

INVESTIGATION OF PASSIVE SAMPLING OF NO₂ AND O₃ IN AMBIENT AIR
AND DETERMINATION OF THE EFFECTS OF METEOROLOGICAL
PARAMETERS TO THE UPTAKE RATE

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**INVESTIGATION OF PASSIVE SAMPLING OF NO₂ AND O₃ IN
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METEOROLOGICAL PARAMETERS TO THE UPTAKE RATE)**

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ABSTRACT

INVESTIGATION OF PASSIVE SAMPLING OF NO₂ AND O₃ IN AMBIENT AIR AND DETERMINATION OF THE EFFECTS OF METEOROLOGICAL PARAMETERS TO THE UPTAKE RATE

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In this study NO₂ and O₃ gases which are the secondary pollutants in ambient air were sampled with designed passive tubes. The collected samples were extracted for UV-VIS spectrometric analysis. NO₂ gases were converted to NO₂⁻ ions by extracting with water and then this solution was colored with Saltzman reagent (5:1 sulfanilamide and N-(1 naphthyl)-ethylenediamine dihydrochloride). Then the absorbance of the solution was measured at 537 nm. O₃ was extracted with 3-methyl-2-benzothiazolinone hydrozone hydrochloride solution which gives yellow color after extraction. The absorbance of the solution was measured at 430 nm.

Before starting the experiment, the exposure time was optimized. For this purpose, 15 days in winter and 65 days in summer samplings were conducted. For both NO₂ and O₃ it was decided that 7 days of sampling period was required as an optimum sampling time in order to reach maximum collection efficiency values for both pollutants.

To determine the uptake rates of the passive tubes, NO₂ was sampled in fifteen weeks and O₃ was sampled in thirteen weeks. During each sampling period passive tubes were placed nearby the active air sampling stations of Refik Saydam

Hygiene Center, Air Quality Control and Research Laboratory in Ulus and Keçiören. Then uptake rates of NO₂ and O₃ passive tubes were determined by comparing passive and active sampler data. The uptake rate was calculated for NO₂ and O₃ as $0.91 \times 10^3 \text{ cm}^3 \text{ h}^{-1}$ and 1.71×10^3 , respectively.

Since sampling was done in ambient air the effect of meteorological parameters should be determined. Each meteorological parameters, wind speed, wind direction, relative humidity, temperature, pressure and solar radiation were correlated with uptake rates. It was found out that none of these parameters had a significant effect on NO₂ passive tube uptake rate. However, O₃ passive tubes were affected from temperature, solar radiation and relative humidity. Temperature and solar radiation showed positive correlation with uptake rate, on the contrary, relative humidity was inversely correlated with uptake rate.

Finally the pollution map of Ankara was created by taking samples from forty points in the city.

Keywords: passive sampling, NO₂, O₃, meteorological parameters, uptake rate

ÖZ

ATMOSFERDEKİ NO₂ VE O₃'ÜN PASİF ÖRNEKLEYİCİLERLE ÖLÇÜMLERİNİN İNCELENMESİ VE METEOROLOJİ PARAMETRELERİNİN TUTUNMA SABİTİNE ETKİSİNİN BELİRLENMESİ

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Bu çalışmada ikincil kirleticiler sınıfından olan NO₂ ve O₃ gazları tasarımı yapılan pasif tüplerle açık havada ölçülmüştür. Toplanan örnekler, ekstrakt edildikten sonra UV-VIS spektrometrik yöntemi ile ölçüldü. NO₂ su ile ekstrakt edildikten sonra NO₂⁻ iyonuna dönüştürülerek Saltzman (5:1 oranında sulfanilamid ve N-(1 naftil)-etilen-diamin dihidroklorür) reaktifıyla renklendirilmiştir. Daha sonra bu örneklerin absorbensı 537 nm'de ölçülmüştür. O₃ ise çözeltiye sarı rengi veren 3-metil-2-benzotiazolinon hidrozon hidroklorür çözeltisiyle ekstrakt edilerek 430 nm'de absorbens ölçülmüştür.

Deneylere başlamadan önce, en uygun maruziyet süresi belirlenmiştir. Bunun için 15 gün kışın, 65 gün yazın olmak üzere iki farklı mevsimsel örnekleme yapılmıştır. Toplama verimliliğinin maksimuma ulaştığı süre hem NO₂, hem de O₃ için 7 gün olarak belirlenmiştir.

Daha sonraki çalışmada pasif tüplerin tutunma sabitleri belirlendi. NO₂ için 15 haftalık, O₃ içinse 13 haftalık ölçüm yapılmıştır. Her örnekleme sırasında pasif tüpler, Refik Saydam Hıfzısıhha Merkezi, Hava Kalitesi Kontrol Laboratuvarı'nın Ulus ve Keçiören'de bulunan aktif ölçüm istasyonlarının yanına yerleştirilmiştir.

Aktif ve pasif ölçüm sonuçları karşılaştırılarak tüplerin NO₂ ve O₃ için tutunma sabitleri sırasıyla $0.91 \times 10^3 \text{ cm}^3 \text{ h}^{-1}$ ve 1.71×10^3 olarak hesaplanmıştır.

Örneklemler açık havada yapılacağı için meteorolojik verilerin pasif tüplere olan etkilerinin belirlenmesi gereklidir. Bunun için her bir meteoroloji verisi ; rüzgar hızı, rüzgar yönü, kısmi nem, sıcaklık, basınç ve güneş radyasyonu, tutunma sabitiyle ilişkilendirilmiştir. Sonuç olarak NO₂ pasif tüpünün tutunma sabitine hiçbir meteorolojik verinin önemli ölçüde etki etmediği bulunmuştur. Fakat sıcaklığın, kısmi nemin ve güneş radyasyonunun O₃ pasif tüpünün tutunma sabitini etkilediği bulunmuştur. Bunlardan sıcaklık ve güneş radyasyonu doğru orantılı olarak, kısmi nem ise ters orantılı olarak tutunma sabitine etki etmişlerdir.

Son olarak dizayn edilen pasif tüpler ile Ankara'nın kırk noktasında örnekleme yapılarak şehrin kirlilik haritası çıkarılmıştır.

Anahtar Kelimeler: pasif örnekleme, NO₂, O₃, meteorolojik veriler, tutunma sabiti

To my family

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CHAPTER 1

INTRODUCTION

1.1 Importance of Atmosphere

Atmosphere is a protective shield that surrounds the Earth in order to provide living areas. The atmosphere is the main source of carbon dioxide for photosynthesis, oxygen for respiration, nitrogen for nitrogen-fixing bacteria and source of essential components for living molecules. Moreover atmosphere is the main part of the hydrologic cycle by transporting water from ocean to land which is the main requirement for heat transfer.

Besides providing vital substances, atmosphere has also a protective role. It protects organisms by absorbing cosmic rays from outer space and electromagnetic radiation below 300 nm wavelength from sun. Atmosphere has a selective permeable character to radiation. It transmits significant amount of radiation in the region between 300-2500 nm wavelength, near-ultraviolet, visible, and near-infrared and 0.01-40 m (radio waves). In addition to that it stabilizes the Earth's temperature by absorbing infrared radiation which absorbs solar energy that is re-emitted to the space (Manahan, 2000).

Figure 1.1 simply exhibits the chemical processes in the atmosphere. As shown in the figure the initiator of the processes is the electromagnetic radiation from the

sun. After that the chain reaction occurs when the molecules absorb this solar radiation (Manahan, 2000).

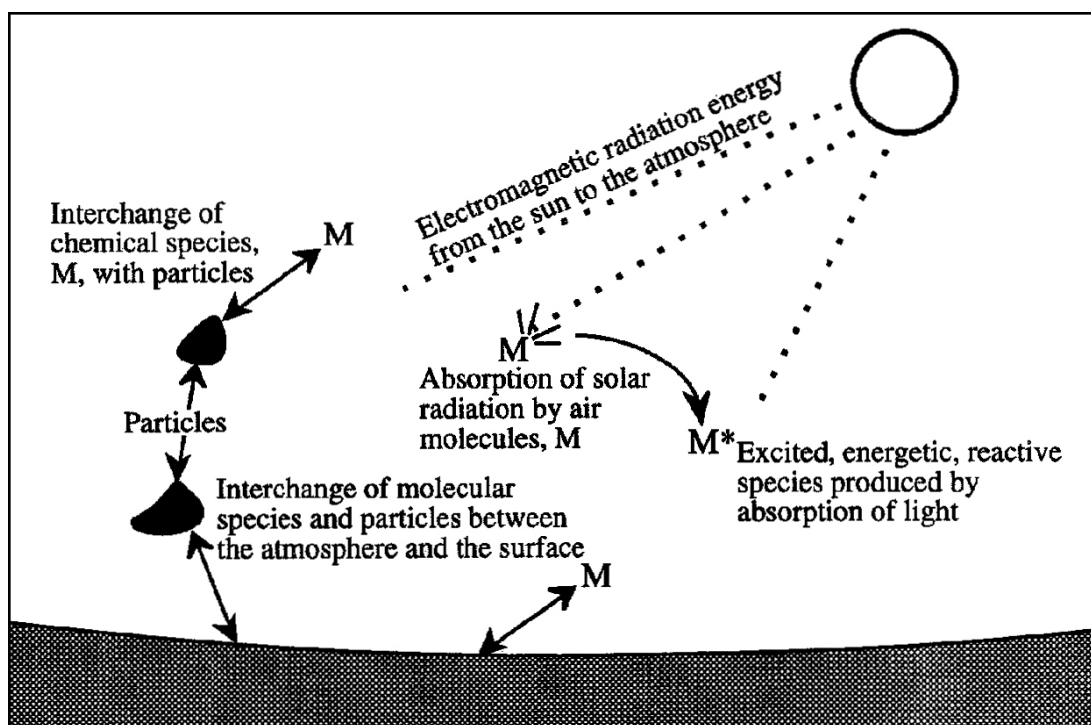


Figure 1.1. Major atmospheric chemical processes (Manahan, 2000).

In this dynamic media there are a lot of species that contribute to the chemical processes individually or with other species. The composition of air exclusive of water is; 78.08 % nitrogen, 20.95 % oxygen, 0.93 % argon, 0.03 % carbon dioxide and 0.01 % other gases. Table 1.1 shows the detailed concentrations (ppm) of main gas phase components in normal dry air. In addition, air contains a large variety of trace gases at levels below 0.002 %, including neon, helium, methane, krypton, nitrous oxide, hydrogen, xenon, sulfur dioxide, ozone, nitrogen dioxide, ammonia, and carbon monoxide (Hodgson, 2004).

Table 1.1. Gaseous components of normal dry air (Hodgson, 2004).

Compound	Percent by Volume	Concentration (ppm)
Nitrogen	78.09	780,900
Oxygen	20.94	209,400
Argon	0.93	9,300
Carbon dioxide	0.00325	32.5
Neon	0.0018	18
Helium	0.0005	5.2
Methane	0.0001	1.1
Krypton	0.0001	1.0
Nitrous oxide		0.5
Hydrogen		0.5
Xenon		0.008
Nitrogen dioxide		0.02
Ozone		0.01-0.04

Atmospheric trace gases are given with percentage volume, their sources and process for removal from atmosphere in Table 1.2. The abundant species are atmospheric methane and carbon monoxide; nitrous oxide and hydrogen gases follow it. As shown in the table most trace gases are both caused and removed by photochemical reactions (Manahan, 2000). As indicated in the name these reactions include ultraviolet radiation from the sun that means these reactions can not take place in the absence of light medium.

Table 1.2. Atmospheric trace gases in normal dry air (Manahan, 2000).

Gas or species	Volume percent	Major sources	Process for removal from the atmosphere
CH ₄	1.6×10^{-4}	Biogenic	Photochemical
CO	$\sim 1.2 \times 10^{-5}$	Photochemical, anthropogenic	Photochemical
N ₂ O	3×10^{-5}	Biogenic	Photochemical
NO _x	$10^{-10} - 10^{-6}$	Photochemical, lightning anthropogenic	Photochemical
HNO ₃	$10^{-9} - 10^{-7}$	Photochemical	Washed out by precipitation
NH ₃	$10^{-8} - 10^{-7}$	Biogenic	Photochemical, washed out by precipitation
H ₂	5×10^{-5}	Biogenic, photochemical	Photochemical
H ₂ O ₂	$10^{-8} - 10^{-6}$	photochemical	Washed out by precipitation
HO·	$10^{-13} - 10^{-10}$	photochemical	Photochemical
HO ₂ ·	$10^{-11} - 10^{-9}$	photochemical	Photochemical
H ₂ CO	$10^{-8} - 10^{-7}$	photochemical	Photochemical
CS ₂	$10^{-9} - 10^{-8}$	Anthropogenic, biogenic	Photochemical
OCS	10^{-8}	Anthropogenic, biogenic, photochemical	Photochemical
SO ₂	$\sim 2 \times 10^{-8}$	Anthropogenic, photochemical, volcanic	Photochemical
I ₂	0-trace	-	-
CCl ₂ F ₂	2.8×10^{-5}	Anthropogenic	Photochemical

1.2 Air Pollution

Development status of the countries can be determined by their pollutant emissions and the concentration of pollutants. Main anthropogenic sources of air pollutants are traffic emission and industrial processes. Taking precautions, monitoring and controlling the pollution exhibit the development of the country.

Air pollution which is a global environmental problem can be defined as the substances that affect the living organisms in negative way. These substances are in the form of particle, gas or solar energy at such concentration, duration and frequency that above the limits. The residence time of some gas phase pollutants are listed in Table 1.3. These durations in air can be determined by the physicochemical properties of the pollutants, their reactivity, solubility, diffusion coefficient and etc. (Schnelle and Brown, 2002; Radojevic and Bashkin, 1999).

As indicated in Table 1.3, NO_2 , SO_2 , NH_3 , HNO_3 and H_2O have short residence time beside O_2 , N_2 and CO_2 which are the main constituents of the air. Short residence time shows the ease in degradation; however, the pollutants having long residence time remain in the air for a long time without the change in the structure. Although the pollutants having long residence time are harmful at concentrations above the limited amount, the degradable pollutants like NO_2 and SO_2 can be as hazardous as the other if they reach their limits.

Pollution concept deals with degradation, increase in quantity, loss of quality and adverse effects on environment (Godish, 1997; WHO, 2000; Yu 2005). The impact of air pollution is mostly on climate, weather, human health, animal life, vegetation and materials. Moreover, if any precautions are not taken, pollution can

damage the resources needed for long-term sustainable development (Godish, 1997; WHO, 2000).

Table 1.3. Residence time of some atmospheric pollutants.

Species	Residence time
O ₂	10 ⁴ years
N ₂	10 ⁶ years
CO ₂	5-10 years
CH ₄	5 years
O ₃	1-3 months
CO	1-2 months
H ₂ O	10 days
SO ₂	2-7 days
NH ₃	5 days
NO ₂	4 days
HNO ₃	1 day

The industrialization of society, the introduction of motorized vehicles, and the explosion of the population, are factors contributing toward the growing air pollution problem. An air pollution problem involves three parts: the pollution source, the movement or dispersion of the pollutant, and the recipient mentioned in Figure 1.2.

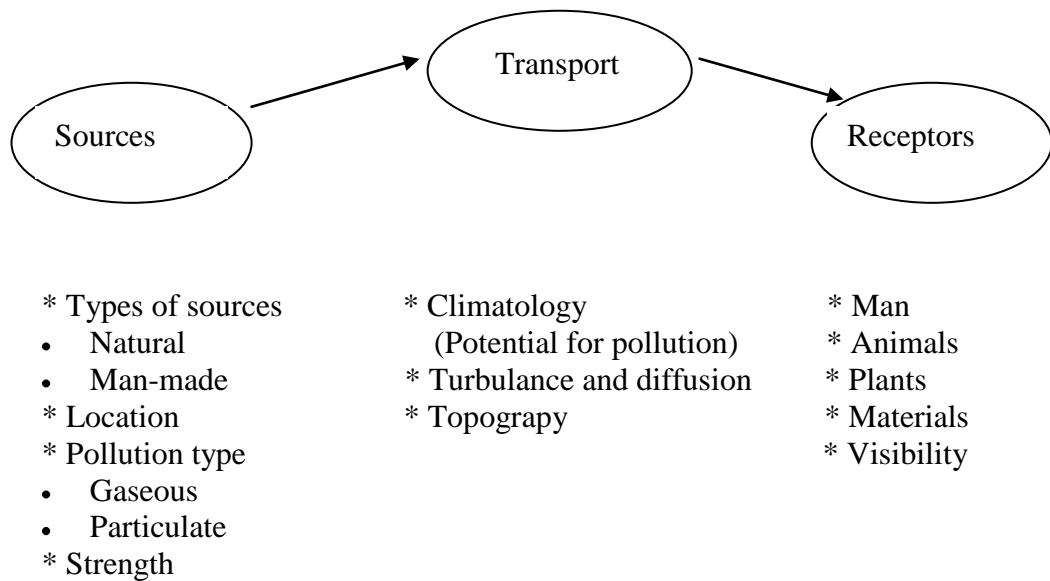


Figure 1.2. Main parts of air pollution (Schnelle and Brown, 2002).

Sources of air pollution are either man-made or natural. In most of the environmental studies man-made sources are much more considered than natural ones because taking precautions and management of the problem can be easy. Knowledge about the source location relative to the receptor allows to calculate the concentration in exposed area. Also, pollution type and strength of them help to recognize the effects on living organisms.

Transportation of the pollutants results within the dispersion that means taking pollutants from source to receptors which can be classified as man, animal, plants, materials and visibility. Meteorological conditions, diffusion and topography are also the important factors in dispersion.

The reason to pollution is ‘pollutant’ which is the species that has an increase in its natural amount. The effects of pollutants can be verified with the composition and impact area. EPA (Environmental Protection Agency) classified six air pollutants that are; particulate matter, ground-level ozone, carbon monoxide, sulfur dioxide, nitrogen dioxide and lead as ‘criteria pollutants’ because these pollutants threat both human health and environment directly.

1.2.1 Inorganic Gas Phase Pollutants

Gas phase pollutants become significant due to their role in acid rain and photochemical smog. The pollutants that are the reason of acid rain are sulfur dioxide (SO_2), nitric oxide (NO and NO_2) and one of the pollutant that causes photochemical smog, ozone (O_3). SO_2 and NO_x are released to the atmosphere from anthropogenic sources as well as natural sources. Once they enter to the atmosphere many chain reactions occur, then sulfate and nitrate ions are formed which are the crucial parameter in acid deposition. Another pollutant, O_3 and its secondary products are important parameters that should be investigated during the air pollution studies beside other gases (Özer et al., 1997).

Concentration Expressions: Atmospheric gases and vapors have been expressed as mixing ratios in air volume. This mixing ratio can be reported as ppmv (parts per million volume), ppbmv (parts per hundred million volume), ppbv (parts per billion volume) and so on which are defining as mixing ratio. Air concentration expressions should not be confused with those used for aqueous solution (weight/volume-mg/L, $\mu\text{g/mL}$ etc.) and solid concentrations (weight/weight-mg/kg, $\mu\text{g/g}$ etc.) (Godish, 1997). For atmospheric concepts volume/volume ratio is used to express gas phase pollutants like;

$$1 \text{ ppmv} = \frac{1 \text{ gas volume}}{10^6 \text{ air volumes}}$$

or with the units;

$$1 \text{ ppmv} = \frac{1 \mu\text{L gas}}{1 \text{ L air}}$$

Since 1970s the gas concentration has been expressed in metric units as mass per unit volume ($\mu\text{g m}^{-3}$, mg m^{-3} etc.)

Although atmosphere is contaminated with hundreds of pollutants, limited amount of them are identified and classified as threatening substances for human health and welfare (Godish, 1997). Gas phase pollutants constitutes the relatively large part of these pollutants.

Most of the inorganic gas phase pollutants are entered into the atmosphere as a result of human activities like traffic emissions, lightening, domestic heating, industrial processes etc. NO_x ($\text{NO} + \text{NO}_2$), N_2O , SO_2 , CO , NH_3 and O_3 are the main inorganic pollutants in both indoor and outdoor (Manahan, 2000; Radojevic and Bashkin, 1999; Alloway and Ayres, 1997). Due to their individual impacts on living organisms and environment, NO_x especially NO_2 and O_3 can be classified as critical inorganic gas phase pollutants. Also, due to their formation and removal mechanisms between each other, they are studied together in order to understand the total effect and to get meaningful result.

1.2.2 Nitrogen Dioxide, NO₂

1.2.2.1 Properties of NO₂

Nitrogen gas is the major gaseous constituent of the atmosphere, making up approximately 78% of the atmosphere's mass. Although its huge portion in the atmosphere most of nitrogen compounds especially the oxides of it have low concentration in the air (Manahan, 2000; Godish, 1997). One of the nitrogen oxides is the NO₂ which is exhibited as an indicator of the air pollution because with depend on its concentrations the concentrations of other pollutants such as carbon monoxide, particulate polycyclic aromatic hydrocarbon, tropospheric ozone etc. will be changed (Cox, 2003; Plaisance et al., 2007; Glasius et al., 1999). Also NO₂ is the precursor for a number of secondary air pollutants. It contributes to acidic deposition in terrestrial ecosystems as dry-deposited gases or in dissolved form in precipitation, fog and cloud; in aerosol form it can also impact visibility (Cox, 2003; Tang et al., 1999; Report on a WHO Working Group, 2003).

NO₂ is one of the most ubiquitous secondary air pollutants that photochemically 'manufactured' in the atmosphere has reddish-brown color at high concentrations (Heal et al., 1999; Levaggi et al., 1973; Santis et al., 1997; Tang et al., 1999; Godish, 1997). It has a pungent, irritating odor and also relatively toxic and is extremely corrosive because of its high oxidation rate (Godish, 1997). Mostly it occurs in the exhausts of automobiles, cigarette smoke; and produced by the reaction of nitric acid with metals and decomposition of nitrates (Patnaik, 1997).

1.2.2.2 Sources of NO₂

The source of nitrogen oxides is the high temperature combination with atmospheric nitrogen and oxygen. Two of these oxides; NO and NO₂ are designated as NO_x and they enter the atmosphere from natural sources, such as lightning, volcanoes, bacterial activity, biomass burning and from pollutant sources. However, these naturally occurring NO_x can be ignored compared to the processes in internal combustion engine, power stations and nitrate fertilizers that produce almost half of the amounts arising from the natural sources (Harrison, 2002; Manahan, 2000; Radojevic and Bashkin, 1999; Alloway and Ayres, 1997). In urban sites the main anthropogenic sources of NO₂ are vehicle exhausts, energy production and domestic heating etc. (Ferm and Svanberg, 1998; Heal and Cape, 1997; Yeşilyurt and Akcan, 2001)

1.2.2.3 Removal Mechanisms of NO₂

The reactive nitrogen oxides in the troposphere are NO, NO₂, HNO₃ that cycle among each other as shown in Figure 1.3. Moreover, the chemistry of these inorganic species is very important in the atmosphere in areas such as formation of photochemical smog, production of acid rain and depletion of stratospheric ozone.

As indicated in the following reactions the atmospheric NO is easily oxidized to NO₂ by ozone and HO₂ radicals.

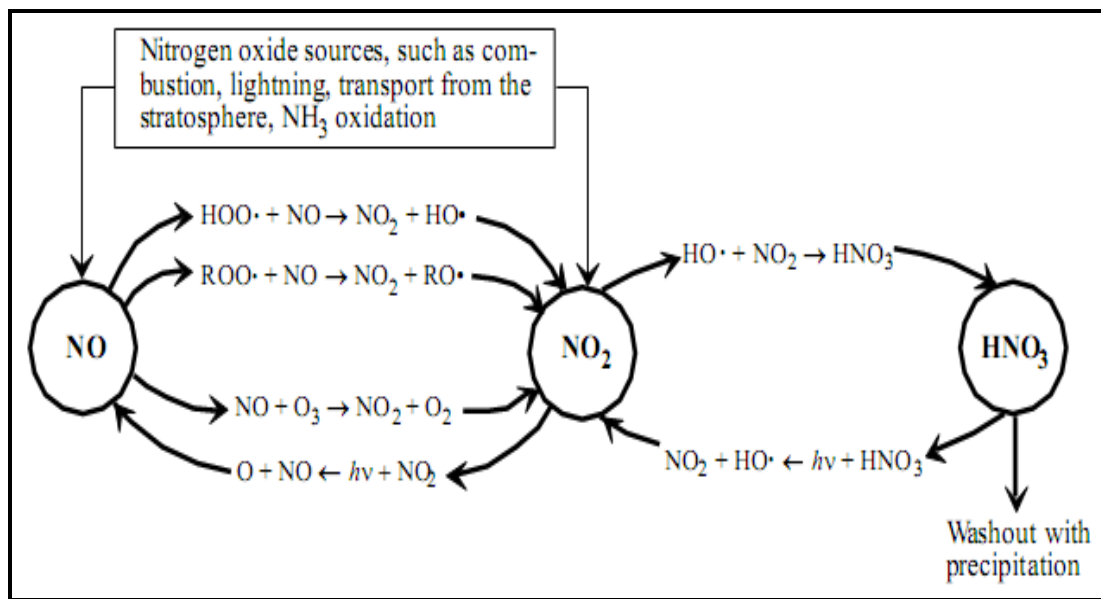
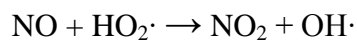
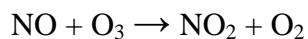
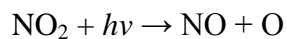
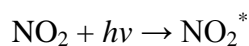


Figure 1.3. Conversion reactions among NO, NO₂ and HNO₃ (Harrison, 2001)

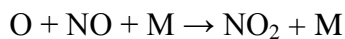
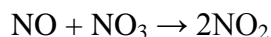
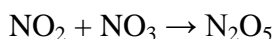
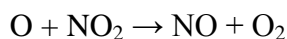
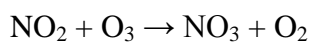
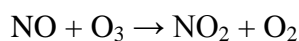
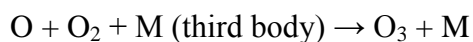
Due to the reactivity of nitrogen dioxide, many photochemical reactions occur in different wavelengths. It absorbs light throughout the ultraviolet and visible spectrum. For instance, at wavelengths below 380 nm, photo-dissociation occurs;



At wavelengths above 430 nm, only excited molecules are formed;

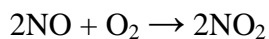


The tendency of NO₂ to photodissociate is shown clearly by the fact that in direct sunlight the half-life of NO₂ is much shorter than that of any other common molecular atmospheric species. The photodissociation of nitrogen dioxide can give rise to the following significant inorganic reactions in addition to a host of atmospheric reactions involving organic species (Harrison, 2001; Manahan, 2000):



Generally nitrogen dioxide is removed from the atmosphere as nitric acid or nitrate (Manahan, 2000).

Beside the photochemical reactions nitrogen dioxide can be formed by direct oxidation of nitric oxide (Harrison, 2001; Godish, 1997).



1.2.2.4 Health Effects of NO₂

Nitrogen oxide (NO_x = NO + NO₂) emissions to the atmosphere have direct impact on the environment and human health through the formation of ozone and some photo oxidants and deposition of acidity (Heal and Cape, 1997). However, health risks from nitrogen oxides generally result from NO₂ itself or its reactions with ozone and other secondary pollutants.

In order to get evidences about health effects of NO₂ some information sources like observational epidemiology, controlled human exposure to pollutant and animal toxicology are benefited (Report on a WHO Working Group, 2003)

During the investigation of effects of NO₂ on human it was found that exposure in indoor is much more easy beside outdoor exposure because of the difficulty in the determination of NO₂ sources (Report on a WHO Working Group, 2003). The main indoor NO₂ source includes unvented combustion appliances. However, outdoor NO₂ sources are much more complicated because in ambient air there are many other pollutants that trigger the formation of NO₂. Moreover, NO₂ can be changed in to other forms by the reaction with other secondary pollutants. Also fuel combustion, lightening and energy production processes are the other sources for outdoor NO₂. Then in order to state the health effects of NO₂ in outdoor exposure detailed and extended study are required.

