

DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED
SCIENCES

DETERMINATION OF OZONE, NITROGEN
DIOXIDE, AND SULFUR DIOXIDE POLLUTION
AROUND ALİAĞA BY PASSIVE SAMPLING

by
Mehtap EVCİ

April, 2009
İZMİR

**DETERMINATION OF OZONE, NITROGEN
DIOXIDE, AND SULFUR DIOXIDE POLLUTION
AROUND ALIAĞA BY PASSIVE SAMPLING**

**A Thesis Submitted to the
Graduate School of Natural and Applied Sciences of Dokuz Eylül University
In Partial Fulfillment of the Requirements for the Master Degree in
Environmental Engineering**

**by
Mehtap EVCİ**

**April, 2009
İZMİR**

M.Sc. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled “**DETERMINATION OF OZONE, NITROGEN DIOXIDE, AND SULFUR DIOXIDE POLLUTION AROUND ALIAĞA BY PASSIVE SAMPLING**” completed by **MEHTAP EVCİ** under supervision of **Prof.Dr. AYSEN MÜEZZİNOĞLU** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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DETERMINATION OF OZONE, NITROGEN DIOXIDE, AND SULFUR DIOXIDE POLLUTION AROUND ALIAĞA BY PASSIVE SAMPLING

ABSTRACT

In this study, the atmospheric concentrations of O₃, NO₂, and SO₂ were measured using passive samplers at 49 different sites in the region. Sampling campaigns were performed two times in summer and three times in winter seasons during the years of 2005-2007.

According to the results, there was a large variation in O₃, NO₂, and SO₂ levels among the sampling points. Measured levels for the pollutants were generally lower than the current long term national limits for human health protection. But, when the data set was compared with the target limits, they were exceeded those long term limit values at some sites and periods, especially for SO₂ and O₃.

Generally, background and rural sites had the lowest SO₂ and NO₂ levels in air during both seasons, while in summer period the residential areas had also low SO₂ levels. The SO₂ distribution map showed that the petroleum refinery and the petrochemical complex are the most important SO₂ sources in Aliağa air. High SO₂ levels were also measured at the urban and residential areas during winter, probably as a result of residential heating emissions and uncontrolled combustion. For NO₂, İzmir-Çanakkale highway, Yeni Foça road, Aliağa town, petroleum refinery and petrochemical industry with high NO₂ levels are the major sources in the region. NO₂ levels at the sites ($n=49$) were generally at the same levels in summer and winter.

Summertime O₃ levels were generally higher than the wintertime ones probably because of the increased solar radiation in summer. The sampling sites on the highway, around the industries and town center had the lowest levels while high O₃ concentrations were generally observed at the background and rural sites.

Keywords: Passive sampling; diffusion tubes; ozone; nitrogen dioxide; sulfur dioxide.

ALIAĞA ÇEVRESİNDEKİ OZON, AZOT DİOKSİT, VE SÜLFÜR DİOKSİT KİRLİLİĞİNİN PASİF ÖRNEKLEME İLE TESPİTİ

ÖZ

Bu çalışmada, O₃, NO₂, ve SO₂'in dış havadaki seviyeleri, Aliğa genelinde 49 farklı noktada pasif örnekleyciler kullanılarak ölçülmüştür. Örnekleme kampanyaları 2005-2007 yılları boyunca, 3 kez kış ve 2 kez de yaz sezonunda gerçekleştirilmiştir.

Sonuçlara bakıldığında O₃, NO₂, ve SO₂ seviyelerinin örnekleme noktalarına göre geniş bir aralıkta değiştiği görülmektedir. Tüm kirleticiler için bölge genelinde ölçülen seviyeler, halen kullanımda olan ve insan sağlığını korumak için belirlenen limitlerden düşüktür. Fakat, elde edilen veri seti hedeflenen limitlerle kıyaslandığında, özellikle SO₂ ve O₃ seviyelerinin, bazı noktalarda ve örnekleme periyotlarında bunlardan daha yüksek olduğu görülmüştür.

Genellikle en düşük SO₂ ve NO₂ seviyeleri, her iki mevsim için, temiz bölgelerde ve kırsal alanlarda ölçülmüştür. Yaz mevsiminde, yerleşim alanlarında ölçülen SO₂ seviyeleri de düşüktür. SO₂ dağılım haritalarına bakıldığında, petrol rafinerisi ve petrokimya tesisinin Aliğa havası için önemli bir kirlilik kaynağı olduğu görülmüştür. Kış mevsimi boyunca kentsel ve yerleşim alanlarında ölçülen SO₂ seviyeleri de, muhtemelen evsel ısınmaya ve kontrolsüz yanmaya bağlı olarak yüksektir. NO₂ seviyelerinin yüksek ölçüldüğü, İzmir-Çanakkale anayolu, Yeni Foça yolu, Aliğa ilçesi, petrol rafinerisi ve petrokimya tesisleri bölge için önemli birer NO₂ kaynaklarıdır. Örnekleme noktalarında ($n=49$) ölçülen NO₂ seviyelerinin önemli bir mevsimsel farklılık göstermediği görülmüştür.

Yazın ölçülen ozon seviyeleri genellikle, muhtemelen güneş radyasyonunun artması nedeniyle, kışın ölçülenlere oranla daha yüksektir. Anayol üzerinde, endüstrilerin çevresinde, ve ilçe merkezindeki noktalarda ölçülen ozon seviyeleri düşükken, temiz ve kırsal alanlarda ölçülenler yüksektir.

Anahtar Sözcükler: Pasif örnekleme; difüzyon tüpleri; ozon; azot dioksit; kükürt dioksit.

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CHAPTER ONE

INTRODUCTION

1.1 Introduction

Inorganic air pollutants including NO_x ($\text{NO}+\text{NO}_2$), N_2O , SO_2 , CO , NH_3 , and O_3 are mainly emitted to the atmosphere from anthropogenic sources such as traffic emissions, residential heating, and industrial facilities. Once emitted, air pollutants are subject to mixing, dispersion, transport and complex chemical interactions and physical transformation processes in the urban atmosphere. For example, atmospheric reactions between emitted nitrogen oxides ($\text{NO}_x=\text{NO}+\text{NO}_2$) and volatile organic compounds (VOCs) result in the formation of ground level ozone (Özden, Döğeroğlu, & Kara, 2008). Besides their deleterious effects on human health, these inorganic pollutants may cause serious negative effects on ecosystems (e.g. leading to injury to plants and reduction in crop yields), materials and the visibility.

Because of the adverse effects of atmospheric pollutants on human beings and the environment, they need to be monitored and controlled. Currently, most air quality monitoring is being carried out at “continuous/active” instrumental monitoring stations. However, these are expensive and mostly limited to urban sites, with only a few in rural locations. Therefore, the use of passive samplers for gas or vapor monitoring has become an attractive alternative when compared to conventional active sampling techniques, due to the advantages such as low cost, flexibility of placement, and needing no power supply (Cox, 2003).

Passive sampling technology has been widely used in ambient monitoring to measure trace gas species such as NO_2 , SO_2 and O_3 at rural, urban, industrial sites in the world (Bhugwant & Hoareau, 2003; Campbell, Stedman, & Stevenson, 1994; Carmichael et al., 1995; Cox, 2003; Cruz, Camposs, Silva, & Tavares, 2004; Delgado-Saborite & Esteve-Cano, 2007; Ferm & Svanberg, 1997; Kasper-Giebl & Puxbaum, 1999; Krzyzanowski, 2004; Miller, 1998; Nerriere et al., 2005;

Seethapathy, Gorecki, & Li, 2008; Zhou & Simith,1997) and in Turkey (Bayram et al., 2008; Güner, Horasan, Tıprıdamaz, & Güllü, 2008; Özden, Koçaker, & Döğeroğlu, 2008; Özden, Yay et al., 2008; Yay et al., 2008). But, there are limited investigations on ambient air levels of NO₂, SO₂ and O₃ and their spatial distributions over large areas in Turkey (Bayram et al., 2008; Özden, Yay et al., 2008).

İzmir is one of the most industrialized cities of Turkey. Especially Aliğa town in İzmir is an industrial district with many iron steel factories, petrochemicals and ship-breaking facilities. In the area, air pollution is a serious problem and because of possible health effects in the region, pollutants must be identified, monitored and controlled. The air pollutants of major concern in the study area are particulate matter (PM), carbon monoxide (CO), sulfur dioxide (SO₂), nitrogen oxides (NO_x), ozone, trace metals, volatile organic compounds (VOC), polynuclear aromatic hydrocarbons (PAH), polychlorinated biphenyls, dioxine-furans, and other chlorinated organics.

This thesis work was part of a project funded by Tübitak. The aims of the main project were to determine the organic and inorganic air pollutant levels around the Aliğa region and find the possible sources and health effects of these air pollutants.

The aim of this thesis work was to measure SO₂, NO₂ and O₃ levels in Aliğa by passive sampling methods. This is the first study that was carried out at multiple points to define distributions of these pollutants in air over a wide coverage in and around Aliğa. In this respect, these measurements were used to evaluate the following:

- Finding ambient air concentrations of SO₂, NO₂ and O₃ at 49 different points in the region,
- Assessing their seasonal variations,
- Mapping the spatial distributions of these pollutants to find out the main polluted sources in the region.

All results were compared with national limits aiming at the human health protection (Air Quality Evaluation and Management Regulation [HKDYY], 2008).

In the scope of this study, ambient air samples were collected using passive sampling method at five different campaigns during both summer and winter seasons. Passive tubes for SO₂, NO₂ and O₃ sampling were obtained from Gradko Company, England and analysed in Gradko Laboratories.

This study consists of five chapters. An overview and objectives of the study were presented in Chapter 1. Chapter 2 reviews the concepts and previous studies related to this work. Experimental work and data analysis procedures are summarized in Chapter 3. Results and discussions are presented in Chapter 4. Chapter 5 includes the conclusions drawn from this study.

CHAPTER TWO

LITERATURE REVIEW

This chapter presents background information on physical-chemical properties, sources, and health effects of the studied inorganic pollutants of SO₂, NO₂ and O₃. Recent studies on their ambient air concentrations measured with passive sampling techniques are also summarized.

2.1 Air Pollutants Measured in This Study

Inorganic gaseous pollutants are the major contributors to the environmental problems. The most common gaseous pollutants are carbon dioxide (CO₂), carbon monoxide (CO), hydrocarbons, nitrogen oxides (NO_x), sulfur oxides (SO_x) and ozone (O₃). Other inorganic pollutant gases include NH₃, N₂O, N₂O₅, H₂S, Cl₂, HCl, and HF. Pollutants may be primary or secondary in origin. Primary pollutants such as CO, NO, and SO₂ are emitted directly into the atmosphere from a variety of sources, whereas secondary pollutants such as O₃ are formed indirectly, from the reaction of other chemical compounds present in the atmosphere. In this study, only atmospheric SO₂, NO₂, and O₃ levels were measured using passive measurement technique.

2.1.1 Sulfur Dioxide (SO₂)

Sulfur dioxide (SO₂) belongs to the family of sulfur oxide gases (SO_x). It is a primary pollutant formed from the oxidation of sulfur contained in fuels during combustion processes. Sulfur is prevalent in all raw materials, including crude oil, coal, and ore that contains common metals like aluminum, copper, zinc, lead, and iron. The majority of SO₂ originates from power stations and industrial sources, although there can be local contributions in areas where coal is used for domestic heating. It is also formed when gasoline is extracted from oil, or metals are extracted from ore (Environmental Protection Agency [EPA], 2008). According to the types of fuel and combustion device, about 15-98% of SO_x in the waste gas is in sulfur dioxide form (Dinçer, 2001).

Sulfur dioxide is a colorless gas with a pungent odor. Its molecular weight is 67 g mol⁻¹ and cas-number is 7446-09-5. It is a liquid when under pressure, and it dissolves in water very easily (Agency for Toxic Substances and Disease Registry [ATSDR], 1998). SO₂ can be released to the air from natural sources (volcanoes, oxidation products of sulfurous gases from plant decomposition) and also by anthropogenic sources, such as the combustion of sulfur containing fossil fuels (coal, oil and natural gas), the smelting of ores (mostly copper, lead and zinc), and other industrial processes (ATSDR, 1998; Dinçer, 2001).

In the air, SO₂ can be converted to sulfuric acid, sulfur trioxide, and sulfates. Once dissolved in water, sulfur dioxide can form acid, and interacts with other gases and particles in the air to form sulfates and other products that can be harmful to people and the environment (EPA, 2008). Acid rain forms when moisture in the air interacts with nitrogen oxide and sulfur dioxide. This interaction of gases with water vapor forms sulphuric acid and nitric acids. Eventually these chemicals fall to earth as precipitation, or acid rain (ATSDR, 2002; Özden, Döğeroğlu et al., 2008).

Exposure to sulfur dioxide occurs from breathing it in the air. It affects the lungs and at high levels may result in burning of the nose and throat, breathing difficulties, and severe airway obstructions (ATSDR, 1998).

2.1.2 Nitrogen Dioxide (NO₂)

Nitrogen oxides (NO_x) are important pollutant gases in air. There are seven oxides of nitrogen: NO, NO₂, NO₃, N₂O, N₂O₃, N₂O₄ and N₂O₅. However, only two are important in air pollution: nitric oxide (NO), which is a primary pollutant, and nitrogen dioxide (NO₂), which can be both a primary and a secondary pollutant. Both are non-flammable and colorless to brown at room temperature. Nitric oxide is a sharp sweet-smelling gas at room temperature, whereas nitrogen dioxide has a strong, harsh odor and is a liquid at room temperature, becoming a reddish-brown gas above 70°F (ATSDR, 2002). NO is produced during high temperatures combustion processes, and oxidises to NO₂ once combined with oxygen in the air. In

this study, only NO₂ levels in ambient air was investigated. Cas-number and molecular weight of nitrogen dioxide are 10102-44-0 and 46 g mol⁻¹, respectively.

Nitrogen oxides in the air may occur both naturally and from human activities. In nature, they result from bacterial processes, biological growth and decay, lightning, as well as forest and grassland fires (Dinçer, 2001). Anthropogenic nitrogen oxides are released to the air from the exhaust of motor vehicles, the burning of coal, oil, or natural gas, and during processes such as arc welding, electroplating, engraving, and dynamite blasting. They are also produced commercially by reacting nitric acid with metals or cellulose (ATSDR, 2002; Dinçer, 2001). Glasius, Carlsen, Hansen, & Lohse (1999) carried out measurements from monitoring sites in the vicinity of a motorway, and indicated that air pollution from the vehicles affects the concentration of NO₂ even at more than 1000 m away downwind.

Nitrogen dioxide is the most effective and poisonous nitrogen oxide molecule (Dinçer, 2001). The reaction of nitrogen dioxide with chemicals produced by sunlight leads to the formation of nitric acid, which is a major constituent of acid rain. Nitrogen dioxide also reacts with sunlight, which leads to the formation of ozone and smog conditions in the air we breathe (ATSDR, 2002; Cox, 2003). It absorbs light and contributes to the colorful haze seen hanging over cities (Dinçer, 2001). This molecule is of particular concern, as it is a precursor to the formation of photochemical oxidants, which directly impact human health. Nitrogen dioxide is also an important indicator of air pollution, because the concentration of NO₂ is well correlated with the concentration of carbon monoxide, particulate polycyclic aromatic hydrocarbons and soot (Glasius et al., 1999).

From the absorbed forms in soil and water, small amounts of nitrogen oxides may evaporate into the air, but most of it will be converted to nitric acid or other compounds. Nitrogen oxides do not build up in the food chain (ATSDR, 2002).

Low levels of nitrogen oxides in the air can irritate the eyes, nose, throat, and lungs, possibly causing a cough and experience shortness of breath, tiredness, and

nausea. Exposure to low levels can also result in fluid build-up in the lungs 1 or 2 days after exposure. Breathing high levels of nitrogen oxides can cause rapid burning, spasms, and swelling of tissues in the throat and upper respiratory tract, reduced oxygenation of body tissues, a build-up of fluid in your lungs, and death. In case of the skin or eye contact with high concentrations of nitrogen oxide gases or nitrogen dioxide liquid, it would likely cause serious burns (ATSDR, 2002).

2.1.3 Ozone (O_3)

Ozone (O_3) is a gas composed of three oxygen atoms. It occurs both in the Earth's upper atmosphere and at ground level and has the same chemical structure whether it occurs in upper atmosphere (the stratosphere) or at ground-level (the troposphere). It has a cas-number of 10028-15-6 and molecular weight of 48 g mol^{-1} . O_3 can be "good" or "bad," depending on its location in the atmosphere. Stratospheric ozone occurs naturally and protects life on Earth from the sun's harmful ultraviolet (UV) rays while ground-level ozone is considered "bad" (EPA, 2009). In this study, only tropospheric (ground level) ozone levels were investigated.

Ground-level ozone is a secondary pollutant that is not usually emitted directly into the air. O_3 is formed by a chemical reaction between oxides of nitrogen ($NO_x=NO+NO_2$) and volatile organic compounds (VOC) in the presence of sunlight (EPA, 2009; Özden, Döğeroğlu et al., 2008; Delgado-Saborit & Esteve-Cano, 2007). Ozone has an inverse relationship with NO_x as it requires NO_2 for its formation, but it is scavenged in the atmosphere by NO. Sunlight and hot weather cause ground-level ozone to form in harmful concentrations in the air. As a result, it is known as a summertime air pollutant (EPA, 2009).

