, the high level of solar irradiation which is the most important reason, leading to the formation of photochemical pollutants. The average seasonal O_3 levels in surroundings of Athens were 100 µg m^{-3} during summer but maximum hourly values exceeding 350 µg m^{-3} were recorded in the afternoon hours during pollution episodes (Kalabokas et al., 2000). In another O_3 level determination study, O_3 was measured in six sampling periods in 1996-1997, mostly during summer in northern of Greece. Mean values in each sampling periods ranged between 86-96 µg m^{-3} which exceeded the European Union 24 h plant protection standard (70 µg m^{-3}). The background O_3

concentration of 86 μg m^{-3} also exceeded the EU plant protection standard (Glavas, 1999).

However, elevated emissions of VOCs from various anthropogenic sources have not only reduced the air quality within source regions, but also have altered the composition of the atmosphere in remote areas due to processes of medium and long-distance transport. VOCs constitute an important group of air pollutants to be studied as they contribute to some of the most serious environmental problems. Some VOCs exert direct adverse effects on either human health, vegetation or both (Fernandez-Martinez, Lopez-Mahia & Muniategui-Lorenzo, 2001). In addition, VOCs also play a significant role in particle formation and, in the presence of NO_x, they react with OH radicals to form O_3 (Atkinson, 2000) thus modifying the oxidizing capacity of the atmosphere. VOCs are oxidized in the atmosphere through very different mechanisms, for example, alkanes and aromatics react only with hydroxyl radicals (HO) in the gas-phase while alkenes react with HO, O_3 and nitrate radicals (NO_3) (Stockwell, Geiger & Becker, 2001).

Consequently, measurement of VOCs in air becomes necessary: to determine the sources of pollutants and the transport mechanics of pollution, and to study health effects and the compliance of regulatory limits. Ambient VOC species have been investigated in many cities around the world (Derwent, Davies, Delaney, Dollard, Field, Dumittrean, et al, 2000; Na & Kim, 2001; Broderick & Marnane, 2002; Cetin, Odabasi & Seyfioglu, 2003; Na, Kim, Moon, & Moon, 2004; Jorquera & Rappenglück, 2004; Buzcu & Fraser, 2006; Filella et al., 2006; Elbir, Cetin, Cetin, Bayram & Odabasi, 2007). In general, main anthropogenic sources of VOCs are engine exhaust gases of vehicles (gasoline and diesel fuels), solvent and gasoline evaporation, natural gas and liquefied petrochemical gas usage in urban areas (Yasssaa, Meklati, Brancaleoni, Frattoni & Ciccioli, 2001; Na et al., 2004; Grant, Fuentes, Chan, Stockwell, Wang & Ndiaye, 2008) and can be a large contributor in some areas in which ethane, propane, propene, n-pentane, benzene, n-heptane, toluene and n-octane are abundant species (Buzcu et al., 2006; Kansal, 2009). In urban areas several industrial sources i.e., petroleum refining, chemical, printing/

packaging industries and paint industry may also contribute significantly to the ambient VOCs (Tsai, Hsu & Yang, 2004; Kume, Ohura, Amagai & Fusaya, 2008).

Several studies (Muezzinoglu, Odabasi & Onat, 2001; Cetin et al., 2003; Odabasi, Ongan & Cetin 2005; Elbir et al., 2007) have reported the characteristics of VOCs around the city of Izmir. There is a high flow of traffic during the daytime especially during the morning and evening rush hours at certain downtown areas. A recent study conducted near highways with heavy traffic indicated that ambient mono aromatic and alkane concentrations in Izmir were relatively high compared to other cities around the world (Muezzinoglu et al., 2001). There are also many industries i.e., a petroleum refinery, a petrochemical complex, paint and varnish plants, and printing/ packaging industries emitting high quantities of VOCs in Izmir area. In addition to mono aromatics and alkanes, oxygenated VOCs are also emitted from these industries. High levels of oxygenated VOCs measured recently near a petroleum refinery and a petrochemical complex in Izmir and their strong dependency on wind direction indicated the association of these compounds with petrochemical products and petroleum processing (Cetin et al., 2003). Recently a receptor modeling (positive matrix factorization) has been performed to estimate the contribution of specific source types to ambient VOCs concentrations in Izmir (Elbir et al., 2007). Six source factors as gasoline vehicle exhaust, diesel vehicle exhaust+residential heating, paint production/use, degreasing, dry cleaning, and an undefined source were identified for the urban area while three source factors (gasoline vehicle exhaust, diesel vehicle exhaust, and paint production/use) were identified for the suburban site (Elbir et al., 2007).

2.3 Chemistry of Tropospheric Ozone

During the pre-industrial era, the O_3 found in the troposphere came essentially from the intrusion of stratospheric air. The main source of O_3 is the middle stratosphere, and ozone is fed into the lower troposphere by the circulation at a rate determined by the dissipation of planetary and gravity wave field in the stratosphere and mesosphere (Guicherit & Roemer, 2000).

The most active regions of stratosphere-troposphere exchange are in cyclonic regions of the upper troposphere, near jet streams, troughs, and cut-off lows. Stratosphere-troposphere exchange is most effective during late winter and spring. Thus one might expect concentration of tropospheric O_3 to be largest in spring in the absence of significant photochemical production of the gas in the atmosphere. This means that the stratospheric O_3 contribution to the tropospheric O_3 budget is dependent on latitude, tropospheric altitude and time of the year, and that in absence of any significant photochemical production of O_3 in the troposphere, the stratospheric source will dominate (Guicherit et al., 2000).

Recent estimates indicate that stratospheric-tropospheric exchanges only account for 20% of the current total tropospheric O_3 (Guicherit et al., 2000), because now it is mainly produced by complex photochemical reactions involving solar radiation and anthropogenic pollutants.

O_3 plays an important role in controlling the chemistry and chemical composition of the atmosphere. Photo dissociation of O_3 by solar UV radiation produces electronically excited $O(^1D)$ atoms by way of the following reaction

$$O_3 + hv \rightarrow O(^1D) + O_2 \quad \lambda \leq 325 \text{ nm} \qquad \text{Eq.2.1}$$

followed by reaction of the atomic oxygen $O(^1D)$ with water

$$O(^1D) + H_2O \rightarrow HO + HO \qquad \text{Eq.2.2}$$

The oxidation efficiency of the atmosphere is primarily determined by hydroxyl (OH) radicals, because a variety of atmospheric species, including the precursor O_3 namely CO, NO_2 and VOCs are removed from the atmosphere by reaction with OH (Guicherit et al., 2000).

A major parts of the atmospheric O_3 is also produced and destroyed in the troposphere by chemical reactions involving free radicals and furthermore by removal at the Earth’s surface by dry deposition (Guicherit et al., 2000).

O_3 in the troposphere is formed by reactions of CO, CH_4, and non-methane volatile organic compounds (NMVOC) in the presence of NO_x and destroyed reactions with HO_x radicals.

The reactions involved are:

$NO_2 + hv \rightarrow NO + O(^3P)$ $\lambda \leq 400$ nm Eq.2.3

$O(^3P) + O_2 + (M) \rightarrow O_3 + (M)$ Eq.2.4

In the presence of NO, O_3 reacts with NO to reproduce NO_2

$O_3 + NO \rightarrow NO_2 + O_2$ Eq.2.5

In the presence of CO and organic compounds, the reactions involved are

$CO + OH(+O_2) \rightarrow CO_2 + HO_2$ Eq.2.6

$RH + OH \rightarrow R + H_2O$ Eq.2.7

$R + O_2 + (M) \rightarrow RO_2 + (M)$ Eq.2.8

$RO_2 + NO \rightarrow RO + NO_2$ Eq.2.9

$RO + O_2 \rightarrow HO_2 + CARB$ Eq.2.10

$HO_2 + NO \rightarrow OH + NO_2$ Eq.2.11

$NO_2 + hv \rightarrow NO + O(^3P)$ Eq.2.3

$O(^3P) + O_2 + (M) \rightarrow O_3 + (M)$ Eq.2.4

---net

$RH + 4O_2 + 2hv \rightarrow RCHO + H_2O + 2O_3$

where an organic compound (CH_4, NMVOC) is denoted as RH in (Eq.2.7). CARB is either a carbonyl species (RCHO) or a ketone (RCRO). Additional O_3 molecules can be produced from degradation of the carbonyl compounds by reaction with OH or photolysis.

Photochemical loss of tropospheric O_3 is accomplished primarily through the following reactions.

$O_3 + hv \rightarrow O(^1D) + O_2$ $\lambda \leq 325$ nm Eq.2.1

$O(^1D) + H_2O \rightarrow 2OH$ Eq.2.2

$HO_2 + O_3 \rightarrow OH + H_2O + 2O_2$ Eq.2.12

$OH + O_3 \rightarrow HO_2 + O_2$ Eq.2.13

From the reactions given it is obvious that the rate of O_3 production depends on the availability of NO_x (Itano, Bandow, Takenaka, Saitoh, Asayama & Fukuyama, 2007). In some parts of the atmosphere the concentration of NO_x is so small that the O_3 destruction exceeds the O_3 production (Guicherit et al., 2000).

Since O_3 is produced and destroyed in the troposphere by reaction involving HO_x (HO_x =OH+HO_2), cloud effects HO_x chemistry should be considered in this respect. HO_2 radicals will be scavenged efficiently by cloud droplets as a result of acid base dissociation of HO_2 (aq):

$$HO_2(g) \Leftrightarrow HO_2(aq) \qquad \text{Eq.2.14}$$

$$HO_2(g) \Leftrightarrow H^+ + O_2^- \qquad \text{Eq.2.15}$$

Followed by electron transfer between HO_2 (aq) and O_2^-

$$HO_2 + O_2^- + H_2O \rightarrow H_2O_2 + O_2 + OH^- \qquad \text{Eq.2.16}$$

and reaction of O_2^- with O_3(aq)

$$O_2^- + O_3 + H_2O \rightarrow 2O_2 + OH + OH^- \qquad \text{Eq.2.17}$$

OH is depleted by clouds relative to clear sky conditions (Guicherit et al., 2000). This depletion is due in part to direct uptake of OH from the gas-phase which is converted in the atmosphere into OH. The depletion of OH will slow down the loss of NO_x due to scavenging of OH by the reaction

$$NO_2 + OH + (M) \rightarrow HNO_3 + (M) \qquad \text{Eq.2.18}$$

Previous studies showed that NO_x emissions are mainly responsible for O_3 formation in rural areas, whilst VOCs are responsible in urban areas. There is a competition between VOC and NO_x for the OH radical. When [VOC]/ [NO_x] is high, OH will react mainly with VOC (NO_x limited), generating new radicals and accelerating O_3 production. Under these conditions, typical of rural areas, an increase in NO_x concentration accelerates O_3 formation. When [VOC]/ [NO_x] is low, the reaction of OH with NO_x can predominate (VOC limited), removing OH from the VOC oxidation cycle and retarding the further production of O_3. Under these conditions, typical of polluted areas, an increase in NO_x concentration leads to O_3 decrease. Therefore, while increasing of VOC concentration always increases O_3 formation, increasing of NO_x leads to more or less O_3, depending on the prevailing ratio between [VOC] and [NO_x] (Gimeno, Hernandez, Rua, Garcia & Martin, 1999; Guicherit et al., 2000; Sadanga, Matsumoto & Kajii, 2003; Alvim-Ferraz et al.,2006; Toro, Cremades & Calbo, 2006).

The analysis of air pollutants characteristics is very important and necessary to monitoring, forecasting and controlling of pollution. As far as the chemical reactions within pollutants concerned, the chemical coupling of O_3, VOCs and NO_x (NO and NO_2) and the levels of O_3, VOCs, NO and NO_2 are inseparably linked. Regarding this topic, the interaction patterns of primary air pollutants, NO_x, NO, NO_2, VOC and O_3 were investigated. The study carried out by Lu & Wang (2003) was based on the database covering two urban area types (residential area, mixed residential commercial/industrial area) in Hong Kong. Statistical analysis indicating that there was a very strong positive, near linear correlation between NO and NO_x and the negative correlation generally existed between O_3 and NO_x (NO and NO_2).

With regard to the relationship between NO_2 and O_3 concentrations Bernard et al., (1999) compared NO_2 and O_3 levels measured with passive samplers at several sites. They noted an inverse correlation between hourly levels of NO_2 and O_3 (r=-0.74). They also identified an inverse correlation between distance from city center and the NO_2 level during winter and summer, and positive correlation was observed between distance from city center and the O_3 concentrations. These results indicated possible influence of the NO_2 sources on O_3 generation in city center and suburban area.

In line with the importance of NO_2 and VOC affect on O_3, their correlation between each other is considered as important. The correlation between NO_2 and VOC was highly significant and consistent with vehicular emissions, the primary local source of emissions of both pollutants. However, correlations were higher during summer months (r=0.77) than during winter (r=0.53) which could be related to the existence of sources other than traffic during this time of the year, such as emissions of NO_2 from house heating. Supporting this idea, benzene-toluene-xylene-ethyl benzene (BTEX) and nitrogen oxides concentrations were found to be highly significantly correlated (r=0.49), whereas a strong negative correlation between BTEX and O_3 was also observed (r=−0.35) (Parra, Gonzalez, Elustondo, Garrigo, Bermejo & Santamaria, 2006).

In a similar study ambient concentrations of VOCs and NO_2 were measured by means of passive sampling at 40 sampling points in a medium-size city in Northern Spain. Annual mean concentrations of benzene, toluene, ethylbenzene, xylenes, propylbenzene, trimethylbenzenes, and NO_2 were 2.84, 13.26, 2.15, 6.01, 0.59, 1.32 and 23.17 $\mu g\ m^{-3}$ respectively, and found to be highly correlated. Their spatial distribution showed high differences in small distances and pointed to traffic as the main emission source of these compounds. The lowest levels of VOC and NO_2 occurred during summer, owing to the increase in solar radiation and to lower traffic densities (Parra, Elustondo, Bermejo & Santamaria, 2009).

2.4 Spatial and Temporal Variation of Troposheric Ozone Concentrations

O_3 is a reactive atmospheric chemical that influenced in many ways by its sources, sinks, and chemical reactions. As a result of the complex series of reactions enhanced by temperature and sunlight, O_3 exhibits significant variations in space and time (hourly, daily, seasonally and annually) (Ribas et al., 2004).

2.4.1 Diurnal Pattern of Tropospheric Ozone Concentration

A good way of unraveling the dynamics of O_3 is by examining its diurnal pattern. Concerning the diurnal variation of O_3, the maximum were observed at daytime while the difference between night and day became considerable during summer months (Kalabokas et al., 2000; Ribas et al., 2004).

The diurnal variation of O_3 showed a typical pattern for polluted urban area, characterized by high concentrations during mid or afternoon, low concentrations during late night or early morning, and big variation magnitude between daytime and nighttime (Shan et al.,2008). The minimum value of yearly average appeared at 6:00 a.m., while that of summer average appeared at 5:00 a.m. Most diurnal maximums in the year appeared in summer, which caused by the high O_3 product rate due to favorable meteorological conditions during daytime in summer (Kalabokas et al., 2000; Duan et al., 2008).

O_3 concentration slowly decreased during nighttime due to the chemical loss by NO and deposition process. However, it started rapidly coinciding with the increase of solar radiation after sunrise by photochemical production. Therefore, the time of sunrise was a turning point of diurnal O_3 variation trend. Both summer average and yearly average showed maximum values at 14:00, as well as summer and yearly maximum, which was the result of solar radiation diurnal variation. Duan et al., (2008) identified throughout their measurements made during August in Beijing, China that O_3 always peaked at 13:00-16:00 in the afternoon. The highest 1h maximum O_3 concentration of 240 $\mu g\ m^{-3}$ was observed at 14:00 on August.

The diurnal cycle of chemical formation and destruction is driven by the pattern of NO_x and VOC as well as solar radiation. The rural site in Athens during all seasons there was a strong diurnal variation, which became more distinct in summer, where the afternoon values were almost 3 times higher than the nocturnal ones. The nocturnal values did not vary significantly from one season to the other. This was not the case for the afternoon values, which had a summer/winter ratio of the order of 2 with the summer concentrations varied between 120 and 130 $\mu g\ m^{-3}$ for about 7 h (12–19 h). The spring afternoon values were higher than the autumn ones and practically lied almost half way between autumn and summer. This sharp contrast of O_3 between day and night in urban site was likely to be attributed almost exclusively to physical processes as the influence of the chemistry is expected to be minimal. The reason for this is that nitrogen oxides at the site did not have concentrations high enough in order to influence the O_3 as the mean monthly values. Therefore, the basic reason of the low night values in rural site was the physical destruction of O_3 by dry deposition enhanced by the nocturnal inversion (Kalabokas et al., 2000).

2.4.2 Seasonal Variation of Tropospheric Ozone Concentration

Photochemical reaction and meteorological parameters affected seasonal variation of O_3 concentrations as well as diurnal variations of them.

So in high and mid-latitudes there are two seasonal maxima. The spring maximum is formed partly from enhanced photochemistry in spring after a wintertime accumulation of air pollutants (Penkett & Brice, 1986) and partly from a stratospheric flux of O_3. The summer maximum is produced by photochemical activity in large pollutant source areas (Logan, 1985; Gimeno et al., 1999) by changing weather conditions (Kalabokas et al., 2000; Shan et al., 2008). As expected, in the study made by Bernard et al. (1999) the mean seasonal O_3 concentrations were higher in summer than the ones in winter, as a result of the climatic conditions. The mean O_3 levels at the 22 sites used for both of the measurement periods were between 24.6-97.3 $\mu g\ m^{-3}$ for summer and between 12.9-42.2 $\mu g\ m^{-3}$ for winter.

The seasonal variation of rural O_3 showed a strong characteristic with summer values being almost double than winter concentrations. Measurements of surface O_3 clearly show a seasonal cycle with a distinct maximum usually in spring-summer which generally occur during July and August and minimum values in October-December periods (Varotsos, Kondratyev & Efstathiou, 2001, Dell-Era, Brambilla & Ballarin-Denti, 1998; Monks, 2000; Yuska, Skelly, Ferdinand, Stevenson, Savage, Mulik et al., 2003).

2.5 Effects of Meteorological Parameters on Ozone and Ozone Precursors

It is well-known that photochemical formation of O_3 through reactions with NO_x, CO and other reactive compounds is increasing with higher air temperature and solar radiation and decreasing in cloudy and rainy periods (Koutrakis, Wolfson, Bunyaviroch, Froehlich, Hirano & Mulik, 1993). Other important parameters are the wind direction and wind speed. Warm and sunny weather conditions enhances the O_3 concentrations because, the higher solar radiation increase photochemical processes, and high temperature results in rapid chemical O_3 formation (Sanz, Calatayud & Sanchez-Pena, 2007).

Temporal variations of surface O_3 and related meteorological factors have been simultaneously studied around the world (Koutrakis et al., 1993; Camalier, Cox & Dolwick, 2007; Saborit & Cano, 2007). These studies have comprehensively analyzed the factors and processes affecting O_3 formation, accumulation, and transport. Periods of high O_3 concentrations are often associated with intense solar radiation, high temperature, stagnant air, and minimum rainfall, which are favorable for photochemical production of O_3 and the accumulation of pollutants in the atmospheric boundary layer (Millan, Mantilla, Salvador, Carratala, Sanz, Alonso et al., 2000; Sanz et al., 2007).

In order to quantitatively assess the influence of meteorological factors on O_3, a regression analysis of the daily averaged values was carried out (Bernard et al., 1999; Wang et al., 2007; Shan et al., 2008). Based on the results of those analyses, O_3 showed negative correlation with relative humidity and positive correlation with temperature, sunshine duration, and wind speed.

High wind speeds often imply high speed transport of air masses, which resulted in rapid dilution of primary pollutants. However, the effect of wind speed on O_3 is much more complex. Shan et al. (2008) noted that wind speed showed positive contribution on O_3 production throughout the year. This result might suggest that the intrusion of stratospheric O_3 and long-range transport might be a reason for the surface O_3 pollution (Shan et al., 2008; Duan et al., 2008).

2.6 Health and Environmental Effects of Ozone

Besides its important role in the physicochemical processes of the troposphere, O_3 is also important because of its strong oxidant properties, which may cause damages to humans, animals, vegetation, and materials at certain concentration levels (Scheeren & Adema, 1996; Yuska et al., 2003; Ras, Marce & Borrull, 2009; Leeuw, 2000). O_3 exposure affects the structure and function of the respiratory tract in several ways. There is evidence from epidemiological studies that significant changes of lung function occurred in many individuals exercising outdoors during photochemical pollution episodes (Krochmal & Kalina, 1997; Shan et al., 2008). Photochemical pollution causes small increases in asthma morbidity and even mortality (Scheeren et al., 1996; Yuska et al., 2003; Ras et al., 2009). The effects of O_3 on plants may include visible leaf injury, reduced plant growth, decreased economic yield, and changes in crop quality (Leeuw, 2000; Alvim-Ferraz et al., 2006). Ambient O_3 concentrations in rural and forested areas cause high levels enough to produce phytotoxic effects in native vegetation (Dell-Era et al., 1998; Yuska et al., 2003; Krzyzanowski, 2004; Sanz et al., 2007).

According to study (Yuska et al., 2003) O_3 effect on forest ecosystems could be synergistic to other stress factors as climate, acid mists, nitrogen deposition and nutrient leaching from the soils. Natural O_3 concentration is dependent on altitude, particularly in mountain sites where it is also affected by exchange processes of air masses among low troposphere, free troposphere and stratosphere. Based on the correlation, most sites clearly defined the relationship that O_3 concentrations increased with elevation.

O_3 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. O_3 affects materials such as natural and synthetic rubbers, coating and textiles. However, there are today serious gaps in knowledge on the mechanisms of damage, the attribution of O_3 to damage in comparison to others and the economic evaluation of such damages (Leeuw, 2000).

Due to the above atmospheric reasons, O_3 guidelines and standards proposed are already used by international organizations like the World Health Organization (WHO), or state authorities (European Union, United States). Limit values of O_3 for human health are 200 µg m^{-3} (1-h average) and 120 µg m^{-3} (8-h average) while for vegetation protection the guidelines are 200 µg m^{-3} for 1-h average and 70 µg m^{-3} for 24-h average proposed by WHO (WHO, 2000). The limit values applied in Turkey and in the world are given in Table 2.1.

A number of studies have indicated that personal exposure to NO_2 is associated with both chronic and acute adverse health effects on lung function, especially in high-risk populations such as children, the elderly and asthmatics. As a consequence, NO_2 as primary pollutant has significant impact on O_3 production mechanisms and NO_2 ambient concentrations are subject to statutory regulation limits (Heal et al., 1999) (Table 2.1).

Table 2.1 Limit values for O_3 and NO_2 (µg m^{-3})

Pollutant	Limit Value (Turkey)[a]		Limit Value (WHO)[b]	Limit Value (EU)[c]	Limit Value (USEPA)[d]
	Hour	Annual			
NO_2	200 (1 hour)	40	200 (1hour) 40 (annual)	200 (1hour) 30[a] (annual)	100 (annual) 30[a] (annual)
O_3	120 (8 hours)[b]	-	120 (8 hours)	180 (1hour) 120 (8 hours)	235 (1hour) 157 (8 hours)

[a] National Air Quality Standard for Turkey, 2008 (2024 target value).

[b] WHO (World Health Organization). Guidelines for air quality. Geneva; 2000).

[c] EU (European Union). Council Directive 1999/30/EC, EU (European Union). Council Directive 2002/3/EC.

[d] USEPA, National Ambient Air Quality Standards (NAAQS); 2006.

VOCs may also represent a potential threat to human health. Although short-term exposure to particular concentrations of some VOCs present in air is not considered acutely harmful to human health, long-term exposure may results in mutagenic and carcinogenic effects. Exposure to VOCs can cause such acute and chronic effects as respiratory damage and can therefore increase, for example, the risk of asthma. They can also affect the nervous, immune and reproductive systems. Classic neurological symptoms associated with VOCs are feelings of fatigue, headaches, dizziness, nausea, lethargy and depression (Ras et al., 2009).

2.7 Ozone Measurement with Diffusive Sampling

Comparability of air quality data on a national scale is usually not satisfactory due to two reasons: (1) site selection criteria in local monitoring network is not uniform; and (2) different analytical methods and equipments are used (Krochmal et al., 1997. These difficulties can be overcome by the use of a diffusive sampling method (Zabiegala, Gorecki, Przyk & Namiesnik, 2002). In this type of sampling, substances of interest are collected in a diffusive sampler. There is a clear need for rapid, effective and low-cost integrated methods that would allow direct monitoring of the fate and concentrations of chemical pollutants in the environment, as well as evaluation of their effects and assessment of the hazards these chemicals pose to the environment and to the human health. Many of these requirements are fulfilled by diffusive sampling techniques.

