

**SOURCE APPORTIONMENT OF PM_{2.5}, PM_{2.5-10} AND OZONE IN BOLU
ATMOSPHERE IN RELATION TO METEOROLOGICAL VARIABLES**

by

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ABSTRACT

SOURCE APPORTIONMENT OF PM_{2.5}, PM_{2.5-10} AND OZONE IN BOLU ATMOSPHERE IN RELATION TO METEOROLOGICAL VARIABLES

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Daily particulate matters in two fractions (PM_{2.5} and PM_{2.5-10}) were collected throughout a year from March 2009 to March 2010. In addition ozone (O₃) and meteorological parameters were monitored between March 2009 and March 2012 in the same site (at high altitude semi-rural region of Bolu). Aerosol samples were collected by one dichotomous sampler (collecting PM_{2.5} and PM_{2.5-10} samples separately) and two particulate matter samplers (one PM₁₀ and one PM_{2.5} sampler) on teflon and micro glass fiber filters, respectively. Ionic species were determined by Ion Chromatography, elemental (trace and major metals) compositions were determined by Flame Atomic Absorption and Emission techniques. Elemental and organic carbon content were investigated by Organic Carbon/Elemental Carbon Analyzer. The statistical analysis results showed that the highest mean concentration of the elements for both fine and coarse particles are Na and Ca. In PM_{2.5}, the concentration values were $5.2 \pm 2.4 \mu\text{g m}^{-3}$ and $4.4 \pm 2.7 \mu\text{g m}^{-3}$ whereas in PM_{2.5-10} the concentration values were $4.4 \pm 1.9 \mu\text{g m}^{-3}$ and $4.2 \pm 3.9 \mu\text{g m}^{-3}$, respectively.

Carbonaceous compositions (total carbon content) nearly composed of 30 % of fine mode aerosol samples and differentiated as organic carbon (OC) (primary and secondary) and elemental carbon (EC) in this study. Annual average concentrations of OC and EC were $7.0 \pm 4.6 \mu\text{g m}^{-3}$ and $1.6 \pm 1.1 \mu\text{g m}^{-3}$, respectively. During three-years sampling, O_3 concentration showed well-defined seasonal pattern and significantly higher values were obtained in summer as compared to winter. Hourly average O_3 concentration ranged from 40 ppb to 48 ppb in summer and ranged from 14 ppb to 20 ppb in winter. Ozone concentration was exceeded AOT_{40} value (40 ppb) in the 26.0 % of total sampling period. Determination of possible sources for the investigated pollutants were carried out by some statistical treatments (Binary Correlation, Multiple Linear Regression) and receptor modelings (Enrichment Factor, Wind Sector and Back-trajectory Analysis, Factor Analysis and Positive Matrix Factorization-PMF). Six possible pollution sources were identified for both fine and coarse fractions by PMF analysis. The pollution sources for $\text{PM}_{2.5}$ were defined as regional background, traffic, soil, secondary compounds/combustion, metal works/sea salt and industrial emissions. In addition, long range transportation, road dust, coal combustion, metal works, crustal and surface soil were defined as sources for $\text{PM}_{2.5-10}$.

Keywords: Aerosol, Ozone, Trace metals, Major ions, Organic and elemental carbon, Receptor modeling, AOT_{40} , Statistical treatments

ÖZET

BOLU ATMOSFERİNDE METEOROLOJİK PARAMETRELERLE İLİŞKİLENDİRİLEREK PM_{2,5}, PM_{2,5-10} VE OZON KAYNAK PAYLAŞIMI

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Bolu'nun yüksek rakımda yarı kırsal bölgesinde, iki fraksiyonda (PM_{2,5} and PM_{2,5-10}) Mart 2009'dan Mart 2010'a kadar bir yıl boyunca günlük partikül örnekleri toplanmıştır. Ek olarak, aynı örnekleme noktasında (Bolu'daki yüksek rakımlı yarı kırsal alan) Mart 2009 ve Mart 2012 tarihleri arasında da ozon (O₃) ve meteoroloji parametreleri izlenmiştir. Aerosol örnekleri bir adet dichotomous (PM_{2,5} and PM_{2,5-10} örneklerini ayrı ayrı topluyor) ve iki adet partikül madde örnekleyicisi (1 adet PM_{2,5} ve 1 adet PM₁₀ örnekleyicisi) ile sırasıyla teflon ve mikro cam fiber filtreler üzerine toplanmıştır. İyonlar, İyon Kromatografi; elementel kompozisyonlar (eser ve temel metaller) ise Alevli Atomik Absorpsiyon ve Emisyon teknikleri ile tayin edilmiştir. Elementel ve organik karbon içeriği ise Organik Karbon/Elementel Karbon Analizörü ile araştırılmıştır. İstatistik sonuçlarına göre, en yüksek ortalama konsantrasyon değerleri ince ve kaba partiküllerde Na ve Ca'ya aittir. Sırasıyla PM_{2,5}'te konsantrasyon değerleri $5,2 \pm 2,4 \mu\text{g m}^{-3}$ ve $4,4 \pm 2,7 \mu\text{g m}^{-3}$ ve PM_{2,5-10}'ta ise $4,4 \pm 1,9 \mu\text{g m}^{-3}$ ve $4,2 \pm 3,9 \mu\text{g m}^{-3}$ 'dür. Karbon kompozisyonu (toplam karbon

içeriği) ince yapılı aerosollerin % 30'unu oluşturmakta ve bu çalışmada organik karbon (OK) (birincil ve ikincil) ve elementel karbon (EK) olarak ayırt edilmiştir. Organik karbon ve EK'nın yıllık ortalama konsantrasyonları sırasıyla $7,0 \pm 4,6 \mu\text{g m}^{-3}$ ve $1,6 \pm 1,1 \mu\text{g m}^{-3}$ 'tür. Üç yıllık örneklerme boyunca, O_3 konsantrasyonu iyi tanımlanmış biçimde bir mevsimsel değişim göstermiş ve kışa göre yazın daha yüksek değerler saptanmıştır. Yazın saatlik O_3 konsantrasyonları 40 ppb ile 48 ppb arasında, kışın ise 14 ppb ile 20 ppb arasındadır. Toplam örnekleme süresinin % 26'sında O_3 konsantrasyonu AOT_{40} değerini (40 ppb) aşmıştır. İncelenen kirleticiler için muhtemel kirlilik kaynaklarının belirlenmesi bazı istatistiksel uygulamalar (ikili korelasyon, çoklu doğrusal regresyon) ve alıcı ortam modellemeleri (Zenginleşme Faktörü, Rüzgar Sektörü ve Geri-trajektöri Analizleri, Faktör Analizi ve Pozitif Matriks Faktörizasyonu-PMF) ile gerçekleştirilmiştir. PMF analizi sonucunda hem ince hem de kaba partiküllerde altı muhtemel kirlilik kaynağı tespit edilmiştir. $\text{PM}_{2,5}$ için kirlilik kaynakları bölgesel arkaplan, trafik, toprak, ikincil bileşikler/yanma, metal işleri/deniz tuzu ve endüstriyel salınım olarak tanımlanmıştır. $\text{PM}_{2,5-10}$ için ise uzun mesafeli taşınım, yol tozu, kömür yanması, meta işleri, toprak ve yüzey toprağı kirlilik kaynakları olarak tanımlanmıştır.

Anahtar Kelimeler: Aerosol, Ozon, Eser metaller, Temel İyonlar, Organik ve elementel organik karbon, Alıcı ortam modellemesi, AOT_{40} , İstatistiksel uygulamalar

To my family

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrometry
AES	Atomic Emission Spectrometry
AGL	Above Ground Level
AMSL	Above Mean Sea Level
AOT ₄₀	Accumulated amount of Ozone exceeding a Threshold of 40 ppbv
APFM	Air Particulate on Filter Media
AQI	Air Quality Index
BCR	Community Bureau of Reference
BDL	Below Detection Limit
BVOCs	Biogenic Volatile Organic Carbons
CC	Carbonate Carbon
CFA	Coal Fly Ash
CL	Confidence Level
CMB	Chemical Mass Balance
CNHS	Carbon Nitrogen Hydrogen Sulfur Analyzer
DMS	Dimethyl sulfate
DRI	Desert Research Institute
E	East
EC	Elemental Carbon
ED-XRF	Energy Dispersive X-ray Fluorescence

EF	Enrichment Factor
ENE	East-North-East
EPA	Environmental Protection Agency
ESE	East-South-East
FA	Factor Analysis
FID	Flame Ionization Detector
GDAS	Global Data Assimilation System
GFAAS	Grafit Furnace Atomic Absorption Spectrometry
HEPA	High-efficiency particulate air
HYSPLIT	HYbrid Single-Particle Lagrangian Integrated Trajectory
IC	Ion Chromatography
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
K-S DN	Kolmogorov –Smirnov
LOD	Limit of Detection
LOQ	Limit of Quantification
MDL	Method Detection Limit
MH	Mixing Height
MLR	Multiple Linear Regression
N	North
NAAQS	National Ambient Air Quality Standards
NE	North-East
NIOSH	National Institute for Occupational Safety and Health
NIST	National Institute of Standard and Technology
NNE	North-North-East
NNW	North-North-West

NOAA	National Oceanic and Atmospheric Administration
NO _x	Nitrogen Oxides
NW	North-West
OC	Organic Carbon
OC _{pri}	Primary Organic Carbon
OC _{sec}	Secondary Organic Carbon
PAN	PeroxyAcetyl Nitrate
PCA	Principle Component Analysis
PIXE	Proton-Induced X-ray Emission
PM	Pariculate Matter
PM _{2.5}	Particulate Matter <2.5 µm in diameter
PM _{2.5-10}	Particulate Matter between 2.5 and 10 µm in diameter
PMF	Positive Matrix Factorization
POCP	Photochemical Ozone Creation Potential
PTFE	Polytetrafluoroethylene
QC/QA	Quality Control and Quality Assurance
RSD	Relative Standard Deviation
S	South
SE	South-East
SFU	Stacked Filter Unit
SRM	Standard Reference Material
SSE	South-South-East
SSW	South-South-West
SW	South-West
TC	Total Carbon

TCD	Thermal Conductivity Detector
TGA	Thermal Gravimetric Analysis
TOT	Thermal Optical Transmission
TSP	Total Suspended Particulate
U	Expanded uncertainty
UN-ECE	United Nations-Economic Commission for Europe
UPM	Urban Particulate Matter
USEPA	United States of Environmental Protection Agency
VOCs	Volatile Organic Carbons
W	West
WHO	World Health Organization
WNW	West-North-West
WSW	West-South-West
XRF	X-ray fluorescence

CHAPTER 1

1. INTRODUCTION

1.1. Air pollution and air quality

Air pollution can be defined as contamination of the indoor or outdoor environment by any chemical, physical or biological agent that modifies the natural characteristics of the atmosphere and affects the living organisms or any material in negative way (http://www.who.int/topics/air_pollution/en/ 18.10.2011). These substances can be in the form of particle, gas or solar energy at such a concentration, duration and frequency above the defined limits in impact areas. If the types of pollutants are mentioned, they divided into two as natural (biomass burning, volcanic eruption etc.) and anthropogenic (traffic, industrial processes, domestic heating etc.). If the formation of them is discussed then they can be classified as primary (emitted directly from source) and secondary pollutants (formed through the chemical reactions in the atmosphere). The pollution concept deals with degradation, increase in quantity, loss of quality and adverse effects on environment (Godish, 1997; WHO, 2000, Yu, 2005). The impact of air pollution is mostly on climate, weather, human health, animal life, vegetation and materials environment (Godish, 1997; WHO, 2000). The pathway of the air pollution and the relations between different process are given in Figure 1.1 (Mayer, 1999).

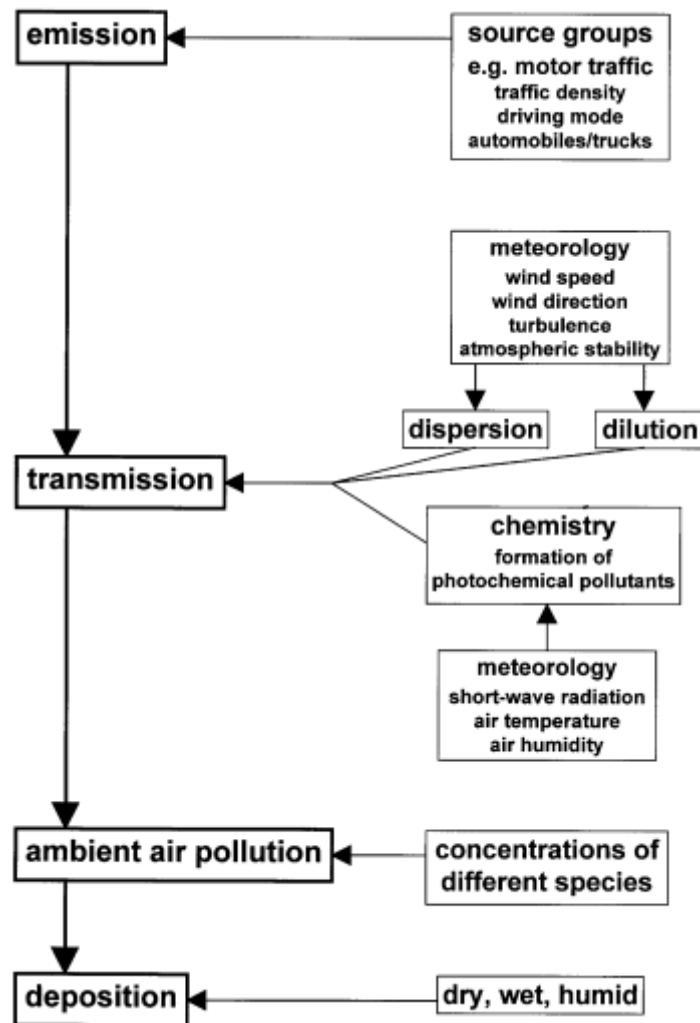


Figure 1.1. Schematic diagram of air pollution pathway

Environmental Protection Agency (EPA) classified six air pollutants that are; particulate matter, tropospheric ozone, carbon monoxide, sulfur dioxide, nitrogen dioxide and lead as ‘criteria pollutants’ due to their threat on both human and environment directly. The increase in air pollution or the decrease in air quality result from being excess than the natural amount. Moreover, pollutants have crucial effects on health due to their length of life time and the degradation rate in this period.