Motor vehicle exhaust and industrial emissions, gasoline vapors, and chemical solvents as well as natural sources emit NO_x and VOC that help form ozone. O_3 is the primary constituent of smog (EPA, 2009). The effect of O_3 on vegetation is also well known. The effects on vegetation appear in the form of visible consequences on the leaves of, for example tobacco, beans, and various species of clover, watermelon,

and spinach. Ozone reduces yields in crops such as carrots, tomatoes, tobacco, beans, spinach, watermelon, wheat and other cereals. Some fruit trees such as peach, orange and lemon, almond and olive are also known to be at risk (Delgado-Saborit & Esteve-Cano, 2007).

Symptoms from exposure to low concentrations of ozone include eye, nose, throat, and lung irritation. At higher concentrations, coughing and breathing problems occur. Even higher concentrations result in chest pain and pneumonia (ATSDR, 2007).

2.2 Passive Sampler

The use of passive samplers for gas or vapor monitoring has become an attractive alternative, due to the advantages that they present when compared to conventional active sampling techniques. In addition to being simple and cost-effective, this device presents the following benefits: i) the possibility of simultaneous sampling of numerous sites; ii) easy transportation to difficult locations (e.g. forests and mountains) due to its small dimensions and light weight; iii) silent operation; iv) reusability; v) a 100% time coverage is obtainable; and vi) does not need field calibration, sampled air volume measurements, electricity nor technical personnel at the sampling site. So, passive samplers are suitable for determining the spatial distribution of gases over large areas, checking atmospheric transport and deposit models, screening studies, establishing atmospheric monitoring networks, personal monitoring, mapping concentrations in cities, and measuring concentrations in remote sites (Cruz et al., 2004; Cox, 2003).

2.2.1 Principle of Operation

Diffusion tube samplers operate on the principle of molecular diffusion, with molecules of a gas diffusing from a region of high concentration (open end of the sampler) to a region of low concentration (absorbent end of the sampler). The movement of gas molecules is described by Fick's law (Cox, 2003; Ferm &

Svanberg, 1997; Kot-Wasik et al., 2007). The free flow of analyte molecules during sampling from one medium to the collecting medium goes on till equilibrium is established in the system or till the sampling session is ended by the user.

Depending on the studied pollutant and passive sampler types (e.g. badge- or tube-type), different kinds of absorbents can be used. Absorbents currently used in O₃ sampler are nitrite, indigo compounds and 1,2-di(4-pyridyl)ethylene (DPE). The most commonly used absorbent for NO₂ sampling is triethanolamine (TEA). Nitrogen dioxide is converted to nitrite ions after reaction with TEA. In addition to TEA, potassium iodide (KI), sodium hydroxide (NaOH), sodium iodide (NaI), and sodium carbonate (Na₂CO₃) in passive sampler for NO₂. Absorbents used for the passive sampling of SO₂ are sodium tetrachloromercurate (Na₂HgCl₄), potassium carbonate (K₂CO₃), TEA, and sodium hydroxide (NaOH) (Cox, 2003).

To prevent negative effects of air currents in order to control analyte mass transfer, the diffusion sampler has to be constructed by materials that minimal resistance to the diffusion process but high resistance to the negative air currents. The geometry of passive sampler affects efficiency of diffusion. Rate of pollutant gas absorption for a diffusion tube sampler is controlled by the diffusion path length and the internal cross-sectional area of the sampler (Cox, 2003). For example, the effect of ambient air velocity decreases and practically disappears when the length:diameter ratio (L:A) reaches 7:1 (Gorecki & Namiesnik, 2002).

Passive samplers are generally protected from external effects such as rain, sun, and mechanical damage during field deployment by a shelter of different designs. They provide a point of attachment to the sampling site (pole or tree) (Cox, 2003; Delgado-Saborit & Esteve-Cano, 2007).

When sampling from air, a sorbent is often chosen that acts like a zero sink (i.e. analyte concentration at the sorbent surface is practically zero). Under such conditions, the amount of the analyte collected by the sampler is proportional to its concentration in the air and to the time for which the sampler was exposed, which

makes time-weighted average concentration determination possible. An essential condition for this is that the sampling rate remains practically constant throughout the entire sampling period (Seethapathy et al., 2008).

Passive (diffusion) sampling is the collection of inorganic pollutants on absorbent by diffusion. The value of data acquired by analyses after passive sampling is not concentration. It is the total mass of the inorganic pollutant collected in a passive sampling tube for a week ($\mu\text{g tube}^{-1}$). In order to convert this value to concentration, diffusion constants (diffusion coefficients or uptake rates) are needed.

2.2.2 Data Analysis

After exposure, atmospheric SO_2 , NO_2 and O_3 concentrations measured by passive samplers can be calculated by applying Fick's first law from the analyte masses adsorbed:

$$C_i = (m_i - m_b) / (U_i t) \quad (2.1)$$

where m_i is the mass of the analyte i (μg) found on the sorbent, t (min) is the sampling time, m_b is the mass of the analyte i (μg) on a non-exposed sorbent (a blank), C_i is the ambient concentration ($\mu\text{g m}^{-3}$) of the analyte i , U_i is the uptake rate of the analyte i ($\text{m}^3 \text{min}^{-1}$).

Uptake rate is calculated from diffusion coefficient and the geometry of the tube as follows:

$$U_i = D_i (A/L) \quad (2.2)$$

where D_i is the diffusion coefficient of the analyte i in air ($\text{cm}^2 \text{min}^{-1}$), A is the cross-sectional area of the sampler (cm^2) and L is the length of the diffusion zone (cm).

For the gas monitored, the diffusion coefficient must be determined, or obtained

from the literature. The area and length of the tube are determined by measurement. In the case of air sampling, molecular diffusion coefficients in air increase with temperature, which results in increased uptake rates of the analytes. The diffusion coefficient of molecules in air is inversely proportional to pressure; hence pressure variations must also be known accurately (Seethapathy et al., 2008).

2.3 Reported Levels of SO₂, NO₂, and O₃ in Ambient Air

For atmospheric SO₂, NO₂ and O₃, the long and short term limit values for human health protection are given in Air Quality Evaluation and Management Regulation in Turkey (HKDYY, 2008). Present day and target limits for these pollutants are given in Table 2.1.

Table 2.1 Present and target short and long term air quality limit values (STL and LTL, respectively; $\mu\text{g m}^{-3}$) for human health protection ([HKDYY], 2008).

Pollutant	Average time	Limit value ($\mu\text{g m}^{-3}$)				Date to be reached limit value
		01.01.2008	01.01.2009	01.01.2014	For the target date	
SO ₂	STL ^a	400	367	250	125	01.01.2019
	LTL ^b	150		20 ^c	20 ^c	01.01.2014
NO ₂	STL	300		300	200	01.01.2024
	LTL	100	93	60	40	01.01.2024
Ozone	LTL				120	01.01.2022

^a Daily average.

^b Annual average.

^c For protection of ecosystem.

According to an earlier emission inventory (Müezzinoğlu, Bayram, & Yıldızhan, 1997) industrial activities caused hourly SO₂ emissions varying between 15 and 20 ton in 1996. The same study pointed out that 85% of this pollutant was produced by the refinery and petrochemicals industries in Aliğa and these industry facilities are responsible for 70% of total emissions in the İzmir region.

A study (Özden, Yay et al., 2008) on weekly NO₂, SO₂, and O₃ measurements were carried out by using passive sampling method during 9-23 January of 2008 in Eskişehir, Turkey. For the sampling studies, 64 points were selected, depending on the parameters such as traffic density, heating system and population density. SO₂,

NO₂, and O₃ concentrations were between 42-79, 10-66, and 12-63 µg m⁻³ and their average values were 54±8.4, 34±10, and 31±11 µg m⁻³, respectively. It was reported by Özden, Koçaker et al., (2008) that SO₂ was the highest levels around the city center, and the levels measured at the sites, where coal was used for the residential heating, were higher than the sites where natural gas was used. They reported the highest NO₂ levels at the city center with an intensive traffic. Ozone was reported at the highest levels at the rural sites.

At 27 points around the iron-steel plants in Aliğa industrial region, Bayram et al. (2008) measured atmospheric SO₂ and NO₂ levels on weekly passive samplers during March-April 2007 (*n*=8 for each sampling point). They reported that the SO₂ and NO₂ levels as a weekly average were between 1-65 and 2-59 µg m⁻³ at the sampling points, respectively.

Using passive samplers, Yay et al. (2008) measured atmospheric levels of SO₂, NO₂, and O₃ at 60 points in the İskenderun-Payas region in Turkey during the period 29 January-11 February 2008. The sampling period was reported as a week for each sampling point. They found the highest levels of SO₂ and NO₂ at the city center of İskenderun with high population and traffic density, and Payas with iron steel industry as the dominating industrial activity. Even though the sampling was done at winter months, ozone levels were found to be very high at some locations. The reported range for SO₂, NO₂ and O₃ levels was between 35-201, 6-49, and 11-395 µg m⁻³, respectively.

Another study was carried out by Güner et al., (2008) at four different points in Nezahat Gökyiğit Botanic Garden which is located at the intersection of highways in Istanbul, Turkey. They measured SO₂, NO₂, O₃ levels between December 2007-June 2008 and in August 2008 and weekly passive samplers were taken once every month. They reported SO₂, NO₂, O₃ levels between 3-24, 48-79, and 15-89 µg m⁻³, respectively. Low SO₂ levels were attributed to the lack of emissions from residential heating around these sites. They found the highest NO₂ levels at the point being the nearest distance to the traffic emissions. The reported ozone levels were higher in summer than in winter.

CHAPTER THREE

MATERIALS AND METHODS

Sampling site and program, meteorology in the area, sampling technique, and the experimental methods used for the measurement of atmospheric SO₂, NO₂ and O₃ levels in this study are discussed in Chapter 3. Quality control studies are also given in this chapter.

3.1 Sampling Site

Aliğa is located approximately 60 km to the north of İzmir located by the Aegean Sea (38° 56' N-37° S and 26° 53' W-27° 10' E). The town is surrounded by Dumanlı Mountain at south-east, Yunt Mountain at north-east. Manisa is at the east, Bergama is at the north, Menemen is at the south and Foça is at the south-west of Aliğa. Güzelhisar Stream is the unique creek in Aliğa borders. Land area of Aliğa is 393 square kilometers and İzmir-Çanakkale Highway passes through the center of the town. The general layout of the sampling area is shown in Figure 3.1.

Aliğa was a small town with 2590 persons in 1960, but today has been converted to a heavily industrialized area. The town grew rapidly and became one of the popular industry centers in Aegean Region. Thus, Aliğa is subject to immigration and this situation is still going on. According to recent report of the Turkish Statistical Institute in 2008, the population was counted 62,258 in Aliğa (Türkiye İstatistik Kurumu [TÜİK], 2008). It is also known that the number of people working but not residing in Aliğa is not negligible. Hence, the number of people during daytime is more than these figures.

Aliğa is a heavily industrialized area. There are a lot of industrial companies in several sectors with different capacities in Aliğa. These sectors are refinery, petro-chemistry, liquid fuel and gas filling facilities, energy generation facilities, iron-steel facilities (steelworks+rolling mill), blooming mills, chemical fertilizer, paper, waste recycling facilities, and ship dismantling facilities (Fig. 3.1).

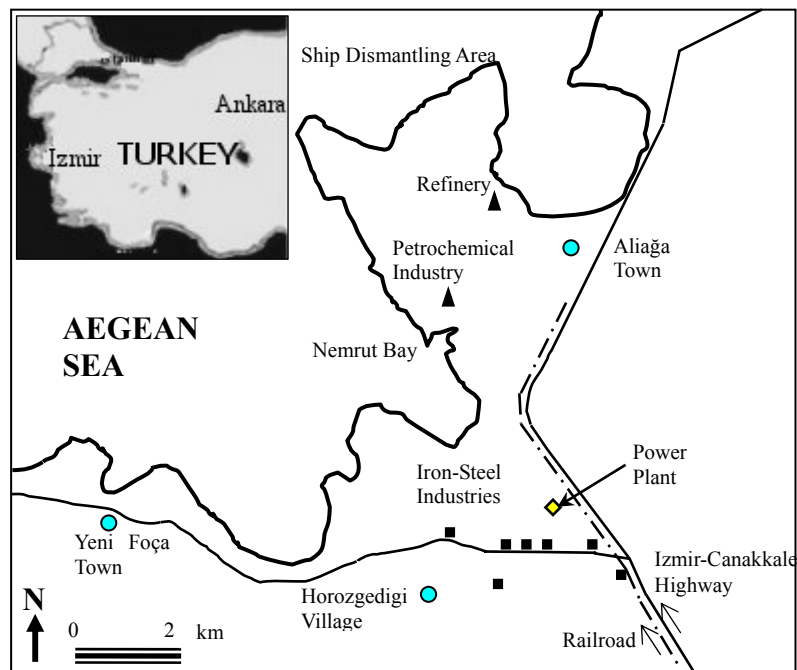


Figure 3.1 General layout of the study site.

Aliğa has an important role at Turkey's refinery capacity; 226,440 ton per day of the 694,115 ton per day crude petroleum processing requirement of Turkey is processed in Aliğa Petroleum Refinery. Natural gas was connected to Aliğa in 2005, and gradually the industry started consuming natural gas. For example, Enka power plant firing natural gas was established to generate electricity with 1100 MW capacity. In addition to Enka, investments over electricity production were made by Petkim petrochemical industry, Tüpraş petroleum refinery and Turkish Electricity Administration to convert from residual fuel oil which is in surplus in the area (Tübitak Project No: 104Y276).

Aliğa has busy ports; 22% of the total export of the Aegean Region is made from Aliğa. Moreover, harbors and ship dismantling facilities also provided high profit to development of the town. Tourism is of less significance in comparison with industry. After industrialization, agricultural activities have decreased in the region.

The traffic is intensive at İzmir-Çanakkale highway, Aliğa-Foça and Aliğa ship dismantling area roads. The traffic on Aliğa-Foça and ship dismantling area roads

contain transportation of steel products, scrap iron and other essential materials for facilities and worker service vehicles.

3.2 Meteorology in the Area

Aliaga area has a typical Mediterranean climate with hot and dry summers and mild rainy winters. The mean temperature in the region is 25 and 7°C in summer and winter, respectively. The coldest month is January. The mean annual rainfall is 700 mm. During the sampling periods, meteorological parameters were taken from the State Meteorological station located near the Aliaga town center. Average temperatures in periods 1 to 5 were 2, 11, 26, 23 and 4°C, respectively. The prevailing wind directions in most part of the year were coming from north-north east and north. Additionally, a southerly direction in summer was noted. Wind-rose diagrams showing annual, summer and winter wind directions are given in Figure 3.2.

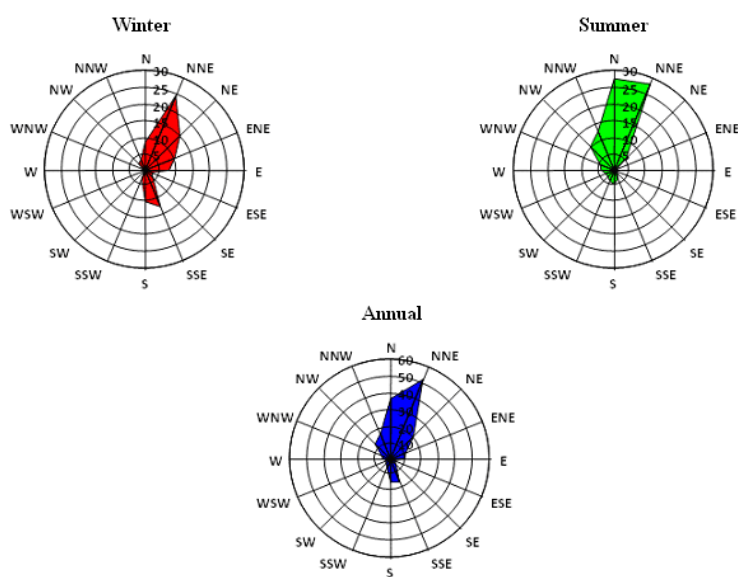


Figure 3.2 Wind-rose diagrams of Aliaga showing wind directions.

3.3 Sampling Program

A total of five sampling campaigns were conducted from December 2005 to February 2007. They were between 19-27 December 2005, 21-28 March 2006, 19-26 June 2006, 29 August-5 September 2006, and 9-16 February 2007, respectively.

Table 3.1 Names and numbers of the sampling points.