A diffusive sampler is a device which is capable of taking samples of gas or vapor pollutants from the atmosphere at a rate controlled by a physical process such as diffusion through a static air layer or permeation through a membrane, but which does not involve the active movement of the air through the samplers (Brown, Harvey, Purnell & Saunders, 1984). The sampling rate is controlled by the rate of diffusion of the substance through an air layer inside the sampler, according to Fick's law of diffusion (Palmes, Gunnison, Di Mattio, & Tomczyk, 1976). The procedures for determining the performance characteristics of a diffusive sampler for outdoor monitoring have been published as EN 13528-1 and EN-13528-2 Pats 1 and 2 (EN 13528-1, 2002, EN13528-2, 2002) (Saborit et al., 2008).

The theoretical basis for diffusive sampling is well established. The mass of an analyte migrating by diffusion to an adsorbent is given by Fick's first law Eq.2.19:

$$m_i = D_i \cdot \frac{A}{l} \cdot (c_i - c_0) \cdot t \qquad \text{Eq. 2.19}$$

where:

m_i= mass of the compound i found on the sorbent (pg)

D_i= diffusion coefficient of the compound i in air (cm^2 min^{-1})

A = cross-sectional area of the sampler (cm^2)

l = length of the diffusion zone (cm)

c_i = ambient concentration of the compound i (µg m^{-3})

c_o = concentration of the analyte above the sorbent surface

t = time of exposure (min)

Once the measurement session is completed diffusive sampling very often significantly simplifies analytical procedures, as it generally combines sampling and sample preconcentration into a single step. Thus, with a few exceptions, diffusive sampling shortens the time between sample collection and analysis, improving the response time of the entire system (Gorecki & Namiesnik, 2002).

Diffusive samplers (also called passive samplers) can be placed at any location and left unattended during sampling as no pumping of air or electricity needed (Krochmal et al., 1997; Kume et al., 2008). Diffusive samplers can also be transferred before and after exposure and stored for periods of at least several weeks.

In the occupational environment, it is more user-friendly, less inclined to influence worker behavior and more amenable to self-assessment of worker exposure. In the ambient environment, it is easier to deploy and less susceptible to damage or theft. However, there are also disadvantages. The main one is a requirement to determine the effective sampling rate of the sampler itself (since the sampling rate is governed by the geometry of the sampler not an attached pump) (Tang & Lau, 2000). Ideally, the uptake rate of a diffusive sampler is a constant, since it should depend only on the geometry of the sampler and the individual pollutant vapor, which has a particular diffusion coefficient in air. In practice, the uptake rate may vary slightly with changes in pollutant concentration, exposure time, atmospheric temperature, pressures, humidity, and turbulence (Brown et al., 1984; Gorecki et al., 2002). The successful practical application of diffusive sampling to ambient air requires an understanding of the operating principles of diffusive sampling and an evaluation of the environmental factors which may affect sampler performance (Brown, 2000; Krupa & Legge, 2000). Krochmal et al. (1997) have determined that relative humidity (ranging from 10 to 80%) and temperature (ranging from 0 to 40 °C) at typical ambient O_3 levels (40-100 ppb) do not influence sampler performance. By using a protective cup which acts as both a wind screen and a rain cover, they were able to obtain a constant collection rate over a wide range wind speeds (Koutrakis et al., 1993).

These positive characteristics indicate that diffusive samplers are suitable for determination of the spatial distribution of gases over large areas, checking atmospheric transport and deposition models, monitoring studies, establishing ambient air quality monitoring networks, human health (personal monitoring) and mapping concentrations in cities (Cruz & Campos, 2002; Carmichael, Ferm, Thongboonchoo, Woo, Chan, Murano, et al., 2003; Cox, 2003; Cruz, Vania, Campos, Silva & Tavares, 2004).

Diffusive sampling has few disadvantages, one of which is the relatively low sampling rate necessitating long sampling times at low concentrations. However, this feature can also be viewed as an advantage of the technique, as it makes it easy to determine time-weighted average (TWA) concentrations of the analytes (Krochmal et al., 1997; Gerboles, Buzica, Amantini & Lagler, 2006; Parra et al., 2006). In the overall assessment of the pollutant impact on human health, TWA concentrations are more useful than short-term concentrations, as they reflect the long-term action of these compounds (Zabiegala et al., 2002).

There are four main types of diffusive samplers: Palmes tube, radial diffusive sampler, badge and double-ended badge (Plaisance, Gerboles, Piechocki, Detimmerman & Saeger, 2007). Among these samplers, radial diffusive sampler has been distinguished. These samplers consist of a coaxial system in which a cylindrical adsorbing cartridge is housed inside a cylindrical diffusive barrier; the diffusion path is parallel to the cartridge radius. A larger diffusive surface along with the short distance between the diffusive barrier and adsorbing surface result in a much higher effective sampling rate compared to their axial counterparts. This makes radial diffusive samplers compatible with low concentration for short duration sampling—an application area previously unsuitable for diffusive devices. Radiello as a radial symmetry diffusive sampler, were evaluated for its potential for ambient air quality monitoring (Bruno, P., Caputi, M., Caselli, M., Gennora, G. & Rienzo, M., 2005; Parra et al., 2006; Plaisance, Gerboles, Piechocki, Detimmerman & de Saeger, 2007). It is also used for VOC sampling (Bates, Gonzales-Flesca, Sokhi & Cocheo, 2000; Simon, Baer, Torres,Olivier, Meybeck & Massa, 2004; Bruno et al., 2005; Pennequin-Cardinal, Plaisance, Locoge, Ramalho, Kirchner & Galloo, 2005; Strandberg, Sunesson, Olsson, Levin, Ljungqvist, Sundgren, Sallsten & Barregard, 2005; Martin, Duckworth, Henderson, Swann, Granshaw, Lipscombe & Goody, 2005; Roukos et al., 2009; Parra et al., 2006), O_3 sampling (Plaisance et al., 2007; Saborit et al., 2007; Buzica, Gerboles & Plaisance 2008) and NO_2 sampling (Gair and Penkett, 1995; Simon et al., 2004).

According to the principles of Radiello diffusive sampling; the O_3 sampler consists of an adsorbing cartridge is formed by a micropore polyethylene tube filled with silica gel coated with 4, 4’-dipyridylethylene and closed at one end by a polytetrafluoroethylene (PTFE) cap. Upon exposure, acid-catalysed ozonolysis of 4,4’-dipyridylethylene leads to 4-pyridylaldehyde (Figure 2.1). Silica gel ensures the presence of water, necessary to complete ozonolysis reactions. The NO_2 sampler cartridge is made of mycroporous polyethylene coated with triethanolamine (TEA). NO_2 is chemiadsorbed onto TEA as nitrite ions. For the VOCs sampling stainless steel adsorbing cartridge is filled with activated charcoal.

The producer of diffusive samplers suggests the exposure time according to pollutants. In outdoor environment, where typical O_3 concentrations range from 2 to 400 µg m^{-3}, the producer suggests exposure time from 24 hours to 14 days. The ideal range is from 3 to 7 days. For the NO_2 sampler exposure up to 15 days is feasible but if relative humidity is higher than 70% for the entire sampling duration it is not advisable to sample for more than 7 days. VOCs cartridge has a very large loading capacity: about 80 mg, corresponding to an overall VOCs concentration of 3,000-3,500 mg m^{-3} sampled for 8 hours or 70,000-80,000 µg m^{-3} sampled for 14 days.

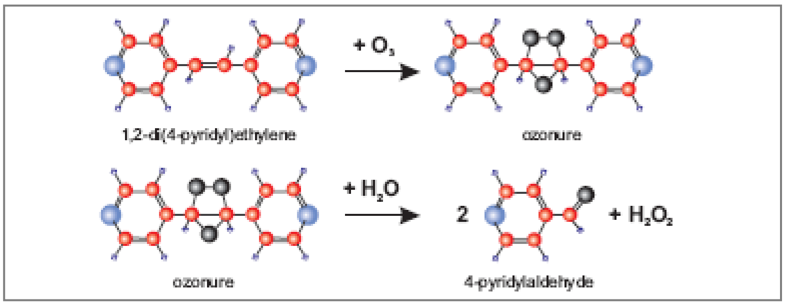

Figure 2.1 O_3 reaction taking place in Radiello cartridge.

The diffusive sampling method is being increasingly used because it provides a simple and inexpensive alternative to online monitoring methods for the determination of air pollution levels and in particular for the screening of air quality in urban or regional areas (Santis, Allegrini, Fazio, Pasella & Piredda, 1997; Dell-Era et al., 1998; Ballach, Greuter, Schultz & Jaeschke, 1999; Heal et al., 1999; Tang, Lau, Brassard & Cool, 1999; Glasius, Carlsen, Hansen & Lohse, 1999; Yuska et al., 2003; Cruz et al., 2004; Gerboles et al., 2006a; Saborit et al., 2007; Sanz et al., 2007; Saborit & Cano. 2008; Buzica et al., 2008). As a supporting study Saborit et al., (2007) aimed to study the performance of diffusive samplers, to compare their results with the ones obtained with an UV-photometric O_3 analyzer in order to validate the diffusive sampler technique to study ground level O_3 in the area of interest. In a similar study Yuska et al., (2003) studied use of diffusive sampling devices to evaluate ambient O_3 concentrations in Pennsylvania. Diffusive samplers and online O_3 monitoring equipments (at 6 sites co-located with the diffusive samplers) were utilized. The relationship between seasonal O_3 concentrations measured with diffusive sampling devices versus the online analyzer showed a highly significant positive correlation (Bernard et al., 1999; Cruz et al., 2004).

Diffusive sampler usage in assessing the ecological effects of tropospheric O_3 has significantly increased in recent years (Manning, Krupa, Bergweiler, & Nelson, 1996; Krupa et al., 2000; Sanz et al., 2007). In the framework of the activities O_3 measurements were recommended, with the following objectives: to produce information on ambient air quality in biological and forest ecosystems and to evaluate the potential risk to biological and forest ecosystems (Dell-Era et al., 1998; Yuska et al., 2003; Saborit et al., 2008). Passive samplers are useful tools for monitoring exposure of ecosystem components to gaseous pollution on different spatial scales, and to verify atmospheric transport and chemistry models and their extension over remote areas (Cox, 2003).

2.8 Maximum Incremental Reactivity (MIR)

The relative contributions of VOCs to O_3 formation vary from one compound to another by virtue of differences in reactivity and structure, since these factors influence the rate of oxidation and the precise oxidation pathway (i.e. the degradation mechanism) (Na, Kim & Moon, 2003, Derwent, Jenkin, Passant & Pilling, 2007).

The volatile organic compounds (VOCs) are emitted into the atmosphere at different rates with different reaction mechanism. Thus, VOCs can differ significantly in their contribution on O_3 formation (Carter et al., 1987; Bowman & Seinfeld, 1994). The contribution of VOCs to the production of the photochemical O_3 is related to their reaction with hydroxyl radicals and O_3 in the complex photo-oxidation mechanism (Na et al., 2003). These differences in effects on O_3 formation are referred to as the O_3 reactivities of the VOCs (Carter, 1994). While a variety of reactivity measures have been proposed, they are usually studied at smog chamber and developed using box model calculations (Carter, 1994; Kelly & Chang, 1999; Hakami, Harley, Milford, Odman & Rusell, 2004; Chang, Chen, Lin, Yuan & Liu, 2005). This has given rise to definition of scales of so-called reactivity of O_3

formation potential of which the most widely published and applied are the Maximum Incremental Reactivity (MIR) scale (Carter & Atkinson, 1987, 1989; Chang & Rudy, 1990; Carter, 1991, 1994; Bowman & Seinfeld, 1995; Kahn, Yang & Russell, 1999; Chang et al., 2005), developed by Carter and co-workers to assess O_3 formation over periods of up to a day in urban scenarios in the USA (Carter, 1994, 1995; Carter, Pierce, Luo, & Malkina, 1995).

The maximum incremental reactivity (MIR) of a VOC compound is defined as the amount of O_3 formed per quantity of an individual VOC compound (i) added to the VOC mixture of a given air parcel:

$$MIR_i = \frac{\Delta_i O_3}{\Delta[VOC_i]} \qquad \text{Eq.2.20}$$

where $\Delta_i O_3$ is the change in maximum O_3 concentration that occurs from the presence of the VOC component i; and $\Delta[VOC_i]$ is the incremental change in concentration of the VOC component i. MIR values reported by Carter (2008) and have been used in the present study to calculate the O_3 formation potentials of VOCs are listed in Table 2.2 for specific organic groups. Alkanes and alkenes including isoprene, trans-2-pentene and cis-2-pentene have the highest three reactivities. Among aromatic compounds 1,2,3-trimethylbenzene, 1,3,5-trimethylbenzene and o-xylene among halogenated VOCs cis-1,3-dichloropropene, cis-1,2,-dicholopropene and trichloroethene have the highest three reactivities. Methyl isobutyl ketone has the highest reactivity among oxygenated groups. Aromatic group is the one with highest reactivity within organic groups. While halogenated group has the lowest reactivity.

To estimate the O_3 forming potential (OFP) of the major VOC species the maximum incremental reactivity (MIR, g O_3/g VOCs) was often used (Carter et al., 1989; Carter, 1994; Hsieh, Chang & Kao, 1999; Stockwell et al., 2001; Duane, Poma, Rembges, Astorga & Larsen, 2002; Na, Kim & Moon, 2002; Hakami et al., 2004; So & Wang, 2004; Hung-Lung et al., 2007).

Table 2.2 Listed of maximum incremental reactivity of VOCs (Carter, 2008)

	MIR [a]		MIR [a]		MIR [a]
Alkanes and alkenes		Aromatic VOCs		Halogenated VOCs	
Isoprene	10.48	1,2,3-Trimethylbenzene	11.94	cis-1,3-Dichloropropene	3.66
trans-2-Pentene	10.47	1,3,5-Trimethylbenzene	11.75	cis-1,2-Dichloroethene	1.66
cis-2-Pentene	10.28	o-Xylene	9.73	Trichloroethene	0.61
1-Pentene	7.07	1,2,4-Trimethylbenzene	8.83	Chlorobenzene	0.31
Methylcyclopentane	2.05	m-Ethyltoluene	7.39	1,2-Dichloroethane	0.21
n-Propylbenzene	1.96	m-Diethylbenzene	7.08	1,2-Dichlorobenzene	0.171
3-Methylpentane	1.69	m,p-Xylene	5.78	1,1,2-Trichloroethane	0.082
Methylcyclohexane	1.56	n-butylbenzene	5.55	Tetrachloroethene	0.029
3-Methylhexane	1.5	o-Ethyltoluene	5.54	Chloroform	0.02
2,4-Dimethylpentane	1.46	p-Isopropyltoluene	4.41	1,1,1-Trichloroethane	0.005
Iso-pentane	1.36	Isopropylbenzene	4.39	Carbon tetrachloride	-
2,3-Dimethylpentane	1.25	p-Ethyltoluene	4.39	Bromochloromethane	-
n-Pentane	1.22	p-Diethylbenzene	4.39	Dibromomethane	-
2,2,4-Trimethylpentane	1.2	Toluene	3.93	Bromodichloromethane	-
Cyclohexane	1.14	Naphthalene	3.28	Dibromochloromethane	-
3-Methylheptane	1.12	Ethylbenzene	2.96	Bromoform	-
2-Methylhexane	1.09	sec-butylbenzene	2.29	1,1,2,2-Tetrachloroethane	-
n-Heptane	0.97	Styrene	1.66	1,3-Dichlorobenzene	-
2-Methylheptane	0.97	Benzene	0.69		
2,3,4-Trimethylpentane	0.95			Oxygenated VOCs	
n-Octane	0.8			Methyl isobutyl ketone	3.78
n-Nonane	0.68			Butyl acetate	0.77
n-Decane	0.59			Ethyl acetate	0.59
n-Undecane	0.52				

[a] MIR denotes maximum incremental reactivity (g O_3/g VOCs)(Carter, 2008)

CHAPTER THREE
MATERIALS AND METHODS

The methods of experimental studies and data analyses were discussed in this chapter.

3.1 Study Area

The city of Izmir is the third biggest urban agglomeration in Turkey. The city with a 3.4 million population and sizeable economic activities including many industries emit high quantities of air pollutants on the Aegean Sea shoreline of Turkey (Elbir et al., 2007). Izmir is located in a basin surrounded by mountains of approximately 1 000–1 500 m in height, with only the west end open to the Aegean Sea. Izmir is a city having high level of pollution during certain periods with its population more than three million and high number of industrial zones. On the other side, Aliaga region has continuous and high level of air pollution during the whole year due to its refinery, petrochemical and iron and steel plants which also affects Izmir atmosphere. Kemalpasa region can also be considered as important for Izmir air pollution with its close location to Izmir and industrial zone. In addition to that industrial plants located in metropolitan area (Bornova, Cigli, Gaziemir), residential heating are also major contributors for air pollution. The traffic of Izmir as third largest city of Turkey should also be monitored as another air pollution source.

The meteorological data i.e. wind speed and direction, relative humidity, temperature, and solar radiation needed to investigate relations between pollutant concentrations and meteorological parameters was obtained from four meteorological stations located in the study area. These stations are located in Aliağa, Güzelyalı, Gaziemir (Adnan Menderes Airport) and Urla. The wind speed and direction, relative humidity and temperature had been measured at each station while solar radiation had been measured only at meteorology station in Izmir Institute of Technology, Urla. Summary of meteorological parameters during sampling periods were given in Table 3.1-3.4 for each station.

The annual average temperature was around 15 °C and the difference between warmer and colder months were about 20°C. Seasonal average values for humidity were 42% in summer and 65% in winter. There were not significant differences in wind speed at winter and summer seasons. Annual average wind speed was 3 m s^{-1} in the city. In the study area where the Mediterranean climate dominates the average solar radiation was 1.8 W cm^{-2} in winter whereas the summer average increased to 4.1 W cm^{-2}. The major air movements over the area are mainly from a northerly direction in summer. However, the predominant wind directions in winter are southerly.

Table 3.1 Summary of meteorological parameters for Aliaga station

Sampling Periods		**Temperature (°C)**	**Relative Humidity (%)**	**Wind Speed (m s^{-1})**
1	22-29 January 2007	10.0	55	5.2
2	05-12 February 2007	10.4	65	3.4
3	19-26 February 2007	9.0	71	3.1
4	09-19 March 2007	10.6	59	4.2
5	19-26 March 2007	15.1	59	5.7
6	02-09April 2007	13.7	58	5.0
7	16-23April 2007	15.8	55	4.9
8	01-08 May 2007	19.7	54	3.2
9	15-22 May 2007	20.3	50	3.5
10	21-28 June 2007	30.1	43	2.5
11	05-12 July 2007	27.9	40	3.3
12	19-26 July 2007	30.8	40	3.2
13	02-10 August 2007	25.6	55	3.2
14	16-23 August 2007	28.9	49	3.5
15	26 September-02 October 2007	22.2	55	3.0
16	02-09 October 2007	21.6	63	2.4
17	16-23 October 2007	17.4	57	2.8
18	30 October-06 November 2007	16.6	73	2.4
19	27 November 2007-04 December 2007	10.4	67	3.3
20	04-12 December 2007	11.2	79	3.1
21	18-25 December 2007	5.2	70	3.1
22	08-15 January 2008	6.0	66	2.2
23	25 Janury-01 February 2008	5.0	58	4.2
24	06-14 February 2008	6.5	68	5.0
25	18-25 February 2008	7.7	56	3.0
26	03-10 March 2008	9.6	65	3.5
27	17-25 March 2008	15.8	67	5.4
28	31 March-07 April 2008	12.9	69	2.6
29	14-21 April 2008	18.7	55	2.8

.

Table 3.2 Summary of meteorological parameters for Güzelyalı station

Sampling Periods		**Temperature (°C)**	**Relative Humidity (%)**	**Wind Speed (m s^{-1})**
1	22-29 January 2007	13.0	57	3.6
2	05-12 February 2007	11.0	63	2.6
3	19-26 February 2007	10.5	69	2.4
4	09-19 March 2007	11.9	57	2.9
5	19-26 March 2007	15.1	59	3.3
6	02-09April 2007	14.9	61	4.8
7	16-23April 2007	17.2	55	4.2
8	01-08 May 2007	21.2	49	3.6
9	15-22 May 2007	21.0	41	3.2
10	21-28 June 2007	32.1	35	2.6
11	05-12 July 2007	29.4	37	2.6
12	19-26 July 2007	32.4	36	2.9
13	02-10 August 2007	26.9	51	2.8
14	16-23 August 2007	30.1	45	2.7
15	26 September-02 October 2007	24.6	47	2.8
16	02-09 October 2007	22.5	60	2.3
17	16-23 October 2007	12.8	62	2.6
18	30 October-06 November 2007	18.2	72	2.3
19	27 November 2007-04 December 2007	12.0	63	2.3
20	04-12 December 2007	11.8	79	2.3
21	18-25 December 2007	6.3	65	1.8
22	08-15 January 2008	7.2	61	1.7
23	25 Janury-01 February 2008	6.3	53	2.4
24	06-14 February 2008	8.3	64	2.4
25	18-25 February 2008	9.0	54	2.0
26	03-10 March 2008	10.9	61	2.3
27	17-25 March 2008	17.0	60	3.4
28	31 March-07 April 2008	13.7	65	2.1
29	14-21 April 2008	20.6	46	2.6

Table 3.3 Summary of meteorological parameters for Adnan Menderes station

Sampling Periods		**Temperature (°C)**	**Relative Humidity (%)**	**Wind Speed (m s^{-1})**
1	22-29 January 2007	9.2	59	4.7
2	05-12 February 2007	8.5	66	3.9
3	19-26 February 2007	9.0	71	4.3
4	09-19 March 2007	10.3	59	6.6
5	19-26 March 2007	12.8	61	5.0
6	02-09April 2007	13.1	59	4.9
7	16-23April 2007	16.0	53	4.2
8	01-08 May 2007	19.9	48	5.0
9	15-22 May 2007	19.4	42	4.0
10	21-28 June 2007	31.4	38	4.5
11	05-12 July 2007	28.4	38	5.2
12	19-26 July 2007	32.5	37	5.8
13	02-10 August 2007	26.6	52	5.6
14	16-23 August 2007	29.7	46	5.5
15	26 September-02 October 2007	23.2	50	4.9
16	02-09 October 2007	21.8	61	3.9
17	16-23 October 2007	16.5	61	3.7
18	30 October-06 November 2007	16.8	72	3.1
19	27 November 2007-04 December 2007	9.7	65	4.1
20	04-12 December 2007	9.9	79	3.5
21	18-25 December 2007	6.0	69	
22	08-15 January 2008	4.2	65	3.9
23	25 Janury-01 February 2008	3.9	59	1.4
24	06-14 February 2008	6.8	65	6.3
25	18-25 February 2008	6.3	54	3.8
26	03-10 March 2008	12.7	60	2.8
27	17-25 March 2008	14.6	58	4.5
28	31 March-07 April 2008	11.3	59	3.1
29	14-21 April 2008	16.9	46	2.7

Table 3.4 Summary of meteorological parameters for Izmir Institute of Technology station

Sampling Periods		**Temperature (°C)**	**Relative Humidity (%)**	**Wind Speed (m s^{-1})**	**Solar Radiation (W cm^{-2})**
1	22-29 January 2007	13.1	65	5.2	1.3
2	05-12 February 2007	10.4	69	3.9	3.6
3	19-26 February 2007	9.2	73	3.8	2.0
4	09-19 March 2007	11.0	61	6.4	2.7
5	19-26 March 2007	14.3	65	5.5	2.5
6	02-09April 2007	13.6	60	4.0	2.5
7	16-23April 2007	15.8	51	3.6	3.1
8	01-08 May 2007	19.4	45	2.9	3.9
9	15-22 May 2007	15.8	38	2.0	4.1
10	21-28 June 2007	30.9	35	2.1	4.4
11	05-12 July 2007	27.9	36	3.3	4.6
12	19-26 July 2007	31.2	36	2.9	4.3
13	02-10 August 2007	25.7	50	3.2	4.5
14	16-23 August 2007	28.8	45	3.1	2.6
15	26 September-02 October 2007	22.3	48	2.9	3.2
16	02-09 October 2007	21.2	60	2.1	2.6
17	16-23 October 2007	17.6	65	2.2	2.1
18	30 October-06 November 2007	17.5	72	1.9	1.4
19	27 November 2007-04 December 2007	11.7	67	2.5	1.2
20	04-12 December 2007	12.0	78	2.1	0.8
21	18-25 December 2007	5.9	71	3.1	1.5
22	08-15 January 2008	5.8	69	2.9	1.3
23	25 Janury-01 February 2008	5.1	65	3.5	3.6
24	06-14 February 2008	7.2	63	4.2	2.1
25	18-25 February 2008	7.7	51	3.3	2.6
26	03-10 March 2008	11.1	55	2.8	2.5
27	17-25 March 2008	15.8	46	2.9	3.5
28	31 March-07 April 2008	12.6	42	3.2	3.7
29	14-21 April 2008	18.7	38	3.8	4.0

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3.2 Sampling Program

The main objective of the measurements in these areas was comparison of the levels of air pollution in different locations of the city. A necessity for such comparisons is the use of data that represent the same type of areas within cities. There are four types of sites: (1) city center or commercial areas, (2) residential areas, (3) industrialized areas, and (4) heavy traffic locations. All the sampling sites (except traffic) were selected far from the sources of air pollution.