Personal exposure to NO₂ is associated with both chronic and acute adverse health effects on children, elder people and asthmatics (Heal et al., 1999). For acute exposures ranging from several minutes to one hour, a level of 50-100 ppm of NO₂ causes inflammation of lung tissue for a period of 6-8 weeks, exposure of the subjects to 150-200 ppm of NO₂ causes bronchiolitis fibrosa obliterations, a

condition fatal within 3-5 weeks after exposure. Death generally results within 2-10 days after exposure to 500 ppm or more of NO₂. “Silo-filler’s disease,” caused by NO₂ generated by the fermentation of ensilage containing nitrate, is a particularly striking example of nitrogen dioxide poisoning (Manahan, 2000; Radojevic and Bashkin, 1999).

However, the effects of short-term exposure are still unclear, but continued or frequent exposure to concentrations that are typically much higher than those normally found in the ambient air may cause increased incidence of acute respiratory illness in children. EPA's health-based national air quality standard for NO₂ is 0.053 ppm (measured as an annual arithmetic mean concentration) (www.epa.gov/ARD-R5/naaqs/no2.htm)

1.2.3 Ozone, O₃

1.2.3.1 Properties of O₃

An essential constituent of the stratosphere, ozone is an undesirable pollutant in the troposphere that causes photochemical smog. Tropospheric ozone is a major secondary air pollutant produced from photochemical reactions and some anthropogenic processes plays a crucial role in atmospheric chemistry. It is a colorless gas at ambient temperature and pressure, and unstable especially at higher concentrations (Sanz et al., 2007; Helaleh et al., 2002; Özer et al., 1997; Grigorieva and Mihalev, 1998).

Until 1980s most of the studies had been based on only stratospheric ozone because it prevents Earth from harmful UV rays. However, nowadays the importance of tropospheric ozone is understood and studies have been conducted about it.

The increase of tropospheric ozone causes many important cases. These are climate change (greenhouse effect), oxidation in plant surfaces and photochemical smog (Özer et al., 1997).

1.2.3.2 Sources of O₃

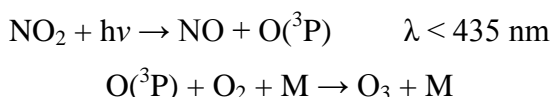
Some O₃ may be found on the earth's surface as a result of its downward transport from the stratosphere but major source of background ozone in troposphere is the photochemical process and the movement of the stratospheric ozone into the lower atmosphere. However, in warmer months human activities play an important role during the formation of tropospheric ozone (Godish, 1997; Godish, 2004) and sources of it are photochemical transformation of nitrogen oxides, carbon monoxide and volatile organic compounds from urban traffic (Bernard, 1999; Harrison, 2001; Report on a WHO Working Group, 2003).

If volatile organic compound is considered individually their contributions depend on their concentrations and reactivity to form OH· radical. The contributions of individual compounds per unit mass of emissions, termed their photochemical ozone creation potential (POCP), and this can be determined from numerical models of atmospheric photochemistry (Harrison, 2001).

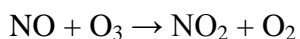
Also ozone is emitted from germicide lamps, copy machine printers, welding and other industrial processes (Helaleh et al., 2002).

1.2.3.3 Removal Mechanisms of O₃

There are two major sink processes for O₃. These are surface deposition (or destruction) and photochemical reactions. Surface deposition includes reaction with plants, bare land, ice and snow, and man-made structures. Deposition of O₃ is of its greatest magnitude over daytime forests and croplands. However, the primary sink for O₃ is its photo-dissociation on absorption of UV light and subsequent formation of OH radical. In polluted atmospheres, there is abundant NO₂ whose photolysis leads to formation of ozone at the wavelength of 435 nm or below (Harrison, 2001). At these wavelengths NO₂ decomposes to NO and excited O atom (³P) and the elevated O atom reacts with O₂ molecules in the presence of third body molecules in order to form O₃.



On the contrary, during night-time hours, O₃ reacts with NO₂ to subsequently produce HNO₃ (Godish, 1997) and also emission of NO leads to ozone removal with the production of NO₂. However, this removal mechanism is the initiator of the formation of O₃ as indicated in Figure 1.4. The removal mechanism concludes that the concentration of ground-level ozone is lower in urban areas than the rural ones (Godish, 1997).



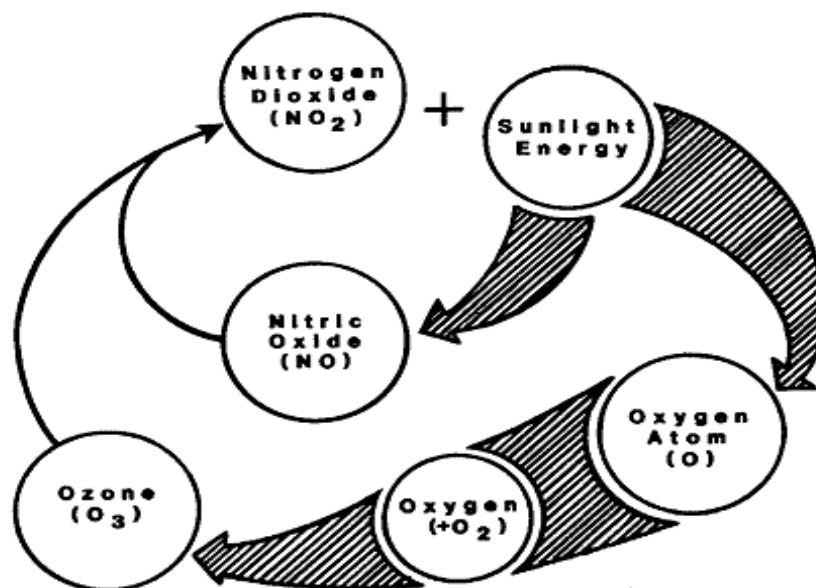


Figure 1.4. NO₂ photolysis and O₃ formation (Godish, 1997).

During the tropospheric ozone formation, chain reactions like in Figure 1.5 may occur. The energetic ultraviolet radiation required to split O₂ molecules in order to produce O atoms that are required for the formation of ozone.

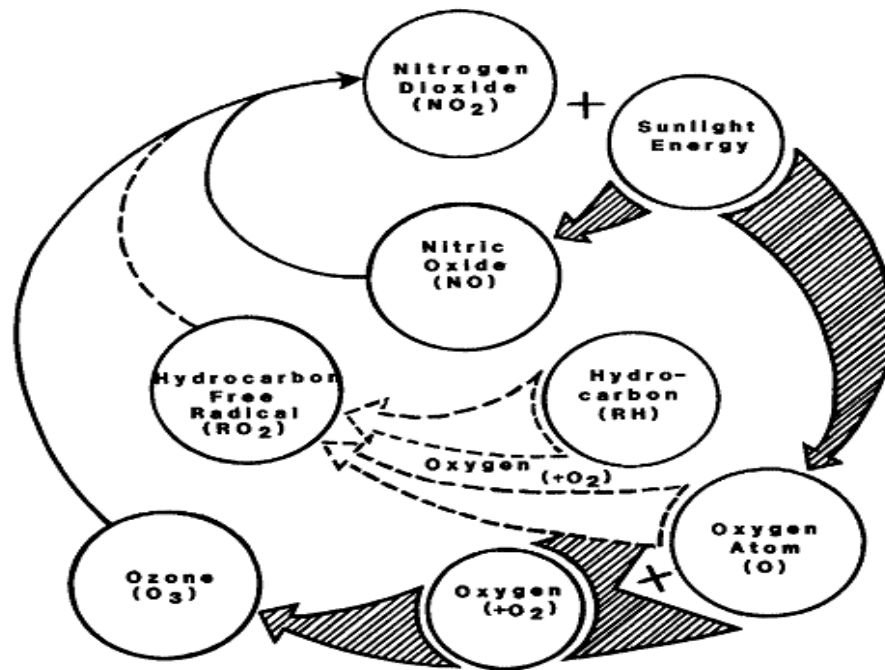
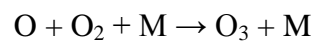
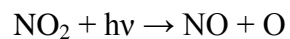
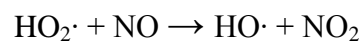
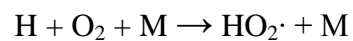
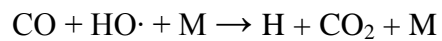


Figure 1.5. Production of tropospheric O₃ (Godish, 1997).

Also other species like hydrocarbons can be included in the ozone formation process. The chain reactions can be more comprehensible by the following reactions (Manahan, 2000)



1.2.3.4 Health Effects of O₃

Air quality index give information about the cleanness or pollution of air in the living zone and also explain the health effects of it. In air quality index these effects are reported with respect to daily or hourly exposure of the polluted air. Republic of Turkey Ministry of Environment and Forestry give air quality index of O₃ and also the health effects of it in 8 hour exposure as in Table 1.4.

Table 1.4. Air Quality index for O₃

Air Quality Index (ppm)	Health Level	Cautions
0.000 - 0.040	Good	None
0.041 - 0.080	Medium	Randomly, sensitive people should decrease the long term and dense effort in outdoor.
0.081 - 0.120	Unhealthy for sensitive groups	Active children, adults and people having respiratory illness should decrease the long term and dense effort in outdoor.
0.121 - 0.160	Unhealthy	All people especially children should decrease the long term and dense effort in outdoor.
0.161 - 0.240	Very unhealthy	All people especially children should decrease the long term and dense effort in outdoor.
0.241 - 0.400	Hazardous	None one should do any physical exercise in outdoor.

Ozone exposure affects mostly the respiratory systems of humans. Adverse health effects associated with ozone concentration in ambient air in short term exposure to 0.11 ppm cause irritation to nose and throat, itchy and watery eyes, swelling within the nasal passages and nasal congestion, and exposure to 0.1-0.3 ppm causes lung damage, asthma and bronchitis (Helaleh et al., 2002, Report on a WHO Working Group, 2003) and 2 hours exposure to concentrations of 1.5 ppm of O₃ is regarded as dangerous (Alloway and Ayres, 1997).

1.3 Overview of Air Sampling

Environmental analysis is made for the following two reasons;

1. to determine the background concentration of chemical constituents
2. to determine the concentration of harmful pollutants

Analysis should be done strategically in order to get the meaningful data. For that reason, sampling, sample treatment, analysis and interpreting the results should be achieved carefully step by step. However, the choice of the method in order to obtain meaningful data depends on the following factors (Schnelle and Brown, 2002):

- type of pollutant
- averaging time specified by air quality criteria or standards
- expected pollutant levels
- available resources
- availability of trained personnel
- interfering materials present in the air

The most important step in environmental analysis is the collection or sampling pollutants. Sampling can be classified in to two as, batch sampling and continuous sampling. *Batch sampling*, involves collecting sample from the environment and performing analysis in the laboratory. It is the easiest and most common method. The other technique is the *continuous sampling* that involves taking sample and analyzing it at the same time. This method is much more expensive and complex due its requirements such as instrument and technical personnel.

The primary consideration for gaseous pollutant sampling is that the sample is not contaminated by incompatibility with the sampling material of the device or the container. Mostly Teflon, stainless steel and glass sample lines are used to avoid reactions with pollutants (Schnelle and Brown, 2002).

1.3.1 Active Sampling

Determination of the detectable level of ambient air pollutants is very difficult due to continuous removal of the gases by physical and chemical process (Reeve, 2002). For that reason in short-term measurements of pollutant concentrations can vary significantly, therefore, only instant concentration can be identified not the cumulative one.

The active sampling method is based on the principle that, air sample introduces to an adsorbing media with a regular flow rate. If the instantaneous amount of pollutant is wanted to be determined, continuing monitoring system is attached to the collecting device. This combination allow to collect and measure the pollutant at that moment (Tang et al., 1999; Schnelle and Brown, 2002). Continuous or automated monitoring instruments offer an advantage to get short-interval data

that is required for the pollutants that vary rapidly (have short residence time) throughout the day by the effect of sunlight or any anthropogenic emissions (traffic, factory, domestic etc.) (Schnelle and Brown, 2002; Reeve, 2002).

In continuous real-time sampling, the analytical technique is usually sensitive enough to detect and quantify the specific pollutants that have small size and amount accurately. As a consequence, flow rates used in such instruments are also relatively low (ml/min), and optimal rates of flow are used to achieve the sensitivity and accuracy for which instruments are designed (Godish, 2004).

In direct and instantaneous measurements of gas phase pollutants can be achieved by solid electrolyte sensors and chemiluminescence are preferred due to their high sensitivity and rapid responds. Wei et al. 2001, explains these methods by the application of each to NO₂ sampling.

For the determination of NO₂ in industry solid-state electrochemical sensors based on sodium superionic conductor was used. The response time of this system is as short as 30 s to 1 min. Although it is a sensitive and rapid method, it must be worked at high temperature which is the main limitation of the system (Wei et al. 2001).

Beside the solid-state electrolytic sensors gas-phase and liquid phase chemiluminescence techniques are used. Chemiluminescence technique is based on the emission of light as a result of a chemical reaction at environmental condition (Schnelle and Brown, 2002). In gas-phase chemiluminescence method catalytic or photolytic reduction of NO₂ to ozone and subsequent gas-phase reaction with O₃ is applied. The instrument permits to measure the concentration below $\mu\text{g m}^{-3}$ with high sensitivity but it is very expensive and not appropriate to apply in large number of sites (Wei et al. 2001).

In liquid-chemiluminescence method H_2O_2 reacts with luminol in order to utilize catalytic oxidation of luminol. After that NO_2 and oxidized luminol give a chemiluminescence reaction in which the reaction takes place between gas and liquid phases and need no catalysis. Although it is a capable and sensitive method, the instrument is complex and expensive. Another limitation is the stability of luminol reagent which make difficult to control the reaction between NO_2 and oxidized luminol (Wei et al. 2001).

1.3.2 Passive Sampling

As the name ‘passive’ indicates that the movement of air is based upon the gas diffusion through the static air or a collection media (Varshney and Singh, 2003; Brown, 1993; Cruz et al., 2004; Ferm and Svanberg, 1998; EN 13528, March 2000).

In conventional environmental monitoring technology, it is common to sample many liters or even cubic meters of air in order to have sufficient sensitivity. Such volumes can only be sampled in reasonable periods by means of a sampling pump. On the other hand, diffusive samplers can be operated at an equivalent of a few milliliters in a minute. It is practical and therefore if blanks can be made extremely low by meticulous attention to cleanliness by having much increased sensitivity in the analytical stage or by sampling for very long times (Brown, 1993).

In contrast to active samplers in which air is brought into contact with a detector or collector device by means of a pump, diffusive samplers has capability 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 samples (Santis et al., 1997; Tang et al., 1999). The capacity of the passive tubes also can be controlled by defining optimum sampling rate (Helaleh et al., 2002; Heal et al., 1997; Sickless et al., 1990; Plaisance, 2004; Miller 1998). For example, Varshney and Singh (2003) sampled NO₂ in single 4-week. NO₂ amount was derived from in two ways; 1) NO₂ values were the summation of consecutive 2-week exposure, 2) NO₂ values were obtained from four parallel weekly exposures. The results show that both consecutive 2-week exposure and four parallel weekly exposures have higher NO₂ value than in single 4-week exposure. Then one and two weeks sampling time was recommended.

In other study that was executed between May-August 1997 by Heal et al., (1999(a)) again one to four week exposure of NO₂ by using passive samplers was evaluated. The same results were found and concluded as 1-week exposure has higher NO₂ concentration values than 4-week exposure.

However, Sanz et. al., (2007) concluded that 2 week exposure is the optimum sampling time for ozone sampling. Their study was carried on in 5 country; France, Italy, Spain, Luxembourg and Switzerland between April-September 2001, 2002 and 2003.

Recently usage of passive sampler in ambient air again became popular although it has been an old-fashioned technique. 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). Beside that being a simple, lightweight and cheap device and operating without power supply, not being required a technician, ideally suited for wide spatial measurement and no calibration in field make passive sampler much more convenient for environmental studies (Varshney and Singh, 2003; Krupa and Legge, 2000; Cox, 2003; Santis et al.,

1997; Ferm et al., 1998; Heal et al., 1999; Tang et al., 1999; Ray, 2001; Patnaik, 1997).

The application areas of the passive sampling method are listed in Table 1.5. with respect to sampling medium, sampling type and the aim of measurements.

Table 1.5. Main application areas of passive sampling (Schnelle and Brown, 2002).

Medium	Sample type	Measurement goals
Gaseous	Atmospheric air	Determination of time-weighted average (TWA) concentrations over long periods of time
	Indoor air	Determination of TWA concentration Determination of momentary concentration (grab sampling by SPME)
	Workplace air	Determination of 8-h TWA concentration Determination of personal exposure (personal dosimeters)
Liquid	Surface water	Determination of TWA concentrations over long periods of time Determination of momentary concentration
Solid	Soil	Determination of volatile organic compounds

On the other hand, not providing real-time values and being less accurate with respect to the chemiluminescence analyzer are the main disadvantages of the passive sampler (Varshney and Singh, 2003). Another serious drawback of it is its low diffusive transport rate which does not allow resolution times lower than one

week even in a moderately polluted environment then it can only provide information on integrated average concentrations over the exposure period not short-term or diurnal fluctuations (Varshney and Singh, 2003; Santis et al., 1997; Helaleh, 2002). The main reason is that; active sampler has a known sampling rate, which is the pump's flow rate; but the passive sampler's sampling rate depends on many factors, such as temperature, relative humidity, wind direction, wind speed, sampler's structure, collection media, and so on (Tang et al., 1999).

In addition to these drawbacks there are two more problems associated with the use of passive samplers. One of them is the interference effect; other chemical constituents in the atmosphere can interfere the adsorbent in the tube (Varshney and Singh, 2003). The second one is the turbulence effect that affect the dispersal of air pollutants. At low face velocities the sampler absorbent can become starved and, thus, not satisfactorily collect the actual air concentration of the pollutant (Varshney and Singh, 2003; Krupa, 2000; Brown, 1993). In contrast, under high face velocities, some samplers are known to be subjected to interferences from other pollutants (Varshney and Singh, 2003; Brown, 1993).

Basically there are three types of diffusive samplers; longitudinal, radial and badge types tubes (Gerboles et al., 2006). Four brands of passive tubes are mostly used world wide, these are Ogawa, Passam, Radiello and, Gradko.

Ogawa passive sampler is a double face badge type as shown in Figure 1.6. The main purpose of the usage is the determination of the NO_2 and O_3 uptake rates. Filters were placed in each side of the sampler between diffusion and support screens. These parts are placed in a diffusive body that has diffusion barrier on two sides Ogawa samplers. Through the laboratory experiments uptake rate of NO_2 is determined as $1.86 \text{ cm}^3 \text{ h}^{-1}$ and for the O_3 it is $21.8 \text{ cm}^3 \text{ h}^{-1}$ (Krupa and Legge, 2000; Gerboles et al., 2006).

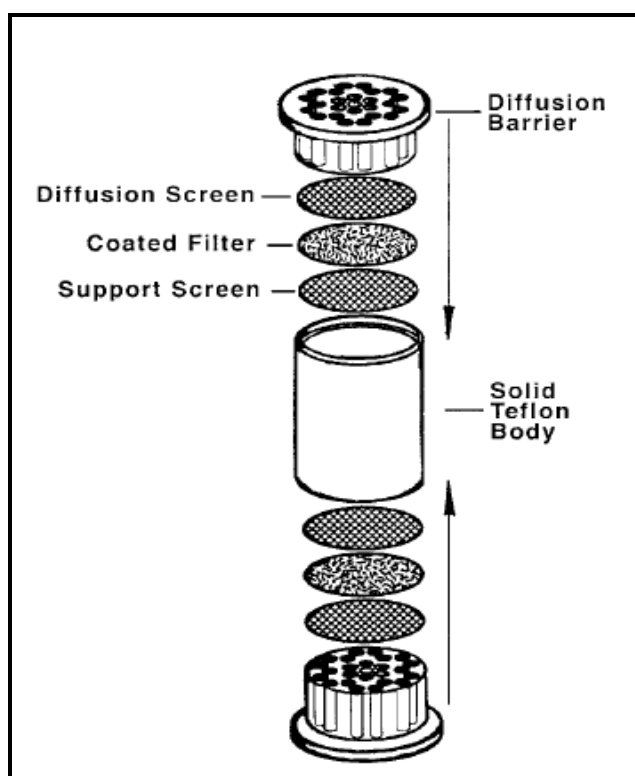


Figure 1.6. Ogawa diffusive sampler (Krupa and Legge, 2000).

Passam passive sampler is composed of 4.9 cm long calibrated tube fixed with a cap. There is a glass fiber filter impregnated with related coating material (e.g. for ozone 1,2-di(4-pyridyl)ethylene (DPE) solution). The other end of the tube is left open for air diffusion and after the exposure it is closed with a stopper. In Figure 1.7, the Passam passive sampler for ozone is given (Bernard et al., 1999). The uptake rates of NO_2 and O_3 is calculated as approximately $0.85 \text{ cm}^3 \text{ h}^{-1}$ and $0.03 \text{ mg m}^{-3} \text{ h}^{-1}$ at temperatures between 9 to 20°C , respectively, with Passam diffusion tubes (Gerboles et al., 2006).

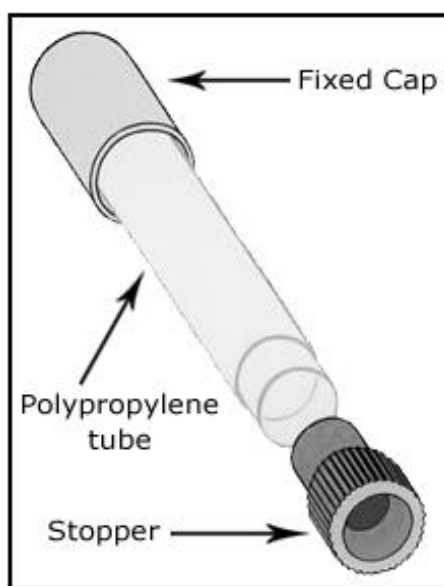


Figure 1.7. Passam passive sampler (Gerboles et al., 2006)

Schematic structure of Radiello diffusion tube is given Figure 1.8. This type of tube differs from the other ones by the air movement through the sampler. In Radiello passive sampler, pollutants diffuse through the micro porous polyethylene membrane to a cartridge where it is trapped (Plaisance et al., 2007; Namiesnik, 2005; Gerboles, 2006). This cartridge is filled with silica gel coated with DPE solution for ozone and triethanolamine (TEA) solution for nitrogen dioxide. Two cellulose caps are soldered to the ends, that lead the direction of diffusion through the membrane (Plaisance, 2007). By Radiello passive tubes the uptake rate for NO_2 is determined as approximately $3 \times 10^3 \text{ cm}^3 \text{ h}^{-1}$ and for ozone it is $1.48 \times 10^3 \text{ cm}^3 \text{ h}^{-1}$ (Piechocki-Minguy, 2006; Gerboles, 2006).

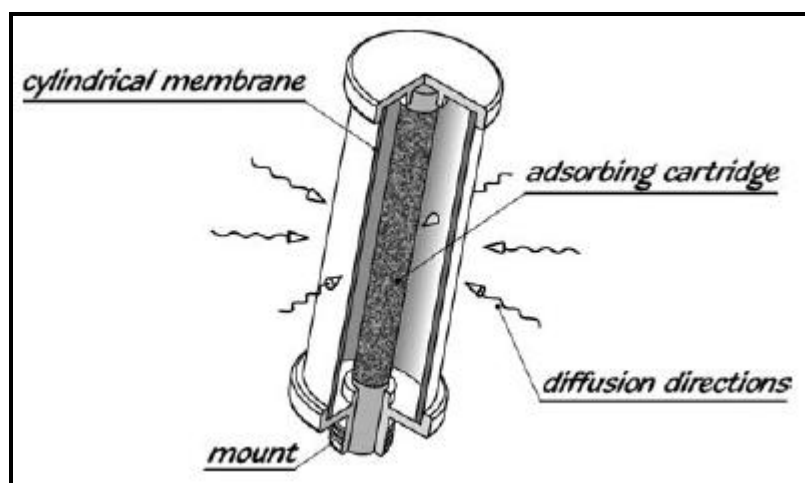


Figure 1.8. Radiello passive sampler (Namiesnik et al., 2005)

The other type of diffusion sampler is Gradko passive tube which is shown in Figure 1.9. As shown in the figure the tube has five parts. The adsorbing media is the stainless steel meshes that are coated with related solution and these parts are fixed to the acrylic tube with a colored plastic cap. Different from the Radiello passive sampler, in Gradko the movement of the air is through the inside of the tube that means the diffusion is longitudinal. The other end is closed with a Teflon membrane and fixed with a holder. This membrane helps to regulate air movement through the tube and also protect tube from big size interferences. The uptake rate of Gradko passive sampler is calculated as $72.8 \text{ cm}^3 \text{ h}^{-1}$ for NO_2 (Heal et al., 1999 (a); Heal et al., 1999 (b); Glasius, 1999; Gerboles, 2006).

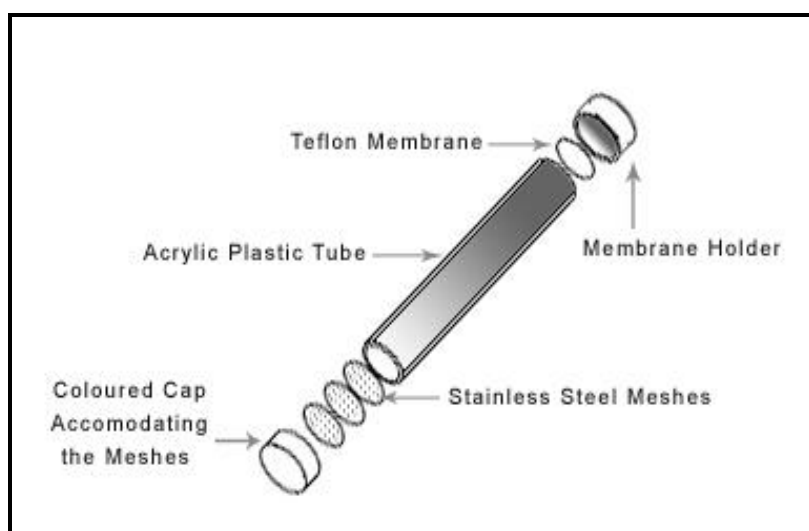


Figure 1.9. Palmes (Gradko) passive tube (Gerboles et al., 2006)

In theoretically by using Fick's law the amount of pollutant in passive tubes can be calculated as directly proportional to the ambient concentration.

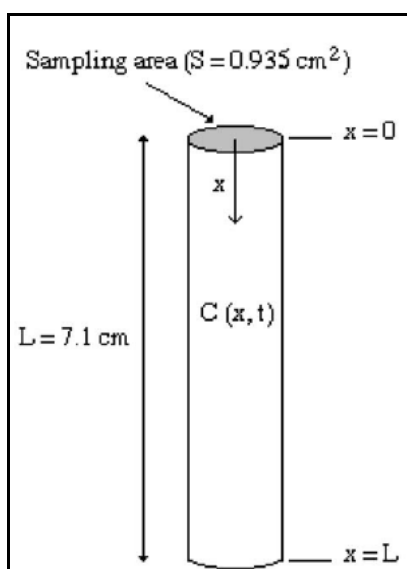


Figure 1.10. Geometry of a diffusion tube

If the passive tube is assumed to be as in Figure 1.10, the terms in the Fick's law expression can be explained as;

$$C = \frac{xL}{StD}$$

C: concentration in air ($\mu\text{g m}^{-3}$)

x: mass of analyte on adsorbent (μg)

L: length of diffusion tube (path length) (mm)

S: cross-sectional area of the tube (mm^2)

t: sampling time (s)

D: diffusion coefficient at 1 atm and 294 K ($\text{cm}^2 \text{s}^{-1}$)

The mass of gas pollutant (x) on the adsorbent surface of the passive tube is converted to the concentration of gas in air (C) by multiplying it with the path

length (L) and dividing to cross-sectional area (S), sampling time (t) and the diffusion coefficient (D) of the gas. In this expression the air is assumed to be in a steady state that means the turbulence effect is neglected. Also the concentration of air on the surface is assumed to be zero as shown in the figure.