Site Number	Sampling Location	Site Number	Sampling Location
S1	Mouth of Güzelhisar Creek	S30	Transformer (Main road)
S2	Forest	S32	Yeni Foça Road
S3	Opposite Asphalt Plant	S33	Sheepfolds
S4	Tüpraş (Security # 6)	S34	Near Betonsa
S5	Aliğa Org. Ind. Dis. Road	S35	Bozköy
S6	Petkim (Restricted zone)	S36	Bozköy entrance
S7	Aliğa Beach	S37	Şehit Kemal entrance
S9	Aliğa Org. Ind. Dis.	S39	Kozbeyli road
S10	Aliğa Org. Ind. Dis.	S42	Main Road
S11	Tüpraş (Opposite to Petkim entrance)	S43	Hatundere
S12	Tüpraş (Main entrance)	S44	Helvacı
S13	Aliğa bus station	S45	Eski Foça Road
S14	Aliğa hospital road	S46	Eski Foça Road (Ilıpınar)
S15	Karaköy	S47	Eski Foça Road
S16	Petkim fences	S48	Eski Foça Road
S17	Petkim entrance to Petkim houses	S49	Hatundere Crossroads
S18	Petkim (Petrol Office's Harbour entrance)	S50	Eski Foça Road
S19	Petrol Office	S53	Buruncuk
S20	Nearby Aliğa Hospital	S54	Türkelli
S22	Güzelhisar	S55	Buruncuk
S23	Field	S56 (A)	Aliğa station
S24	Çakmaklı	S57 (AB)	ENKA road
S25	İDÇ Harbour entrance	S58 (i-1)	İncirlik
S26	Village entrance	S59 (i-2)	Çandarlı
S29	Horozgediği		

To represent air quality at the study area, 49 points were selected over a grid system. These sampling points were located at the corners of a 15 x 20 km rectangular matrix subdivided into 2000 m grids to the best that could practically be done. Otherwise, a nearby location was chosen. Also, the junction points quite far

away from pollutant sources were preferably moved to more important receptor areas. Therefore, some of the sampling points were somewhat displaced from the junction points of the grid. The selected sampling points had different site characteristics (such as background, rural, urban, and industrial) due to distances from the main pollutant sources. Locations of the sampling points are shown in Figure 3.3; their numbers and names are given in Table 3.1.

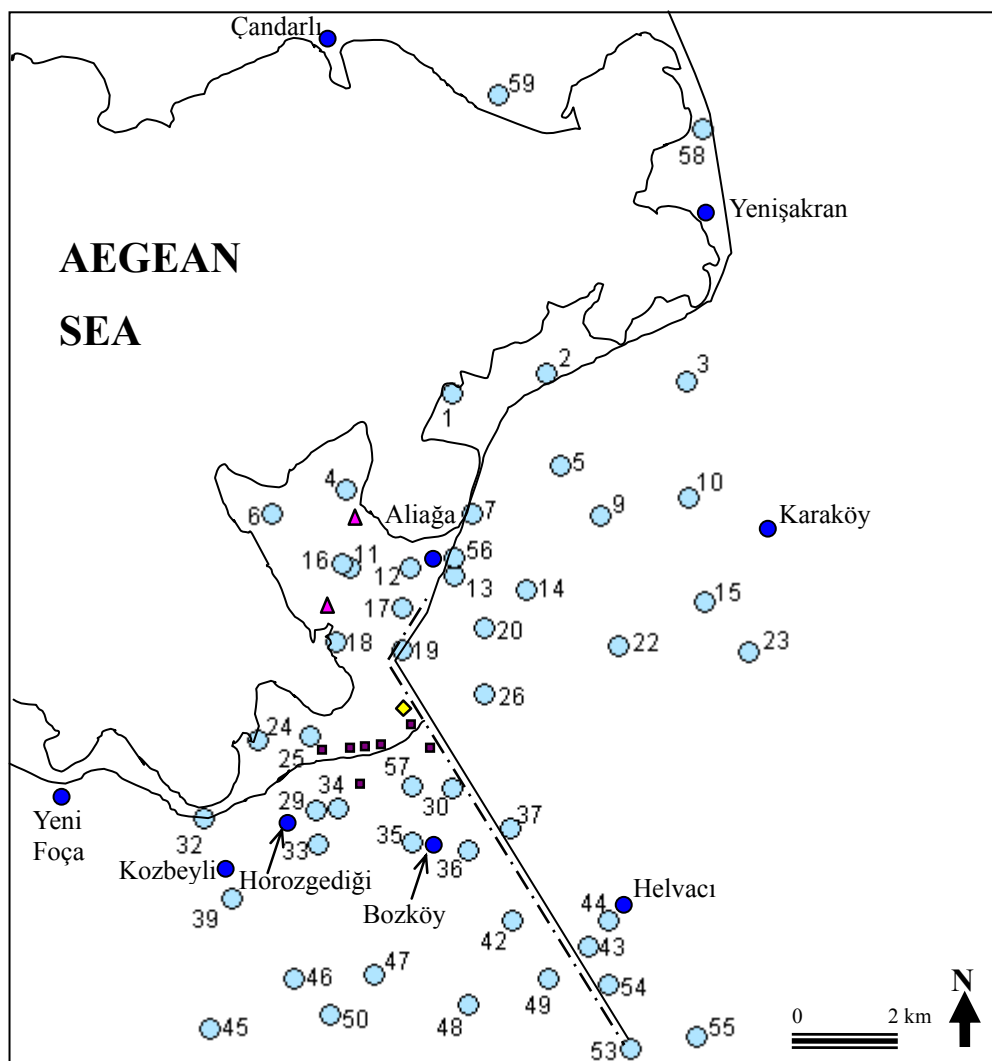


Figure 3.3 Location of the sampling points ($n=49$) in the study area. (○: passive sampling points, ●: residential areas, ▲: refinery and petrochemical industry, ◆: power plant, ■: iron-steel industries).

3.4 Passive Sampling Method

Passive diffusive type samplers for SO_2 , NO_2 , and O_3 were obtained from Gradko in England. After sample collection, all tubes were also sent for analysis to England in order to assure the quality of the data as they have a reliable accredited laboratory. Gradko is a well known and an internationally recognized company and they sell the tubes with the cost of analysis included.

The tubes used for all of the studied inorganic compounds are 71 mm length with an internal diameter of 11 mm and they are shown in Figure 3.4.



Figure 3.4 The diffusion tubes used in this study.

Sulfur dioxide tubes were made of fluorinated ethylene polymers fitted with purple and white thermoplastic rubber caps. The colored cap contains a potassium hydroxide absorbent. Desorption efficiency of absorbent is given as 0.99. A filter with 1 micron porosity is fitted to the white cap to prevent particulates loading together with sulfur. The concentrations of sulfate ions chemically adsorbed are quantitatively determined by ion chromatography with reference to a calibration curve derived from the analysis of standard sulfate solutions. Uptake rate for sulphur dioxide was reported by Gradko as $0.95 \text{ cm}^3 \text{ hr}^{-1}$ (Gradko, 2008a).

Nitrogen dioxide tubes are made of acrylic material and fitted with grey and white thermoplastic rubber caps. During sampling the white cap was removed and the tube was left for exposure period. At the completion of the sampling the white cap is replaced. The colored caps contained an absorbent made up of 20% triethanolamine solution in deionized water. Desorption efficiency of the absorbent is given as 0.98. The concentrations of nitrite ions and hence NO_2 chemically adsorbed are quantitatively determined by UV/Visible Spectrophotometry with reference to a calibration curve derived from the analysis of standard nitrite solutions. Uptake rate for NO_2 was given by Gradko as $72.0 \text{ cm}^3 \text{ hr}^{-1}$ (Gradko, 2008b).

Ozone tubes consisted of fluorinated ethylene polymer and fitted with black and white thermoplastic rubber caps. The colored caps contained the absorbent. Desorption efficiency of the absorbent was given as 0.99. A filter with 1 micron porosity was fitted to the white cap to prevent the inclusion of airborne particulate nitrate. The concentrations of nitrate ions chemically sorbed were quantitatively determined by ion chromatography with reference to a calibration curve derived from the analysis of standard nitrate solutions. Uptake rate for ozone was given by Gradko as $0.93 \text{ cm}^3 \text{ hr}^{-1}$ (Gradko, 2008c).



Figure 3.5 Shelter located at study sites.

Passive sampling tubes were kept at the sampling locations for one week. They were placed approximately 1.5-2.0 m from the ground which is the human nose level. Shelters were used to protect the tubes from the bad weather condition and to keep them vertically with the colored cap facing up during exposure period in the field. These shelters were made of aluminum and were fixed by steel wire to a post, wall, streetlamp, or tree. These shelters together with the passive tubes are shown in Figure 3.5.

The time and date from the beginning to the end of the sampling period were recorded on the supplied monitor sheets for each pollutant at each sampling point. At the end of the exposure period, collected passive samplers were stored in their protective polyethylene caps after label records were made. Then, they were packaged in airtight plastic bags for transportation back to the laboratory. Their exposure times for each sampling point were calculated in hours and recorded on the sheets.

All the tubes and monitor sheets were shipped to England to analyze in Gradko laboratories. The average ambient air concentrations were calculated using the indicated uptake rates for SO_2 , NO_2 , O_3 ; amount of nitrite (NO_2^-), sulfate (SO_4^{2-}) and nitrate determined in the extract; and the exact period of exposure (Eq. 2.1).

3.5 Quality Control

Some tubes were used as laboratory and field blanks at each sampling period. Laboratory blanks ($n=2$ for each studied compound) were unopened, unused and left in the refrigerator in the laboratory, while field blanks ($n=3$ for each studied compound) were prepared and taken to the field in their protective polyethylene caps during the sampling period. All blanks were extracted and analyzed in the same manner as the exposed samples to determine the possibility of contamination during sample preparation, handling and transfer to-and- from the sampling points.

All samples were blank-corrected by subtracting the mean blank amount from the sample amount using the blank data set of each period. Since the amounts found in laboratory and field blanks were generally close to each other, blank correction were made using the mean blank amount of all blanks. Average SO_2 , NO_2 and O_3 amounts measured in blanks for each sampling period are presented in Table 3.2.

Table 3.2 Average SO_2 , NO_2 and O_3 amounts (μg) measured in blanks ($n=5$ for each compound at each sampling period) (average \pm SD).

Sampling Periods	SO_2	NO_2	O_3
P1	0.02 \pm 0.01	0.09 \pm 0.12	0.03 \pm 0.01
P2	0.05 \pm 0.02	0.005 \pm 0.007	0.05 \pm 0.02
P3	0.03 \pm 0.01	0.003 \pm 0.006	0.06 \pm 0.01
P4	0.02 \pm 0.005	<i>nd</i>	0.02 \pm 0.01
P5	0.01 \pm 0.002	<i>nd</i>	0.01 \pm 0.02

nd: Not detected.

Limit of detections given by Gradko were between 0.04-0.07 $\mu\text{g S0}_4^{2-}$ for SO_2 ; 0.01 $\mu\text{g N0}_2^-$ for NO_2 ; 0.04 μg nitrate for O_3 over all sampling periods. The measurement uncertainties for the same pollutants were also reported by Gradko and they were between ± 6.9 -11%, ± 3.5 -4.4%, and $\pm 6.9\%$, respectively over all sampling periods.

A number of duplicate passive samplers for each studied pollutant were placed the same sampling site during the same exposure time to see whether all tubes are measured at the same levels for each compound. For this aim, a total of five tubes for each studied pollutant were kept side by side at the sampling site (point 29) during a week. Observed SO₂, NO₂, and O₃ concentrations at the duplicate tubes ($n=5$ for each compound) were approximately in the same levels and between 15-22, 18-22, 38-44 $\mu\text{g m}^{-3}$, respectively.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

In this chapter, ambient air concentrations of SO₂, NO₂, and O₃ measured at 49 different sites in the region are presented and their levels are compared with the long term limit values in HKDYY (2008). A total of five sampling periods, two times in summer (periods 3 and 4) and three times in winter (periods 1, 2, and 5) are compared between each other in order to investigate the seasonal variation of the pollutants. Spatial distribution of the atmospheric pollutant levels around the study region mapped out using MapInfo with Vertical Mapper software are also given in this chapter. Finally, the results are evaluated by separating the sampling points depending on the site characteristics (e.g. rural, industrial, and urban).

4.1 Ambient Air Concentrations of SO₂

SO₂ levels in air measured during five sampling periods at 49 different sites around the study area and their seasonal averages are given in Table 4.1. Atmospheric SO₂ concentrations ($\mu\text{g m}^{-3}$) were between 2 (S9) and 125 (S16) for period 1; 3 (S10) and 121 (S16) for period 2; 3 (S9) and 152 (S11) for period 3; 5 (S9, S10, S58) and 121 (S11) for period 4; and 4 (S9, S15, S23) and 136 (S4) for period 5. They showed a large variation between the sampling points, probably due to their proximity to the sources of pollutants and other environmental conditions such as air temperature and wind direction.

For all the sampling periods, measured SO₂ levels in the region were generally less than the long term limit values in present Air Quality Evaluation and Management Regulation of Turkey ($150 \mu\text{g m}^{-3}$), except obtained level at site 11 in period 3 (HKDYY, 2008). Natural gas usage for industrial utilization started in 2005 in Aliağa. Thus, measured low levels can be attributed to this change. However, it should take into account that these values were measured weekly and thus, peak values during the passive sampling periods cannot probably be detected at the sampling points.

According to HKDYY (2008), the present long limit value ($150 \mu\text{g m}^{-3}$) for SO_2 levels in ambient air were aimed to gradually be decreased until 2014 to the target limits of $20 \mu\text{g m}^{-3}$. When the data set from this study was compared with this new limit, it was shown that the levels measured at lots of sampling points exceeded the target long term limit value. In winter, SO_2 levels were found to be higher than $20 \mu\text{g m}^{-3}$ at the sites of 2, 4, 6, 11, 13, 16, 29, 33, 35, 44, 56 for period 1; 3, 4, 11, 12, 14, 16, 18, 23, 24, 29, 32, 33, 36, 39, 44, 45, 47, 48, 50, 54, 55, 56, 59 for period 2; and 1, 3, 4, 10, 11, 13, 16, 19, 20, 26, 30, 36, 48, 49 for period 5. In summer, they were observed at the sites of 11, 12, 16, 17, 18, 19, 20, 24, 25, 26, 32, 39, 45, 59 for period 3; and 4, 7, 11, 12, 16, 17, 18, 19, 24, 25, 29, 30, 33, 34, 39, 42, 45 for period 4.

Also, in order to compare the measured annual average pollutant levels with the present and target long term air quality limit values given by HKDYY (2008) (Table 2.1), obtained levels during the sampling periods ($n=5$) were then averaged for each sampling site. The overall average SO_2 levels were less than the present long term limit value for all the sampling points. However, when the obtained data set was compared with the target long term limit value for 2014, it can be said that the SO_2 levels especially at the points around the refinery and petrochemical industry, at site 25 close to the iron-steel industries, at the residential areas such as Aliğa city center and Helvacı, at site 19 on main road, and the sites of 3 (opposite the asphalt plant), 24 (Çakmaklı) and 39 (Kozbeyli road) were exceeded this long term limit value.

To see the seasonal differences in pollutant levels, average atmospheric SO_2 concentrations obtained in periods of 1, 2, and 5 (winter) and in periods of 3 and 4 (summer) were averaged for each sampling point. They ranged from 4 ± 0.2 (S15) to 114 ± 15 (S16) $\mu\text{g m}^{-3}$ in winter and from 4 ± 1 (S9) to 137 ± 22 (S11) $\mu\text{g m}^{-3}$ in summer, (average \pm SD).

The highest SO_2 levels were generally measured around petroleum refinery and petrochemical industry during both sampling periods. This may probably be due to emissions from the processes that are used fuel oil for the operations. The lowest SO_2

levels were generally measured background and rural sites in both periods, while in summer period the residential areas had also the lowest ones. Observed low levels around the residential areas during summer can be explained by the lack of emissions from residential heating during this season. For example, SO₂ level in Aliğa town center measured during winter decreased dramatically during summer, reflecting a decrease in emissions associated with residential heating (Table 4.1).

Spatial distribution maps of atmospheric SO₂ levels in the region ($n=49$) for the sampling periods of 1-5 are illustrated in Figure 4.1-4.5, respectively. The maps showed that the petroleum refinery and petrochemical industry with the highest SO₂ levels are the major sources in the study area. However, high SO₂ concentration at S3 only for period 2 (March) was also observed (Fig. 4.2). This site was opposite to the asphalt plant. Excess asphalt production or uncontrolled production may cause peak levels at this sampling period. In winter periods, relatively higher SO₂ levels were measured around the residential areas (e.g. Aliğa town, Horozgediği, Helvacı, and Bozköy), probably due to the emissions from residential heating (Fig. 4.1, 4.2, and 4.5).

Table 4.1 SO₂ concentrations (µg m⁻³) measured during 5 sampling periods at 49 sites in the region.

