MEASUREMENT AND SOURCE DETERMINATION OF AIR POLLUTANTS IN ULUDAĞ NATIONAL PARK

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ABSTRACT

MEASUREMENT AND SOURCE DETERMINATION OF AIR POLLUTANTS IN ULUDAĞ NATIONAL PARK

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An air pollution monitoring station was set up at Uludağ Mountain which is located Northwest of Turkey. Hourly measurements of NO, NO_2, SO_2, SPM and O_3 were done starting from March 1993.

The long and short term trends in the concentrations of measured parameters were investigated to understand sources contributing to the observed concentrations of these pollutants. Higher concentrations of O_3 during summer months were consistent with higher photochemical production with increased solar flux. Seasonal patterns observed in other parameters were consistent with their source strengths in different periods of the year. The O_3 showed a peak at approximately 3 pm together with SO_2 and NO_2. The SPM on the other hand showed different diurnal pattern with maximum concentrations occurring during night hours. The main sources of O, SO, NO in the Mt

High concentrations of O_3 were observed during night hours. Unlike day-time peaks, these peaks were sporadic and did not correlate with the SO_2 and NO_2. These night-time O_3 were suspected to be due to injection from the stratosphere.

Keywords: Ozone, Nitrogen Oxides, Sulphur Dioxide, Suspended Particle Diurnal Variation, Photochemical Ozone Formation, Rural areas.

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ÖZ

ULUDAĞ MİLLİ PARKINDA KİRLETİCİ GAZ KONSANTRAYONLARININ VE KAYNAKLARININ BELİRLENMESİ

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Türkiyenin kuzey batısında bulunan Uludağ Milli Park'ında bir hava kirliliği ölçüm istasyonu kurularak, NO, NO_2, O_3, SO_2 ve AKM (Askıda Katı Madde) konsantrasyonları saatlik olarak mart 1993' ten itibaren ölçülmeye başlandı.

Bu kirlecilerin konsantrasyonlarındaki uzun ve kısa vadeli değişimlere bakılarak, kirletici kaynakları belirlenmeye çalışıldı.

Yaz aylarında görülen yüksek ozon konsantrasyonu, yüksek güneş akısı ile paralellik göstermektedir. Bu durum fotokimyasal ozon üretiminin varlığını açıkca ortaya koymaktadır.

Öğleden sonra saat 15^{00} civarında NO_2, SO_2 ve O_3 derişimleri en yüksek değerlerine ulaşmaktadırlar. AKM ise gece en yüksek konsantrasyona ulaşmaktadır.

Ozon için öğleden sonra görülen yüksek konsantrasyon, daha az olmakla beraber gecede görülmektedir. Ancak bu tepecik gündüz görülen ozon tepeciği gibi NO_2 ve SO_2 ile korelasyon içerisinde değildir. Gece güneş akısı olmadığı için, fotokimyasal ozon üretiminden söz etmek mümkün değildir. Gece görülen bu yüksek ozon konsantrasyonuna Stratosfer'den Tropsfer'e injeksiyon yolu ile geçen ozonun neden olduğu sanılmaktadır.

Yapılan ölçümler sunucunda O_3, SO_2 ve NO_2'nin esas kaynağının Bursa şehri ve istasyon yakınındaki oteller bölgesi olduğu ortaya konulmuştur.

Ozon ve ozon üretimini sağlayan NO_x(NO ve NO_2) için diğer bir kaynakta Bursa'yı oteller bölgesine bağlayan yol üzerinde motorlu araçların egsoz gazlarıdır.

Anahtar Kelimeler: Ozon, Azot Oksitler, Kükürt Dioksit, Askıda Katı Madde, Saatlik Degişim, Fotokimyasal Ozon Üretimi, Hava Kirliliği, Kırsal Araziler

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INTRODUCTION

1.1 Air Pollution

The role of atmosphere changes with its composition. This gaseous mixture becomes polluted by the addition of particles, gases etc. The presence of one or more contaminants in the atmosphere in such quantities and such duration tends to be injurious to human health or welfare animal or plant life, or would reasonably interfere with the enjoyment of life.

Pollution of ambient air results from natural and anthropogenic (that is caused by man) processes:
Volcanoes, forest fires, decomposition of plants and animals, soil erosion, pollens, ocean spray, volatile hydrocarbon's emitted by vegetation, O_3 from electrical storms, stratospheric intrusion and photochemical reactions are examples for natural processes.

Although nature pollutes more than man, it has low significance because:

1) levels of contaminants associated with natural emissions are very low,
2) large distance separate of natural emission and large human populations,
3) major sources of natural emission are episodic and transient,
4) atmosphere has a capability of cleaning itself of all known pollutants given sufficient time. As a result, emission due to natural processes can be cleaned by the atmosphere [1,2].

Anthropogenic sources are the most important sources of air pollution. Because potentially harmful pollutant levels are produced in environments where harm to human health and welfare is the most likely. The major cause of all air pollution is combustion which is essential to man.

The air pollution problem involves a system consisting of three basic components:

1) Sources; responsible for emission of pollutants,

2) Atmosphere; is a medium for mixing and chemical transformations of pollutants,

3) Receptors; are receivers of airborne pollutants [3].

1.2 Gas Phase Air Pollutants

Pollutants in the atmosphere may have been released from an identifiable source or they may have been produced in the atmosphere as a result of chemical reactions. The former are classified as being Primary Pollutants, the latter as Secondary Pollutants [1]. A general list of major primary air pollutants is given in Table 1.1.

The most important of these major primary pollutants are Nitrogen Compounds, Sulphur Compounds and Aerosols. The sources of these pollutants are different, they may be both natural and anthropogenic. Major sources of these primary pollutants are given in Table 1.2.

Table 1.1 General Primary Pollutants

- Particulate Matter
  - Fine dust:less than 100μ[a] in diameter
  - Coarse dust:above 100μ in diameter
  - Fumes:0.001 μ in diameter
  - Mist:$0.01\text{-}10\mu$ in diameter
- Sulphur compounds
- Organic compounds
- Nitrogen compounds
- Carbon compounds
- Halogen compounds
- Radioactive compounds

[a] Note $1\mu = 10^{-4}$cm

W.Kenneth et al. (1976) [2]

Table 1.2 Major Sources of Primary Pollutants

Natural	Man-made
Volcanoes	Combustion processes
Fires	Chemical processes
Breaking seas	Nuclear or atomic processes
Blowing dust	Roasting, heating and refining processes
Pollens, terpenes-bacteria, viruses	Mining, quarrying, farming

Lutgens et al, (1989) [4]

Adverse effects of pollution associated with Secondary Pollutants are more than that of Primary Pollutants. For example; SO_2 as a primary pollutant has itself many harmful effects, H_2SO_4 (Sulphuric Acid), which is secondary pollutant formed by the oxidation of SO_2, is even more damaging to the environment(as in the case of NO_X - O_3 system) [7].

The most important of the primary pollutants in local and regional scale are Nitrogen Compounds, Sulphur Compounds, and Aerosols. Primary and Secondary products of major pollutant source is given in Table 1.3. Certain halogen compounds such as HF, HCl are produced in metallurgical and other operation. Fluoride compounds are harmful and irritating to human beings, animals and plants even when they are present at low concentrations.

Global man - made and natural emissions of various pollutants are given in Table 1.4. As it is seen from the Table, in several cases global natural emissions (but not local emissions in an urban areas) of a particular pollutant far exceed man made (anthropogenic) emissions. This is the case for all the pollutants given in the Table. However for some pollutants which are due to combustion process, the emission difference between natural and anthropogenic combustion process, is smaller than that of others. The small difference is true for CO, CO_2, NO_x, CH_4 and Hydrocarbon's which are the major combustion product. In the Table, only the made emission of SO_2 is higher than natural emission. This reasonable because the major natural source of SO_2 is the mostly volcanic eruptions but there are several anthropogenic sources for SO_2 such as; fuel combustion, transportation, coal burning, agricultural burning etc.

Table 1.3 Primary and Secondary Products of Major Pollutants

Class	Primary pollutants	Secondary pollutants
Sulphur containing-compounds	SO_2, H_2S	SO_3, H_2SO_4, MSO_4**
Nitrogen containing-compounds	NO, NH_3	NO_2, MNO_3**
Carbon containing-compounds	C_1 - C_5 compounds	Aldehydes, ketones, acids
Oxides of Carbon	CO, CO_2	None
Halogen compounds	HF, HCl	None

**MSO_4 and MNO_3 denote general sulfate and nitrate compounds.

J.H. Seinfeld (1975) [5].

Table 1.4 Global Man-made and Natural Emissions of Various Species (Estimated for 1976)

	Emission estimate (10^9 kg/yr)	
Species	Man-made	Natural
CO_2	$2*10^4$	10^6
CH_4, hydrocarbons	188	1800
CO	600	2500
SO_2	207	10
H_2S	2	50
NO_X (as NO)	90	1200
NH_3	7	1200

P.R.Wayne (1985) [6].

National Ambient Air Quality Standards (NAAQS) set by the Turkish Air Quality Regulation and United States Federal Government and comparison of concentration levels between clean and polluted air are given Table 1.5, 1.6 and 1.7 respectively. If Table 1.5 and 1.6 are compared, it will be seen that Turkish Air Quality Standards are higher than that of USA. If the economic status of two countries are compared, this is reasonable result for Turkey as a developing country.

In Table 1.7, concentrations of some major pollutants in remote, rural, moderately polluted and heavily polluted areas. The concentrations of the pollutants are increasing in the same order, lowest in remote and highest in heavily polluted areas.

1.2.1 Ozone

Ozone is a secondary photochemical pollutant produced from a variety of natural anthropogenic precursors that include industrial and vehicular emissions of volatile organic compounds (VOC) and oxides of nitrogen (NO_x) [9,10]. Ozone has both natural and anthropogenic sources in the troposphere. The primary natural source is injection from the stratosphere. The anthropogenic source is photochemical production from precursors emitted by industrial and transportation combustion sources.

Ozone is a key element in atmospheric photochemistry. Until 1980, the main interest was centred upon the stratospheric O_3 due to its importance in the heat budget of the stratosphere and absorption of the dangerous UV radiation.

Table 1.5 Turkish Air Quality Standards [8]

	Longterm*		Shortterm**	
	Ambient	Industrial	Ambient	Industrial
SO_2(ppm)	0.05	0.1	0.15	0.15
SPM($\mu g/m^3$)	150	200	300	400
NO(ppm)	0.16	0.17	0.50	0.50
NO_2(ppm)	0.053	0.053	0.16	0.16

* Annual Arithmetic Average

** Daily Maximum in one Year

Table 1.6 National Ambient Air Qulaity Standards (NAAQS) by USA

	Primary		Secondary	
Pollutant	Concentration	Time	Concentration	Time
CO	9.0 ppm	8 h	9.0 ppm	8 h
	35.0 ppm	1 hr	35.0 ppm	1 h
SO_2	0.03 ppm	Annual arithmetic mean	—	—
	0.14 ppm	24 h	0.5 ppm	3 h
O_3	0.12 ppm	1 h	0.12 ppm	1 h
NO_2	0.05 ppm	Annual arithmetic mean	0.05 ppm	Annual arithmetic mean
NMHC[b]	0.24 ppm	Average from 6 to 9 a.m.	0.24 ppm	Average from 6 to 9 a.m.
Total suspended particles	75 $\mu g\ m^{-3}$	Annual geometric mean	60 $\mu g\ m^{-3}$	Annual geometric mean
	260 $\mu g\ m^{-3}$	24 h	150 $\mu g\ m^{-3}$	24 h
Lead	1.5 $\mu g\ m^{-3}$	Quarterly average	1.5 $\mu g\ m^{-3}$	Quarterly

[a] NAAQS in effect in 1984.

[b] NMHC = non-methane hydrocarbons; expressed as ppm carbon (ppmC).

J.F.Pitts (1986) [7].

Table 1.7 Typical Peak Concentrations of Gas Phase Criteria Pollutants Observed in the Troposphere Over the Continents

	Type of Atmosphere				U.S. Primary Federal Air Quality Standard
Pollutant	Remote	Rural	Moderately Polluted	Heavily Polluted	
CO	$\leqslant 0.2$ ppm[f]	0.2–1 ppm[h]	~ 1–10 ppm[g]	10–50 ppm	9.0 ppm for 8 h 35.0 ppm for 1 h
NO_2	$\leqslant 1$ ppb[b,f,j]	1–20 ppb[c,d]	0.02–0.2 ppm[g]	0.2–0.5 ppm	0.05 ppm annual average
O_3	$\leqslant 0.05$ ppm[b,f]	0.02–0.08 ppm	0.1–0.2 ppm	0.2–0.5 ppm	0.12 ppm for 1 h
SO_2	$\leqslant 1$ ppb[e]	~ 1–30 ppb[d]	0.03–0.2 ppm	0.2–2 ppm	0.14 ppm for 24 h 0.03 ppm annual average
NMHC	$\leqslant 65$ ppbC[f]	100–500 ppbC[h]	300–1500 ppbC[i]	$\geqslant 1.5$ ppmC	0.24 ppmC average from 6–9 a.m.

[b] Kelly et al., 1980.

[c] Spicer et al., 1982; Pratt et al., 1983.

[d] Martin and Barber, 1981.

[e] Ludwick et al., 1980; Maroulis et al., 1980.

[f] Kelly et al., 1982; Hoell et al., 1984.

[g] Ferman et al., 1981.

[h] Seila, 1979.

[i] Sexton et al., 1982.

[j] Johnston and McKenzie, 1984.

J.F.Pitts (1986) [7].

Now, people have realized the importance of tropospheric O_3 in relation to several subjects;

1) elimination of pollutants by OH radicals (initiated by O_3 photolysis),
2) climatic action upon the troposphere (green - house effect),
3) air quality (Max = 120 ppb),
4) oxidizing attack of vegetation (reductions in crop yield and forest decline),
5) boundary conditions for stratospheric O_3.

Due to these important reasons, Tropospheric Ozone is therefore monitored at many stations and data are collected by individual scientists, sometimes by certain nationwide services and recently also at an international level. An example is the EUROTRAC (European Experiment on Transport and Transformation of Environmentally Relevant Trace Constituents in the Troposphere over Europe [11,12].

In the lower troposphere, O_3 is derived from three sources;

1) Transport from the stratosphere,
2) Photochemical formation in the free troposphere,
3) Photochemical formation in the boundary layer:

The photochemical formation mechanism of O_3 is as follows:

$$O_2 + O('D) + M \rightarrow O_3 + M \text{ (where M is a third body)}$$

$$NO_2 + hv \rightarrow NO + O\ ('D) \quad (295nm < \lambda < 430nm)$$

$$NO + O_3 \rightarrow NO_2 + O_2$$ [13,14,15,16,17,18,19].

The lower tropospheric O_3 is removed two processes ;

1) deposition to the earth surface,
2) homogeneous photochemical destruction

But, the rates of photochemical formation and elimination of tropospheric O_3 are far greater than contributions from stratosphere and soil deposition. One of the scavengers of O_3 is NO. Related reactions is given above (first reaction).

Night time reactions of NO_2 reaction, destroy O_3 and causes the formation of HNO_3 (Nitric Acid). Also, terpene and isoprene are emitted from conifer and deciduous trees in significant quantities react with O_3 to oxidize SO_2 to H_2SO_4 [20,21].

In Fig 1.1, ozone producing process and related reactions are given schematically. As it is seen from the figure, ozone formation and destruction occur continuously. It is a cyclic process.

In clean atmosphere of rural areas, O_3 concentrations near the ground are estimated to be in the range of 10-20 ppb during the warm months of the year. But the concentration of O_3 is higher in Rural areas than that in Urban areas, because;

1) Ozone formation and accumulation occurs over-time scales of several hours resulting in the highest O_3 concentrations downwind in the urban plume (emitted NO_2 during this transportation, photodissociate and produce O_3),

2) when influenced by the long-range transport of O_3 from upwind sources, cities may act as O_3 sinks since the emission of fresh precursors may scavenge O_3 in the early stages of oxidation. Guicherat et al. (1977) suggested that typical transport distances for O_3 are of the order of 1000-2000 km and several thousands of kilometres for its precursors [22].

1.2.2 Nitrogen Compounds

There are five major gaseous forms of nitrogen in the atmosphere. These include N_2, NH_3, N_2O, NO and NO_2. Among these, NO and NO_2 have been identified as important pollutants of lower atmosphere [1].

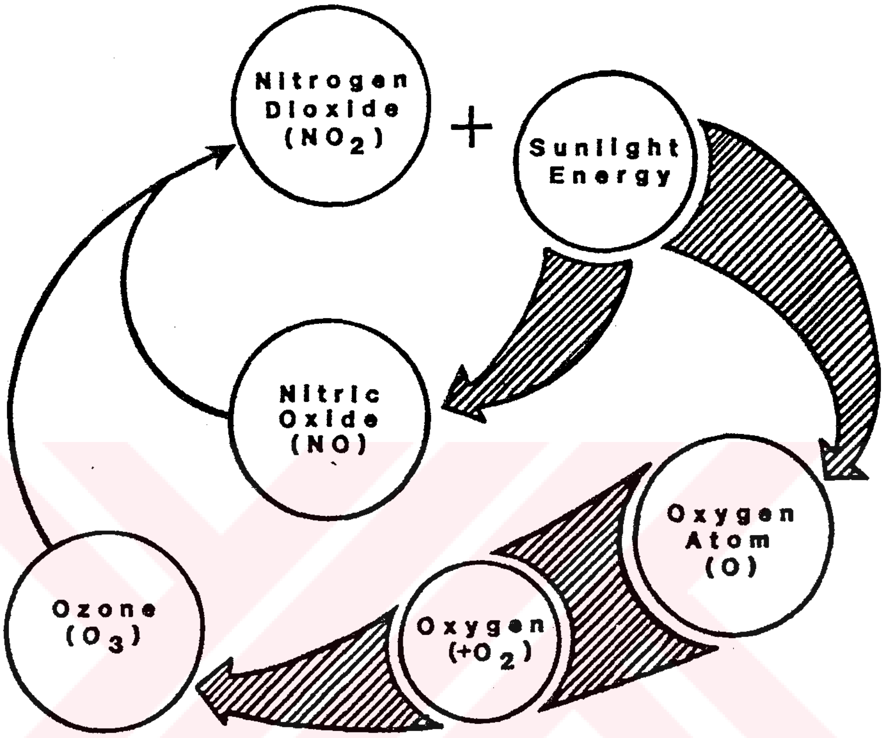


Figure 1.1 Photolysis of NO_2 and Generation of O_3 T.Godish (1991) [1].

Nitric oxide (NO) is a colourless, odourless, tasteless, relatively nontoxic gas. It is produced naturally by anaerobic biological processes in soil and water, by combustion processes (automobile) and by photochemical destruction of nitrogen compounds in the stratosphere. On a global basis, natural emissions of NO are estimated to be approximately $5*10^8$ tons/yr.

Nitric oxide is a product of high temperature combustion:

$$N_2 + O_2 \rightleftarrows 2NO(g)$$

Nitrogen dioxide (NO_2) has a colour of light yellowish orange to reddish brown at relatively low and high concentrations, respectively. It has a pungent, irritating odour and it is also relatively toxic.

There are two major routes of NO_2 concentrations from anthropogenic emissions in the ambient atmosphere. One is the so-called primary emission of NO_2 along with the usually dominant NO, the NO_2 being formed from

$$2NO + O_2 \rightleftarrows 2NO_2$$

shortly after combustion. Typically the NO_2 content of combustion effluent is about 5-10% of the total NO_x.

The second major route is the secondary oxidation of NO to NO_2 in the ambient atmosphere in a long term basis. This can occur in three ways:

1) the reaction with ambient O_2,

$$2NO + O_2 \rightleftarrows 2NO_2$$

2) direct reaction with ambient Ozone,

$$NO + O_3 \rightleftarrows NO_2 + O_2$$

3) photochemical oxidation of NO,

This last reaction occurs when reactive Hydrocarbon's following attack from OH radicals and subsequent reactions, form peroxy radicals which can oxidize NO to NO_2

$$RO_2 + NO \rightleftarrows RO + NO_2 \text{ [23]}$$

The dry and wet deposition rate of NO is generally considered to be very slow. However, the major chemical sink for NO_2 during the day is the reaction with OH radicals to form HNO_3.

$$OH + NO_2 + M \rightleftarrows HNO_3 + M$$

NO_2 can also be photo-dissociated by light of wavelength ≤ 400nm.

$$NO_2 + h\nu \rightleftarrows NO + O$$

This reaction leads to the formation of O_3 (details are given in Ozone part above).