1.4 Aim of the study

The aim of this study is to investigate the relationship among meteorological parameters and uptake rate of the passive tubes. In this study passive tubes for NO₂ and O₃ will be designed and uptake rate of these passive tubes will be determined. For this purpose weekly sampling of NO₂ and O₃ will be performed in Ulus and Keçiören where the air sampling station of Refik Saydam Hygiene Center, Air Quality Control and Research Laboratories are located. For O₃, 13 weeks sampling and for NO₂, 15 weeks sampling are performed. Then passive tubes are calibrated with active samplers and the definite uptake rates for each tube are determined and these uptake rates are associated with meteorological parameters. Finally, the developed passive tubes will be located in many points in Ankara to collect O₃ and NO₂ in order to create the pollution map of the city.

CHAPTER 2

METHODS and MATERIAL

2.1 Sampling strategies

The good sampling strategy based upon considering two main factors, selection of sampling sites and determining the optimum sampling period. Both factors make unable to predict the pollutants' character and the amount efficiently if they are not conducted effectively.

2.1.1 Sampling sites

Weekly sampling was performed in two different places nearby the active air sampling station of Ministry of Health, Refik Saydam Hygiene Center. In winter sampling samplers was conducted near the Ulus station between January and April in 2008, and for summer sampling samplers were placed nearby the Keçiören station between June and September.

To create the NO₂ and O₃ pollution map of Ankara, samples were collected from 40 different points of the city. During the selection of the sites equal distance from each other was considered and labeled as in Figure 2.1.

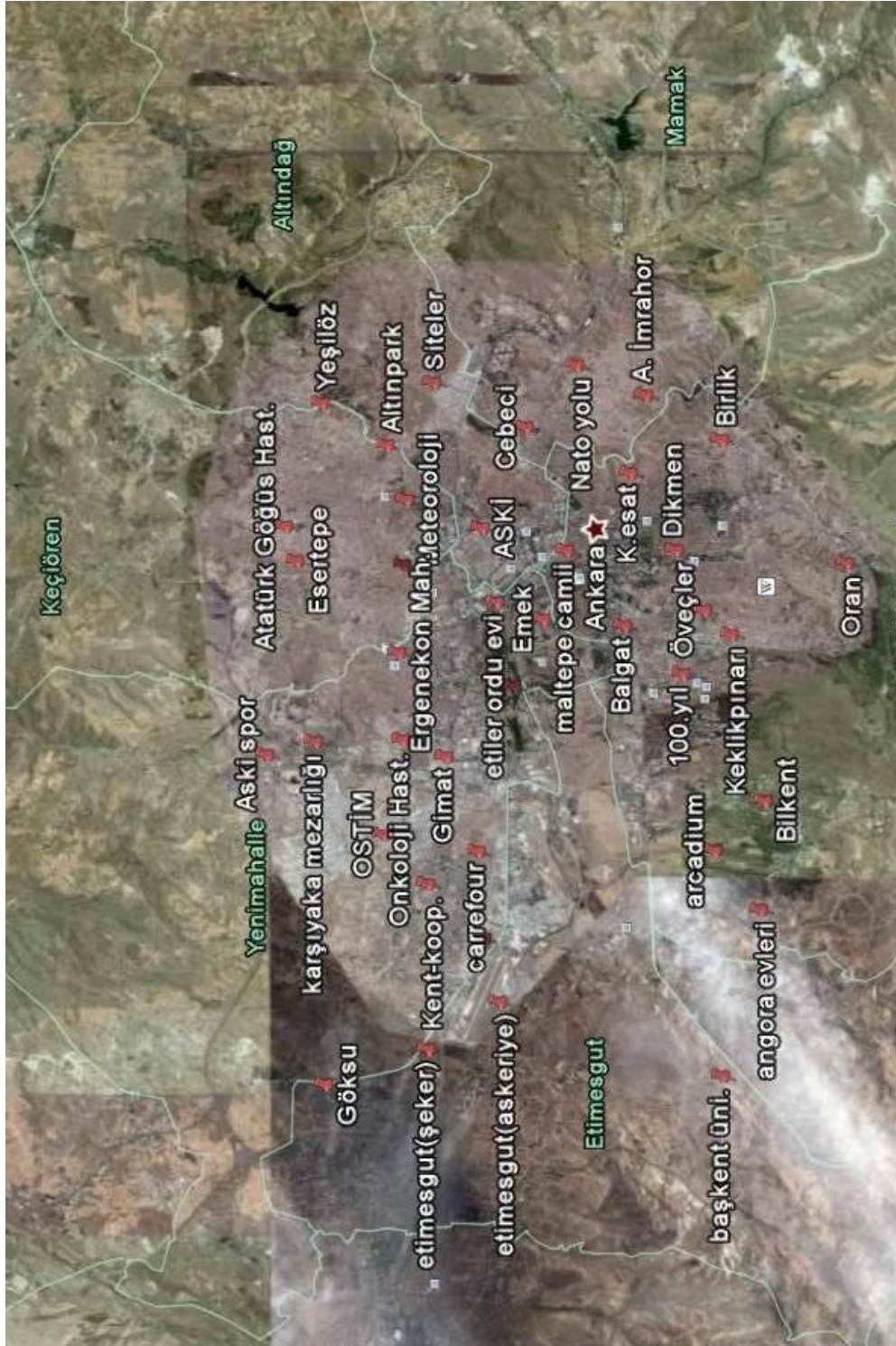


Figure 2.1. Passive sampling points in Ankara (September 20-September 26, 2008)

In order to determine the sampling points Ankara city map was divided into grids (nearly 2 x 2 km) and from each grid one sampling point was selected. The coordinates from Google Earth were not consequent with the surface coordinates. Then exact coordinates of each point was determined by Garmin 12 XL GPS personal navigator system.

For outdoor air sampling, the passive sampler was located at 1.5-2 m from the ground and was shielded from the rain by a small roof Figure 2.2 in order to eliminate the direct meteorological effects like solar radiation and rain.



Figure 2.2. Protective shelter for NO₂ and O₃ passive tubes

2.1.2 Sampling period

Meteorological conditions, locations and exposure time may affect collection efficiency. In order to define the collection efficiency of both ozone and nitrogen dioxide, the optimum sampling time should be determined first. For this purpose passive sampling tubes were exposed to the ambient air in two different periods, 15 days in winter and 65 days in summer. Seasonal variation also helped understand the effect of meteorological parameter effects. The tubes were collected in different time intervals. Initially sampling was performed diurnally, after the first week this period was expanded. Finally for both pollutants 7 days sampling was found to be the optimum exposure period. Then the sampling was performed 7 days regularly.

In each sampling average 5 (can be changed between 3 to 7) tubes were prepared and placed in Ulus (winter) and Keçiören (summer). After 7 days all tubes were collected and closed with their stoppers. Then they brought to the laboratory in plastic bags.

Time interval for each sampling was extended for optimizing sampling period. In winter (March 8, 2008 – March 23, 2008) totally 24 tubes were placed in Ulus station initially and each time 3 tubes were collected diurnally. At least 3 tubes were required for precision. After 15 days all tubes had been collected and prepared for the analysis. However, in summer (July 12, 2008 – September 4, 2008) initially 21 tubes were placed in Keçiören station in each time 3 tubes were collected and finished 65 days later. As shown in Figure 3.7 the sampling period was 2, 4, 6, 11, 18, 44 and 65 days. The extension in sampling period also allowed to understand the change in pollutant concentration in long term sampling.

2.2 Reagents

In passive tubes triethanolamine solution (TEA) and 1,2-Di(4-pyridyl)ethylene solution (DPE) were used as coating reagents, and sodium nitrite (NaNO_2) and 4-pyridylaldehyde solutions were used as standard solutions for NO_2 and O_3 , respectively. All solutions were prepared with double distilled deionized water obtained from Nanopore, Ultrapure Water Purification System.

Triethanolamine solution (TEA): 25 mL of acetone (Fluka[®]) and 22.7 mL extra pure triethanolamine from Merck[®] were mixed with acetone (Fluka[®]) (Varshney and Singh, 2003; Levaggi et al., 1973; Vinjamoori and Ling, 1981; Glasius, 1999; Tang, 1999; Patnaik, 1997). TEA has very high viscosity and it melts at 18°C, then in outdoor sampling. In order to decrease the melting point of TEA extra pure ethylene glycol (Merck[®]) was added to the solution and diluted to 100 mL with deionized water (Levaggi, 1973; Sickless et al., 1990; Tang, 1999).

1,2-Di(4-pyridyl)ethylene solution (DPE): 0.375 gr DPE (Fluka[®]) was dissolved in 5 mL 100 % pure glacial acetic acid (Merck[®]).

Sulfanilamide solution: 5 g of sulfanilamide (Fluka[®]) was dissolved in 50 mL of 37 % extra pure HCl (Merck[®]) and diluted to 500 mL with deionized water.

N-(1 naphthyl)-ethylene-diamine dihydrochloride solution (NEDA): 0.253 g of NEDA (Merck[®]) was dissolved and diluted to 250 mL with deionized water. NEDA solution was prepared in every month.

3-methyl-2-benzothiazolinone hydrozone hydrochloride solution (MBTH): 2.502 g of MBTH (Merck[®]) was dissolved in deionized water. 2.5 mL concentrated H₂SO₄ was added and diluted to 500 ml with deionized water.

4-pyridylaldehyde solution (O₃ standard solution): 100 µL (112.2 mg at 20°C) of 4-pyridylaldehyde (Merck[®]) was diluted to 1 L with deionized water (25 ppm).

NaNO₂ solution (NO₂ standard solution): 1.5026 g of NaNO₂ was dissolved and diluted to 1 L with deionized water (1000 ppm stock solution).

2.3 Apparatus and materials

All passive samplers have the common working principle; movement of air through the diffusion path length. In this study a new passive sampler that has the similar properties as the commercial ones was designed. For NO₂ and O₃ the similar passive tubes with different coating materials were constructed as shown in Figure 2.3.

As an adsorption medium stainless steel meshes with 24.6 mm in diameter were used. From the same material which has 26.4 mm diameter meshes were used on the entrance of the tube supported with a stopper having a hole. This screen was not coated with any chemicals however, only cleaned with deionized water before using.

In all sample preparation and analysis ultrafiltered deionized water that was produced by Barnstead nanopure deionization unit was used. The system is equipped with two ion exchange cartridges to remove ions, a third cartridge to

remove organics, and a fourth one to remove particulate matters. The produced deionized water has final resistance of 18.3 M Ω .

Samples and standards were weighed by Sartorius A210P sensitive analytical balance with 4 digits after decimal and during the extraction of the samples Nuvemix vortex was used.

During sampling Garmin 12 XL GPS personal navigator system was used for the sampling point determination.

2.4 Analytical Methodology

During sampling period near the passive tubes active sampling was done. Comparing active and passive sampling results permit determination of the uptake rates. After sampling, passive tubes were extracted and analyzed in UV-VIS spectrophotometer.

2.4.1 Preparation of passive tubes

The body of the passive tubes is made of polypropylene with a length of 8.5 cm. As an adsorbing medium stainless steel meshes in a 24.6 mm diameter were used. Also uncoated 26.4 mm stainless steel meshes were used on the entrance of the tube during sampling in order to prevent the adsorption surface from interferences and also to allow homogeneous diffusion of air through the path length.

Before coating the screens were cleaned with deionized water in a water bath at 15°C about 10 minutes and were dried under HEPA filters in clean-room at Environmental Engineering Department at METU. After cleaning of the screens they were coated with required solutions. For O₃ sampling screens were immersed in DPE (1,2-di(4-pyridyl)ethylene) and for NO₂ they were immersed in TEA (triethanolamine) solution (Varshney and Singh, 2003; Cadoff and Hodgeson, 1983) and waited 30 minutes for drying under Hepa Filters.



Figure 2.3. Passive tubes designed for NO_2 and O_3 sampling

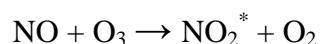
After the coating of the screens as an adsorbing surface they were placed into the stopper and prepared for sampling. Before sampling all tubes were stored under HEPA filters in plastic bags that can be locked. However, sampling was performed immediately after coating and also analysis was done directly after the sampling. Then there was no need to prepare lab blank tubes.

2.4.2 Active samplers

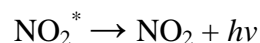
Passive tubes were placed nearby the active sampling stations of Ministry of Health, Refik Saydam Hygiene Center in Ulus and Keçiören. For NO₂ Chemiluminescent NO_x analyzer and for O₃ UV photometric ozone analyzer was used for active sampling. In every 10 minutes O₃ and NO₂ concentration results were received from these analyzers. Weekly averages of these results were calculated and compared with passive ones in order to determine the uptake rate of the passive tubes.

2.4.2.1 Chemiluminescent NO_x analyzer

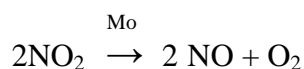
The AC32M NO_x analyzer is a nitrogen monoxide and nitrogen dioxide analyzer designed to monitor low concentration of these pollutants in ambient air. The monitor operates on the principle that NO will emit light (chemiluminescence) in the presence of highly oxidizing ozone molecules. Chemiluminescence corresponds to an oxidation of NO by ozone molecules as;



The return to a fundamental electronic state of the excited NO_2^* molecules is made by luminous radiation in 600-1200 nm.



In order to be measured by chemiluminescence, the NO_2 must be first transformed into NO and in order to carry out the reaction molybdenum is used.



The concentration of nitrogen monoxide can be determined by measuring the intensity of this chemiluminescence. If the sample air is passed through a converter to convert nitrogen dioxide into nitrogen monoxide, the concentration of nitrogen oxides (nitrogen monoxide and nitrogen dioxide) can be obtained by measuring the intensity of the chemiluminescence. The concentration of nitrogen dioxide in the sample air can be obtained by calculating the difference between the two measured values. The schematic expression of NO_x analyzer was shown in Figure 2.4 and the technical information of AC32M NO_x analyzer was given in Table 2.1.

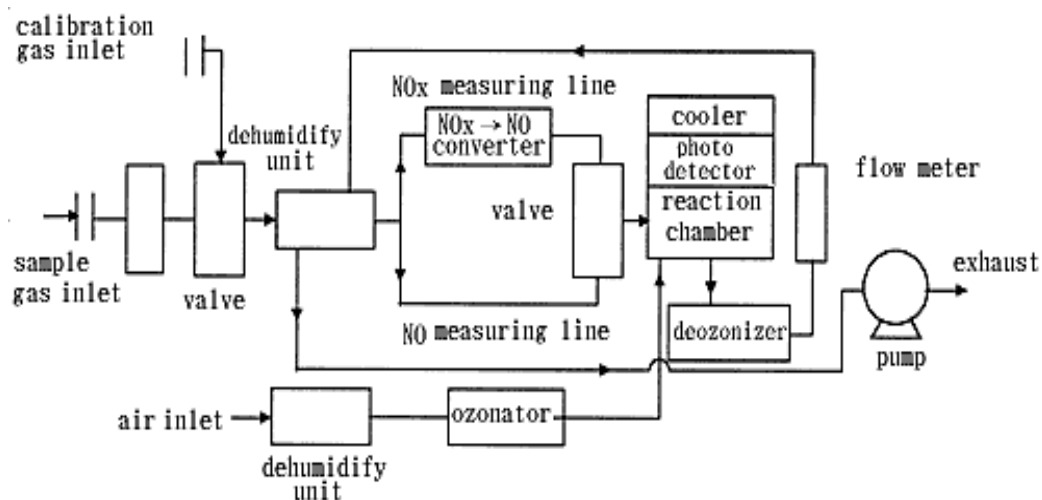


Figure 2.4. Schematic diagram of NO_x analyzer

Table 2.1. Technical notes for AC 32M NO_x analyzer

Measurement range (max.)	50 ppm	Sample flow rate	0.66 L / min
Units	ppb, ppm or $\mu\text{g}/\text{m}^3$, mg/m^3	Ozone flow rate	0.06 L / min
Noise	0.2 ppb	NO₂ → NO converter	Molybdenum at 340 °C
Min. detection limit	0.4 ppb	Reaction chamber temperature	60 °C
Min. response time (0-90 %)	40"	Operating temperature	+5 °C to 40 °C
Linearity	± 1 %		

2.4.2.2 UV photometric ozone analyzer

The O₃ 42M is a continuous analyzer and specific for low concentration of ozone in ambient air. It uses the principle of O₃ detection by absorption quantity of ultraviolet rays and measure the variation of absorbing in 253.7 nm. This method is not subject to interference from any of the common gaseous air pollutants.

The sample is drawn into the absorption cell through a scrubber which removes all ozone and light intensity (I₀) is determined. The valve is then switched to allow ambient air to fill the cell. During this measurement cycle the light intensity (I) is determined.

The Beer-Lambert Law gives the relationship between these measurements and the ozone concentration as following expression.

$$O_3(\text{ppm}) = \frac{10^6}{K \cdot L} \cdot \log \frac{I_0}{I} \cdot \frac{760}{P} \cdot \frac{T}{273}$$

K : Absorption coefficient = 134cm⁻¹ atm⁻¹

I : Transmitted light quantity

I₀ : Incident light quantity

L : Cell length (cm)

T : Cell outlet temperature

P : Cell outlet pressure (corrected to 760 mm Hg)

UV photometric ambient ozone analyzer should be composed of filter, ozone scrubber, three-way-valve, UV absorption cell, UV source lamp, detector, flow meter, sample ambient air suction pump and this composition was shown in Figure 2.5 and technical notes are given in Table 2.2.

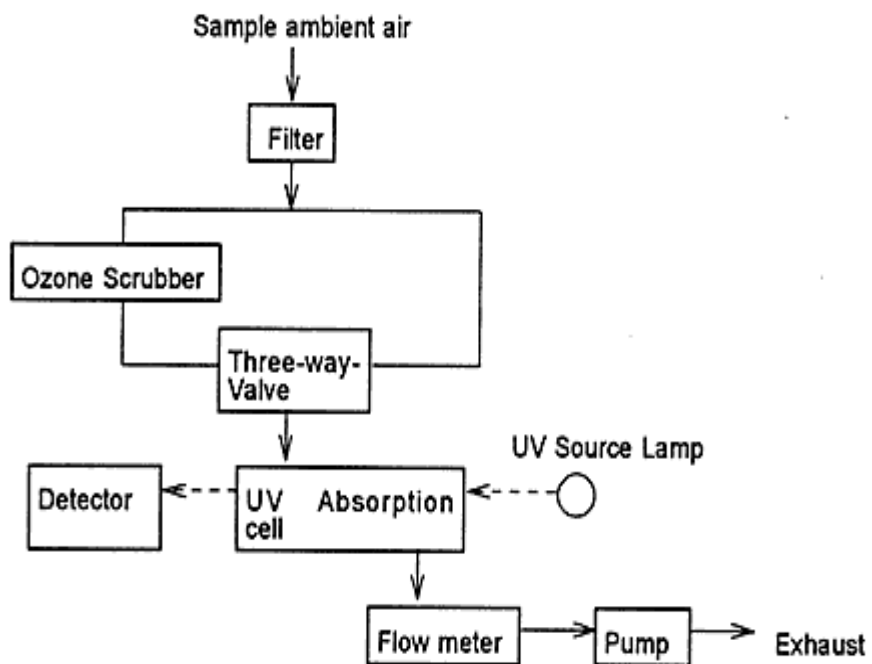


Figure 2.5. Schematic diagram of O₃ analyzer

Table 2.2. Technical notes for O₃ 42 Module UV photometric ozone analyzer

Measurement range (max.)	10 ppm
Units	ppm, mg/m ³
Noise	0.0005 ppm
Min. detection limit	0.001 ppm
Min. response time (0-90 %)	10-90 s
Linearity	± 1 %
Sample flow rate	1 L / min
Working temperature	+10 °C to 35 °C
O₃ internal generator	Conc. Generated 150 to 400 ppb
Adjusted accuracy	± 5 %

2.4.3 Analysis of NO₂ and O₃ in laboratory

After sampling, the passive tubes were brought to the Chemistry Department of METU. Then NO₂ and O₃ passive tubes were extracted with deionized water and 3-methyl-2-benzothiazolinone hydrazone solution, respectively and then coloring reagents were added to the solutions for VIS spectrometric analysis.

2.4.3.1 NO₂ Analysis

NO₂ in ambient air was collected on the adsorbent surface which was coated with TEA solution. The reaction between NO₂ and TEA was given in Figure 2.6 (Varshney and Singh, 2003; Glasius et al., 1999; Tang et al., 1999). As a product of this reaction NO₂⁻ ion was obtained. The collected tubes were sent to the laboratory for the analysis.

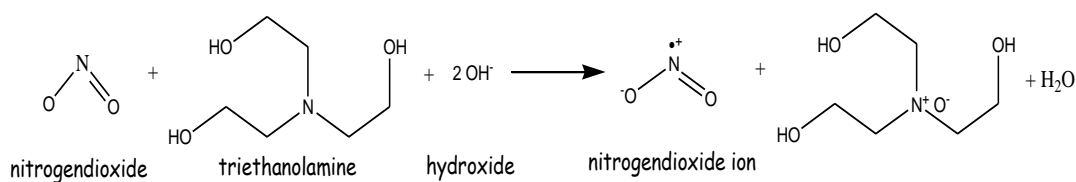


Figure 2.6. Reaction between nitrogendioxide and TEA on adsorbent surface

Each tube was extracted with 5 mL deionized water and was stirred about 1 minute in vortex. Then 500 μ L of sample was transferred to 10 mL glass test tubes. To each test tube 5 mL sulfanilamide solution and 1 mL NEDA solution which are called as a Griess-Saltzman reagent were added (Varshney and Singh, 2003; Glasius et al., 1999; Tang et al., 1999; Patnaik, 1997). The nitrite ion in the solution reacts with sulfanilamide and forms diazonium compound and this compound reacts with NEDA to form purple azodye. This colored solution was then measured at a wavelength of 537 nm in UV/VIS spectrophotometer (Varshney and Singh, 2003; Glasius et al., 1999).

Instrument calibration was achieved by NaNO_2 for NO_2 analysis. The same procedure as mentioned for sample analysis was applied for calibration standard solutions. Working range for standards was 0.05-4.00 ppm. To each 500 μ L of standard solution 5 mL sulfanilamide solution was added and was left for about 5 minutes and 1 mL NEDA solution was added. As a blank deionized water was used because it was the extraction solution. Then the colored solution was then measured at a wavelength of 537 nm in UV/VIS spectrophotometer. The calibration curves of the standards are shown in Figure 2.7.

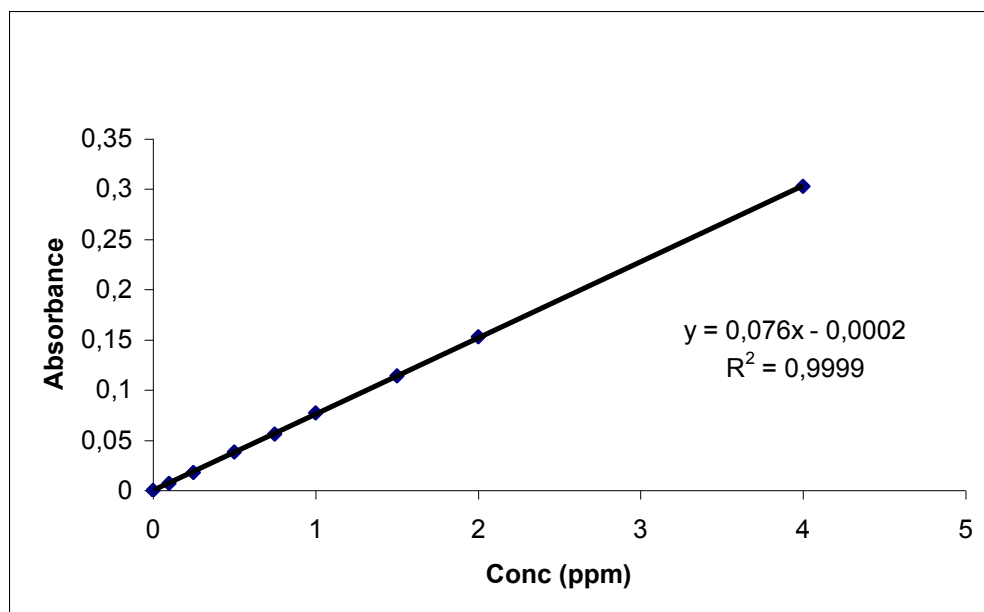
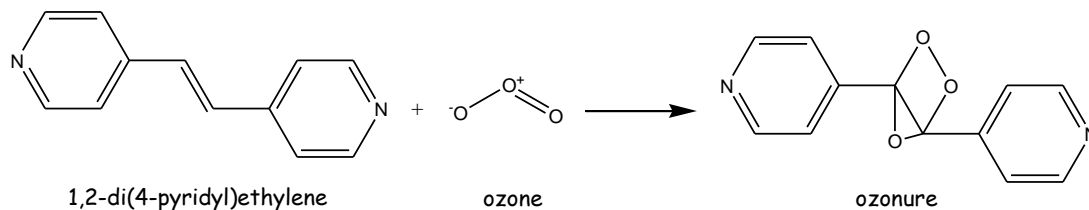


Figure 2.7. Calibration curve for NO₂

2.4.3.2 O₃ Analysis

O₃ reacts with 1,2-di(4-pyridyl)ethylene on the adsorption surface to give ozonure and the water molecules (humidity) in the air breaks the O-O bond to give 4-pyridylaldehyde and hydrogen peroxide (H₂O₂) as shown in Figure 2.7.



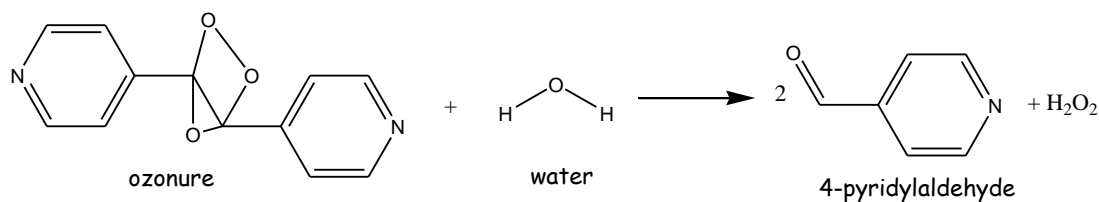


Figure 2.8. Ozonolysis mechanism on the passive tube adsorption surface

Then passive tubes were extracted with 7 mL MBTH solution which was also used as coloring reagent. The reaction of MBTH with 4-pyridylaldehyde is shown in Figure 2.9. The product from this reaction was MBTH-azide which has a yellow color. Then the extracted solution was transferred directly to the test tubes and absorbances were measured at a wavelength of 430 nm in UV/VIS spectrophotometer (Bernard et al., 1999; Hauser and Brandley, 1966; Helaleh, 2002).

Instrument calibration was performed by 4-pyridylaldehyde solution for O_3 analysis. Working range for standard solutions was 0.05-1.00 ppm and the calibration curve is given in Figure 2.10. To each 500 μ L standard solutions 5 mL MBTH solution was added and was left 1 hour then measured at a wavelength of 430 nm.