Site N.	Winter				Summer		
	P1	P2	P5	Avg±SD	P3	P4	Avg±SD
S1	7	7	65	26±34	4	7	6±2
S2	40	4	18	21±18	6	9	8±2
S3	6	116	38	53±57	8	7	8±0.1
S4	36	73	136	82±51	13	45	29±23
S5	4	5	8	6±2	8	6	7±1
S6	28	8	8	15±12	6	8	7±2
S7		13	13	13±0.3	10	27	18±13
S9	2	6	4	4±2	3	5	4±1
S10	7	3	47	19±25	5	5	5±0.1
S11	73	115	90	93±21	152	121	137±22
S12	15	34	19	23±10	38	21	29±12
S13	28	19	22	23±5	11	10	11±0.0
S14	7	27	12	15±11	13	6	10±4
S15	4	4	4	4±0.2	4	9	7±4
S16	125	121	96	114±15	36	74	55±27
S17	12	12	19	14±4	50	62	56±8
S18	16	34	17	22±10	110	50	80±42
S19	14	17	22	18±4	23	26	25±2
S20	13	16	20	16±3	27	14	21±10
S22	6	14	7	9±4	10	6	8±2
S23	6	34	4	15±17	5	8	7±2
S24	16	25	13	18±6	44	25	35±13
S25	15	14	15	15±0.4	30	27	28±2
S26	17	15	21	17±3	30	15	22±10
S29	24	21	5	16±10	12	24	18±8

Site N.	Winter				Summer		
	P1	P2	P5	Avg±SD	P3	P4	Avg±SD
S30	7	11	28	15±11	4	20	12±11
S32	16	30	13	19±9	20	19	20±0.4
S33	20	23	5	16±10		23	23
S34	9	15	12	12±3	19	25	22±5
S35	27	15	13	19±8	12	10	11±1
S36	10	27	22	20±9	10	16	13±4
S37		7	12	10±4	8	7	8±1
S39	14	28	14	19±8	23	32	28±6
S42	5	10	8	8±2	8	23	15±11
S43	19	13	11	15±4	13	10	11±2
S44	29	40	17	29±12	12	12	12±1
S45	8	24	9	14±9	30	27	29±2
S46		15	9	12±4	10		10
S47	7	24	11	14±9	12	12	12±0.3
S48	11	35	30	25±13	9	6	7±2
S49	11	11	24	15±7	16	19	17±2
S50	9	32	7	16±14	9	10	9±0.3
S53	7	11	11	10±2	18	17	17±0.5
S54	12	20	17	16±4	8	9	8±1
S55	16	21	11	16±5	7	10	8±2
S56 (A)	38	39		38±1	13	12	13±1
S57 (AB)		11		11			
S58 (i-1)	5	8	12	8±3	8	5	7±2
S59 (i-2)	7	25	5	12±11	27	17	22±7

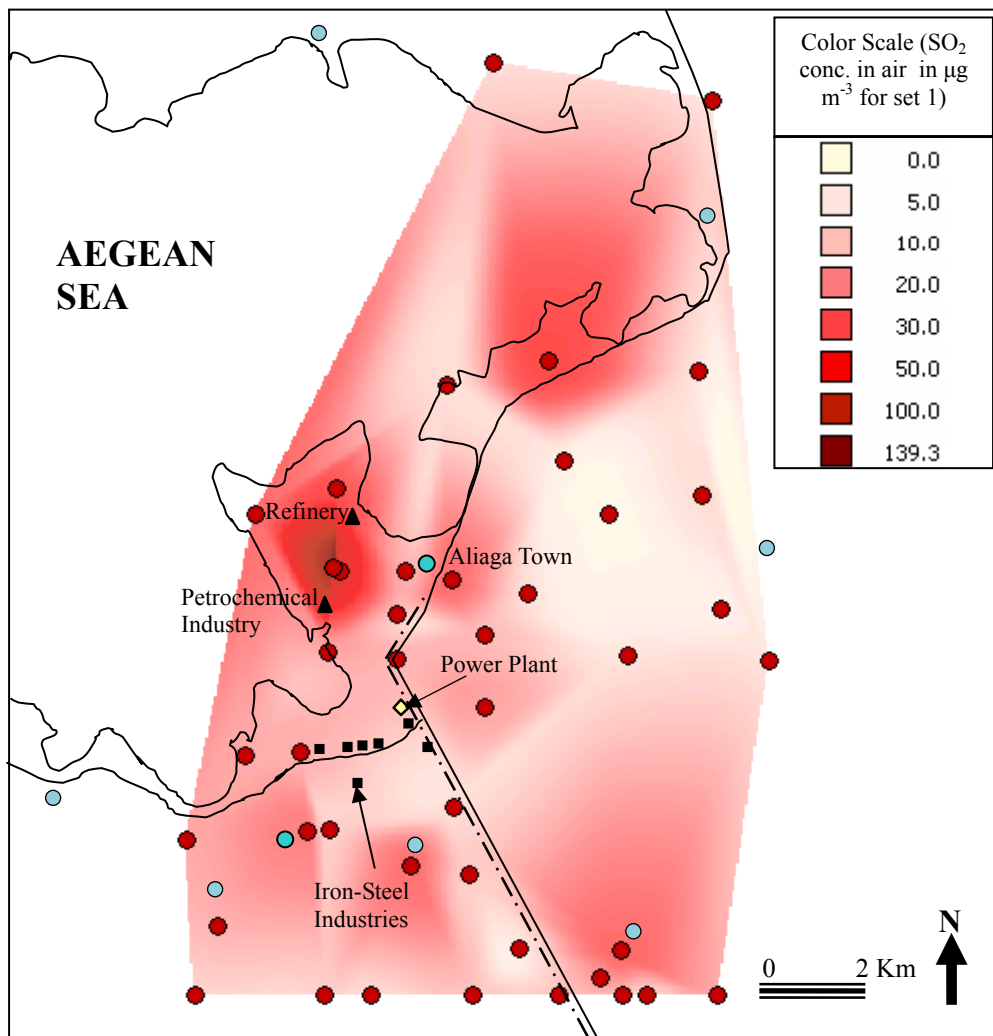


Figure 4.1 Spatial distribution map of atmospheric SO₂ levels (µg m⁻³) for set 1 ($n=49$). (●: sampling points, ○: residential areas).

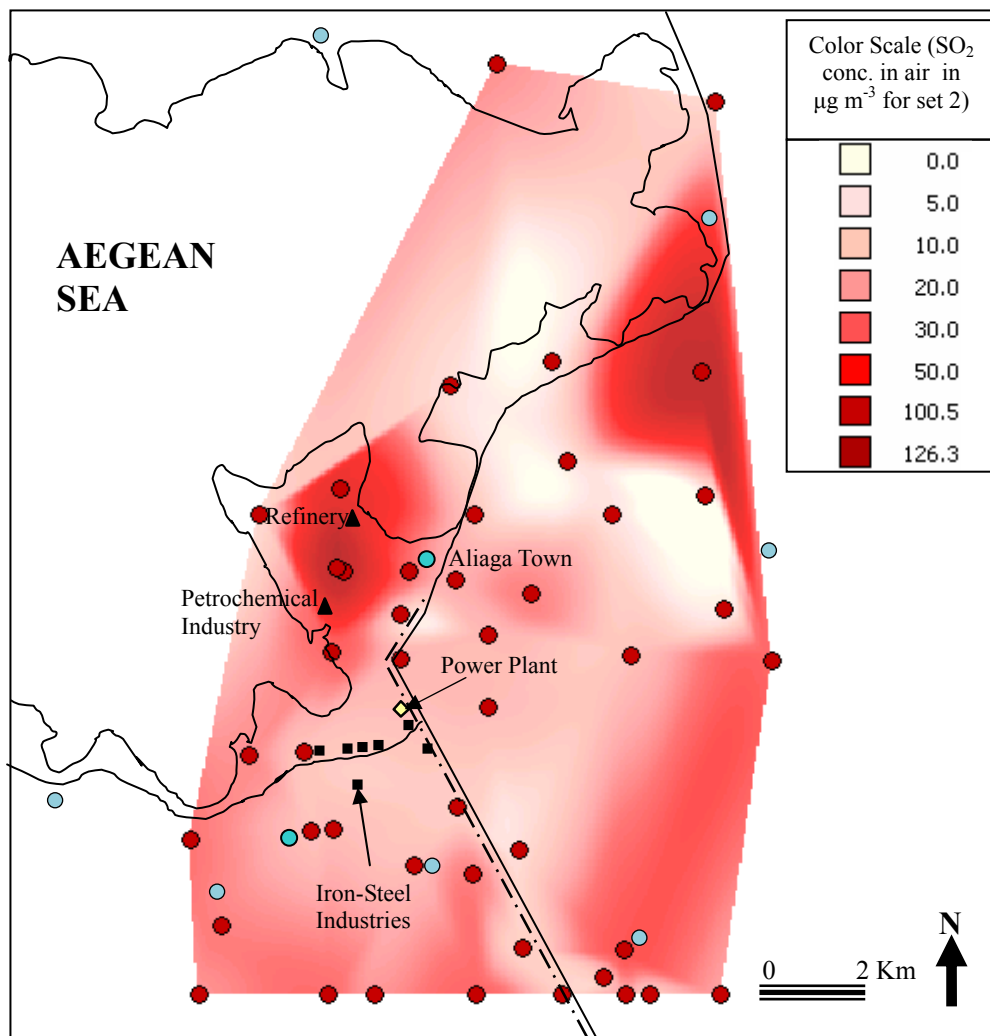


Figure 4.2 Spatial distribution map of atmospheric SO₂ levels ($\mu\text{g m}^{-3}$) for set 2 ($n=49$). (●: sampling points, ○: residential areas).

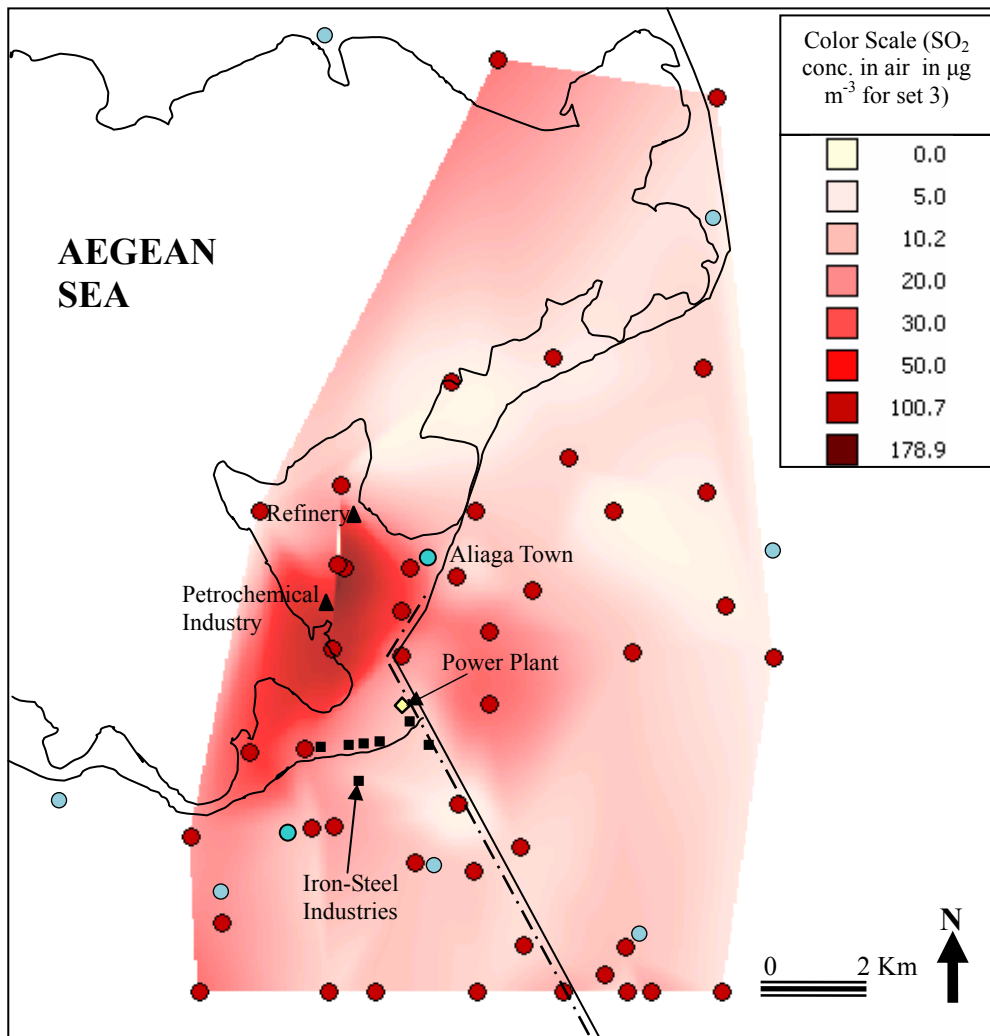


Figure 4.3 Spatial distribution map of atmospheric SO₂ levels ($\mu\text{g m}^{-3}$) for set 3 ($n=49$). (●: sampling points, ○: residential areas).

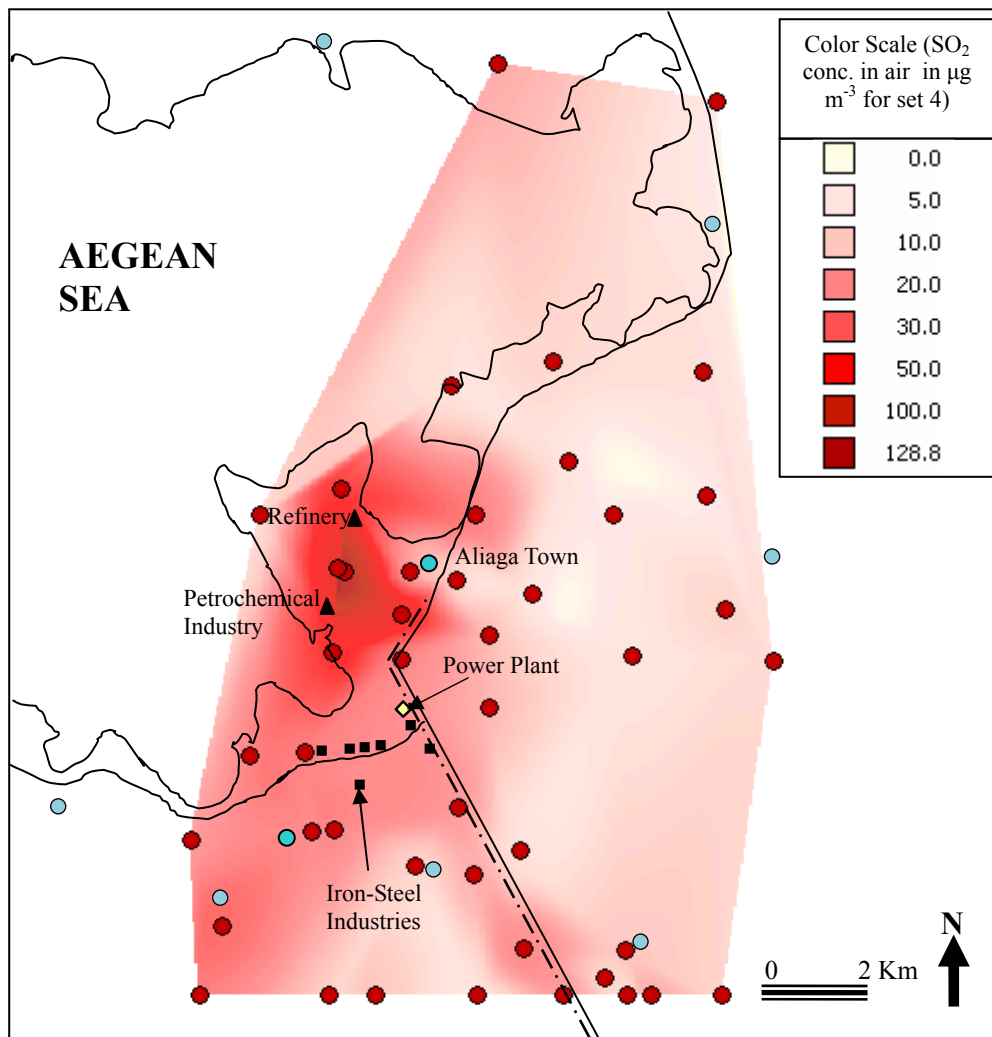


Figure 4.4 Spatial distribution map of SO₂ concentrations in air in $\mu\text{g m}^{-3}$ for set 4 (n=49). (●: sampling points, ●: residential areas).