Night - time reactions with NO_2 destroys O_3 according to subsequent reactions (int these reactions NO_3 is the free radical and it is key factor for night time chemistry.

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$NO_2 + NO_3 \rightarrow N_2O_5$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \text{ (Nitric Acid)}$$

1.2.3 Sulphur Compounds

Sulphur dioxide (SO_2) is recognized as one of the primary air pollutants, it is a major atmospheric pollutant in many parts of the world.

The concentration of SO_2 is significantly elevated by anthropogenic sources such as the combustion of sulphur-containing fossil fuel. Another important source of SO_2 is the volcanic eruptions. Because most of the volcanic sulphur is emitted as SO_2, with smaller and highly variable amounts of H_2S and $(CH_3)_2S$.

In the troposphere, SO_2 is almost all oxidized to H_2SO_4 (sulphuric acid), and the atmospheric sulphur cycle is closed by wet precipitation of the H_2SO_4 (acid rain) according to following oxidation reactions;

$$S + O_2 \rightleftarrows SO_2$$

$$2SO_2 + O_2 \rightleftarrows 2SO_3$$

$$SO_3 + H_2O \rightleftarrows H_2SO_4 \text{ (acid rain) [1]}$$

In the USA, major contribution on acidity in precipitation appears to be due to sulphuric acid (65 %) and nitric acid (30 %).

Sulphur dioxide is a major air pollutant which is harmful to vegetation and its effect have been well described in terms of foliar injury, physiological and biomedical perturbations and growth reductions, degradating effect on soil system and on plant growth. It kills leaf tissue. Chronic exposures of plants to SO_2 causes chlorosis, a bleaching or yellowing of the normally green portions of the leaf [24]. Sulphur dioxide pollution may affect plant growth either directly when it is absorbed by the plants or indirectly through the changes brought about in the soil system. SO_2 in the atmosphere has its primary effect upon the respiratory system, producing irritation and increasing airway resistance. Therefore, exposure to SO_2 may increase the effort required to breathe and it causes bronchitis.

1.3 Suspended Particulate Matter (SPM):

Particulate matter is collective term used to describe very small solid or liquid particles dispersed in the atmosphere. Individual particles vary considerably in size, geometry, chemical composition and physical properties. They may be produced by natural processes and human activity.

Based on the origin and methods of formation, particulate matter can be classified as either primary or secondary. Primary particles are produced by physical and chemical processes within a source and are emitted directly in to the atmosphere. Secondary particles are formed in the atmosphere as a result of chemical reactions that involve gases. Oxyhydrocarbons, sulphates and nitrates are the most common secondary aerosol particles produced from anthropogenic emissions. The sulphates and nitrates may be of considerable concern because of their irritation to humans, their role in visibility reduction and their effect on precipitation acidity. They are main particles of the fine particle fraction of atmospheric aerosols. The sulphate fraction consists of a variety of sulphur compounds; $(NH_4)_2SO_4$, H_2SO_4 , $CaSO_4$ etc. The nitrate fraction consists of mostly HNO_3.

Two major sources of primary particles are industrial sources (mineral rock crushing and processing, coal cleaning, ferrous and nonferrous metal smelting operations and cement and lime production etc.) and fuel combustion.

Secondary particles are produced from anthropogenic emissions of gases or they are generated from natural emissions from sea water, volcanoes, biological decomposition and trees. Over 50 % of the total atmospheric aerosol is estimated to be secondary particles produced from gaseous emissions of natural sources.

The size distribution of particles in the atmosphere has been characterized as being trimodal. As it is seen from Fig 1.2, two of the peaks characterize the fine particle fraction ($<2\mu m$), the third is the coarse fraction ($>2\mu m$). The fine particle fraction consists of a aitken nuclei and accumulation mode of particles. Aitken nuclei mode particles range in size from 0.005 to 0.1 μm and they are formed by the condensation of vapours produced such as fuel combustion and photochemical reactions. Accumulation mode particles vary in size from 0.1 to 1 μm. They are formed by the coagulation and agglomeration of nuclei mode particles and growth of nuclei mode particles by vapour condensation.

Under calm atmospheric conditions, the fine particle mass begins to exceed the mass of coarse particles with increasing downwind distance from urban areas. Because of their low settling velocities, fine particles may be transported 1000km or more from their source region. Size ranges of common atmospheric particles is shown in Fig. 1.3.

Air quality standards for particulate matter are now written in terms of suspended particulate matter (SPM). SPM is non size-fractionated particles and they are generally <15 μm.

SPM causes visibility degradation, respiratory problems in humans, wide damage to materials. Particulate dusts may cause injury to vegetation both directly and indirectly. For cement kiln dust, a variety of plant responses have been observed, including;[1]

1) indirect beneficial effects from soil neutralization,
2) reduction in yield and growth without visible injury,
3) increase in disease incidence,
4) severe injury to leaf cells,
5) suppression of photosynthesis,
6) death of trees.

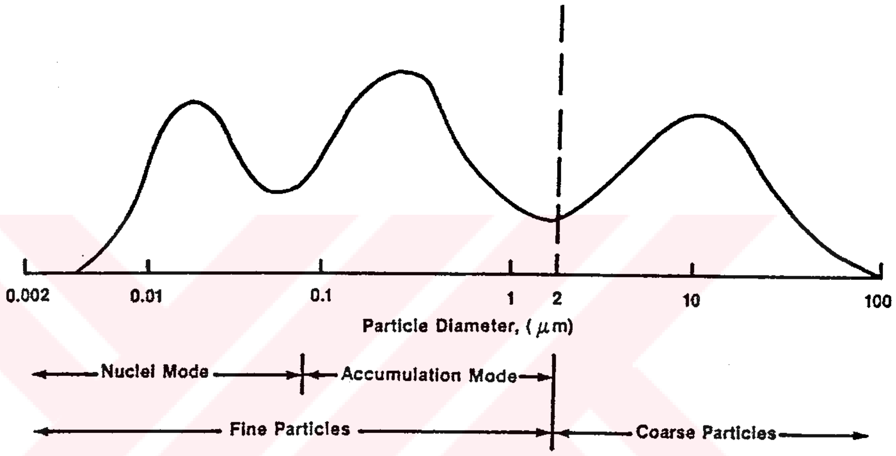


Figure 1.2 Modal Distribution of Atmospheric Particles[1]

T.Godish (1991) [1]

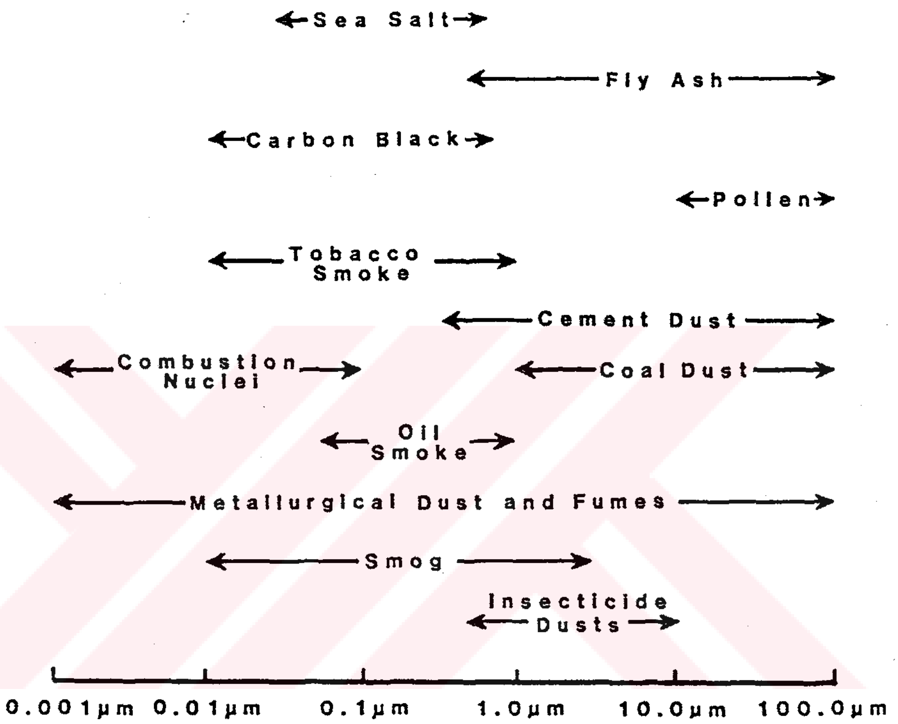


Figure 1.3 Size and ranges of Common Atmospheric Particles [1]
Godish (1991) [1]

1.4 Work Done on Measurement of Gaseous Pollutants at Rural Areas

Emissions from urban areas can also be transported to more rural downwind locations. This can result in elevated O_3 concentrations at considerable distance from urban centres [25,26,27,28]. During the period of 1977 to 1984, average O_3 concentrations at rural and urban stations of the USA were measured as 29 ppb and 21 ppb respectively [12]. In 1984, Kelly measured O_3 concentrations at three rural stations as 41,49 and 51 ppb which are higher than typical concentrations of urban, 17 ppb [13].
Data presented from two complete years of monitoring O_3 concentrations at two sites in Northern England, one a hill top site and the other a valley site indicated that the ozone dosage was significantly greater at the higher elevation site which are 28 ppbv and 61 ppbv [29]. Another important source of O_3 is the photochemical production. Ozone concentration shows a peak around hour ending 13 GMT. This is typical ozone peak for rural areas [30].

Due to importance of NO_x in photochemical smog formation, both in urban and rural areas, its concentration was measured in many countries. In many works, mean, rural, surface NO_x concentrations ranging from 0.1 ppb to 7.2 ppb have been reported. Mean urban concentrations may be as much as one order of magnitude larger [31,32.33]. For three rural stations of USA, NO and NO_2 concentrations were measured as 3.41, 3.97 and 3.17 for NO and 1.83, 3.41 and 5.93 ppb for NO_2 [9]. NO and NO_x concentrations were measured for Zurich (Urban) 35 and 65 ppb and for Davos (Rural) 2 and 8 ppb [28] respectively.

In addition to NO_x and O_3, There are a lot of work related with SO_2 and SPM, found in rural areas. In 1977, SO_2 was measured for three years periods as 10,12 and 11 ppb in rural areas of UK [30]. Another study were done by Lefohn A.S for periods of 1979-88 in USA and similar results was observed [34], as in UK.

SPM levels may vary from around 0.002-10 $\mu g/m^3$ under exceptionally clean atmospheric conditions to 1500 $\mu g/m^3$ or more in very dirty environments. In monitoring studies conducted in 1978 at 1448 sampling sites (both in urban and rural areas)in the United States, annual mean SPM values ranged from 9 to 288 $\mu g/m^3$. Fifty percent of these sites had mean values were of less than 60 $\mu g/m^3$, 25% had means greater than 76 $\mu g/m^3$ and 10 % were over 96 $\mu g/m^3$. The lowest values have been reported at remote sites such as Glacier National Park, and high values are associated with industrial settings [1]. SPM values were also measured in Brazil but this study was done for rural areas [35]. Similar work was also done (for SO_2 and SPM) in west part of Turkey by Tuncel G.(1992) [36].

The range of annual average sulphate concentrations varies from less than 1 $\mu g/m^3$ in same states to 20 $\mu g/m^3$ in industrialized cities in the northeast of USA. Highest annual average concentrations of sulphate (>15 $\mu g/m^3$) occur in an area extending trough the Ohio Valley of USA [36].

Unlike H_2SO_4, HNO_3 formed in the atmosphere tends to remain in the gas phase. As a consequence, nitrate concentrations in the atmospheric aerosol samples are considerably lower than those reported for sulphate, it is about one-tenth those of sulphate. The highest average annual nitrate is about 3-4 $\mu g/m^3$ for USA [1].

1.5 The Aim of This Work

Most of the gas-phase chemical reactions occurring in the atmosphere are due to very reactive radicals and oxidants. One of the most important radical in the atmosphere is hydroxyl radical (OH^-). This radical is produced at the end of photochemical reaction of NO_2 gas in the atmosphere. Other product of this photochemical reaction is O ('D) atoms which give very rapid reaction with O_2 in the atmosphere and produce O_3 gas. The net result of this reactions are the formation of H_2SO_4 and HNO_3 from SO_2 and NO_X.

Although concentrations of SO_2 and NO_X and O_3 are extremely low in the rural area, their effect on the plant is very important. Today, in Europe due to this effect very large amounts of forest were destroyed.

The main goal of this work is to set up a monitoring station to determine the ambient concentrations of NO_x, O_3, SO_2 and TSP and their harmful effect on forest ecosystem in Uludağ National Park. Short and long term trends observed in the concentrations of measured pollutants are discussed in relation to their potential sources.

Bursa-Uludag region was selected as a working area due to its unorganized urbanization and industrialization and geographical location. Due to these reasons, Bursa has severe big air pollution problem. In addition to this, in this region it is possible to see the effects of both soil and marine. As a result of above problems, Uludağ forest are destroyed for many years. Although there are regular monitoring of air quality parameters such as the SO_2, Suspended Particulate Matter (SPM), and NO_x in most of the Turkish cities, no data are available on O_3 concentrations in urban or rural areas.

CHAPTER II

EXPERIMENTAL

2.1 Selection of Sampling Site:

The sampling site, Uludağ mountain is 2540m high at 40^{o}N 20^{o}E and located at about 10km south of Bursa, which is the fifth largest city in Turkey with the population of around two million. Because of its unorganized industrialization and geographical location, Bursa is one of the polluted cities of country. Major sources of air pollution in the city are large number of industries located around and domestic local burning. In addition to industrial emissions, motor vehicle emission is also important, particularly during the summer period as the town is located on the cross road of east-west north-south highways, connecting eastern and southern cities to Istanbul. In Uludag mountain one can study the influence of both land and marine environment as it is located about 40km south of the Marmara Sea and 200km east of Aegean Sea. Depending on the time of the day, and direction of wind, it is possible to sample high pollution, high oxidant and clear air conditions.

Another potential source area that may influence the station is the ski resort which is located 2 kms to south of the station and the road that connect the city of Bursa to the ski resort.

Sampling Station was installed at Sarıalan region of Uludag mountain which has an 1685m altitude. This point is below the boundary layer mountain which has an 1685m altitude. This point is below the boundary layer (whose length depends on the temperature, topographical features of the region). By this way, it is possible to determine anthropogenic and natural air pollutants before inversion. This region is about 2km from hotels which is one of the well known ski resorts in Turkey and about 35km from the city. Station is located to south of the Bursa and nourth of hotels. So, around station there is no predominant source contributors. We can measure the concentrations pollutants which are transported from Europe, Bursa and Hotels. At this point, in addition to the gaseous pollutants coming from Bursa city, gaseous pollutants coming from Europe can also be determined. This region is selected after examination of several spots; considering mountain height, local meteorology, distance to the local sources and distance to the forest. Finally a bare land of about 1km^2 is selected, the nearest human activity is about 1.5 km away. Because of the hard winter conditions (average snow height is about 1.5m), it was not possible to be very far away from the roadway and electricity. Fig 2.1 shows the location of the station in Turkey. In this figure, the place of Bursa city and the Mt.Uludağ is shown. Fig 2.2 shows the topographical features in the region. The height difference and topographical features of Mt.Uludağ is shown in this Figure. The place of Bursa, station and ski-resort area (Hotels region) are also shown.

2.2 Construction of Sampling Station:

Installation and maintenance program are the most important part of the monitoring program. Installation of monitoring equipment was done in August 1992 and took place in two steps. At first, the infrastructure of the station (construction of meteorology tower, arrangement of station area, construction of electricity line etc.) was completed.

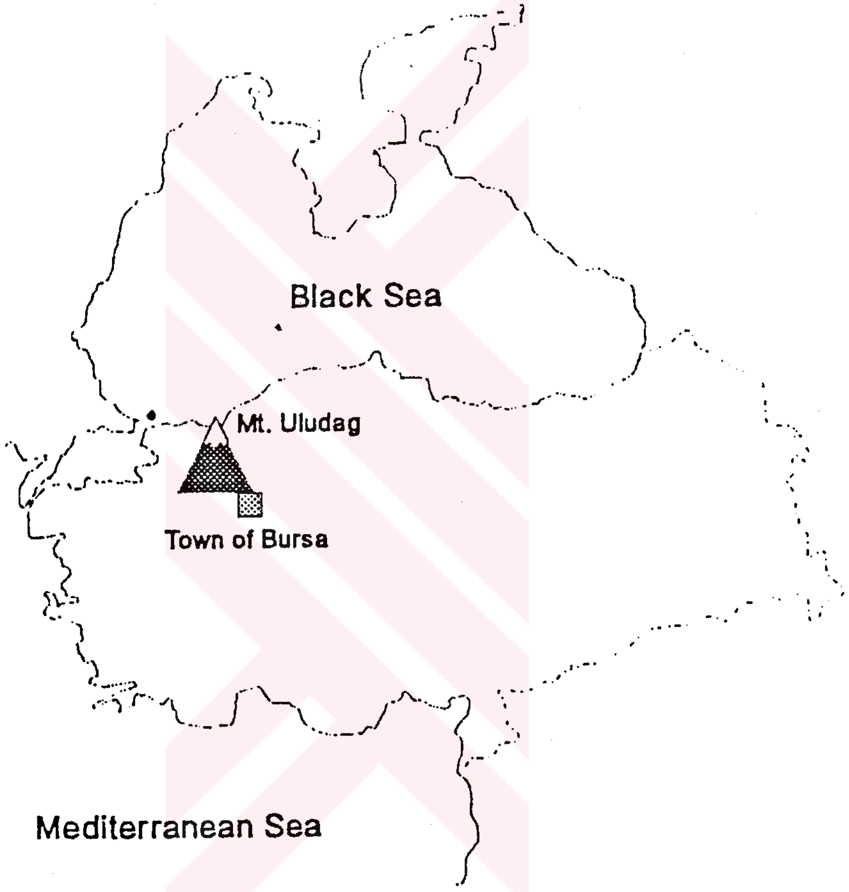


Figure 2.1 Location of The Station

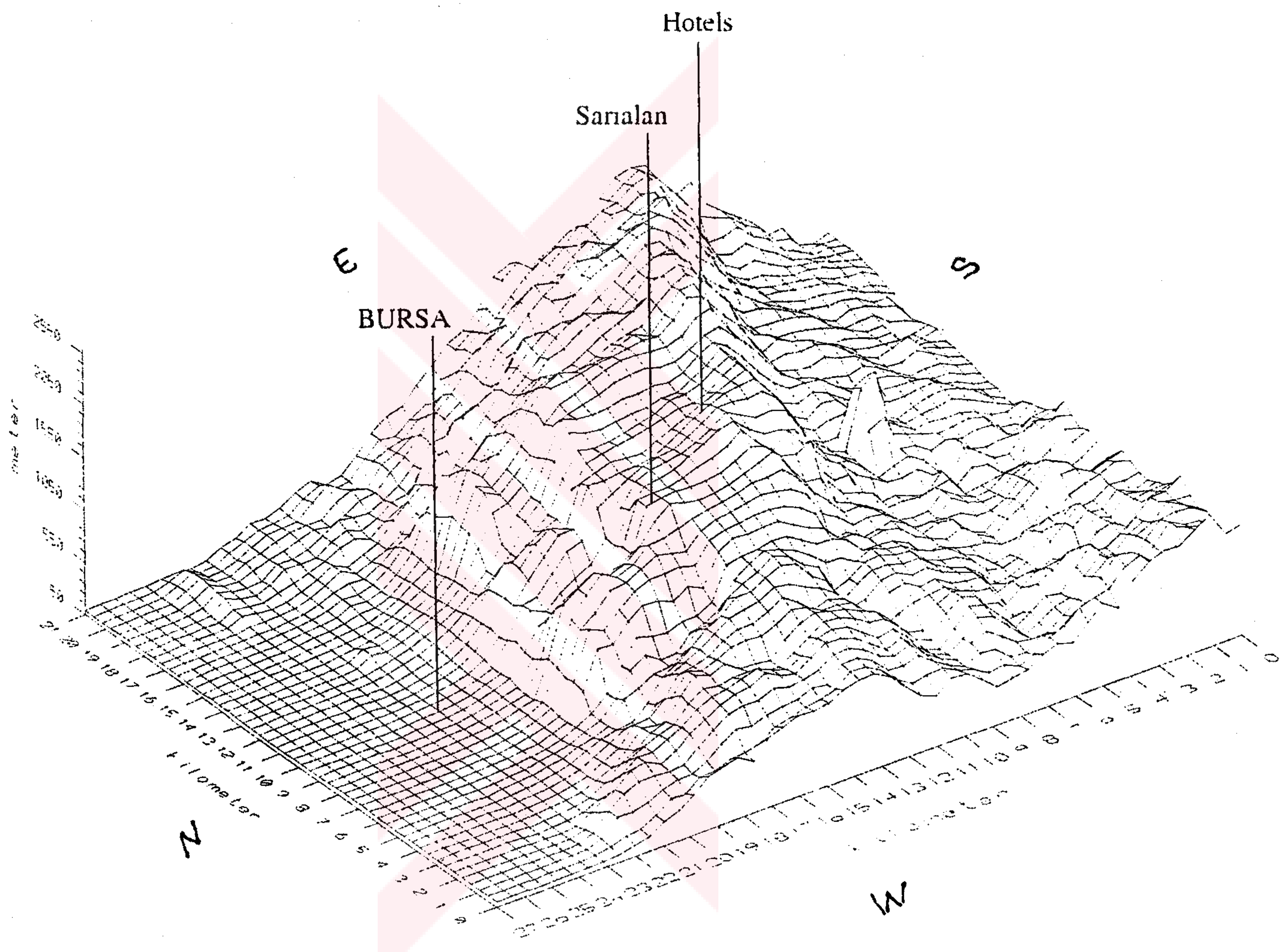


Figure 2.2 Topographical Features in the Region

There are instruments for wind speed, wind direction, temperature and humidity measurements on the meteorology tower. By this way, variation and correlation between meteorological parameters and measured pollutant will be investigated. For photochemical ozone formation, the relation between ozone and temperature will be investigated. Second step was the stand up of monitoring equipments.