Industrialization of society, introduction of motorized vehicles and explosion of the population are factors that grow the air pollution problem. Air pollution involves three parts: the pollution source, the movement or dispersion of the pollutant and the recipient as indicated in Figure 1.2 (Schnelle and Brown, 2002).

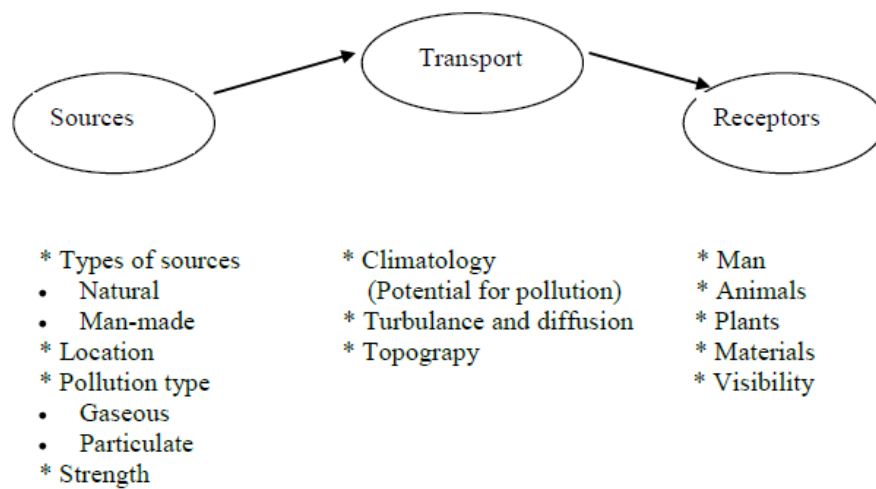


Figure 1.2. Main concepts in air pollution

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

Transportation of the pollutants results within the dispersion that makes taking pollutants from source to receptors which can be classified as human, animals,

plants, materials and visibility. Meteorological conditions, diffusion and topography are also the important factors in transportation.

The concentrations of the pollutants should be measured at sites where representative population exposures are present. However, the magnitude of the effects of air pollutants are uncertain due to the complexity and non-linear nature of the troposphere (Tang et al., 1998). The dependence on the vicinity to the specific pollution sources like traffic, industrial zones, etc. the pollution levels may be higher. Then, the protection of this population requires special treatment (WHO, 2005).

An air quality standard is defined as the concentration of an air pollutant below the level that negligibly effects the human health. This standard is accepted for sensitive individuals like asthmatics however, most sensitive groups are not included which means the designed standards are used to protect the health of population rather than every individual (Sanhueza et al., 2002).

Air quality index (AQI) gives information about the cleanness or pollution of air in the living zone and also explains the health effects of it. In air quality index these effects are reported with respect to daily or hourly exposure of the polluted air. Environmental Protection Agency (EPA) assigned the AQI levels with their concerns (Table 1.1) (<http://cfpub.epa.gov/airnow>, 26/06/2014).

Table 1.1. Air quality index levels

AQI levels of health concern	Numerical value	Meaning
Good	0-50	Air quality is considered satisfactory, and air pollution poses little or no risk.
Moderate	51-100	Air quality is acceptable; however, for some pollutants there may be a moderate health concern for a very small number of people who are unusually sensitive to air pollution.
Unhealthy for sensitive groups	101-150	Members of sensitive groups may experience health effects. The general public is not likely to be affected.
Unhealthy	151-200	Everyone may begin to experience health effects; members of sensitive groups may experience more serious health effects.
Very unhealthy	201-300	Health warnings of emergency conditions. The entire population is more likely to be affected.
Hazardous	301-500	Health alert: everyone may experience more serious health effects

An air quality index can be calculated by using the following equation (Eq (1.1)).

$$I_p = \frac{I_{Hi} - I_{Lo}}{BP_{Hi} - BP_{Lo}} (C_p - BP_{Lo}) + I_{Lo} \quad Eq (1.1)$$

Where,

I_p =the index value for pollutant p

C_p = the rounded concentration of pollutant p

BP_{Hi} =the breakpoint that is greater than or equal to C_p

BP_{Lo} =the breakpoint that is less than or equal to C_p

I_{Hi} = the AQI value for corresponding BP_{Hi}

I_{Lo} = the AQI value for corresponding BP_{Lo}

The breakpoint values for ozone and particulate matter are given in Table 1.2.

Table 1.2. Breakpoint values for each AQI

O ₃ (ppb)		PM _{2.5} (µg m ⁻³)	PM ₁₀ (µg m ⁻³)	AQI
8-hour	1-hour	24 h		
0-64	-	0.0-15.4	0-54	0-50
65-84	-	15.5-40.4	55-154	51-100
85-104	125-164	40.5-65.4	155-254	101-150
105-124	165-204	65.5-150.4	255-354	151-200
125-374	205-404	150.5-250.4	355-242	201-300
-	405-504	250.5-350.4	425-504	301-400
-	505-604	350.5-500.4	505-604	401-500

The higher the AQI value, the greater the level of air pollution and the greater the health concern. The AQI value of 100 (Moderate limit) is the national air quality standard for a given pollutant which EPA defined to protect public health.

Besides national air quality, global air-quality issues exist only in regard to those pollutants whose residence times are long enough (at the order of 1 week) for them to be transported at least to another continent. Ozone is one of the pollutants that has

this criteria. Due to its long atmospheric life it is transported to other continents through a year (Akimoto, 2003).

Recent time series studies of daily mortality and hospitalization have found significant relationships with most common constituents of urban air and that the effects of air pollution on health can occur at levels below the standards (Sanhueza et al., 2002).

1.2. Tropospheric ozone

1.2.1. General properties of tropospheric ozone

Ozone was first identified in 1840 by Schönbein who described its formation by electrolysis when an electric discharge passes through the oxygen of the air (Alloway and Ayres, 1997; Wallace and Hobbs, 2006). The structure of it is composed of charge separated species which arises from the donation of a shared electron pair from one terminal bond to the other (Figure 1.3).

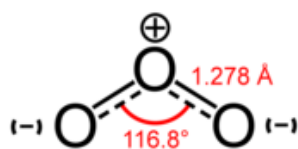


Figure 1.3. Principle structure of O₃ molecule

An essential constituent of the stratosphere, O₃ is an undesirable pollutant in the troposphere that causes photochemical smog. On the other hand, O₃ is also a crucial substance to control the chemical composition of troposphere (Duenas et al., 2002).

Ozone is an irritating and highly reactive gas (Markovic and Markovic, 2005) that has negative effects on biosphere (Duenas et al., 2002), human health (Shanhueza et al., 2002; Tu et al., 2007) and vegetation (Latif et al., 2012; Zhang, 2011; Barrero et al., 2006; Kovac-Andric et al., 2009). Tropospheric O₃ is a major secondary air pollutant that plays a crucial role in atmospheric chemistry produced from photochemical reactions involving nitrogen oxides (NO_x) and volatile organic carbons (VOCs) in the presence of sunlight and some anthropogenic processes (Zhang and Rao, 1999). It is a colorless gas at ambient temperature and pressure and unstable especially at higher concentrations (Sanz, 2007; Helaleh, 2002; Özer et al., 1997; Grigorieva and Mihalev, 1998).

The first tropospheric O₃ measurements were conducted between 1876 and 1910 at Montsouris near Paris showed background levels of ~20 ug m⁻³ (Bytnerowicz et al., 2002; Hunova I., 2003). However, 1980s most of the studies had been based on only stratospheric ozone because there is a lack of knowledge about the effects of tropospheric ozone. The only important aspect about O₃ had been its protective role for harmful ultra-violet rays from Sun (Hunova et al., 2003). In the middle of the 20th century, stratospheric O₃ was suggested as the primary source for tropospheric O₃ (Wallace and Hobbs, 2006). Nowadays the importance of tropospheric O₃ is understood and studies have been conducted about it. Ozone is a specific pollutant that there are no compounds other than O₃ in the troposphere that has a small range

between the natural and toxic levels. That means effects of O₃ can be occur at lower levels than current ambient concentrations (Hunova et al., 2003; WHO, 2000).

1.2.2. Sources of tropospheric ozone

Tropospheric O₃ is the secondary air pollutant however in some cases direct emissions of O₃ can be occurred. The examples of direct emissions can be listed as; copy machine printers, welding and other industrial processes (Helaleh, 2000). The main sources of this pollutant beside the direct emissions (Helaleh et al., 2002) are;

- i) photochemical production by the reaction with NO_x, CO and VOCs (Tuncel et al., 1996; Kovac-Andric, 2009; Bernard et al., 1999; Harrison, 2001; Grigorieva and Mihalev, 1998; Godish, 2004; Helaleh et al., 2002; Özer et al., 1997; Sanz et al., 2007; Shan et al., 2008; Gerosa et al., 2009; Tang et al., 1998; Sicard et al., 2011).
- ii) vertical transport from stratosphere (Alloway and Ayres, 1997; Kovac-Andric et al., 2009).
- iii) horizontal transport (dispersion) from local sources by winds (Tuncel et al., 1996; Duenas et al., 2002).
- iv) biomass burning and long range transport (Latif et al., 2012; Shan et al., 2009).
- v) dry deposition and chemical destruction (Bytnerowicz et al., 2002).
- vi) human activities (Godish, 2004).

vii) biogenic emissions (Sicard et al., 2011).

1.2.3. Chemistry of tropospheric ozone

Tropospheric O₃ is sensitive to climate change due to its dependence on temperature and sunlight for the formation (Bell et al., 2007) and also it is a precursor to the formation of the hydroxy radicals which affects the oxidizing capacity of the troposphere (Oltmans et al., 2006; Tang et al., 1998; Satsangi et al., 2004; Wallace and Hobbs, 2006). Ozone is one of the atmospheric trace gases (NO₂, H₂O₂, HCHO, HNO₃, etc.) whose photolytic products; O, NO, OH, H, HCO, HO₂ and organic peroxy radicals are very reactive.

The oxidation of non-methane hydrocarbons in the presence of NO_x are the responsible photochemical processes. Moreover, ultraviolet-B radiation (UV-B, 290-320 nm) is very energetic that can be the other parameter for the processes. The detection of the effects of UV-B on tropospheric constituents will be difficult because the concentrations of the species can be also influenced by many factors especially like anthropogenic emissions (Solomon et al., 2003).

The residence time of O₃ is 1 to 2 weeks in summer and 1 to 2 months in winter. This can cause O₃ concentration levels in urban sides where traffic is much more dense are lower than in rural sides (Bayındır, 2008; Paoletti, 2009; Tuncel et al., 1996; Akimoto et al., 2003). The main reasons could be listed as:

- a) ozone is a secondary pollutant that means it does not emitted directly then, it can be formed at a certain distance from the precursor sources.

b) ozone can be depleted by NO_x in polluted areas.

c) biogenic hydrocarbons (BVOCs) are reactive than anthropogenic hydrocarbons then, in remote or green areas the contribution of BVOCs are favorable in the O₃ formation.

1.2.3.1. Formation and removal mechanism of ozone

In literature, generally two processes are mentioned for the formation of tropospheric ozone; one of them is the downward transport from the stratosphere and the other one is the photochemical production from the oxidation of hydrocarbons or carbon monoxide in the presence of nitrogen oxides and UV radiation.

In addition, there are two sink processes for the tropospheric ozone; deposition at the Earth's surface and photolysis of ozone (Tang et al, 1998; Harrison, 2001). Surface deposition includes the reaction with plants, bare land, ice and snow and man-made structures. However, the primary sink for tropospheric O₃ is its photo-dissociation on absorption of UV radiation and subsequent formation of radicals, especially OH.

The potential for tropospheric O₃ formation can be related not only local sources but also, non-local origin that means the transported air masses in large scale. Non-local sources include natural and anthropogenic O₃ as well as the precursor compounds required for photochemical reactions (Williams et al., 2009).

The absorption of higher energy radiation at shorter wavelength, typically at 200 nm, leads to cleavage of the molecule and the formation of very reactive atomic oxygen (R1). When atomic and molecular oxygen collide, ozone is formed (R2) and survives

the collision provided that a third inert entity (M), normally nitrogen present in excess, is available to take up excess energy (Alloway and Ayres, 1997).



The above reactions occur in clean air however, in polluted atmosphere there is an abundant NO₂ whose photolysis leads to formation of O₃ at the wavelength of 435 nm or below (Harrison, 2001). The conversion of NO to NO₂ by peroxy radicals (HO₂ and RO₂) is the pioneer reaction for the formation (R4.1 and R4.2). Peroxy radicals are provided by the oxidation of hydrocarbons and carbon monoxide (CO) (R3.1 and R3.2). Then photolysis of produced NO₂ is occurred and excited oxygen atom (O(³P)) is produced (R5). Finally, the elevated oxygen atom collide with oxygen molecule in the presence of third body molecule in order to form ozone (R6) (Bernard et al., 1999; Godish, 1997; Harrison, 2001). During the whole process NO₂ acts as a catalyst. Figure 1.4 summarized generation of tropospheric O₃ by free radical catalyzed oxidation of hydrocarbons. Moreover, the removal mechanism of tropospheric O₃ in daytime was given in Figure 1.5 (Jenkin and Clemitshaw, 2000).