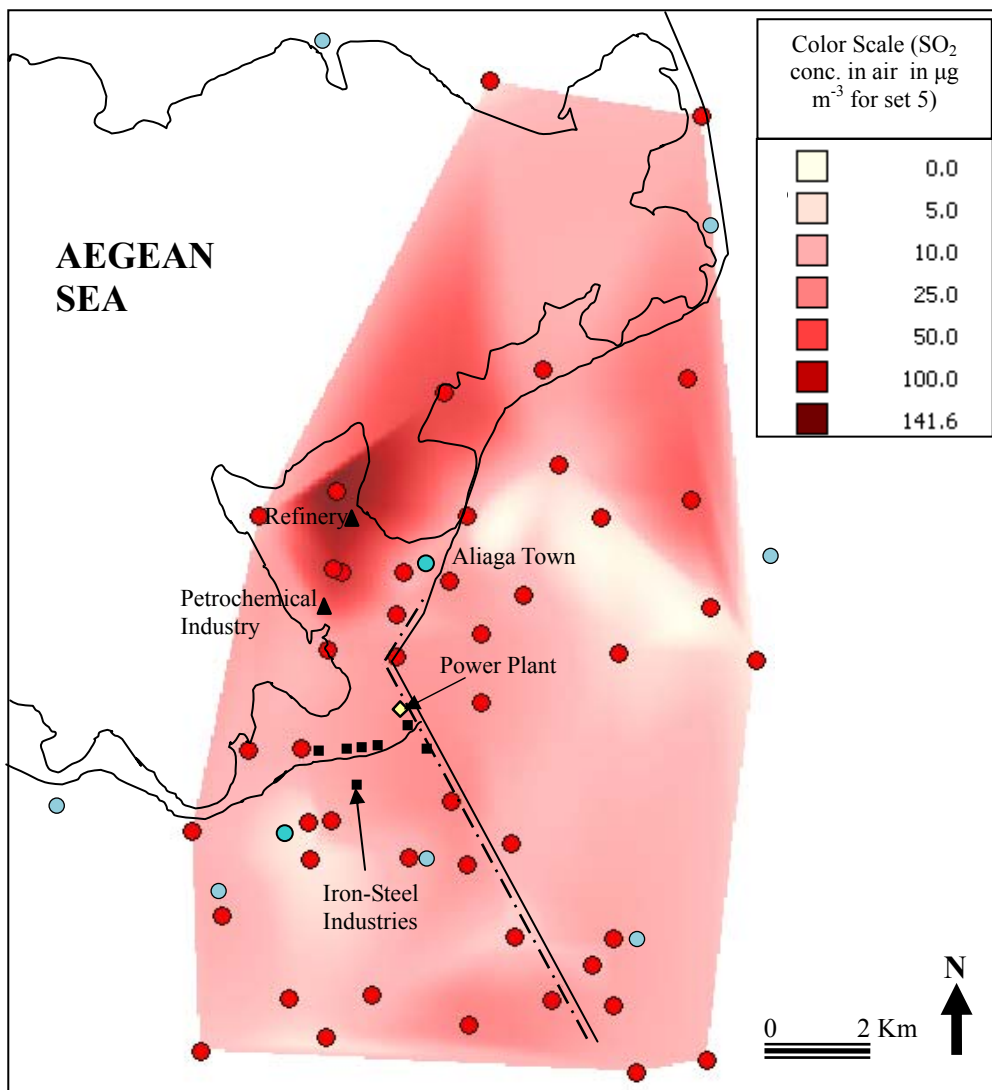


Figure 4.5 Spatial distribution map of atmospheric SO₂ levels (µg m⁻³) for set 5 ($n=49$). (●: sampling points, ○: residential areas).

4.2 Ambient Air Concentrations of NO₂

Atmospheric NO₂ levels measured during five sampling periods at 49 different sites in the region and their seasonal averages are given in Table 4.2. NO₂ concentrations showed a large variation among the sampling points, and they ranged from 4 (S2, S15, S23) to 42 (S25) for period 1; 1 (S6) to 48 (S53) for period 2; 5 (S2, S23) to 63 (S53) for period 3; 1 (S17) to 47 (S53) for period 4; and 0.4 (S17, S50) to 48 (S25) µg m⁻³ for period 5.

For all sampling periods, NO₂ levels measured in the region ($n=49$) were less than the present long term limit value of 100 in HKDYY (2008). When the data set was compared the target (2024) long term limit value of 40 $\mu\text{g m}^{-3}$, measured levels at the sites of 25 for period 1; 19, 25, 49, 53 for period 2; 18, 53 for period 3; 53 for period 4; and 4, 19, 25, 53 for period 5 exceeded this limit.

To compare the measured annual average NO₂ levels with the present and target long term air quality limit values given by HKDYY (2008) (Table 2.1), obtained levels during the sampling periods ($n=5$) were also averaged for each sampling site. It may be said that the overall average NO₂ levels were low at all sites around Aliğa. Their values were lower than the long term limits given for the years of 2008-2014. But considering the target long term limit value for 2024, it was seen that the levels measured at the points on İzmir-Çanakkale highway and at site 25 on Yeni Foça road with intensive transportation activity of scrap iron materials were exceeded or close to this target value.

Atmospheric NO₂ concentrations obtained in periods of 1, 2, and 5 (winter) and in periods of 3 and 4 (summer) were averaged for each sampling point. They ranged from 5 ± 1 (S3, S15, and S23) to 45 ± 3 (S25) $\mu\text{g m}^{-3}$ in winter and from 4 ± 3 (S59) to 55 ± 11 (S53) $\mu\text{g m}^{-3}$ in summer (Table 4.2).

The highest NO₂ levels in winter were measured at site 25. This site was located on the road with a very dense transportation activity of scrap iron trucks. High NO₂ levels were also observed at the sites of 53, 19, 49, 56, and 11, respectively. Site 11 was around refinery. Sites 19, 49, and 53 were on İzmir-Çanakkale highway and site 56 was in Aliğa town center where the traffic would be expected intensive. Generally, high NO₂ levels were also observed at these points during summer. In this period, the highest levels were measured at site 53, followed by 19, 25, 11, 49, 42, and 18. Site 42 was also on the highway and site 18 was around petrochemical industry. Low NO₂ concentrations were generally observed at background and rural sites (e.g. S2, S58, and S59) during both seasons (Table 4.2).

Table 4.2 NO₂ concentrations ($\mu\text{g m}^{-3}$) measured during 5 sampling periods at 49 sites in the region.

Site N.	Winter				Summer		
	P1	P2	P5	Avg \pm SD	P3	P4	Avg \pm SD
S1	6	10	12	10 \pm 3	7	7	7 \pm 0.3
S2	4	6	7	6 \pm 2	5	4	5 \pm 1
S3	5	5	6	5 \pm 1	9	6	8 \pm 2
S4	17	22	43	27 \pm 14	8	15	11 \pm 5
S5	6	6	10	7 \pm 2	7	18	12 \pm 8
S6	11	1	16	9 \pm 7	6	7	7 \pm 0.5
S7		28	30	29 \pm 2	24	27	25 \pm 2
S9	5	7	8	7 \pm 2	6	6	6 \pm 0.0
S10	6	6	8	7 \pm 1	6	7	6 \pm 0.5
S11	26	29	37	31 \pm 6	36	36	36 \pm 0.3
S12	13	18	31	21 \pm 9	15	13	14 \pm 2
S13	21	30	33	28 \pm 7	17	19	18 \pm 2
S14	6	10	8	8 \pm 2	7	3	5 \pm 3
S15	4	6	5	5 \pm 1	6	5	5 \pm 0.5
S16	31	31	18	27 \pm 7	15	17	16 \pm 1
S17	15	18	0.4	11 \pm 10	17	1	9 \pm 11
S18	18	20	21	19 \pm 2	42	17	30 \pm 18
S19	31	47	40	39 \pm 8	35	39	37 \pm 3
S20	9	10	11	10 \pm 1	11	8	10 \pm 2
S22	5	8	6	6 \pm 1	8	6	7 \pm 1
S23	4	6	4.7	5 \pm 1	5	5	5 \pm 0.2
S24	21	20	17	19 \pm 3	22	20	21 \pm 2
S25	42	45	48	45 \pm 3	33	39	36 \pm 4
S26	9	11	7	9 \pm 2	11	8	9 \pm 2
S29	22	23	15	20 \pm 4	17	16	17 \pm 1

Site N.	Winter				Summer		
	P1	P2	P5	Avg \pm SD	P3	P4	Avg \pm SD
S30	16	35	36	29 \pm 11	21	25	23 \pm 2
S32	15	19	11	15 \pm 4	13	14	14 \pm 1
S33	17	19	12	16 \pm 4		15	15
S34	24	21	17	21 \pm 3	20	22	21 \pm 1
S35	12	21	12	15 \pm 6	18	15	17 \pm 2
S36	16	21	15	17 \pm 4	16	17	16 \pm 0.5
S37	11	16	14	14 \pm 3	8	11	10 \pm 2
S39	16	18	13	15 \pm 3	17	14	16 \pm 2
S42	26	32	25	27 \pm 4	35	29	32 \pm 4
S43	14	19	12	15 \pm 3	14	14	14 \pm 0.1
S44	20	20	17	19 \pm 2	12	13	12 \pm 1
S45	16	18	13	15 \pm 2	18	15	16 \pm 2
S46		20	15	18 \pm 4	14		14
S47	15	15	12	14 \pm 2	13	14	13 \pm 1
S48	13	17	17	16 \pm 3	12	10	11 \pm 1
S49	27	43	39	36 \pm 8	34	37	35 \pm 2
S50	18	23	0.4	14 \pm 12	21	13	17 \pm 5
S53	37	48	45	43 \pm 6	63	47	55 \pm 11
S54	15	19	16	17 \pm 2	16	13	15 \pm 2
S55	13	17	12	14 \pm 3	14	9	12 \pm 4
S56 (A)	26	38		32 \pm 8		27	27
S57 (AB)		25		25			
S58 (i-1)	12	18	13	15 \pm 3	8	9	9 \pm 1
S59 (i-2)	7	13	8	9 \pm 3	6	2	4 \pm 3

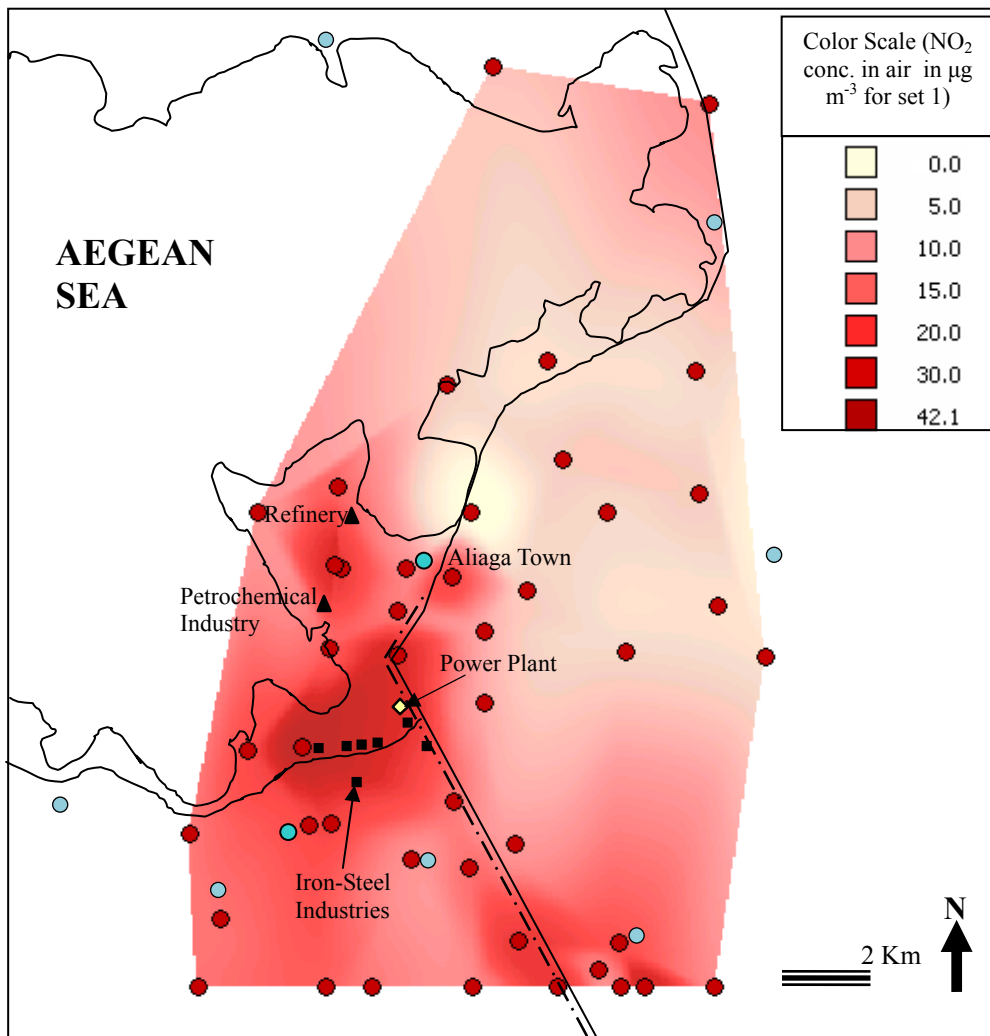


Figure 4.6 Spatial distribution map of atmospheric NO₂ levels ($\mu\text{g m}^{-3}$) for set 1 ($n=49$). (●: sampling points, ○: residential areas).

Spatial distribution maps of atmospheric NO₂ levels in the region ($n=49$) for the sampling periods of 1-5 are illustrated in Figure 4.6-4.10, respectively. The maps showed that İzmir-Çanakkale highway, Yeni Foça road, Aliaga town, the petroleum refinery and petrochemical industry with high NO₂ levels are the major sources in the study area.

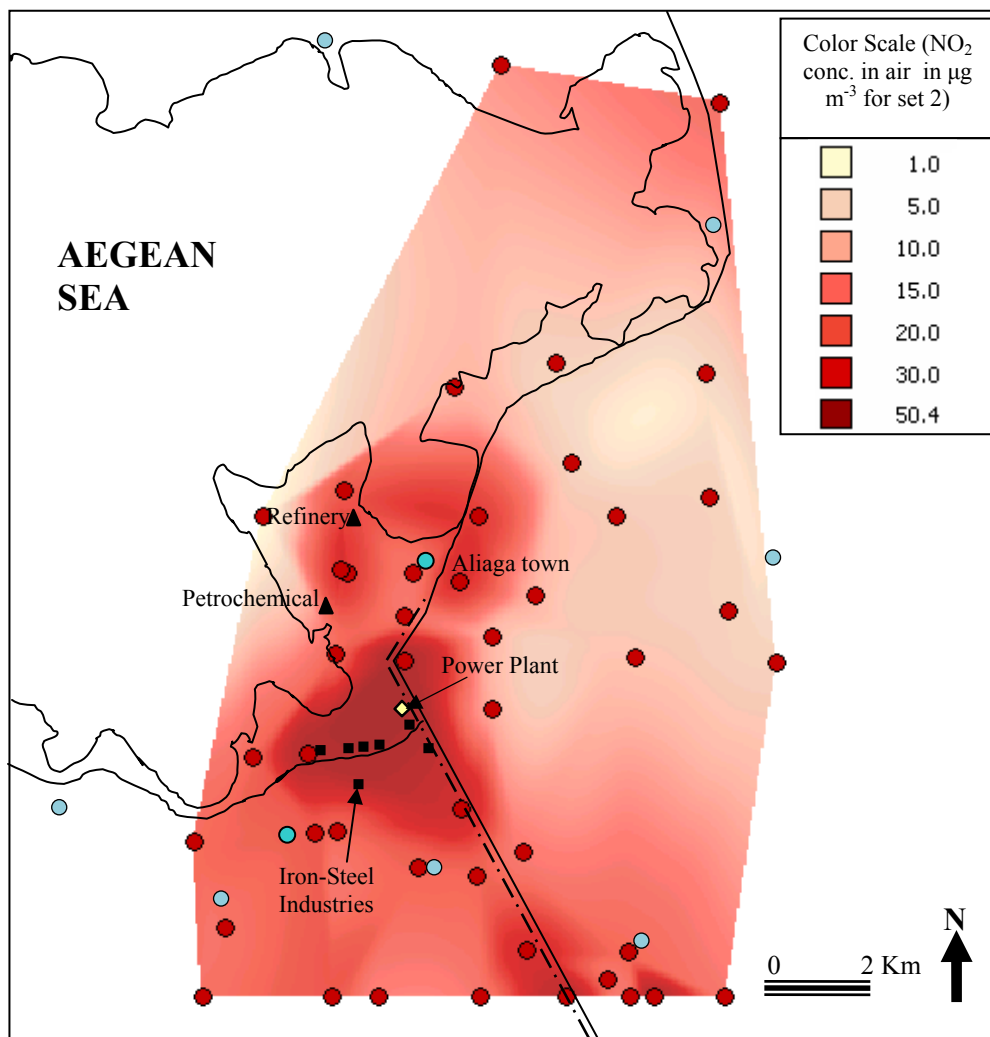


Figure 4.7 Spatial distribution map of atmospheric NO₂ levels ($\mu\text{g m}^{-3}$) for set 2 ($n=49$). (●: sampling points, ○: residential areas).