Station is made up of an caravan which is equipped with a heater and ventilator to keep the temperature in a convenient range to instruments. The caravan is surrounded by fences for safety purposes. Inside the caravan, NO_X, SO_2, O_3, and TSP analyzers were installed in a rack . Data acquisition is done by the help of two computers, one for transferring of data from the analyzers, the other one is for data storage.

A number of difficulties have arise at the beginning of the study which affected operation of station for a certain period of time. Most of the problems came out in the first months of operation. At the beginning of the study, analyzers worked without continuous power supply. Because of remoteness of the region and hard winter conditions, very frequent breaks and voltage fluctuations on electricity were observed. This problem was solved by installing a continuous power supply and a voltage regulator.

Another problem that is related with electricity was the main fuse on the electric tower. When the rain was started fuse combines with rain as a result short circuit occurred on the tower and electricity was cutting down. This problem was solved by changing the main fuse with the new one.

Due to electricity fluctuations, communication fuse (RS 232) was burned out twice. For the first, we changed the RS 232 fuse of our computer and for the second we took data acquisition system main board to Ankara and changed with new one (which was sent from France in one month). After construction of continuous power supply, data acquisition system and computer worked without any major problems.

Another important problem we faced that was the hard winter conditions. For the summer there is no problem. Because the height of the snow was about 1.5m for November to May. It was difficult to reach the station. Then we used PTT special car (with which we go on the snow).

Fig 2.3 shows the picture of station rack from 20 m away. In this Fig, the height of the snow (which was about 1.5 m) during winter season can be seen clearly. The tower near the station is the meteorology tower. The other one is the electricity tower. As it is seen from the figure there are two sample inlets. The one at the top of the caravan is for dust analyzer, the one on the left side of the analyzer is for NO_x, O_3 and SO_2.

2.3 Analyzers

A picture of analyzers is given in Fig 2.4. As it is seen, all the analyzers were installed in a rack. The SPM analyzer is at the top then NO_x ,SO_2, O_3 and at the bottom there is data acquisition system. At the back, calibration gas bottles are seen.

Figure 2.3 The Picture of Station

Figure 2.4 The Picture of Analyzer

2.3.1 O_3 Analyzer

The O_3 measurements were done using Environment S.A. Model 41M UV photometric (Ultraviolet (UV) absorption) O_3 analyzer with a detection limit of 1 ppb for 30 seconds response time which is programmable from 10 to 90 seconds. Our working response time is 60 seconds.

The programmable measurement range of the analyzer is between 0.1 to 10 ppm. The 0.1 ppm range was chosen as working range for our work. The span and zero drift and noise of this analyzer are less than 1%/7 days, less than 1 ppp/7 days and 0.0005 ppm respectively.The zero (the gas that does not contain O_3) and span gas calibrations were done in each two weeks manually. The MnO_2 filter was used to obtain zero air. In addition to these calibrations, every day, zero and span check of the analyzer was done automatically. By this way, it was possible to understand whether the last zero and span gas calibrations were okey or not. The required span gas was produced by the ozone generator inside the analyzer. A UV radiation of a wavelength of 184.9 nm emitted by the lamp, transforms a portion of the oxygen contained in the zero air in to zone according to the following reactions:

$$O_2 + hv \rightarrow O + O$$

$$O_2 + O \rightarrow O_3 + W$$

At the end, ozone which has a concentration of 0.134 ppm, is sent to the reaction chamber.

The absorption spectrum of ozone contains a maximum at the wavelength of 253.7 nm, which is the main emission line of mercury. The absorption coefficient of ozone at 253.7 nm is;

$$\propto = 308\ \text{atm}^{-1}\ \text{cm}^{-1} \text{ at } 101.3 \text{ kPa and } 0^{0}\text{C}$$

$$C_{ppm}(O_3) = \frac{10^6}{\alpha L} * \ln\left(\frac{I_0}{I}\right) * \left(\frac{P_0}{P}\right) * \left(\frac{T}{T_0}\right) \quad (1)$$

where;

L: is optical path length in cm,

I_o: UV energy for air sample that does not contain O_3 molecules,

I : UV energy for air sample that contains O_3 molecules.

P_o: 101.3 kPa

P: Pressure inside measurement chamber

T_o:0^0C

T: Temperature of the gas

Flow Chart of Ozone Analyzer is shown in Fig 2.5

2.3.2 NO_x Analyzer

The NO and NO_2 measurements were done using Environment S.A. Model AC 31M chemiluminescence analyzer. Programmable measurement range of 0.1 to 10 ppm, with a minimum detectability of 0.35 ppb for 60 seconds response time which is programmable from 12 to 120 seconds. Our working response time and working range are 60 seconds and 0.1 ppm respectively. The calibration process of NO_x analyzer is same with the O_3 and SO_2 analyzers. But for this analyzer, we used both permeation tube and calibration gas which has a fixed concentration in the bottle. Zero and span gas calibrations were done in each two weeks manually (with bottle) and every day zero and span check were done automatically (with

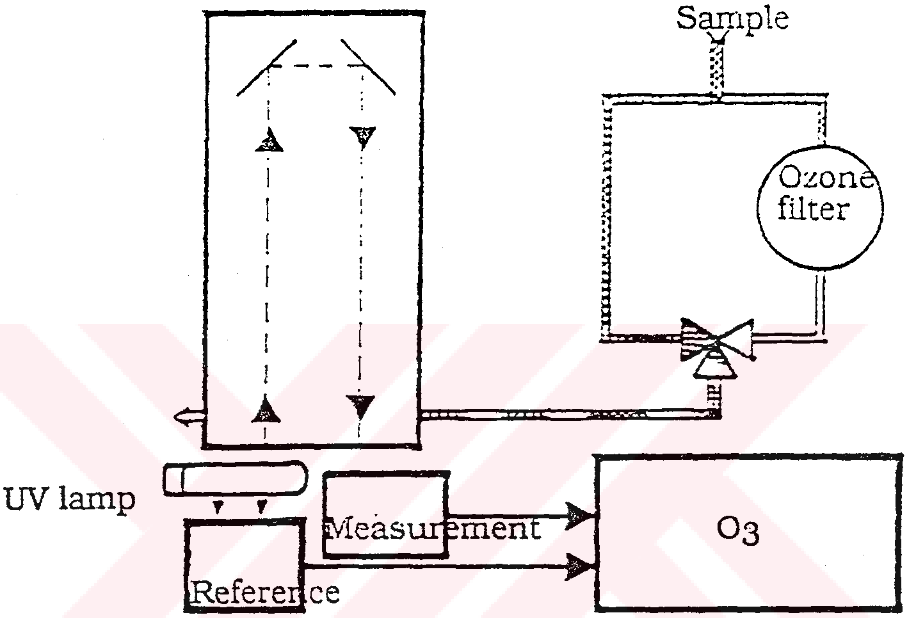


Figure 2.5 The Flow Chart of Ozone Analyzer

permeation tube). The concentration of calibration gas for NO and NO_x were 0.825 ppm and 0.840 ppm. The purafil filter was used to obtained zero air for this analyzer. The span and zero drift and noise of NO_x analyzer are less than 1%/24 hours, 1 ppb/24 hours and 0.17 ppb respectively. Chemiluminescence corresponds to an oxidation of NO molecules in ambient air by ozone molecules (from ozone generator):

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

The returning of the excited NO_2^* molecules to fundamental electronic state (ground state) is accompanied by luminous radiation with a spectrum of 600 to 1200nm:

$$NO_2^* \rightarrow NO_2 + hv \ (\lambda = 600\text{-}1200nm)$$

In order to measure NO_2 concentration in ambient air, it is transformed in to NO. A converter oven heated to approximately 320 ^oC is used to carry out this reduction according to following reaction:

$$3NO_2 + Mo \rightarrow 3NO + MoO_3$$

The air, sampled by a pump goes in to two separate chambers. One part toward NO_x chamber (Converter Oven), other part directly in to the NO chamber. The difference between NO_x and NO chamber gives NO_2 concentration in sampled air. The flow chart of NO_x analyzer is shown in Fig 2.6.

The NO and NO_2 concentrations in Sarıalan Region sometimes are very low. Most of the times, NO and NO_2 concentrations were not measured as they were below the detection limits. This resulted in large number of missing points in both NO and NO_2 concentrations.

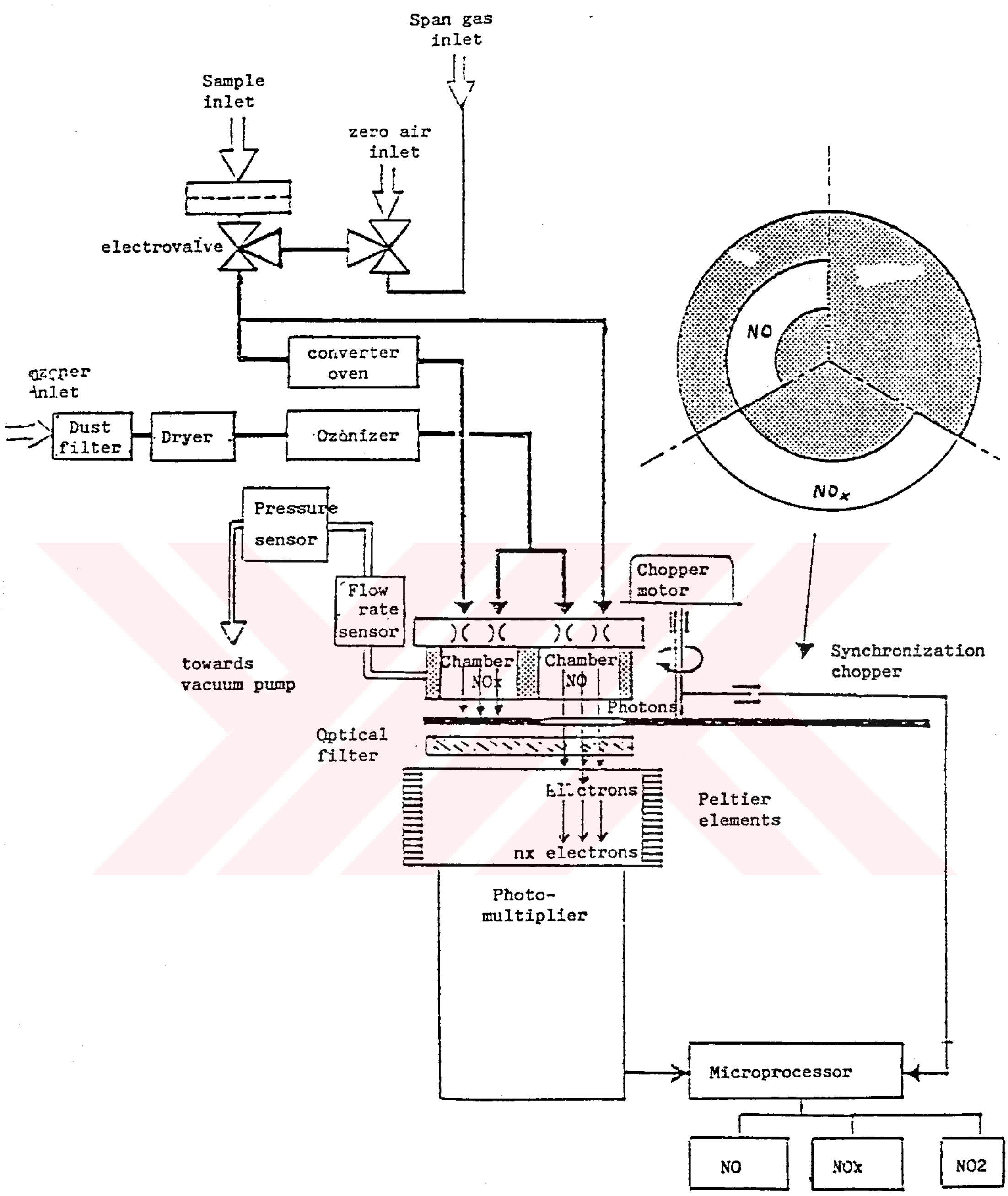


Figure 2.6 The Flow Chart of NO$_x$ Analyzer

2.3.3 SO_2 Analyzer

The SO_2 was measured using Environment S.A. Model AF 21M fluorescent specific monitor. The lower detection limit of the analyzer is 1 ppb for 60 seconds response time which is programmable from 10 to 90 seconds. The programmable measurement ranges changes from 0.1 to 10 ppm as in the case of O_3 and NO_x analyzer. Our working range is 0.1 ppm. The span and zero gas calibrations were done in each two weeks manually and checks were done everyday automatically. The concentration of calibration gas was 0.114 ppm. The span, zero drift and noise are less than 1%/7days, less than 1 ppb/7days and 0.0005 ppb respectively.

The hydrocarbon-free sample (sample to be analyzed is first filtered through a carbon kicker to eliminate aromatic hydrocarbons) is sent to a reaction chamber where it is irradiated with ultraviolet radiation centred around 213.9 nm. This wavelength is specific for absorption by SO_2 molecules.

$$SO_2 + h\nu \rightarrow SO_2^* \quad (\lambda_{abs} = 213.9\text{nm})$$

$$SO_2^* \rightarrow SO_2 + h\nu \quad (\lambda_{emiss} = 330\text{nm})$$

$$\text{Cppm}\,(SO_2) = (GI_oK_f\propto L)/(K_f+K_q+K_d) \qquad (2)$$

where,

G:constant dependent on the lighted portion of the chamber seen by the PM,

I_o:the intensity at the entrance of the chamber,

$\propto$:the characteristic absorption coefficient of SO_2 molecule,

K_f:quantum yields for fluorescence,

K_d:quantum yields for dissociation,

K_q:quantum yields for quenching.

L:the length of the chamber

The flow chart of SO_2 analyzer is shown in Fig 2.7.

2.3.4 SPM (Suspended Particulate Matter) Analyzer:

The SPM measurements were accomplished using Environment S. A. Model MPSI100 Beta - Atteunation. The lower detection limit is 10 $\mu g/m^3$ for 2 hours response time. The calibration of analyzer was done in every six months, in some cases it was done in every 3 months. For calibration standard filter paper which has a dust concentration of 870 $\mu g/m^3$. was used. The measurement response time of analyzer from 1/2 to 24 hours. Our working response time was 2 hours because this range was suitable for the dust concentration around the station. The flow chart of TSP analyzer is shown in Fig 2.8. The sample air (dust) collected on a fibreglass filter at high air flow (25 L/min). Particle concentrations are expressed as $\mu g/m^3$ and reported as total suspended particulate (TSP) levels. The size of the particles that has been measured by this analyzer is less than 10 μm.

Beta attenuation is composed of a soft beta rays transmitter, such as Pm 147, and a radiation receiver which as Gauger Muller. The intensity difference in light for filter table with no dust and with dust, gives the concentration of dust collected on the filter.

$$\Delta m = (1/k) \log (N_1/N_2) \qquad (3)$$

where,

N_1:transmission on filter (c/s),

N_2:transmission on filter with collected (c/s),

k:mass absorption coefficient taking in to account the beta source used (cm^2/mg),