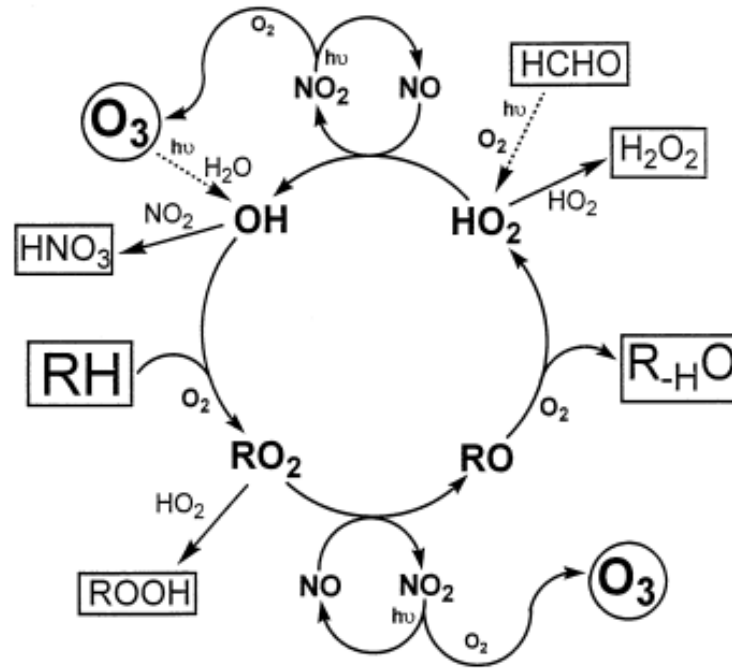
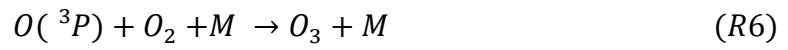
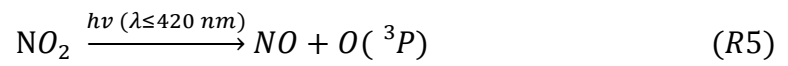


Figure 1.4. Generation and removal mechanisms of tropospheric O_3

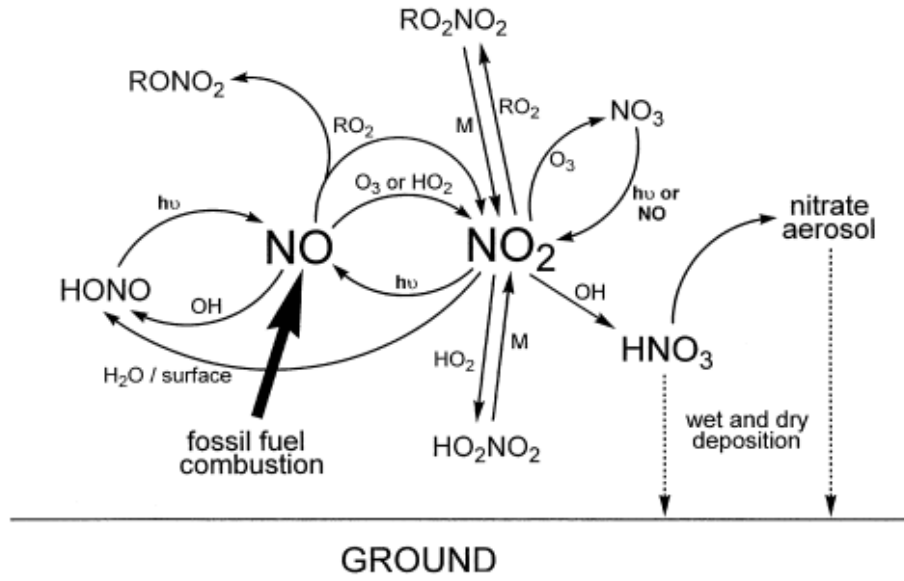
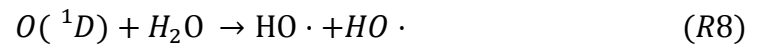
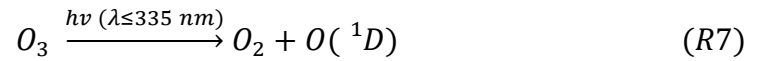


Figure 1.5. Removal mechanisms of tropospheric O_3 in daytime.

The photolysis of O_3 (R7) followed by the reaction of $O(^1D)$ atoms with water vapor is the major sink for O_3 and the main source for hydroxy radicals (R8) (Latif et al., 2012; Tang et al., 1998).



However, only a small fraction of $O(^1D)$ atoms with water vapor, then most of the $O(^1D)$ atoms undergo relaxation reaction to ground state oxygen atom ($O(^3P)$) by collision with N_2 or O_2 (R9) (Latif et al., 2012; Tang et al., 1998). After that, sixth reaction (R6) will occur.



In the absence of sunlight (during night time), O_3 reacts with NO and NO_2 to produce HNO_3 (R10-R13) which remains in the gas phase until it reacts with NH_3 to form ammonium salt (R15). The removal of the ammonium nitrate is achieved by wet or dry deposition processes. In Figure 1.6 the removal of tropospheric O_3 at nighttime was given (Jenkin and Clemitshaw, 2000).

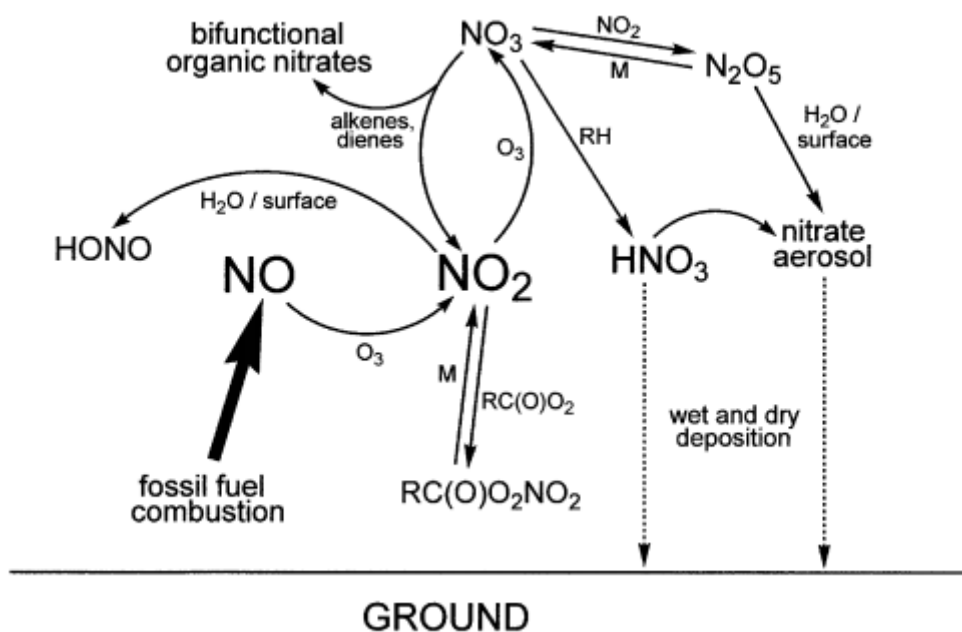
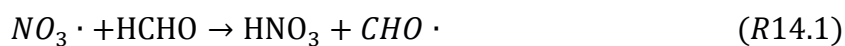


Figure 1.6. Removal mechanisms of tropospheric O_3 in night time.

Reactions between O_3 and NO_2 produce nitrate radical ($NO_3\cdot$) that reacts with NO_2 to produce N_2O_5 . Then, dinitrogen pentaoxide react rapidly and produce HNO_3 . Nitric acid also produced by reaction between $NO_3\cdot$ and formaldehyde ($HCHO$) or hydrocarbon radicals (R14.1 and R14.2).



Nitrate radical is a key component in tropospheric O_3 chemistry because it is placed in the production of biogenic VOCs in nighttime (Godish, 2004).



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

1.2.4. Effect of meteorological parameters on ozone concentration

Meteorology plays a crucial role in the air pollutants formation, dispersion, transport and dilution (Duenas et al., 2002; Tu et al., 2007). In literature, the evaluation of tropospheric ozone is generally related with meteorological parameters however, there is a difficulty in the detection of changes in O_3 concentration due to change in emissions in the presence of meteorological fluctuations (Rao and Zurbenko, 1994).

Brönnimann and Neu (1997) found that some meteorological conditions like intense solar radiation and high temperature are the suitable ones for ozone production in rural and urban areas in Switzerland. In addition, high ozone levels are also related with stagnant air and zero rainfall, which are favorable for photochemical production and accumulation of ozone (Thompson et al., 2001; Vukovich, and Sherwell, 2003; Duenas et al., 2002, Shan et al., 2009). Also, it is indicated that meteorological parameters affect the ozone circulation in a short time interval (Kovac-Andric et al., 2009). However, the chemistry of O₃ and the effects of meteorological conditions could vary depending on the characteristics of the climate and air pollutants emissions in the place of interest (Tu et al., 2007).

1.2.5. Possible health and environmental effects of tropospheric ozone

Tropospheric O₃ can be a major environmental problem when it exceeds the threshold value. It is well known that higher concentrations of O₃ have harmful impact on human health, biosphere, human health, animal populations, agriculture productivity and forest ecosystem (Sillman, 1999; Duenas et al., 2002; Latif et al., 2012; Zhang et al., 2011). The danger of tropospheric ozone to human, animal and plant health at molecular and cellular level results from oxidative damage to lipids, proteins and nucleic acid depending on the dose (Kovac-Andric et al., 2009).

Since O₃ has adverse health effects on humans and vegetation, the European Community Directive sets health protection, information and alert threshold levels at 120 ug m⁻³ (8 h average), 180 ug m⁻³ (1 h average) and 240 ug m⁻³ (1 h average), respectively. Also for vegetation protection the threshold value of O₃ was 200 ug m⁻³ for 1 hour average and 65 ug m⁻³ for 24 hour average period (EU, 2002).

Even though EPA established the value of 80 ppb ($160 \mu\text{g m}^{-3}$) as a threshold for significant health effects, the standards in other developed countries have adopted more stringent levels as 65 ppb ($130 \mu\text{g m}^{-3}$) in Canada and 50 ppb ($100 \mu\text{g m}^{-3}$) in U.K (Sanhueza et al., 2002). Then, forecasting atmospheric O_3 concentration has great importance, especially in populated areas, so that the population may be warned in advance and preventive measures can be taken (Barrero et al., 2006).

1.2.5.1. Human health

Ozone is one of the most powerful oxidizing agent in the atmosphere which releases free oxygen radicals during the photochemical reactions. These radicals defense the body from the harmful bacteria by inflammatory reactions. Oxygen radicals are toxic to bacteria however, they also have the ability to damage normal tissues if the dose of them are higher (Sanhueza et al., 2002). Moreover, it is the third most important greenhouse gas that contributes the climate change (Sicard et al., 2011).

In studies on animals and human about repeated exposure to O_3 have been shown that most of the diseases are related with respiratory systems (Kovac-Andric et al., 2009). Shanhueza et al., 2002, listed the diseases as chronic obstructive pulmonary diseases (asthma, bronchitis, emphysema), cough and chest pain, lung inflammation, allergic airway diseases (Kovac-Andric et al., 2009).

Helaleh et al., 2002 and WHO, 2003, elaborated the adverse health effects with exposure dose. Ozone concentration in ambient air in short term exposure to 0.11 ppm cause irritation to nose and throat, itchy and watery eyes, swelling within the nasal passages and nasal congestion. The exposure to 0.1-0.3 ppm causes lung

damage, asthma and bronchitis and 2-hour exposure to concentration of 1.5 ppm of O₃ is regarded as very dangerous (Alloway, 1997).

Environmental Protection Agency (EPA) gives the air quality index of O₃ and also the possible health effects of each level in 8-hour exposure as in Table 1.3. An air quality index of 100 for O₃ corresponds to an O₃ level of 80 ppb.

Table 1.3. Air Quality Index of tropospheric O₃.

Index Values	Levels of Health Concern	Cautionary Statements
0-50	Good	None
51-100*	Moderate	Unusually sensitive people should consider reducing prolonged or heavy exertion outdoors
101-150	Unhealthy for sensitive groups	Active children and adults and people with lung disease, such as asthma, should reduce prolonged or heavy exertion outdoors.
151-200	Unhealthy	Active children and adults and people with lung disease, such as asthma, should reduce prolonged or heavy exertion outdoors. Everyone else, especially children, should reduce prolonged or heavy exertion outdoors.
201-300	Very unhealthy	Active children and adults and people with lung disease, such as asthma, should avoid prolonged or heavy exertion outdoors. Everyone else, especially children, should avoid prolonged or heavy exertion outdoors.
301-500	Hazardous	Everyone should avoid all physical activity outdoors

* Air Quality Index value 100 = 80 ppb O₃ (averaged over 8 hours)

1.2.5.2. Forests and vegetation

Tropospheric ozone is recognized as one of the most toxic compounds for plants in the atmosphere (Fuhrer et al., 1997; Kovac-Andric et al., 2009; Grünhage et al., 1999). Like other atmospheric gases, O₃ is taken up by plants through transpiration and stomatal diffusion (Hunova et al., 2003; Gerosa et al., 2009; Sicard et al., 2011;

Grünhage et al., 1999). Penetration through stomata depends on hydric condition of air (Sicard et al., 2011; Hunova et al., 2003; Gerosa et al., 2009), air temperature, photosynthetic active radiation; indirectly, to wind velocity (Gerosa et al., 2009), pH of the wetted surface, the surface temperature and the water solubility of O₃ (Grünhage et al., 1999). One of the major factor to determine the sensitivity of plant to O₃ is the determination of stomatal conductance genetically and environmentally (Hunova et al., 2003).