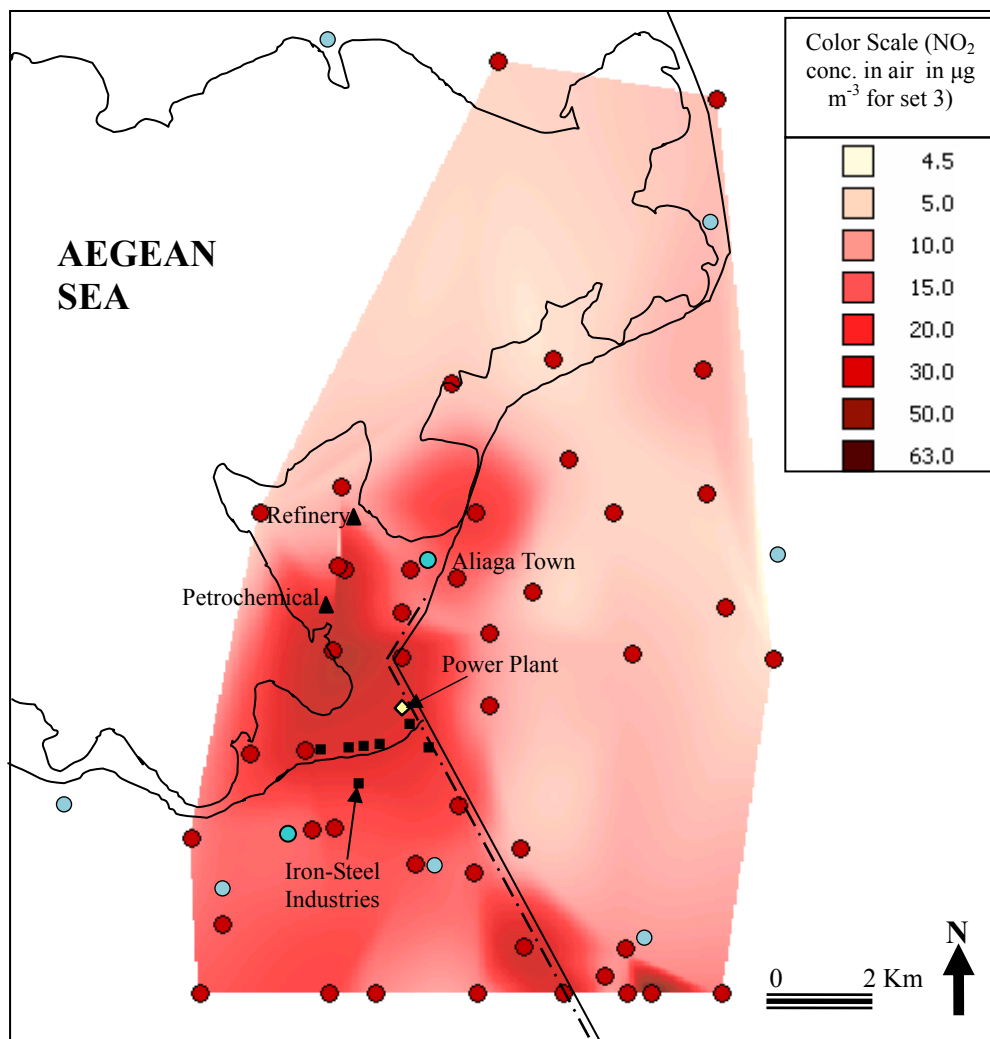


Figure 4.8 Spatial distribution map of atmospheric NO₂ levels ($\mu\text{g m}^{-3}$) for set 3 ($n=49$). (●: sampling points, ○: residential areas).

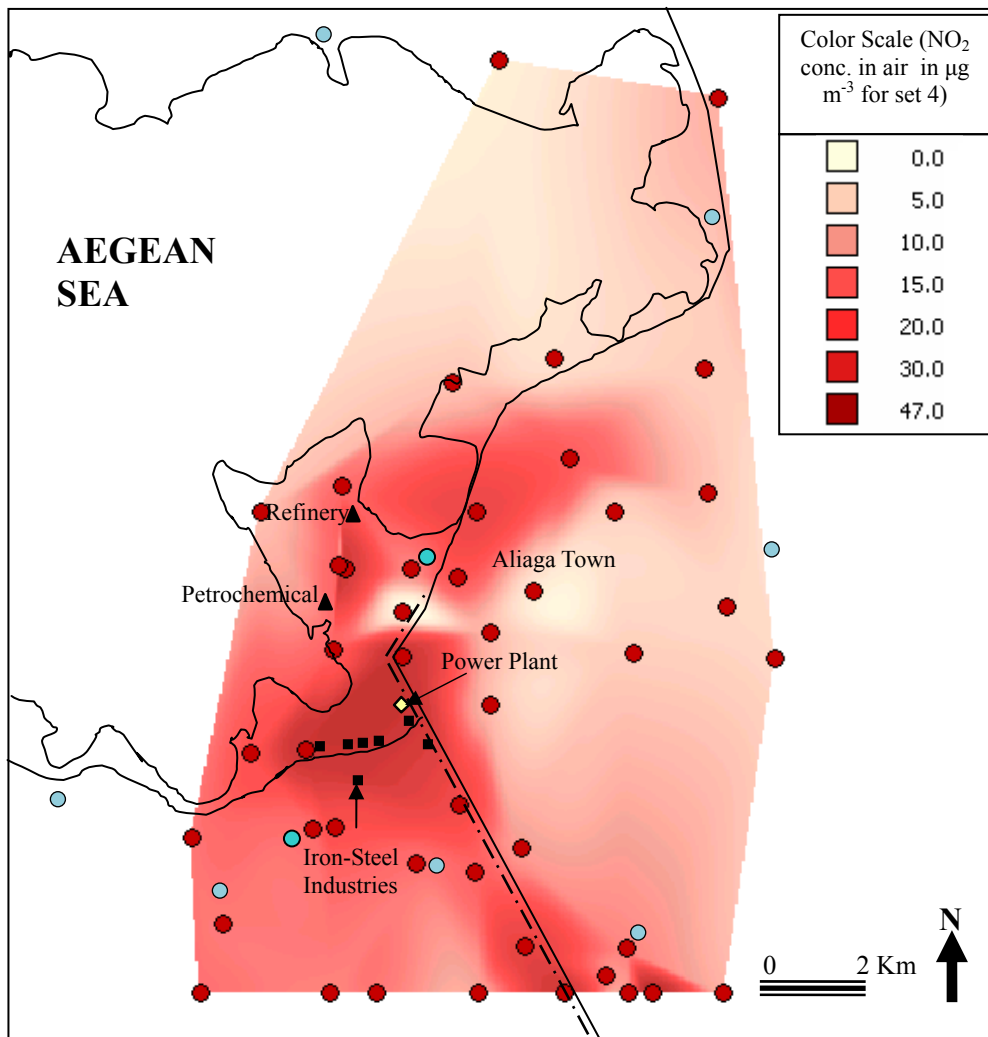


Figure 4.9 Spatial distribution map of atmospheric NO₂ levels (µg m⁻³) for set 4 ($n=49$). (●: sampling points, ○: residential areas).

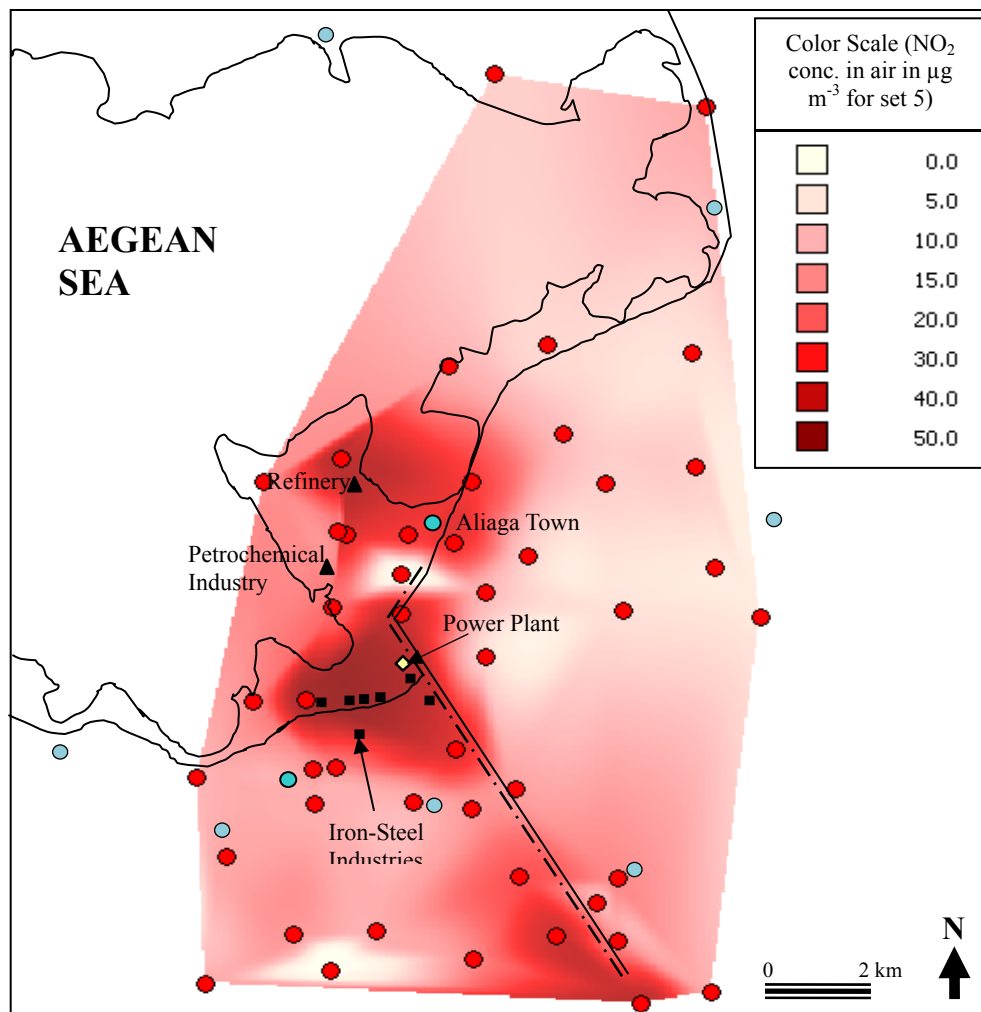


Figure 4.10 Spatial distribution map of atmospheric NO₂ levels (µg m⁻³) for set 5 ($n=49$). (●: sampling points, ○: residential areas).

4.3 Ambient Air Concentrations of O₃

Atmospheric O₃ levels measured during five sampling periods at 49 different sites in the region and their seasonal averages are presented in Table 4.3. O₃ levels in air (µg m⁻³) showed a large variation between the sampling points and they ranged from 10 (S53) to 62 (S1, S20) for period 1; 21 (S19, S25) to 90 (S37) for period 2; 2 (S24) to 147 (S44, S45, S54) for period 3; 59 (S49) to 136 (S12) for period 4; and 24 (S25) to 82 (S26) for period 5. It should be considered that these ozone levels were obtained using weekly measurements. So, it can be said that hourly O₃ concentrations (especially at midday hours) would probably be higher than the observed levels.

For all sampling periods, measured O₃ levels in the region were generally less than the target (2022) long term limit values of 120 µg m⁻³ in HKDYY (2008), except obtained levels in summer at sites of 1, 2, 4, 10, 12, 14, 16, 22, 23, 26, 29, 30, 35, 36, 39, 43, 44, 45, 47, 48, 50, 54, 55, 56, 58 and 59 in period 3, and at sites of 4, 12, 15, 54 in Period 4. All measured ozone levels in winter were lower than this limit value (Table 4.3).

To compare the measured annual average ozone levels with the target long term air quality limit value of 120 µg m⁻³ in HKDYY (2008) (Table 2.1), obtained levels during the sampling periods ($n=5$) were also averaged for each sampling site. It may be said that the overall average ozone values around the study area were under this limit value.

To see the seasonal differences in pollutant levels, atmospheric O₃ concentrations obtained in periods of 1, 2, and 5 (winter) and in periods of 3 and 4 (summer) were averaged for each sampling point. They ranged from 24±3 (S25) to 87 (S57) µg m⁻³ in winter and from 46±62 (S24) to 134±18 (S54) µg m⁻³ in summer. Observed low ozone levels in winter season may probably because of the solar radiation decline. Much higher ozone levels measured during summer season may be attributed to its formation in the presence of precursors and sunlight. In winter, the highest O₃ concentrations measured at site 57 (around the power plant), followed by 56, 59, 45, and 35, respectively. S13 and S19 had the lowest levels. In summer, the highest ozone levels were measured site 54 (rural), followed by sites of 44, 45, 12, 4, 43, 47, 58, 56, 55, 15, and 10, respectively. Sites of 24, 25, 32, 37, 49 and 53 had the lowest levels in this season (Table 4.3).

Table 4.3 O₃ concentrations ($\mu\text{g m}^{-3}$) measured during 5 sampling periods at 49 sites in the region.

Site N.	Winter				Summer		
	P1	P2	P5	Avg±SD	P3	P4	Avg±SD
S1	62	55	75	64±10	137	101	119±26
S2	59	52	62	57±5	127	104	115±16
S3	52	45	69	55±12	114	102	108±9
S4	59	52	62	58±5	130	126	128±3
S5	52	45	73	57±14	107	94	101±9
S6	45	38	58	47±10	111	115	113±3
S7		38	55	46±12	89	118	103±21
S9	52	45	59	52±7	107	98	102±6
S10	35	28	59	40±16	121	119	120±1
S11	41	35	55	44±10	96	84	90±8
S12	48	42	58	49±8	120	136	128±12
S13	35	28	44	36±8	99	80	90±14
S14	45	38	79	54±22	127	112	119±11
S15	55	48	79	61±16	116	126	121±7
S16	55	49	69	58±10	131	84	108±34
S17	38	31	59	43±14	111	91	101±14
S18	52	45	62	53±9	107	109	108±1
S19	27	21	38	29±9	111	81	96±21
S20	62	55	69	62±7	103	101	102±1
S22	48	42	69	53±14	137	108	123±20
S23	52	45	62	53±8	123	91	107±23
S24	41	35	69	48±18	2	91	46±62
S25	27	21	24	24±3	100	70	85±21
S26	45	38	82	55±24	130	101	116±20
S29	34	76	68	60±22	130	102	116±20

Site N.	Winter				Summer		
	P1	P2	P5	Avg±SD	P3	P4	Avg±SD
S30	52	62	37	50±12	120	90	105±21
S32	45	80	55	60±18	61	105	83±31
S33	52	80	65	66±14		119	119
S34	38	83	62	61±23	117	98	107±14
S35	58	73	75	69±9	120	101	111±13
S36	48	69	58	59±11	120	98	109±16
S37	51	90	58	66±21	44	104	74±43
S39	48	76	72	66±15	120	98	109±16
S42	27	52	48	42±13	113	101	107±9
S43	21	76	75	57±32	140	115	127±18
S44	31	79	58	56±24	147	118	133±21
S45	48	84	79	70±19	147	114	131±23
S46		80	72	76±6	106		106
S47	48	77	69	65±15	137	111	124±18
S48	35	66	34	45±18	133	80	106±38
S49	51	38	34	41±9	102	59	81±31
S50	48	70	65	61±11	137	101	119±26
S53	10	38	41	30±17	57	80	69±16
S54	38	38	62	46±14	147	121	134±18
S55	44	73	72	63±16	140	104	122±25
S56 (A)		80		80	137	109	123±20
S57 (AB)		87		87			
S58 (i-1)		70	65	68±4	144	104	124±28
S59 (i-2)		84	68	76±11	130	104	117±19

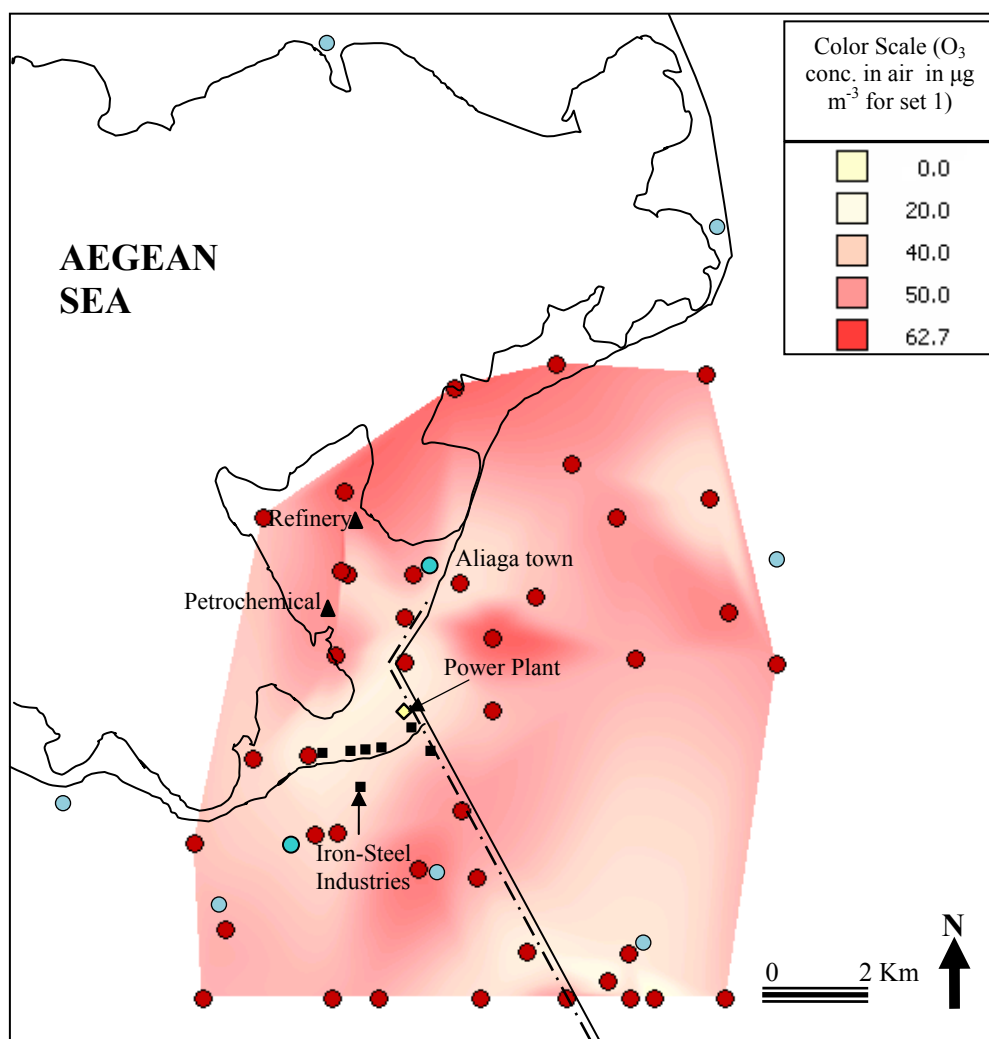


Figure 4.11 Spatial distribution map of O_3 concentrations ($\mu\text{g m}^{-3}$) in air for set 1 ($n=49$). (●: sampling points, ●: residential areas).