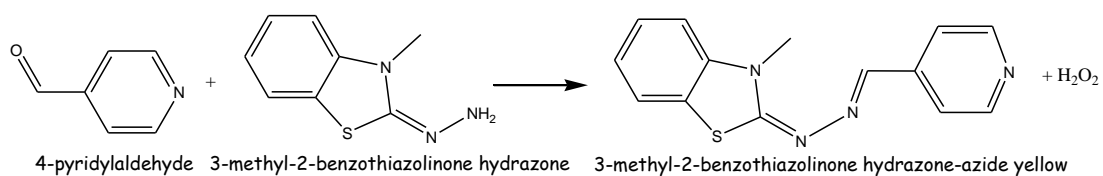


Figure 2.9. Reaction mechanism between MBTH and 4-pyridylaldehyde

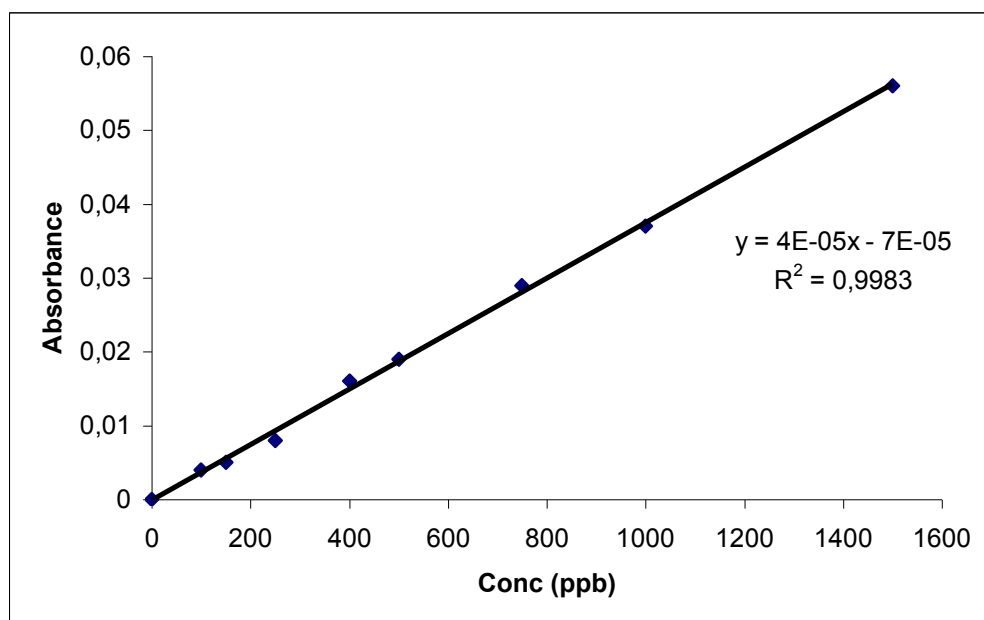


Figure 2.10. Calibration curve for O_3

CHAPTER 3

RESULTS and DISCUSSION

3.1. Reproducibility of sampling

Reproducibility refers to the ability of a system to be accurately replicated by somebody else in different conditions (apparatus, laboratory, time intervals etc.) with the same method. Repeatability is the variation in measurements by a single person or instrument on the same item and under the same conditions. As indicated in Figure 3.1 reproducibility and repeatability have two-way relationship. Both of them are used to express the data in a meaningful way. Systematic and random errors from the measurement results are determined and the final data are given with them as deviation.

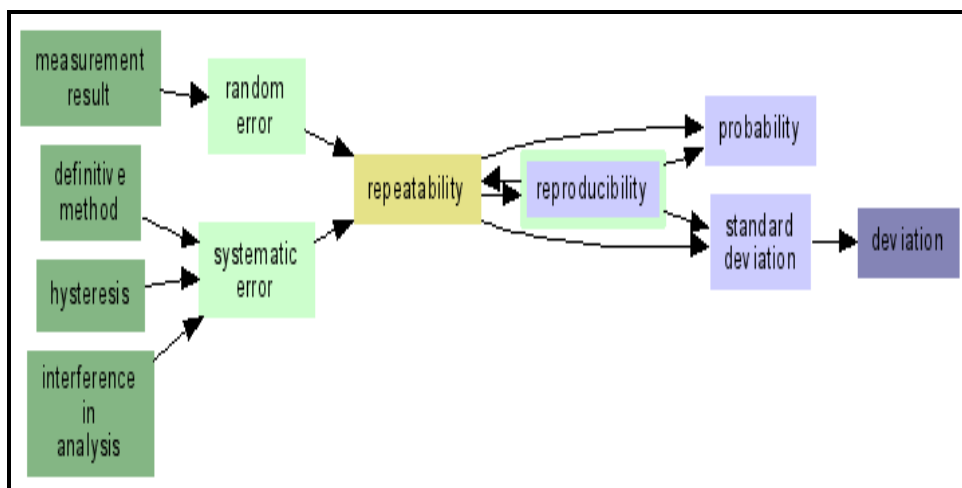


Figure 3.1. Schematic diagram of data validation

Measurement results can be identified as reproducible if repeatability is achieved. In our passive sampling system air samples were collected in the same points with the same time intervals (one week). Table 3.1 and Table 3.2 exhibit number of sampling tubes, weekly concentrations of ozone and nitrogen dioxide calculated by Fick's law (passive) with % RSD and concentrations calculated by using active samplers and the. Each week 3 – 7 passive tubes for each parameter were co-located with an automated NO₂ and O₃ monitors. Average concentrations for each gas pollutant were obtained after the subtraction of blank concentrations. Blank tubes were transported with sampling tubes during the placement of the tubes to the sampling points. Then they were brought to the laboratory and left under HEPA filter where the coating process was performed until the analysis. Laboratory blanks (tubes in refrigerator) were not included in the calculation. At the beginning of the analysis the effective storage was investigated. Although in literature storage in refrigerator at 4 °C was recommended, in the laboratory under HEPA filter at room temperature was decided to be more effective storage place. However, sampling was achieved immediately after coating and analysis were done just after sampling, it was not required to include the laboratory blank values during the calculation of the average concentration of gas pollutants and then only transport blanks are given in Table 3.1 and 3.2. Concentrations, calculated using Fick's law in 7 tubes were used to calculate relative standard deviation for precision of the analytical system. % RSD (percent Relative Standard Deviation) or CV (Coefficient of Variance) calculated with this approach is not only measure of the spectrometric measurement, but it also includes repeatability of the passive sampling.

The low value in percent relative standard deviation indicates the high precision that exhibits the closeness of the measurements for each sampler. For O₃ sampling in two dates % RSD were higher than 40 % however, in other dates these values changed approximately between 25 to 30 % which can be acceptable in environmental sampling analysis. Only in one sampling period blank value was

higher than the average concentration value. The reason may be due to the experimental error. In NO₂ sampling, % RSD changes between 10 to 15 %. The reason of high % RSD value may be due to personal and/or instrumental errors and also other atmospheric constituents may interfere the diffusion tube (Varshney and Singh, 2003). Other effects were minimized by using same methods and same laboratory conditions. Before each analysis with UV-VIS spectrophotometer, the instrument was calibrated with O₃ and NO₂ standard solutions.

Meteorological parameters are key factors in determining outdoor concentrations of air pollutants. However, they are more important in passive sampling, since there is no pump pulling air containing pollutants at a certain rate, pollutant molecules has to be transferred to the surface of the adsorbent, via diffusion and physical motion of the air. Any meteorological parameter that affects diffusion and physical motion of air may have strong influence on concentrations of pollutants measured by passive sampling.

In outdoor studies, the effect of meteorological parameters should not be ignored, however in passive sampling the amount of pollutant expressed as ‘time-weighted average’ concentration (Heal, 1999(a); Cox and Brown, 1984; Harper and Purnell, 1987; Schnelle and Brown, 2002; Manahan, 2000) that means the fluctuations in all day can not be observed then the cumulative amount is considered. In order to obtain meaningful values the average concentrations were related with the average value of the meteorological parameters in sampling days.

Table 3.1. Weekly O₃ concentrations

Date	# of tubes	Blank conc (µg m ⁻³)	Active O ₃ conc (µg m ⁻³)	Passive O ₃ conc (µg m ⁻³)	% RSD
31.12.08-07.01.08	7	-	6	3	35
11.01.08-18.01.08	5	8	5	18	49
02.02.08-09.02.08	5	5	11	8	18
16.02.08-23.02.08	4	13	17	18	26
23.02.08-01.03.08	5	20	12	12	0
08.03.08-16.03.08	3	12	12	27	37
23.03.08-30.03.08	6	11	26	11	26
29.03.08-05.04.08	6	-	14	15	35
11.04.08-19.04.08	4	-	8	18	22
13.06.08-20.06.08	3	1	58	12	43
03.07.08-11.03.08	4	9	72	16	19
12.07.08-18.07.08	3	-	67	22	10
23.07.08-30.07.08	3	2	75	3	35

Table 3.2. Weekly NO₂ concentrations

Date	# of tubes	Blank conc (µg m ⁻³)	Active O ₃ conc (µg m ⁻³)	Passive O ₃ conc (µg m ⁻³)	% RSD
31.12.08-07.01.08	7	-	-	146	30
11.01.08-18.01.08	7	126	-	577	7
02.02.08-09.02.08	6	40	252	901	6
16.02.08-23.02.08	7	110	259	790	10
23.02.08-01.03.08	7	297	322	722	6
08.03.08-16.03.08	3	45	272	724	24
23.03.08-30.03.08	7	-	177	594	9
29.03.08-05.04.08	7	-	222	859	13
11.04.08-19.04.08	5	-	365	743	5
13.06.08-20.06.08	5	57	61	367	30
03.07.08-11.07.08	5	0	81	139	22
12.07.08-18.07.08	3	-	131	305	9
23.07.08-30.07.08	4	0	176	397	9
30.07.08-06.08.08	5	9	158	293	16
07.08.08-14.08.08	5	129	280	450	11

3.2 Determination of uptake rate

Various studies have been performed to use passive samplers in ambient air. One of the risks for ambient air sampling is to find the exact concentration value of the pollutant due to meteorological condition effects. Beside the meteorological parameter effect also the tube itself has a great influence on the concentration determination. Then in literature for each type of the passive tubes the uptake rates were defined. For O_3 the uptake rate changes between $0.02-1.5 \times 10^3 \text{ cm}^3 \text{ h}^{-1}$ (Gerboles et al., 2006; Yamada et al., 1999) and for NO_2 the uptake rate changes between $0.07-9.24 \times 10^3 \text{ cm}^3 \text{ h}^{-1}$ (Gerboles et al., 2006; Plaisance et al., 2003; Campbell et al., 1994; and Mulik et al., 1989).

The working principle of passive tubes is based on the diffusion of gas phase pollutants through the defined path length. According to the Fick's law it can be calculated that the trapped amount is directly proportional to the ambient pollutant concentration, the exposure time, the diffusion coefficient in air for the pollutant in question and the cross-sectional area of the tube. The collected amount is further inversely proportional to the distance that the gas has to pass by molecular diffusion (Ferm and Svanberg, 1998).

In order to define the collection efficiency uptake rate of the tubes should be determined. As indicated in expression 3.1 theoretical uptake rate depends on diffusion coefficient of gas, concentration in ambient air, geometry of the tube and the exposure time.

$$\text{Uptake rate} = D \times C \times A \times t / z \quad (3.1)$$

D : diffusion coefficient of vapor in air

C : ambient concentration of gas

A : cross-sectional area of passive tube

t : time of exposure

z : path length of diffusion (length of passive tube)

In Fick's law it is assumed that the adsorption of the pollutants on the collecting medium is due to only the diffusion of air and the effects of meteorological parameters are neglected although they are the most significant factor in ambient air analysis. Due to the complex mechanism in air high variation in the concentration of pollutants calculated from Fick's law was expected.

Temperature, solar radiation, humidity and wind speed affect the adsorption of the pollutants on the collecting medium and also they can cause decomposition from the surface after sampling. In an exposure chamber tests were performed under field and extreme conditions of controlling factors (Gerboles, 2006). Then in passive sampling the uptake rates obtained from the exposure chamber systems were used (Krupa and Legge, 2000; Cadoff and Hodgeson, 1983; Royset, 1998; Helaleh et al., 2002).

In this study uptake rates of O₃ and NO₂ were determined experimentally in ambient air conditions instead of using Fick's law. For this purpose passive tubes were placed nearby the active sampling station. The concentration results obtained from active samplings were used in the uptake rate equation.

Uptake rates of O₃ and NO₂ in literature and also in this study are listed in Table 3.3 and 3.4., respectively. In Table 3.3 the commercial passive tubes with different dimensions and same coating material are listed. Theoretical sampling

rates of each passive tube differ with respect to each tube size. This implies the importance of tube dimensions in the determination of sampling rate.

Table 3.3. Some passive samplers used for NO₂ with same adsorbent and different dimensions (Cox, 2003).

Sampler type	Dimensions L (cm) x A (cm²)	Absorbent	Theoretical uptake rate (cm³ h⁻¹)
Palmer type diffusion tube	7.1 x 0.95	Triethanolamine	0.72×10^2
Ogawa badge	0.6 x 0.79	Triethanolamine	0.73×10^3
Radiello radial sampler	4.0 x 1.3	Triethanolamine	0.47×10^3
Krochmal badge	1.0 x 4.91	Triethanolamine	0.27×10^4
In this study	8.5 x 4.98	Triethanolamine	0.91×10^3

Gerboles et al., (2006) reported some of the NO₂ and O₃ passive tubes with their uptake rates as shown in Table 3.4. In their study passive tubes were analyzed in different laboratories and some laboratories found different uptake rate values for the same passive tube.

In addition to Gerboles et al., (2006), the early studies of NO₂ uptake rates reported as Plaisance et al., (2003) $72.6 \text{ cm}^3 \text{ h}^{-1}$, Campbell et al., (1994) $7.049 \times 10^6 \text{ cm}^3 \text{ h}^{-1}$. Mulik et al., (1989) calculated NO₂ uptake rate by using Fick's law of diffusion as $9.24 \times 10^3 \text{ cm}^3 \text{ h}^{-1}$.

Beside NO₂ uptake rates, Plaisance, 2007 and Gerboles et al., (2006) found O₃ uptake rate as 5.502 cm³ h⁻¹ for 8 hours exposure and Yamada et al., (1999) calculated O₃ uptake rate as 1.47 x 10³ cm³ h⁻¹ for 30 days exposure.

Table 3.4. Some passive tubes with their uptake rates

Passive tubes	Uptake rates	
	O ₃	NO ₂
Gradko	-	72.80 cm ³ h ⁻¹ (lab 1) *
	-	72.00 cm ³ h ⁻¹ (lab 2) *
Passam	0.0255 mg m ⁻³ h ⁻¹	0.85 cm ³ h ⁻¹ (lab 1)
	-	0.90 cm ³ h ⁻¹ (lab 2)
Radiello	1.48 x 10 ³ cm ³ h ⁻¹	-
Ogawa	21.80 cm ³ h ⁻¹	3.82 x 10 ³ cm ³ h ⁻¹
Analyst	1.56 x 10 ³ cm ³ h ⁻¹	2.86 x 10 ³ cm ³ h ⁻¹
In this study	1.71 x 10 ³ cm ³ h ⁻¹	0.91 x 10 ³ cm ³ h ⁻¹

* lab1 and lab 2 indicates different laboratories

3.2.1 Variation of uptake rate with analyte concentration

The uptake rate of the sampler is not expected to be changed with analyte concentration and if the source of the collected pollutant on adsorbent is the only air diffusion (Cox and Brown, 1984). The above statement does not hold if all of

the active sites on the sampler are filled. In such a saturation case uptake rates are expected to decrease after the saturation is reached. A separate experiment was not performed to investigate the saturation point. However, since uptake rates were determined over a long period, we simply plotted the uptake rates as a function of analyte concentrations measured in the course of this study, measured with automated O₃ and NO₂ monitors. Results are presented in Figures 3.2 and 3.3, for NO₂ and O₃, respectively. According to the simple regression analysis no significant relationship between uptake rate and concentration was obtained for both O₃ and NO₂. Respectively p-values were found as 0.09996 and 0.09568 which are lower than 0.10 at 90 % confidence level. This demonstrates that the uptake rates are not variable at NO₂ and O₃, concentrations encountered in Ankara atmosphere, during 1 year-long study period.

Experimental weekly average uptake rates are given in Figures 3.4 and 3.5 for NO₂ and O₃ respectively. Experimental uptake rates were determined by using the concentration values obtained from active air samplers. The bars in figures are weekly average uptake rates, because sampling period was fixed at one week. Uptake rates that bases on Fick's law are also depicted in the figures. The most important point in these two figures is that while the Fick's law uptake rates were the same throughout the study period, due to nature of its calculation, experimentally determined uptake rates were variable. This variability is largely due to variations in meteorological conditions as will be discussed later in the manuscript.

Theoretical uptake rates, which were based on Fick's law, were $0.033 \times 10^3 \text{ cm}^3 \text{ h}^{-1}$ for NO₂ and $0.032 \times 10^3 \text{ cm}^3 \text{ h}^{-1}$ for O₃. In theoretical uptake rate determination all meteorological parameters were eliminated and only the diffusion of air is considered. Experimental uptake rates on the other hand are highly variable for both NO₂ and O₃. For NO₂ the average uptake rate was calculated as $0.91 \times 10^3 \text{ cm}^3 \text{ h}^{-1}$ and for O₃ it was found as $1.71 \times 10^3 \text{ cm}^3 \text{ h}^{-1}$.

In Figure 3.4 and 3.5 the lines on the bars indicate variability of 7 parallel sampling in that particular week. High variability in uptake rates is very important and signifies the high uncertainty associated with the use of theoretical uptake rates in calculating concentrations of pollutants. The reason for observed variability is not due to problems in experimental measurements. Fairly good reproducibility of data generated from 7 parallel passive tubes collected each week is an indication of this. The observed variability in uptake rates is due to variations in meteorological conditions as will be discussed in coming sections of this manuscript.

Uptake rates calculated for O_3 is more variable than the uptake rates calculated for NO_2 . This is not surprising and is due to relative instability of atmospheric ozone. As pointed out before, accurate measurement of O_3 using passive samplers is not possible no matter which method is used in uptake rate calculations due to its instability on the adsorbent and fast desorption from the sampler.

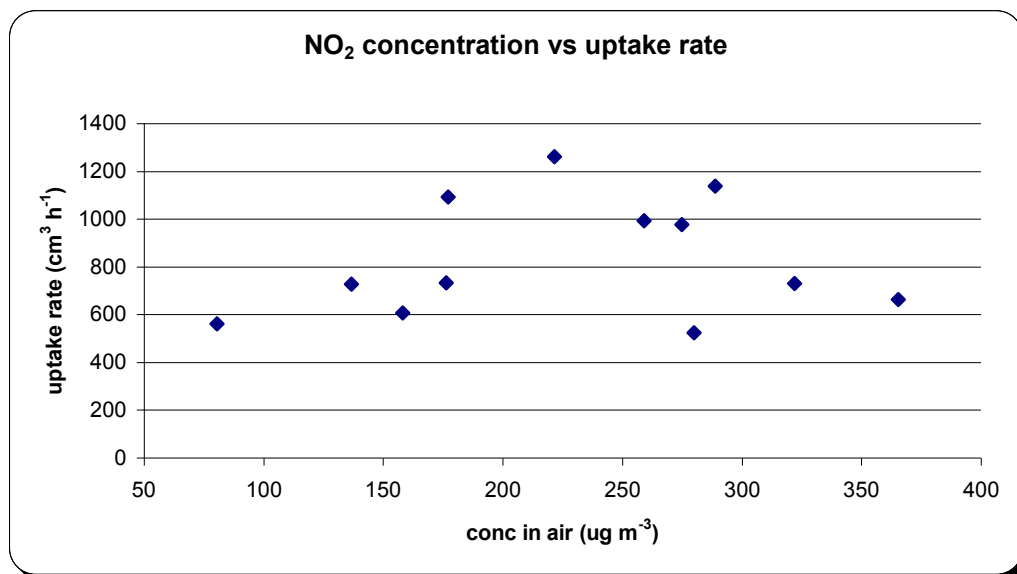


Figure 3.2. Relationship between NO₂ passive uptake rates and NO₂ concentrations in passive tube

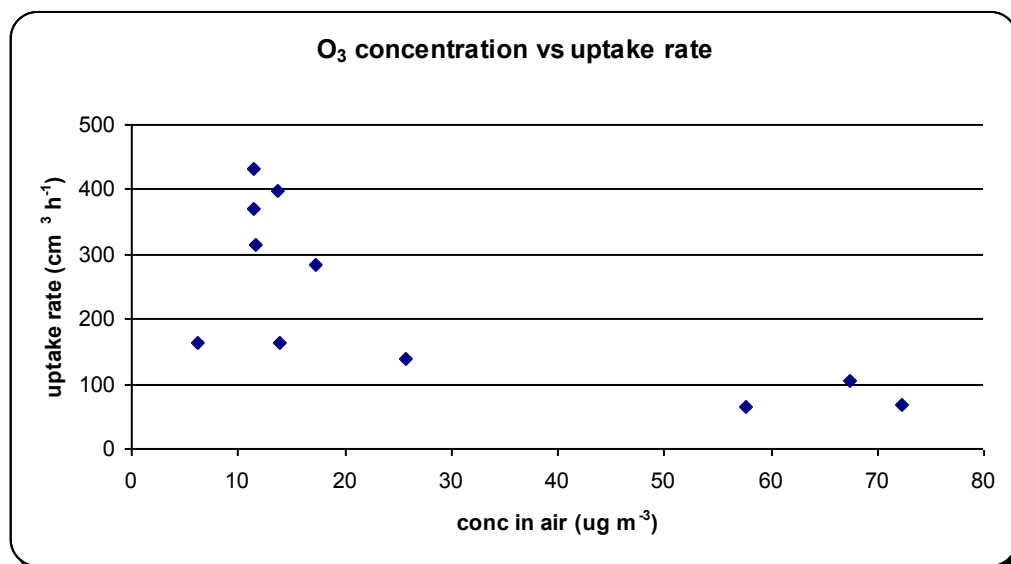


Figure 3.3. Relationship between O₃ passive tube uptake rates and O₃ concentrations in passive tube

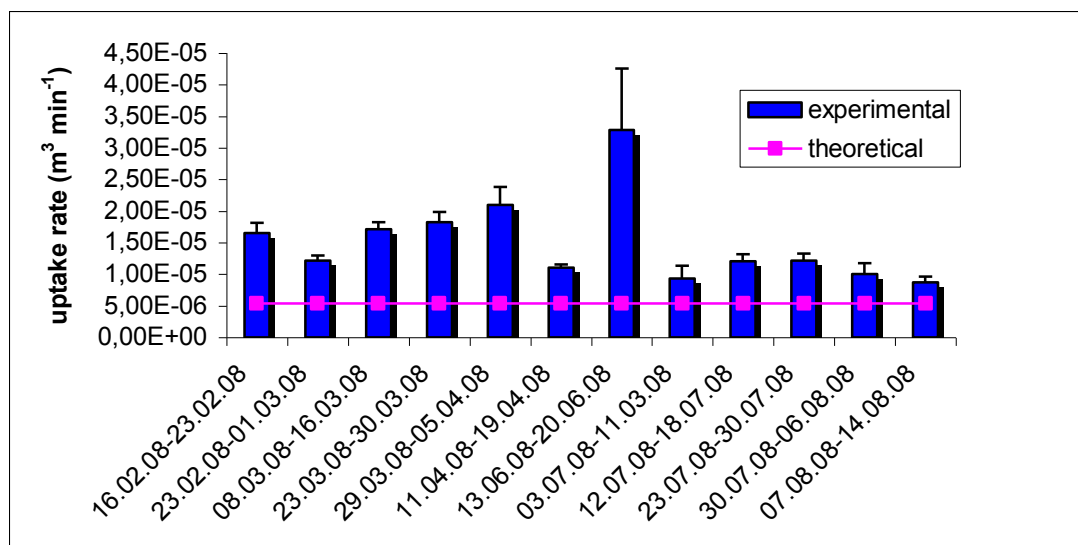


Figure 3.4. Experimental uptake rates calculated by using active sampling results and theoretical uptake rates that were calculated by using concentration value derived from Fick's law values of NO_2 uptake rates

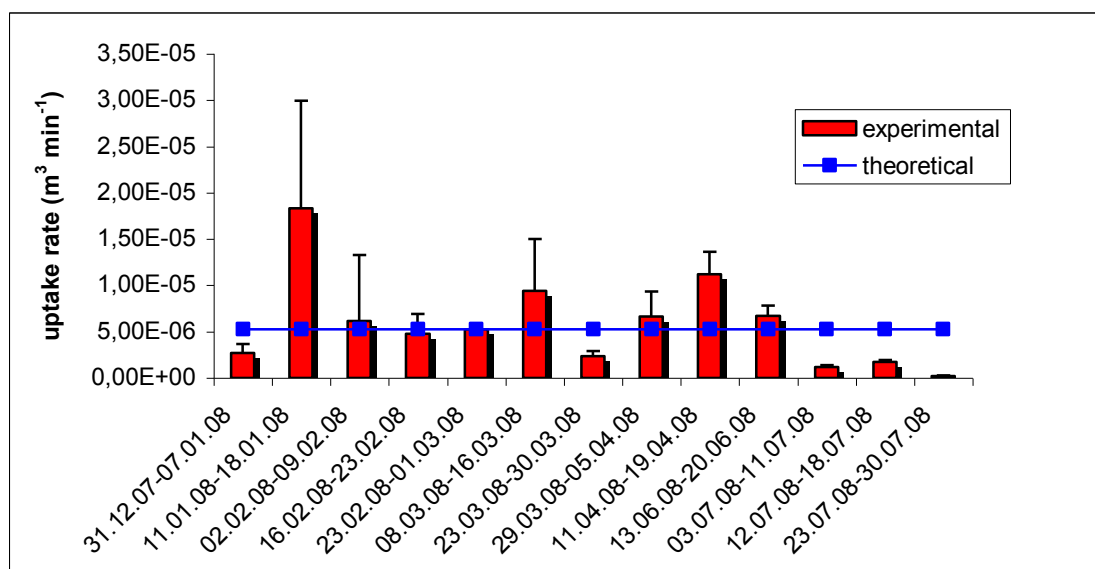


Figure 3.5. Experimental uptake rates calculated by using active sampling results and theoretical uptake rates that were calculated by using concentration value derived from Fick's law values of O_3 uptake rate

3.3 Determination of collection efficiency

Extended sampling periods are required in order to overcome the manual and periodic collection and analysis of the samples. By this way, concentration values are integrated or averaged over the sampling period. Sampling periods required to collect samples, and intended use of the data, determine the averaging time (Godish, 2004).

One of the limitations in passive sampling is the capacity of the adsorbent (Harper and Purnell, 1987). In order to evaluate the performance of a passive tube, optimum exposure period should be determined otherwise overestimation or underestimation may happen (Varshney and Singh, 2003).

For pumped samplers, sampling efficiency will be reduced or leaking in tubes will occur if the adsorbent becomes saturated. A similar phenomenon occurs with diffusive samplers, and may occur earlier than full saturation if a significant vapor pressure exists at the adsorbent surface relative to the ambient concentration of pollutant. In long exposure times desorption from the surface and photochemical process for removal of the pollutant may be observed. Then the efficiency of the sampler is decreased. However, it is not a problem for commonly reagent-coated screen or a strong surface adsorbent (Brown, 1993; Heal et al., 1999(a)). As this situation was observed in this study, sampling period was considered as 5 to 10 days.

Different studies were done in order to find the effective sampling period. In most of the studies one week passive sampling is recommended as an optimum sampling time otherwise decrease in the concentration of pollutant could be observed (Plaisance, 2004; Miller, 1988; Sickless et al., 1990; Heal et al., 1999(b); Helaleh et al., 2002). Bush et al., (2001), Ayers et al., (1998), Varshney and

Singh, (2003) and Heal et al., (1999) were examined 1-week to 4-week NO₂ exposure. Also Plaisance, (2004); Royset, (1998) and Sanz et al., (2007) examined one to two week exposure of NO₂ and O₃.

In this study the collection efficiency with respect to uptake rates were examined in order to determine the capacity of the passive tubes. The main hypothesis is that the meteorological parameters are the significant factors to determine the collection efficiency of the tubes. For that purpose different sampling periods were examined. In two seasons, winter and summer the different time exposures for NO₂ and O₃ were applied and collection efficiencies were investigated separately.

First sampling was done in winter between March 8-March 23, 2008 and the second sampling was done in summer between July 12-October 14, 2008. The collection efficiency of both O₃ and NO₂ passive tubes differ from each other and also there was a great difference in collection efficiency during sampling in summer and winter as seen in Figure 3.6 to Figure 3.9.

When the change of O₃ concentration with respect to exposure time was examined it was seen that both in winter and summer O₃ concentrations decreased in a few days (Figure 3.6 and 3.7). The interesting thing is that decrease in concentration was faster in higher temperatures in summer rather than in other days. In winter sampling the maximum O₃ concentration was obtained in 4 days and the concentration reached acceptable values in the first week. However, in summer sampling the maximum O₃ concentration was obtained in the first two days and then the concentration decreased fast after 2 days. The reason of rapid change in O₃ concentration can be the decomposition of O₃ by temperature and also solar radiation.