The exposure of O₃ reduces the photosynthetic activity rate, affect the cultures productivity and at sites with high O₃ concentration severe defoliation and foliar symptoms have been observed (Sicard et al., 2011). According to the United Nations-Economic Commission for Europe (UN-ECE) definition, the critical levels for crops and semi-natural vegetation are related to the ozone concentrations measured at the top of the canopy (the upper surface boundary of the (quasi-)laminar layer (Grünhage et al., 1999).

Although O₃ exposure affects trees, trees also affect O₃ in the air. The effects of urban trees on O₃ concentration can be listed as (Paoletti, 2009).:

- Trees reduce air temperature through shading and evapotranspiration thus they reduce emissions of O₃ precursors. Decrease in temperature also affect the emissions of hydrocarbons from biogenic and anthropogenic sources which change the reaction rate of O₃ formation (Nowak et al., 2000).
- Inside the leaf, O₃ diffuses into the intercellular spaces and dissolves in water content to form toxic reactive oxygen species. Generally, deposition of gaseous pollutants is greater in woodlands than in shorter vegetation. In

addition, in greater leaf areas turbulent mixing of the air passing over land gets higher.

- Emission of biogenic volatile organic compounds (BVOCs) contributes to O₃ formation. Biogenic volatile organic compounds include the isoprenoids (isoprene and monoterpenes as well as sesquiterpenes and homoterpenes) and minor compounds such as alkanes, alkenes, carbonyls, alcohols, esters, ethers and acids. Isoprenoids protect plant membranes against oxidative stressors, like O₃. The amount of BVOCs in major urban areas is minimal or negligible when compared to anthropogenic sources. However, they are estimated to be 2-3 times more reactive than a weighted average hydrocarbons from gasoline combustion.

1.2.6. Ozone exposure index (AOT₄₀)

Within the framework of the United Nations Economic Commission for Europe (UNECE) Convention on long-range transboundary air pollution, the concepts for critical levels for ozone has developed and steadily improved. Under the idea of “Critical Loads” and “Critical Levels”, it is understood that scientifically based values of pollutants concentration or deposition. Critical levels are the concentrations of pollutants in the atmosphere above which direct adverse effects on receptors, such as human beings, plants, ecosystems or materials, may occur according to present knowledge. Critical levels can be compared with local, regional and international levels. The comparisons could also be used to implement policies that balance out and compensate for air pollutants (Ferretti et al., 2007).

During the 1990s, the concept of 'Critical Levels for Ozone' has been introduced by UNECE and defined as the AOT₄₀ exposure index " Accumulated amount of Ozone exceeding a threshold of 40 ppbv ". The index is defined as the sum of the differences, in each hour, between the measured hourly mean O₃ concentration and a value of 40 ppb when the concentration exceeds 40 ppb and net radiation is above 50 W m⁻² (Eq 1.2) (Matyssek et al., 2004; Fuhrer et al., 1997; Grünhage et al., 1999).

$$AOT_{40} = \sum (C_{O_3} - X) \cdot T \quad C_{O_3} \Rightarrow 40 \text{ ppb} \quad Eq (1.2)$$

The AOT₄₀ concept is most widely used in Europe where it is believed to be the best available approach in identifying geographical areas that may be potentially impacted by ozone (Ashmore and Fuhrer, 2000). Moreover, it corresponds to ozone exposures associated with significant negative effects on the yields of crops, the biomass increment of forest trees and species composition of semi-natural plant communities (Fuhrer et al., 1997; Matyssek et al., 2007).

For forest trees, exposure is generally limited to the period when the stomata will be open and so AOT₄₀ is calculated for daylight hours during the growing season. Different exposure periods may be used to allow for differences in phenological development – for example, in the Mediterranean region, plants are often active during the winter months, with limited conductance during the summer as a result of water limitation.

Based on the AOT₄₀ concept, the critical level for crops and semi-natural vegetation is exceeded over most of Europe except for the far North and North-West, while the exceedance of the critical level for forests is confined to the European mainland. The highest values represent a six-fold exceedance of the critical level for crops and

semi-natural vegetation and a threefold exceedance of the critical level for forests (Hunova et al., 2003, Gottardini et al., 2010) .

On the other hand, one of the disadvantages of the AOT_{40} exposure index is its high sensitivity resulting in stringent requirements for the quality of measured data. Inevitably uncertainties in both observed and calculated ozone concentrations and a high sensitivity of the ozone index results in instability of the exposure estimate and create problems (Sofiev and Tuovinen, 2001).

A value of 40 ppbv (AOT_{40}) has been employed in impact assessment research in Europe, while a higher value of 60 ppbv (AOT_{60}) has been used in the USA. There is evidence that ozone may affect vegetation at concentrations well below 40 ppb, and a lower threshold of 30 ppbv (AOT_{30}) has been proposed as more appropriate.

AOT_x values (typically AOT_{40}) which were based upon the model's predicted grid-average ozone concentrations at a height of 1 m is the sum of the difference between the hourly mean ozone concentration (in ppbv) at the top of the canopy and a selected criteria value of 40 ppbv for all daylight hours accumulated within a specified time period.

1.3. Particulate matters (Aerosols)

1.3.1. General information about aerosols

Particulate matter (PM) or aerosols are technically defined as a suspension of the fine solid or liquid particles in gaseous medium (Raes et al., 2000; Seinfeld and Pandis, 2006). Particles in the atmosphere are distinguished by their physical (size, shape), chemical (composition) properties and also their origins (probable emission sources).

Besides emitting directly from sources (primary aerosols), aerosols can also be formed in the atmosphere by gas to particle conversion or physicochemical processes (secondary aerosols) (Seinfeld and Pandis, 2006; Salma and Maenhaut, 2006).

Air pollution due to particulate matters is the main problem not only because of health effects but also for the reduction in visibility. Moreover, on global scale particulate matters affect the global radiation balance by scattering, reflecting and absorbing the coming light as shown in Figure 1.7 (Rastogi and Sarin, 2009; Marcazzan et al., 2003; Swami et al., 2001). Absorption of radiation by fine particles causes heating whereas, scattering causes cooling. Moreover, they have action on the global radiation balance by affecting the micro structure of clouding (Rastogi and Sarin, 2009). Then the size of aerosols again becomes crucial.

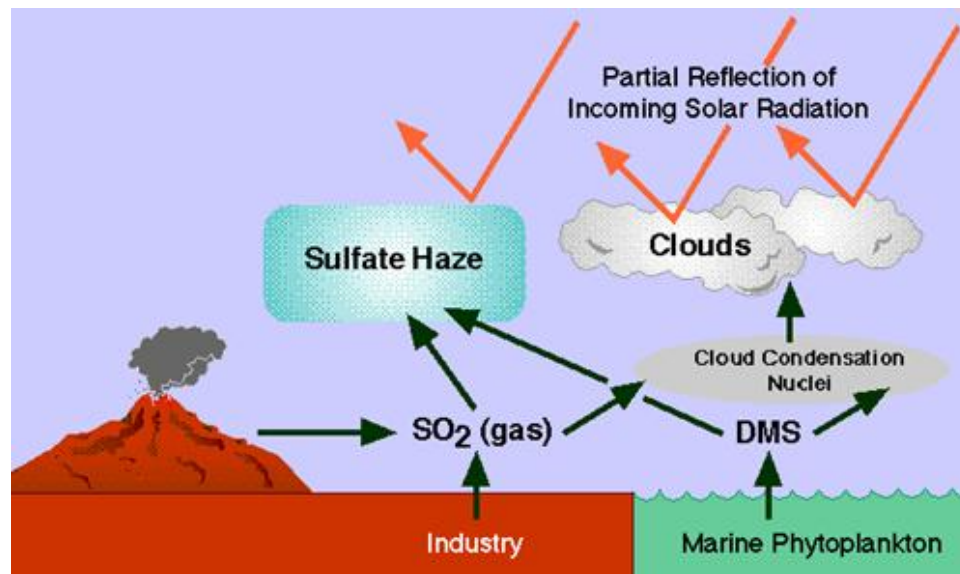


Figure 1.7. Climatic effect of tropospheric aerosols

European Council set air quality standards for PM_{10} mass concentration in 1999 and in the Daughter directive (Directive 1999/30/EC), the request for a first characterization of $PM_{2.5}$ was added. The EU standard fixes for 2010 an annual PM_{10} mean limit value of $20 \mu g m^{-3}$ and a daily PM_{10} value of $50 \mu g m^{-3}$ which should not be exceeded more than 7 days year⁻¹ (Marcazzan et al., 2003). Marcazzan et al., 2003 explained that in order to reduce PM levels in air, a deep knowledge of the contributing sources, of the influence of the meteorological conditions and of PM formation and transport processes are needed.

1.3.2. Aerosol size

Figure 1.8 which is adopted from Seinfeld and Pandis (2006) summarizes the aerosol size and composition that can be changed by physical and chemical transformation processes, condensation, evaporation, coagulation, sedimentation and impaction (Harrison and Grieken 1998; Seinfeld and Pandis, 2006; Colbeck, 2008). In

coagulation, small particles form larger ones, when coagulated particles reach their sufficient size to settle, *sedimentation* will occur as *dry deposition*. Another type of coagulation, scavenging, is obtained by rain drops and they deposited with washout/rainout processes.

Atmospheric particulate matters were described with respect to their sizes by National Ambient Air Quality Standards (NAAQS) in Table 1.4. Besides these sizes aerosols are also defined as inhalable size and respirable size (Colbeck, 2008).

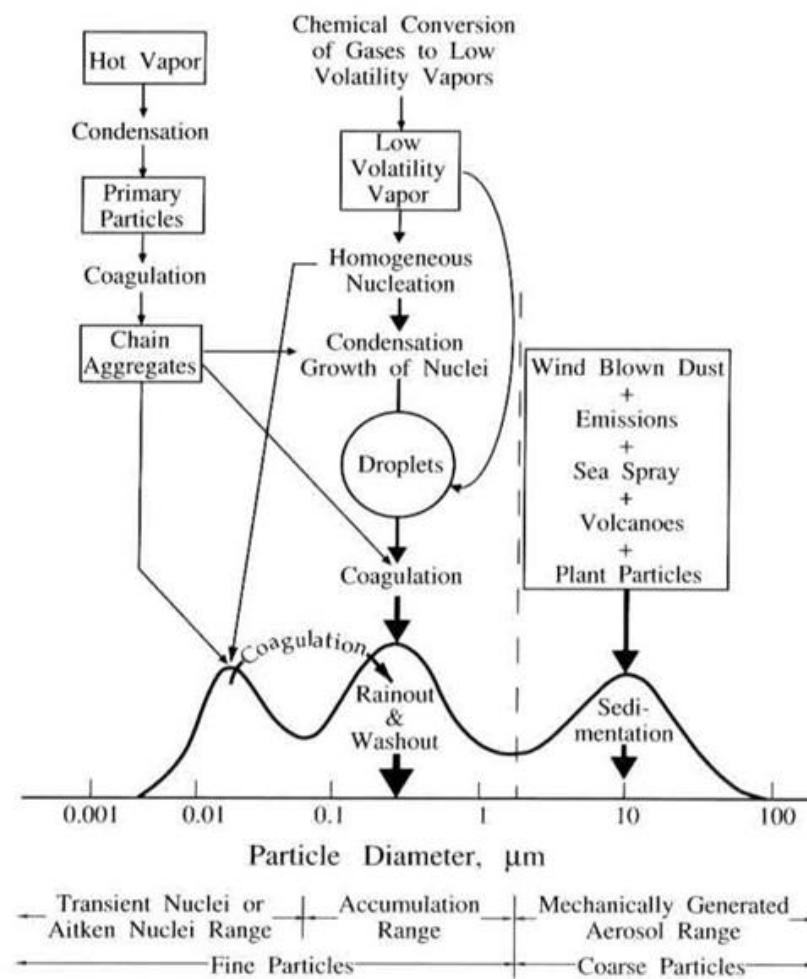


Figure 1.8. Schematic diagram of the distribution of aerosols

Size distribution varies from place to place with altitude and time (McMurry, 2000; Colbeck, 2008). Combustion and other high-temperature processes are generally responsible for primary emissions of the fine-mode particles ($< 2.5 \mu\text{m}$), while mechanical processes such as grinding of rocks generate coarse-mode particles ($> 2.5 \mu\text{m}$) (Colbeck, 2008; Heard, 2006). Then atmospheric aerosol can be considered as the particle whose size varies from a few nanometers to tens of micrometers (Manahan, 2005; Wallace and Hobbs, 2006; Seinfeld and Pandis, 2006).

Table 1.4. Size definition of the aerosols.