Spatial distribution maps of atmospheric O_3 levels in the region ($n=49$) for the sampling periods of 1-5 are illustrated in Figure 4.11-4.15, respectively. The maps showed that the sampling sites on the highway and around the iron-steel industries, petroleum refinery, petrochemical industry and town center with high NO_2 concentrations had the lowest ozone levels. However, high O_3 concentrations were generally observed at the background and rural sites. Measured low ozone levels at the roadsides or urban sites are probably due to the reaction between ozone (O_3) and nitric oxide (NO) which goes on producing NO_2 especially at roadsides where nitric oxide concentrations are relatively high and sufficient ozone is present (Helaleh, Ngudiwaluyo, Korenaga, & Tanaka, 2002).

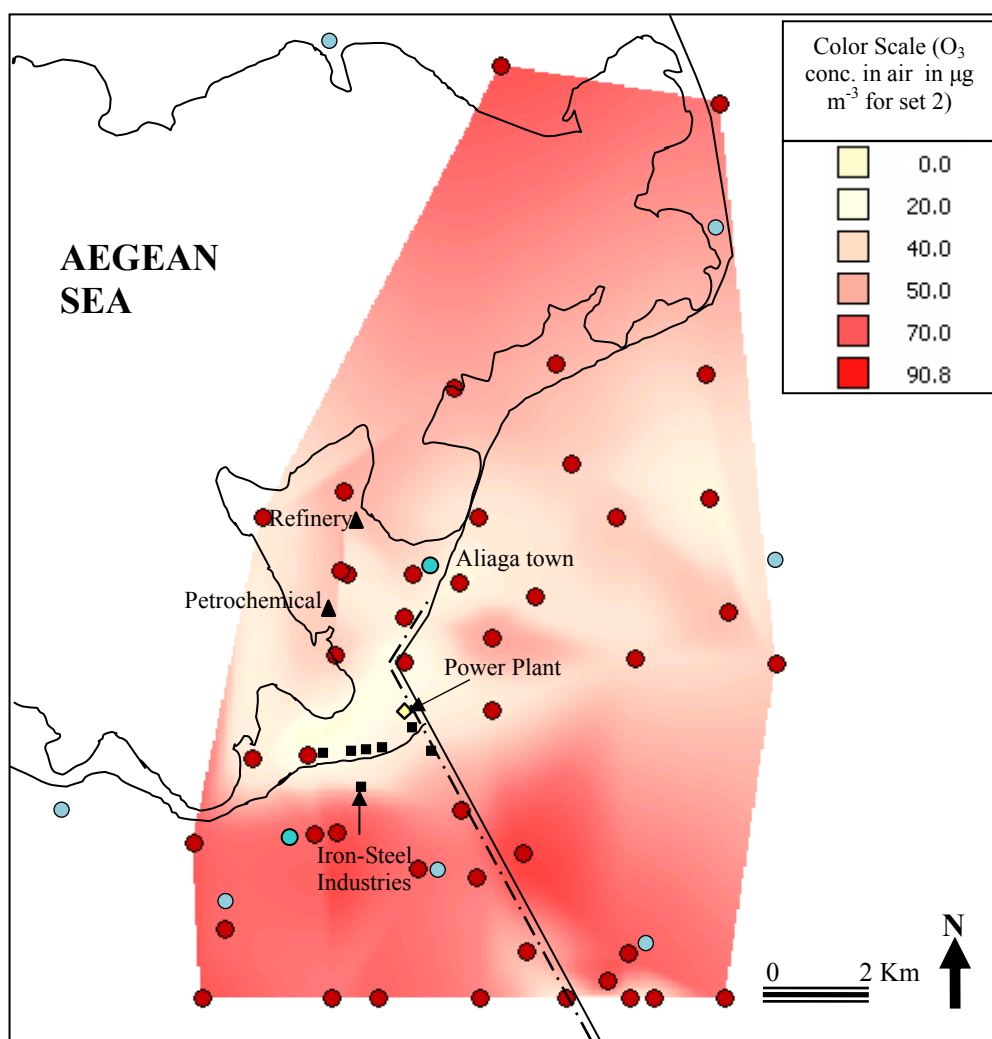


Figure 4.12 Spatial distribution map of O_3 concentrations ($\mu\text{g m}^{-3}$) in air for set 2 ($n=49$). (●: sampling points, ●: residential areas).

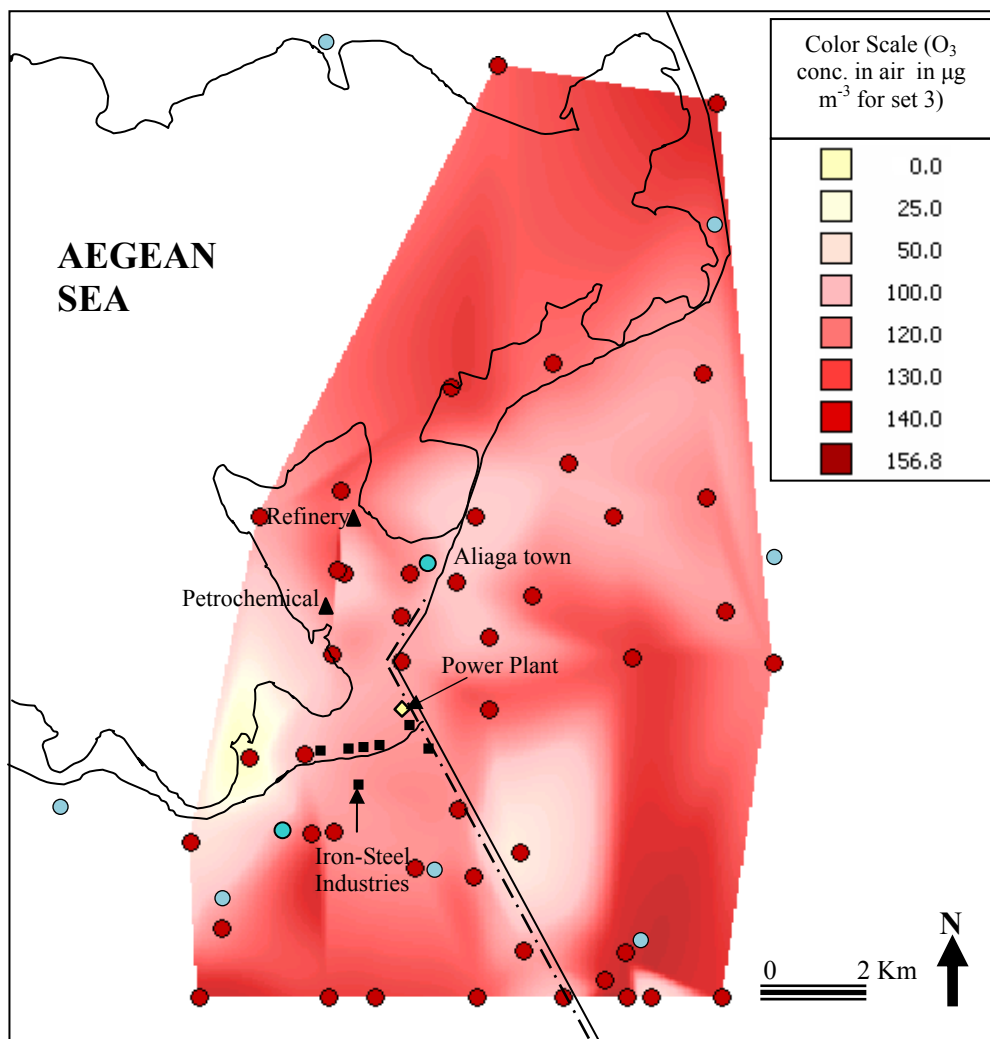


Figure 4.13 Spatial distribution map of O_3 concentrations ($\mu\text{g m}^{-3}$) in air for set 3 ($n=49$). (●: sampling points, ●: residential areas).

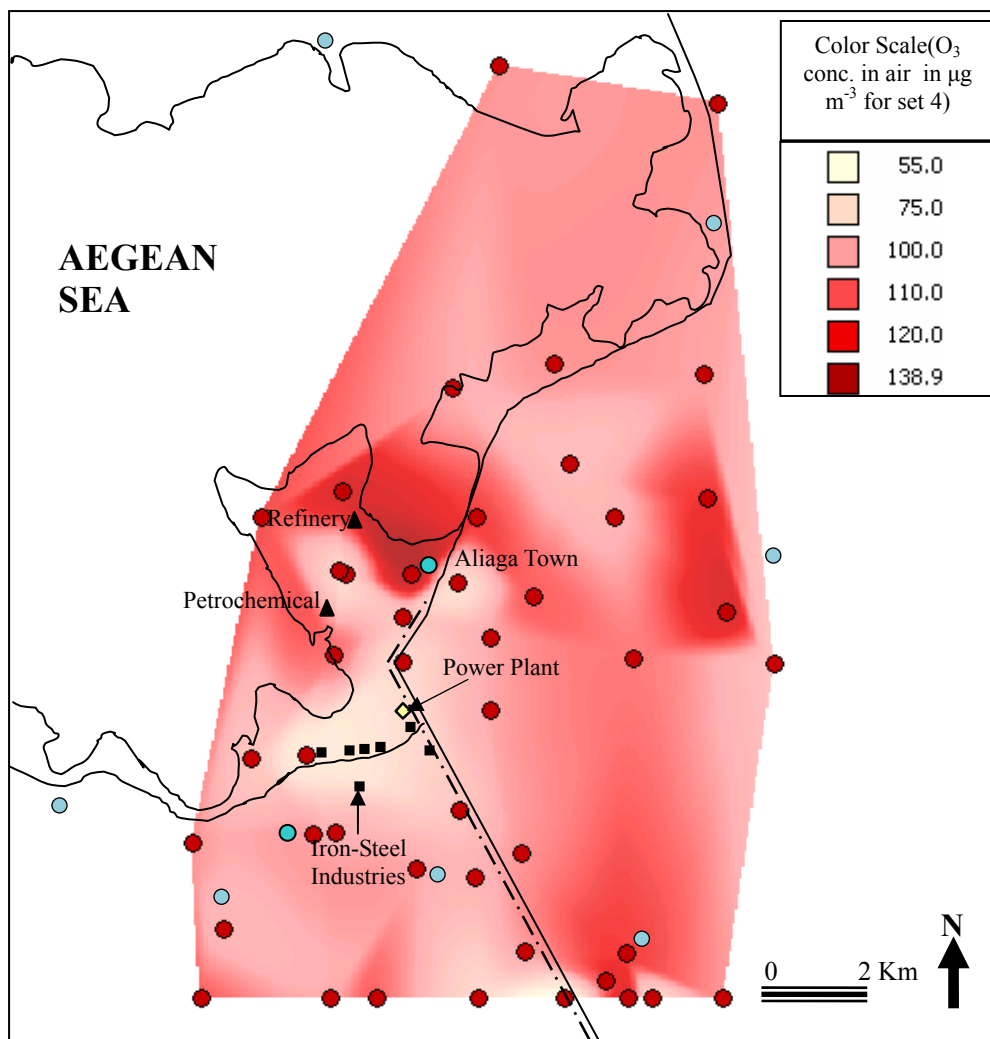


Figure 4.14 Spatial distribution map of O₃ concentrations ($\mu\text{g m}^{-3}$) in air for set 4 (n=49). (●: sampling points, ●: residential areas).

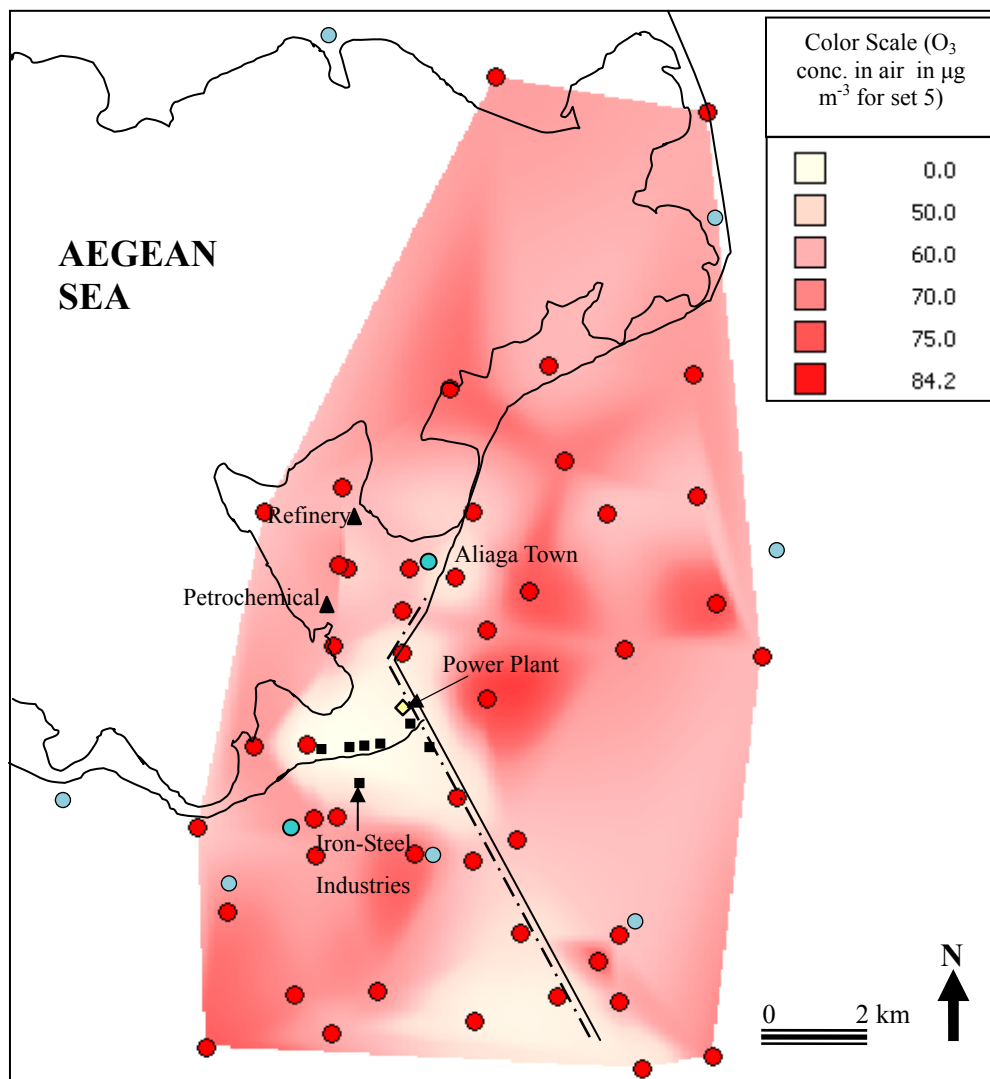


Figure 4.15 Spatial distribution map of O_3 concentrations ($\mu\text{g m}^{-3}$) in air for set 5 ($n=49$). (●: sampling points, ●: residential areas).

4.4 Pollutant Concentrations Depending on the Site Classification

In this study, all the sampling sites ($n=49$) were classified as industrial, roadside, urban, and rural depending on the site characteristics. This classification is based on the proximity to major industrial sources of petroleum refinery/petrochemicals, iron-steel plants, main roads, and no close by industries which are named rural. Also industrial sites were separated into two main groups i) iron-steel plants and ii) refinery and petrochemical industry. Since the northerly winds were prevailing in the region, rural sites were also classified as downwind and upwind of the main pollutant

sources (i.e. iron-steel plants, refinery, and petrochemical industry).

According to this classification, list of the sampling sites at each category are given in Table 4.4 and average atmospheric concentrations determined for SO₂, NO₂, and O₃ during all the sampling periods ($n=5$) are given in Table 4.5. Locations of the sampling points are illustrated in Figure 3.3.

Table 4.4 List of the sampling points at each category.

Site Classification		Site No
Industrial	Refinery-Petrochemical Industry	4, 6, 11, 12, 16, 17, 18
	Iron-Steel	25, 29, 32, 33, 34
Roadside		19, 30, 36, 37, 42, 48, 49, 53, 57, 58
Urban		7, 13, 20, 56
Rural	Downwind	22, 24, 26, 35, 39, 43, 44, 45, 46, 47, 50, 54, 55
	Upwind	1, 2, 3, 5, 9, 10, 14, 15, 23, 59

Table 4.5 Depending on the different site characteristics, average atmospheric concentrations ($\mu\text{g m}^{-3}$, average \pm SD) of SO₂, NO₂, and O₃ measured at all the sampling periods ($n=5$).