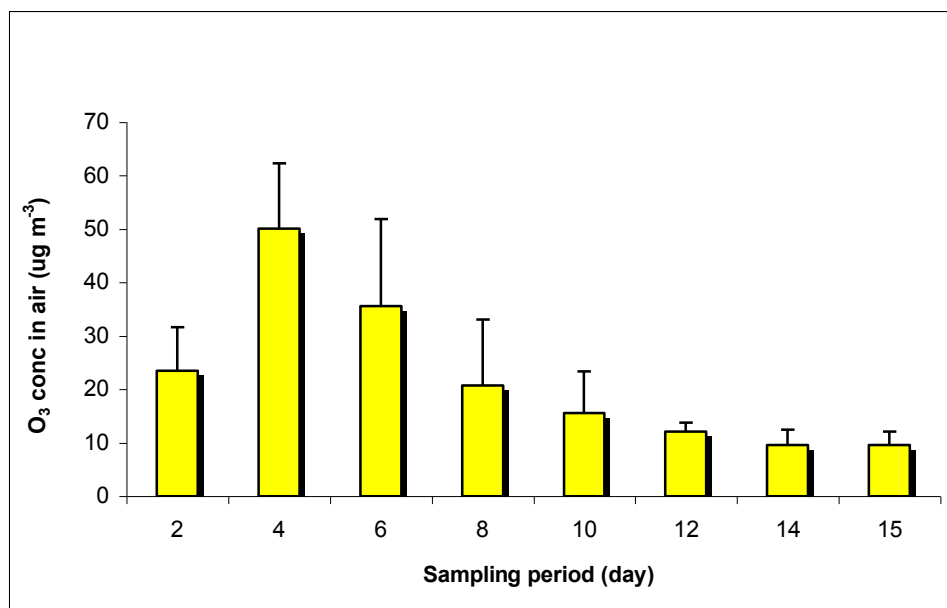


Figure 3.6. Concentration distribution of O₃ in winter (March 8, 2008 – March 23, 2008)

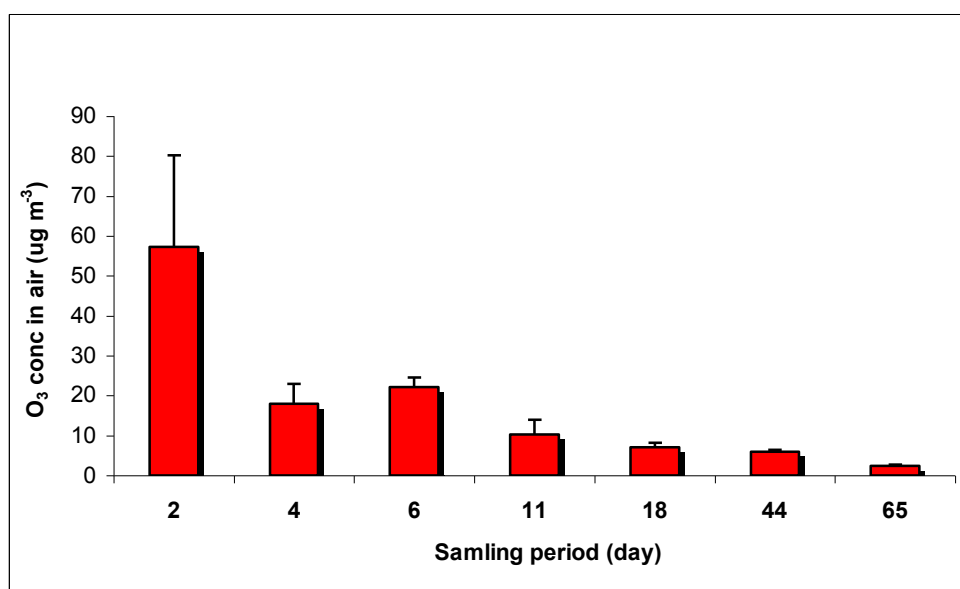


Figure 3.7. Concentration distribution of O₃ in summer (July 12, 2008 – September 4, 2008)

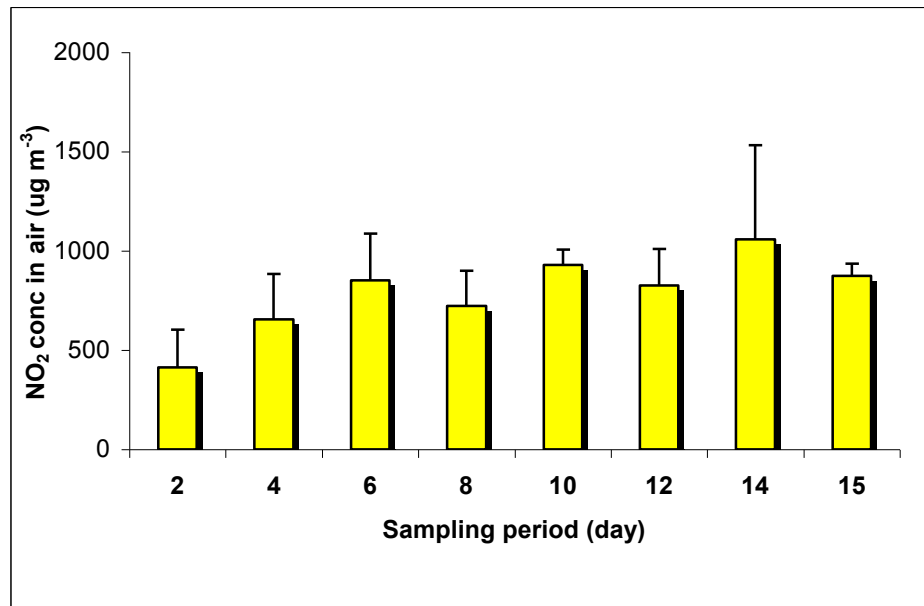


Figure 3.8. Concentration distribution of NO₂ in winter (March 8, 2008 – March 23, 2008)

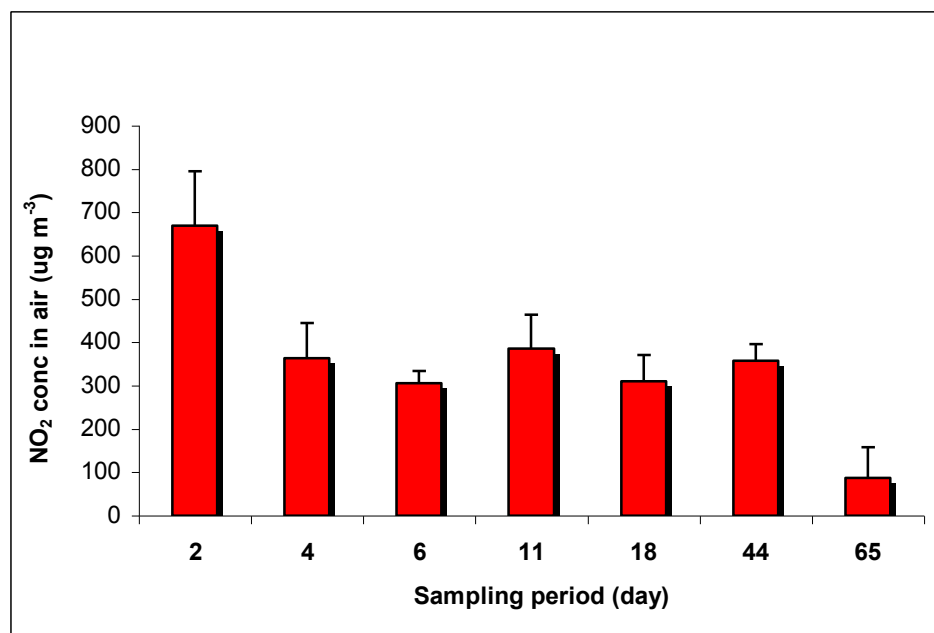


Figure 3.9. Concentration distribution of NO₂ in summer (July 12, 2008 – September 4, 2008)

Nevertheless, these observations showed that O₃ sampling in summer may not be reliable enough. Although the exposure time would be extended until the constant concentration value was obtained, the same conditions during this rapid change could not be maintained.

On the other hand, different situation in NO₂ concentrations was observed in seasonal sampling. In winter the change in NO₂ concentration could be considered as negligible in first 15 days which was expected (Figure 3.8). However, in summer sampling NO₂ concentration decreased in first 2 days but in the following 40 days the change in NO₂ concentration was neglected (Figure 3.9). Decrease in first 2 days could be explained only with the contamination during sampling or during the analysis. Despite of this situation use of NO₂ passive tubes in summer can be accepted as available because during 40 days there was no change in concentration.

As mentioned before, optimization of sampling time was determined by considering the collection efficiency of the passive tubes. For that purpose both concentration and uptake rate values of O₃ and NO₂ were calculated. The reason to determine the uptake rate beside concentration during both winter and summer sampling is that, concentration values during extended sampling periods can not be reliable itself because during exposure the concentration of the pollutant in ambient air may not be constant. The change in obtained concentration may be due to change in ambient air concentration with respect to time not due to the capacity of the passive tube.

During the whole sampling each 3 passive tubes were collected in stated time intervals. For example in first sampling X concentration was found, however, in other days very high concentrations of pollutants were found although the collection efficiency of the tubes was low. As a result concentration itself can not be used to determine the collection efficiency of passive tubes.

Then the uptake rates of the passive tubes were determined. For the determination of uptake rates, active sampling systems were used as a reference. Passive tubes were placed nearby the active air sampling stations of Refik Saydam Hygiene Center and Air Quality Control Station. The ambient air concentration results during whole sampling were obtained from the station and then the uptake rates for O₃ and NO₂ were determined. As seen in Figure 3.10 to 3.13, the change in uptake rate with respect to time show similar distribution as concentration.

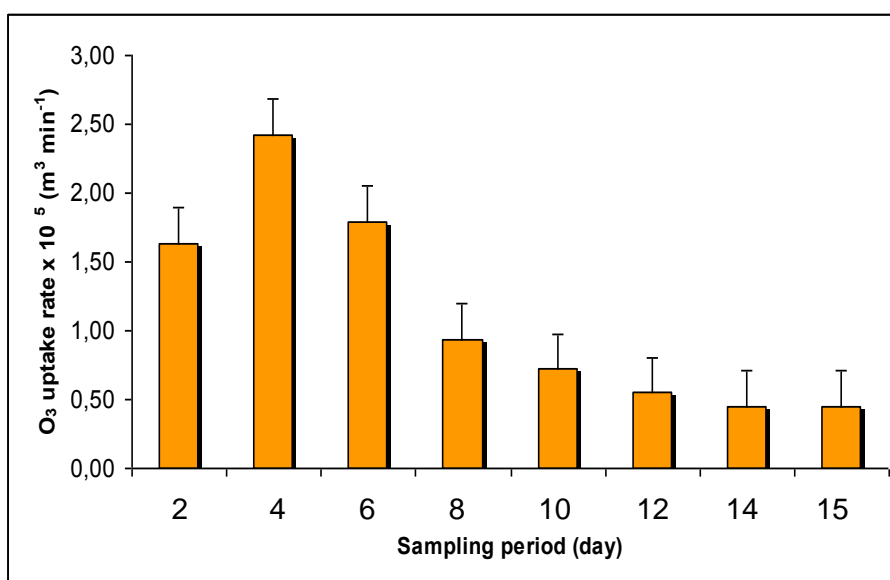


Figure 3.10. Uptake rate distribution of O₃ in winter (March 8, 2008 – March 23, 2008)

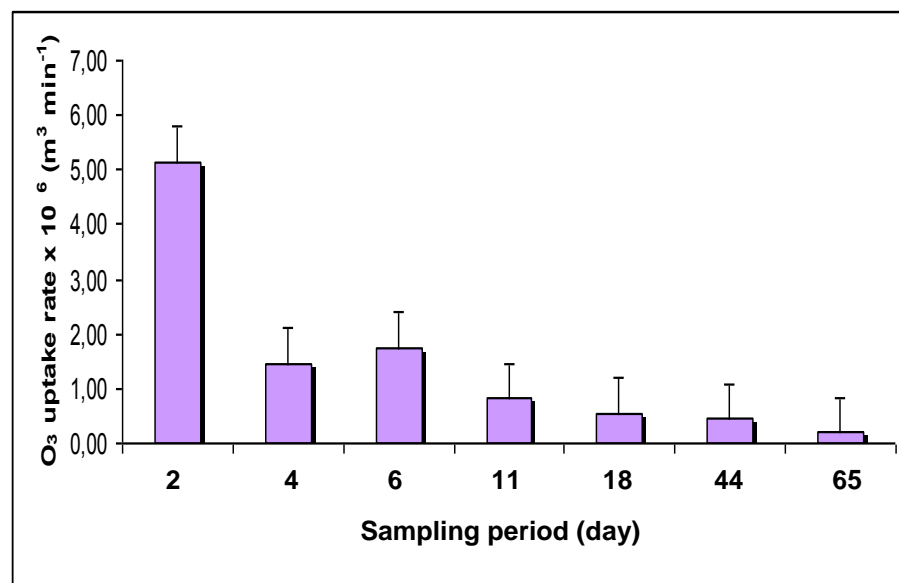


Figure 3.11. Uptake rate distribution of O₃ in summer (July 12, 2008 – September 4, 2008)

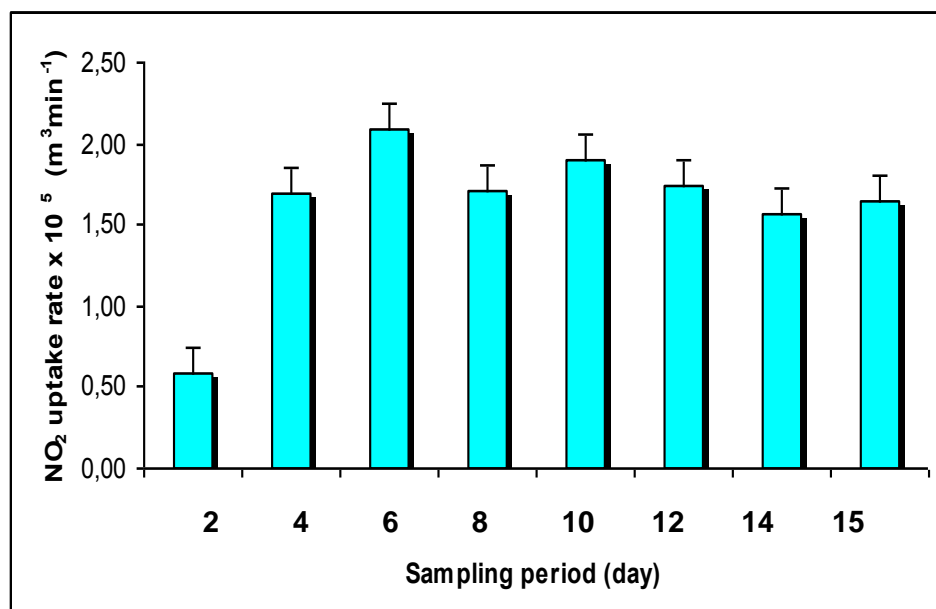


Figure 3.12. Uptake rate distribution of NO₂ in winter (March 8, 2008 – March 23, 2008)

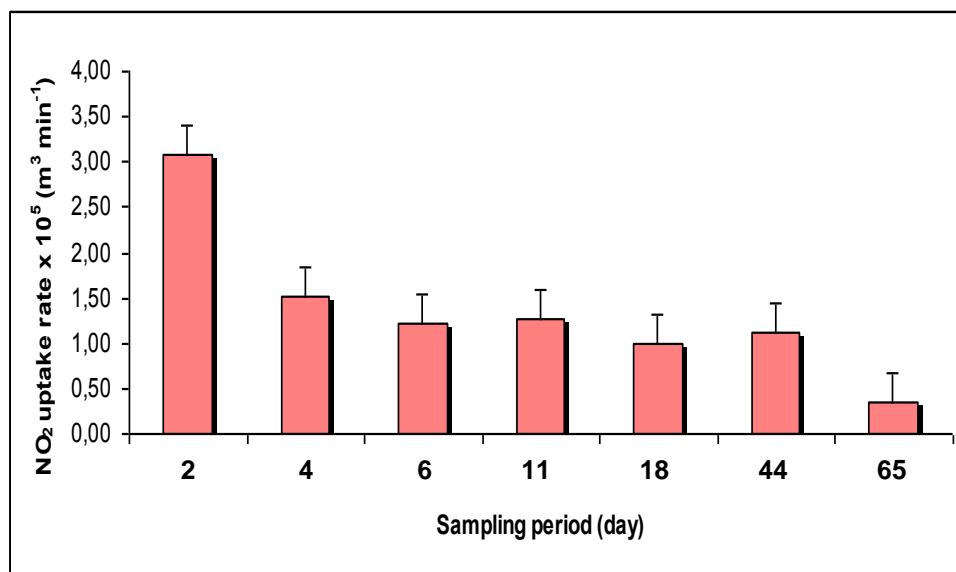


Figure 3.13. Uptake distribution of NO₂ in summer (July 12, 2008 – September 4, 2008)

3.4 Dependence of uptake rate on meteorological parameters

Meteorological parameters including, wind speed (WS), wind direction (WD), temperature (T), pressure (P), percent relative humidity (% RH) and solar radiation (rad) are shown to impact collection efficiency of passive sampling tubes for both NO₂ and O₃ (Varshney and Singh, 2003; Krupa and Legge, 2000; Cox, 2003; Brown, 1993; Plaisance et al., 2004; Cox and Brown, 1984; Gair and Penkett, 1995; Vinjamoori and Ling, 1981; Yamada et al., 1999; Santis et al., 1997; Ferm and Svanberg, 1998; Glasius et al., 1999; Tang et al., 1999; Ray, 2001; Royset, 1998; Godish, 1997). These studies, where meteorological variables were related to collection efficiency of samplers, are generally performed in exposure chambers where both concentrations of pollutants and meteorological

parameters can be carefully controlled (Krochmal and Gorski, 1991; Sanz et al., 2007; Ferm and Svanberg, 1998; Ray, 2001; Namiesnik et al., 2005).

In chamber studies value of the meteorological parameters were varied at a time, assuming all other meteorological parameters and concentrations of pollutants remain the same throughout the sampling period. This is the main weakness of the uptake rates determined through chamber studies. In real life various parameters vary simultaneously and their impacts on uptake rate are not necessarily independent from each other.

The influence of meteorological parameters on uptake rates of pollutants can also be determined in real life conditions. In this approach, passive sampling tubes are co-located with active measurement devices and parallel active and passive measurements are performed at the same location. In this way, uptake rates can be determined using active measurement results under different meteorological conditions. Dependence of uptake rates on meteorological parameters can then be determined by applying statistical tools, mainly multiple linear regression and correlation analysis. One drawback of this more realistic approach is the need for large data base, which means fairly long sampling period.

In this study, fifteen weeks of sampling was performed to assess the impact of meteorological parameters on uptake rates of NO₂ and O₃. These parameters were received from Refik Saydam Hygiene Center, Air Quality Control and Research Laboratory. In these 15 sampling intervals 3 – 7 passive tubes were placed to the Ministry of Health monitoring station at Sıhhiye (later samplers were moved to Keçiören station when ozone monitor at Sıhhiye station was malfunctioned). Average meteorological conditions during each passive sampling period and corresponding average uptake rates (average of uptake rates calculates from 3 – 7 passive samplers) are given in Table 3.5. In order to prevent tubes from direct impact of solar radiation, rain-snow and wind speed a protective shelter was used.

Table 3.5. Meteorological parameters during sampling.

date	NO ₂ uptake rate (cm ³ h ⁻¹)	O ₃ uptake rate (cm ³ h ⁻¹)	Wind speed (ms ⁻¹)	Temperature (°C)	Relative humidity (%)	Solar radiation (Wm ⁻²)
31.12.08-07.01.08	-	2.72x10 ³	1.17	-3	66.5	51.2
11.01.08-18.01.08	-	1.10x10 ³	1.75	-6	72.2	61.9
02.02.08-09.02.08	-	0.04x10 ³	1.31	1	61.0	94.7
16.02.08-23.02.08	0.99x10 ³	0.29x10 ³	1.87	-2	70.6	84.5
23.02.08-01.03.08	0.73x10 ³	0.32x10 ³	1.18	4	58.0	128.9
08.03.08-16.03.08	1.03x10 ³	0.56x10 ³	1.36	9	50.0	109.2
23.03.08-30.03.08	1.09x10 ³	0.14x10 ³	1.90	12	45.5	121.3
29.03.08-05.04.08	1.26x10 ³	0.40x10 ³	1.29	7	71.4	82.8
11.04.08-19.04.08	0.66x10 ³	1.79x10 ³	0.95	19	46.8	151.7
13.06.08-20.06.08	1.97x10 ³	0.06x10 ³	1.90	22	39.8	267.2
03.07.08-11.03.08	0.56x10 ³	0.07x10 ³	2.22	23	32.8	298.4
12.07.08-18.07.08	0.73x10 ³	0.10x10 ³	2.20	23	39.5	265.7
23.07.08-30.07.08	0.73x10 ³	0.01x10 ³	2.30	26	35.1	316.5
30.07.08-06.08.08	0.61x10 ³	-	2.68	24	35.2	289.9
07.08.08-14.08.08	0.52x10 ³	-	2.24	24	39.4	260.7

3.4.1 Dependence of uptake rate on wind speed

Wind is an important meteorological parameter affecting dispersal of air pollutants and also the efficiency of passive sampling (Varshney and Singh, 2003; Krupa and Legge, 2000; Cox, 2003; Heal et al., 1999 (a); Brown, 1993; Plaisance et al., 2004; Plaisance et al., 2007; Palmes et al., 1976; Tang, 1999; Godish, 1997). For instance, Koutrakis et al., (1993) found that the collection rate of the sampler was affected from the wind velocity at the sampler surface. This effect can be over-estimation of gas concentration on the adsorbent surface. Campbell et al., (1994) determined that the wind incursion into the open-ended tube sampler caused a decrease in diffusion length and caused 30 % over-estimation of gas phase pollutants. Since both wind speed and tube geometry are variable, the impact of wind speed on sampling efficiency is not always 30% (Varshney and Singh, 2003; Cox, 2003)

In this study direct influence of wind speed on designed samplers was minimized by placing a protective screen at the open end of the sampler and by placing passive tubes at sheltered locations. The relationship between uptake rate and wind speed in the course of the study are depicted in Figures 3.14 and 3.15 for O₃ and NO₂, respectively.

Figures demonstrate a slight increase of NO₂ uptake rate and a slight decrease in O₃ uptake rate with increasing surface wind speed. However, these trends, observed in NO₂ and O₃ uptake rates versus wind speed are not statistically significant at 90% confidence level, indicating that the effect of wind speed on passive NO₂ and O₃ measurements are negligible, as long as a screen is placed in front of the sampler and the sampler is located under a protective shelter.

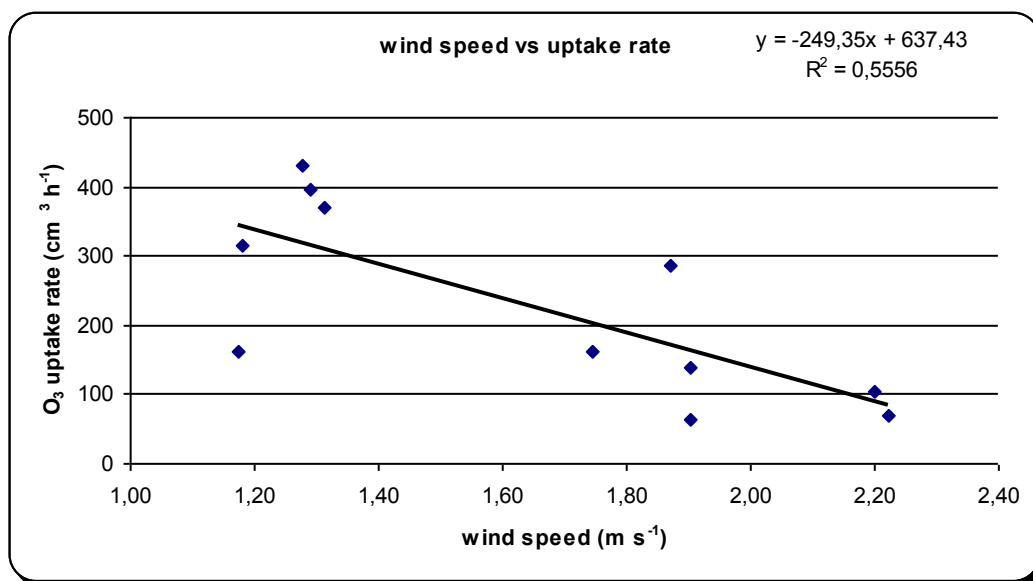


Figure 3.14. Relationship between wind speed and uptake rate of O₃ passive tube.

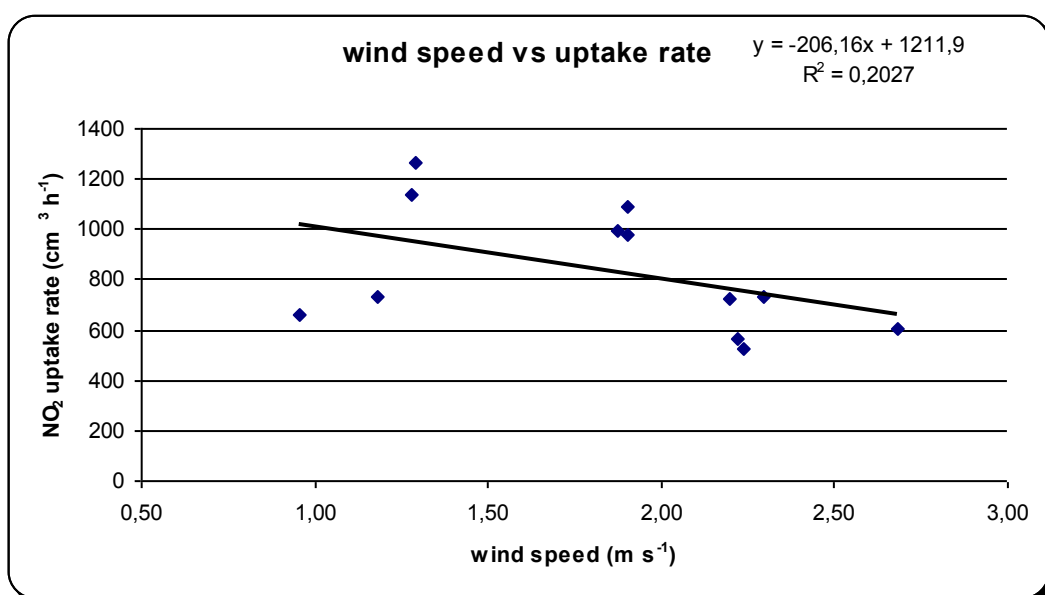


Figure 3.15. Relationship between wind speed and uptake rate of NO₂ passive tube.

3.4.2 Dependence of uptake rate on relative humidity

Another parameter that affects the uptake rate of the passive sampler is the relative humidity (Varshney and Singh, 2003; Krupa and Legge, 2000; Plaisance, 2004; Krochmal and Gorski, 1991; Cox and Brown, 1984; Krochmal and Kalina, 1997; Tang, 1999; Helaleh, 2002). In the literature the individual effect of relative humidity on passive samplers is generally neglected since it is difficult to measure exact value of it in ambient air (usually it is more than 40 %)..

The general outcome of all studies is that the effect of relative humidity on passive NO₂ sampling is not significant. For example in chamber studies it was demonstrated that the NO₂ uptake increased by only 25% when relative humidity changes dramatically from 0% to 100% (Varsney and Singh, 2003).

The O₃ uptake rate seems to be more related on the variations in relative humidity. For example the following relation was used to relate ozone uptake rate on meteorological parameters (Krupa and Legge, 2000).

$$R_s = 12.769 T^{1/2} - 0.540 RH + 0.276 WS - 135 \quad (3.2)$$

Where R_s is the sampling rate T is the temperature and WS is the wind speed. This equation demonstrates that ozone sampling rate is inversely related with the relative humidity.

The variation of uptake rate with relative humidity is depicted in Figure 3.16 for ozone and in Figure 3.17 for NO₂.

The relative humidity varied between 32% and 72% during our sampling period (January – September, 2008). Ozone uptake consistently decreased by an order of

magnitude, from 1×10^{-5} to 1×10^{-6} , in this RH range. The NO_2 uptake rate, on the other hand did not change significantly with relative humidity. The slight decrease that can be seen in Figure 3.19 is not statistically significant at 95% confidence level. These variations in NO_2 and O_3 uptake rates with relative humidity are consistent with the variations reported in literature which was briefly discussed in above paragraphs.