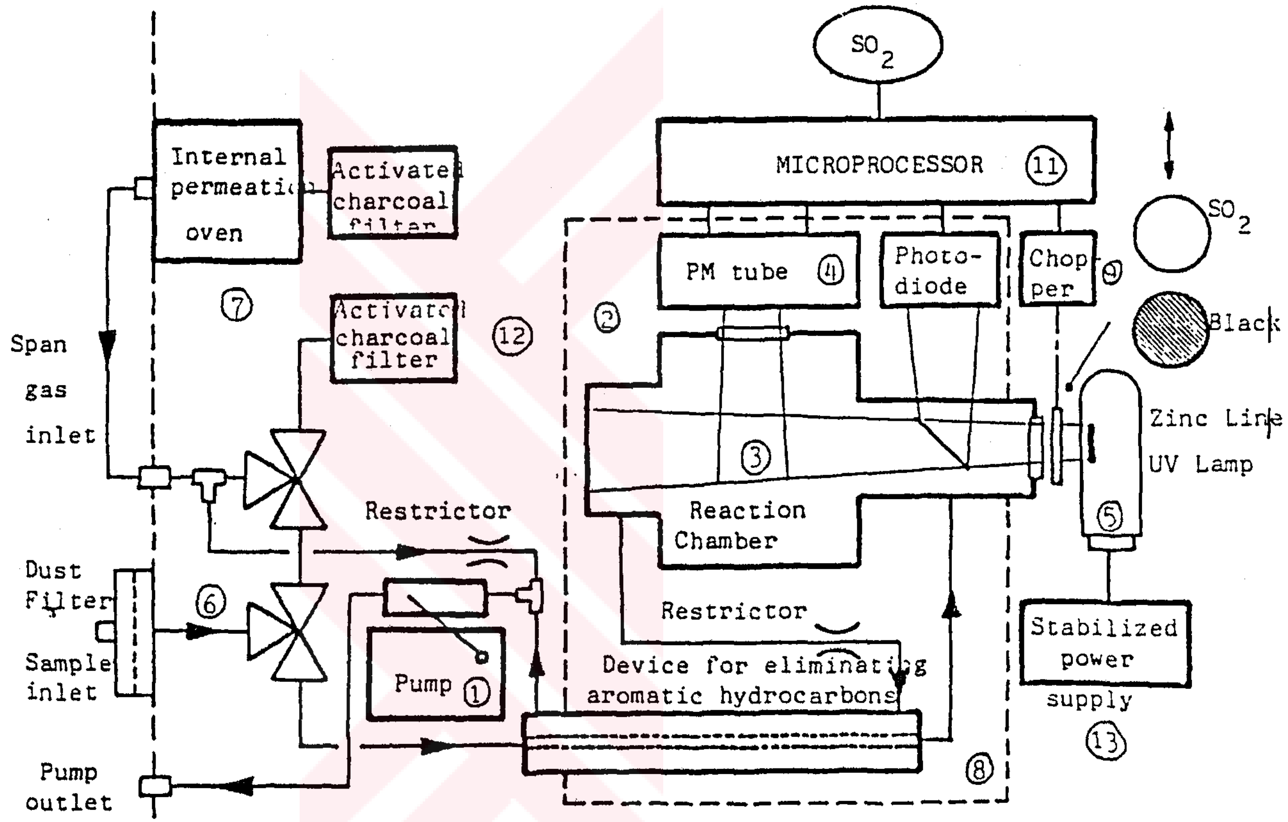


Figure 2.7 The Flow Chart of SO$_2$ Analyzer

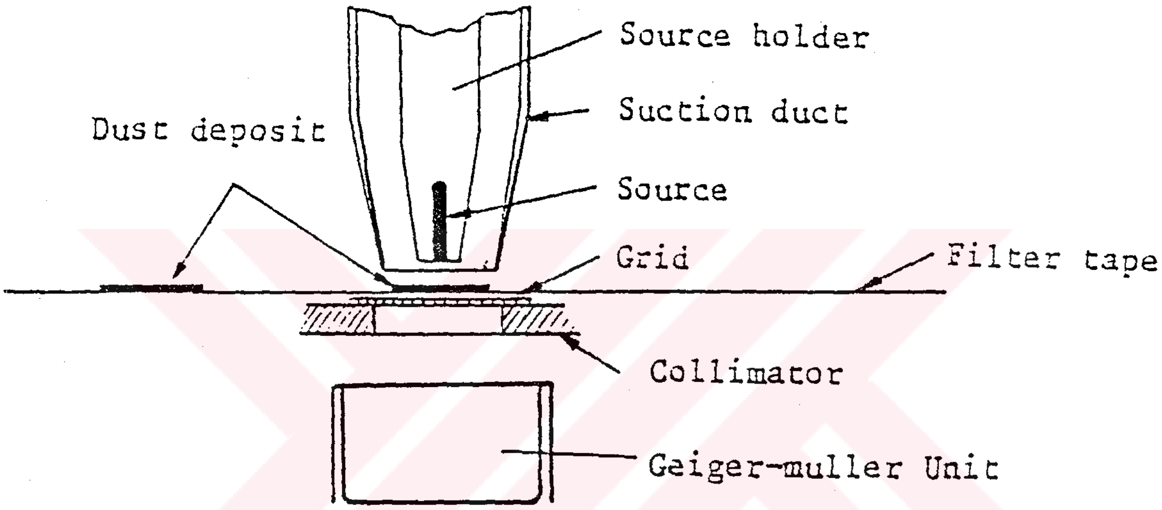


Figure 2.8 The Flow Chart of SPM Analyzer

2.4 Analytical Methods

In order to see the relation or correlation between gases and ions, NO_3^- and $SO_4^=$ concentration were also measured by Ion Chromatography for a one month period. The spot on the glass fibre filter of TSP analyzer is used for both dust and ion measurements.

The Ion Chromatography is a combination of the ion exchange liquid chromatography, UV detector and software for area calculations. This method has been successfully applied to the analysis of ions in many types of sample such as; rain, aerosol, tap water, fog, sewage etc.

Sample were directly injected to ion chromatography without any pretreatment because the ions are in simple matrices.

The instrument used was non-suppressed type ion chromatography. Operating parameters are given in Table 2.1. To determine the low concentrations in ppm level, different eluents are used in literature. For this purpose, in this research, potassium hydrogen phthalate (KHP) was used. Detection depends on the existence of a significant and measurable difference in UV absorption between the eluent ions and sample ions. One analysis is finished at most 12 minutes. The lower detection limit of our Ion Chromatography was 0.1 ppm. The working range was between 0.1 and 1000 ppm. For calibration of analyzer, NaCl, Na_2SO_4 and $NaNO_3$ with 1, 2, 3, 5, 10, 15, 20, and 25 ppm concentrations were used.

Sample manipulations were carried out under double filtered air. Samples were brought from Bursa to Ankara in polyethylene bags.

For analysis, each spot is washed with 10 mL deionized water and filtered with membrane filters in clean room then injected to the analyzer.

Class-100 clean room in Environmental Engineering Department was used for sample handling. There are four High Efficiency Particulate filters (HEPA Filters) which remove particles greater than 0.1 μm with 99.999% efficiency. One of the HEPA filters pulled air from outside the room and after filtering send it inside. Other three filters re-filters the filtered air in the room. Sample manipulations were carried out under double filtered air. Samples on filter paper were brought from Bursa to Ankara in polyethylene bags.

For analysis, each spot on the filter paper was washed with 10 mL deionized water and filtered with membrane filters in clean room then injected to the Ion Chromatography.

Table 2.1 Operating Parameters in Ion Chromatographic Analysis

Ion Chromatography: Varian Model with Peak II Software
Injector: Manual loop valve, 100 μL loop size
Mobile Phase: 1 mM KHP adjusted to pH 4.95 with 4 mM NaOH soln.
Flowrate: 3 mL/min
Temperature: Ambient
Column Type: Vydac 302 IC Anion
Detector: Jasco 875 UV Detector

CHAPTER III

RESULTS AND DISCUSSION

3.1 Overview of Measured Parameters

3.1.1 Seasonal Variation

Averages, standard deviations and number of samples for the measured parameters in different seasons are summarized in Table 3.1. As can be seen from the Table 3.1, except SO_2 and NO_x (as NO due to fuel combustion), other pollutants show highest concentrations in summer. Sulphur dioxide is highest in winter due to increasing domestic coal burning and decreasing rate of photochemical conversion of SO_2 to $SO_4^{=}$. More than tenfold decrease of SO_2 concentration in summer and autumn as compared to winter could be explained decreased coal burning and faster rate of conversion to $SO_4^{=}$.

Mean seasonal variation of SPM is less pronounced as compared to other variables. Maximum values are observed for summer months as expected due to increase in wind blown dust. Lowest mean value is observed for winter as a result of snow coverage of the soil. Autumn and spring seasons are relatively rainy seasons as compared to the summer, but still high values are observed. The same trend was also observed in Izmir between 1975 and July 1975 by Sen [38]. This is because of the high rate of emissions of Terpenes from the trees.

Photochemical production, destruction and rate of emission determines the seasonal behaviour of NO and NO_2, which is highest in winter and lowest in spring.

High solar flux during the summer promotes photochemical O_3 formation and lead to an increase in ambient concentrations. But low ambient concentrations are more frequently observed during the winter. This is due to the greater overall atmospheric stability and increased incidence of nocturnal inversions during this season, which in turn result in higher scavenging with rain and snow.

The mean seasonal variation of O_3, NO_x, SO_2 and SPM are given in Fig 3.1.

3.1.2 Monthly Trends

The mean monthly concentrations of O_3, NO, NO_2, SO_2 and SPM in each month between March 1993 and February 1994 are given in Table 3.2.

On monthly basis at this site, the highest ozone and lowest NO concentrations are observed. During July, August and September, Ozone concentration is at maximum and SO_2, NO and SPM show minimum. Actually these gases are at maximum during January and February. In general, each months, ozone is more than that of both NO and NO_2.

Table 3.1 Mean Seasonal Concentrations, Standard Deviations (in parenthesis)and Number of Samples (in square brackets) of O_3, NO_x, SO_2 (ppb) and TSP(μg/m^3) at Mt.Uludağ

	Winter	Autumn	Spring	Summer
NO_x	3.4(±5.7)[33]	0.84(±0.23)[38]	0.50(±0.30)[45]	2.7(±1.5)[34]
O_3	20(±6.1)[52]	33(±10)[61]	26(±6.7)[58]	41(±12)[46]
SO_2	17(±9.6)[40)	1.3(±0.20)[61]	3.5(±1.8)[45]	1.2(±0.10)[13]
TSP	14(±12)[47]	17(±7.5)[61]	16(±4.4)[75]	20(±13)[46]

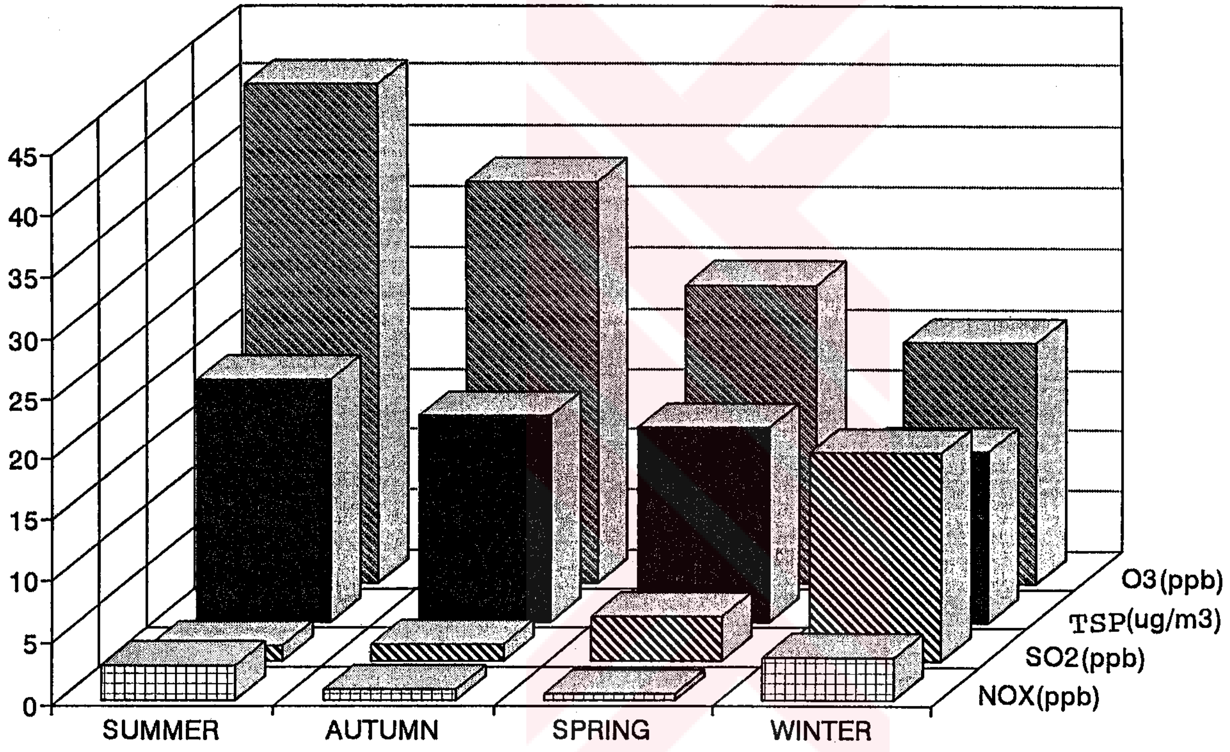


Figure 3.1 The Mean Seasonal Variation of NO_x, O_3, SO_2 and SPM at Mt.Uludağ Between Spring 1993 and Winter 1994

Table 3.2 The Monthly Average Concentrations of O_3, NO, NO_2, SO_2 (ppb) and SPM ($\mu g/m^3$) at Mt.Uludağ

	NO	NO_2	O_3	SO_2	SPM
March	-	-	25	1.5	16
April	BDL	BDL	27	3.4	17
May	BDL	BDL	22	6.2	16
June	-	-	21	-	14
July	0.4	2.7	51	-	22
August	0.4	1.9	44	1.1	22
September	BDL	0.7	41	1.3	14
October	BDL	0.5	24	1.3	20
January 94	3.2	1.3	18	14	6.0
February 94	BDL	BDL	21	21	20

BDL : Below Detection Limit

The O_3 peak in july corresponds to a minimum in NO and the largest ratio of NO_2/NO. The O_3 is at maximum in July 22, which is 62 ppb. On the same day, temperature and wind speed are also maximum, and humidity is minimum. So, for the photochemical formation of O_3, all conditions are satisfied. Ozone shows low concentrations in May, June, January and February.

Generally, NO_2 concentrations are higher than NO for all the months for which we have data. This indicates that the sources of NO_x are not very close to the site. During the trapping process, almost all NO is converted to NO_2. The small amount of NO shows the transportation of NO from ski resort to the station.

On a monthly basis, the SO_2 and NO concentrations show peaks in winter months (December, January and February) but the O_3 show a peaks in summer months (July, August and September).

The NO concentrations are at a maximum in January. This is expected result because in addition to the vehicular emissions, fuel combustion is also high during this season. The NO_2 concentrations are less than those of NO in winter, but become larger in spring (May) and summer (July), Autumn (September and October).

SPM has a maximum in July and August (22.0 and 22.0 $\mu g/m^3$) and minimum in January (6.0 $\mu g/m^3$). This is expected result because during winter months vicinity of the station is covered by snow, which result in reduced contribution of wind blown dust. The mean monthly variation of O_3, NO, NO_2, SO_2 and SPM between March 1993 and February 1994 is given in Fig 3.2.

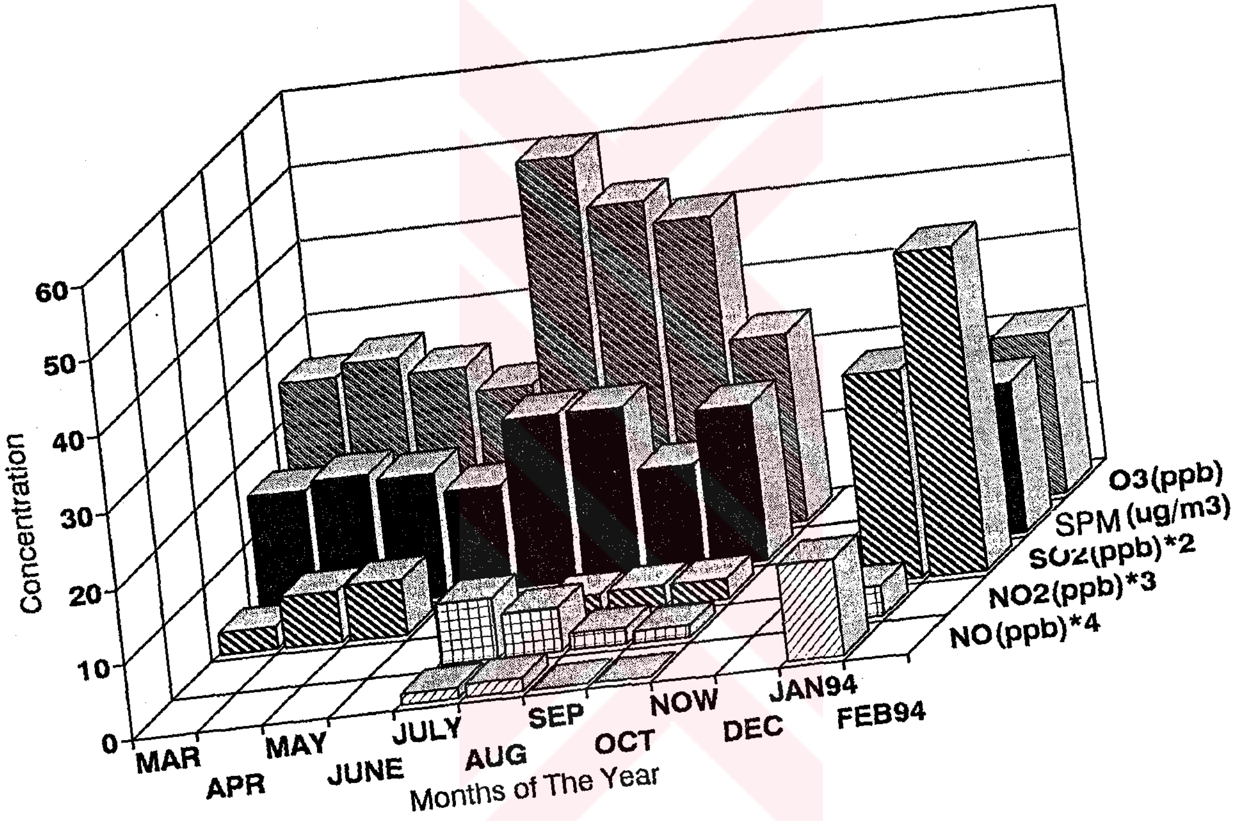


Figure 3.2 The Mean Monthly Variation of O_3, NO, NO_2, SO_2 and SPM at Mt.Uludağ Between March 1993 and February 1994

3.1.3 Daily Variations

In addition to seasonal and monthly variations of measured parameters, daily variations were also examined in order to see day to day fluctuations. Twenty four hour average concentrations of SO_2 for winter, spring and autumn season are compared in order to see the changes from one day to another. On the average highest daily values are obtained for winter months as expected. The concentrations are scattered about the mean value ±1 SD which indicates moderate fluctuation as can be seen from Fig 3.3, very small fluctuation in daily concentrations of SO_2 was observed for spring and summer season.

Daily averages of SPM for winter, spring,summer and autumn is shown in Fig 3.4. On the average the concentration of SPM is higher in summer. The maximum was seen in August of 1993. The lowest concentrations and more fluctuations were observed in winter. The explanation for this observation is given in the previous chapters, as the amount of contribution from soil dust which is reduced and during winter due to coverage of soil by snow. The date of each data point both for SO_2 and SPM are given in Table 3.3.

3.2 Comparison of Measured Parameters

The mean monthly concentrations of in O_3, NO, NO_2, SO_2 in Mt.Uludağ is compared with values obtained in Bottesford (UK) which is also a rural site.