Studied Pollutants	Industrial		Roadside	Urban	Rural	
	Refinery-Petrochemical Industry	Iron-Steel			Downwind	Upwind
SO ₂	53 \pm 36	18 \pm 2	14 \pm 4	19 \pm 4	16 \pm 5	14 \pm 9
NO ₂	19 \pm 8	22 \pm 13	26 \pm 12	23 \pm 9	14 \pm 3	7 \pm 1
O ₃	74 \pm 8	72 \pm 14	70 \pm 15	77 \pm 32	82 \pm 11	80 \pm 8

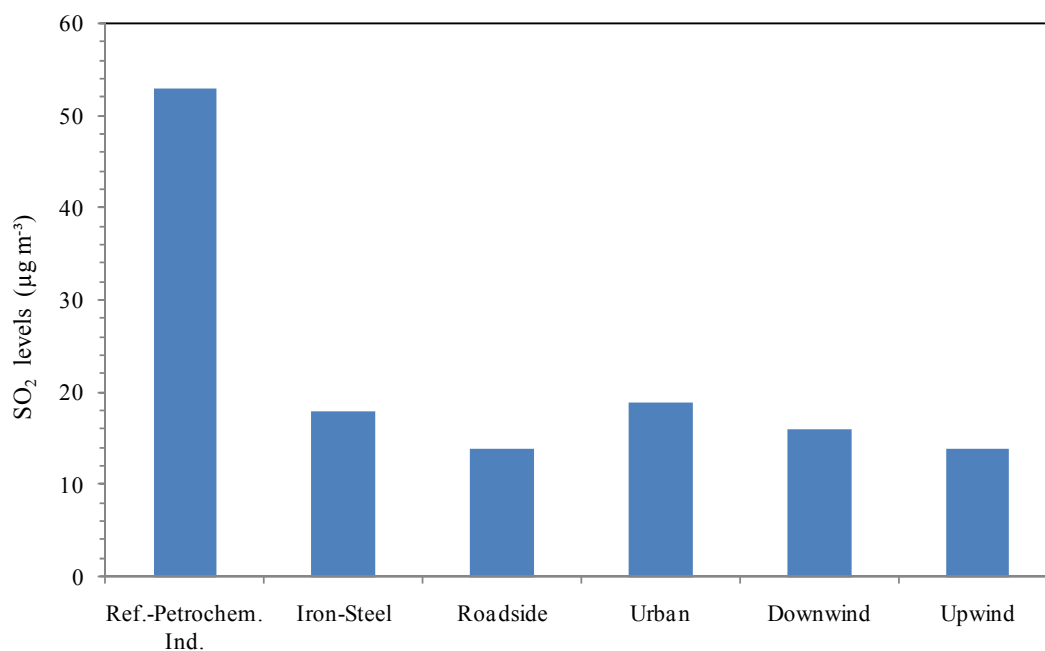


Figure 4.16 Average SO₂ concentrations depending on the different site characteristics in the region.

The average atmospheric concentrations of NO₂ and SO₂ (Table 4.5) were found to be higher around the industrial and urban sites than those measured at the rural sites in the region. The average atmospheric NO₂ levels at roadsides was also observed at higher levels.

Figure 4.16 shows that SO₂ levels measured around the refinery and petrochemical industry were significantly higher than those measured at the other sites. They were followed by the urban, iron-steel industries, roadsides, and rural sites, respectively. This indicated that main SO₂ sources in the region were the refinery and petrochemical industry, probably as a result of fuel oil usages at some processes. Relatively low SO₂ levels measured around the iron-steel plants can be attributed to the electrical power and natural gas usage for most of the operations in these plants, although some coal and fuel oil is also used in insignificant amounts. This is also true for refinery and petrochemicals industries, too. Measured levels around these plants can also be affected to the residential heating emissions released from nearby residential areas such as Horozgediği and Bozköy. SO₂ levels measured

at the roadsides were similar to those measured the rural sites (Fig. 4.16). This indicated that traffic emissions had no significance in terms of SO₂ pollution. However, SO₂ levels around the urban were slightly higher than the rural sites, probably because of the residential heating emissions in these areas. SO₂ concentrations at up-wind and down-wind rural sites were similar to each other (Fig. 4.16). Natural gas usage for the industrial facilities located in the region was started in 2005. Therefore, it may be said that there was no serious effect of industrial facilities to these sites.

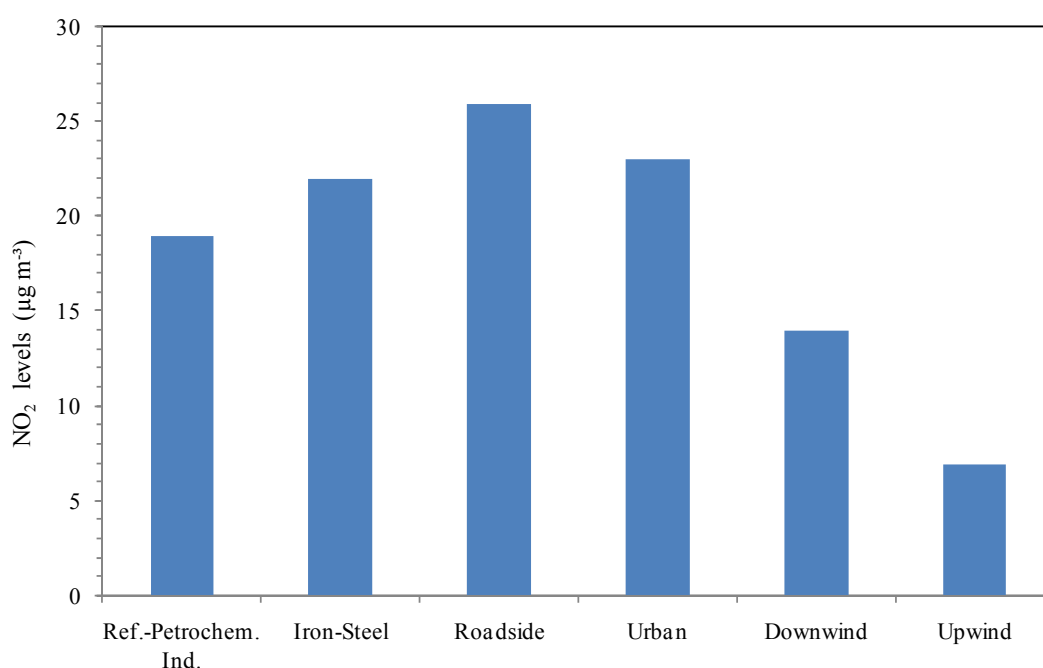


Figure 4.17 Average NO₂ concentrations depending on the different site characteristics in the region.

According to Figure 4.17, the highest NO₂ levels were found at the roadsides, followed by the urban sites, iron-steel industries, refinery and petrochemical industry, and rural sites respectively. This indicates that roadsides with traffic emissions were the main NO₂ sources in the region. Average NO₂ levels at the sites near the industrial and urban areas were found to be close to each other. This may be because of the emissions from the industrial processes and heavy traffic around the industrial areas. Average NO₂ concentrations at the rural sites were measured approximately two times higher at the down-wind sites than those measured at the up-wind sites.

This may be as a result of the higher traffic intensity at down-wind sites and prevailing northerly winds in the region.

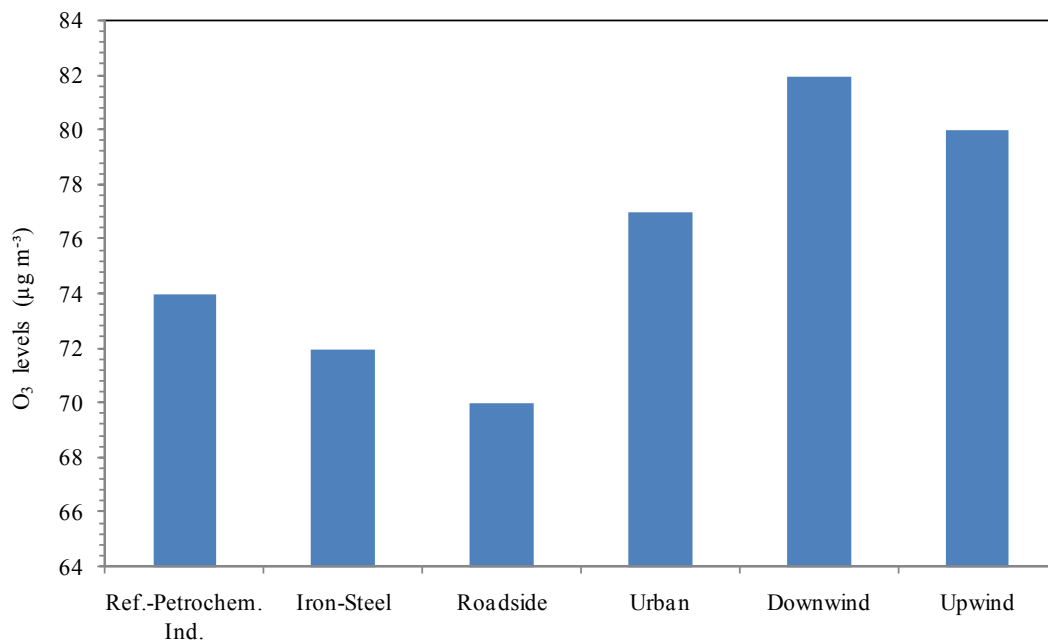


Figure 4.18 Average O₃ concentrations depending on the different site characteristics in the region.

Average ozone levels measured at the different sites in the region are illustrated in Figure 4.18. Roadside sites with the highest NO₂ pollution had the lowest ozone levels. Lower ozone concentrations are noted in areas where the concentrations of traffic exhaust gases are high, possibly the result of O₃ being trapped by NO from exhaust emission (Bernard, Gerber, Astre, & Saintot 1999; Pehnec, Vadjic, & Hrsak, 2005). The highest ozone concentrations were measured in the rural areas where local sources of ozone precursors were insignificant. In addition, ozone levels measured at down-wind rural areas were slightly higher than those measured at up-wind ones. The long-range transport of ozone and its precursors from polluted areas may be responsible for the higher ozone concentrations found in down-wind areas.

4.5 The Relationship between the Atmospheric O₃ and NO₂ Levels

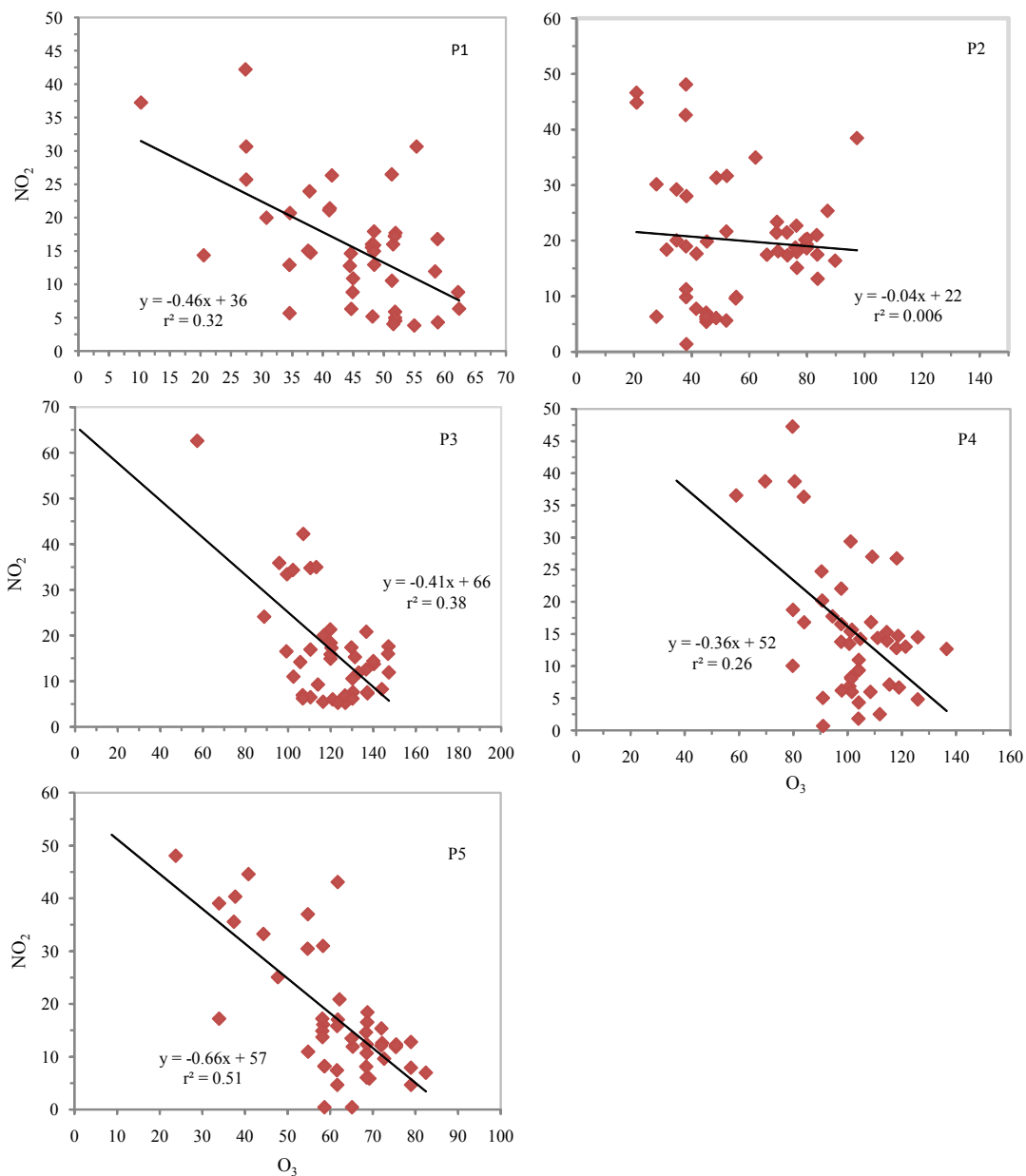


Figure 4.19 The correlations between the atmospheric O₃ and NO₂ concentrations measured five sampling periods.

The relationship between the atmospheric O₃ and NO₂ concentrations measured at all the sampling sites were investigated for each sampling period and statistically significant negative correlations ($p < 0.01$, $n = 43-49$ for each period) were found (Fig. 4.19). This is probably because ozone was formed as a result of the reactions

involving NO_x in the ambient air. Relatively weak correlation was observed only for period 2 ($r^2=0.006$, $p<0.01$, $n=49$). Figure 4.19 clearly showed that there is a reverse relationship between atmospheric NO_2 and ozone concentrations. Ozone concentration increased with decreasing NO_2 concentration in the air.

CHAPTER FIVE

CONCLUSIONS

In this study, passive samplers were used to measure the ambient air concentrations of SO₂, NO₂, and O₃ at 49 different sites in the Aliğa region. Sampling campaigns were performed two times in summer and three times in winter seasons during the years of 2005-2007. Spatial distributions of SO₂, NO₂, and O₃ levels in the region were also mapped using MapInfo with Vertical Mapper software.

The result showed there was a large variation in pollutant levels among the sampling points. This indicated that different sampling points were under influence of different pollution sources and had different pollutant compositions. Generally, low SO₂ and NO₂ levels were measured around the study area, probably due to the natural gas usage for the industrial facilities. But, relatively higher levels were observed especially around the refinery and petrochemical complex for SO₂.

For all the sampling periods ($n=5$), measured SO₂ and NO₂ levels in the region were generally less than the present long term limit values in national regulation (HKDYY, 2008). However, when the data set from this study was compared with the target limits, it was shown that the levels measured at lots of sampling points exceeded the long term limit value for SO₂. For NO₂, measured levels on İzmir-Çanakkale highway, around the refinery and petrochemical complex and at site 25 exceeded the target (2024) long term limit. Measured O₃ levels in the region were generally less than the target (2022) long term limit value in HKDYY (2008), except obtained levels in summer, especially at the rural sites. In addition, all measured ozone levels in winter were lower than this limit value.

The SO₂ distribution maps showed that the petroleum refinery and petrochemical complex with the highest SO₂ levels are the most important sources of pollutant in the region. The SO₂ pollution around these industries can be related to the emissions from the processes that are used fuel oil for the operations. High SO₂ levels were also measured at the urban and residential areas during winter periods, probably as a

result of residential heating emissions and/or uncontrolled combustion. Background and rural sites had the lowest SO₂ levels, while in summer period the residential areas had also the lowest ones.

SO₂ levels at the sites around the iron-steel plants were relatively lower than those around the refinery and petrochemical industry. This can be attributed to the usages of electricity and natural gas at lots of productions in these factories. Horozgediği village, Yeni Foça road and İzmir-Çanakkale highway are located close to these sites. So, the measured pollutant levels around the iron-steel plants may also be influenced by the intensive traffic emissions on the roads, residential heating in the village and by transportation of pollutants by advection especially from the refinery and petrochemical industry.

The NO₂ distribution maps showed that İzmir-Çanakkale highway, Yeni Foça road, Aliğa town, the petroleum refinery and petrochemical industry with high NO₂ levels are the major sources in the study area. However, rural and background sites had the lowest NO₂ levels. Generally, there was not a big difference between the observed NO₂ levels in summer and winter.

According to the maps, the sampling sites on the highway and around the iron-steel industries, petroleum refinery, petrochemical industry and town center with high NO₂ concentrations had the lowest ozone levels. This may probably be due to the reaction between O₃ and NO producing NO₂. However, high O₃ concentrations were generally observed at the background and rural sites. Summertime ozone levels were generally higher than the wintertime ones, probably because of the elevated solar radiation during hot summer months.

Results from this study also demonstrated that diffusive samplers are suitable for measurements of inorganic pollutants at large areas with more sampling points and for mapping pollutant level in a region.

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