Ambient air samples were collected between January 2007 and April 2008 at 16 selected sites around the city of Izmir. Figure 3.1 shows the study area and the locations of the sampling sites. The selected sites in this study (n=16) could be grouped into four categories; i.e. rural (site 2), suburban (sites 4, 5, 6, 10, 14), urban (sites 1, 7, 8, 9, 12, 13) and industrial (sites 3, 11, 15, 16). Site 3 was located in an organized industrial zone. The iron and steel rolling mill, chemical industry, plastics industry, paper industry are located this industrial zone. A petroleum refinery which is the major pollutant source, and a petrochemical complex and iron - steel industries were located at the area around the sites 11, 12, 15 and 16. Other sampling sites 7, 8, 9 and 13 were selected in the urban area and generally surrounded by several high buildings. Site 8 was located at the center of a metropolitan area. To avoid direct contamination by direct pollutant sources, the station was placed in a public park where major roads and buildings were several tens to hundred meters away. Site 5 was at the southeast of the city center and near a major highway whereas site 14 was at southwest of the city center.

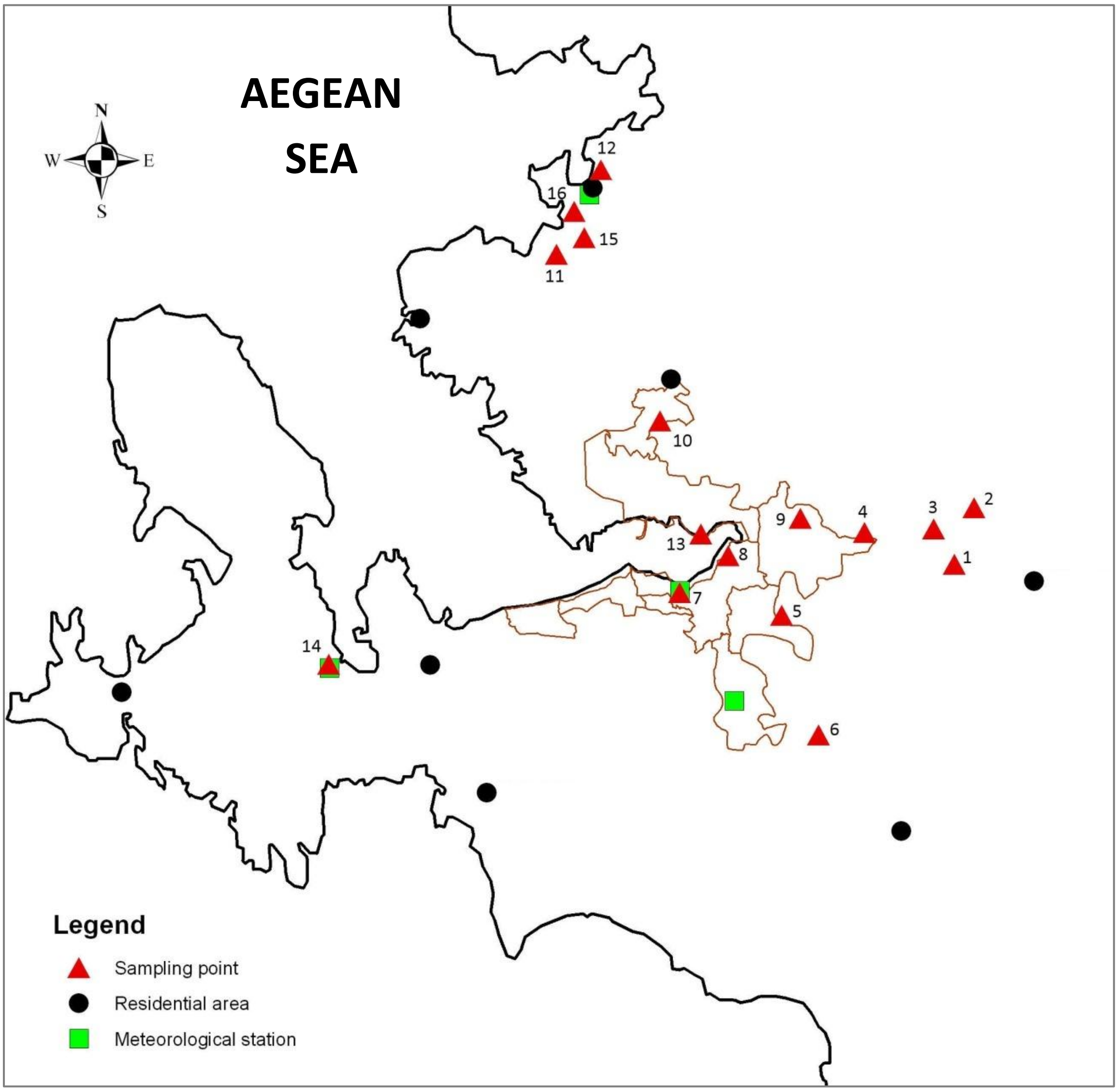


Figure 3.1 The study area and the locations of the selected sampling sites in Izmir.

At 16 different sampling sites selected, O_3, NO_2 and VOCs concentrations were measured. During the measurement of those pollutants radial diffusive samplers (Radiello® models) (Figure 3.2) were used during the sampling campaigns. All diffusive sampling measurements were conducted simultaneously at all sampling sites. Twenty-nine samples were collected at each sampling site (total 16×29 samples). All diffusive sampling measurements were performed for one-week and twice in a month.

At two sampling sites out of 16 where diffusive sampling was used, O_3 and NO_x (NO, NO_2) were measured with online sampling. This online sampling program was used simultaneously with passive sampling at two sites. These online sampling devices were established at urban (Site-8) and suburban (Site-5) areas. In urban area O_3 concentration and in suburban area O_3 and NO-NO_2-NO_x concentrations were measured by online sampling devices. At both sites O_3 measurement was made by Thermo Scientific Model 49i devices. At suburban site NO_x measurement was made by Thermo Scientific Model 46i device. Online sampling program was applied simultaneously with diffusive sampling program between January 2007 and April 2008 at suburban site. At the urban site O_3 measurements were conducted between March 2007 and April 2008. The measurements were not made in September and October 2007 due to O_3 device problem at the urban site and in January 2008 due to NO_x device problem at the suburban site.

3.3 Sampling Methods

3.3.1 On-Line Monitoring

O_3 and NO_x (NO and NO_2) samples were collected by using on-line gas analyzer. An ultraviolet light absorption-based detector (Model 49i, Thermo Scientific) was used for O_3 measurement. Instrument detection limit is 1 parts per billion (ppb) and its response time is 20 s (10 s averaging time). Nitrogen oxide levels were monitored with a chemiluminescence based instrument (Model 46i, Thermo Scientific). The probes were placed at 1.5 m above the ground and had a filter holder which contained a 1.5 µm pore size Teflon filter to keep the Teflon sampling lines free of dust and pollen. The gas analyzer and the probe, the length of the sampling tubing was 2.5 m. Filters were changed weekly throughout the field campaigns. This instrument has external valve manifold and external calibration sources. Instrument calibration and zero check were performed with external calibrator. This instrument meets the technical specifications for US EPA (Environmental Protection Agency). Quality control checks were performed every week including instrument zero and span checks. The O_3 analyzer was calibrated by generating known O_3 amounts using a generator (Model 146i, Thermo Scientific). The NO_x analyzer was calibrated using a three-point linear regression calibration obtained by passing through the analyzer two gas mixtures standards, and zero-nitric oxide air (generated by scrubbing the nitrogen oxides using activated charcoal). Ozone and NO_x measurements were made every second and were processed to produce 1-min averages. The O_3 and NO_x levels reported in this study represent 30-min averages.

3.3.2 Diffusive Sampling

In the 16 sampling sites O_3, NO_2 and VOCs concentrations were measured with Radiello® diffusive samplers (R&P-Co, Radiello, 2001). The main parts of Radiello are the adsorbing cartridge, the diffusive body, the supporting plate and the adhesive label with the bar code indication (Fig 3.2). Apart from the adsorbing cartridge, if not differently stated, all of the other components can be repeatedly used for several sampling experiments. Depending on the pollutants to be sampled, many different adsorbing cartridges are available. The VOCs adsorbing cartridge was placed in a sealed glass tube, the O_3 and NO_2 adsorbing cartridge was placed in a polypropylene tube suitable for short-term storage and transport.

During measurement, cartridges for each pollutant were placed in a different diffusive body and these diffusive bodies were fixed onto a triangular polycarbonate supporting plates. A polypropylene mountable shelter protected sampler from rain and direct sunlight during sampling. The mountable shelter and samplers were placed at 1.5 m above the ground.

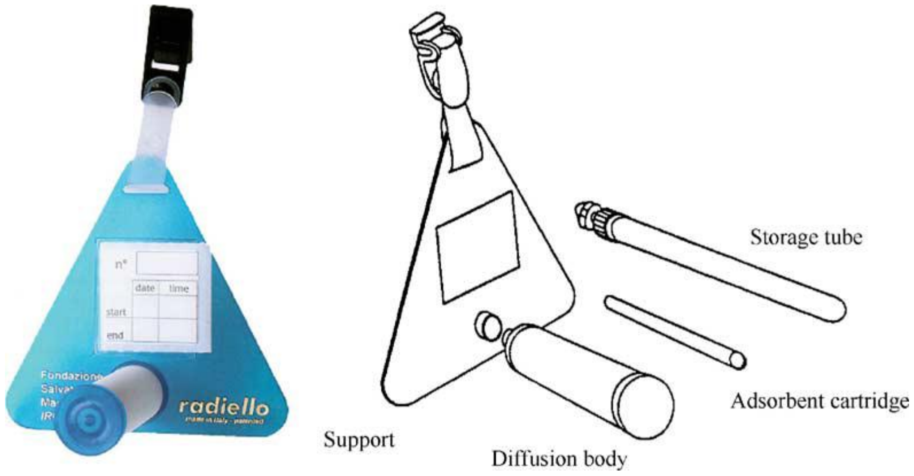


Figure 3.2 Radiello diffusive sampler.

3.3.2.1 Extraction of Samples for Analysis

After sampling program adsorption cartridges were labeled and placed into the capped vial containers to avoid contamination and desorption. Then, they were placed into tightly closed plastic bags and kept in a freezer until they were processed.

For the extraction of O_3 samplers before analysis, 3-methyl-2-benzothiazolinone hydrazone hydrochloride (MBTH) dissolved 5 g per liter in water and 5 ml of concentrated sulfuric acid was added. This solution should be prepared daily. The cartridge was drawn out from the plastic tube, the PTFE cap was discarded and the silica gel was poured into the tube. Five ml MBTH solution was added into the sample, the tube was caped and stirred vigorously. Under these conditions 4-pyrilaldehyde was condensed with MBTH to yield the yellow colored azide, (Figure 3.3). The tube left for at least one hour to react while, stirring it occasionally. After stirring, the solution was filtered with a pre-filter (Alltech 13 mm, 0.45 micron, Nylon) and a syringe.

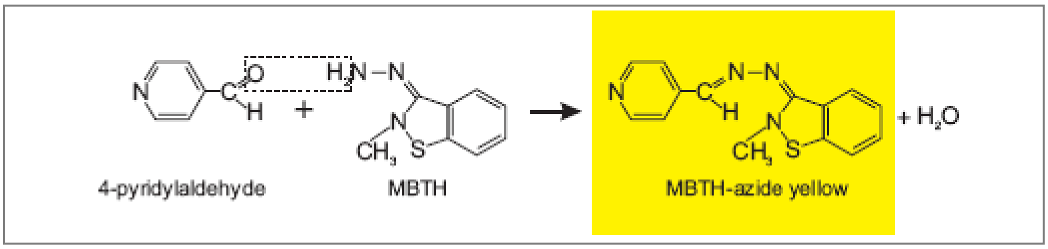


Figure 3.3 Reaction of 4-pyridylaldheyde and MBTH.

For the extraction of NO_2 samplers, 5 ml deionized water was added in the plastic tube with the cartridge and stirred vigorously in a by shaker for 30 min. In the samplers used in the present study triethanolamine N-oxide is the reaction product as described by. The following proposed reaction scheme:

$$2NO_2 + N(CH_2CH_2OH)_3 + 2OH^- \rightarrow 2NO_2^- + {}^-O - {}^+N(CH_2CH_2OH)_3 + H_2O$$

This reaction is in accordance with the observed 1:1 conversion of NO_2 to nitrite ions. Hydroxyl-ions in the reaction probably stem from the dissociation of

Triethanolamine (TEA) in water, and the reaction will therefore not take place in completely dry air (Glasius et al., 1999). These extracts were filtered from syringe filters and then analyzed by ion chromatography.

For the extraction of VOCs samplers before analysis, 2.0 ml carbon disulfide (CS_2, Aldrich 34227) was added as the extraction solvent into the sampler containers. Samples were extracted in an ultrasonic bath for 15 min. Then they were centrifuged for another 15 min to obtain a clear phase at the top. One ml of the clear phase was transferred into a 2 ml vial. The extracted samples were stored in a freezer until they were analyzed.

3.3.2.2 Analysis of Samples

To determine the O_3 concentration the absorbances of yellow hidrazide sample extracts were determine immediately using a spectrophotometer (Pharmacia Biotech 80-208864 Spectrophotometer) at 430 nm. Production of 4-pyrilaldehyde is a specific reaction of O_3; neither nitrogen oxides nor organic compounds, if present, do interfere (Radiello, 2006).

For the calibration of the method a calibration solution was prepared in the laboratory. One hundred µl (112.2 mg at 20°C) of 4- pyridylaldehyde was dissolved in 1 liter of water and the solution was diluted to prepare five different calibration solutions. Half ml of each calibration solution was transferred in a plastic tube together with 4.5 ml MBTH solution. They were stirred and let stand for one hour, then the absorbance was read at 430 nm. The calibration curve was plotted for O_3 mass vs. measured absorbance, taking into account that:

$$1\ \mu g \text{ of 4- pyridylaldehyde} = 0.224\ \mu g \text{ of } O_3 \qquad \text{Eq.3.1}$$

During the analysis of O_3 cartridge, in some cases absorbance of sample solutions were higher than the calibration curve upper limit. In the cases, the samples were diluted with the MBTH solution to ensure that they were in the calibration range.

Following the analysis, the O_3 average concentrations (µg m^{-3}) over the whole exposure time were calculated according to the following equation:

$$C_{O_3} = \frac{m_{O_3}}{24.6 \times t} \times 10^6 \qquad \text{Eq.3.2}$$

where m is O_3 mass in µg sampled by diffusive sampler and *t* is exposure time in minutes. The sampling rate value Q_{298} at 298 °K (25°C) and 1013 mbar is 24.6 ml min^{-1}. Sampling rate is linear in the exposure range from 10 000 to 4 000 000 µg m^{-3} min^{-1}. Sampling rate could be corrected for different temperatures using the following equation:

$$Q_K = Q_{298} \times \left(\frac{K}{298}\right)^{1.5} \qquad \text{Eq.3.3}$$

where Q_K is the sampling rate at the temperature K and Q_{298} is the references value at 298 °K. Sampling rate is not influenced by humidity or wind speed.

The NO_2 samplers were analyzed with ion chromatography (IC) (Dionex ICS 3000) equipped with conductivity detector. The chromatography column was ASRS-9 and the carrier eluent was 9 Mm Na_2CO_3 at 1 ml min^{-1}. Compounds were identified based on their retention times (within ±0.02 min of the retention time of calibration standard). Identified compounds were qualified using the external standard calibration procedure.

Following the analysis, the NO_2 concentrations in air were calculated by the following equation:

$$C_{NO_2} = \frac{m_{NO_2}}{Q_K \times t} \qquad \text{Eq. 3.4}$$

where m_{NO_2} is nitrite mass in ng found on the cartridge, t is exposure time in minutes and Q_K is the sampling rate value at the temperature K in Kelvin. The sampling rate of NO_2 varies from the value at 298 °K on the effect of temperature following the equation 3.5

$$Q_K = Q_{298} \times \left(\frac{K}{298}\right)^{7.0} \qquad \text{Eq. 3.5}$$

where Q_K is the sampling rate (ml min^{-1}) at the temperature K ranging from 263 to 313 K (from -10 to 40 °C) and Q_{298} is the references values at 298 °K and 1013 mbar (0.141±0.007 ng ppb^{-1} min^{-1}). On the contrary sampling rate is invariant with humidity in the range 15 - 90% and with wind speed between 0.1 and 10 m s^{-1} for NO_2.

Ambient air samples were analyzed for 83 VOCs. The selection of VOCs was based on a list suggested by the USEPA for Photochemical Assessment Monitoring Stations (PAMS) program located in O_3 nonattainment areas (USEPA, 1999).

The VOC samples were analyzed with a gas chromatograph (GC) (Agilent 6890N) equipped with a mass selective detector (Agilent 5973 inert MSD). The chromatographic column was HP5-MS (30 m, 0.25 mm, 0.25 μm) and the carrier gas was Helium at 1 ml min^{-1} and 36 cm s^{-1} linear velocity with a split ratio of 1:20. The inlet temperature was 240°C. Temperature program was: initial oven temperature 40°C, hold for 3 min, 40 to 120°C at 5°C min^{-1}, hold 1 min. Ionization mode of the MS was electron impact (EI). Ion source, quadrupole, and GC/MSD interface temperatures were 230, 150, and 280°C, respectively. The MSD was run in selected ion monitoring. Compounds were identified based on their retention times (within ±0.05 min of the retention time of calibration standard), target and qualifier ions. Identified compounds were quantified using the external standard calibration procedure.

Following the analysis, the VOCs concentrations in air were calculated (Eq.3.6) by applying Fick's first law from the pollutant masses retained on the cartridge (Pennequin-Cardinal et al., 2005)

$$C_{VOC} = \frac{m_d - m_b}{Q_K \times t} \times 10^6 \qquad \text{Eq. 3.6}$$

where m_d is the adsorbed mass of compound (µg) sampled during time t (min) under the concentration in air C_VOC(µg m^{-3}), m_b the mass of compound(µg) on a non-exposed cartridge (a blank) and Q_K is the sampling rate of the compounds (ml min^{-1}).

The sampling rates of some VOC compounds were listed in Radiello® manual. These listed values were experimentally measured in a standard atmospheric chamber under laboratory conditions. For these compounds, whose diffusion coefficient is known, sampling rate was calculated using the equation (Eq.3.7) suggested by the manufacturer. Several experiments performed in the standard atmosphere chamber demonstrate that the calculated sampling rates seldom deviate by more than ± 10% from the experimentally measured values.

$$\mathrm{Q} = \mathrm{D} \times \left[\frac{2\pi\mathrm{h}}{\ln\left(\frac{\mathrm{r_d}}{\mathrm{r_a}}\right)}\right] \qquad \text{Eq.3.7}$$

Q=Sampling rate (ml min^{-1})

D=Diffusive coefficient (related to the molar volume and molecular weight of compound) ($\mathrm{cm}^2\ \mathrm{s}^{-1}$)

$\left[\frac{2\pi\mathrm{h}}{\ln\left(\frac{\mathrm{r_d}}{\mathrm{r_a}}\right)}\right]$=Geometric constant of Radiello® diffusive sampler (14.145±0.110 cm)

Sampling rate varies from the value at 298 °K on the effect of temperature (in Kelvin) as expressed by the following Equation 3.8

$$Q_K = Q_{298} \times \left(\frac{K}{298}\right)^{1.5} \qquad \text{Eq. 3.8}$$

where Q_K is the sampling rate at the temperature K and Q_{298} is the reference value at 298 °K this produces a variation of ±5% for 10 °C variation (upwards or downwards) from 25 °C. Sampling rate is invariant with humidity in the range 15-90% and with wind speed between 0.1 and 10 m s^{-1}.

3.4 Data Analysis

Statistical analysis was done for all available VOC, O_3 and NO_2 data. Pearson's correlation coefficient was used to evaluate the relations among O_3, O_3 precursors and meteorological factors. All descriptive computations and statistical analyses were made by Statistica 6.0 (Statsoft, Inc., Tulsa, OK, USA). Bar chart maps were prepared to illustrate the spatial distribution of VOCs, O_3 and NO_2, using a Geographic Information System (Arc GIS 9.2) program. Differences in pollution concentrations between the sites and the sampling periods were determined with one-way analysis of the variance (ANOVA) by using Statistica 6.0.

Correlation and regression analyses were used to compare weekly and seasonal O_3 concentrations as were measured via the passive samplers to the continuously monitored O_3 and NO_x concentrations.

3.5 Quality Control and Assurance

Field blanks were transported along with samplers to the field and stored in the laboratory during the exposure period. For this purpose three diffusive samplers were carried to the sampling site and returned to the laboratory and treated as an environmental sample. Blank sample cartridges were extracted and analyzed as process blank to determine if there was any contamination in the sampling tubes. Additionally extraction solvent (CS_2) and deionized water were also analyzed for the same purposes. None of the VOCs, nitrite and sulfate ions were detected in the solvent and water blanks while only a few compounds were detected in cartridge blanks. The blank amounts were <1% of the sample amounts. For the compounds detected in blanks the limit of detection of the method (LOD) was defined as the mean blank mass plus three standard deviations. Instrumental detection limits were used for the compounds that were not detected in blanks. Sample quantities exceeding the LOD were quantified and corrected by subtracting the mean blank amount from the sample amount. For seven days sampling period LODs for analyzed VOCs ranged between 0.005-4 µg m^{-3}. LODs were 0.71 µg m^{-3} and 1.6 µg m^{-3} respectively for O_3 and NO_2.

Quantifiable VOC amounts were determined from linear extrapolation from the lowest standard in calibration curve using the area of a peak having a chromatographic signal/noise ratio of 3. These amounts ranged from 2 to 5 pg (1 µl injection, split ratio 1:20).

The performance of passive samplers were investigated by, comparing their results with those obtained with an UV-photometric O_3 analyzer and chemiluminescence NO_2 analyzer. This was conducted at two air quality stations (urban, suburban). Regression of the diffusive sampler data vs. the active sampler data, as shown in Figures 3.4, 3.5, and 3.6, confirms quantitative agreement between the two types of samplers. When the complete data set was considered, significant correlations between diffusive sampler and active monitor measurements were found for all the plots. The relationship shows a trend between the two variables with a correlation coefficient of 0.81 (Site-8 and Site-5) for O_3 and 0.78 (Site-5) for NO_2.