Aerosol size	Definition
TSP	Total suspended particulate matter (up to $\sim 35 \mu\text{m}$ in diameter)
PM ₁₀	Particulate matter smaller than $10 \mu\text{m}$ in diameter
PM _{2.5}	Particulate matter smaller than $2.5 \mu\text{m}$ in diameter
Fine PM	Particles smaller than $1\text{-}3 \mu\text{m}$ in diameter; operationally defined as PM _{2.5}
Coarse PM	Particles larger than $1\text{-}3 \mu\text{m}$ in diameter; operationally defined as PM ₁₀ minus PM _{2.5} but it is actually the PM ₁₀ contribution to the coarse PM mode
Ultrafine PM	Particles smaller than about 100 nm
Nuclei mode	Particles in the range $5\text{-}100 \text{ nm}$
Accumulation mode	Particles in the range of $100 \text{ nm}\text{-}2 \mu\text{m}$

The fine and the coarse particles originated and transformed separately, are removed from the atmosphere by different mechanisms, require different techniques for their removal from sources, have different chemical compositions, have different optical properties and differ significantly in their deposition pattern in the respiratory tract.

Therefore, the distinction between fine and coarse particles is a fundamental aspect for the discussion of the physics, chemistry, measurement and health effects of aerosols (Seinfeld and Pandis, 2006; Rastogi and Sarin, 2009). Seinfeld and Pandis, (2006), compare the properties of both fractions as in Table 1.5.

Table 1.5. Comparison of ambient fine and coarse particles.

	Fine	Coarse
Formation pathway	Chemical reactions Nucleation Condensation Coagulation Cloud/fog processing	Mechanical disruption Suspension of dust
Composition	Sulfate Nitrate Ammonium Hydrogen ion Elemental carbon Organic carbons Water Metals (Pb, Cd, V, Ni, Cu, Zn, Mn, Fe, etc.)	Resuspended dust Coal and oil fly ash Crustal elements (Si, Al, Ti, Fe) oxides CaCO ₃ , NaCl Pollen, mold, spores Plant, animal debris Tire wear debris
Solubility	Largely soluble, hygroscopic	Largely insoluble and non-hygroscopic
Sources	Combustion (coal, oil, gasoline, diesel, wood) Gas to particle conversion of NO _x , SO ₃ and VOCs Smelters, mills, etc.	Resuspension of industrial dust and soil Suspension of soil (farming, mining, unpaved roads) Biological sources Construction/demolition Ocean spray
Atmospheric lifetime	Day to weeks	Minutes to days
Travel distance	100 s to 1000 s of km	< 10 s of km

Aerosol size range also determines the residence time which is approximately 1 to 2 weeks (Akimoto, 2003), and the characteristics of atmospheric transport of aerosols. Some chemical compounds reside on larger particles thus they have a short residence time and transported only regionally. Other parameters like some radioactive loads are confined to smaller particles thus have longer residence times and can be transported to intercontinental places (Harrison et al., 1996). However, in some cases horizontal and vertical distribution of aerosols are limited and they are mostly concentrated near their sources (Akimoto, 2003).

1.3.3. Classification of aerosols with respect to their origins

Aerosols arise from natural sources such as windborne dust, sea spray, volcanoes, biomass burning, soil and deserts, also from anthropogenic sources such as combustion of fuels and direct emission from industrial processes (Harrison, 1998; Seinfeld and Pandis, 2006). Fogg and Sangster, (2003) estimates the rate of emissions of primary (Table 1.6) and secondary (Table 1.7) particulate matters.

In primary aerosols carbonaceous particles consist of two major components as organic carbon and black or elemental carbon. The identification of the sources of organic particulate is very difficult due to the variation in composition. The basic sources are burning processes like biomass and fossil fuel and biogenic. Harrison and Grieken (1998) described the biological aerosols as the particulate matters that "derived from living organisms, including microorganisms and fragments of all varieties of living things". The only source for black carbon is the combustion processes.

Industrial dust is produced by various industrial and human activities. The activities include cement manufacture, waste incineration and metallurgy (Fogg and Sangster, 2003). On the other hand, mineral dust aerosols arise from the action of wind on soil surface (Seinfeld and Pandis, 2006). The main sources of mineral dust are deserts, dry lake beds, dry areas where vegetation has been removed, soil surface that disturbed by agricultural activities and semi-arid fringes of deserts (Fogg and Sangster, 2003).

Finally, aerosols that composed sea salt originate from the evaporation of aerosol droplets of sea water into the air by bursting of air bubbles on sea surface (Wallace and Hobbs, 2006; Fogg and Sangster, 2003).

The composition and the concentration of aerosol vary day to day. Then, long term monitoring must be required in order to gather more accurate source identification (Okuda et al., 2004).

Table 1.6. Rate of emissions of primary aerosols during 2000 (Tg yr⁻¹).

Material	Northern Hemisphere	Southern Hemisphere	Global	Min-Max in literature
Carbonaceous aerosols				
<i>Organic matter (0-2 μm)</i>				
Biomass burning	28	26	55	45-80
Fossil fuel	28	0.4	28	10-30
Biogenic			56	0-90
<i>Black carbon</i>				
Biomass burning	2.9	2.7	5.7	5-9
Fossil fuel	6.5	0.1	6.6	6-8
Aircraft	0.005	0.0004	0.006	
Industrial dust (>1 μm)			100	40-100
Sea salt				
Diameter <1 μm	23	31	54	18-100
Diameter 1-16 μm	1420	1870	3290	1000-6000
Mineral dust				
Diameter <1 μm	90	17	110	
Diameter 1-2 μm	240	50	290	
Diameter 2-20 μm	1470	282	1750	

Secondary aerosols are composed of particulate matters that has formed in the atmosphere by chemical conversions or reactions in order to form a condensed particulates. This condensation may be in new form or changing in concentration on the existing particles (Harrison and Grieken, 1998). The most abundant components of the secondary aerosols are sulfate, nitrate (Harrison and Grieken, 1998; Fogg and Sangster, 2003) and chloride (Harrison and Grieken, 1998).

Table 1.7. Estimated emissions of precursors of secondary aerosols.

Substance	Northern Hemisphere	Southern Hemisphere	Global	Min-Max in literature
NO _x (Tg N yr ⁻¹)	32	9	41	
Fossil fuel	20	1.1	21	
Aircraft	0.54	0.04	0.58	0.4-0.9
Biomass burning	3.3	3.1	6.4	2-12
Soils	3.5	2.0	5.5	3-12
<i>Agricultural soil</i>			2.2	0-4
<i>Natural soil</i>			3.2	3-8
Lightning	4.4	2.6	7.0	2-12
NH ₃ (Tg N yr ⁻¹)	41	13	54	40-70
Domestic animals	18	4.1	21.6	10-30
Agriculture	12	1.1	12.3	6-18
Human	2.3	0.3	2.6	1.3-3.9
Biomass burning	3.5	2.2	5.7	3-8
Fossil fuel and industry	0.29	0.01	0.3	0.1-0.5
Natural soil	1.4	1.1	2.4	1-10
Wild animals	0.10	0.02	0.1	0-1
Oceans	3.6	4.5	8.2	3-16
SO ₂ (Tg S yr ⁻¹)	76	12	88	67-130
Fossil fuel and industry	68	8	76	60-100
Aircraft	0.06	0.004	0.06	0.03-1.0
Biomass burning	1.2	1.0	2.2	1-6
Volcanoes	6.3	3.0	9.3	6-20
DMS and H ₂ S (Tg S yr ⁻¹)	11.6	13.4	25.0	12-42
Oceans	11	13	24	13-36
Land biota and soils	0.6	0.4	1.0	0.4-5.6
VOC (Tg C yr ⁻¹)	171	65	236	100-560
Anthropogenic	104	5	109	60-160
Terpenes	67	60	127	40-400

Sulfate in the atmosphere mainly arises from the oxidation of sulfur dioxide to sulfuric acid. The sources and conversion mechanisms of SO_2 is given in Figure 1.9 which is adopted from Wallace and Hobbs (2006). The direct sources of SO_2 are biomass burning, fossil fuel combustion and volcanoes whereas, the indirect sources are H_2S from soil, CS_2 from biogenic and industry and finally DMS from marine planktons.

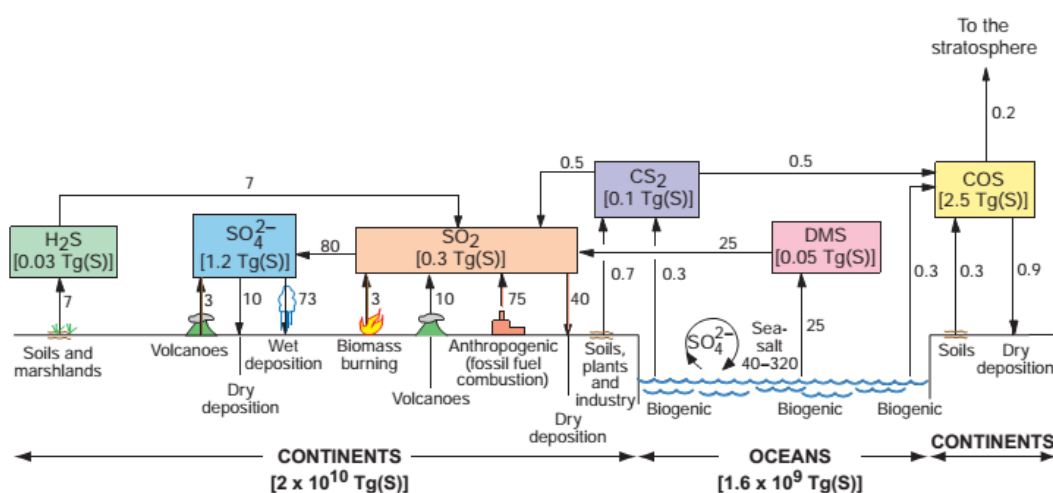


Figure 1.9. Sources and fluxes ($\text{Tg(S)} \text{ y}^{-1}$) of sulfur containing compounds.

The second most abundant secondary aerosol component is nitrate which arises from the oxidation of nitrogen oxides to nitric acid. After the reaction with NH_3 and NaCl , HNO_3 is converted to ammonium nitrate or sodium nitrate. Sources and fluxes of nitrogen containing compounds were given in Figure 1.10.

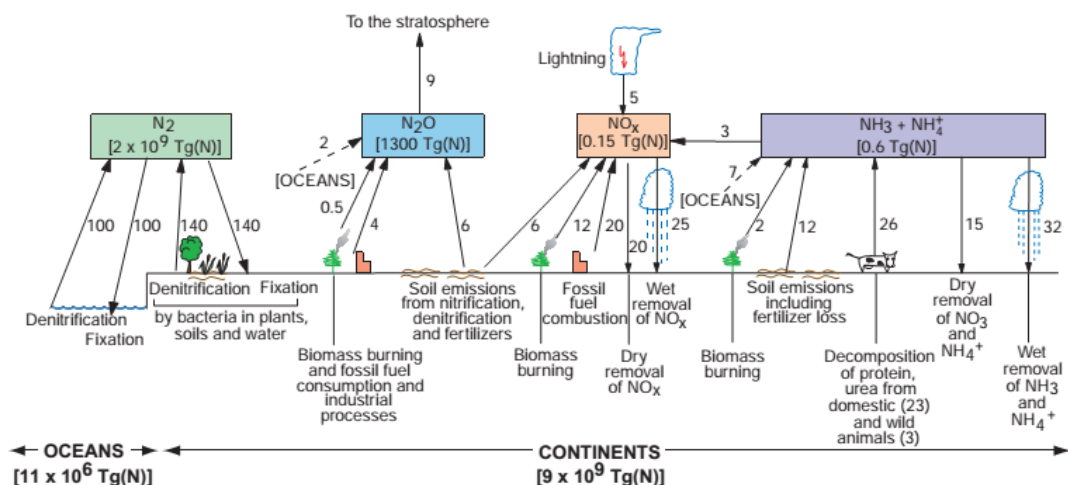


Figure 1.10. Sources and fluxes ($\text{Tg(N)} \text{ y}^{-1}$) of nitrogen containing compounds.

The third commonly observed secondary aerosol component is chloride which is generally in the form of ammonium chloride. Near to the marine, chloride is in the primary aerosols as NaCl however, by the emission hydrogen chloride gas near to the industrial zones (refuse incineration, coal combustion etc.) and the presence of sufficient ammonia, ammonium chloride is formed.

1.3.4. Classification of aerosols with respect to their composition

Tropospheric aerosols contain mostly, sulfate, ammonium, nitrate, sodium, chloride, trace metals, carbonaceous species, crustal elements and water (Seinfeld and Pandis, 2006) or simply organic and inorganic compositions. Inorganic composition of atmospheric particles and their sources were given in Figure 1.11 which is adopted from Manahan (2005). Identification of pollutant sources is very difficult and not accurate then the sources in the figure are commonly observed ones. For example, I, Na, Si, Fe, Cl and Ti are natural elements; Br, Cu, Mn, Ba, Mg, Ca, Zn, Pb, V, Be,

Fe, Ti are introduced to the atmosphere mainly by human activities and finally NH_4^+ , NO_3^- and SO_4^{2-} are originated from the chemical reactions within the atmosphere.

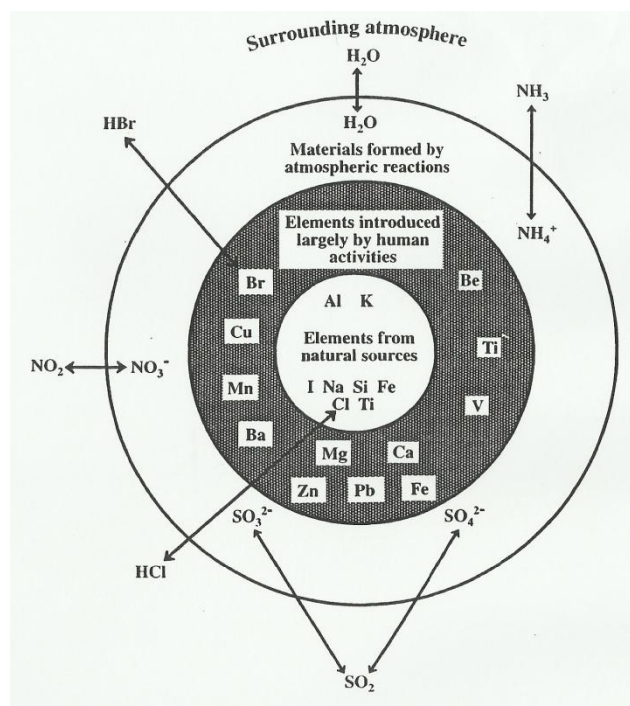


Figure 1.11. Inorganic composition of particulate matters and their origins.