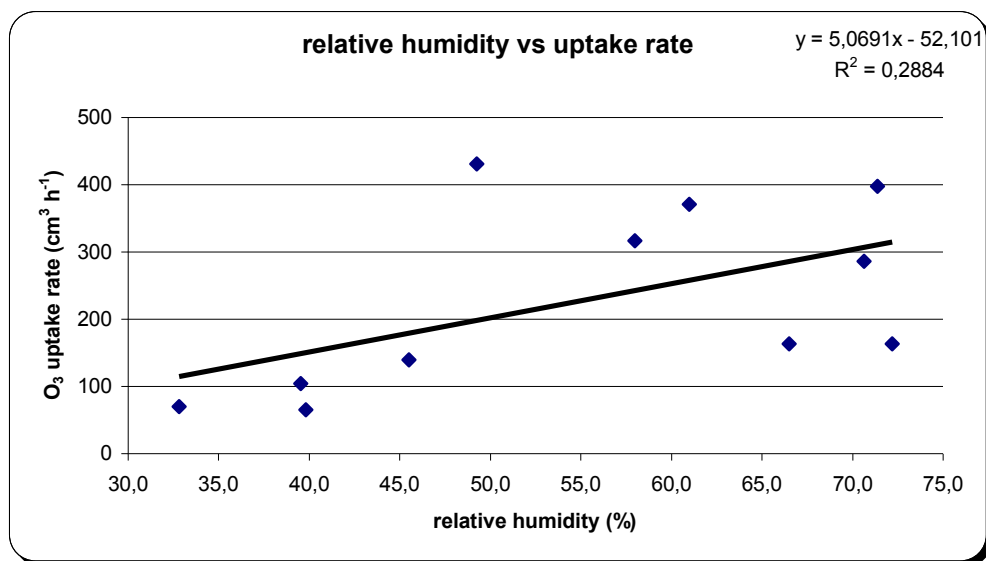


Figure 3.16. Relationship between relative humidity and uptake rate of O₃ passive tube

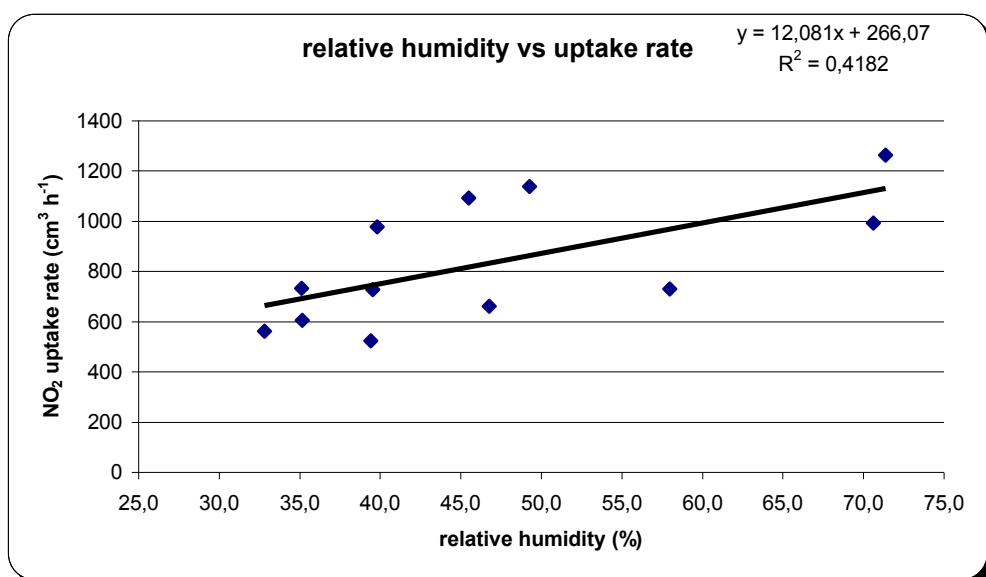


Figure 3.17. Relationship between relative humidity and uptake rate of NO₂ passive tube

3.4.3 Dependence of uptake rate on temperature

There has been several studies that investigate the effect of temperature on uptake rate (Varshney and Singh, 2003; Krupa and Legge, 2000; Plaisance et al., 2004; Krochmal and Gorski, 1991; Plaisance et al., 2007; Ray, 2001; Royset, 1998; Reeve, 2002). However, conclusions reached on the effect of temperature on pollutant uptake rates are contradictory. Some authors reported a significant change in passive sampling rates of pollutants even with small temperature changes, such as 10°C (Varneshney and Singh, 2003; Tang et al., 1999). However, other researchers reported that uptake rates of pollutants are not significantly affected by temperature (Palmer et al., 1976; Atkins et al., 1986; Hargreaves, 1989).

Temperature and relative humidity are related to each other. This relationship between relative humidity and temperature in Ankara is depicted in Figure 3.18 for sampling period (January to September, 2008). During the sampling period temperature changes from -6 to 24 °C. As indicated in the figure relative humidity showed an opposite trend. This observed trend is not surprising, because the humidity in the atmosphere is defined as the ratio of actual H₂O vapor pressure to that of saturation vapor pressure (when this ratio is multiplied with 100, the term becomes “percent relative humidity”). At high temperatures both fractional humidity and relative humidity are increased, because saturation vapor pressure of H₂O increases.

Since relative humidity and temperature are inversely related with each other, the effect of temperature on uptake rates of NO₂ and O₃ should also be the opposite of the impacts discussed for RH in the previous section.

The effect of temperature on O₃ and NO₂ tube uptake rates are shown in Figure 3.19 and 3.20, respectively. The graphs shown in these figures are indeed opposite of the trends depicted for RH in Figures 3.18 and 3.19. The increase in temperature from -2°C to 25°C results in approximately an order of magnitude increase in ozone uptake rate (the R² value given in the figure indicate a statistically significant correlation at 95 % confidence interval), but it does not cause a substantial change in NO₂ uptake rate (the R² value in the figure does not indicate a statistically significant correlation between temperature and NO₂ uptake rate).

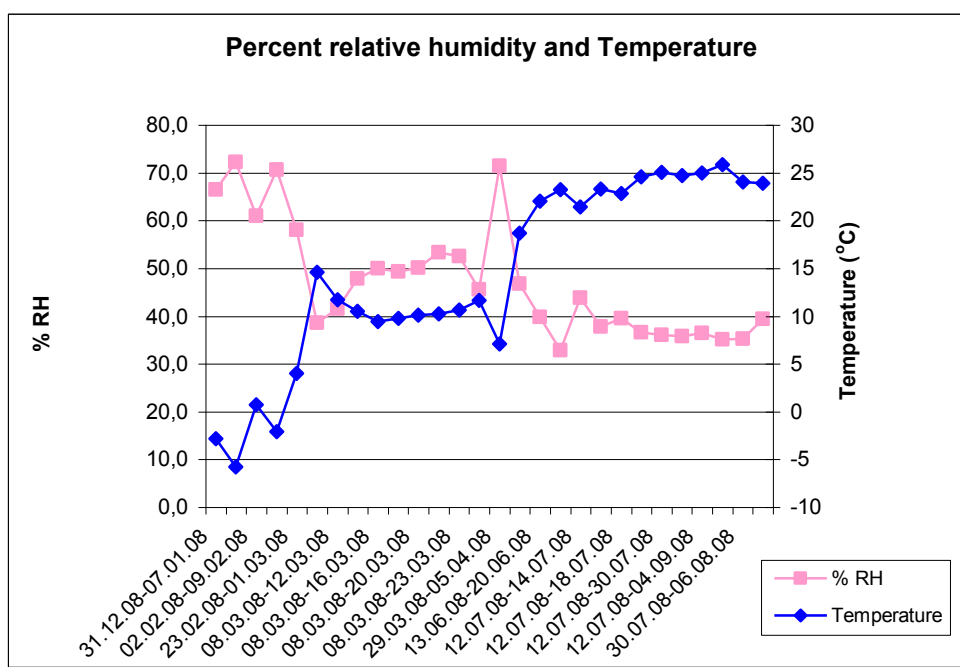


Figure 3.18. Relationship between relative humidity and temperature

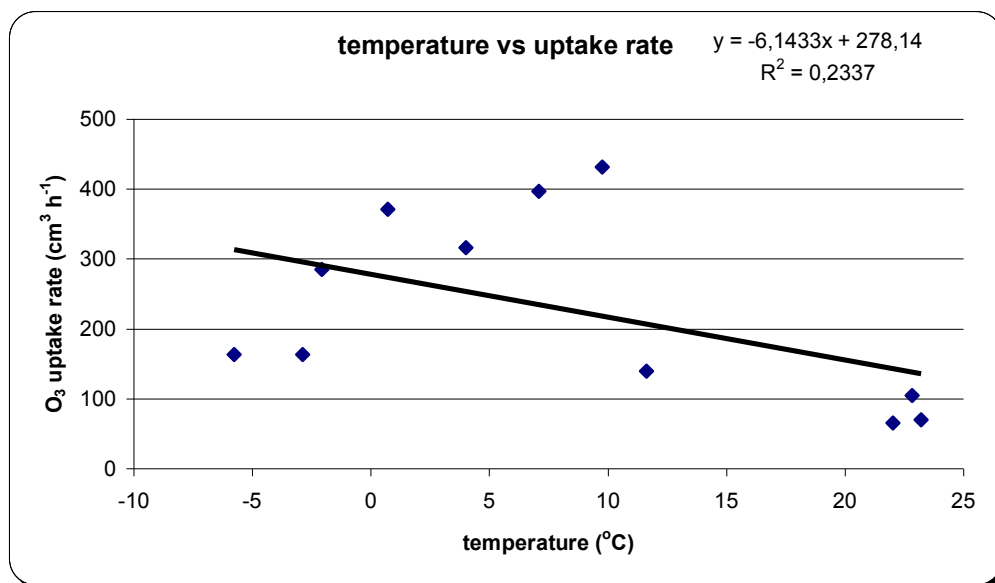


Figure 3.19. Relationship between temperature and uptake rate of O₃ passive tube

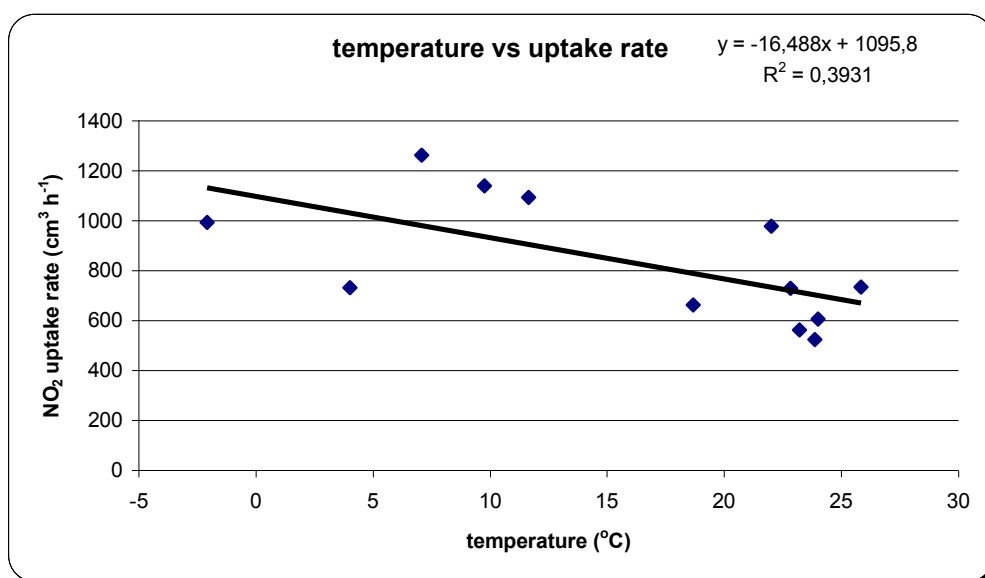


Figure 3.20. Relationship between temperature and uptake rate of NO₂ passive tube

3.4.4 Dependence of solar radiation on uptake rate

Another meteorological parameter that can potentially affect the uptake rate in passive sampling is the solar radiation. Solar radiation is known as the initiator for O₃ production (Sickless et al., 1990; Royset 1998). For that reason O₃ is called as photochemical pollutant (Harrison, 2001; Krupa et al., 2003; Bernard et al, 1999; Helaleh et al., 2002).

Concentration of NO₂ in the atmosphere also depends on solar flux, because NO₂ is formed by photochemical oxidation of NO. Consequently uptake rates of both parameters measured in this study can be affected from the solar flux at the sampling point. However, any relation between solar flux and uptake rates is not necessarily a direct one. Solar flux is expected to be strongly related with atmospheric temperature, which is another parameter that may affect uptake rate, particularly that of ozone, as discussed previously. The relation between atmospheric temperature and solar flux, during our sampling period, is depicted in Figure 3.21.

Theoretically solar flux is expected to be high in summer when temperature is high and it is expected to be low in winter when temperature is low. However, it is clear from the figure that the expected relation between solar flux and ambient temperature can be seen at temperatures higher than 15°C, but solar flux appears to be independent of temperature below 15°C. This behavior is probably due to presence of overcast conditions at intermediate temperatures. Direct relation between solar flux and temperature holds when there is no clouds. In the presence of clouds temperature can increase, but solar flux can remain low. Direct relation between solar flux and temperature greater than 15°C probably indicates that it is rare to have overcast conditions at temperatures higher than 15°C.

The relation between O_3 and NO_2 uptake rates and solar flux is depicted in Figures 3.22 and 3.23, respectively. As can be seen from Figure 3.22, there is a statistically significant correlation between solar flux and O_3 uptake rate at 95% significance interval. However, it is not clear whether the figure indicates direct dependence of O_3 uptake rate on solar flux, or it demonstrates an indirect effect of temperature. The relation between solar radiation and NO_2 uptake rate is not statistically significant at 90 % confidence level.

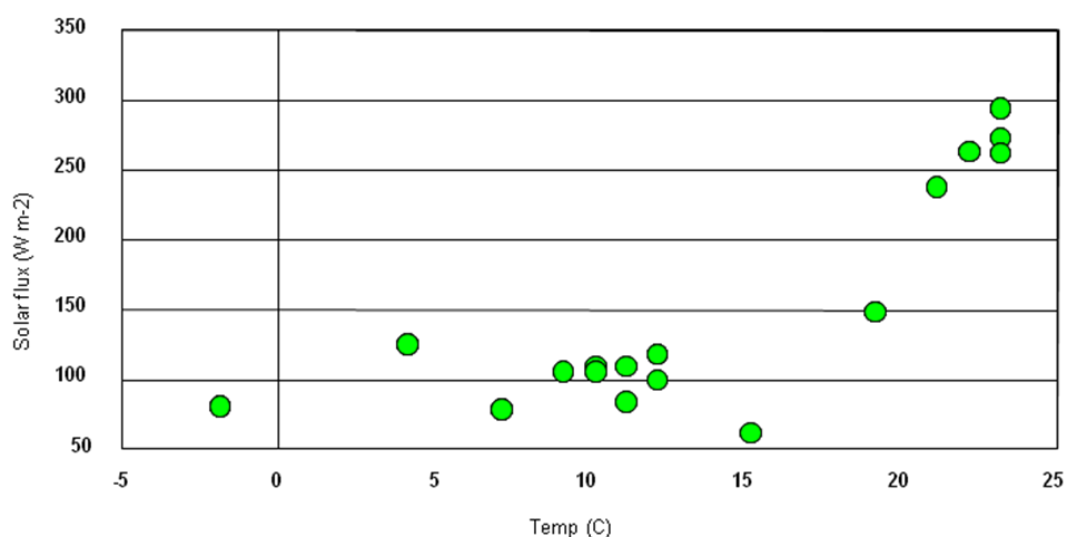


Figure 3.21. Relationship between temperature and solar flux

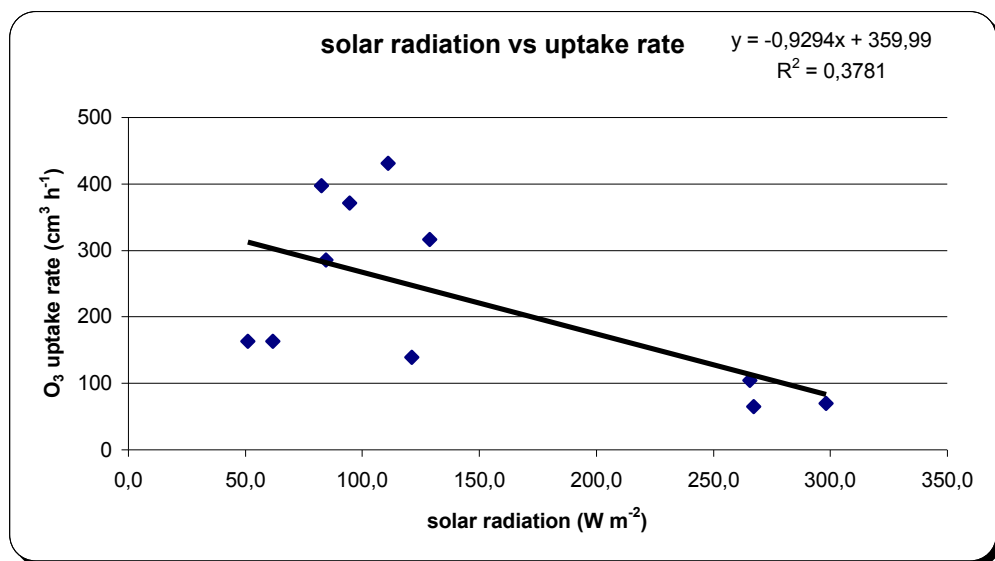


Figure 3.22. Relationship between solar radiation and uptake rate of O₃ passive tube

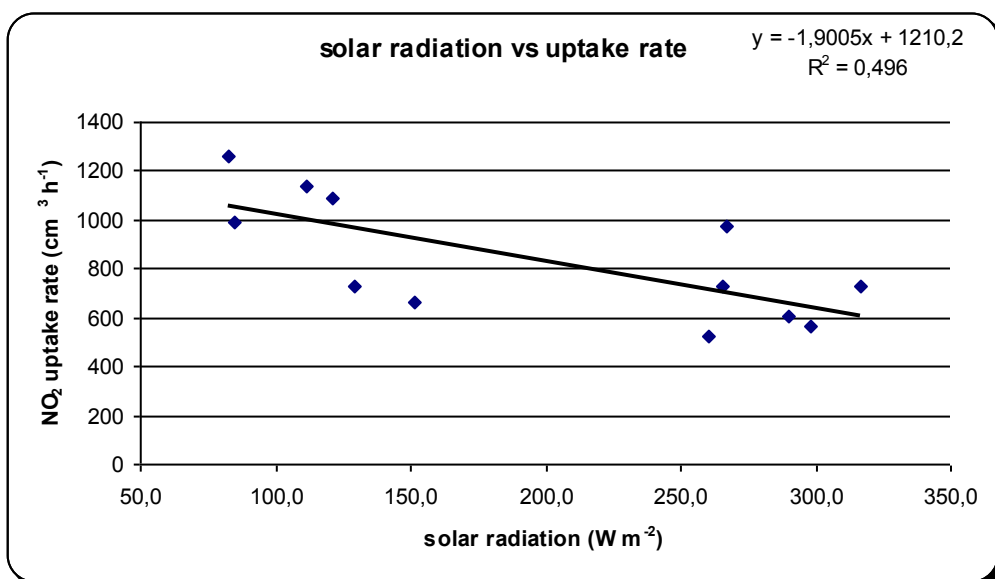


Figure 3.23. Relationship between solar radiation and uptake rate of NO₂ passive tube

Effects of wind speed, relative humidity, temperature and solar radiation flux on O₃ and NO₂ uptake rates were investigated in previous sections. Although these tests demonstrated impacts of individual parameters on uptake rates of NO₂ and O₃, impacts of individual meteorological parameters may not be identical with collective impacts of all meteorological parameters. Those collective impacts determine if the uptake rate of a given pollutant can be said to be affected from meteorological parameters.

As a last part in this section of the manuscript multiple linear regression tests were applied on the uptake-rate data set to determine if there is a statistically significant relation between NO₂ and O₃ uptake-rates and meteorological parameters in general. In fact for multiple regression analysis this data set is not suitable then some troubles might have been occurred. In these multiple regression test, dependent variables were NO₂ and O₃ uptake-rates and the independent variables were wind speed, wind direction, temperature, pressure, relative humidity and solar radiation flux. The wind direction and pressure were not included in the discussion of the relation between individual meteorological parameters and uptake-rate, in the previous sections, because their effect on NO₂ and O₃ uptake rates were believed to be insignificant. These two meteorological parameters were included in multiple regression analysis, just in case they may have a synergetic effect together with other meteorological parameters.

The following regression equation was obtained for NO₂

$$\text{NO}_2 (\text{uptake rate} \times 10^6) = 630.14 - 0.6663 P - 0.0080 \text{ rad} + 0.0851 \text{ RH} - 0.3111 T - 0.0016 \text{ WD} - 2.7648 \text{ WS} \quad (3.3)$$

Where, P is ambient pressure, rad is radiation flux, RH is relative humidity, T is temperature, WD is wind direction and WS is wind speed. Observed vs. predicted uptake-rate scatter plot based on the above equation is given in Figure 3.24.

Reasonable agreement between observed and predicted values demonstrates that, the above regression relation can explain observed variations in NO₂ uptake rate. Although the agreement between observed and predicted uptake-rates is fairly good, their statistical significance is not equally encouraging. The values of the regression coefficients in equations 3.3 are given in Table 3.6 for both NO₂ and O₃. The p values of the individual regression coefficients in above relation are all higher than 0.1 indicating that they are not statistically significant at 90% confidence level. The overall regression coefficient in both NO₂ and O₃ regression models were calculated with Analysis of Variance. ANOVA is used to test the significant differences between different group means. The ANOVA results are given in Table 3.7. The overall multiple linear regression coefficient in NO₂ model has a p value of 0.1721. This suggests that there is no statistically significant relation between NO₂ uptake-rate and meteorological parameters.

The multiple linear regression models for O₃ uptake-rate is given as:

$$\begin{aligned} \text{O}_3 \text{ (uptake rate} \times 10^6) = & -499.307 + 0.1862 \text{ WS} - 0.0272 \text{ WD} + 0.6821 \text{ T} \\ & + 0.0223 \text{ RH} - 0.0621 \text{ rad} + 0.5552 \text{ P} \end{aligned} \quad (3.4)$$

Where the terms used in the model are identical with the ones used in NO₂ model. Observed vs. predicted uptake-rate scatter plot based on the equation 3.4 is given in Figure 3.25. The ANOVA table demonstrate that, like in the case of NO₂, the overall p value of the model is 0.1083, indicating that the relation between O₃ uptake rate and meteorological parameters are not statistically significant at 90% confidence level and statistical significance of individual regression coefficients given in Table 3.6.

In simple regression analysis the effects of each meteorological parameter were investigated. Although direct or inversely proportionality obtained between each parameter and the uptake rates of each tube, the total effect of all meteorological

factors can be neglected according to the multi regression analysis because all parameters have p-value greater than 0.1 which implies that there is not statistically significant relation between uptake rates of pollutants and the meteorological parameters.

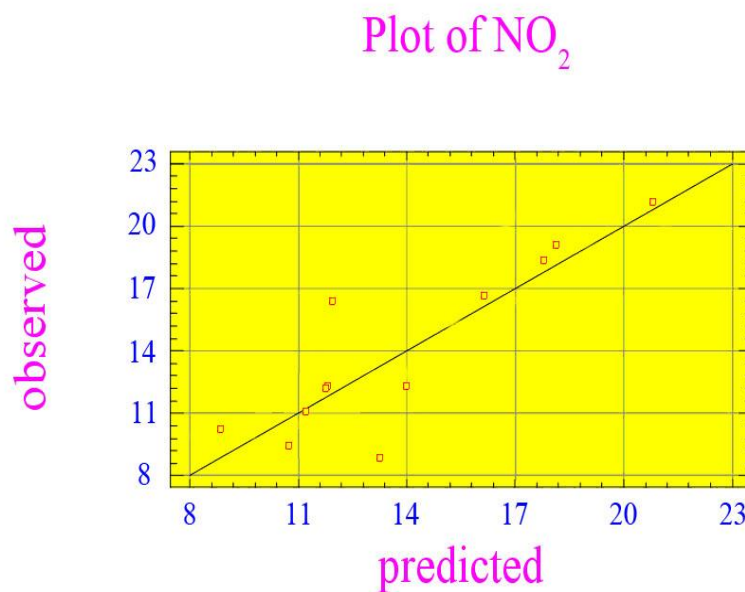


Figure 3.24. Model for observed and predicted value for NO₂ multiple regression analysis. Dependent variable: NO₂ (uptake rate x 10⁶), independent variable: meteorological parameters

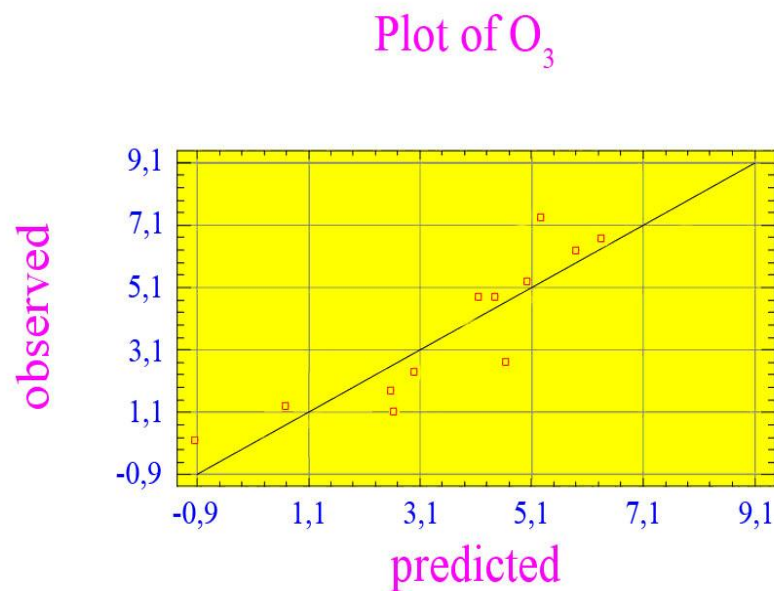


Figure 3.25. Model for observed and predicted value for O₃ multiple regression analysis. Dependent variable: O₃ (uptake rate x 10⁶), independent variable: meteorological parameters

Table 3.6. Multiple Regression Analysis for NO₂ and O₃

Dependent variables	Parameters	Standard error	p-value
NO ₂ (uptake rate x 10 ⁶)	Pressure	0.364	0.1267
	Temperature	0.316	0.5727
	Wind speed	0.516	0.5835
	Wind direction	0.042	0.9708
	Solar radiation	0.045	0.8644
	Relative humidity	4.720	0.6814
O ₃ (uptake rate x 10 ⁶)	Pressure	0.357	0.1809
	Temperature	0.446	0.1866
	Wind speed	2.540	0.9444
	Wind direction	0.036	0.4841
	Solar radiation	0.037	0.1546
	Relative humidity	0.112	0.8492

Table 3.7. Analysis of Variance for NO₂ and O₃ uptake rates (x10⁶)

NO ₂					O ₃				
Source	Sum of Squares	Mean Square	p-value	R ²	Source	Sum of Squares	Mean Square	p-value	R ²
Model	139.425	23.238	0.172	74.613	Model	50.616	8.436	0.108	79.599
Residual	4.439	9.488	-	-	Residual	12.972	2.594	-	-

3.5 Distribution of NO₂, and O₃ in Ankara atmosphere

3.5.1 Temporal distribution of O₃ and NO₂ in Ankara atmosphere

In order to determine the temporal distribution of O₃ and NO₂ in Ankara atmosphere weekly sampling was applied both in winter and summer. As shown in Table 3.8 and 3.9 concentrations of O₃ and NO₂ with median, geometric mean, minimum and maximum values, respectively, in a given sampling period were given. For each tube the given concentration results were calculated by using Fick's diffusion expression. High standard deviation is not a surprise. In O₃ sampling only in three periods shown with asterisk high standard deviation was observed, however, in NO₂ sampling deviation was seen as small.