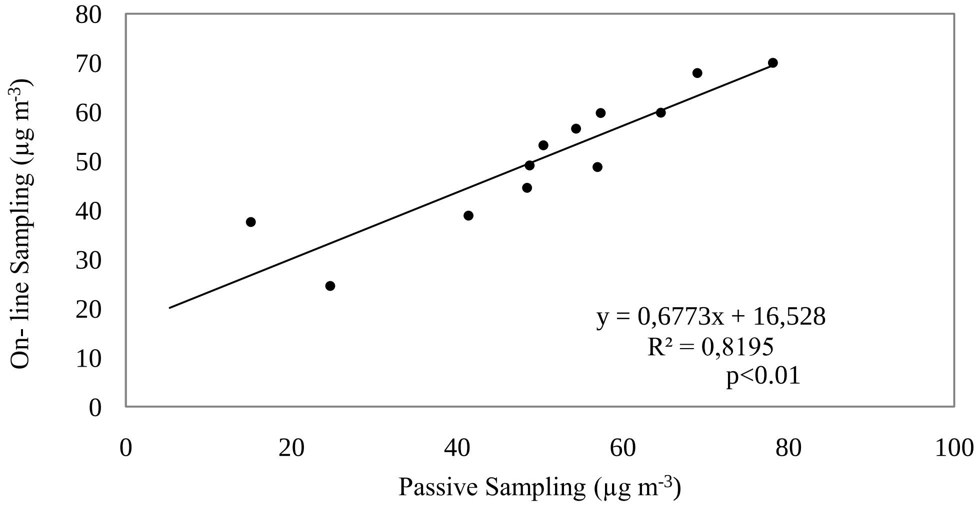


Figure 3.4 Diffusive sampling and on-line sampling comparison for O_3 , S-8.

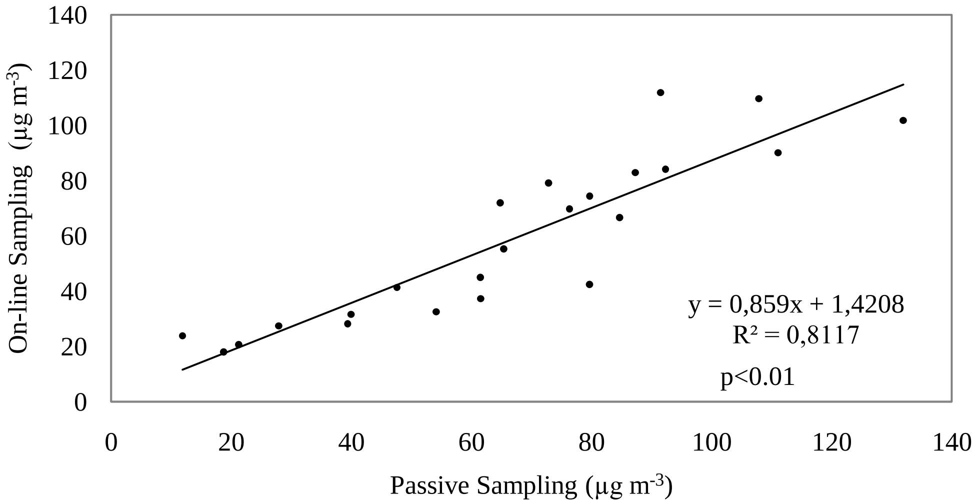


Figure 3.5 Diffusive sampling and on-line sampling comparison for O_3, S-5.

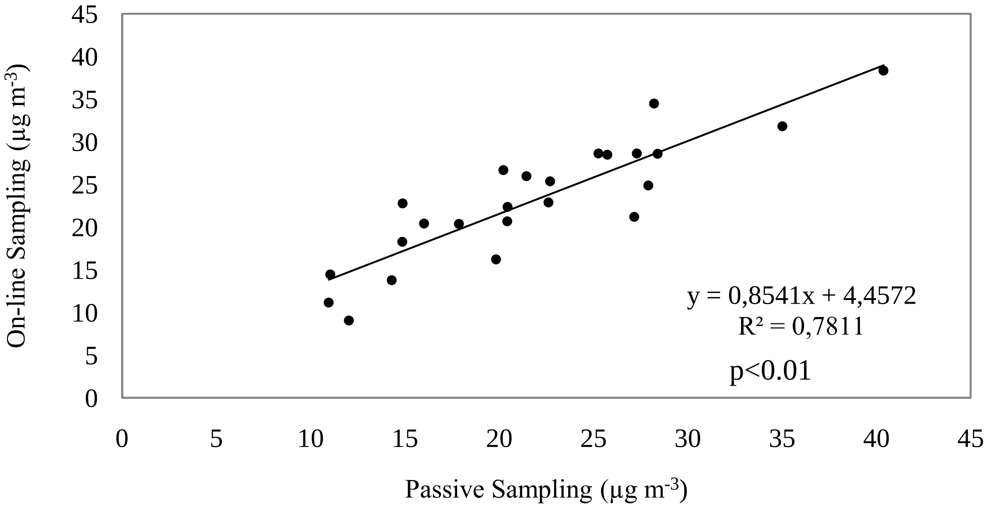


Figure 3.6 Diffusive sampling and on-line sampling comparison for NO_2, S-5.

During the sampling period repeatability tests were performed in different sampling points at different sampling time. In these tests, three different diffusive samplers were used. Repeatability tests were performed in various locations which had high O_3, VOC and NO_2 levels as well as low levels. Differences between duplicate samples were less than 10%. No significant variance was noted in repeatability values at different levels (Figures 3.7, 3.8, and 3.9).

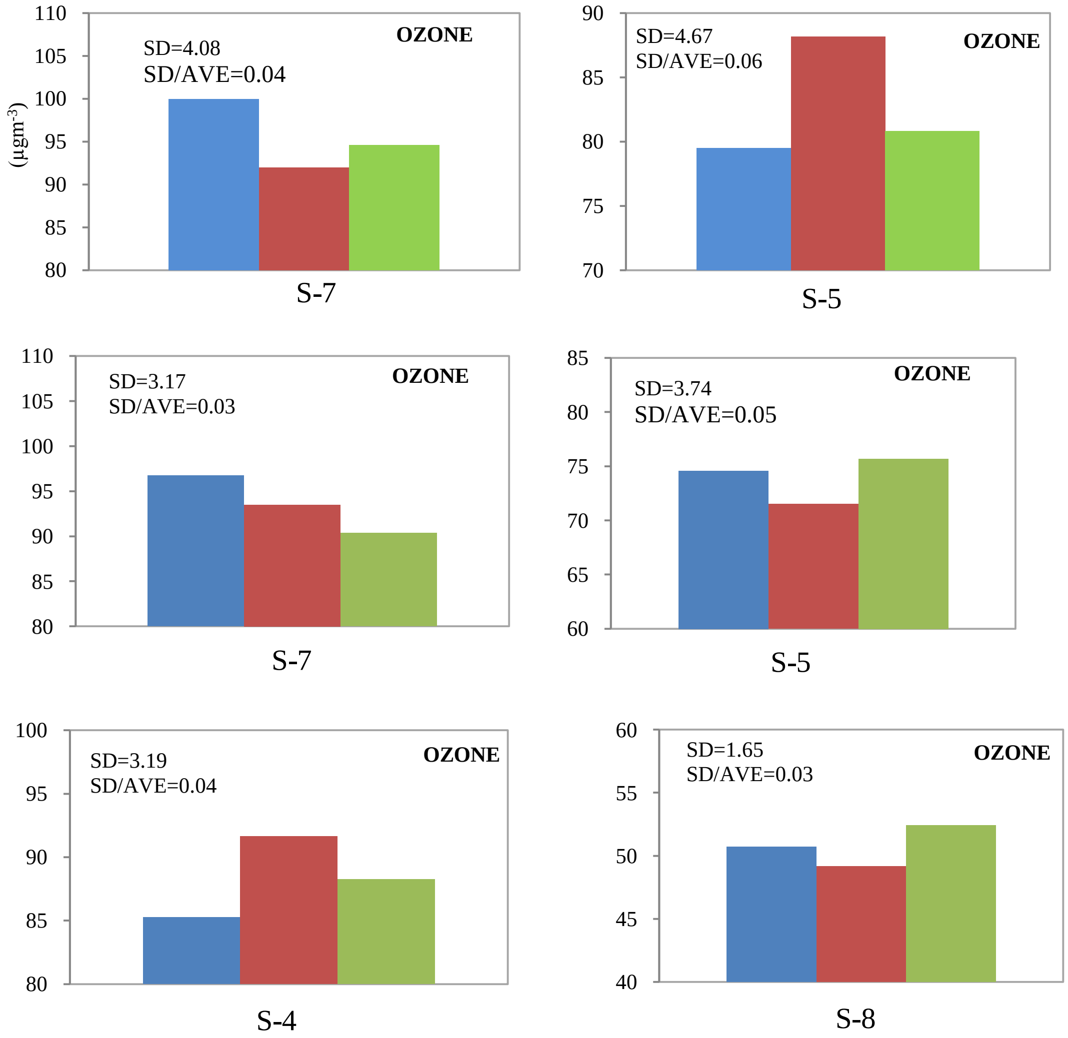


Figure 3.7 Repeatability of results of O_3 measurement with diffusive sampling.

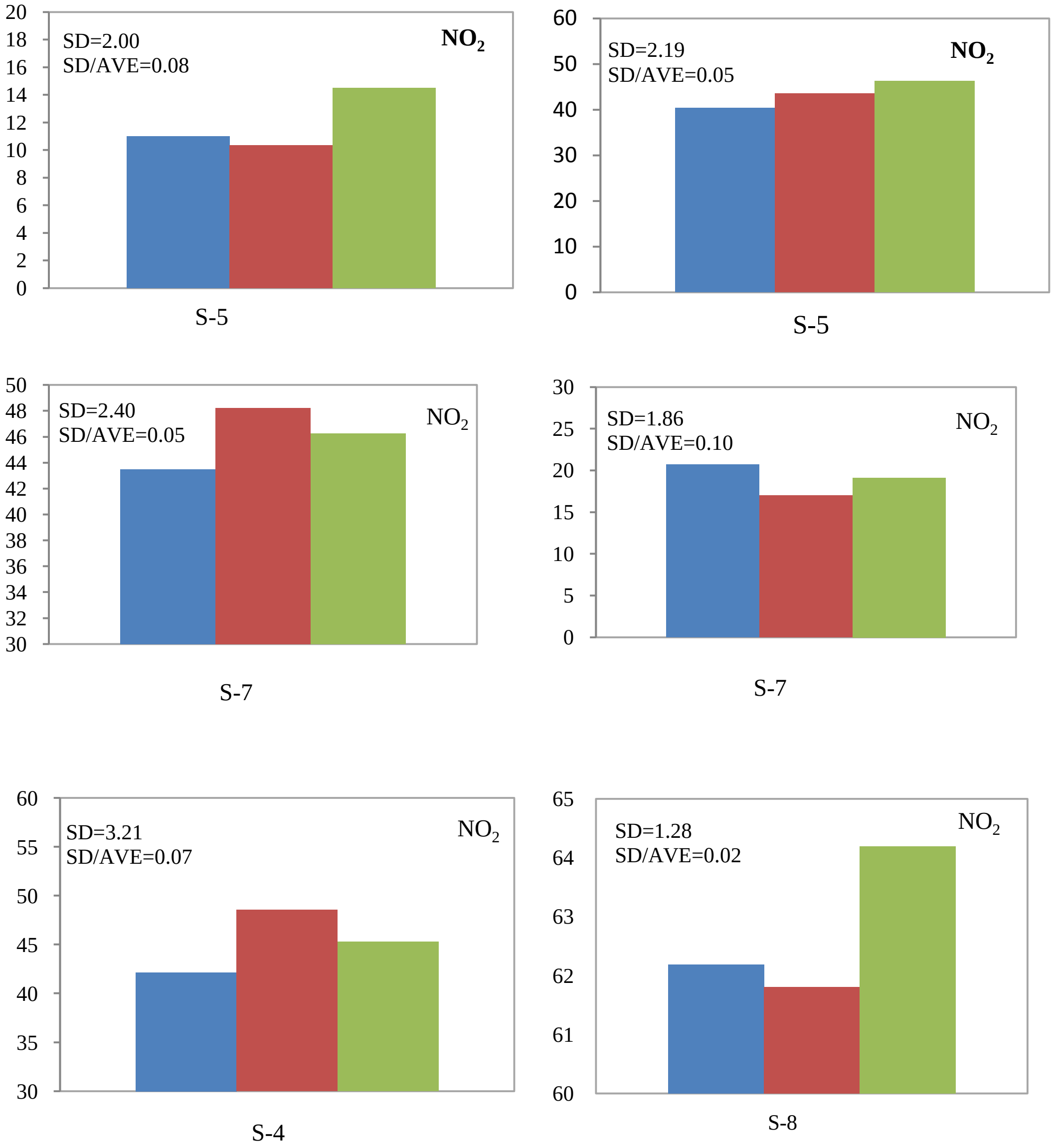


Figure 3.8 Repeatability of results of NO_2 measurement with diffusive sampling.

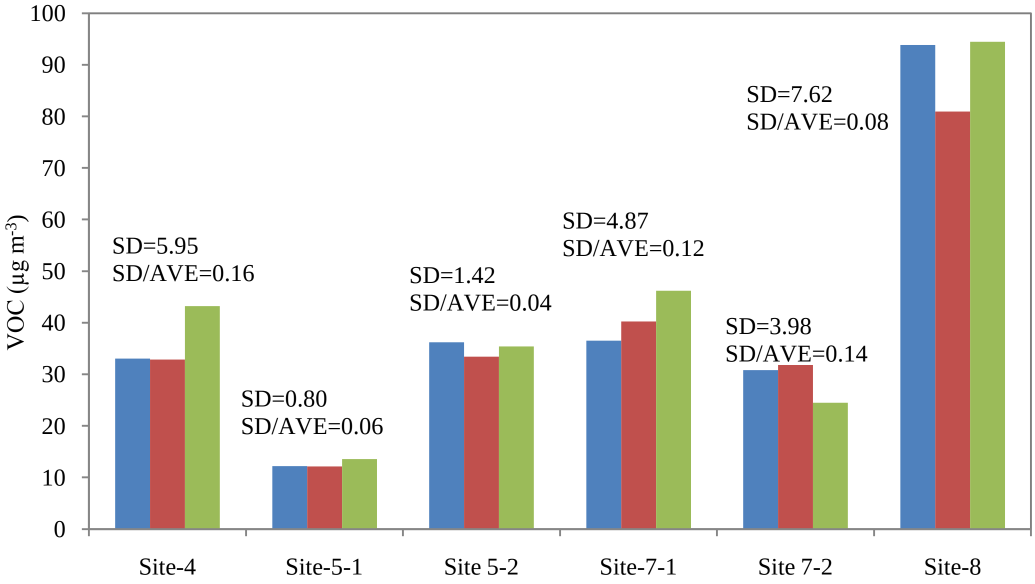


Figure 3.9 Repeatability of results of VOCs measurement with diffusive sampling.

3.6 Maximum Incremental Reactivity (MIR)

Ozone formation potential was calculated in order to identify the effect of each measured VOC on ozone formation. These values were calculated by using MIR factors developed by Carter (Carter, 2008). These MIR factors for each VOC measured were listed in Chapter 2 Table 2.2. Ozone formation potential was calculated by multiplication of relevant MIR factor with concentration of each detected VOC. During this study ozone formation potentials were observed at 16 different sampling sites for 29 sampling periods against each VOC.

CHAPTER FOUR
RESULTS AND DISCUSSION

This chapter presents the results of diffusive sampling and online monitoring of ozone and ozone precursors. The spatial and temporal variation of ozone, nitrogen dioxide and volatile organic compounds were investigated. Hourly variations of ozone and nitrogen oxide concentrations were analyzed and identified the relationship between ozone and nitrogen oxide. Effect of meteorological parameters and ozone precursor on ozone formation was research.

4.1 Hourly Variation of Ozone and NO_x Concentrations

Ozone concentrations vary during hours of the day. Previous studies show that these variances are due to changes in primary pollutants concentrations and meteorological parameters. In this section hourly variation of O_3, NO and NO_2 concentrations in suburban (Site-5) site and hourly variation of O_3 concentrations in urban (Site-8) were reviewed according to online measurement results.

The hourly average variation of ozone at urban and suburban sites for all season is presented in Figure 4.1. This figure shows that the ozone concentrations were consistently lower in the urban site than in the suburban site during the winter and summer season, suggesting that there were constant ozone depressing processes in the urban site. Ozone concentrations tended to increase during afternoon hours around 14:00–16:00, decrease during rush hours. During rush hour traffic between 07:00 a.m. and 09:00 a.m., increasing NO_x emissions cause the O_3 levels to reach their minimum due to NO_x titration, and then O_3 begins to build-up due to increasing solar radiation and in turn increasing chemical reaction rate. This diurnal cycle is typical of urban stations (Gimeno et al., 1999). Hourly O_3 concentrations during afternoon hours were above 100 $\mu g\ m^{-3}$ in spring and summer season, above 30 $\mu g\ m^{-3}$ in winter and autumn season and followed a typical diurnal O_3 cycle in site-5. This gradual increase in the duration of the afternoon maxima from winter to summer is in accordance with the increases in daylight duration, temperature and height of the boundary layer. During the summer site-8 average concentration values reached up to 80 μg m^{-3} and during the winter reached up to only 20 μg m^{-3}. Ozone concentrations were always observed at low levels at site-8 where there was high level of NO emission sources. Moreover there was no high level of ozone concentrations afternoon time which was supported by lower level of solar radiation during winter compared to summer season.

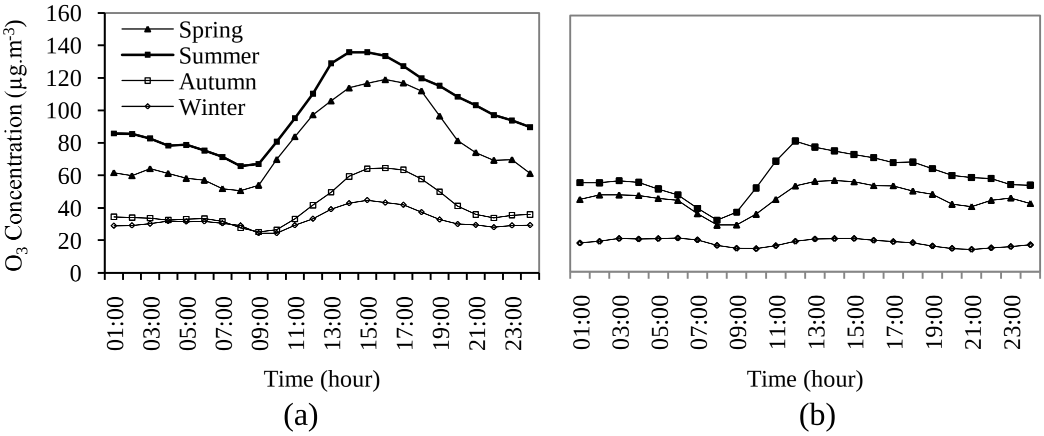


Figure 4.1 Hourly variation of average ozone concentrations in each season for site-5 (a) and Site-8 (b).

At site-5 for all seasons there was a strong hourly variation which became more distinct in summer, where the afternoon values were almost approximately 3 times higher than the nocturnal ones. The nocturnal values did not vary significantly from one season to the other (summer seems to be an exception showing higher values). This was not the case for the afternoon values, which have a summer/winter ratio of the order of 2. The spring afternoon values were higher than the autumn ones and practically lied almost half way between autumn and summer. This sharp contrast of ozone between day and night in site-5 was likely to be attributed almost exclusively to physical processes as the influence of the chemistry was expected to be minimal. The reason for this was that nitrogen oxides at the site did not have concentrations high enough in order to influence the ozone curve. Therefore, the basic reason of the low night values in Site-5 was the physical destruction of ozone by dry deposition enhanced by the nocturnal inversion.

Concerning the hourly variation of suburban ozone the maxima were observed at daytime while the difference between night and day became considerable during summer months. Daytime (08:00-17:00) average was 35 µg m^{-3}, and night time (18:00-07:00) average was 30 µg m^{-3} during the winter. These values were daytime (07:00-20:00) average 106 µg m^{-3}, and night time (21:00-06:00) average 87 µg m^{-3} respectively during the summer. The reason was that the warm, sunny anticyclonic conditions bringing elevated ozone levels during the day were also associated with the formation of nighttime inversions due to radiative cooling at the surface. This situation established a shallow stable layer near the ground and vertical mixing of air was severely restricted. Vertical ozone soundings have shown that above the inversion ozone was not destroyed, while below the inversion ozone was removed by dry deposition enhanced by chemical destruction from emitted substances. Following the disappearance of the inversion in the morning, the downward mixing of air from the ozone reservoir in the upper layers resulted in a rapid increase in ozone at ground level (Kalabokas et al., 2000).

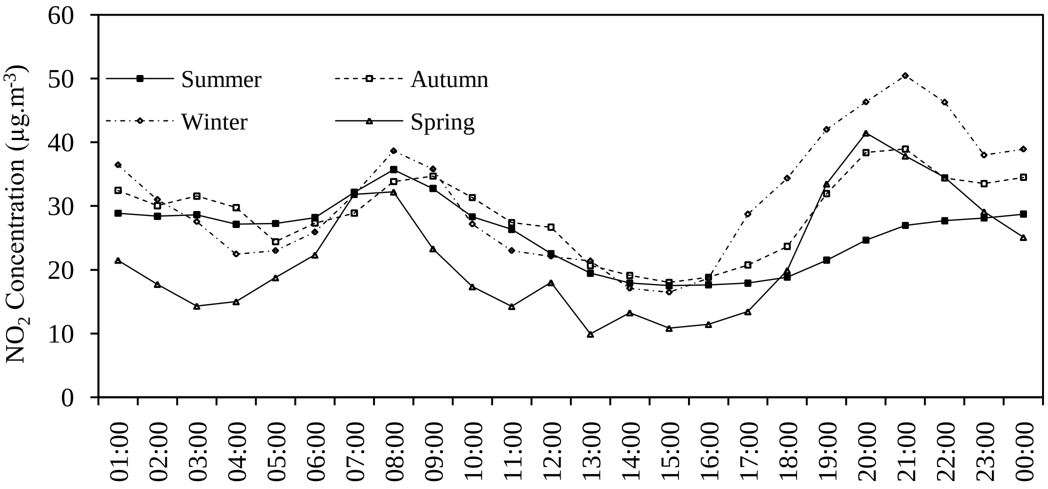


Figure 4.2 Hourly variation of average NO_2 concentrations in each season for site-5.

Figure 4.2 shows the hourly profiles for NO_2, obtained from Site-5 at each seasons. The daily variation was determined by traffic since the time series plots followed a typical pattern characterized by maximums registered during peak hours. The variations of the daily NO_2 levels were characterized by a maximum in the morning, between 7:00 and 9:00 a.m., and a second and slightly lower peak in their concentrations in the evening between 7:00 and 9:00 p.m. Although there was no seasonal change observed in NO_2 values of 07:00-09:00 a.m., it was noted that night time values were higher in winter compared to summer. NO_2 concentrations of summer period were always observed at a lower level compared to winter time. A relatively higher level of NO_x concentration at nighttime during winter was due to residential heating in addition to traffic. On the other hand, the increase in solar radiation during summer supported photo-dissociation of NO_2. The current EU limit for the protection of human health is expressed as an hourly limit of 200 µg m^{-3} of NO_2 not to be exceeded more than 18 times a calendar day. During our measurements, the maximum NO_2 concentrations never reached 200 µg m^{-3}. The NO_2 mean values in Izmir were similar to those reported by Baldasano et al. (2003) for the major Spanish cities (50–63 µg m^{-3}), but higher than those reported by Fernández-Villarenaga et al. (2001) for La Coruña, (13.4 µg m^{-3}).