The composition of the aerosols varies significantly with size (Manahan, 2005). Natural and anthropogenic sources of particulate matter with compositions in different size fractions and abundances were listed in Table 1.8 (Chow, 1995). For instance, in coarse fraction Si composed most of the particulate matter that has the abundance over 10 %. As seen in the table some parameters can be emitted from more than one source. Then, the knowledge about the quality of parameter is not enough for source apportionment, also the size of particle should be considered as indicated.

Table 1.8. Composition of particles in different size and sources.

Source Type	Dominant Particle Size	Chemical Abundances in Percent Mass			
		<0.1 %	0.1 to 1 %	1 to 10 %	>10 %
Paved road dust	Coarse	Cr, Sr, Pb, Zr	SO ₄ ²⁻ , Na ⁺ , K ⁺ , P, S, Cl, Mn, Zn, Ba, Ti	EC, Al, K, Ca, Fe	OC, Si
Unpaved road dust	Coarse	NO ₃ ⁻ , NH ₄ ⁺ , P, Zn, Sr, Ba	SO ₄ ²⁻ , Na ⁺ , K ⁺ , P, S, Cl, Mn, Ba, Ti	OC, Al, K, Ca, Fe	Si
Construction	Coarse	Cr, Mn, Zn, Sr, Ba	SO ₄ ²⁻ , K ⁺ , S, Ti	OC, Al, K, Ca, Fe	Si
Agriculture Soil	Coarse	NO ₃ ⁻ , NH ₄ ⁺ , Cr, Zn, Sr	SO ₄ ²⁻ , Na ⁺ , K ⁺ , S, Cl, Mn, Ba, Ti	OC, Al, K, Ca, Fe	Si
Natural Soil	Coarse	Cr, Mn, Sr, Zn, Ba	Cl ⁻ , Na ⁺ , EC, P, S, Cl, Ti	OC, Al, K, Ca, Fe	Si
Lake Bed	Coarse	Mn, Sr, Ba	K ⁺ , Ti	SO ₄ ²⁻ , Na ⁺ , OC, Al, S, Cl, K, Ca, Fe	Si
Motor Vehicle	Fine	Cr, Ni, Y, Sr, Ba	Si, Cl, Al, Si, P, Ca, Mn, Fe, Zn, Br, Pb	Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ , NH ₄ ⁺ , S	OC, EC
Vegetative Burning	Fine	Ca, Mn, Fe, Zn, Br, Rb, Pb	NO ₃ ⁻ , SO ₄ ²⁻ , NH ₄ ⁺ , Na ⁺ , S	Cl ⁻ , K ⁺ , Cl, K	OC, EC
Residual Oil Combustion	Fine	K ⁺ , OC, Cl, Ti, Cr, Co, Ga, Se	NH ₄ ⁺ , Na ⁺ , Zn, Fe, Si	V, OC, EC, Ni	S, SO ₄ ²⁻
Incinerator	Fine	V, Mn, Cu, Ag, Sn	K ⁺ , Al, Ti, Zn, Hg	NO ₃ ⁻ , Na ⁺ , EC, Si, S, Ca, Fe, Br, La, Pb	SO ₄ ²⁻ , NH ₄ ⁺ , OC, Cl
Coal-fired boiler	Fine	Cl, Cr, Mn, Ga, As, Se, Br, Rb, Zr	NH ₄ ⁺ , P, K, Ti, V, Ni, Zn, Sr, Ba, Pb	SO ₄ ²⁻ , OC, EC, Al, S, Ca, Fe	Si
Oil-fired power plant	Fine	V, Ni, Se, As, Br, Ba	Al, Si, P, K, Zn	NH ₄ ⁺ , OC, EC, Na, Ca, Pb	S, SO ₄ ²⁻
Smelter fine	Fine	V, Mn, Sb, Cr, Ti	Cd, Zn, Mg, Na, Ca, K, Se	Fe, Cu, As, Pb	S
Antimony roaster	Fine	V, Cl, Ni, Mn	SO ₄ ²⁻ , Sb, Pb	S	None reported
Marine	Coarse and Fine	Ti, V, Ni, Sr, Zr, Pd, Ag, Sn, Sb, Pb	Al, Si, K, Ca, Fe, Cu, Zn, Ba, La	NO ₃ ⁻ , SO ₄ ²⁻ , OC, EC	Cl ⁻ , Na ⁺ , Na, Cl

In order to investigate the properties of atmospheric pollution and also for taking precautions, the studies concerning concentration and composition of inhalable particles (PM_{10}) and fine particles ($PM_{2.5}$) are required (Kushrestha et al., 2009).

Atmospheric aerosol may be divided into three by their solubilities. First group is “water soluble inorganic salts”, second group is “minerals from the Earth’s crust that are insoluble in water or organic solvents” and the third group is composed of “organics, some of which are soluble in water and others insoluble”. If size of the particles is considered, generally giant particles are composed of roughly equal amounts of water soluble compounds and insoluble minerals. The amount of water soluble compounds increase by decreasing particle size at the expense of the mineral component (Hobbs, 2006).

Fine particles contain sulfates, ammonium, organic and elemental carbon and certain transition metals. Crustal minerals including silicon, calcium, magnesium, aluminum and iron and biological particles like pollen, spores and plant fragments are found in coarse fraction. Nitrate can be found in both fine and coarse fraction. Fine nitrate is usually the result of the nitric acid and ammonia reaction for the formation of ammonium nitrate while coarse nitrate is the product of nitric acid reactions (Seinfeld and Pandis, 2006).

1.3.4.1. Elements (Metals)

The most of the trace elements are found in atmospheric particulate matter samples. They have also been used as indicators of pollutant transport. These elements arise from many different sources including combustion of coal, oil, wood burning, steel

furnaces, boilers, smelters, dust, soil erosion, sea spray, vegetation, volcanic activity and many man made activities like waste incineration (Seinfeld and Pandis, 2006; Harrison and Grieken, 1998; Colbeck, 2008). Depending on their sources and the transformation processes these trace elements can be found in either fine or coarse particles. The trace element concentrations in different areas are given with their size mode in Table 1.9 (Seinfeld and Pandis, 2006).

Table 1.9. Concentration and size distributions of some elements in aerosols.

Element	Mode (F=fine, C=coarse)	Concentration (ng m ⁻³)		
		Remote	Rural	Urban
Fe	F and C	0.6-4,200	55-14,500	130-130,800
Pb	F	0.01-65	2-1,700	30-90,000
Zn	F	0.03-450	10-400	15-8,000
Cd	F	0.01-1	0.4-1,000	0.2-7,000
As	F	0.01-2	1-25	2-2,500
V	F and C	0.01-15	3-100	1-1,500
Cu	F and C	0.03-15	3-300	3-5,000
Mn	F and C	0.01-15	4-100	4-500
Ni	F and C	0.01-60	1-80	1-300
Sb	F	0-1	0.5-7	0.5-150
Cr	F and C	0.01-10	1-50	2-150
Co	F and C	0-1	0.1-10	0.2-100
Se	F and C	0.01-0.2	0.01-30	0.2-30

Trace elements that are in fine fractions are non volatile in general and also they have less tendency to go chemical transformations. Then, they mostly remain in their emitted form and can undergo long range atmospheric transport (Kulshrestha et al., 2009).

Various analytical methodologies have been applied for the elemental content of environmental samples. X-ray fluorescence (XRF) and proton-induced X-ray emission (PIXE) are the direct measurement however, atomic absorption-emission

(AAS-AES) spectroscopy and inductively coupled plasma (ICP) techniques are required preparations before the analysis. The most common interference in the direct measurement techniques is the matrix effects. Inductively coupled plasma techniques are rapid and multi element analysis at the same time is feasible and also matrix effect or chemical interferences are negligible in this technique. Main disadvantage of the technique is the lack of sensitivity and selectivity for less abundant elements in environmental samples. However, AAS and AES techniques give more accurate results but individual analysis is required for each element.

1.3.4.2. Ions

The most important ions in atmospheric particulate matters are Cl^- , NO_3^- , SO_4^{2-} , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} . These ions can be originated from both natural and anthropogenic sources. For instance, Cl^- can be emitted to the atmosphere from coal burning as well as from sea salt. Nitrate is formed by the oxidation of some nitric oxides. Ammonium is formed as the product of neutralization reactions of ammonia and some acids. The main sources of ammonia are organic degradation and fertilization. The important crustal ions are Ca^{2+} and Mg^{2+} . Potassium can be also crustal but the main source of it is biomass burning as sulfate. Moreover, the reactive gases, SO_2 and NO_x from industrial processes and traffic emission can be converted to SO_4^{2-} and NO_3^- with humidity (Baltensperger and Nyeki, 1998, Wang ve Shooter, 2001). Secondary sulfate and nitrate are accumulated in coarse particles, and then they can be easily swept by wet and dry deposition.

1.3.4.3. Carbonaceous species

Carbon is the dominant element in aerosol composition. The carbonaceous fraction of aerosol can be differentiated as elemental, organic and inorganic carbon.

1.3.4.3.1. Elemental carbon

Especially, in atmospheric pollution studies elemental and organic carbon are focused on. Elemental carbon (EC or black carbon) has a crucial role in order to balance the temperature of Earth by absorbing the sunlight. However, this effect is the main reason of global warming after the effect of CO₂ (Li et al., 2002; Cao et al., 2004). Elemental carbon is emitted from combustion at high temperature and it is classified as primary air pollutant due to its inert structure. The concentrations of EC in urban areas are generally higher than in rural and remote areas.

1.3.4.3.2. Organic carbon

In addition to elemental carbon, organic carbon (OC) is the other important parameter. In atmospheric particles organic compounds contribute significantly to the total aerosol mass (Colbeck, 2008; Cao et al., 2004). Organic compounds can be emitted directly to the atmosphere or its structure can be changed by photochemical reactions after emitted from the source and affect the receptors with its secondary composition. Secondary organic compounds are produced especially from the oxidation of organic compounds

During the determination of primary and secondary organic carbons elemental carbon is used as tracer (Cao et al., 2004). As indicated in the following equations, total organic carbon can be separated as primary and secondary organic carbon by using the factor calculated from the ratio of organic carbon and elemental carbon (Dusek, 2000; Turpin and Huntzicker, 1995; Na et al., 2004; Satsangi et al., 2012; Salma et al., 2004).

$$OC_{primary} = \left(\frac{OC}{EC}\right)_{primary} \times EC \quad Eq (1.3)$$

$$OC_{secondary} = OC_{total} - OC_{primary} \quad Eq (1.4)$$

Secondary organic fraction of carbonaceous aerosols can be estimated by assuming that the lowest OC/EC ratio found for a location is representative for primary OC/EC ratio (Schaap et al., 2007) because primary OC and EC have the same source (Salma et al., 2004). This approach generally used for urban locations where the ratio of OC/EC is near to 1. However, it is difficult to conclude the presence of secondary OC from the absolute values of OC/EC alone (Na et al., 2004) and also the amount of secondary OC aerosol depends not only on the ratio, but also on ambient carbon concentrations (Turpin and Huntzicker, 1995). Hence, extrapolation of the minimum OC/EC value to the whole sampling period as a substitute for the primary OC/EC ratio can not be accepted for any locations other than heavily pollutant urban sides.

These calculations can be used in fine fraction of aerosols because in coarse mode OC originates from other sources like pollen, spores paved road dust, tyre rubber. The weakness of this approach is the variation of $(OC/EC)_{pri}$ emission rates. This ratio can be influenced by local sources and meteorology (Salma et al., 2004).

Determination of OC_{pri} was achieved by using scatter plot graphs of OC versus EC. Slope of the graph estimates the primary OC/EC ratio. Intercepts represent the residual OC from sources like biogenic emissions and other non combustion sources (Turpin and Huntzicker, 1995).

1.3.4.3.3. Carbonate carbon

Carbonate has crucial roles in atmospheric chemistry, global climate and radiative forcing (Ho et al., 2011 and references therein). Moreover, carbonate can also affect the chemical processes and aerosol characteristics due to its neutralizing capacity. It facilitates the heterogeneous conversion of sulfur and nitrogen oxides to particulate sulfate and nitrate (Wang et al., 2005). Despite being important, a few studies about atmospheric carbonate have been conducted.

Carbonate is a prominent component of the soils and it is often associated with calcium and magnesium which can be found in coarse fraction of aerosol. Common types of natural carbonate structures with their volatilization temperatures are given in Table 1.10.

Table 1.10. Volatilization temperature ranges of some natural carbonated materials

Material	Initial volatilization temperature (°C)	Maximum volatilization temperature (°C)
Calcite (stalagnite)	643	841
Dolomitic limestone	601	803
Oolitic limestone	654	703

Soluble carbonates can be easily determined by using ion chromatography as CO_3^{2-} form. However, this convenience can not be obtained in insoluble ones. Some thermal optical methods have been used to determine carbonate carbon along with both organic and elemental fractions (Ho et al., 2011; Jankowski et al., 2008; DRI, 2005). One of the most important problems is the interference of CC with the signal of EC or OC. Although it has been mentioned in several EC/OC intercomparison studies, the assessment is not mentioned (Jankowski et al., 2008).