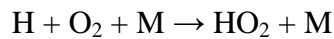
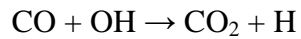
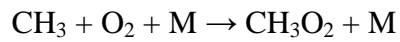
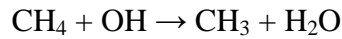
Figure 3.26 and 3.27 show the passive sampling results of O₃ and NO₂ in Box-and-Whisker plot. A box-and-whisker plot is a good device for showing various features of a sample of data. The rectangular part of the plot extends from the lower quartile to the upper quartile, covering the center half of the sample. The center line within the box shows the location of the sample median. The plus sign indicates the location of the sample mean. The whiskers extend from the box to the minimum and maximum values in the sample, except for any outside or far outside points, which will be plotted separately. Outside points are points which lie more than 1.5 times the interquartile range above or below the box and are shown as small squares. Far outside points are points which lie more than 3.0 times the interquartile range above or below the box and are shown as small squares with plus signs through them. In this case, there are no outside points and no far outside points.

The concentration of the pollutant is determined by mixing height. In winter mixing height becomes low which results in high pollutant concentration. On the

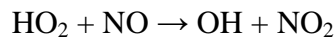
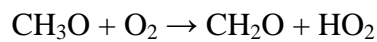
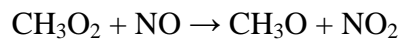
other hand in summer the mixing height ratio becomes high which causes the dilution of the pollutants although there was no change in the concentration of O₃ both in winter and summer sampling as seen in the Figure 3.26. The main reason can be the photochemical processes of O₃ in summer. If O₃ is considered as the main source and the product of the photochemical reactions then dilution of pollution was diminished by photochemical processes. For that reason the concentration of O₃ was seen as same as it was in winter.

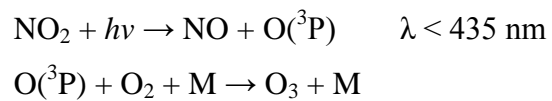
During summer in rural and remote areas the presence of NO_x and hydrocarbons contribute the formation of O₃ that leads to local photochemical pollution (Helalah et al., 2002; Kelly et al., 1984). Moreover, in the previous studies done by the Environmental Research Group in Environmental Engineering Department of METU, an increase in O₃ concentration in summer was also observed (Project No: 104Y276, March 2008).

However, in this study increase in the concentration of O₃ was not observed in summer sampling. The main reason can be the sampling area. In literature the rise in O₃ concentration was mostly seen in rural areas while our sampling points were in the center of Ankara. In addition to photochemical formation of O₃ from HC and other pollutants, one more reaction between O₃ and NO should be considered (Harrison, 2001).

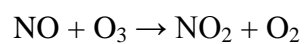


In the presence of NO;





Although NO is one of the constituents responsible in the formation of O₃, it also contributes to the removal mechanism of O₃.



This reaction is also photochemical then the rate of the reaction increases with the light intensity that means NO₂ concentration increases and O₃ concentration decreases in summer.

Table 3.8. Weekly O₃ concentrations in Ankara atmosphere

Date	O ₃ concentration in air (µg m ⁻³)					
	# of tubes	Average	Median	Geometric mean	Min.	Max.
31.12.08-07.01.08	7	3 ± 1	3	3	2	5
11.01.08-18.01.08*	7	19 ± 12	14	16	5	37
02.02.08-09.02.08*	5	13 ± 15	7	9	3	41
16.02.08-23.02.08	5	16 ± 7	15	14	5	23
23.02.08-01.03.08	7	12 ± 0	12	12	12	12
08.03.08-16.03.08*	3	21 ± 12	20	18	9	34
23.03.08-30.03.08	6	11 ± 3	10	11	8	16
29.03.08-05.04.08	7	17 ± 7	15	16	12	29
11.04.08-19.04.08	4	18 ± 4	19	17	12	21
13.06.08-20.06.08	3	12 ± 5	9	11	8	18
03.07.08-11.03.08	4	16 ± 3	16	16	12	19
12.07.08-18.07.08	3	22 ± 2	21	22	20	25
23.07.08-30.07.08	3	3 ± 1	4	3	2	4

Table 3.9. Weekly NO₂ concentrations in Ankara atmosphere

Date	NO ₂ concentration in air (µg m ⁻³)					
	# of tubes	Average	Median	Geometric mean	Min.	Max.
31.12.08-07.01.08	9	146 ± 43	159	140	78	206
11.01.08-18.01.08	7	577± 40	589	575	504	617
02.02.08-09.02.08	6	901 ± 56	905	899	831	970
16.02.08-23.02.08	7	790 ± 77	807	786	672	896
23.02.08-01.03.08	7	722 ± 44	733	721	675	805
08.03.08-16.03.08	3	724 ± 176	726	709	547	899
23.03.08-30.03.08	7	594 ± 52	565	592	551	681
29.03.08-05.04.08	7	859 ± 113	852	853	717	1031
11.04.08-19.04.08	5	743 ± 37	743	742	702	797
13.06.08-20.06.08	5	367± 109	346	354	239	514
03.07.08-11.03.08	5	139 ± 30	141	136	100	183
12.07.08-18.07.08	3	305 ± 28	311	304	275	330
23.07.08-30.07.08	4	397 ± 34	405	395	348	428
30.07.08-06.08.08	5	293 ± 47	302	290	217	344
07.08.08-14.08.08	5	450 ± 49	440	448	409	535

Due to the complexity of O₃ formation and removal mechanism, the exact amount and the source of O₃ could not be determined in this limited study. However, we can conclude the change in O₃ level depends on the seasonal variation.

Unlike O₃, NO₂ concentration showed a difference between winter and summer sampling. Although O₃ degradation is high in summer which resulted with the formation of NO₂, concentration of NO₂ in summer was obtained lower than in winter. Winter concentration of NO₂ was 400-900 µg m⁻³ due to low mixing height and summer concentration of NO₂ was 150-400 µg m⁻³ because of high mixing height. Then we can say that the photochemical production of NO₂ can be ignored in summer because dilution of it due the low mixing height is generally more predominant.

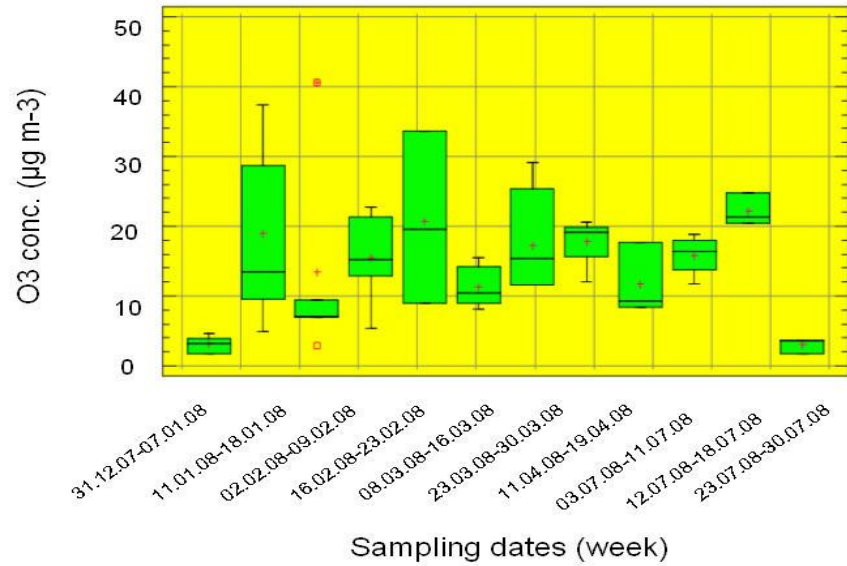


Figure 3.26. Passive O₃ concentration results in Box-and-Whisker plot

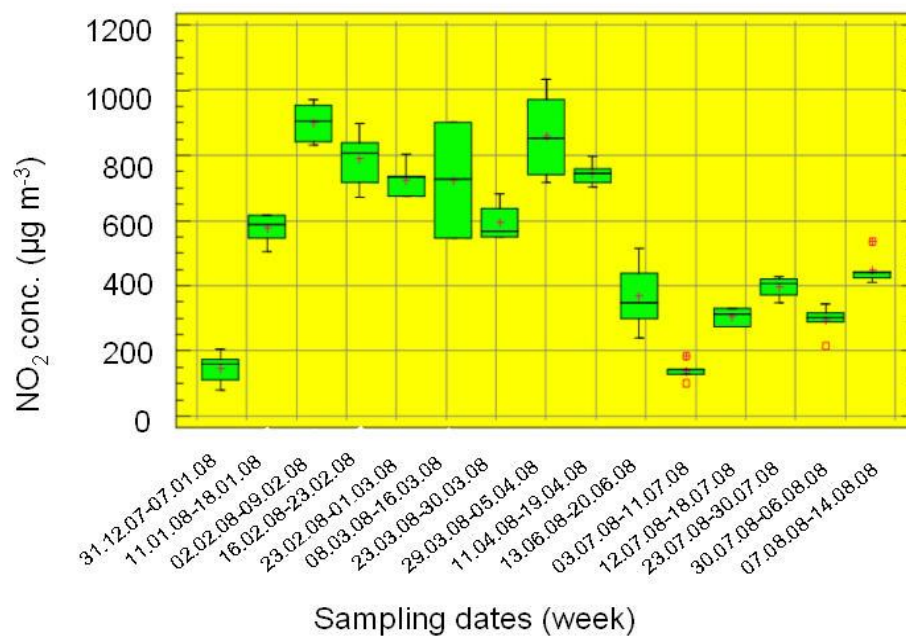


Figure 3.27. Passive NO₂ concentration results in Box-and-Whisker plot

3.5.2 Spatial distribution of O₃ and NO₂ in Ankara atmosphere

Using passive samplers is ideal to study the spatial distribution of pollutant concentrations. Active measurement systems are too expensive for simultaneous deployment in many locations whereas, passive samplers are cheap enough for that particular purpose.

A study on spatial distribution of pollutants can be performed at two separate levels. Such a study can be performed with few passive samplers to get general information on how certain pollutants are distributed in the study area, or the same passive sampling campaign can be performed with many samplers. In such a case information obtained will have high resolution. Furthermore, pollution maps can be prepared using interpolation or extrapolation techniques.

However, passive samplers are not being used widely together with the interpolation techniques. Probably it will be used more extensively in the future, because interpolation when coupled with dense passive measurement can provide concentration data at every point in the study area. Then this information can be fed to health risk models to understand the health effects due to air pollution.

Obviously this would be very valuable data provided that the concentrations obtained by interpolation are accurate. The accuracy of interpolation or extrapolation results depends on the density of measurements. This means that results would not be accurate if interpolation is based on few measurements. This point is where passive sampling comes in. Since passive measurements are relatively inexpensive, data can be obtained from large number of points to generate reliable data for health effect modeling, or for the calibration of numerical models.

In this study a passive sampling was conducted in Ankara to demonstrate the importance of passive measurements at large number of points. Since the objective was not to evaluate current status of air pollution in Ankara, passive sampling was performed only once and not repeated in different seasons.

For this exercise passive samplers were located at 40 different points in the city. The main roads were accepted as boundary and 40 points with approximately equal distance from each other were selected. The points were labeled as shown Figure 2.1.

Placement of passive samplers through the whole city took 2 days. Passive tubes were brought to the sites in a plastic bags stored in refrigerator until sampling at 4 °C. Samplers were placed on trees or masts, 1.5-2 m from the ground and at least 1 m far away from the buildings in protective shelters. After 6 days the tubes were collected and the open ends were closed with their own stoppers and transferred to the laboratory in plastic bags.

The concentration distributions of the pollutants were exhibited on Ankara city map as in Figure 3.30 by using Mapinfo programme.

3.5.2.1 Distribution of NO₂ in Ankara and its relation to sources

Weekly average NO₂ concentrations measured in Ankara atmosphere are given in Table 3.11. As seen in the table concentration of NO₂ in Ankara is very high compared to Hava Kalitesi Değerlendirme ve Yönetimi Yönetmeliği, (2008). In the report short term exposure (hourly) limit value of NO₂ was given as 200 µg m⁻³ and tolerant limit was given as 100 µg m⁻³ whereas, in this study weekly average NO₂ was found as approximately 300 µg m⁻³.

In Table 3.10 monthly NO₂ concentrations in Etlik and Kavaklıdere crossroads in 1999 is given. For Etlik average concentration was 34 µg m⁻³ and in Kavaklıdere it was measured as 45 µg m⁻³. The smooth increase in concentration attracts attention. In 2008 this value reached to 176 µg m⁻³ and as a result NO₂ concentration shows sharp increase in 10 years. This could be the cause of being the main product of traffic emission.

Table 3.10. Average monthly NO₂ concentrations (µg m⁻³) in Etlik and Kavaklıdere in 1999

	Etlik	Kavaklıdere
January	29	40
February	30	41
March	31	42
April	32	43
May	33	44
June	34	45
July	35	46
August	36	47
October	37	48
November	38	49
December	39	50

Before starting to create pollution map of Ankara we should be sure about the reliability of our passive samplers. As mentioned previously during weekly sampling passive tubes were placed nearby the active air sampling systems and the concentrations of each system was compared as indicated in Figure 3.28. According to this graph concentrations of NO₂ obtained by passive tubes

(calculated by Fick's law) are nearly two times higher than that of the active ones. This situation implies the importance of determination of uptake rate for NO₂ passive tubes. Then the NO₂ concentration results of Ankara sampling were calculated by using uptake rate.

Theoretical calculation of NO₂ concentrations (by using Fick's law) and experimental determinations are listed in Table 3.11 with respect to the points and they are compared in Figure 3.29. As mentioned in previous sections NO₂ concentration results obtained by using Fick's law is two times higher than the results calculated by using the determined uptake rate of the tubes.

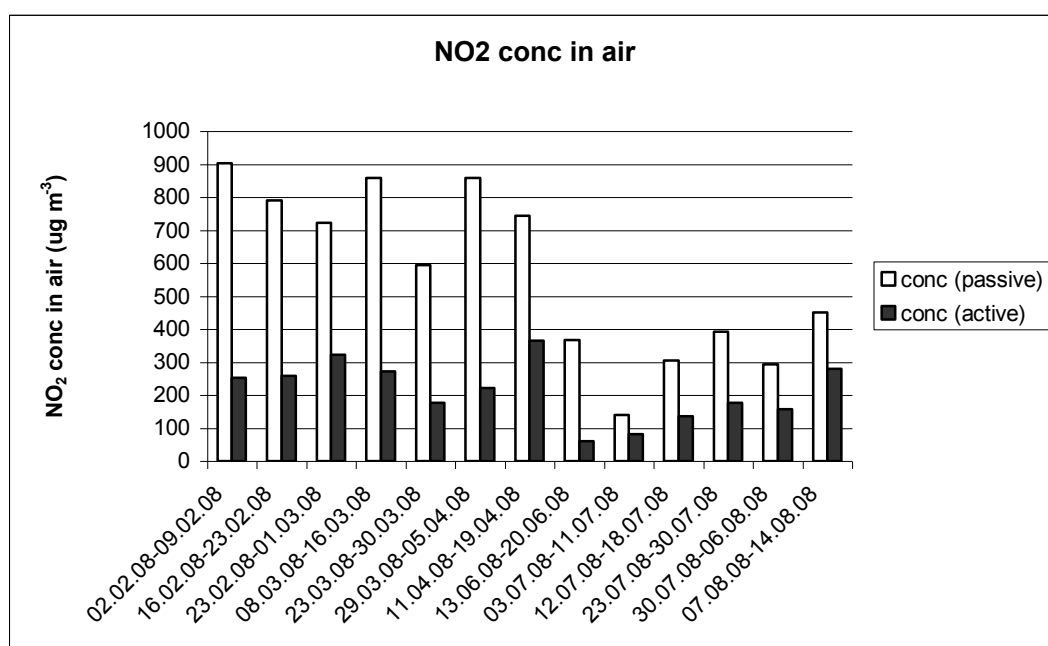


Figure 3.28. Comparison NO₂ concentrations by calculating Fick's law and by using uptake rate expression.

Table 3.11. NO₂ concentration in air in Ankara sampling (September 20, 2008 – September 26, 2008)

Sampling points	Coordinates		NO2 conc. ($\mu\text{g m}^{-3}$) theoretical	NO2 conc. ($\mu\text{g m}^{-3}$) experimental
	East	North		
ODTÜ	32° 46.90'	39°53.75'	664	234
Bilkent	32° 45.32'	39°52.52'	460	162
Angora evleri	32° 42.98'	39°52.38'	199	70
Arcadium	32° 44.25'	39°53.13'	255	90
Başkent	32° 39.42'	39°53.00'	293	103
Etimesgut	32° 40.98'	39°56.63'	537	189
Etimesgut	32° 39.96'	39°57.80'	555	195
Göksu Parkı	32° 39.20'	39°59.46'	388	137
Etimesgut	32° 42.34'	39°56.88'	370	130
Batıkent	32° 44.23'	39°56.98'	464	163
Batıkent	32° 43.53'	39°57.80'	578	204
Ostim	32° 44.59'	39°58.52'	409	144
Gimat	32° 46.27'	39°57.49'	599	211
Demetevler	32° 46.64'	39°58.20'	447	157
İvedik	32° 46.61'	39°59.63'	372	131
İvedik	32° 46.33'	40°00.42'	354	125
Ergenekon Mah.	32° 48.52'	39°58.26'	774	272
Esertepe	32° 50.50'	39°59.91'	564	199
Altınpark	32° 52.98'	39°58.44'	604	213
Siteler	32° 54.32'	39°57.67'	567	200
Cebeci	32° 53.35'	39°56.17'	608	214
AOÇ	32° 47.77'	39°56.38'	417	147
K.esat	32° 47.70'	39°56.30'	645	227
Emek	32° 49.22'	39°55.90'	614	216
Maltepe	32° 47.77'	39°56.38'	525	185
Gazi mah.	32° 47.77'	39°56.38'	579	204
Ulus	32° 47.77'	39°56.38'	671	236
Keçiören	32° 51.81'	39°58.12'	507	178
Keçiören	32° 51.81'	39°55.13'	397	140
Yeşilöz	32° 51.29'	40°00.13'	619	218
Nato yolu	32° 51.29'	40°00.13'	567	199
A. imrahor	32° 54.75'	39°54.86'	456	161
Birlik	32° 53.06'	39°53.00'	457	161
Oran	32° 53.06'	39°53.00'	382	135
Keklikpınarı	32° 53.06'	39°53.00'	438	154
Dikmen	32° 50.70'	39°53.81'	569	200
Öveçler	32° 49.43'	39°53.35'	496	175
Balgat	32° 49.08'	39°54.58'	737	260
100. yıl	32° 48.04'	39°53.64'	347	122

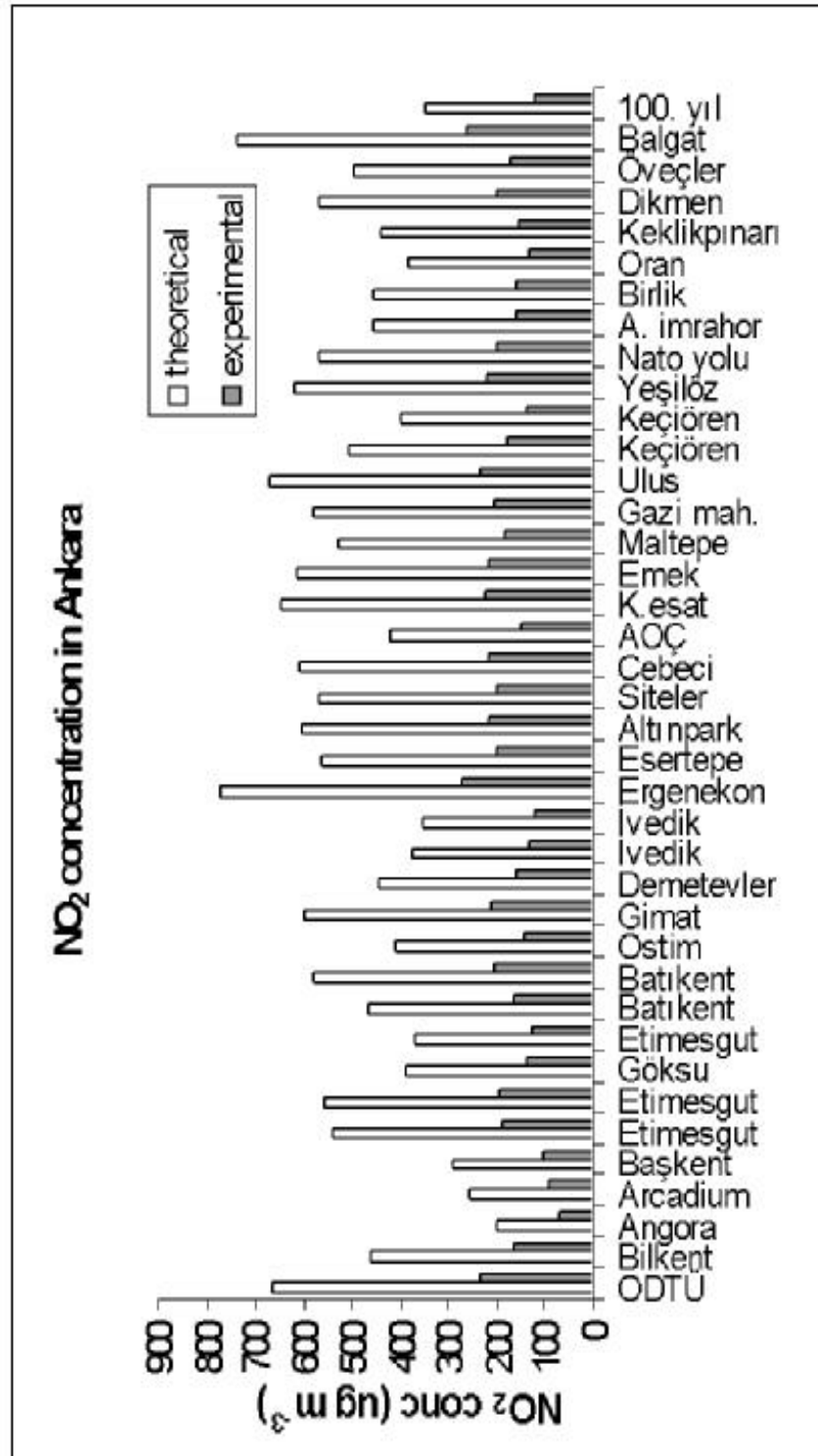
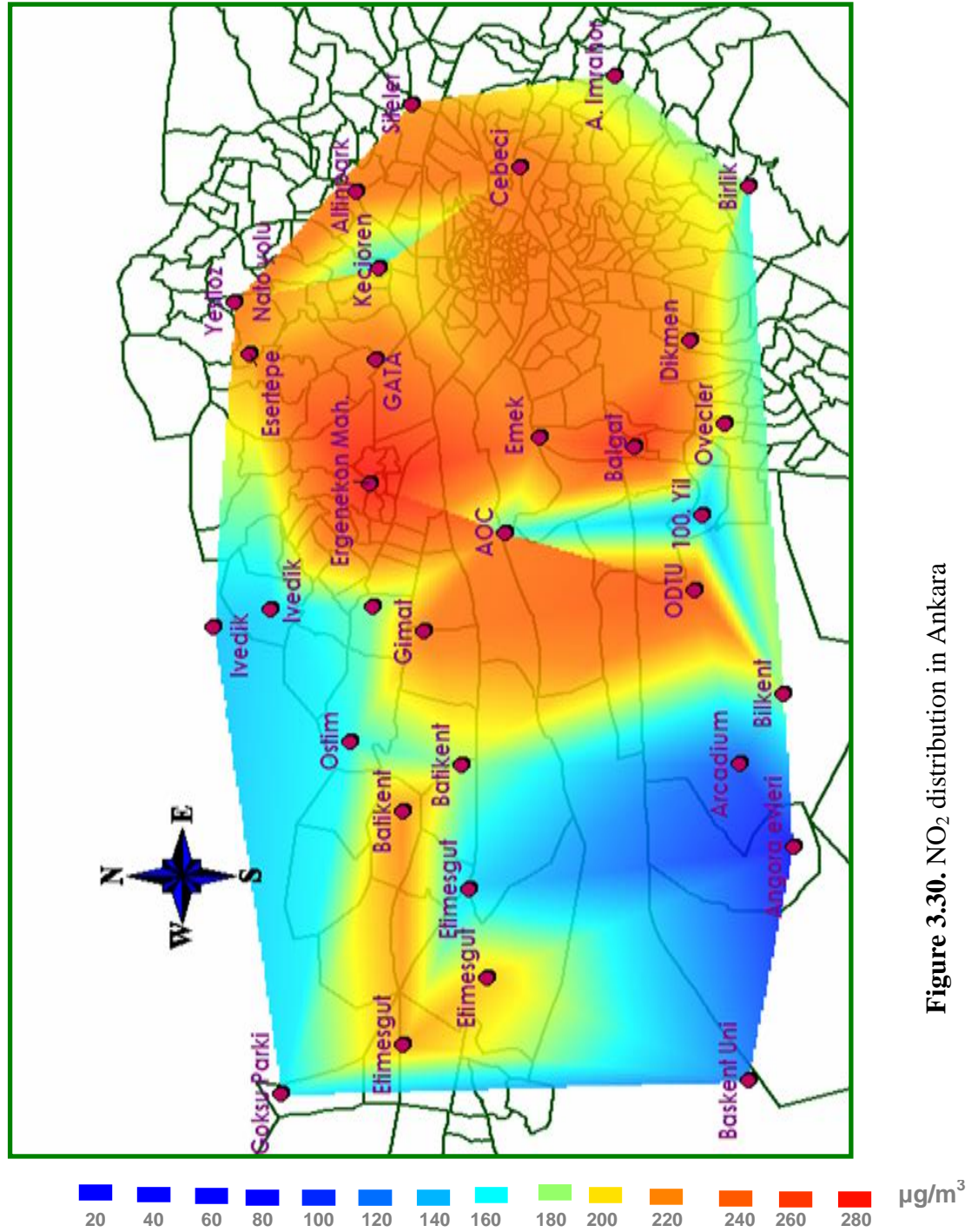


Figure 3.29. Theoretical (Fick's law) and experimental distribution of NO₂ in Ankara

Ankara is a polluted city with respect to the pollutants emitted from traffic. If the theoretical calculation of NO₂ concentration was considered, unreliable and worse situation than the real would be obtained. Most of the associations could not obtain uptake rates of the passive tubes by using active systems as a reference.

Then they apply to Fick's law to calculate the pollutant concentrations. However, the difference between experimental and theoretical values should be considered.

NO₂ concentration distribution in Ankara is given in Figure 3.30. Another important point to constitute a pollution map is the location and the closeness of the sampling stations. As seen in the map high concentration of NO₂ was obtained in the center of the city. Due to the dense traffic in center of the city, the NO₂ concentration is found high in wide area and then, the importance of distribution and the quantity of the stations can be ignored. However, if there are more stations located in strategic points the difference in the center of the city may be observed.



In suburban areas aside from Konya-Samsun freeway dependence of concentration on sampling stations was also observed. Here, there are different characteristics points like, main roads with dense traffic and residential areas far away from these roads. Moreover, from Etimesgut through the İstanbul arterial roads and the center of the city, high concentration of NO₂ was measured that is probably due to high traffic emissions. On the other hand this situation was not observed in Eskişehir main road which is also as busy as İstanbul main road. The reason of this difference may be the location of the sampling stations. On the İstanbul arterial road there are several stations and the interpolation among these stations exhibit high NO₂ concentrations through the west of the city. However, near Eskişehir road there are a few stations as Angora Houses, rural areas nearby Etimesgut and Arcadium. Since the concentrations in these points were low, Eskişehir main road between these stations was seen as clean area.

All these discussions above exhibits the importance of quantity and the selection of the sampling stations during passive sampling.

3.5.2.2 Distribution of O₃ in Ankara and its relation to generation

Short term exposure limit of photochemical O₃ concentration was reported as maximum 240 µg m⁻³ (Hava Kalitesi Değerlendirme ve Yönetimi Yönetmeliği, 2008). In this study weekly average O₃ concentrations found as 15 µg m⁻³ (Table 3.9). This low value of O₃ concentration shows that photochemical pollution caused by O₃ can be negligible in Ankara atmosphere. However, as mentioned in previous section, the reliability of passive tubes should be determined. The active and passive sampling results were compared as in Figure 3.31.