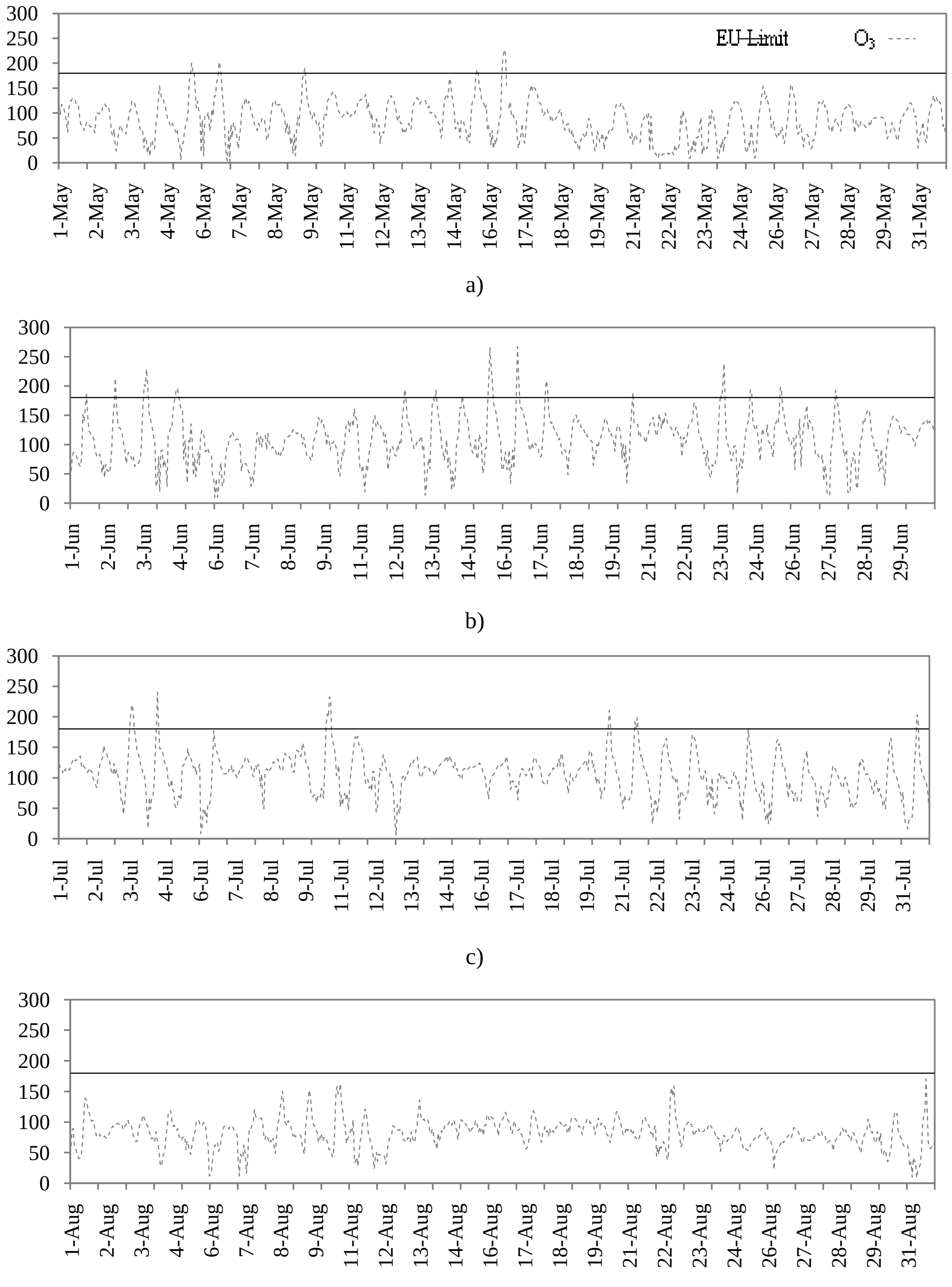


Figure 4.3 Diurnal variations of ozone concentrations (µg m^{-3}) in May (a), June (b), July (c), August (d) and EU Limit in Site-5.

May-August period has the highest concentrations throughout the year. Figure 4.3 shows hourly average values during those months and the current EU limit for hourly average ozone of 180 μg m^{-3}. When we look into our hourly average values we seen that EU limit was exceeded for 5 times in May, 13 times in June and 5 times in July whereas August values were within the limits.

The seasonal variation of ozone concentrations was analyzed using the values of monthly averages for the examined 1yr period (April 2007- April 2008), shown in Figure 4.4 for the data series of Site-5 and Site-8 showing a strong characteristic seasonal variation with summer values being almost double than winter concentrations. Similar patterns of seasonal variation have also been observed in Europe (Kalabokas et al., 2000; Pehnec, Vadjic & Hrsak, 2005). The shift of the ozone maximum from spring to summer is a signal that the photochemical production of ozone due to the emissions of the man-made ozone precursors is the determining factor in the tropospheric ozone budget. The site-5 monthly average ozone concentrations calculated as minimum 18 μg m^{-3} and maximum 108 μg m^{-3} at December and June respectively. The site-8 monthly average ozone concentrations calculated as minimum 12 μg m^{-3} maximum 62 μg m^{-3} at January and July respectively which were lower than the annual average values (40–70 μg m^{-3}) referred by WHO (2000). There was a similar trend at both stations whereas concentrations of site-5 were always higher than site-8 (no data available in months 9 and 12 due to equipment failure).

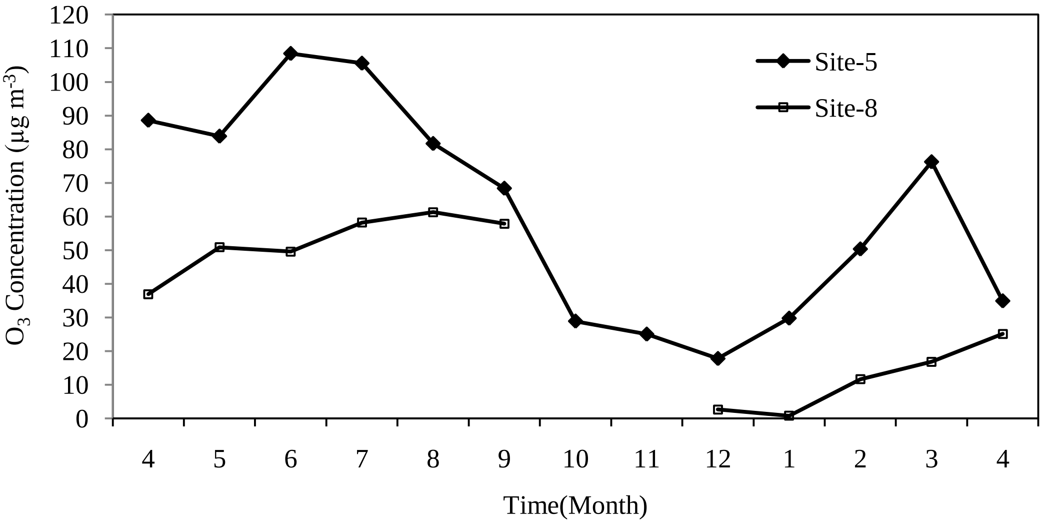


Figure 4.4 Seasonal variations of monthly average ozone concentrations for from April 2007 to April 2008 in an urban and suburban station.

Sampling data simultaneously obtained at both sites during March-August 2007 period were investigated in this study. Daily average O_3 concentrations for urban and suburban sites between March and August were presented in Figure 4.5. As shown in the figure, in suburban site daily average O_3 concentration generally above 60 µg m^{-3} in suburban site, above 20 µg m^{-3} in urban site. The highest daily average O_3 concentration was calculated to be 133 µg m^{-3} on June 22, 2007, at Site-5 and 90 µg m^{-3} on June 14, 2007, at Site-8. These averages show that the Site-5 was exposed to higher O_3 levels as compared to the Site-8. Figure 4.5 shows that site-5 experienced higher concentration levels than those in site-8. This can be explained by the geographical characteristics of the two stations. The site-8 station was exposed to traffic emissions leading to NO-titration of ozone which results in lower ozone concentrations. According to the daily average values calculated during 6 months, it was monitored that there was an increasing trend in ozone concentrations of suburban site from March to July. There was also a similar increasing trend in urban site.

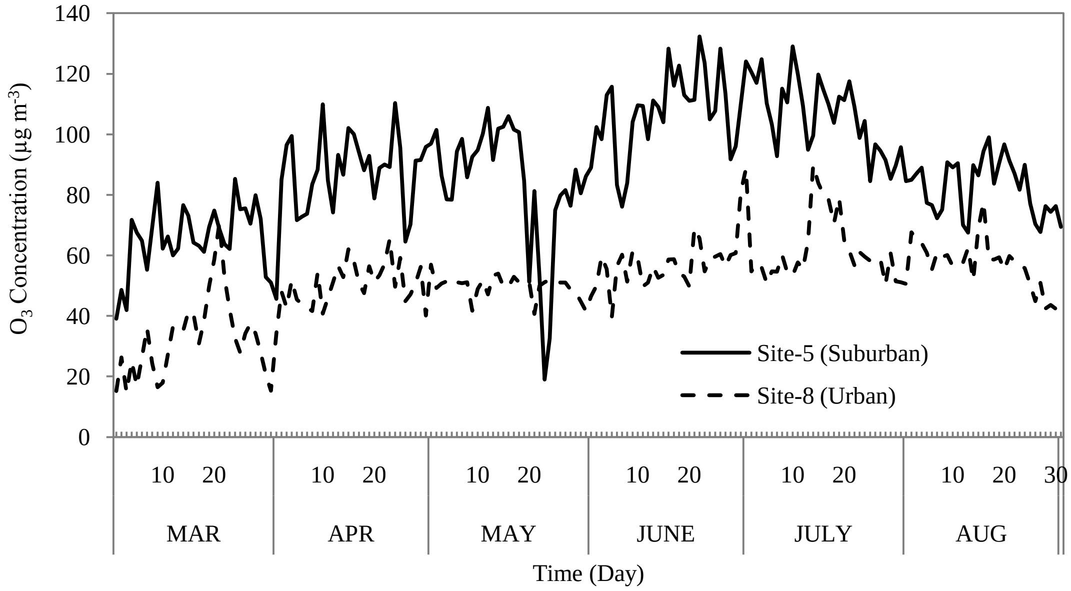


Figure 4.5 Daily average concentrations of surface ozone in the urban and suburban sites.

During the measurement of urban and suburban ozone concentration suburban NO and NO_2 concentrations were also measured. Daily average NO and NO_2 concentrations for suburban sites between March and August 2007 were presented in Figure 4.6. As shown in this figure daily average of NO_2 concentration changed between 10 µg m^{-3} and 50 µg m^{-3}. Besides that daily average of NO concentrations were approximately 10 µg m^{-3}. There was a parallel trend in NO_2 and NO daily average concentration changes. There was no change observed in two pollutants during March-August period. This was due to their anthropogenic source that is not showing seasonal changes. NO is a pollutant occurring upon combustion process and especially upon traffic. On the other hand, NO_2 is a pollutant coming out from oxidation of NO. NO_2 concentrations were always observed higher than NO concentrations during the whole sampling period. When Figure 4.5 and Figure 4.6 are compared NO_x concentrations were showing a constant trend during sampling period, O_3 concentrations were showing an increasing trend during summer period which can be explained by temperature and solar radiation impact on complex reactions.

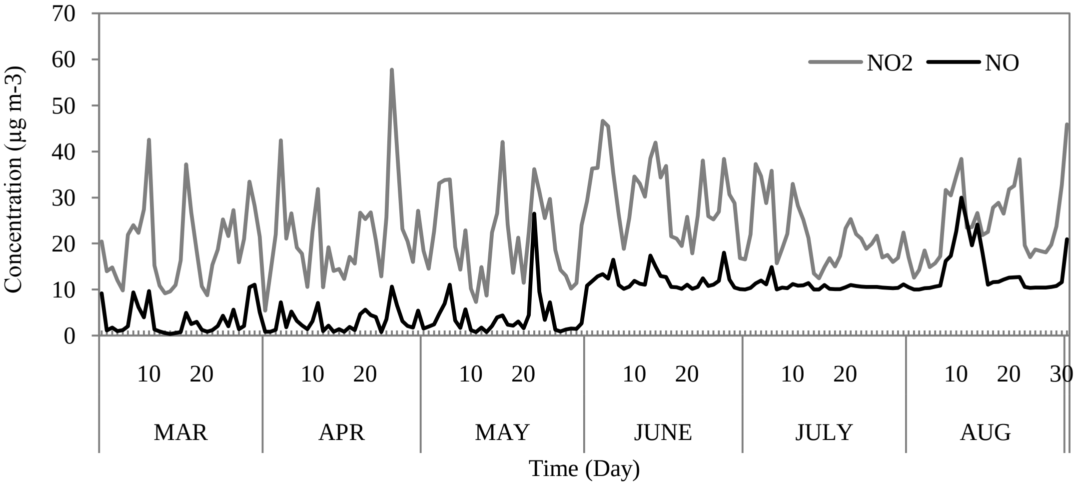


Figure 4.6 Daily average concentrations of NO_2 and NO in suburban sites.

In this study, daily variations of ozone concentrations were characteristic for photochemically originated ozone concentrations would reach the peak in early afternoon when the sunlight is the most intense and fall overnight due to reaction of ozone with NO. Pehnec et al. (2005) and Geng, Tie, Xu, Zhou, Peng, Gao, Tang & Zhao (2008) studies suggested that ozone concentrations are depressed by the reaction of $NO+O_3$ and are converted to NO_2. During day time, NO_2 can be quickly photo-disassociated (in a few minutes) to form back to O_3. However, during early morning, the sunlight is very weak, and NO_2 is not been photo-disassociated. As a result, NO_2 is being transported in other regions, and then is photo-dissociated to form O_3 when sunlight is enhanced.

Figure 4.7 shows the hourly average ozone concentrations at the two sites in Izmir atmosphere. At site-5 and site-8, there was a remarkable hourly variation with a maximum in the afternoon. The generated profile was a typical hourly changing trend for O_3 (Geng et al., 2008; Im, Tayanc & Yenigün, 2008), reaching maximum concentrations during afternoon hours due to high solar radiation, which triggered the chemistry. Some smaller increases in O_3 concentrations were also observed in early morning hours due to a buildup of O_3 in the absence, or decreased levels, of NO_x. These results suggested that both stations were more influenced by urban sources than desirable and that hourly cycle could be produced by these sources. There was no significant change in ozone concentrations of site-8 afternoon time unlike to site-5. This can be explained by site-8 being located close to a car parking area and in city center where high traffic (source of NO concentrations) did not change. There were values higher than 100 µg m^{-3} in site-5 afternoon hours during spring period whereas the values of site-8 during summer period (high temperature and solar radiation) were higher than 80 µg m^{-3}.

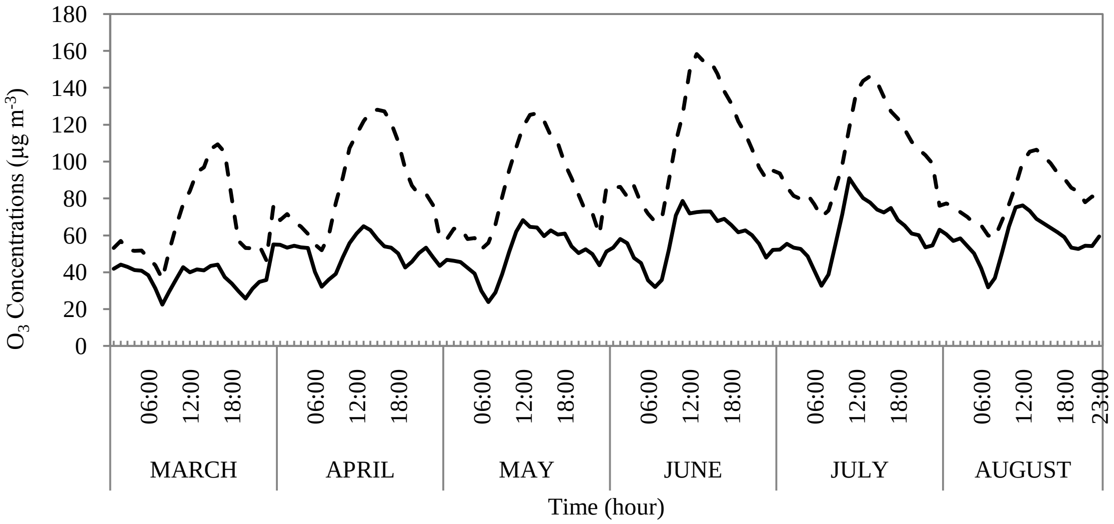


Figure 4.7 Variations of hourly average ozone concentrations at March- August 2007, at site-5 (dashed line), site-8(straight line).

Figure 4.8 shows the NO_2 and NO average hourly concentrations the day at the suburban site. There was a parallel increase in NO and NO_2 concentrations noted in two time spots during the whole day. One peak value was during the morning time (heavy traffic hours) and the second value was during the night time. NO concentrations reached up to 15-20 µg m^{-3} at these morning time peak values. During these high values being obtained, it was noted that ozone concentrations had a decreasing trend. NO_x concentrations decreased at midday because of vertical dilution and chemical processing. Traffic sourced increases at morning and evening hours reduced due to holiday period at the campus between June-July and August period.

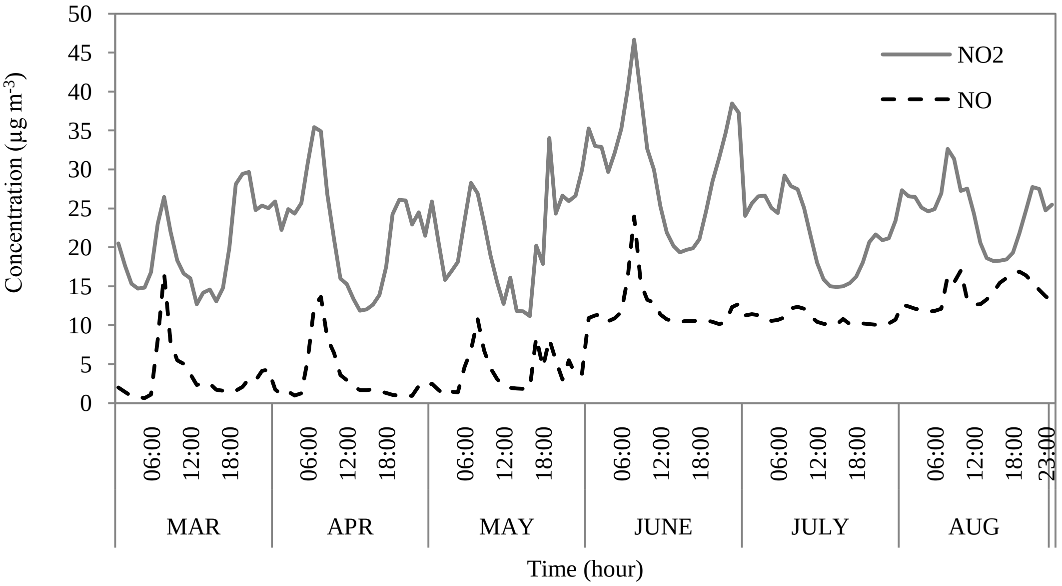


Figure 4.8 Variation of hourly average NO_2 and NO concentrations at March- August 2007 in suburban site.

Coinciding with increased traffic in the morning, NO concentrations started increasing and peaked at around 8:00–10:00 a.m. After sunrise, NO concentrations started to decrease – because of its participation in the photochemical production of O_3 – and O_3 concentrations rose rapidly. At midday there were high concentrations of O_3 because of NO_x emissions from the study site. From evening to the end of the day the intensity of solar radiation decreased sharply and photochemical reactions were inhibited, thereby producing a depletion of O_3 due to reaction with NO, whose emission increases again coinciding with the evening traffic peak. During the night, photochemical and meteorological processes such as inefficient vertical mixing and the ceasing of chemical NO_x removal led to nighttime NO_x increases. Atmospheric circulation in the studied area exhibited marked diurnal cycles with highly stable conditions at night alternating with strong vertical mixing by day in summer. In cold seasons, low temperatures and low solar radiation did not favor the development of the mixing layer by day and at night temperature inversion layers frequently form near the ground.

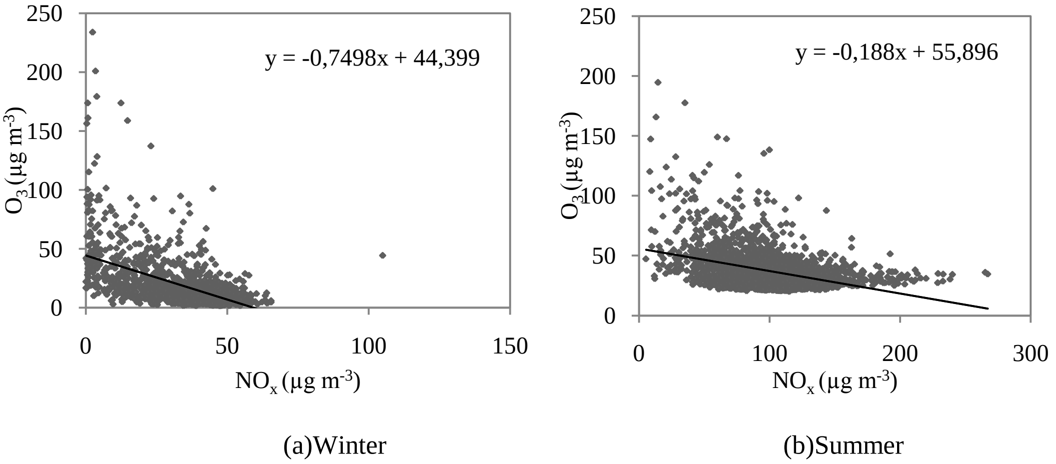
4.2 Correlation Between Hourly O_3 and Hourly NO_x Concentration

In order to identify the correlation between ozone and precursors (NO and NO_2) the overall correlation factors between O_3 and its precursors were calculated and are presented in Table 4.1. As expected, negative correlations resulted and agreed with the chemistry. Correlations between O_3 and NO_x were calculated to be -0.51 and -0.39 in winter and summer respectively in suburban area. If the values were compared, it would be found that there was a higher negative correlation for winter than for summer. High correlations between ozone and NO_x species indicate that ozone formation was predominantly local and relied on photochemical processes.

Table 4.1 Correlation between O_3, NO_2, NO and O_x

WINTER	**NO_2**	**NO**	**NO_x**	**O_3**	**$O_X(NO_2+O_3)$**
NO_2	1				
NO	0.58	1			
NO_x	0.89	0.89	1		
O_3	-0.56	-0.36	-0.51	1	
$O_X(NO_2+O_3)$	0.31	0.14	0.26	0.62	1
SUMMER	**NO_2**	**NO**	**NO_x**	**O_3**	**$O_X(NO_2+O_3)$**
NO_2	1				
NO	0.47	1			
NO_x	0.94	0.74	1		
O_3	-0.39	-0.24	-0.39	1	
$O_X(NO_2+O_3)$	0.29	-0.07	0.18	0.93	1

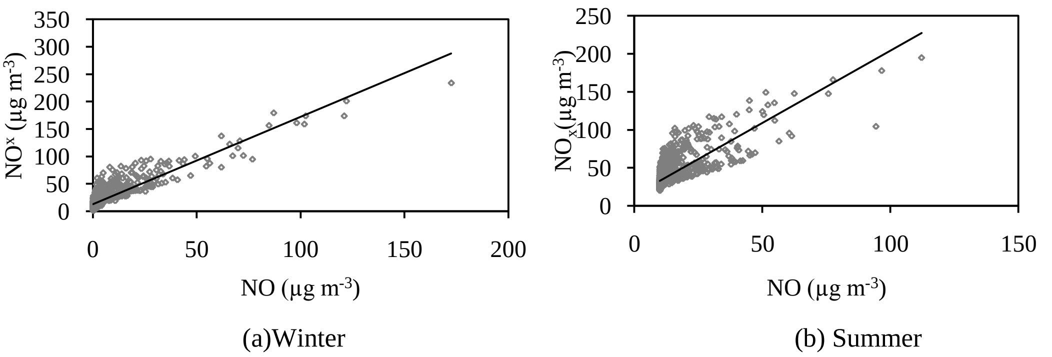
To get a clearer understanding of the chemistry, the scatter diagrams of O_3 and NO_x are presented in Figure 4.9. It can be seen that the slopes of O_3 change against NO_x with changes of -0.749 and -0.188 for winter and summer, respectively. Thus, it is possible to say for winter season that the change in NO_X concentration have as much effect on O_3 formation especially in winter in suburban site which was also observed in the study of Matsumoto, Kosugi, Nishiyama, Isozaki, Sadanaga, Kato, Bandow & Kajii, (2006).



(a)Winter (b)Summer

Figure 4.9 Sensitivity of O_3 formation to NO_x changes in winter (a) and summer (b).