1.3.4.3.4. Oxalate carbon

In literature, oxalic acid is cited as one of the major components of organic aerosols (Kawamura et al., 2010 and references therein; Yang et al., 2014 and references therein; Laongsri and Harrison, 2013). It has been reported as both a product of primary emissions from combustion processes (biomass burning and anthropogenic emissions) and as a secondary product of in-cloud formation (transformation of precursors in the gaseous and condensed phases) (Yang et al., 2014 and references therein; Laongsri and Harrison, 2013 and references therein).

Oxalate can be obtained from the dissociation of oxalic acid or the ionization of water soluble metal oxalates in aerosol samples. In most studies oxalate is determined as oxalate ion ($\text{C}_2\text{O}_4^{2-}$) (Yang et al., 2014; Wang et al., 2007) by using ion chromatography. In this study a new method was improved to determine the oxalate by thermal optical analysis (Sunset OC/EC Analyzer).

1.3.5. Health effects of aerosols

Fine particulate matters have adverse health effects on human and other living things. The reasons are the reactive reagents in the structure of the particle and also the other pollutants adsorbed in the surface of it. The concentrations of adsorbed pollutants are higher than the concentrations in the atmosphere then they destruct the ascendance surface directly. Especially, particles with the size of 2.5 μm and smaller than this size introduce to the human's respiratory system and damage the lungs. Especially, heavy metals in higher concentrations can have severe toxic and carcinogenic effects on human when inhaled (Kulshrestha et al., 2009). The health effects of particulate matters on human health in the range of concentration is summarized in Table 1.11 (EPA, 2006).

Table 1.11. Air quality index values and health effects statements.

AQI Values	24 h ($\mu\text{g m}^{-3}$)		Levels of Health Concern	Cautionary Statements
	PM _{2.5}	PM ₁₀		
0-50	0-15	0-50	Good	None
51-100	>15-40	>50-150	Moderate	Respiratory symptoms possible in unusually sensitive individuals, possible aggravation of heart or lung disease in people with cardiopulmonary disease and older adults.
101-150	>40-65	>150-250	Unhealthy for sensitive groups	Increasing likelihood of respiratory symptoms in sensitive individuals, aggravation of heart or lung disease and premature mortality in people with cardiopulmonary disease and older adults.
151-200	>65-150	>250-350	Unhealthy	Increased aggravation of heart or lung disease and premature mortality in people with cardiopulmonary disease and older adults; increased respiratory effects in general population.
201-300	>150-250	>350-420	Very unhealthy	Significant aggravation of heart or lung disease and premature mortality in people with cardiopulmonary disease and older adults; significant increase in respiratory effects in general population.
301-500	>250-500	>420-600	Hazardous	Serious aggravation of heart or lung disease and premature mortality in people with cardiopulmonary disease and older adults; serious risk of respiratory effects in general population.

In addition to the health effects, particulate matters also affect the environment and materials in negative way. The effects of them are explained with criteria in Table 1.12 (Ayvaz Kahramantekin, 2006).

Table 1.12. Effects of particulate matters on materials, environmental and health.

Concentration ($\mu\text{g m}^{-3}$)	Effects	Criteria
60-180*	Corrosion on metal surfaces	-
150*	Visibility decreases under 9 km	When relative humidity is under 70 %
100-150*	Decrease the solar radiation in a ratio of 1/3	-
100-130*	Respiratory problems occur in children	When SO_2 is higher than $120 \mu\text{g m}^{-3}$
300**	Increase in crisis in chronic bronchitis patients	When SO_2 is higher than $630 \mu\text{g m}^{-3}$
750**	Increase in death and become ill	When SO_2 is higher than $715 \mu\text{g m}^{-3}$

* annual average, ** diurnal average

1.3.6. Source apportionment calculations

The accurate measurement of the composition of atmospheric particulate matter samples is very important in environmental monitoring (Swami et al., 2001) and source apportionment calculations are prerequested to develop effective air quality strategies (Kulkarni et al., 2003).

1.3.6.1. Statistical treatments

1.3.6.1.1. Bivariate linear regression

Bivariate linear regression is used to measure the degree of linear relationship between two variables. Scatter plots in Figure 1.12 shows the possible relationships between the variables. In all linear regressions one variable is dependent on the other(s) and by convention it is in the vertical axis (Y-axis) and the other component(s) are independent variable(s) and lies in horizontal axis (X-axis) (Shaw, 2003). In Figure 2.12 graph a) and b) the relationship between the variables are positive and negative, respectively. Graph c) shows no relation among data and graph d) and c) shows a systematic but non-linear (curvilinear) relationships between the variables.

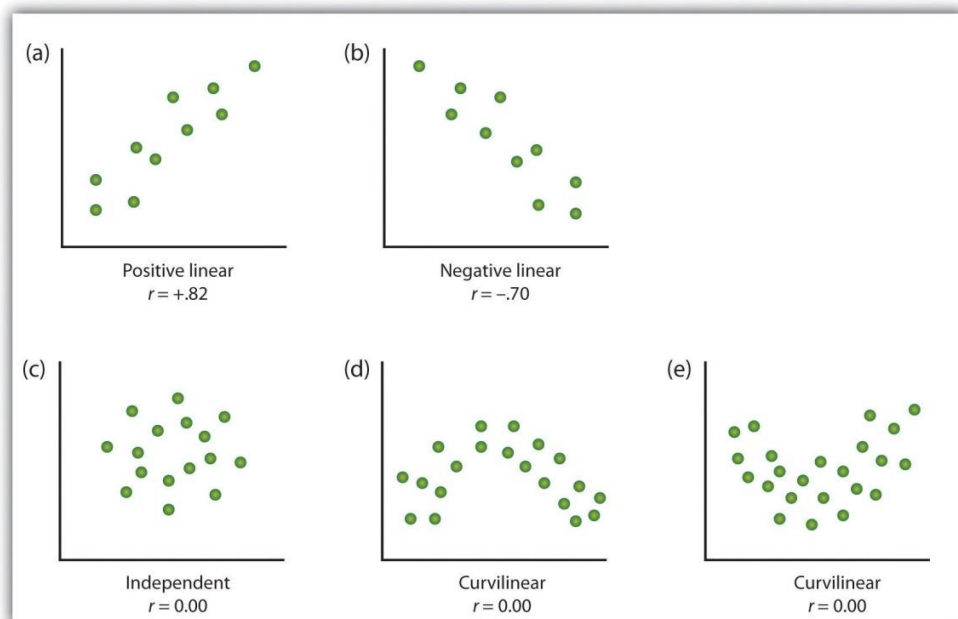


Figure 1.12. Scatter plots of binary correlations

One of the most common method in linear regression that is used to predict how well the experimental points fit a straight line is Pearson product moment correlation (Miller and Miller, 2005). The value of the product moment correlation coefficient is given in the following equation.

$$r = \frac{\sum_i \{(x_i - \bar{x})(y_i - \bar{y})\}}{\{[\sum_i (x_i - \bar{x})^2][\sum_i (y_i - \bar{y})^2]\}^{1/2}} \quad Eq (1.4)$$

Covariance measures the joint variation and calculated by the division of the numerator of the above equation to n . If the variables x and y , are not related with each other then, the covariance will be close to zero. Correlation coefficient is equal to the division of covariance by the standard deviations of the variables. Then, if there is no relation between x and y , r will also close to zero (Miller and Miller, 2005).

The value of the correlation coefficient, r , can range from -1.00 to + 1.00 and the sign of the correlation coefficient (+ , -) defines the direction of the relationship, either positive or negative. A positive correlation coefficient means that as the value of one variable increases, the value of the other variable increases; as one decreases the other decreases. A negative correlation coefficient indicates that as one variable increases, the other decreases, and vice-versa. In addition, taking the absolute value or the squared value of the correlation coefficient, r^2 , measures the strength or the magnitude of the relationship. In this study the relationship between each parameter in each size fraction of particulate matter will be discussed. High correlation coefficient between any of two measured parameter will be concluded as these parameters may be emitted from similar sources, they may be follow the similar transport patterns and also they may be formed in similar mechanisms.

1.3.6.1.2. Multiple linear regression

The regression model Multiple linear regression (MLR) is used to determine the contribution of each parameters to the pollution by predicting the variability between independent and dependant variables (Wahid, et al., 2013). The equation 1.5 shows the calculation of the regression.

$$c_i = b_{0i} + b_{1i}A_1 + b_{2i}A_2 + \dots + b_{6i}A_6 \quad Eq (1.5)$$

The first term, b_{0i} , is the intercept, b_i values are slopes or coefficients. In MLR the number of samples must be grater than the number of the variables (Miller and Miller, 2005).

Although there may be a strong relationship between two or more variables, a regression model does not imply any cause-effect relationship. In order to establish a causality, the relationship may be suggested by theoretical considerations (Montgomery et al., 2012).

1.3.6.2. Crustal enrichment factor analysis

Chemical compositions of atmospheric particulate matters are originated from both natural and anthropogenic sources. However, they can be varied spatially and temporally. Crustal elements compose the high percentage of the particulate matters. Then it should be considered that parameters obtained in soil affect less or more the concentrations of other parameters. Before the source apportionment of aerosols crustal originated elements and their amounts should be determined. Then the

participation of these elements to others is evaluated. For that purpose, one of the common method, enrichment factor (EF) analysis is used. This analysis provides information about the compositions and their origins. The enrichment factor is obtained by the following equation (Yatkin and Bayram, 2007; Yatin et al., 2000; Yenisoy-Karakaş and Tuncel, 2008).

$$EF = \frac{(C_x/C_{Al})_{PM}}{(C_x/C_{Al})_{crustal}} \quad Eq (1.6)$$

In this equation C_x is the concentration of sought parameter in particulate matter and crustal and C_{Al} is the concentration of Al in crustal and particulate matter. The concentrations of crustal elements are obtained from Taylor's average crustal composition (Karakaş, 1999). Aluminum is generally selected as reference crustal element due to its high concentration in soil. However, other crustal elements like Fe, Ca, Sc, Ti can be used. As shown in the above equation, the enrichment factor of an element is based on the ratio of the concentration of the test element to the reference element in the same sample divided by the same ratio in reference material like soil.

According to the enrichment factor analysis elements were divided into three general categories with respect to their mean EF values; non-enriched elements ($EF < 10$), moderately enriched elements ($10 < EF < 100$), and highly enriched elements ($EF > 100$).

1.3.6.3. Transportation of pollutants

1.3.6.3.1. Long range transportation (Back trajectory analysis)

Back trajectory analysis is used to determine the sources of long range transported air pollutants. For back trajectory analysis HYSPLIT model will be used. The HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) model is a complete system for computing simple air parcel trajectories to complex dispersion and deposition simulations. The model is designed to support a wide range of simulations related to the atmospheric transport and dispersion of pollutants and hazardous materials, as well as the deposition of these materials (http://www.arl.noaa.gov/HYSPLIT_info.php, 2011).

The selection of meteorological parameters and starting location for HYSPLIT trajectory model is selected by using the from in Figure 1.13. REANALYSIS archived data file was used in this study. REANALYSIS data covers the globe from 1948 to the present with a horizontal resolution of about 2.5 degree altitude. The latitude and longitude values in degrees was entered. In the next step (Figure 1.14) archived meteorology file was selected for given location. The format of file was year/month (RP200910.glb). Then, the model run details were entered to the form in Figure 1.15. This form requires trajectory direction, vertical motion, start time of trajectory, total run time (as hour), latitude and longitude values and finally, the altitude(s) of air parcel from above ground level (AGL) or above mean sea level (AMSL). An example of HYSPLIT back trajectory graph is given in Figure 1.16.

The movement of air parcel through 5 days until it reached to the sampling location at different altitudes were shown in different colors (red-500m, blue-1000m, green-1500m).