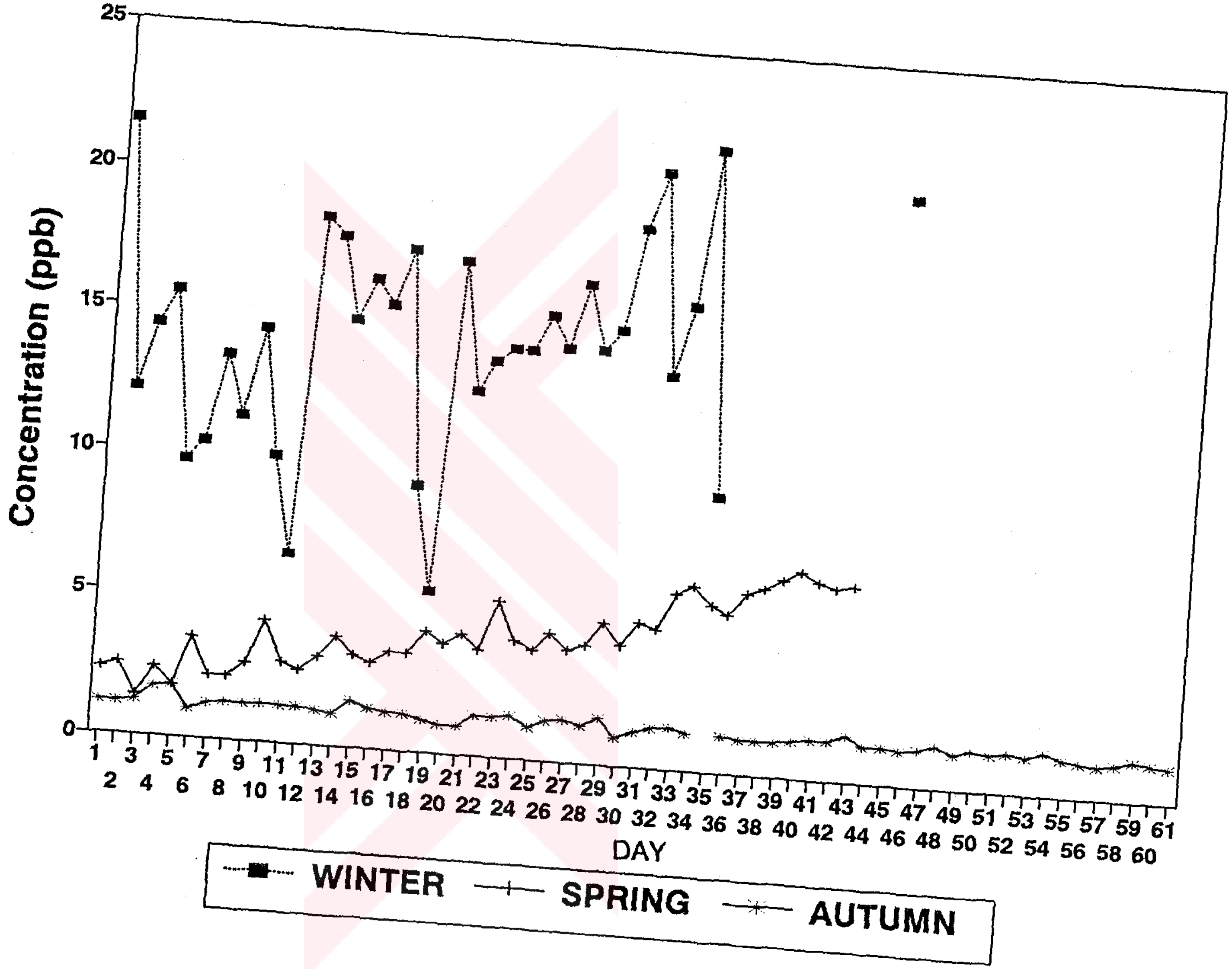


Figure 3.3 The Daily Variation of SO_2 For Seasons at Mt.Uludağ

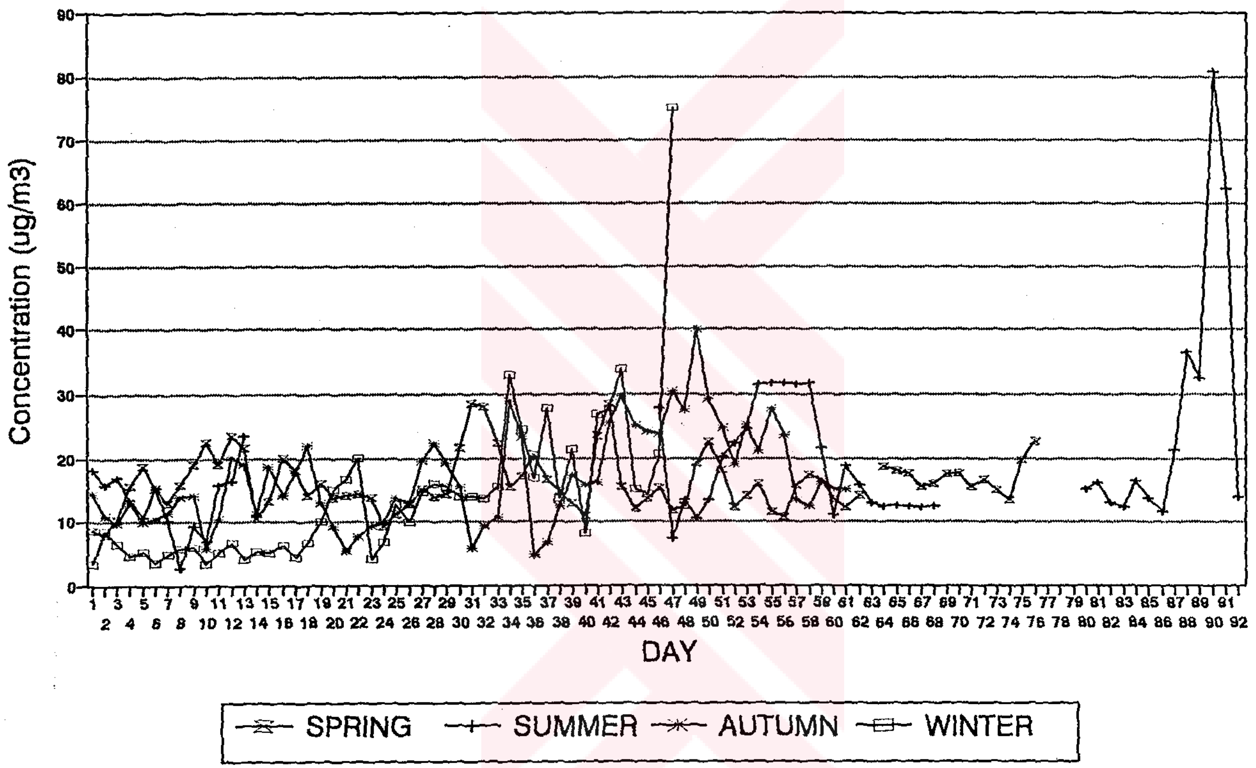


Figure 3.4 The Daily Variation of SPM For Seasons at Mt.Uludağ

Table 3.3 The date of SO_2 and SPM for Daily Variations

SO2

Sample #	Winter	Autumn	Spring
1	Jan 12	Sep 1	Apr 1
2	Jan 13	Sep 2	Apr 2
3	Jan 14	Sep 3	Apr 3
4	Jan 15	Sep 4	Apr 4
5	Jan 16	Sep 5	Apr 5
6	Jan 17	Sep 6	Apr 6
7	Jan 18	Sep 7	Apr 7
8	Jan 19	Sep 8	Apr 8
9	Jan 20	Sep 9	Apr 9
10	Jan 21	Sep 10	Apr 10
11	Jan 22	Sep 11	Apr 11
12	Jan 23	Sep 12	Apr 12
13	Jan 24	Sep 13	Apr 13
14	Jan 25	Sep 14	Apr 14
15	Jan 26	Sep 15	Apr 15
16	Jan 27	Sep 16	Apr 16
17	Jan 28	Sep 17	Apr 17
18	Jan 29	Sep 18	Apr 18
19	Jan 30	Sep 19	Apr 19
20	Jan 31	Sep 20	Apr 20
21	Feb 1	Sep 21	Apr 21
22	Feb 2	Sep 22	Apr 22
23	Feb 3	Sep 23	Apr 23
24	Feb 4	Sep 24	Apr 24
25	Feb 5	Sep 25	Apr 25
26	Feb 6	Sep 26	Apr 26
27	Feb 7	Sep 27	Apr 27
28	Feb 8	Sep 28	Apr 28
29	Feb 9	Sep 30	Apr 29
30	Feb 10	Oct 1	Apr 30
31	Feb 11	Oct 2	May 1
32	Feb 12	Oct 3	May 2
33	Feb 13	Oct 4	May 3
34	Feb 14	Oct 6	May 4
35	Feb 15	Oct 7	May 5
36		Oct 8	May 6
37		Oct 9	May 7
38		Oct 10	May 8
39		Oct 11	May 9
40		Oct 12	May 10
41		Oct 13	May 11
42		Oct 14	May 12
43		Oct 15	May 13
44		Oct 16	
45		Oct 17	
46		Oct 18	
47		Oct 19	
48		Oct 20	
49		Oct 21	
50		Oct 22	
51		Oct 23	
52		Oct 24	
53		Oct 25	
54		Oct 26	
55		Oct 27	
56		Oct 28	
57		Oct 29	
58		Oct 30	
59		Oct 31	

spm

Sample #	Winter	Autumn	Spring	Summer
1	Jan 13	Sep 1	Mar 8	Jun 1
2	Jan 14	Sep 2	Mar 9	Jun 2
3	Jan 15	Sep 3	Mar 10	Jun 3
4	Jan 16	Sep 4	Mar 11	Jun 4
5	Jan 17	Sep 5	Mar 12	Jun 5
6	Jan 18	Sep 6	Mar 13	Jun 6
7	Jan 19	Sep 7	Mar 14	Jun 7
8	Jan 20	Sep 8	Mar 15	Jun 8
9	Jan 21	Sep 9	Mar 16	Jun 9
10	Jan 22	Sep 10	Mar 17	Jun 10
11	Jan 23	Sep 11	Mar 18	Jun 11
12	Jan 24	Sep 12	Mar 19	Jun 12
13	Jan 25	Sep 13	Mar 20	Jun 13
14	Jan 26	Sep 14	Mar 21	Jul 16
15	Jan 27	Sep 15	Mar 22	Jul 17
16	Jan 28	Sep 16	Mar 23	Jul 18
17	Jan 29	Sep 17	Mar 24	Jul 19
18	Jan 30	Sep 18	Mar 25	Jul 20
19	Jan 31	Sep 19	Mar 26	Jul 21
20	Feb 1	Sep 20	Mar 27	Jul 22
21	Feb 2	Sep 21	Mar 28	Jul 23
22	Feb 3	Sep 22	Mar 29	Jul 24
23	Feb 4	Sep 23	Mar 30	Jul 25
24	Feb 5	Sep 24	Mar 31	Jul 26
25	Feb 6	Sep 25	Apr 1	Jul 27
26	Feb 7	Sep 26	Apr 2	Jul 28
27	Feb 8	Sep 27	Apr 3	Jul 29
28	Feb 9	Sep 28	Apr 4	Jul 30
29	Feb 10	Sep 29	Apr 5	Jul 31
30	Feb 11	Sep 30	Apr 6	Agu 1
31	Feb 12	Oct 1	Apr 7	Agu 2
32	Feb 13	Oct 2	Apr 8	Agu 3
33	Feb 14	Oct 3	Apr 9	Agu 4
34	Feb 15	Oct 4	Apr 10	Agu 5
35	Feb 16	Oct 5	Apr 11	Agu 6
36	Feb 17	Oct 6	Apr 12	Agu 7
37	Feb 18	Oct 7	Apr 13	Agu 19
38	Feb 19	Oct 8	Apr 14	Agu 20
39	Feb 20	Oct 9	Apr 15	Agu 21
40	Feb 21	Oct 10	Apr 16	Agu 22
41	Feb 22	Oct 11	Apr 17	Agu 23
42	Feb 23	Oct 12	Apr 18	Agu 24
43	Feb 24	Oct 13	Apr 19	Agu 25
44	Feb 25	Oct 14	Apr 20	Agu 26
45	Feb 26	Oct 15	Apr 21	Agu 27
46	Feb 27	Oct 16	Apr 22	Agu 28
47	Feb 28	Oct 17	Apr 23	Agu 29
48		Oct 18	Apr 24	Agu 30
49		Oct 19	Apr 25	
50		Oct 20	Apr 26	
51		Oct 21	Apr 27	
52		Oct 22	Apr 28	
53		Oct 23	Apr 29	
54		Oct 24	Apr 30	
55		Oct 25	May 1	
56		Oct 26	May 2	
57		Oct 27	May 3	
58		Oct 28	May 4	
59		Oct 29	May 5	

spm

Sample #	Winter	Autumn	Spring	Summer
60		Oct 30	May 6	
61		Oct 31	May 7	
62			May 9	
63			May 10	
64			May 11	
65			May 12	
66			May 13	
67			May 14	
68			May 15	
69			May 16	
70			May 17	
71			May 18	
72			May 19	
73			May 20	
74			May 21	
75			May 22	
76			May 23	
77			May 24	
78			May 25	
79			May 26	
80			May 27	
81			May 28	
82			May 29	
83			May 30	
84			May 31	

The concentrations of O_3, NO, NO_2, SO_2 and SPM are comparable with the results of Bottesford (UK) as it is seen from Table 3.4. Except O_3, the concentrations of NO, NO_2 and SO_2 are lower than those of Bottesford. For winter and spring months, the O_3 results in Mt. Uludağ are lower than that of Bottesford. But during summer and autumn O_3 concentration in Mt. Uludağ is higher than that of Bottesford.

In Table 3.5, The Turkish Air Quality Standards set by Air Quality Regulation is given. In this table, ambient and industrial quality standards are given as longterm and shortterm trends. In this table, longterm means that the daily averages of one year of each pollutant. Shortterm means that the daily maximum averages of each pollutant in one year. Except the O_3, for the other pollutants, NO, NO_2, SO_2 and SPM Turkish air quality standards are given. The O_3 standards are not given because there is no work related with O_3 both in rural and urban areas in Turkey up to now. As it is explained before, this work is the first work for the measurement of ozone. So, the comparison of our O_3 results with Turkish Ozone Quality standards is not possible. Although the given standards for NO_2, NO and SO_2 are for urban ambient air, we compared our values to obtain a roughly information. The best thing is that the comparison of our results with other rural area results of Turkey. But unfortunately there is no such a work. Daily averages of our whole data for NO, NO_2, SO_2 and SPM were lower than that of Turkish Air Quality Standard for ambient air. The only interesting situation is for the shortterm ambient concentration (maximum daily average) of SO_2. These day were the 16th, 19th and 26th of the February 1994. The average wind direction for these days were 175.3, 178.4 and 188.5^0 (from south of the station) respectively. This indicates that in these day, there was strong wind coming from ski resort area to the station (ski resort is at the south of the station).

Table 3.4 The Comparison of Mean Monthly Concentrations of O_3, NO, NO_2, SO_2 (ppb) in Bottesford UK For 1979 and at Mt Uludağ*

	NO	NO_2	O_3	SO_2
January	15(3)	19(5)	20(18)	26(14)
February	5	17	26(21)	15(21)
March	7	8	38(25)	12(2)
April	4	6	43(27)	12(3)
May	3	7	40(22)	8(6)
June	4	7	35(21)	9
July	4(0.4)	6(3)	29(51)	7
August	4(0.4)	4(2)	28(44)	8(1)
September	3	5(1)	28(41)	9(1)
October	7	12(1)	21(24)	8(1)
November	10	14	20	11
December	7	7	29	11

A.Martin et all.,(1981) [27].

* Uludağ data are given in parenthesis

Table 3.5 The Turkish Air Quality Standards Set by Air Quality Regulation and Mt. Uludağ Results (in paranthesis)

	Longterm		Shortterm	
	Ambient	Industrial	Ambient	Industrial
SO_2 ($\mu g/m^3$)	150(16.5)	250	400(150)	400
SPM ($\mu g/m^3$)	150(16.6)	200	300(80.8)	400
NO ($\mu g/m^3$)	200(1.0)	200	600(24)	600
NO_2 ($\mu g/m^3$)	100(2.10)	100	300(15.4)	300

Türk Çevre Vakfı [8]

3.3 Diurnal Variations of Pollutants

Hourly mean concentrations of measured parameters are calculated to see the behaviour during the day. Concentrations of NO_2, O_3, SO_2 and SPM show well defined diurnal variations. But the NO concentrations do not show and significant diurnal trend which is consistent with the short residence time of NO in the atmosphere due to fast conversion.

The diurnal variation in O_3, NO, NO_2, SO_2 and SPM concentrations and Meteorological Parameters (Wind Speed, Wind Direction, Temperature and Humidity) are shown in Fig 3.5 and Fig 3.6.

The O_3 concentration peaks between 3-4 pm. The NO_2 and SO_2 follows the same general pattern and peaks at the same time with the O_3. Such synchronized variations of NO_2 and O_3 with SO_2 indicates that the O_3 is being transported from a distant urban or industrial area where SO_2 is being emitted. As mentioned in the earlier sections, potential source regions in the area are the town of Bursa and ski resort where NO_x is being emitted from motor vehicles and SO_2 is being emitted from industrial activities and from residential heating units. Consequently, the O_3 observed in the Mt.Uludağ is being transported from one of these source regions. In addition to photochemical production which will be discussed more in the following sections.

The lack of diurnal variation is characteristics of remote locations which are above the nocturnal inversion and are not influenced by local emissions.