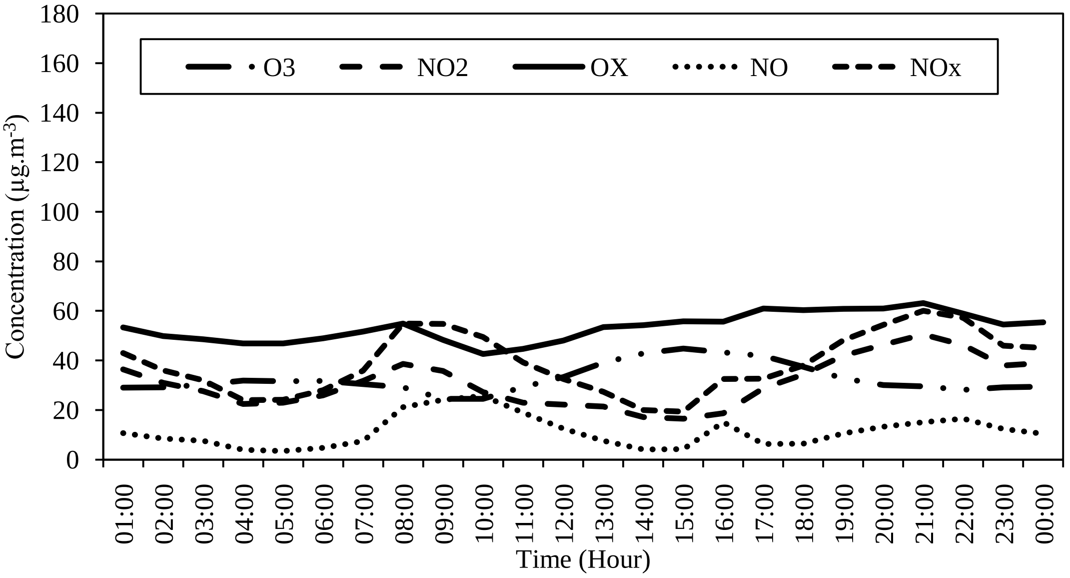
The relation between NO and total NO_x species gives clues about the origin of the NO_x precursors. As seen in Figure 4.10 and Table 4.1, there is a very strong correlation between NO and NO_x, showing that the NO_x species were mainly from local sources (Lu et al., 2003; Im et al., 2008). Thus, we can say that emissions within the city are an important contributor to the chemistry that takes place in the lower atmosphere. Since the atmospheric lifetime of NO_x species (hours) is relatively shorter than the lifetime of O_3 (days), we can expect that air masses transported to the region may contain significant levels of O_3 together with small amounts of NO_x.



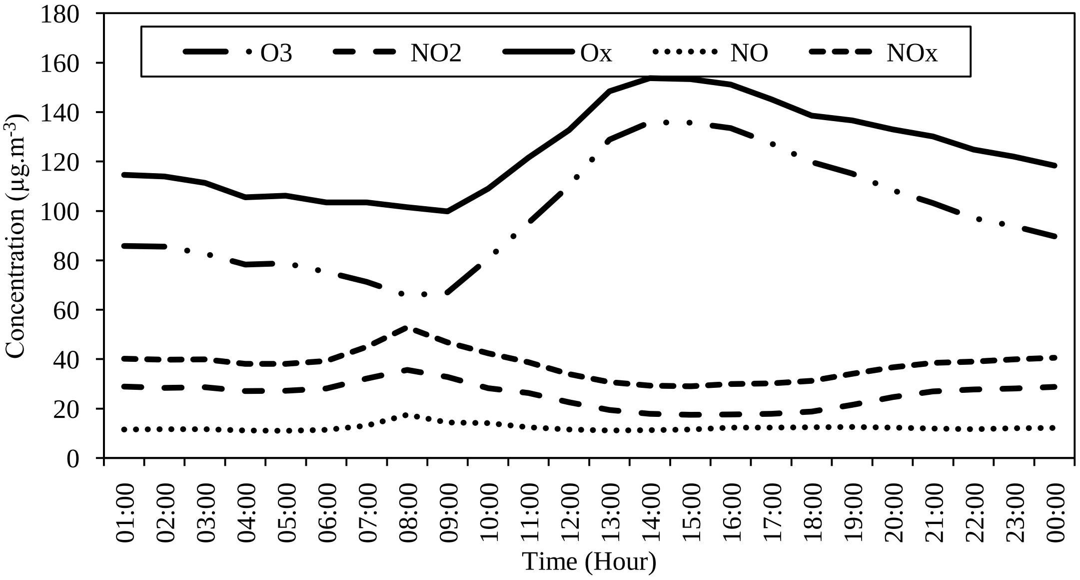
(a)Winter (b) Summer

Figure 4.10 Relationship between NO_x and NO levels in (a) winter and (b) summer.

The results showed that the ozone concentration peaked around 15:00. In contrast to O_3, NO had two peaks, one between 7:00 and 8:00 a.m. and the other between 21:00 and 22:00 the next day. The first peak of ambient NO in early morning was the larger one and was probably caused by emissions from motor vehicles. The second peak was smaller and likely due to emissions and to the lower boundary layer at night. The diurnal pattern of NO_2 was more complex e a result of the influence of emissions and photochemical reactions. As indicated in Figure 4.11, the NO and NO_2 concentrations are consistently higher in winter than in summer. During winter time, the planter boundary layer (PBL) height is shallow, and the shallow PBL height partially leads to the higher NO concentrations near the surface. During morning, there is a strong NO maximum, especially in winter. Because the chemical production of NO is very small in morning, the peak of NO is morning is mainly resulted from higher surface emissions trapped in a shallow PBL as a suggested by Geng et. al., (2008). The successive daytime peaks shown in Figure 4.11 for NO, NO_2 and O_3 very clearly illustrate the active photochemistry at Izmir.



(a) Winter



(b) Summer

Figure 4.11 Diurnal variation of O_3, NO_2, NO, O_x and NO_x concentrations at site-5 in winter and summer.

To determine the dominant channel for NO_2 formation in a particular environment, it is useful to consider the oxidant concentration ($[O_x]$, where $[O_x] = [O_3] + [NO_2]$). Because O_x concentration is conserved by reaction

$$NO_2 + O_2 \rightarrow NO + O_3$$

and increased by reaction

$$NO + ROO\cdot \rightarrow NO_2 + RO\cdot$$

an increase in O_x concentrations implies the occurrence of the reactions (Itano et al.,2007). As shown in Table 4.1 and Figure 4.12 ozone concentrations have a higher impact on O_x compared to NO_2.

The O_x concentration was controlled largely by the city's background O_3, and local O_3 production though the radical reaction was minor. The reaction of background O_3 with locally emitted NO through the O_3 channel controlled the city's NO_2 concentrations. As a consequence, the background O_3 remaining after reaction with NO accounted for the city's O_3 concentrations.

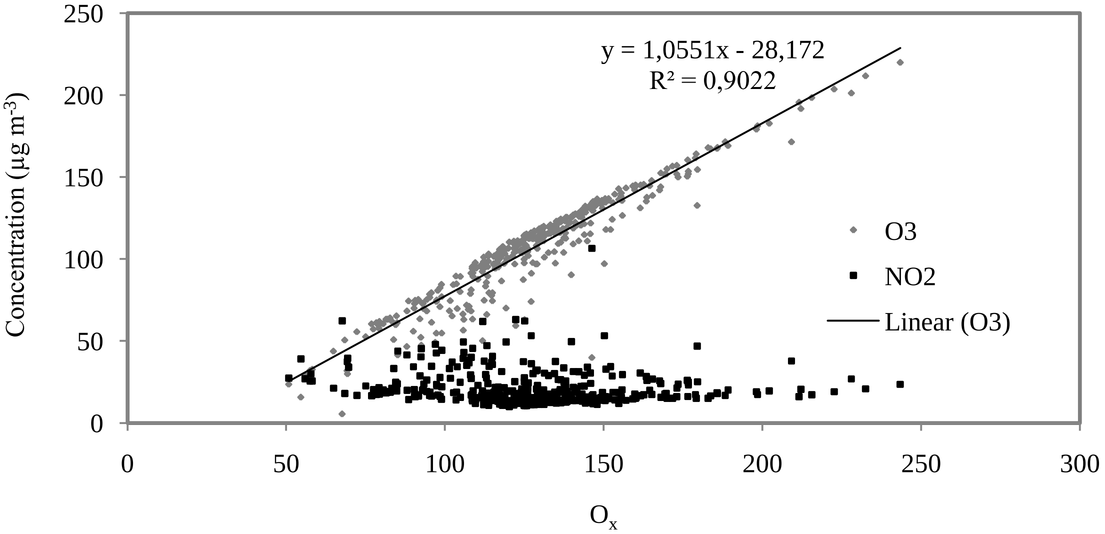


Figure 4.12 Correlation between O_x and NO_2-O_3 concentrations.

4.3 Spatial Distribution of Pollutants

In this section results of diffusive sampling simultaneously made at 16 sites in Izmir were investigated. Spatial distribution of O_3, NO_2 and VOC were reviewed by using 29 values at 16 different sampling sites.

4.3.1 Ozone

The geographical distributions of O_3 concentrations in Izmir are shown in Table 4.2. The weekly average concentrations of O_3 measured in industrial sites range between 63.4-73.0 µg m^{-3}, 39.3-73.6 µg m^{-3}, 48,4-79.9 µg m^{-3} and in urban and in suburban sites, respectively. The average concentration in rural site was 76.4 µg m^{-3}. Considering the average concentration values, it is seen that the highest values were measured in suburban and rural sites which are not subject to vehicle traffic and they are far from the industrial areas. O_3 concentration was measured at an average of 65 µg m^{-3} in four sites located in industrial region and there were no significant differences among those sites. The average value of 39 µg m^{-3} was measured at site 8 where there was heavy traffic and located in downtown location whereas a value of 74 µg m^{-3} was measured at another urban site. Different concentration values were also measured in suburban sites like in urban sites. Among minimum values measured at all sampling sites the lowest concentration was 0.3 µg m^{-3} (site 4, suburban), the highest concentration was 17.5 µg m^{-3} (site 7, urban). On the other hand, the lowest value was 75.1 µg m^{-3} (site 8, urban), the highest value was 162 µg m^{-3} (site 14, suburban) among maximum values measured. In the remaining area, which is mainly rural, ozone levels were always high. These results are consistent with the literature, where rural sites tend to have higher long-term ozone exposures because polluted air masses are transported downwind of urban/industrial centers and the photochemical generation system continues to develop with little scavenging of ozone precursors (Saborit et al., 2008).

Table 4.2 Weekly Average O_3 concentrations (μg m^{-3}) in Izmir

Sampling Sites		**Min**	**Max**	**Average**	**SD**	**Median**	**95%**
Urban	S-1	7.7	126.1	72.8	31.8	77.1	114.5
	S-7	17.5	96.1	57.3	23.5	63.5	92.7
	S-8	5.7	75.1	39.3	21.1	45.4	66.5
	S-9	2.0	78.9	44.4	25.3	48.7	76.5
	S-12	12.8	106.0	73.6	23.4	78.4	100.9
	S-13	10.8	121.4	58.3	30.3	65.0	100.3
Rural	S-2	11.2	134.8	76.4	29.4	78.9	115.2
Suburban	S-4	0.3	102.6	55.5	24.9	59.2	83.4
	S-5	11.9	131.9	67.1	30.6	69.1	110.6
	S-6	11.3	100.2	48.4	22.9	51.4	77.5
	S-10	14.5	116.3	66.1	25.6	68.8	99.4
	S-14	15.4	161.9	79.9	35.4	79.8	118.6
Industrial	S-3	9.9	142.4	64.2	33.4	60.7	108.4
	S-11	12.0	127.0	70.7	29.9	71.6	106.4
	S-15	7.4	151.8	63.4	36.8	65.8	101.5
	S-16	16.5	127.7	73.0	32.7	66.5	119.8

4.3.2 NO_2

The geographical distributions of NO_2 concentrations in Izmir are shown in Table 4.3. The weekly average concentrations of NO_2 measured in industrial sites were at 14.9-25.6 μg m^{-3}, in urban sites they were at 13.3-50.6 μg m^{-3}, in suburban sites they were at 6.4-31.7 μg m^{-3} and in rural site 2 it was 7.8 μg m^{-3}. It should be noted that high concentrations were measured at urban sites where due to residential heating and high level of traffic as NO_2 is considered as a pollutant originated from traffic. NO_2 concentration was measured at the highest level (51 μg m^{-3}) at site 8 located in opposite to minimum O_3 concentration during the same sampling period. At all sampling sites among minimum values measured the lowest concentration was 1.0

µg m^{-3} (site 14, suburban), the highest concentration was 20.4 µg m^{-3} (site 8, urban). On the other hand, the lowest value was 17.8 µg m^{-3} (site 2, rural) and, the highest value was 241.1 µg m^{-3} (site 6, suburban) among maximum values measured. This study showed that the concentration of NO_2 near busy roads was 2.5 times higher than those measured in rural site. When NO_2 and O_3 concentrations were compared it was seen that low NO_2 concentrations were accompanied by high O_3 concentrations. Low O_3 concentrations were noted in areas with dense traffic, possibly the result of O_3 being titrated by NO.

The average levels of NO_2 showed that the National Air Quality Standard for Turkey, Threshold for the protection of human health (40 µg m^{-3}) for the year of 2008 (2024 target value) was exceeded in two of the selected sites (8 and 13) with mean levels of 50.6 and 43.1 µg m^{-3} respectively.

Table 4.3 Weekly Average NO_2 concentrations (μg m^{-3}) in Izmir

Sampling Sites		Min	Max	Average	SD	Median	95%
Urban	S-1	5.1	26.3	13.3	5.3	12.1	20.8
	S-7	14.6	75.8	36.3	13.5	32.1	56.7
	S-8	20.4	77.8	50.6	14.6	52.1	72.1
	S-9	6.2	66.6	34.8	11.6	33.9	51.8
	S-12	6.6	30.8	15.9	5.8	15.6	25.6
	S-13	16.3	78.7	43.0	16.1	40.1	67.5
Rural	S-2	1.9	17.8	7.8	3.8	6.8	13.6
Suburban	S-4	4.6	53.3	29.6	11.7	30.7	46.4
	S-5	14.6	42.8	24.6	7.3	23.0	38.7
	S-6	9.3	41.1	31.7	41.1	22.6	40.7
	S-10	7.7	28.4	16.3	5.3	14.9	24.9
	S-14	1.0	20.2	6.4	5.4	4.9	17.5
Industrial	S-3	13.9	50.4	25.6	7.9	24.8	38.3
	S-11	4.1	31.6	14.9	6.3	15.1	24.0
	S-15	14.0	45.0	22.2	6.9	20.0	32.8
	S-16	6.6	41.3	18.8	8.3	19.6	33.4

4.3.3 VOCs

Several compounds (alkanes-alkenes, aromatics, halogenated and oxygenated VOCs) were also analyzed (the total number of analyzed compounds was 83). Sixty four of the 83 VOCs were detected in most of the samples collected at 16 sampling sites. The geographical distributions of average total VOCs of ($\sum_{64}$VOCs) concentrations in Izmir are shown in Table 4.4. The weekly average concentrations of $\sum_{64}$VOCs measured in industrial sites range between 85.1-122.7 μg m^{-3}, 72.1-113.3 μg m^{-3}, 49.2-95 μg m^{-3} and in urban and in suburban sites, respectively. The average concentration in rural site was 76.5 μg m^{-3}. As it is noted, values decreased respectively from industrial to urban and suburban sites. At all sampling sites among minimum values measured the lowest concentration was 9.8 µg m^{-3} (site 5, suburban), the highest concentration was 47.1 µg m^{-3} (site 3, industrial). On the other hand, the lowest value was 130.2 µg m^{-3} (site 14, suburban), the highest value was 374.6 µg m^{-3} (site 16, industrial) among maximum values measured.

Table 4.4 Weekly Average $\sum_{64}$ VOCs concentrations (µg m^{-3}) in Izmir

Sampling Sites		**Min**	**Max**	**Average**	**SD**	**Median**	**95%**
Urban	S-1	11.9	324.7	77.6	65.5	57.8	158.0
	S-7	21.3	224.5	87.6	55.4	64.3	193.2
	S-8	31.8	246.4	101.9	51.0	93.9	186.9
	S-9	22.9	360.1	113.3	93.1	68.2	285.1
	S-12	19.2	327.1	100.3	72.7	76.8	228.1
	S-13	15.0	162.8	72.1	48.0	50.0	149.4
Rural	S-2	11.5	303.1	76.5	78.0	38.5	243.9
Suburban	S-4	15.6	201.5	73.3	52.17	57.2	188.1
	S-5	9.8	313.9	90.9	81.1	74.4	278.5
	S-6	13.3	320.2	95.0	91.0	49.3	278.1
	S-10	11.3	373.9	78.3	73.1	48.9	166.6
	S-14	11.1	130.2	49.2	36.0	36.4	123.4
Industrial	S-3	47.1	203.9	122.7	46.4	134.3	185.1
	S-11	16.1	219.6	86.6	63.4	57.1	208.7
	S-15	18.1	275.1	85.1	69.8	46.1	225.9
	S-16	20.8	374.6	98.0	83.0	66.5	259.8

4.3.4 BTEX and 1,3,5-trimethylbenzene

The BTEX mean concentration (sum of the concentrations of benzene, toluene, ethylbenzene, m/p-xylene and o-xylene) measured in Izmir was 12.11±10.11 µg m^{-3} (mean±s.d.). The mean concentrations of benzene, toluene, ethyl benzene, m/p-xylene and o-xylene were 2.36±1.87, 6.30±5.66, 0.70±0.83, 2.28±2.92 and 0.50±0.59 µg m^{-3}, respectively. The mean concentration for 1,3,5-trimethylbenzene was 0.42±0.46 µg m^{-3}. The highest levels of BTEX were measured in sites 3 and 8, which were located near a major street. In a previous study of Matysik, Ramadan & Schlink (2010) a strong correlation between sites with high traffic volume and the concentration of aromatic compounds was also noted. Sites 14 and 2 had the lowest concentrations. The same trend of 1, 3, 5-trimethylbenzene with BTEX were obtained in the same sampling sites. BTEX and 1, 3, 5-trimethylbenzene contributed 10% of $\sum_{64}$ VOCs concentrations.

Weekly average concentrations of BTEX are presented in Table 4.5. Toluene, ethyl benzene, xylenes also revealed a similar distribution between sampling sites. These three compounds with high concentrations were measured at sites 3, 8, and 12 (industrial and urban sites). Apart from these three compounds high benzene concentrations were measured at sites 8, 16 and 7 (industrial and urban sites); while high 1,3,5-trimethylbenzene concentrations were measured at sites 8, 12 and 3 (urban and industrial). Furthermore, benzene can show a different distribution as its lower reactivity with OH radicals allows it to be transported long distances without degradation (Hellen, Hakola, Laurila, Hiltunen & Koskentalo, 2002). Toluene was the most abundant aromatic in all sampling sites with the highest concentration corresponding to a spot with high density traffic, industrial zone (Chang et al., 2005). Toluene is the most dominant species in many emission sources of aromatic VOCs (i.e., vehicle exhaust, solvent usage, gasoline evaporation, fossil fuel combustion, adhesives, etc.) (Na et al., 2004). Lowest concentrations were measured in sites 2 and 14 (rural and suburban sites). The lowest toluene, ethyl benzene, xylene concentrations were measured at site 2, the lowest benzene and 1,3,5-trimethylbenzene concentration were measured at site 14. The highest contribution of

BTEX to total VOCs was found in sites 3 (26%) and 8 (24%). The results clearly indicate the predominance of toluene among all the VOCs investigated, since it exhibits the highest mean concentration with 6.30 μg m^{-3}. This major presence has also been reported in other studies conducted in urban atmospheres (Yamamoto, Okayasu, Murayama, Mori, Hunahashi & Suzuki, 2000; Ho & Lee, 2002; Gou, Wang, Simpson, Blake, Yu, Kwok & Li, (2004); Parra et al., 2009).

According to Directive 2000/69/EC (EC, 2000), the annual mean benzene concentrations in ambient air must not exceed 5 μg m^{-3}. The concentration of benzene did not exceed this limit value for toluene at any site, while site 8 was close to this limit (4.06 μg m^{-3}). WHO establishes a guideline value for the protection of human health as 260 μg m^{-3} (Parra et al., 2009), expressed as weekly average, that indeed remains far above the levels measured in this study.

Table 4.5 Mean concentrations of BTEX and 1,3,5-trimethylbenzene at 16 sites

Sampling Site		**Benzene**	**Toluene**	**Ethylbenzene**	**m/p-xylene**	**o-xylene**	**BTEX**	**1,3,5-TMB[*]**
Urban	1	2.60	4.57	0.43	1.16	0.30	8.75	0.23
	7	3.51	7.43	0.82	2.36	0.73	14.85	0.71
	8	4.06	13.89	1.31	3.99	1.17	24.42	1.13
	9	1.77	6.52	0.71	2.01	0.52	11.12	0.51
	12	3.29	9.98	0.97	2.89	0.80	15.45	0.79
	13	2.09	4.23	0.37	0.98	0.24	7.37	0.20
Rural	2	1.03	2.14	0.24	0.59	0.13	3.85	0.11
Suburban	4	1.67	7.03	0.59	2.10	0.35	11.75	0.27
	5	1.84	6.02	0.74	2.11	0.61	10.96	0.45
	6	2.04	5.07	0.41	1.08	0.28	8.88	0.22
	10	2.43	3.10	0.28	1.21	0.27	7.28	0.16
	14	1.05	1.22	0.18	0.44	0.13	2.50	0.10
Industrial	3	2.29	17.39	2.80	8.47	1.39	32.34	1.04
	11	2.39	2.54	0.37	1.43	0.33	6.04	0.26
	15	2.18	3.72	0.32	1.22	0.27	6.12	0.18
	16	3.46	3.51	0.37	3.89	0.38	9.60	0.25
	Mean	2.36	6.30	0.70	2.28	0.50	12.11	0.42
	Sdev	1.87	5.66	0.83	2.92	0.59	10.11	0.46
	Median	1.87	4.50	0.47	1.48	0.34	9.01	0.27

[*] TMB: Trimethylbenzene

In Table 4.6, aromatic VOCs concentrations in Izmir were compared with the concentrations measured in major cities in different countries. Helsinki, Toulousse, Pamplona and Izmir have almost same patterns for the mean concentrations of five aromatic VOCs in their urban sites. The highest concentration belongs to toluene while the lowest belongs to o-xylene. The concentrations of BTEX measured in this study were in the range of the BTEX concentrations measured in other cities. Some cities have generally lower concentrations, as those found in Helsinki and Pamplona, while large Mediterranean cities (i.e. Rome and Athens) are characterized by higher pollution levels. In Toulousse, France, the levels were similar to those measured in Izmir, but measurements were performed during summer, when concentrations are generally lower.

Table 4.6 Comparison of aromatic VOCs concentrations (µg m^{-3}) in Izmir and different cities

City		**Benzene**	**Toluene**	**Ethylbenzene**	**m/p-xylene**	**o-xylene**
Izmir,Turkey	Urban	2.36	6.30	0.70	2.28	0.50
Hong Kong (Lee et al., 2002)	Industrial	15.07	139.4	24.68	27.88	13.39
Pamplona, Spain (Parra et al., 2009)	Urban	2.84	13.26	2.15	3.38	2.63
Fuji,Japan (Kume et al., 2008)	Industrial	2.06	14.0	1.52	1.83	0.62
Karachi, Pakistan (Barletta et al., 2002)	Urban, traffic	18.2	27.2	-	13.5	4.8
Ottawa, Canada (Zhu et al., 2005)	Urban, residential	1.19	2.48	0.58	-	0.31
Algiers, Algeria (Kerbachi et al., 2006)	Urban	9.6	15.2	0.9	3.2	-
Athens, Greece (Chatzis et al., 2005)	Residential	13.3-26.0	-	-	-	-
Roma, Italy (Brocco et al., 1997)	Urban	35.5	99.7	17.6	54.1	25.1
Toulousse, France (Simon et al., 2004)	Urban	2.0	6.6	-	1.2	3.7
Helsinki, Finland (Hellen et al.,2002)	Urban, residential	2.1	6.6	1.3	4.1	1.6

4.4 Seasonal Variation of Pollutants

4.4.1 Ozone

Maps of spatial distribution of O_3 concentrations in far from areas throughout Izmir were plotted for the summer, autumn, winter and spring seasons. Figure 4.13 shows the seasonal variations of the average concentrations of O_3. Ozone concentrations showed typical annual variations at all sites reaching the highest values in summer when the sunlight was the most intense. Similar observations have been reported recently by Godzik (1997) and Pehnec et al. (2005). These differences were found as 4 times higher in sites close to pollutant sources, 2 times higher in sites far from pollutant sources.