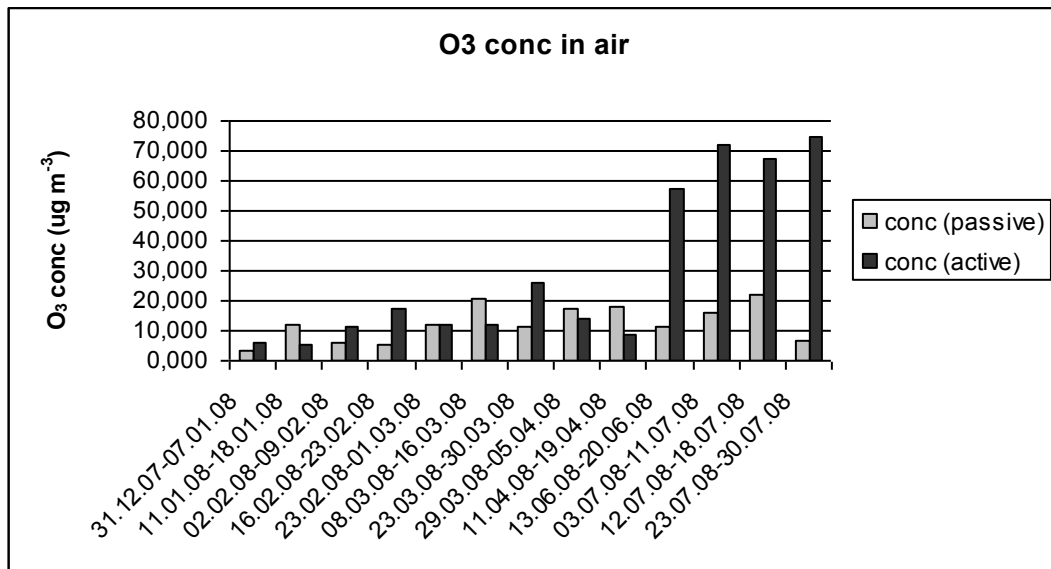


Figure 3.31. Comparison of active and passive O₃ concentrations

As shown in figure except the last four sampling, O₃ concentrations calculated by Fick's law (passive) were nearly same as concentrations obtained by active sampling. Then, we can conclude that during measurement of O₃ concentration in ambient air, uptake rate determination is not as significant as in NO₂

concentrations calculation. In Ankara sampling both theoretical and experimental concentration results of O_3 were given in listed in Table 3.12 and shown as graph in Figure 3.32. However, it should not be neglected that, the obtained data from passive sampling may not be the exact value. In passive tubes O_3 can be decomposed on the surface of the adsorbent due to photochemical reactions and this can make the analysis difficult.

In general O_3 concentration was low all the parts of the city but if it is investigated in detail at the center of the city has lower concentration than the other points (Figure 3.33). Decomposition of O_3 in photochemical reaction by reacting with NO can explain this situation. Then higher O_3 concentrations (approximately 20-30 $\mu\text{g m}^{-3}$) were obtained in the stations that are far away from the center like rural areas in Etimesgut. Then it can be concluded O_3 concentration may be high at outside of the city that has less dense traffic.

Table 3.12. O₃ concentration in air in Ankara sampling (September 20, 2008 – September 26, 2008) (BDL = Below Detection Limit)

Sampling points	Coordinates		O ₃ conc (µg m ⁻³) theoretical	O ₃ conc. (µg m ⁻³) experimental
	East	North		
ODTÜ	32° 46.90'	39°53.75'	4	4
Bilkent	32° 45.32'	39°52.52'	11	10
Angora evleri	32° 42.98'	39°52.38'	14	13
Arcadium	32° 44.25'	39°53.13'	4	3
Başkent Üniversitesi	32° 39.42'	39°53.00'	5	5
Etimesgut	32° 40.98'	39°56.63'	4	3
Etimesgut	32° 39.96'	39°57.80'	4	3
Göksu Parkı	32° 39.20'	39°59.46'	5	5
Etimesgut	32° 42.34'	39°56.88'	20	18
Batıkent	32° 44.23'	39°56.98'	2	2
Batıkent	32° 43.53'	39°57.80'	BDL	BDL
Ostim	32° 44.59'	39°58.52'	16	14
Gimat	32° 46.27'	39°57.49'	4	4
Demetevler	32° 46.64'	39°58.20'	4	4
İvedik	32° 46.61'	39°59.63'	BDL	BDL
İvedik	32° 46.33'	40°00.42'	16	14
Ergenekon Mah.	32° 48.52'	39°58.26'	18	16
GATA	32° 50.41'	39°58.17'	BDL	BDL
Altınpark	32° 52.98'	39°58.44'	40	35
Siteler	32° 54.32'	39°57.67'	16	15
Cebeci	32° 53.35'	39°56.17'	3	2
AOÇ	32° 47.77'	39°56.38'	16	15
K.esat	32° 47.70'	39°56.30'	1	1
Emek	32° 49.22'	39°55.90'	10	9
Maltepe	32° 47.77'	39°56.38'	BDL	BDL
Gazi mah.	32° 47.77'	39°56.38'	7	6
Ulus	32° 47.77'	39°56.38'	BDL	BDL
Keçiören	32° 51.81'	39°58.12'	15	13
Keçiören	32° 51.81'	39°55.13'	BDL	BDL
Yeşilöz	32° 51.29'	40°00.13'	20	18
Nato yolu	32° 51.29'	40°00.13'	12	11
A. imrahor	32° 54.75'	39°54.86'	13	12
Birlik	32° 53.06'	39°53.00'	3	3
Oran	32° 53.06'	39°53.00'	20	18
Keklikpınarı	32° 53.06'	39°53.00'	6	5
Dikmen	32° 50.70'	39°53.81'	BDL	BDL
Öveçler	32° 49.43'	39°53.35'	11	10
Balgat	32° 49.08'	39°54.58'	13	12
100. yıl	32° 48.04'	39°53.64'	11	10

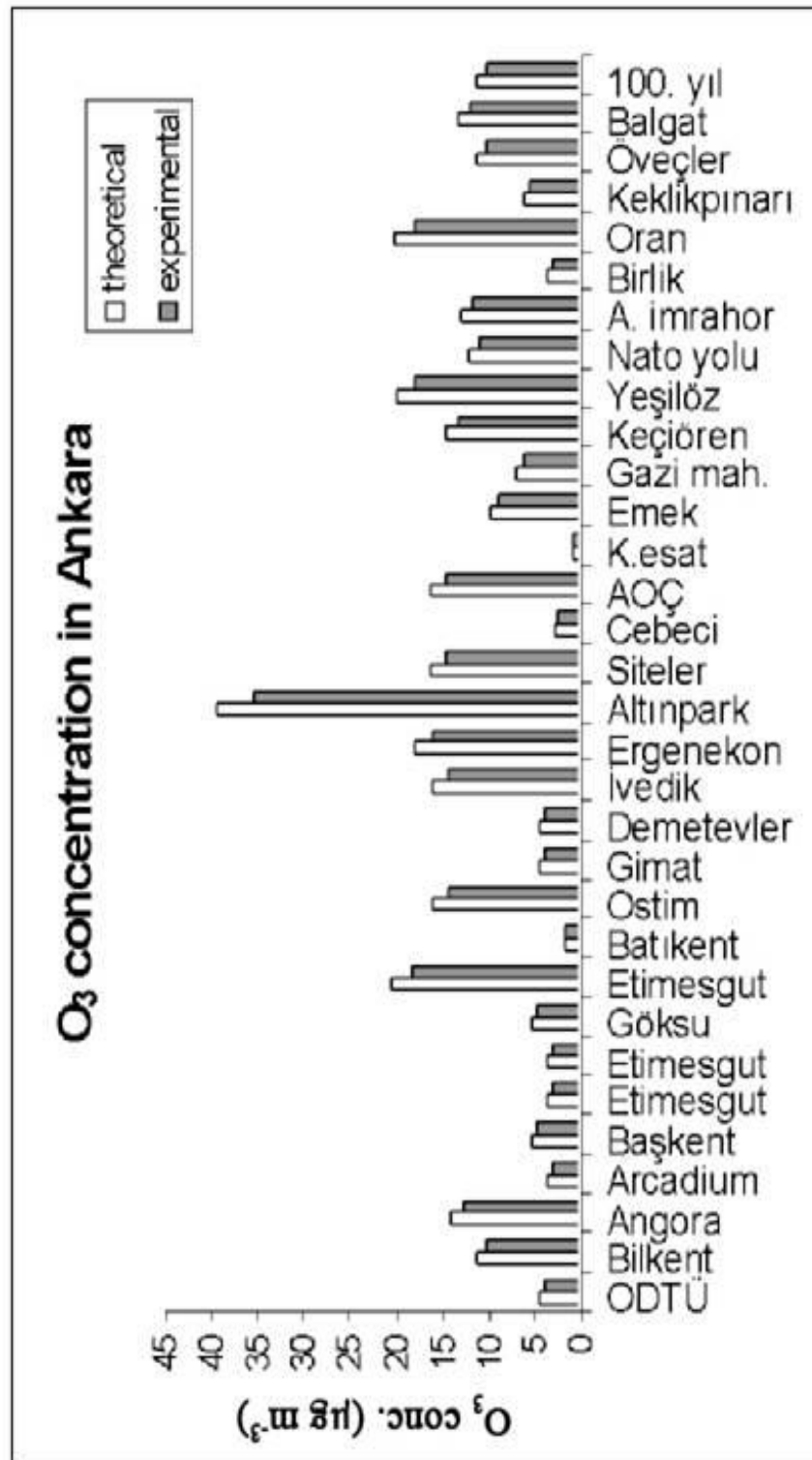


Figure 3.32. Theoretical (Fick's law) and experimental distribution of O₃ in Ankara

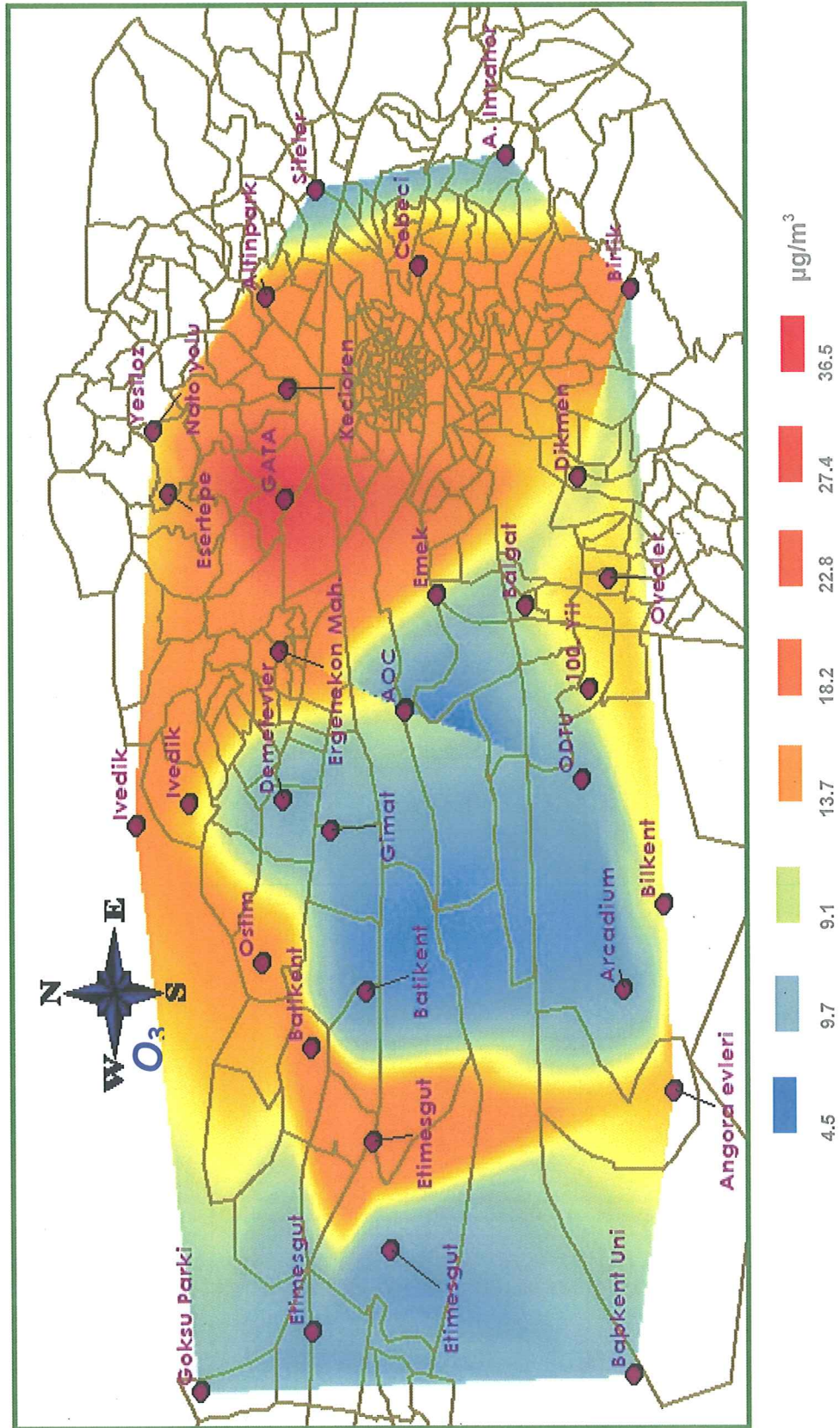


Figure 3.33. O₃ distribution in Ankara

CHAPTER 4

CONCLUSION

In this study, NO₂ and O₃ were sampled by passive samplers that were designed at Chemistry Department of METU. The optimum sampling time was determined for each tube. For this purpose in winter and in summer two sampling periods were applied for 15 and 65 days, respectively. The optimum exposure period was determined as 7 days for each tube.

Then, the uptake rates were determined by using the active sampling values near the passive tubes. These values for NO₂ and O₃ were $0.91 \times 10^3 \text{ cm}^3 \text{ h}^{-1}$ and $1.71 \times 10^3 \text{ cm}^3 \text{ h}^{-1}$, respectively. These values were then discussed with the uptake values determined from Fick's law which is based on diffusion of air. Both experimental and theoretical uptake rate values were similar in O₃ tubes. However, this situation was not observed in NO₂ tubes. Theoretical values were nearly three times higher than the experimental ones.

After the determination of uptake rate, effect on meteorological parameters on uptake rate was investigated. None of the meteorological parameters has any effect on NO₂ uptake rate. On the other hand, the effect of temperature, percent relative humidity and, solar radiation flux on O₃ uptake rate were observed. The effects of temperature and solar radiation flux were directly proportional with O₃ uptake rate. However, relative humidity was inversely proportional with uptake rate of O₃.

Finally the pollution map of Ankara was constructed using passive sampling of NO₂ and O₃. Concentration of NO₂ was observed to be higher through Konya-Samsun

main road where the O_3 concentration was low. High concentration of O_3 was observed in the center of the city, although the traffic is generally denser in here.

FUTURE WORK

In future studies these passive tubes will be improved and modified for commercial use. Obtained values showed that these tubes are not affected from any meteorological factors which allow us to use them in outdoor sampling efficiently. Then the same sampling strategies will be applied for wider sampling areas. The spatial distribution determination provides to estimate the source and the movement of the pollutants.

Moreover, these tubes will be designed for other inorganic and organic pollutants. For instance, SO_2 and NH_3 are the considered inorganic gas pollutants and BTEX are the organic gas pollutants. If it is achieved, O_3 distribution will be compared with VOCs and by this way the relationship between O_3 and other organic pollutants can be related.

In this study the effectiveness of the passive tubes for O_3 and NO_2 was investigated and as a result passive tubes can be considered as a useful technique for air sampling. It is practical and cost efficient, then in large spatial studies it can be conducted easily.

REFERENCES

Alloway B. J., Ayres D. C., 1997, *Chemical Principles of Environmental Pollution*, Second Edition, Times by Thomas Pres, UK, pg:17-245

Bernard N.L., Gerber M.J., Astre C.M., Saintot M.J., 1999, *Ozone Measurement with Passive Samplers: Validation and Use for ozone Pollution Assessment in Montpellier, France*, Environmental Science and Technology Vol:33, 217-222

Brown, R.H., 1993. *The use of diffusive samplers for monitoring of ambient air*, Pure&Applied Chemistry Vol:65(8), 1859-1874

Bush T., Smith S., Stevenson K., Moorcroft S., 2001, *Validation of nitrogen dioxide diffusion tube methodology in the UK*, Atmospheric Environment vol:35 289-296

Cadoff, B.C., Hodgeson J., 1983. *Passive Sampler for Ambient Levels of Nitrogen Dioxide*, Analytical Chemistry Vol:55, 2083-208

Campbell, G.W., Stedman, J.R. and Stevenson, K., 1994. *A Survey of Nitrogen Dioxide Concentration in the United Kingdom Using Diffusion Tubes July-December 1991*, Atmospheric Environment Vol:28(3), 477-486

Cox P.C. and Brown R.H., 1984. *A Personal Sampling Method for the Determination of Nitrous Oxide Exposure*, American Industrial Hygiene Association Journal Vol:45(5), 345-350

Cox, R.M., 2003. *The use of passive sampling to monitor forest exposure to O₃, NO₂ and SO₂: a review and some case studies*, Environmental Pollution Vol:126, 301-311

Cruz, L.P.S., Campos, V.P., Silva, A.M.C. and Tavares, T.M., 2004. *A field evaluation of SO₂ passive sampler in tropical industrial and urban air*, Atmospheric Environment Vol:38, 6425-6429

EN 13528-1.4, March 2000, *Ambient Air Quality-Diffusive samplers for the determination of concentrations of gases and vapours- Requirements and test methods, Part 1: General requirements*

Ferm, M. and Svanberg ,P.A. 1998. *Cost-Efficient Techniques for urban and background measurements of SO₂ and NO₂*, Atmospheric Environment Vol:32(8), 1377-1381

Gair, A.J. and Penkett, S.A., 1995. *The Effects of Wind Speed and Turbulence on the Performance of Diffusion Tube Samplers*, Atmospheric Environment Vol:29(18), 2529-2533

Gerboles M., Buzica D., Amantini L., Lagler F., 2006, *Laboratory and field comparison of measurements obtained using the available diffusive samplers for ozone and nitrogen dioxide in ambient air*, Journal of Environmental Monitoring, Vol: 8, pg:112-119

Glasius, M., Carlsen, M.F., Hansen, T.S. and Lohse, C., 1999. *Measurement of nitrogen dioxide on Funen using diffusion tubes*, Atmospheric Environment Vol:33, 1177-1185

Godish, T., 1997, *Atmospheric Pollutants, Air Quality*, Boca Raton: CRC Press LLC

Godish T., 2004, *Air Quality*, 4th Edition, Lewis Publisher, pg: 23-55

Grigorieva V., Mihalev M., (1998), *Seasonal Surface Ozone Pattern at Sofia, Bulgaria*, In: Borrel P. M., Borrel P. (Ed): Proceedings of EUROTRAC

Symposium'98, Transport and Chemical Transformation in the Troposphere, Vol:1, WIT Press Computational Mechanics Publications, Southampton

Harper M. and Purnell C.J., 1987. *Diffusive Sampling- A Review*, American Industrial Hygiene Association Journal Vol:48(3), 214-218

Harrison, R. M., 2001, *Pollution; Causes, Effects and Control*, Fourth Edition, Royal Society of Chemistry

Hauser T.R., Bradley D.W., 1966, *Specific Spectrophotometric Determination of Ozone in the Atmosphere Using 1,2-di-(4-pyridyl)ethylene*, Analytical Chemistry, Vol: 38, No: 11, pg:1529-1532

Hava Kalitesi Değerlendirme Ve Yönetimi Yönetmeliği, June 6, 2008, Çevre ve Orman Bakanlığı, Türkiye

Heal, M.R and Cape, J.N., 1997. *A Numerical Evaluation of Chemical Interferences in the measurement of ambient nitrogen dioxide by passive diffusion sampling*, Atmospheric Environment Vol:31(13), 1911-1923

Heal, M.R., O'Donoghue, M.A. and Cape, J.N., 1999 (a). *Overestimation of urban nitrogen dioxide by passive diffusion tubes: a comparative exposure and model study*, Atmospheric Environment Vol:33, 513-524

Heal, M.R., O'Donoghue, M.A., Agius, R.M. and Beverland, I.J., 1999 (b). *Application of Passive Diffusion Tubes to short-term indoor and personal Exposure Measurement of NO₂*, Environment International, Vol. 25, 3-8

Helaleh M. I. H., Ngudiwaluyo S., Korenaga T., Tanaka K., 2002, *Development of passive sampler technique for ozone monitoring. Estimation of indoor and outdoor ozone concentration*, Talanta, Vol:58, Pg:649-659

Hodgson, E., 2004, *A Textbook of Modern Toxicology*, Third Edition, John Wiley & Sons, Inc., Publication, pg: 33-40

Kelly N. A., Wolff G. T., Ferman M. A., 1984, *Sources and Sinks of Ozone in Rural Areas, Atmospheric Environment*, Vol: 18, No: 7, Pg: 1251-1266

Krochmal, D. and Gorski, L., 1991. *Determination of Nitrogen Dioxide in Ambient Air by Use of a Passive Sampling Technique and Triethanolamine as Absorbent*, Environmental Science and Technology Vol:25, 531-535

Krochmal, D. and Kalina, A., 1997. *A method of nitrogen dioxide determination in ambient air by use of passive samplers and ion chromatography*, Atmospheric Environment Vol:31, 3473-3479

Krupa, S.V and Legge, A.H., 2000. *Passive sampling of ambient, gaseous air pollutants: an assessment from ecological perspective*, Environmental Pollution Vol:107, 31-45

Krupa, S., Nosal, M., Ferdinand, J.A., Stevenson, R.E. and Skelly, J.M., 2003. *A multi-variate statistical model integrating passive sampler and meteorology data to predict the frequency distributions of hourly ambient ozone (O₃) concentration*, Environmental Pollution Vol:124, 173-178

Levaggi D.A., Siu W., Feldstein M., 1973. *A New Method for Measuring Average 24-Hour Nitrogen Dioxide Concentrations in the Atmosphere*, Journal of the Air Pollution Control Association Vol:23(1), 30-33

Manahan, Stanley E. , 2000, *Environmental Chemistry, Chapter 9 & 11*, Boca Raton: CRC Press LLC

Miller, D.P., 1988. *Low-Level Determination of Nitrogen Dioxide in Ambient Air by Using the Palmes Tube*, Atmospheric Environment Vol:22(5), 945-947

Mulik, J.D., Lewis, R.G., McClenny, W.A. and Williams, D.D., 1989. ***Modification of High-Efficiency Passive Sampler to Determine Nitrogen Dioxide or Formaldehyde in Air***, Analytical Chemistry Vol:61, 187-189

Namiesnik J., Zabiegala B., Kot-Wasik A., Partyka M., Wasik A., 2005, ***Passive sampling and/or extraction techniques in environmental analysis: a review***, Anal. Bioanal. Chem, Vol:381, pg:279-301

Özer U., Tuncel S. G., Baykal A., Karakaş Y. S., 1997, ***NO_x, O₃, SO₂ ve Askıda Katı Maddenin, Uludağ Milli Parkında Dış Hava Konsantrasyonlarının ve Kuru Çökelme Akıplarının Belirlenmesi***, Proje No: KTYÇAG-34

Palmes E.D., Gunnison A.F., DiMattio J. and Tomczyk C., 1976. ***Personal Sampler for Nitrogen Dioxide***, American Industrial Hygiene Association Journal Vol:37 570-577

Patnaik P. 1997, ***Handbook Environmental Analysis: Chemical Pollutants in Air; Water; Soil, and Solid Wastes***, Lewis Publishers, pg:391, 411

Plaisance, H., 2004. ***Response of a Palmes tube at various fluctuations of concentration in ambient air***: Atmospheric Environment Vol:38, 6115-6120

Plaisance, H., Piechocki-Minguy, A., Garcia-Fouque, S. and Galloo, J.C., 2004. ***Influence of meteorological factors on the NO₂ measurements by passive diffusion tube***, Atmospheric Environment Vol:38, 573–580

Plaisance H., Gerboles M., Piechocki A., Detimmerman F., Saeger de E., 2007. ***Radial diffusive sampler for the determination of 8-h ambient ozone concentrations***, Environmental Pollution XX 1-9

Piechocki-Minguy, A., Plaisance, H., Schadkowski C., Sagnier I., Saison J.Y., Galloo, J.C., Guillermo R., 2006, **A case study of personal exposure to nitrogen dioxide using a new high sensitive diffusive sampler**, Science of the Total Environment Vol:366, 55-64

Project number: 104Y276, *İzmir Aliğa Endüstri Bölgesinde hava kirliliğine neden olan organik ve inorganik kirlleticilerin düzeylerinin, kaynaklarının ve sağlık etkilerinin belirlenmesi*, TÜBİTAK, Mart 2008

Radojevic M., Bashkin V. N., 1999, *Practical Environmental Analysis*, The Royal Society of Chemistry, UK, pg: 74,117

Ray D. J., 2001, *Spatial Distribution of Tropospheric Ozone in National Parks of California: Interpretation of Passive-Sampler Data*, Proceedings of the International Symposium on Passive Sampling of Gaseous Air Pollutants in Ecological Effects Research, *TheScientificWorld* Vol:1, pg:483–497

Reeve R., 2002, *Introduction to Environmental Analysis*, John Wiley & Sons, Inc., England, pg: 175-206

Report on a WHO Working Group, 2003, *Health Aspects of Air Pollution with Particulate Matter, Ozone and Nitrogen Dioxide*, Germany, pg:30-56

Royset O., 1998, *Comparison of passive and active sampling methods for the determination of nitrogen dioxide in urban air*, Fresenius J. Anal. Chem., Vol:360, pg:69-73

Santis, F.D., Allegrini, I., Fazio, M.C., Pasella, D. And Piredda, R., 1997. *Development of passive sampling technique for the determination of nitrogen dioxide and sulphur dioxide in ambient air*, Analytica Chimica Acta Vol:346, 127-134

Sanz M.J., Calatayud V., Sanchez-Pena G., 2007, *Measures of ozone concentrations using passive sampling in forests of South Western Europe*, Environmental Pollution Vol: 145, 620-628

Schnelle K. B., Brown C. A., 2002, *Air Pollution Control Technology Handbook*, CRC Pres. Pg: 81-82

Sickless II, J.E., Grohse, P.M., Hodson, L.L., Salmons, C.A., Cox, K.W., Turner, R. and Estes, E.D., 1990. *Development of a Method for the Sampling and Analysis of Sulfur Dioxide and Nitrogen Dioxide from Ambient Air*, Analytical Chemistry Vol:62, 338-346

Tang H., Lau T., Brassard B., Cool W., 1999, *A New All-Season Passive Sampling System for Monitoring NO₂ in Air*, Field Analytical Chemistry and Technology Vol:3 Issue: 6 338-345

Varshney, C. K. and Singh, A.P., 2003. *Passive samplers for NO_x monitoring : A critical Review*, The Environmentalist Vol:23, 127-136

Vinjamoori, D.V. and Ling, C.S., 1981. *Personal Monitoring Method for Nitrogen Dioxide and Sulfur Dioxide with Solid Sorbent Sampling and Ion Chromatographic Determination*, Analytical Chemistry Vol:53, 1689-1691

Wei Y. L., Oshima M., Simon J., Motomizus S., 2001, *Application of Chromamembrane Cell to Flow Injection Analysis of Trace Pollutant in Ambient Air*, Analytical Sciences, Vol: 17, pg: 325-328

WHO, *Guidelines for Air Quality*, 2000, Geneva, pg:3-60

Yamada, E., Kimura, M., Tomozawa, K. and Fuse, Y., 1999. *Simple analysis of atmospheric NO₂, SO₂ and O₃ in Mountains by using passive samplers*, Environmental Science and Technology Vol:33(23), 4141-4145

Yeşilyurt C., Akcan N., 2001, *Hava Kirliliği İzleme Metodolojileri Ve Örneklem Kriterleri*, T.C Sağlık Bakanlığı Refik Saydam Hıfzıssıhha Merkezi Başkanlığı Çevre Sağlığı Araştırma Müdürlüğü, pg:6-163

Yu M. H., 2005, *Environmental Toxicology: Biological and Health Effects of Pollutants*, Second Edition, CRC Press, USA, Pg:15-16, 111-125

<http://www.epa.gov/air/urbanair/> (last access date: September, 2008)