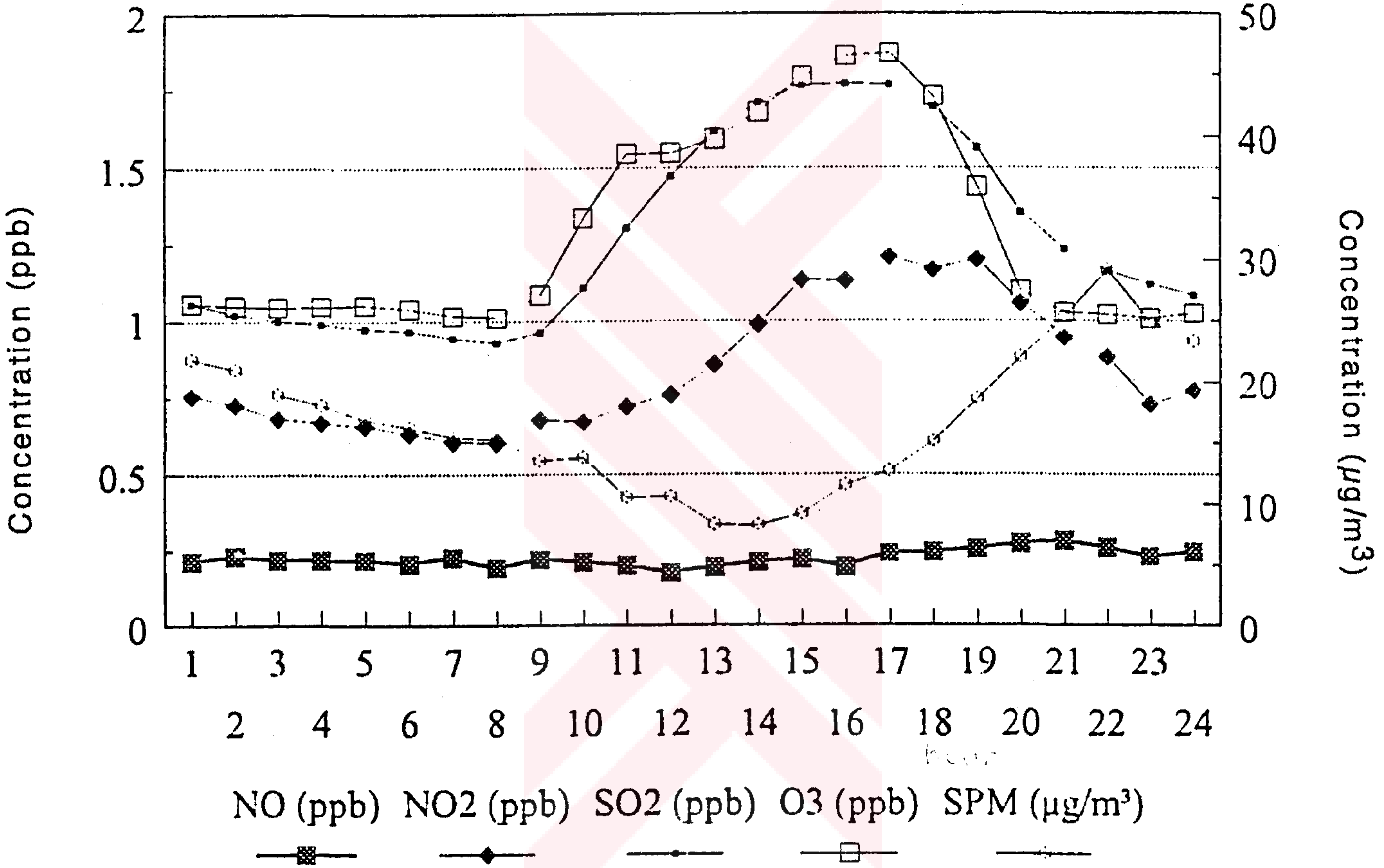


Figure 3.5 The Diurnal Variation of O_3, NO_2, NO, SO_2 and SPM at Mt.Uludağ

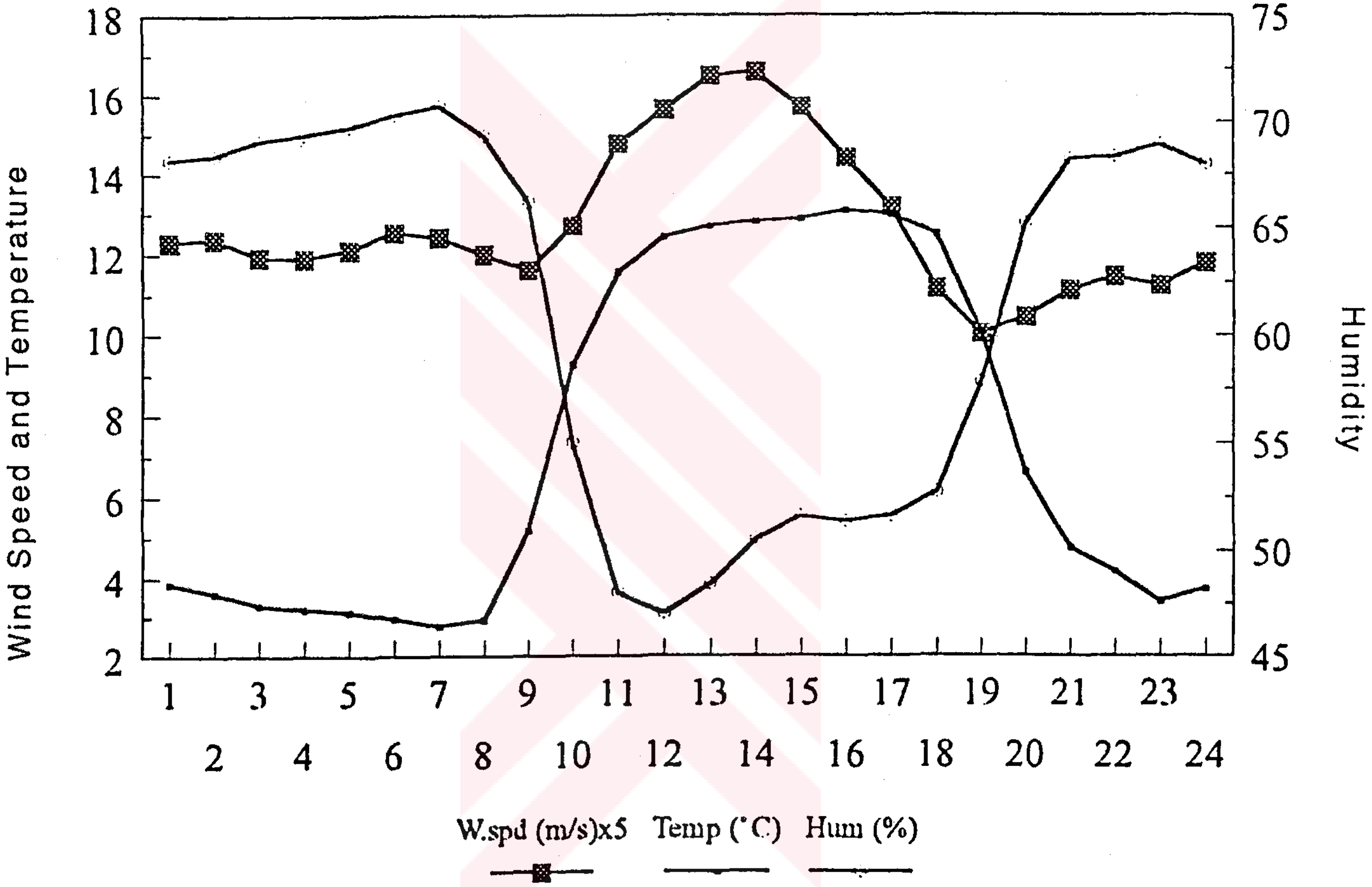


Figure 3.6 The Dİurnal Variation of Meteorological Parameters at Mt.Uludağ

But at Mt.Uludağ, The situation is opposite. The diurnal variation in O_3 concentration(the difference between maximum and minimum concentration for whole data) was about 14.5 ppb. So, the vicinity of station is under influence of local emissions like Bursa and ski resort.

Fig 3.7. shows diurnal variation of O_3 for different seasons. This figure clearly indicates photochemically produced O_3 was transpoted from Bur sa to the station. During the morning hours NO_x is emitted from motor vehicles and in the following hours NO is converted to NO_2 which produces O_3 and both of them are transported to the Mt. Uludağ in the afternoon hours. That is why the O_3 concentration shows a steady value during morning hours and peak in the afternoon. The amplitude of the peak is higher during the summer due to faster production in summer at which solar flux is also high. Peak height decreases as the solar flux decreases, and lowest in the winter. In the vicinity of the station, photochemical O_3 production was also possible. As it seen from the figure, there was a good shift for the peak time of ozon during day time. This depends on the shift of the solar flux during day time in each season.

In addition to this afternoon ozone peak, in some cases, night time O_3 peak was also observed (at 24 pm, midnight). Although the afternoon ozone peak correlate well with the SO_2 and NO_2, the night time ozone peak does not correlate with any of them. As the station is situated at approximatelly 2 000 m altitude, the O_3 night-time O_3 peaks are suspected to be due to the stratospheric injection the stratospheric O_3 to troposphere (Fig 3.8).

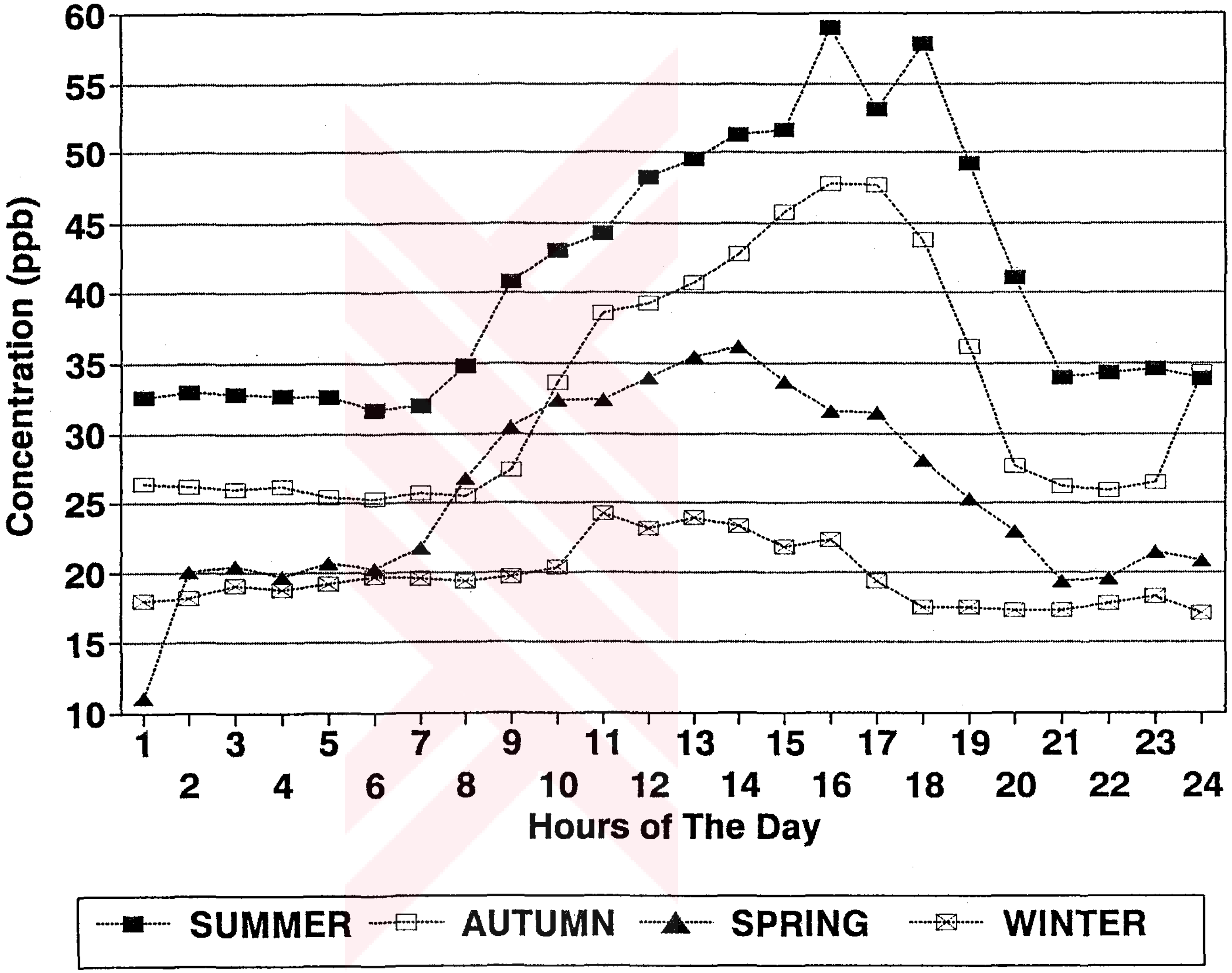


Figure 3.7 The Diurnal Variation of O_3 Concentration For Sesaons at Mt.Uludağ

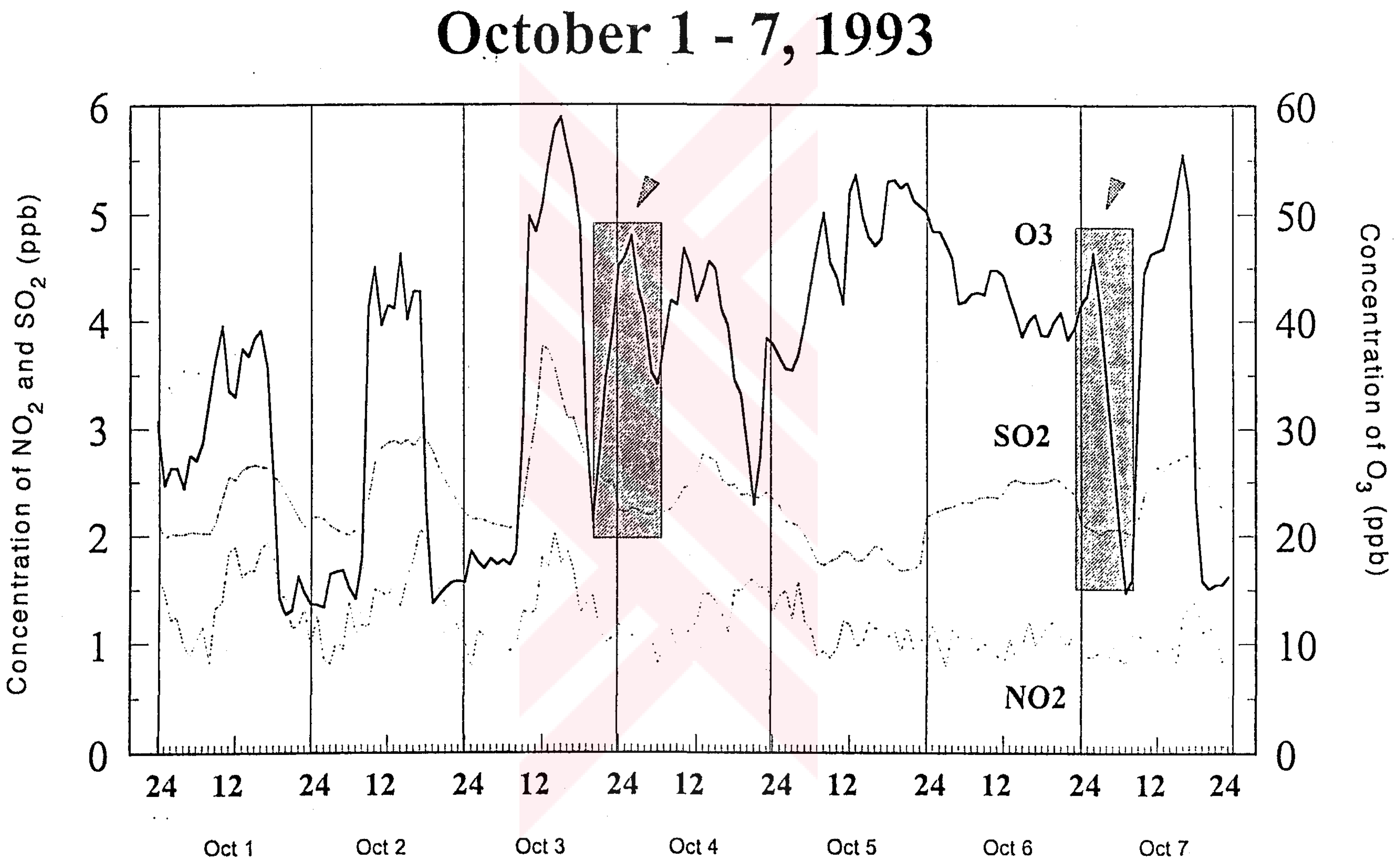


Figure 3.8 Night-time O_3 Peaks Which are Suspected to be the Stratospheric Injection at Mt.Uludağ

The NO concentrations do not show any significant diurnal trend which is consistent with the transport scenario (Fig 3.9). The distance between the town of Bursa and station is approximately 20 km's. Since the average wind speed during day-time changes between 2-3 m/s, the transport time of the pollutants to the station is 1-3 hours. During 3 hours most of the NO is converted to NO_2.

The more vigorous conversion of NO to NO_2 during summer months can also explain high NO_2 concentrations in the summer season. Concentrations of NO do not change significantly in four seasons included but winter concentration is a little higher than that of other seasons. In addition to this, winter values for NO_2 is lower.

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

The diurnal variation of NO_2 is the same with the O_3. The peak for NO_2 was also observed in the afternoon (at 3 pm). As it is seen from the Fig 3.10, the diurnal variation of NO_2 for different seasons, due to lack of conversion during morning hours, the NO_2 shows steady state during this time of the day. The same steady trend was also observed during night due to the same reason. The diurnal variation of O_3 and NO_2 with error bars for autumn 1993 were given in Fig 3.11 and 3.12.

The diurnal variation of SO_2 for seasons is given in Fig 3.13. As it is seen from the fig, for winter, spring and autumn seasons the observed trend of SO_2 is nearly same in which there is SO_2 peak maximum at 3 pm. But this observed trend is more clear in winter than in spring and autumn. The diurnal variation of SO_2 is steady in summer due to decreased emissions of domestic heating systems.