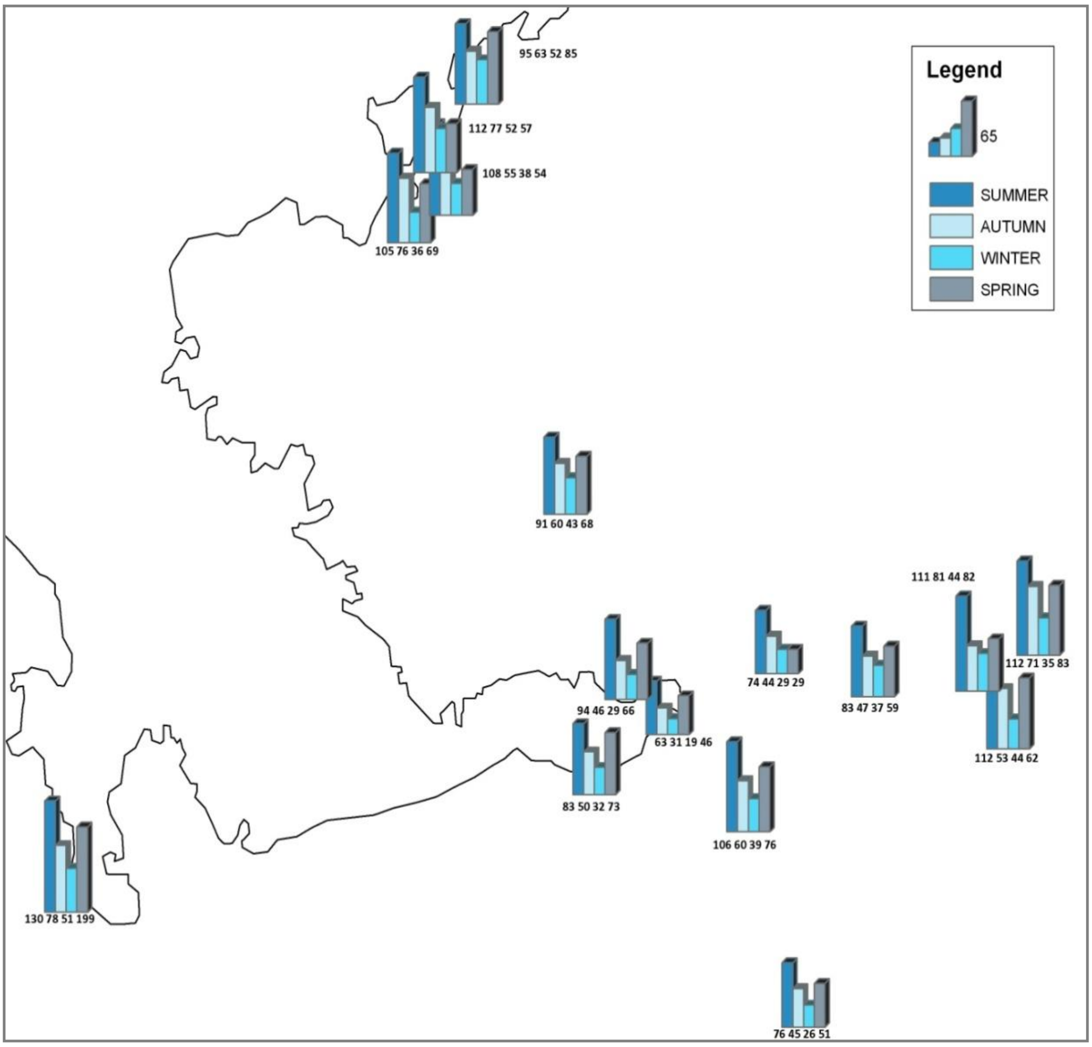


Figure 4.13 Seasonal variation of O_3 concentration (µg m^{-3}) at 16 sampling sites in the city of Izmir.

The highest ozone concentrations were measured at site 14 during summer and winter, 132 µg m^{-3} and 47 µg m^{-3}, respectively. At site 8 where the lowest average weekly concentrations were measured, the values were 65 µg m^{-3} for summer and 18 µg m^{-3} for winter.

The comparison of ozone concentrations with concurrent measurements in the city showed that suburban concentrations were higher throughout the measurement period. Lower ozone concentrations in the city, where the concentrations of traffic exhaust gases was high, were probably the results of ozone reaction with nitrogen oxide from exhaust emission. Maximum concentrations usually occurred away from the sources of primary pollutants. High ozone concentrations have been measured in rural areas where local sources of ozone precursors were insignificant. Pehnec et al. (2005) stated that the long-range transport of ozone and its precursors from upwind areas or from a stratospheric origin might be responsible for the higher ozone concentrations found in the suburban site.

4.4.2 NO_2

Figure 4.14 shows the seasonal variations of the average concentrations of NO_2. The concentration of NO_2 shows differences between seasons. The highest values were measured at sites close to dense traffic sources during summer. During this period NO_2 concentrations varied between 4-65 $\mu g\ m^{-3}$. On the other hand, high concentrations were measured at the areas where residential heating was important in addition to traffic. In this season concentrations ranged between 11-57 $\mu g\ m^{-3}$. Generally, NO_2 concentrations were higher in winter and autumn than in spring and summer, as found in many other cities (Glasius et al., 1999; Batterman, Peng, & Braun, 2002; Kourtidis, Ziomas, Zerefos, Kosmidis, Symeonidis, Christophilopoulos et al., 2002; Pankow, Luo, Bender, Isabelle, Hollingsworth, Chen, et al., 2003). NO_2 concentrations reach a maximum in the winter due to higher atmospheric stability, and a minimum in summer, when atmospheric dispersion is more important whereas it was the opposite at sites 4-6 and 12. Those sites were affected by increased traffic during summer holiday period. Seasonal change between ozone concentrations were lower compared to other sampling sites.

The NO_2 levels depend mainly on chemical reactions and not on direct emissions, since this pollutant is produced mainly from the oxidation of traffic-emitted NO. However, it is also directly emitted by traffic in a minor proportion. This view was also supported by previous studies of Mayer, Haustein, & Matzarakis (1999), Glasius et al. (1999) and Zabalza, Ogulei, Elustondo, Santamaria, Alastuey, Querol et al. (2007).

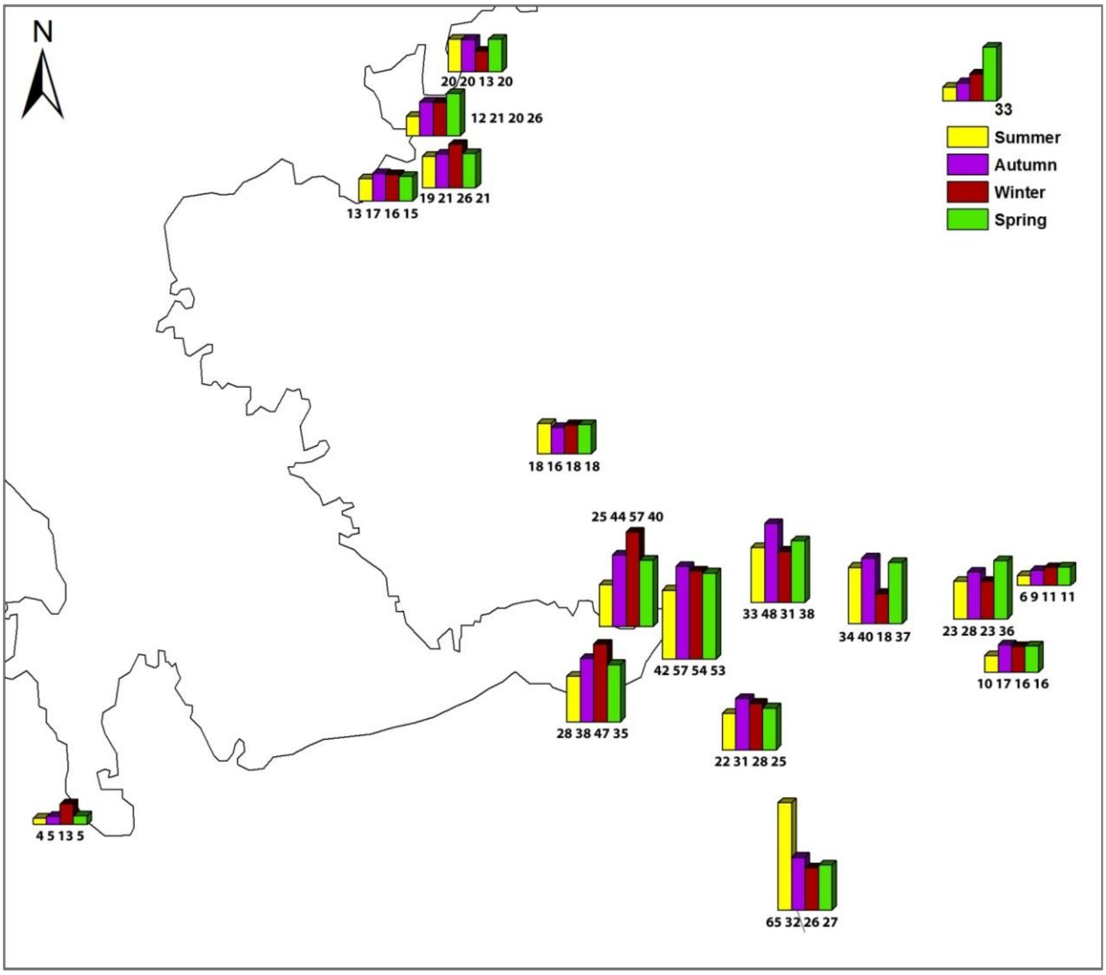


Figure 4.14 Seasonal variation of NO_2 concentration ($\mu g\ m^{-3}$) at 16 sampling sites in the city of Izmir.

4.4.3 VOCs

Figure 4.15 shows the seasonal variations of the average concentrations of $\sum_{64}$ VOCs. The concentration of total VOCs shows seasonal differences. Higher concentrations were measured in winter and lower concentrations were measured in summer, as found in many other cities (Pankow, Luo, Bender, Isabelle, Hollingsworth,Chen, et al., 2003; Na et al., 2003-2005; Filella et al., 2006; Parra et al., 2009). These differences were found as 1.5 times higher in sites 6 and 13; 2 times higher in sites 1, 3, 8, 10, 12 and 14; 3 times higher in sites 2, 4, and 9; 4 times higher in site 5 in winter. According to previous studies four additional factors can affect the seasonal VOC concentrations (1) seasonal abundance of the OH- radicals (chemical removal of VOC by OH radicals is faster in summer than in winter since more sunlight and higher temperatures produce higher chemical removal reaction rates (Ho et al., 2004; Glasius et al., 1999); (2) changing VOC source strengths; and (3) changing atmospheric mixing pattern such as enhancement of vertical mixing through increased convection during the summer months (4) higher atmospheric stability in winter (Cheng et al., 1997; Na et al., 2005).

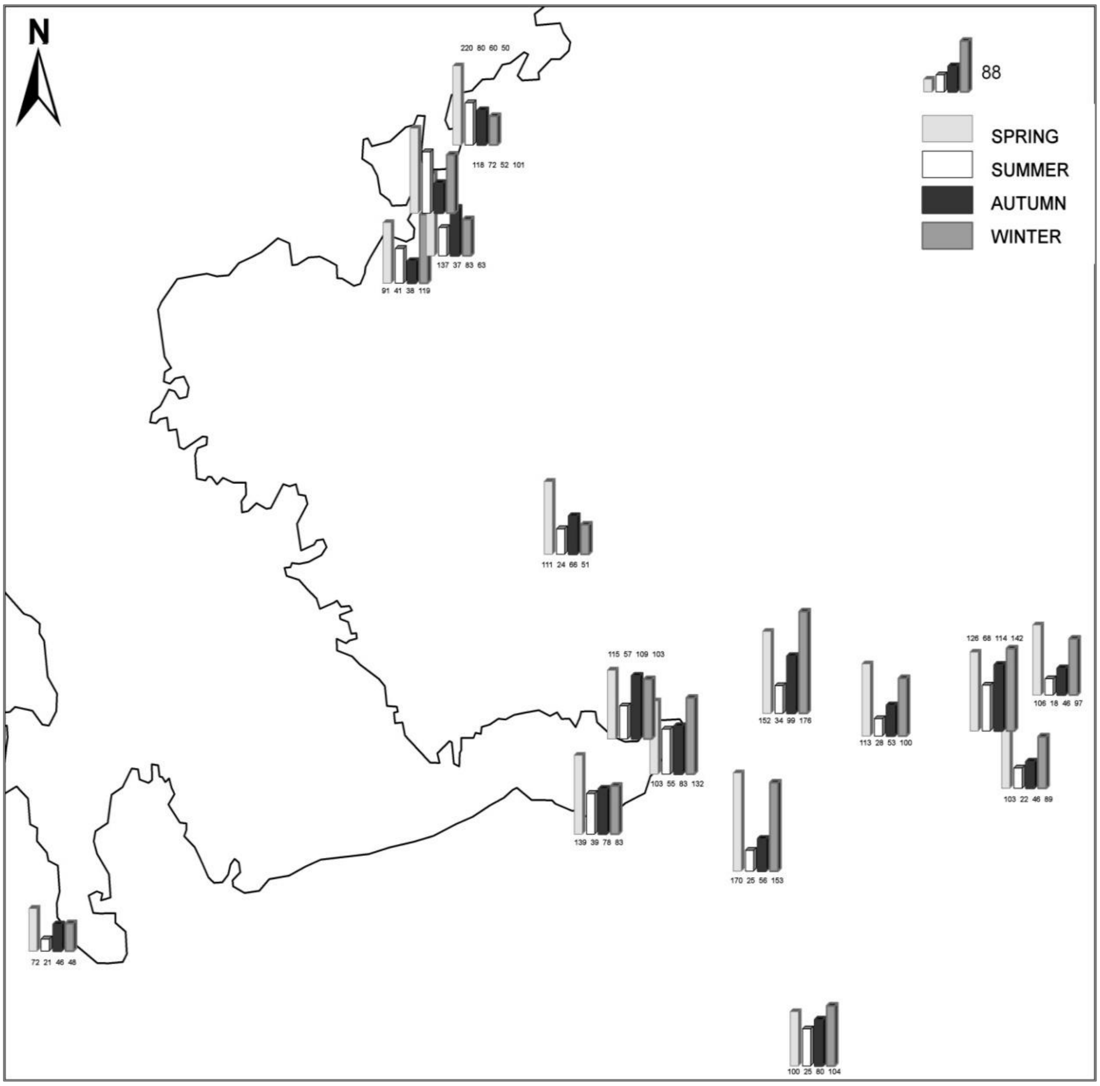


Figure 4.15 Seasonal variation of VOCs concentration (μg m^{-3}) at 16 sampling sites in the city of Izmir.

In order to identify the impact of mixing height parameter on seasonal variation of VOC concentration, upper air sounding and hourly surface temperatures were used to calculate daily mixing heights (method of Holzworth (1972)) in the city of Izmir. It was noted that there were significant differences between summer and winter season ($p<0.01$). It was also identified that mixing heights were higher in summer (1440 m) than in winter (940 m). This difference supported higher VOCs concentration in winter, lower concentration in summer season in the city of Izmir.

On the other hand, at sites 11, 15 and 16 concentrations were higher in summer compared to winter season. Evaporative emissions emitted from gasoline spills, gasoline evaporation, and the use of solvents (e.g., in painting, printing, and dry cleaning) are strongly affected by changes in ambient temperature (Cheng, Fu, Angle & Sandhu, 1997). Accordingly at these sites that were close to petroleum refinery and petrochemical plants where, high concentrations were measured during summer.

The seasonal variations of each VOCs group and percentages of total VOCs observed at the sampling sites in Izmir, are given in Figure 4.16. At all sampling sites, the sum of alkane and alkenes were generally, above 60% of total VOCs, throughout the summer and winter periods. Similar observations have been reported recently (Brocco, Fratarcangeli, Lepore, Petricca & Ventrone, 1997). Contribution of aromatics to the total concentration range between 15%-35% while contribution of halogenated VOCs was 5% and contribution and of oxygenated VOCs was about 15%. At the sampling sites 3, 4 and 12, contribution of these groups to the total concentrations were different from other sites in summer. Contributions of aromatic and oxygenated compounds were above 20%. There were high aromatic and oxygenated concentrations in both summer and winter at site 3.

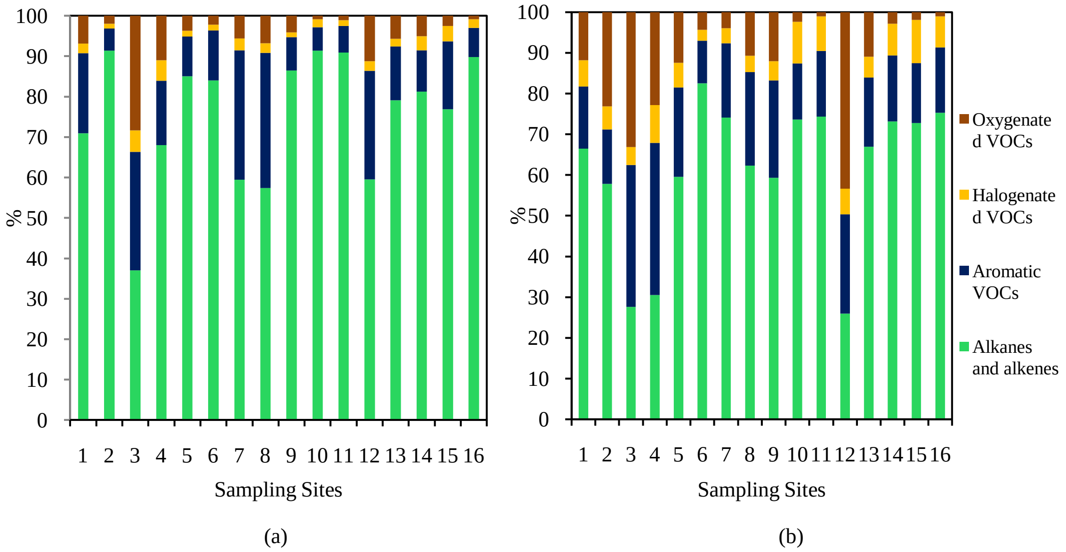


Figure 4.16 Contribution of alkane and alkene, aromatic, halogenated and oxygenated compounds to total VOCs during winter (a), and summer (b).

The contribution of aromatics decreased in winter whereas the contribution of alkane-alkanes increased generally. Oxygenated compounds measured at sampling sites decreased in winter. There was same contribution trend for total concentrations at all sites during both seasons. However there was significant change at site 12 during the summer. The contribution of oxygenated compounds was 11% in winter whereas this increased to 43% in summer. At the downtown site, the sum of alkane-alkenes and aromatic contributions was almost constant, about 84% to 86% of total VOCs, throughout the study period. At the industrial site alkane-alkenes and aromatic make up 89% to 94% of VOCs and there were no consistent seasonal variation.

4.5 Sources of VOCs

Emission sources have different VOC profiles. The ratios of different VOC can be used as tracers to distinguish among diverse VOC emission sources. Some researchers have consistently used diagnostic VOC compound ratios to help them identifying the possible emission sources (Christensen, Skov, Nielsen & Lohse, 2000; Correa, Martins & Arbilla, 2003; Hsieh & Tsai, 2003; Ho et al., 2004; Elbir et al., 2007). The Toluene/Benzene ratios in ambient air for most non-industrialized cities, in which vehicle exhaust could be the main source of toluene, ranged from 1 to 2 (Barletta et al., 2002; Simon et al., 2004; Zhu et al., 2005).In this study, toluene/benzene (T/B) ratios for Izmir were calculated for different sites and they were compared to those reported for other cities (Table 4.7). T/B ratios measured in industrial zones of Hong Kong (9.2) and Fuji (8.7) were similar to the T/B ratio obtained in site 3 (11,7 in summer, 5.0 in winter). It can be seen from Table 4.7 that T/B ratios increase during the summer period due to the reduced emissions of benzene. The rate of decrease of benzene concentrations is however significantly higher than that of toluene. Low T/B ratios obtained during winter can be explained by relatively increasing benzene emissions due to residential heating in winter season (Elbir et al., 2007). There was no seasonal variation in the sites of 11, 12, 15 and 16 which were located closed to the petroleum refinery and petrochemical industry.

Table 4.7 Ambient T/B ratios in Izmir

Sampling Site		**T/B Ratio (Summer)**	**T/B Ratio (Winter)**
Uban	S-1	4.2	0.9
	S-7	3.9	1.1
	S-8	4.4	2.3
	S-9	5.4	2.3
	S-12	0.8	0.9
	S-13	2.6	1.8
Rural	S-2	3.9	1.0
Suburban	S-4	7.2	2.0
	S-5	3.6	2.3
	S-6	5.2	1.6
	S-10	2.4	1.2
	S-14	1.1	1.1
Industrial	S-3	11.7	5.0
	S-11	1.3	1.0
	S-15	1.1	1.7
	S-16	1.0	1.0

In this study, 64 VOCs were measured between 2007-2008 at the 16 sampling sites. Most abundant 5 compounds were: n-pentane, methylcyclopentane, 3-methylpentane, ethyl acetate, iso-pentane and toluene. Table 4.8 summarizes the mean values of these compounds. The contribution of these compounds on

$\sum_{64}$ VOCs varied between 73% and 86%. In general, these results are similar to the ones found in other big cities around the world (Brocco et al., 1997; Derwent et al., 2000; Durana, Navazo, Gomez, Alonso, Garcia, Ilardia, Gangoiti & Iza, 2006). Several studies have noted that refinery plant, motor vehicle exhaust and fuel evaporation that are also available in the study area may be the sources of iso-pentane and n-pentane emissions (Watson, Judith & Fujita, 2001; Schauer, Kleeman, Cass & Simoneit, 2002; Buzcu et al., 2006; Hung-Lung et al., 2007; Ras, Marce & Borrull, 2009). The highly reactive biogenic isoprene was below detection limit at many sites.

Correlation between measured VOCs compounds was also studied. Correlation was successfully performed between 50 compounds out of 64 VOCs measured. Other 14 compounds (1-pentene, trans-2-pentene, isoprene, cis-2-pentene, 2,4,-dimethylpentane, 2,3,4-trimethylpentane, styrene, p-diethylbenzene, cis-1,2-dichloroethene, bromochloromethane, bromodichloromethane, cis-1,3-dichloropropene, dibromochloromethane, 1,1,2,2-tetrachloroethane) were not generally detected during sampling campaigns.

Correlation was identified in alkanes-alkenes group among isopentane, 2-methylhexane, 2,3-dimethylpentane, 3-methylhexane, methylcyclohexane, 2-methylheptane, 3-methylheptane, n-octane, n-nonane, n-propylbenzene, n-undecane, $p<0.01$. Correlation was also identified between the compounds mentioned above with aromatic group and halogenated groups. Especially n-nonane, n-propylbenzene, n-decane and n-undecane from alkanes-alkenes groups had higher positive correlation ($r>0.80$) with aromatic compounds. On-road vehicles are the sources of n-undecane (Hung-Lung et al., 2007). This correlation level could be the result of alkanes-alkenes and aromatics having the same source. From oxygenated groups only methyl isobutyl ketone had significant correlation with alkanes-alkenes groups.

Table 4.8 Average concentrations of top 5 VOCs at 16 sampling sites

	Compound	Concentration (µg m^{-3})	Ratio (Σ/Σ_{64}VOC)
Urban			
Site-1	n-Pentane	38.22	0.80
	Methylcyclopentane	12.79	
	Ethyl acetate	12.57	
	3-Methylpentane	6.62	
	Iso-pentane	6.46	
Site-7	n-Pentane	21.70	0.74
	Methylcyclopentane	17.98	
	Ethyl acetate	9.58	
	3-Methylpentane	8.77	
	Toluene	7.43	
Site-8	n-Pentane	32.87	0.75
	Methylcyclopentane	17.97	
	Toluene	13.89	
	3-Methylpentane	8.64	
	Ethyl acetate	7.95	
Site-9	n-Pentane	76.36	0.86
	Methylcyclopentane	17.95	
	Iso-pentane	8.93	
	3-Methylpentane	8.60	
	Ethyl acetate	8.07	
Site-12	n-Pentane	46.20	0.86
	Methylcyclopentane	19.03	
	3-Methylpentane	13.33	
	Iso-pentane	7.24	
	Ethyl acetate	6.36	
Site-13	n-Pentane	38.94	0.81
	Methylcyclopentane	19.06	
	Ethyl acetate	17.10	
	3-Methylpentane	14.53	
	Toluene	9.98	
Rural			
Site-2	n-Pentane	43.27	0.86
	Methylcyclopentane	13.00	
	Iso-pentane	8.29	
	Ethyl acetate	8.25	
	3-Methylpentane	6.74	
	Toluene	7.03	

Table 4.8 (continuous)

	Compound	**Concentration (μg m^{-3})**	**Ratio (Σ/Σ$_{64}$VOC)**
Suburban			
Site-4	n-Pentane	31.12	0.77
	Methylcyclopentane	18.52	
	3-Methylpentane	9.37	
	Ethyl acetate	8.87	
	Toluene	7.03	
Site-5	n-Pentane	49.83	0.79
	Methylcyclopentane	16.57	
	3-Methylpentane	9.33	
	Iso-pentane	6.35	
	Toluene	6.02	
Site-6	n-Pentane	62.61	0.88
	Methylcyclopentane	17.97	
	3-Methylpentane	8.74	
	Ethyl acetate	6.59	
	Toluene	5.07	
Site-10	n-Pentane	33.58	0.83
	Methylcyclopentane	17.94	
	3-Methylpentane	8.48	
	Ethyl acetate	7.70	
	Toluene	4.23	
Site-14	n-Pentane	22.44	0.86
	Methylcyclopentane	18.35	
	3-Methylpentane	13.86	
	Ethyl acetate	3.99	
	Iso-pentane	3.08	
Industrial			
Site-3	Ethyl acetate	29.44	0.73
	n-Pentane	25.83	
	Methylcyclopentane	18.30	
	Toluene	17.39	
	3-Methylpentane	9.23	
Site-11	n-Pentane	42.13	0.83
	Methylcyclopentane	18.69	
	3-Methylpentane	12.69	
	Iso-pentane	6.04	
	Ethyl acetate	3.45	
Site-15	trans-2-Pentene	39.00	0.85
	n-Pentane	32.87	
	Methylcyclopentane	18.35	
	3-Methylpentane	13.71	
	Iso-pentane	10.47	
Site-16	n-Pentane	55.08	0.83
	Methylcyclopentane	18.34	
	3-Methylpentane	13.73	
	Iso-pentane	12.70	
	m.p-Xylene	3.89	

N-pentane, 3-methylpentane, methylcyclopentane and cyclohexane that were most abundant compounds of all sampling sites had significant correlation with neither each groups nor other groups.

There were significant correlation between measured aromatic groups (r value above 0.80, $p<0.0001$). There were lower correlations between benzene and other aromatic compounds, although this lower correlation could also suggest another possible origin for benzene in the study area. Other aromatics (toluene, xylene) have a high reactivity with the radicals relative to benzene.

Aromatic compounds had significant correlation with halogenated compounds apart from dibromomethane. These correlations were positive between compounds. There was no correlation between dibromomethane with other measured VOCs compounds.

Only methyl isobutyl ketone from oxygenated compounds (ethyl acetate, methyl isobutyl ketone, butyl acetate) had significant correlation with alkanes-alkenes and halogenated compounds. But there were significant correlation with all aromatic and oxygenated compounds. These correlations were supported through identified relations between aromatics and oxygenated compounds in section 4.4.3.

4.6 Ozone Formation Potential of VOCs

Recent studies showed that volatile organic compounds (VOCs) limit the rate of ozone formation in some urban areas (Huang, Shao, Lu & Liu, 2004). Therefore it has been of increasing concern to identify reactive VOCs species through ambient measurements. Reactivity of VOCs could be assessed by ozone formation potentials (OFPs).

The OFPs of VOCs in 16 sampling sites were calculated by summing up the products of individual VOCs amounts and their corresponding MIR factors. Figure 4.17 and Figure 4.18 shows the highest 10 OFPs of VOCs calculated by the MIR method in the 16 sampling sites in the city of Izmir for summer and winter seasons. In both figures species of 1,3,5-trimethylbenzene, 3- methylpentane, ethyl acetate, iso-pentane, m,p-xylene, methylcyclopentane, n-pentane, toluene, o-xylene are top 9 species out of the highest 10 whereas last compound is benzene during winter and cyclohexane during summer. The highest 10 OFPs of VOCs in Izmir accounted for more than 85% of the total OFPs of all measured species. The measurement results showed species with relatively high concentrations were n-pentane, methylcyclopentane, 3-methylpentane, iso-pentane and ethyl acetate. However, after taking into account the photochemical reactivity of each VOCs 3-methylpentane, isopentane, m,p-xylene, n-pentane, toluene became the key species in terms of OFPs in Izmir during the sampling periods.

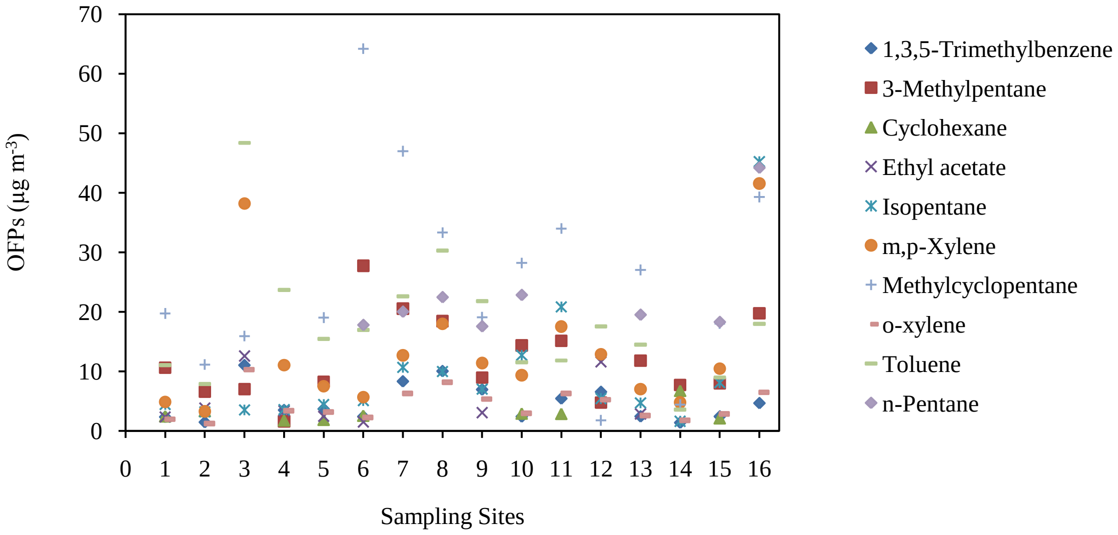


Figure 4.17 The top 10 OFPs in sampling sites in summer.

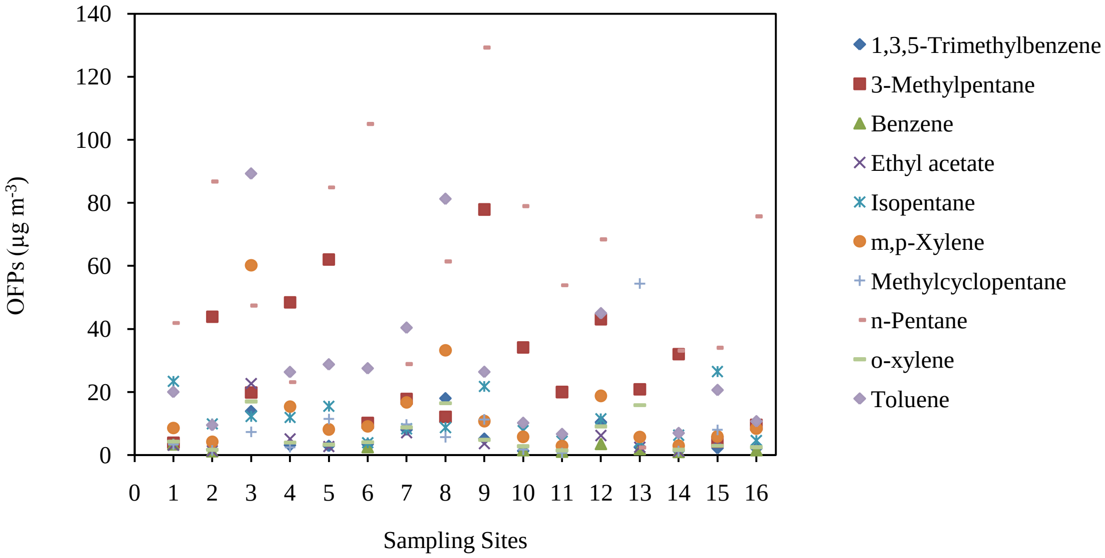


Figure 4.18 The top 10 OFPs in sampling sites in winter.

The highest OFPs during summer on all sampling sites were methylcyclopentane (18%), o-xylene (15%), 3-methylpentane (10%) and m,p-xylene (10%). OFP contribution was noted close to average in all sampling sites. During winter season n-pentane (34%) was the first, 3-methylpentane (16%) was the second and toluene (13%) was the third compound for OFPs of VOCs. The OFPs contribution of these three compounds were similar to each other, especially contribution of n-pentane were 60% in site 16 and were above 50% in sites 6, 10 and 11.

Four groups of VOCs namely as OFPs alkanes and alkenes, aromatics, halogenated compounds and oxygenated compounds were calculated. The contributions of the OFPs of these groups are shown in Figure 4.19. The alkenes and higher molecular weight aromatics are generally the most important species in terms of ozone generation potential in the previous studies of Cheng et al. (1997), Wu, Chang, Sree, Chiu & Lo (2006) and Duan et al. (2008). However alkanes account for about half of the total MIR at the industrial site because of their high concentrations. Alkanes and alkenes often played the most important role in ozone formation and accounted for 69% of total ozone formation potential, followed by aromatic hydrocarbons (28%) oxygenated VOCs (3%) and halogenated VOCs (less than 1%). On the other hand, the contribution of aromatics to OFPs was exactly the same with alkanes and alkenes in sites 8, 12 and 5 whereas the contribution of site 3 was higher for aromatics compared to others. Especially in this sites toluene and m,p-xylene concentrations and OFPs differ significantly compared to other sampling points. Those sites (sites 3-8) were closed to traffic and industry. Sampling site 12 was affected from the petroleum refinery and petrochemical industry. In sampling site 3 where aromatic groups have high OFPs, oxygenated groups' OFPs has also increased in parallel and reached values above average (7%).

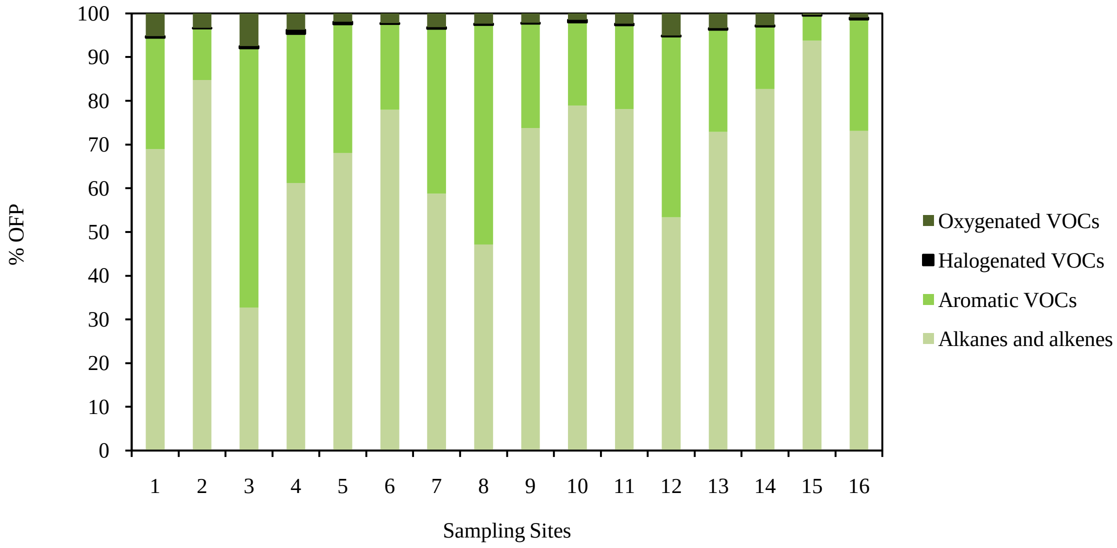


Figure 4.19 OFPs contribution of VOC groups at sampling sites in the city of Izmir.

4.7 Correlation Between O_3, NO_2, VOC and Meteorological Parameters

Within the scope of this study the correlation between ozone, NO_2, VOCs and meteorological parameters (temperature, wind speed, relative humidity and solar radiation) was also investigated. This study describes an improved statistical methodology for ozone trends as well as characterizes the relationships between individual meteorological parameters, ozone, NO_2 and VOCs. Each variable plays a unique role in explaining variations in ozone through its own particular response, or effect. For example, increasing temperature is usually associated with increasing ozone, while increasing wind speed is usually associated with decreasing ozone (i.e. dilution effect).

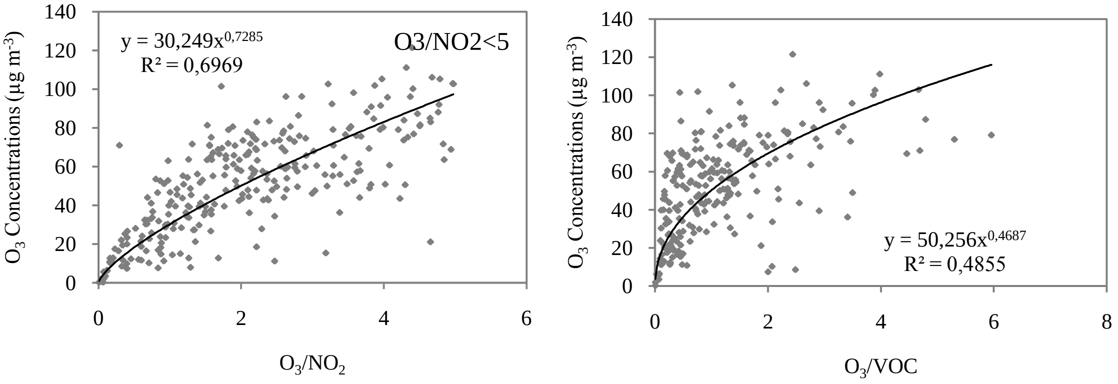
The relationship between VOCs and ozone levels was studied. In this case, there was a significant negative correlation between them. Although BTEX are known to be ozone precursor and, therefore, increases in their concentrations should imply intensification of the ozone formation, this behavior was not observed in this case. This finding may be attributable to the association of VOC emissions with those of NO, a compound emitted into the atmosphere from road traffic which disappears by reaction with ozone (Parra, et al., 2006). Therefore, NO concentrations were high enough to reduce ozone concentration. Consequently, traffic is confirmed as the main source for BTEX.

VOCs and NO_2 atmospheric chemistry are not strongly affected by temperature. There is a temperature effect on reaction rates, but it is less important than for emissions. However, a significant negative correlation between temperature and VOCs concentration were determined (Table 4.9). This relates to increases in temperature correspond to higher radiation, conditions that favor the loss of VOCs by photochemical degradation and, consequently, a decrease in their concentration.

In general, temperature and solar radiation showed a positive influence on O_3 values, as expected. Relative humidity is negatively correlated with O_3. This behavior, also observed in previous studies, suggests that high concentrations of water vapor partially remove pollutants from the atmosphere by means of chemical reaction (acid rain) or condensation (promoting deposition) (Felipe-Sotelo, Cal-Prieto, Gomez-Carracedo, Andrade, Carlosena & Prada, 2006; Ras et al.,, 2009).

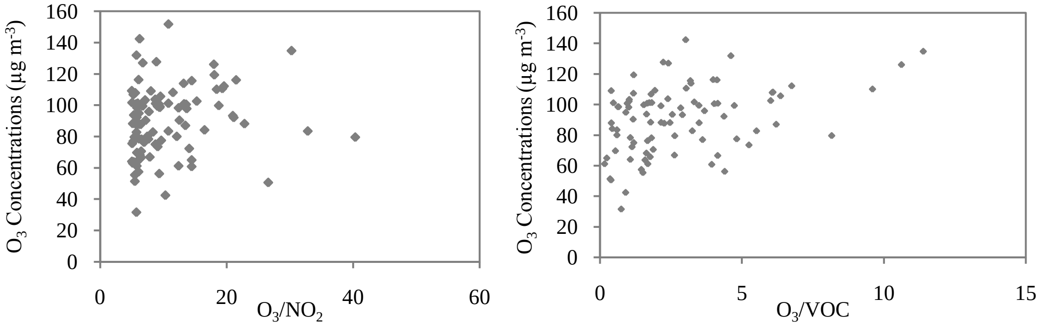
Table 4.9 Correlation coefficients between Ozone, VOC and NO_2 with meteorological parameters

Parameters	**O_3**	**NO_2**	**VOC**	**O_3**	**NO_2**	**VOC**	**O_3**	**NO_2**	**VOC**	**O_3**	**NO_2**	**VOC**
	Site-1			**Site-2**			**Site-3**			**Site-4**		
T	0.75	-0.32	-0.20	0.74	-0.27	-0.38	0.76	0.13	-0.50	0.65	0.45	-0.37
RH	-0.60	0.26		-0.44	0.13	0.20	-0.49		0.30	-0.61	-0.43	0.30
WS	0.39	-0.26	0.36	0.41	-0.44	-0.01	0.25		-0.16	0.35		0.16
SR	0.67	-0.11		0.54	-0.02	-0.27	0.58	0.22	-0.24	0.66	0.53	-0.21
	Site-5			**Site-6**			**Site-7**			**Site-8**		
T	0.76	-0.12	-0.31	0.71	-0.11	-0.17	0.75	-0.45		0.67	-0.14	-0.21
RH	-0.67	0.14		-0.53		0.15	-0.52	0.32		-0.53		
WS	0.40	-0.27		0.47	-0.23		0.44	-0.19	0.11	0.48		-0.10
SR	0.72			0.63			0.55	-0.14		0.52	-0.12	
	Site-9			**Site-10**			**Site-11**			**Site-12**		
T	0.63		-0.45	0.54			0.71	-0.12	-0.17	0.61	0.46	
RH	-0.38		0.21	-0.45			-0.55			-0.56	-0.25	
WS	0.37	0.12	-0.16	0.53	-0.28	0.46	0.49			0.54		0.35
SR	0.39			0.51			0.55	0.26		0.63	0.50	
	Site-13			**Site-14**			**Site-15**			**Site-16**		
T	0.73	-0.71	-0.34	0.78	-0.52	-0.30	0.64	-0.37		0.75	-0.39	
RH	-0.37	0.30		-0.54		0.23	-0.57		0.21	-0.62	0.38	-0.34
WS	0.53	-0.25		0.33	-0.50	0.29	0.34		0.40	0.61		
SR	0.46	-0.27	-0.30	0.53		-0.24	0.62			0.62		0.43



(a) (b)

Figure 4.20 Correlation with O_3 concentrations and O_3/NO_2 <5 ratios(a), O_3/VOC ratios (b).



(a) (b)

Figure 4.21 Relationship between O_3 concentrations and O_3/NO_2>5 ratios(a) ,O_3/VOC ratios (b).

We have observed the change of ozone concentrations against O_3/NO_2 and O_3/VOC ratios in order to identify the impact of VOC and NO_2 concentrations on ozone production (Figure 4.20 and Figure 4.21). When we consider the relationship between ozone concentrations and O_3/NO_2 ratio it is noted that there was a nonlinear correlation (r^2=0.69) in case the ratio was higher than 5. During identification of this relationship it was also noted that there was another nonlinear correlation between O_3 and O_3/VOC ratio (r^2=0.48) but this relationship was not captured in case O_3/NO_2 ratio was higher than 5. The concentration varied between 60-140 µg m^{-3} when there was no nonlinear correlation.

CHAPTER FIVE
CONCLUSIONS

Ozone, NO_2 and VOCs were measured through diffusive sampling method in 16 sampling sites to investigate the geographical distributions of pollutant concentrations in Izmir. The average concentrations of O_3 measured in industrial sites were in 63.4-73.0 $\mu g\ m^{-3}$ range, at urban sites they were in 39.3-73.6 $\mu g\ m^{-3}$ range, at suburban sites they were in 48.4-79.9 $\mu g\ m^{-3}$ range, and the concentration was 76.4 $\mu g\ m^{-3}$ in the rural site. Considering the average concentration values, the highest values were measured in suburban and rural sites, which are not subject to vehicle traffic and they are relatively far from the industrial areas. In the remaining rural area, ozone levels were always the highest. Seasonal variation of ozone concentrations showed typical annual variations at all sites, reaching the highest values in summer, when the sunlight is the most intense. The comparison of ozone concentrations with concurrent measurements in the city showed that there were higher concentrations throughout the measurement period in suburban. Lower ozone concentrations were measured in the city where the traffic emissions are high. This was probably the results of ozone reaction with nitrogen oxide from exhaust emissions. Maximum concentrations usually occur away from the sources of primary pollutants.

Similar to ozone, the geographical distributions of NO_2 concentrations were investigated. It would be noted that high concentrations were measured at urban sites where residential heating and high level of traffic existed as NO_2 is a traffic sourced pollutant. The present work shows that the concentration of NO_2 near busy roads is on average 2.5 times higher than in rural site. When all NO_2 and O_3 concentrations compared it was seen that low NO_2 concentrations were accompanied by high O_3 concentrations.

When spatial distribution of $\sum_{64} \mathrm{VOCs}$ was investigated, the concentrations were decreased from industrial to rural areas. The lowest concentration was measured at site 5 a suburban site (9.8 µg m^{-3}), and the highest concentration was measured at site 16 an industrial site (374.6 µg m^{-3}) in the city of Izmir. The concentration of $\sum_{64}$VOCs shows differences between seasons. On the average, the concentrations were 2 times higher in winter those measured in summer. On the other hand, near the petroleum refinery and petrochemical complex the higher concentrations were measured in summer than in winter. This was attributed to increased evaporative VOC emissions as a result of higher temperatures in summer at these sampling sites. The seasonal differences were investigated on the basis of VOCs chemical speciation classes, at all sampling sites, the contribution of alkanes and alkenes to total VOCs were generally above 60% throughout the summer and winter periods.

The relationship of measured all VOC compounds with the meteorological parameters was investigated using a correlation matrix. Most of the VOC classes generally were correlated with each other. From meteorological parameters wind speed and temperature affected VOC concentrations negatively and positively, respectively.

Another objective of this work was to characterize the annual and diurnal cycles of ozone surface concentrations with the aim of finding the main mechanisms responsible for these cycles. Ozone measurements were performed with online monitoring devices in two sampling sites, one located in the city center (Site-8) and the other one in a suburban site (Site-5). Daily O_3 concentrations for urban and suburban sites were calculated between March and August. O_3 levels, generally above a daily average of 60 µg m^{-3}, were observed in suburban site; above 20 µg m^{-3}, were in urban site. These averages show that the Site-5 was exposed to higher O_3 levels as compared to the Site-8. This can be explained by the geographical characteristics of the two stations. The site-8 station was exposed to traffic emissions leading to NO_x-titration of ozone which results in lower ozone concentrations.

Additional measurements of nitrogen oxides (NO, NO_2 and NO_x) were also performed continuously in the suburban site. Daily NO and NO_2 concentrations for suburban sites between March and August were calculated. NO_2 concentration ranged between 10 and 50 μg m^{-3}. Besides that daily average of NO concentrations were approximately 10 μg m^{-3}. There was a parallel trend in NO_2 and NO daily average concentration changes. While NO_x concentrations were relatively constant during the sampling period, O_3 concentrations showed an increasing trend during summer period which can be explained by increasing temperature and solar radiation, favoring the ozone formation reactions.

At Site-5 and Site-8, there was a marked diurnal O_3 variation with a maximum in the afternoon. The generated profile was a typical diurnal trend for O_3 reaching maximum concentrations during afternoon hours due to high solar radiation, which triggered the photochemical reactions. Some smaller increases in O_3 concentrations were also observed in early morning hours due to a build-up of O_3 in the absence or low levels, of NO_x. These results suggested that sampling sites were significantly influenced by urban sources than expected (especially the suburban site) and the diurnal cycle was produced by these sources. There were usually two daily peaks of NO_x emissions, early in the morning and then in the evening, which corresponded to peaks in traffic levels (morning and evening rush hours). NO_x concentrations decreased at midday because of vertical dilution and chemical processing, even though emissions of NO_x were probably remained high parallel to the traffic density.

The significant correlations were obtained when the diffusive sampling and online monitoring results compared. This shows that the diffusive sampling methods can be used at large areas to determine the geographical distribution of pollutant concentrations simultaneously.

VOCs concentrations were lower in suburban areas compared to the urban areas having a higher level of industrial activity, traffic sources and residential heating. To determine the contribution of each VOC sources to ambient concentrations, VOC profiles of sources should be investigated and receptor modeling should be performed.

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