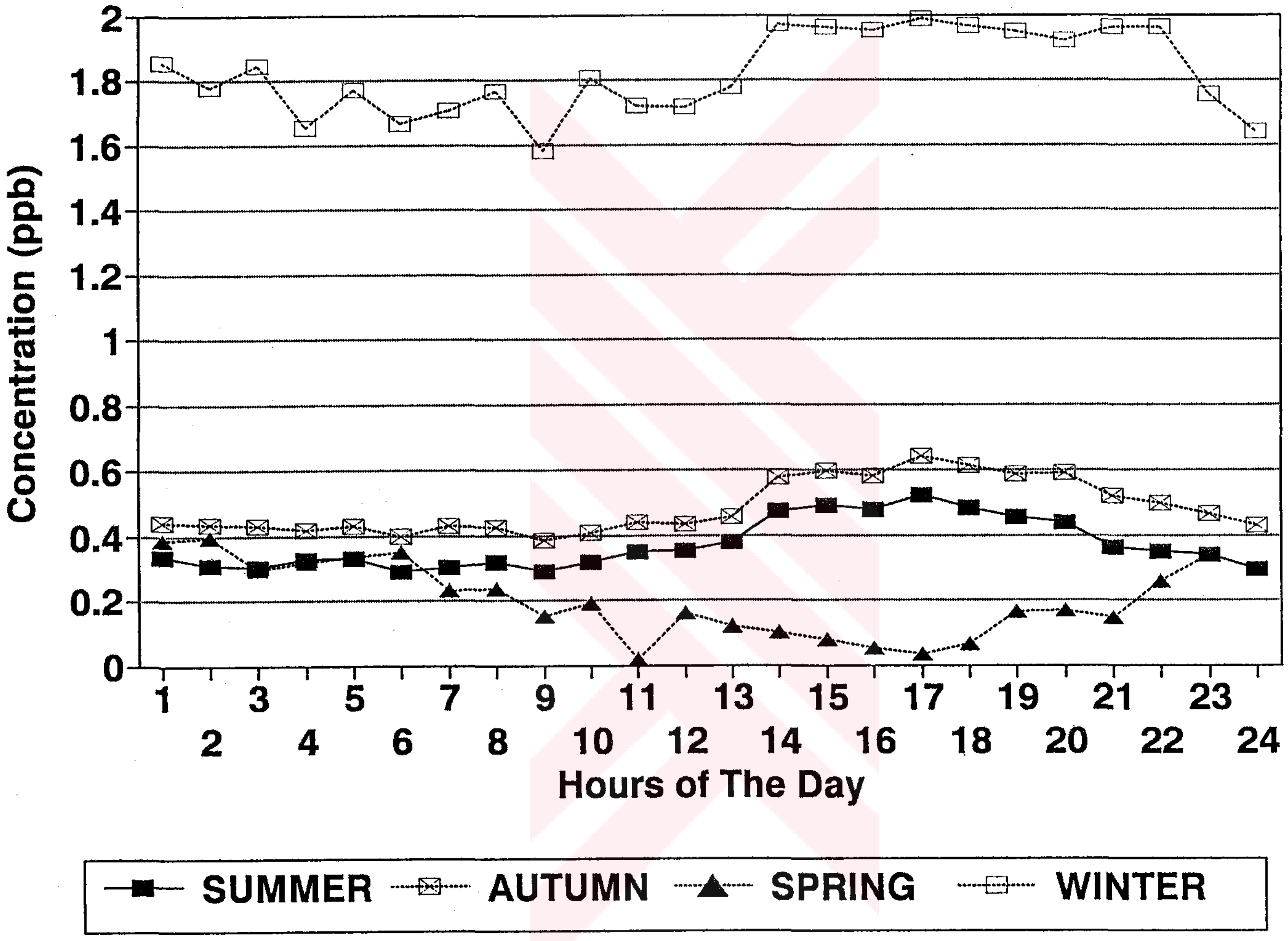


Figure 3.9 The Diurnal Variation of NO Concentration For Seasons at Mt.Uludağ

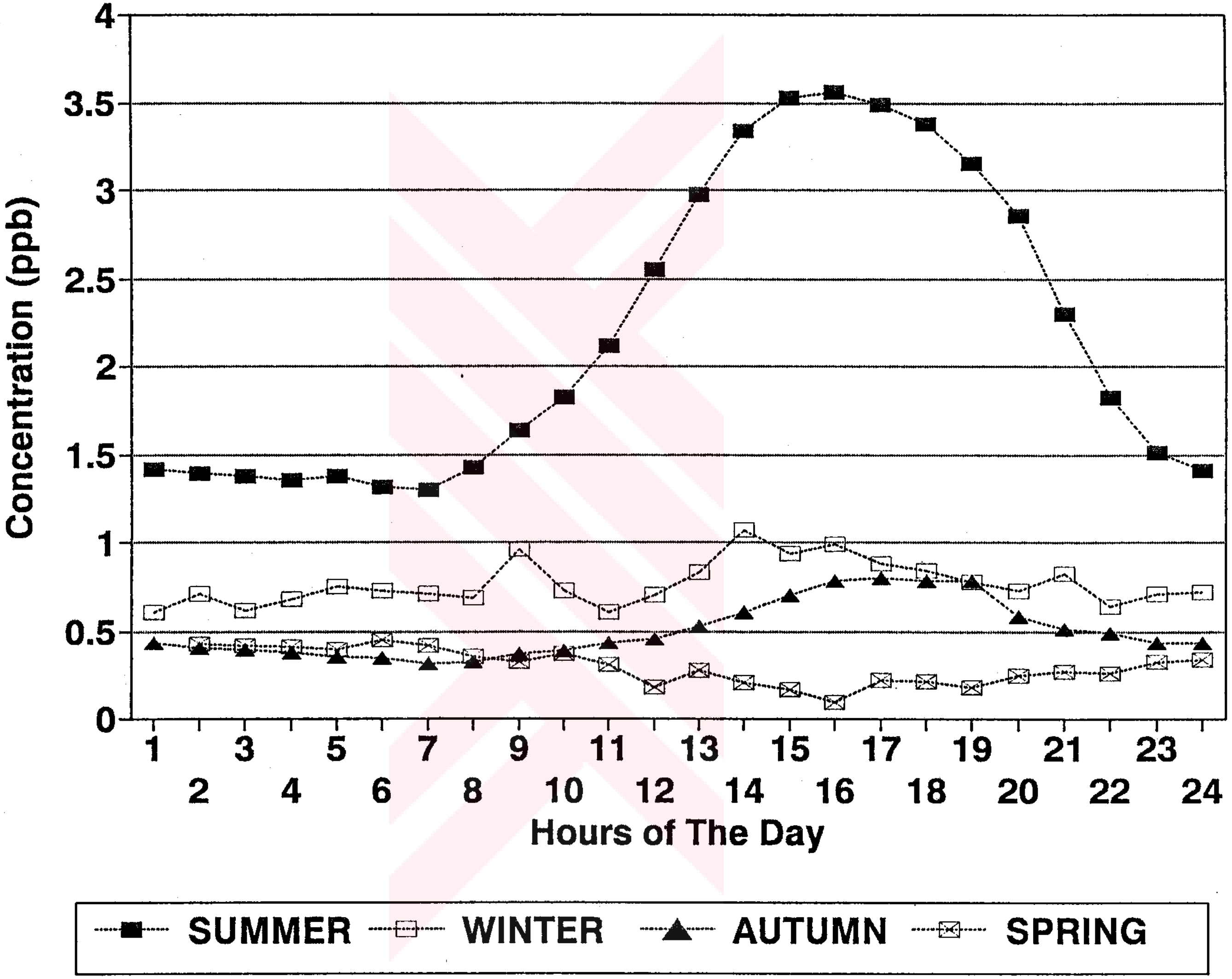


Figure 3.10 The Diurnal Variation of NO_2 Concentration For Seasons at Mt.Uludağ

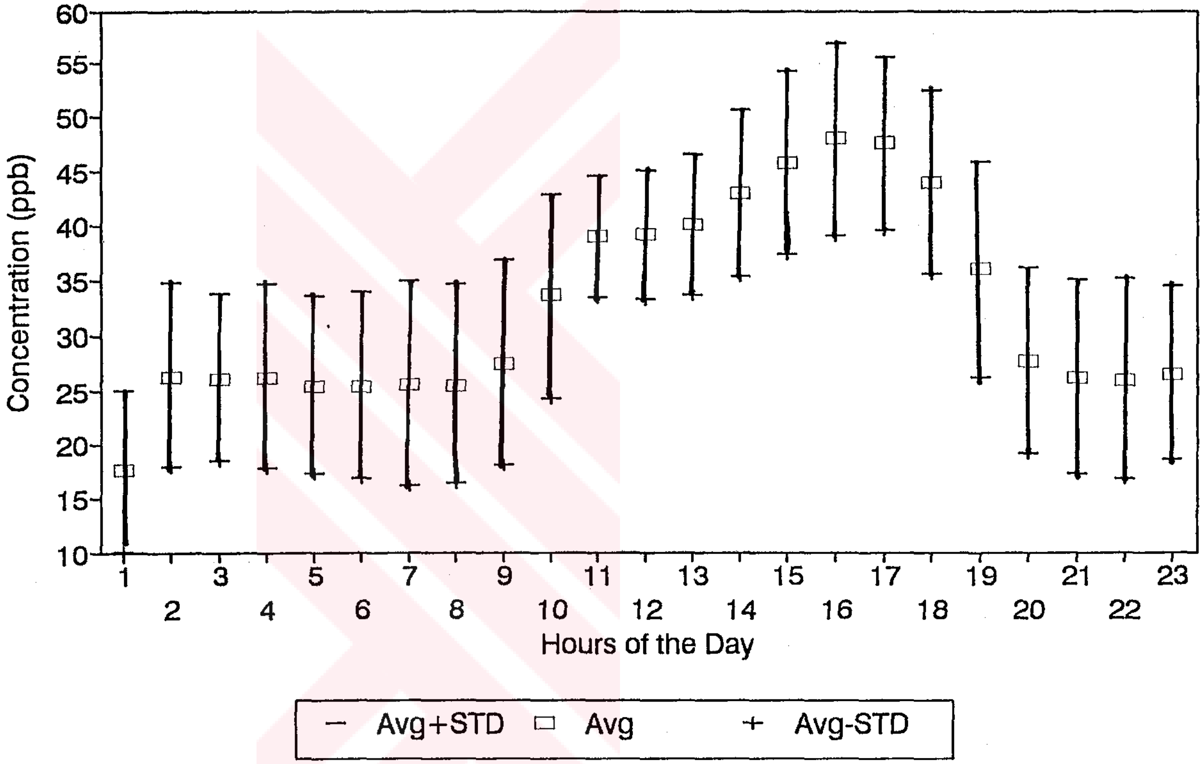


Figure 3.11 The Diurnal Variation of O_3 for Autumn at Mt.Uludağ

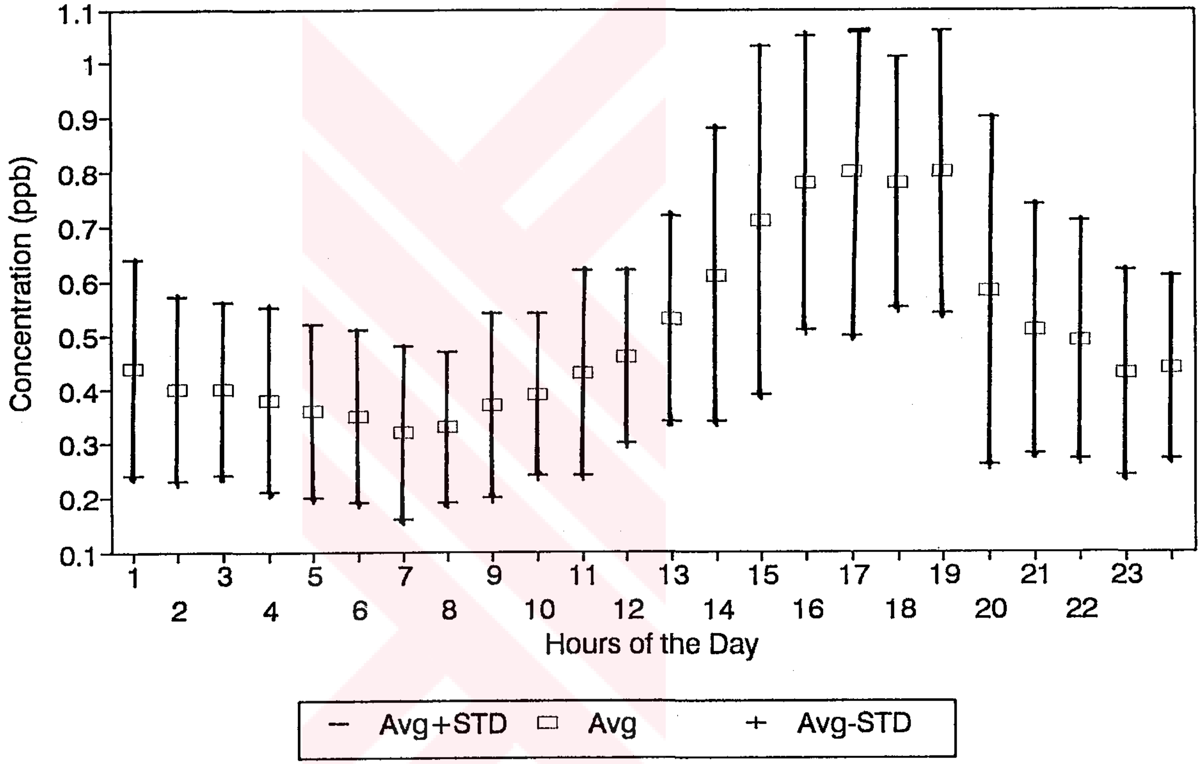


Figure 3.12 The Diurnal Variation of NO_2 for Autumn at Mt.Uludağ

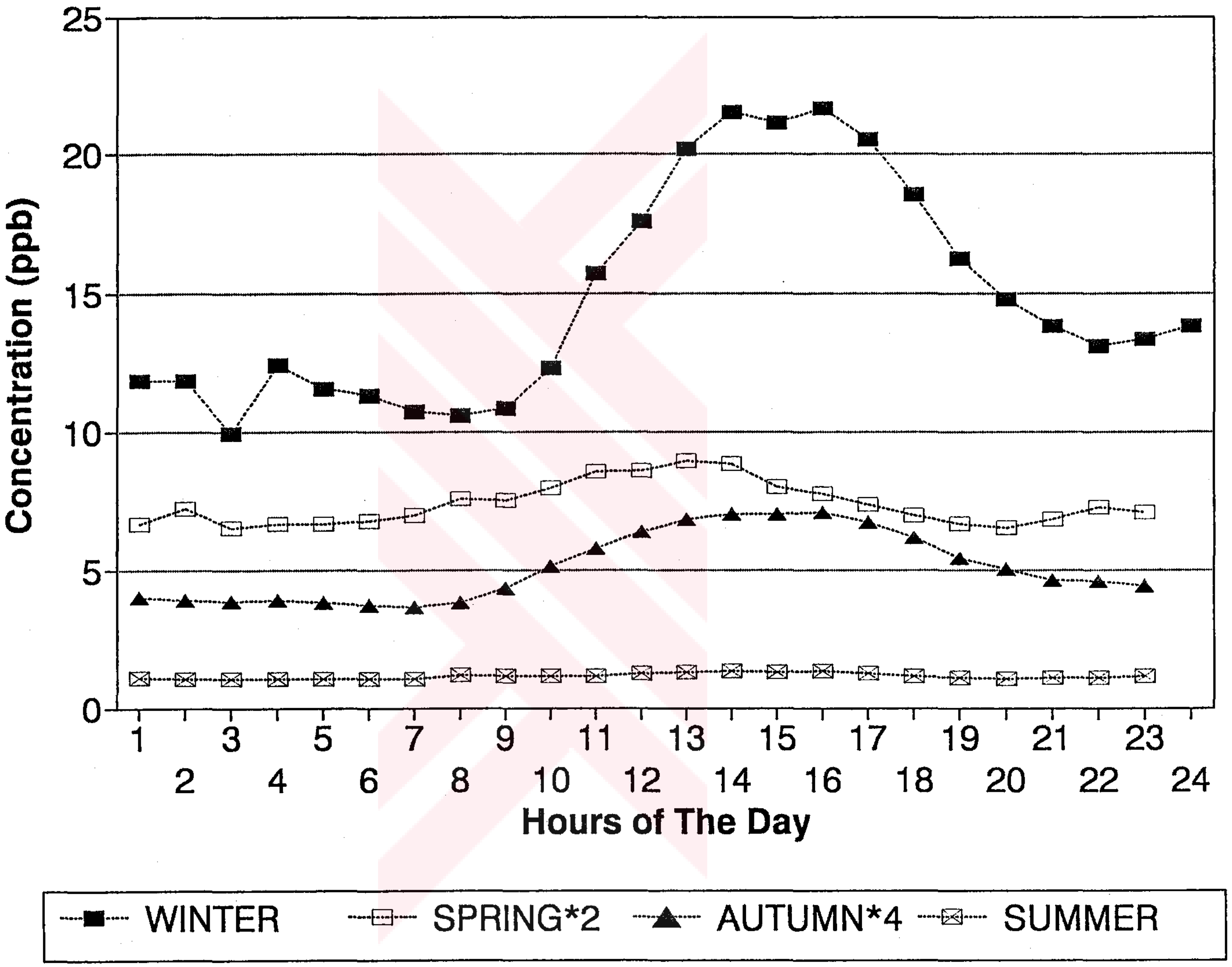


Figure 3.13 The Diurnal Variation of SO_2 Concentration For Seasons at Mt.Uludağ

The wind pattern in the station is N to NW direction during morning hours. If the distance between the station and the town of Bursa is considered as about 20 km and normal wind speed is 2-3 m/s,the observed peak around 3 pm is reasonable. As it is seen from the Fig 3.13, the steady trend in the night is higher than it is in the morning.

In Fig 3.14, the diurnal variation of SPM for seasons is given. As it is seen from the figure, diurnal variation of SPM in summer and spring is steady but there is high variation in winter and autumn. Due to high fluctuations in the direction and speed of wind, the observed fluctuation in autumn and summer is reasonable. But during dry season which are spring and summer, there is considerable no fluctuation in wind direction and wind speed.

The SPM concentrations also show a well defined diurnal cycle. However, the SPM concentrations peak at approximately 21 pm which is out of phase with the diurnal behaviour of NO_2, O_3, and SO_2. The out of phase behaviour of SPM concentrations is not sporadic and can be consistently seen everyday as depicted in Fig 3.15, where the SO_2 and SPM concentrations are plotted for the month of september 1993. Such consistent behaviour of particles indicates that the main source of particulate material in the Mt.Uludağ is different from the sources of gaseous pollutants. At this point, sources of particulate pollutants other than wind blown dust are not clear.

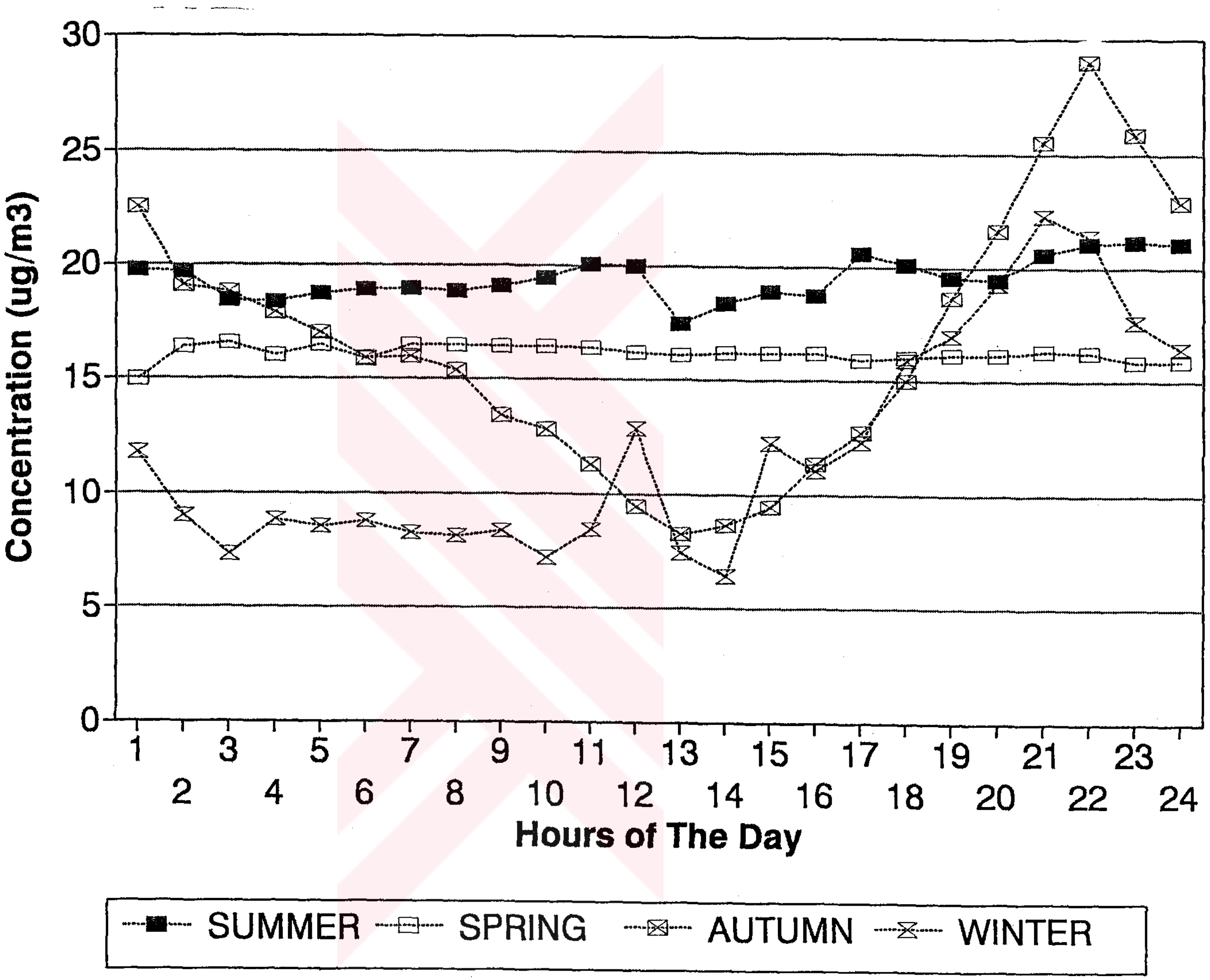


Figure 3.14 The Diurnal Variation of SPM Concentration For Seasons at Mt.Uludağ

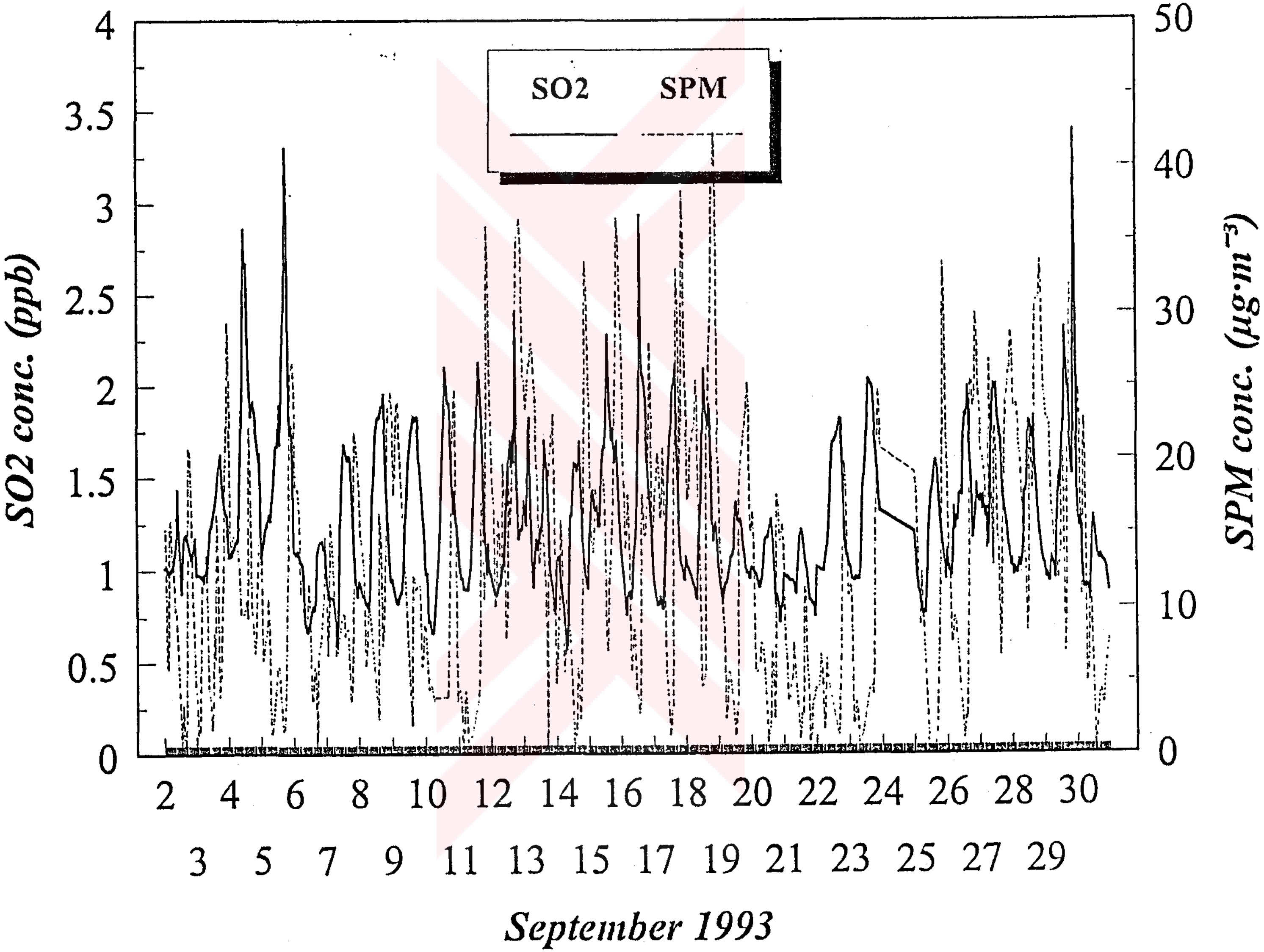


Figure 3.15 The Diurnal Variation of SO_2 and SPM Concentration in September 1993 at Mt.Uludağ.

3.4 Correlations Between Measured Parameters

The correlation coefficient between SPM and SO_2 during summer is 0.61. This modaretely high correlation is expected because during summer SO_2 and dust particles due to wind and wind patterns travel with the same air masses. But for winter it is 0.12. This is also expected result because the vicinity of the station is covered by snow during this season. This small correlation is due to unburned fuels from sources. The corelation between SO_2 and SPM is given in Table 3.6.

The SPM and relative Humidity shows anticorrelation with each other both for winter and summer which is shown in Table 3.7. The correlation between SPM and Relative Humidity for winter and summer are -0.50 and -0.053 respectively. Due to snow, anticorrelation between them for winter is higher than that of summer (there is no wind blown dust in winter).

The correlation between O_3 and temperature, and NO_2 is given in Table 3.8. In all months, there is very high correlation between O_3 and temperature (which could be taken as the intensity of solar radiation). Although during warm months the correlation between O_3 and NO_2 is high which shows photochemical ozone production, for cold months there is anticorrelation between them due to the lack of photochemical reaction. High concentration of O_3 occurs when the relative humidity of ambient air is low, the ambient temperature (solar flux) is high, and the air is stable. These correlations are also supporting the idea of photochemical production of O_3.

Table 3.6 The Correlation Coefficient Between SO_2 and SPM (Number Samples are given in paranthesis)

	SO_2 and SPM
Winter	0.12(61)
Autumn	0.12(61)
Spring	-0.040(58)
Summer	0.61(15)

Table 3.7 The Correlation Coefficient Between SPM and Humidity (Number of Samples are given in paranthesis)

	SPM and Humidity
Winter	-0.50(61)
Autumn	-0.073(49)
Spring	-0.10(75)
Summer	-0.53(49)

Table 3.8 The Correlation Cofficient Between O_3 and Temperature, and NO_2 (Number of Samples are given in paranthesis)

	O_3 and Temperature	O_3 and NO_2
March	0.65(15)	-
April	0.70(30)	-0.44(30)
May	0.74(30)	-0.33(15)
June	0.89(13)	-
July	0.84(15)	0.96(14)
August	0.94(19)	0.86(18)
September	0.93(30)	0.81(30)
October	0.98(31)	0.77(10)
January 94	0.89(24)	0.38(24)
February 94	0.56(28)	0.31(10)

3.5 Possible Source Regions Effecting Sampling Area

There are no nearby strong sources of SO_2 and SPM around the station. Consequently, the observed concentrations of these pollutants could be explained by transport from the town of Bursa or from the resort area where fossil fuel is burned for residential heating.

As it is seen from the mean seasonal variation of SO_2 in (Fig 3.1), the concentration of SO_2 is directly proportional with the residential heating. A sharp increase in the concentration of SO_2 during winter months proves above explanation. Low concentrations of SO_2 in the station during summer months are probably due to lack of residential heating during this period. This idea is supported by the directional variations of the pollutants measured in Uludağ Mountain.

Fig 3.16 shows concentration variations with different wind directions. Although the SO_2 does not show high variation with wind direction, slightly higher concentrations are observed when wind blows from SSW and WNW indicating transport from Bursa and ski resort.

Concentration of the SPM in the Mt.Uludağ most probably is due to airborne dust particles in the summer when the soil is dry. But In spring, autumn and winter it should be explained by the transport of anthropogenic emissions when the soil in the vicinity of the station is either damp or covered by snow. Source of anthropogenic emissions is either the town of Bursa or ski resort.

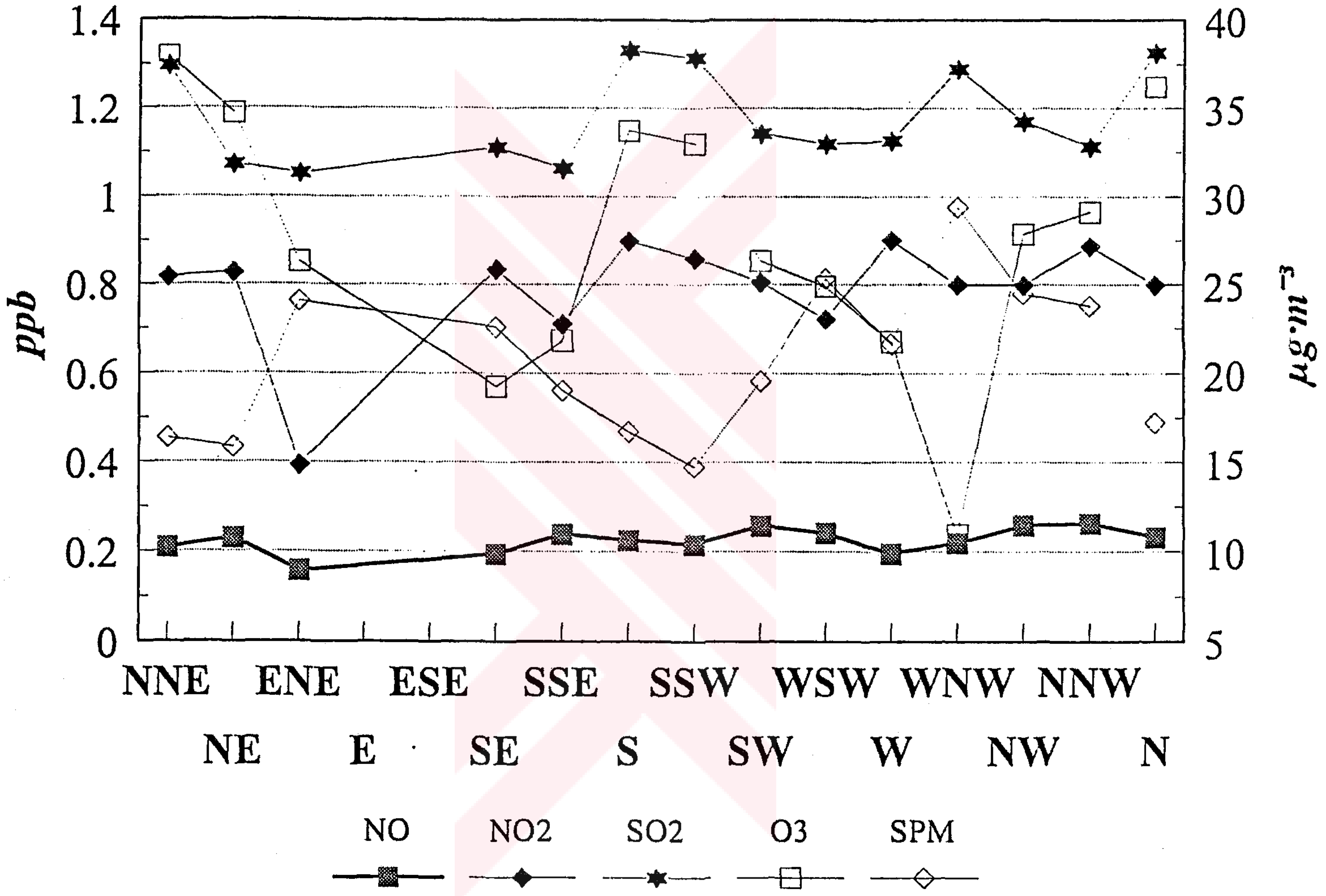


Figure 3.16 Variation of Concentration of Pollutants With Different Wind Directions

The SPM concentrations show a totally different directional dependence. Lowest SPM concentrations are associated with southerly and northerly wind sectors which correspond to the highest concentrations of NO_2, SO_2, O_3. The highest concentration of SPM is observed when the winds blow from WNN sector, indicating that observed pattern of SPM concentrations are also due to fossil fuel combustion. The source which lies to the WNN of the station is not clear. A small village which is located in that sector is a candidate for the observed high concentrations of SPM and SO_2. However it is not certain whether such a small source can determine the tempororal variation of the SPM concentrations at the station-site.

The main potential sources of O_3 observed in the station-site is the local photochemical generation and some transport from Bursa. Since the town of Bursa lies to the north west of the station, this type of transport is expected to be associated with northerly winds and should correlate well not only with NO_2, but also with other conventional pollutants from fossil fuel combustion, like SO_2 and SPM. The ozone from the resort area should be associated with southerly winds and again correlate well with SO_2 and SPM. Although pollutants emitted in the town of Bursa and O_3 are produced from them are several orders of magnitude higher than that produced in the resort area, it is important source due to short distance to the station.

In addition to the ozone transported from the settlement areas (ski resort and Bursa), some can also be generated in the vicinity of the station either from precursor gases from the previous day or from the NO_x and hydrocarbons emitted by the vehicles passing from the road that connects the town of Bursa to hotels and which lies within one km to the west of the station. As a fourth alternative some of the ozone may be due to stratospheric injection as the station is approximately 2 kms from the sea level and above the boundary layer. Such ozone intrusions can only be observed during night-time when tropospheric ozone is at its minimum. The O_3 which is transported from settlement areas correlate well with the SO_2 and NO_2. The stratospheric ozone can not be observable during day time as O_3 concentrations increase due to pollution transport. However, it may be observable during night-time when tropospheric O_3 concentrations is at its minimum. A few O_3 peaks which occurred during night-time and which did not correlate with the SO_2 and NO_2 were detected. The average night-time and day-time O_3 concentrations are 38± 14 ppb and 26±13 ppb respectively. These peaks which occur during night-time have maximum concentrations resembling day-time peak concentrations. However, since the SO_2 and NO_2 do not show a synchronized maxima, the ozone observed is not due to transport from urban sources. Since the ozone can not survive in the night, these peaks can be due to injection from the stratosphere. However, the appearance of these peaks are not frequent and stratospheric O_3 is probably not a significantly source for the observed concentrations of O_3.

Short and long term temporal variations and close association between the observed ozone and SO_2 concentrations were discussed in the previous sections (Diurnal Variation Part). Suggested that transport from the settlement areas is the main source of O_3 in the Mt.Uludag. However, short and long term trends is not sufficient to discriminate between the two potential source regions, namely the town of Bursa and resort areas, the relation between wind direction the wind coming from Bursa and ski resort) and observed concentrations can provide information on relative importance of these source areas.

The NO concentration does not show any directional behaviour. Concentrations are more or less equally distributed. But, NO_2 is minimum when wind blows from the East. Concentration increases with westerly winds and almost the same trend in the angle of NW to SW.

The high concentrations of SO_2, NO_2 and O_3 observed when winds blow from N and NNW are due to transport of pollutants from the town of Bursa, whereas high concentrations associated with southerly transport is due to pollutants emitted in the ski resort.

Although the transport of pollutants from the town and ski resort are the main mechanisms that define long and short term variations in the concentrations of O_3 and other pollutants, other sources of O_3,such as the vehicular activities around the station and injection from the stratosphere may also contribute to the observed concentrations of O_3. The linear regression between SO_2 and NO_2 are depicted in Figure 3.17. The SO_2 is correlated with NO_2 ($r = 0.5$) as expected from the similar temporal variations of the two parameters. However, two different populations of data points appears when the same plot is prepared for high concentrations only (also shown in Fig 3.17). One of the populations consisted of data with high NO_2 but low SO_2 concentrations, and the second population consisted of data points with high SO_2 and low NO_2 concentrations. In each group the SO_2 and NO_2 are correlated with each other indicating two different sources for the SO_2 and NO_2 observed in the station. Although they are not included in the figure, the regression between NO vs. SO_2 and O_3 vs. SO_2 show the same trend. These two groups of data which is apparent in all regression plots when only high concentrations are included indicates that the presence of two different sources for O_3, SO_2 and NO_2.

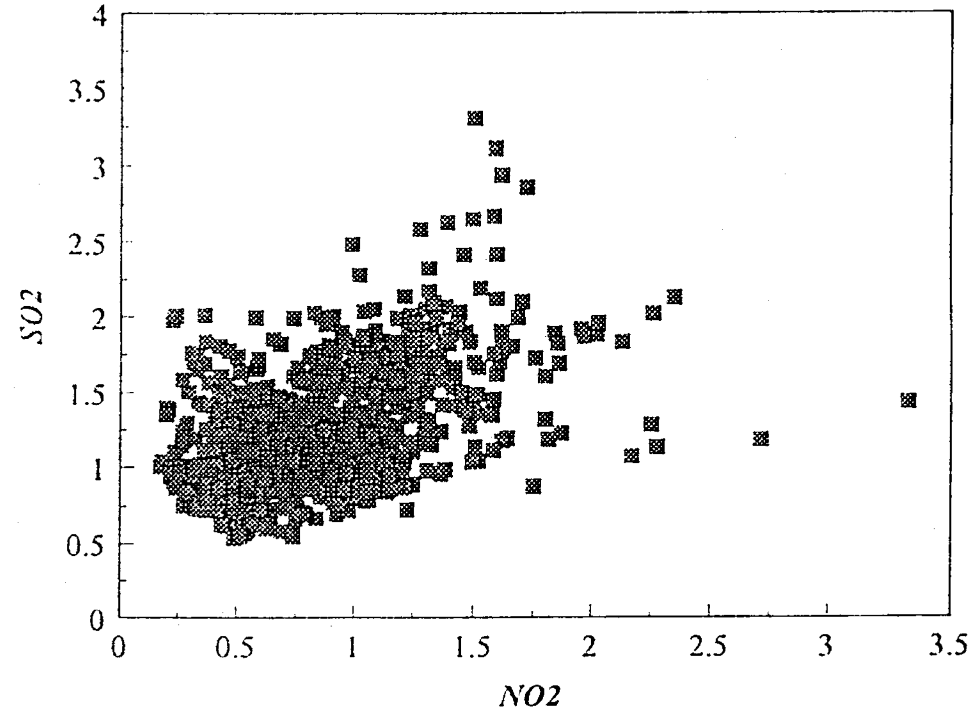
The group which have high concentrations of SO_2 and low concentrations of O_3 and its precursors probably represent transport from town of Bursa and ski resorts.

The group with low concentrations of SO_2 and high concentrations of O_3, NO_2 probably represent emissions from motor vehicles in the vicinity of the station.

The data with low concentrations of parameters and which are not included in the second regression is expected to be to transport from settlement areas because there is a relatively strong correlation between the parameters when these data are included. The uncertainty in the conclusion reached on this minor source of O_3 is high due to the small number of data points included in the regression between high concentrations of parameters. As the monitoring programme continues, these two groups of data will become more populated and will allow us to reach more definite conclusion on the contribution of motor vehicles on the observed concentrations.

3.6 Ions

Atmospheric $SO_4^{=}$ concentrations are seasonally dependent. Concentrations increase in summer, as do the areas of elevated levels. Seasonal differences are primarily due to the increased photochemical oxidation of SO_2 to $SO_4^{=}$ during the summer months. There are two important chemical reaction mechanisms for $SO_4^{=}$ and NO_3^- formation in the atmosphere; photochemical and aqueous phase reactions. Photochemical reactions occur only in hot season, summer.



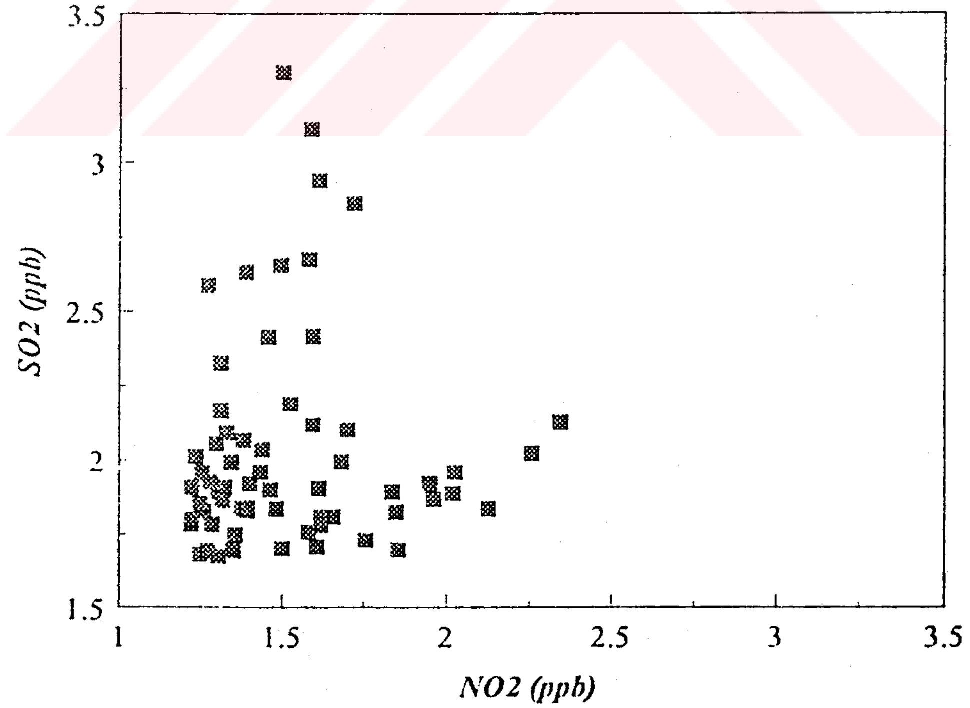


Figure 3.17 Linear Regression Between SO_2 and SPM

Because conversion of SO_2 to $SO_4^=$ and NO_2 to NO_3^- depend on the solar radiation as in the photochemical formation of ozone formation. Aqueous phase reactions occur only during winter season.

Our $SO_4^=$ and NO_3^- data were taken in autumn, September of 1993. During this month of the year, there is neither enough solar radiation for photochemical reactions nor enough humidity for aqueous phase reactions. So, as it is expected, there is poor correlation between SO_2 and $SO_4^=$ (r=0.04) and between NO_2 and NO_3^-(r=0.03). But the correlation between NO_3^- and $SO_4^=$ is 0.6 because both of them are aerosols. Two days within the month is below the detection of analyzer. The comparison of SO_2, $SO_4^=$, NO_2 and NO_3^- is given in Table 3.9.

Our $SO_4^=$ and NO_3^- concentrations are comparable with other rural area results. In 1984, atmospheric concentration of $SO_4^=$ and NO_3^- was measured in Berkshire Mountain by Wolff T.G.et all [39] as 9.7 ppm and 2.6 ppm respectively. The same $SO_4^=$ trend was also observed in Virginia (11.9 ppm), Delaware (7.2 ppm) and Whiteface Mountain (7.7 ppm) [39].

Table 3.9 Comparison of Gases and Aerosols

	SO_2 (ppb)	$SO_4^{=}$ (ppm)	NO_2 (ppb)	NO_3^- (ppm)
Num.of Sample	30	25	28	25
Average	1.3	9.6	0.7	3.3
Min	1.3	1.6	0.3	0.7
Max	1.8	21.2	1.1	9.6
STD	0.2	5.2	0.2	2.1

CHAPTER IV

CONCLUSION

In Uludağ national park at 2000m high, one monitoring was station was constructed for the measurement of O_3, SO_2, NO, NO_2 and SPM concentrations.

The O_3, SO_2, NO, NO_2 and SPM concentrations were measured at a 2,000m high mountain station (Uludağ, Sarılan Region) in the northwestern Turkey.

The long term trends observed in the O_3 concentrations were consistent with the photochemical generation mechanism. The short term variations in the concentrations on the other hand were explained by the sources and transport to the station.

The O_3 concentration showed similar temporal variation with the pollution derived parameters such as the SO_2 and NO_2 indicating that the transport from urban areas is the main source of O_3 and other pollutants in the station. The two source regions, namely the town of Bursa which lies to the northwest of the station and ski resort which is located to the south of the station both contribute to observed concentrations of the O_3, SO_2, and NO_2. Although the resort area was a minor source for pollutants, its contribution is approximately the same with that of the town of Bursa due to its closer proximity to the station.

The regression plots between pollutants have suggested the existences of two populations of data points, one representing transport of pollutants from urban areas and the other one representing emissions from motor vehicles which travel on the road that connects the town to the ski resort.

Several O_3 peaks were identified which occur during night time and which do not correlate with the SO_2 and NO_2 peaks. The peaks were believed to be due to injection of O_3 from the stratosphere.

Concentrations of the suspended particles showed totally different temporal pattern which showed peak at night Although, the sources for such a different behaviour is not certain, a small village which lies to the WNW of the station was suspected to be the source.

This work also shows that acid rain is not the only source for the destruction of trees. The effect of acid rain in winter is more due to wet deposition but in summer photochemical smog is important problem for the destruction of trees.

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