Meteorology: REANALYSIS (global, 1948-present) [More info ▶](#)

Source Location (enter using one of the following methods):

☒ Decimal Degrees Latitude: 40.42 N Longitude: 31.31 E

 **Hold mouse over icon to get Lat/Lon from MapQuest map.**

☐ DDD/MM/SS Latitude: Deg. Min. Sec. N Longitude: Deg. Min. Sec. W

☐ City (Country or State: name: lat: lon):

☐ Airport or WMO ID (i.e., dca): ID Lookup

[Reset Form](#) [Next>>](#)

Figure 1.13. Meteorology and starting location(s) form for HYSPLIT trajectory

Meteorology: Archived reanalysis
Source Location: Lat: 40.000000 Lon: 31.000000

Choose an archived meteorological file

Archive File: RP200910.gbl

[Next>>](#)

Figure 1.14. The selection of archived meteorology files for given location

Model Parameters

Trajectory direction: ☐ Forward ☒ Backward (Change the default start time!) [More Info](#)

Vertical Motion: ☐ Model vertical velocity ☐ Isobaric ☒ Isentropic [More Info](#)

Start time (UTC): Current time: 07:43
 year: 09 month: 10 day: 20 hour: 7 [More Info](#)

Total run time (hours): 150 [More Info](#)

Start a new trajectory every: 0 hrs **Maximum number of trajectories:** 24 [More Info](#)

Start 1 latitude (degrees): 40.42 [More Info](#)

Start 1 longitude (degrees): 31.31 [More Info](#)

Start 2 latitude (degrees):

Start 2 longitude (degrees):

Start 3 latitude (degrees):

Start 3 longitude (degrees):

Level 1 height: 500 ☒ meters AGL ☐ meters AMSL [More Info](#)

Level 2 height: 1000

Level 3 height: 1500

Figure 1.15. Model run details form for HYSPLIT trajectory

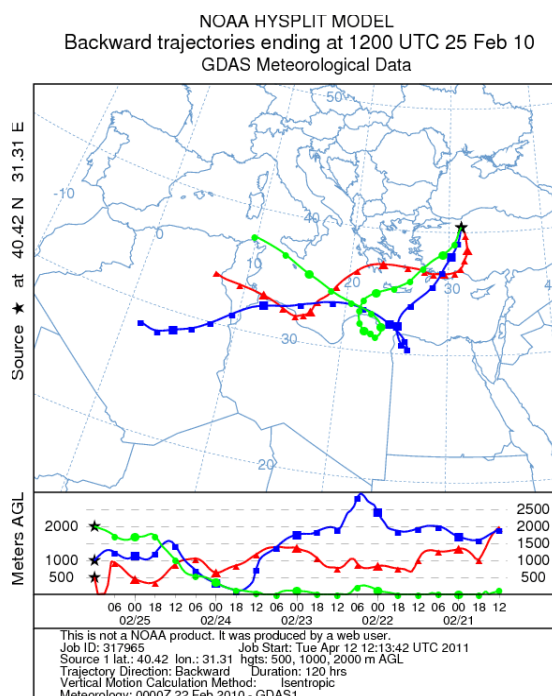


Figure 1.16. An example of back trajectory result

1.3.6.3.2. Local scale transportation (Wind sector analysis)

Wind sector analysis is used to explain the local sources of the pollutants. In the analysis average concentrations of the pollutants in each wind directions is taken. If the concentration of a pollutant is high, then at this direction there will be a possible source for that pollutant. In Table 1.13 the possible sources for air pollution with the directions are given (Öz, 2009).

Table 1.13. Possible local sources for air pollution

Wind Direction	Pollutant Sources
North (N)	Traffic (E-80 ve D-100 highways), Forests
North-North-East (NNE)	Traffic (E-80 ve D-100 highways), Forests
North-East (NE)	Residential areas (Bolu), Agricultural areas (Karaköy), Industrial zone (Isopoly, PVC, aluminum carpentry, petrochemical, motor oil)
East-North-East (ENE)	Residential areas, Agricultural areas, Asphalt manufacturing plant
East (E)	Residential areas, Agricultural areas (Dörtdivan), Industrial zone, Leather factory (Gerede), cement factory
East-South-East (ESE)	Industrial zone (potato factories), Residential areas (Karaköy, Doğancı)
South-East (SE)	Agricultural areas (Karacasu, Seben, Kıbrıscık), Industrial zone (wood-pulp factory),
South-South-East (SSE)	Agricultural areas, Industrial zone (wood-pulp factory),
South (S)	Agricultural areas (Seben), Gököy Lake
South-South-West (SSW)	Forest and Agricultural areas (Mudurnu, Göynük)
South-West (SW)	Agricultural areas (Mudurnu), Forest, Residential areas (Gököy), Heating center of university (A.İ.B.Ü)
West-South-West (WSW)	Forest
West (W)	Residential areas (Bolu, Adapazarı)
West-North-West (WNW)	Traffic (E-80 ve D-100 highways), Forests
North-West (NW)	Traffic (E-80 ve D-100 highways), Forests, Düzce
North-North-West (NNW)	Traffic (E-80 ve D-100 highways), Forests

If there is not any source in the direction of high concentration of a pollutant, then this pollutant came to the receptor zone by a long range transport and it can be determined by a back trajectory analysis.

In this study the local sources for each parameter will be investigated by using wind sector analysis.

1.3.6.4. Receptor modeling

Receptor models are used to identify qualitatively and estimate quantitatively the source contributions to ambient air pollutants by utilizing the abundances of chemical compositions, particle sizes and air concentration variations (Guo et al., 2009; Okuda et al., 2004; Karaca et al., 2009). Most common receptor models are Chemical Mass Balance (CMB), Principle Component Analysis (PCA), Factor analysis (FA) and Positive Matrix Factorization (PMF).

Fundamentally, all these receptors models are based on measured mass concentrations and the use of appropriate mass balances (Seinfeld and Pandis, 2006). Seinfeld and Pandis (2006) explain this situation with an example. For example, the total concentration of particulate iron is assumed to be the combination of the contributions from a number of independent sources.

$$Fe_{total} = Fe_{soil} + Fe_{auto} + Fe_{coal} + \dots \quad Eq (1.7)$$

This example is very simple but it demonstrates the utility of receptor modeling.

Chemical Mass Balance model was first proposed 30 year ago. The assumption of the model is that the ambient chemical concentrations are expressed as the sum of the products of species abundances and source contributions (Okuda et al., 2004; Watson et al., 2002). One of the drawbacks of the model is the difficulty to choose the adequate number of sources and to obtain accurate and representative source profiles (Okuda et al., 2004).

Principle component Analysis (PCA) is the other commonly used receptor model. It is especially useful to investigate the variance structure of a particular data set which means how much data variance can be explained by a particular number of components. However there are two problems with the application of PCA in environmental studies:

(a) the interpretability of the sources

(b) noise propagation effects on PCA results (Tauler et al., 2009)

1.3.6.4.1. Factor analysis

Factor analysis (FA) is one of the multivariate statistical technique to obtain preliminary information about the sources of pollutants that influence a particular receptor. The basic principle of factor analysis is to combine the variables that are related with each other and then reduce the amount of variables for classification (Wang et al., 2006; Huang et al., 1999). Factor analysis is also a variance analysis because it focuses on the common source of components that have similar variance. Then the classification is based on the variance of the components. Factor loading is

the value that is used to determine the relation between each pollutant and emission source and factor score is the value that is used to determine the contribution of emission source to the total concentration (Harrison et al., 1996). Both PCA and FA are used to reduce the amount of variables in a data set. However, in some case they differ in many respects (Rencher, 2002) as in Table 1.14.

Table 1.14. Main differences between PCA and FA.

Principle Component Analysis	Factor Analysis
The principle components are defined as linear combinations of the original variables.	The original variables are expressed as linear combinations of the factors.
The total variance of variables are explained	The covariances or correlations among the variables are explained.

In FA, a linear combination of different factors in the matrix A with factor scores in the matrix F can produce the data matrix X with matrix residuals E. The communality explain the weight of variance that is explained by the factor solution.

$$X = A \cdot F + E \quad Eq (1.8)$$

The matrix notation of the analysis is given in the following equation.

$$\begin{pmatrix} x_{11} & x_{12} & \dots & x_{1n} \\ x_{21} & x_{22} & \dots & x_{2n} \\ \dots & \dots & \dots & \dots \\ x_{m1} & x_{m2} & \dots & x_{mn} \end{pmatrix} = \begin{pmatrix} a_{11} & \dots & a_{1s} \\ a_{21} & \dots & a_{2s} \\ \dots & \dots & \dots \\ a_{m1} & \dots & a_{ms} \end{pmatrix} x \begin{pmatrix} f_{11} & f_{12} & \dots & f_{1n} \\ \dots & \dots & \dots & \dots \\ f_{s1} & f_{s2} & \dots & f_{sn} \end{pmatrix} + \begin{pmatrix} e_{11} & e_{12} & \dots & e_{1n} \\ e_{21} & e_{22} & \dots & e_{2n} \\ \dots & \dots & \dots & \dots \\ e_{m1} & e_{m2} & \dots & e_{mn} \end{pmatrix} \quad \text{Eq (1.9)}$$

In spite of the utility of it, factor analysis also has some drawbacks. One of them is the requirement of a dense and meaningful data set. The other one is that factors that are considered as sources should be certain (Harrison et al., 1996). Moreover, there are some limitations in the identification of sources;

- a) the selection of variables to be included in the model can significantly influence the results
- b) the unavailability of some tracers can yield to subjective source interpretations
- c) ambiguous tracers can be erroneously interpreted because they can be representative for more than one emission source
- d) covariant sources might not be efficiently separated, resulting in mixed source profiles
- e) some factors may have no physical meaning (Masiol et al., 2010).

Analysis will be achieved with Statgraphics Plus 3.1 program.

1.3.6.4.2. Positive matrix factorization (PMF)

Positive Matrix Factorization (PMF) is one of the receptor modeling that has been applied to a wide range of data like daily speciated $PM_{2.5}$, size resolved aerosols, air toxics, deposition of pollutants, VOCs, etc. (EPA PMF 3.0 User Guide, 2008; Brown et al., 2007; Bernardoni et al., 2011) which were determined in the same time interval (Karanasiou et al., 2009). It is also a multivariate factor analysis which decomposes a matrix of speciated sample data into two matrices as factor contributions and factor profiles. (EPA PMF 3.0 User Guide, 2008; Brown et al., 2007; Bernardoni et al., 2011). In PMF analysis the main consideration is to obtain a good fit of the model to the original data (Chueinta et al., 2000). Then, the following steps should be applied to the model.

1. Preparing data to be modeled.
2. Processing the data with PMF to develop feasible and robust results.
3. Interpreting the results (Reff et al., 2007).

The aim of multivariate receptor modeling is to identify the number of sources that contributes to all chemical species for each sample (Kim et al., 2003 (a); Kim et al., 2003 (b); Ramadan et al., 2000; Brown et al., 2007). The following equation (Eq (1.10)) is the general formula that is used in receptor model calculations.

$$x_{ij} = \sum_{k=1}^p g_{ik}f_{ik} + e_{ij} \quad Eq (1.10)$$

Where;

x_{ij} = j^{th} species concentration measured in the i^{th} sample

g_{ik} = particulate mass concentration from the k^{th} source contributing to the i^{th} sample

f_{ik} = j^{th} species mass fraction from the k^{th} source

e_{ij} = residual associated with the j^{th} species concentration measured in the i^{th} sample

p = total number of independent sources.

The matrix equation of this model (Eq (1.11)) is similar with factor analysis ((Eq (2.8)).

$$X = G \cdot F + E \quad \text{Eq (1.11)}$$

Where;

X = n by m data matrix with n measurements and m number of elements

G = n by p matrix of source chemical compositions (source profiles)

F = p by m matrix of source contributions (factor scores)

E = part of the data variance unmodeled by the p -factor model (Ramadan et al., 2000; Kim et al., 2003 (a); Kim et al., 2003 (b); Bernardoni et al., 2011).

In PMF model any sample can not have a negative source contribution and then no species can have a negative concentration in any source profile (Brown et al., 2007; Reff et al., 2007). Weighing each data point is one of the advantage of PMF model.

During the weighing data set, any samples with missing values or values below detection limit are not excluded and alternatively uncertainty of the individual species are evaluated. Then, the impact of the species with missing value or below detection value can be observed as negligible (Bernardoni et al., 2011; Brown et al., 2007; Ramadan et al., 2000).

Generally, values below the method detection limit (MDL) are substituted with MDL/2 (Polissar et al., 2001; Brown et al., 2007; Kim et al., 2004), missing values are substituted with median (Brown et al., 2007) or geometric mean (Polissar et al., 2001; Kim et al., 2004) of concentrations. Uncertainties for the values above MDL are substituted with analytical uncertainties plus one-thirds of the MDL, uncertainties for values below MDL are substituted with one and a half times of MDL (Brown et al., 2007) or 5/6 of MDL (Kim et al., 2004) and finally uncertainties for missing values are substituted with four times the median (Brown et al., 2007; Kim et al., 2004).

Positive matrix factorization provides a solution to minimize an object function, $Q(E)$ based on uncertainties for each observation as in Eq 1.12.

$$Q(E) = \sum_{i=1}^n \sum_{j=1}^m \left[\frac{x_{ij} - \sum_{k=1}^p g_{ik} f_{ik}}{u_{ij}} \right] \quad Eq (1.12)$$

Where u_{ij} is an uncertainty estimate in the j^{th} element measured in the i^{th} sample. The model relies on both concentration and error estimates then, the calculation of uncertainty becomes crucial due to the quality of data (Kim et al., 2003 (a); Kim et al., 2003 (b); Ramadan et al., 2000). Estimation of uncertainties either directly or using equations generally requires knowledge of analytical uncertainties and method

detection limits. Reff et al., (2007) explained that the choice of species to include in the data matrix and the uncertainties to associate with them depend on the aim of the study and the quality of the measurements.

CHAPTER 2

2. MATERIALS AND METHODS

2.1. Field studies

2.1.1. Sampling site

Bolu is placed in the North Eastern Part of Black Sea Region between 30° 32' and 32° 36' east longitudes and 40° 06' and 41° 01' north latitudes. The altitude of the city center and the campus from sea level is 726 m and 874 m, respectively. The city is bordered by Zonguldak, Karabük, Çankırı, Ankara, Bilecik, Eskişehir, Düzce and Sakarya and it has 8 districts except for the city center. According to the Turkish Statistical Institute, the total population of Bolu was 281,080 at the end of 2012 (www.tuik.gov.tr).

Total area of the city is 834,100 hectare, 13 % of the total (~109,185 hectare) is used for agricultural applications and approximately 40 % of total area is composed of forests. Flora of the city contains 89 family, 363 genus and 771 species (Bolu Province Environmental Perspective Report, 2008). According to 2008 reports, 69,813 vehicles have been enrolled and the number of motor vehicles that undergo mandatory emission measurement is 19,850 (Bolu Province Environmental

Perspective Report, 2008). Bolu is located between two metropolitan cities, Istanbul and Ankara, and two international highways TEM and D-100 pass through the city center. Consequently, the density of traffic in these roads affects the air quality of the city. Coal, wood and diesel oil have been used for domestic heating in Bolu. However, utilization of natural gas was started in Abant İzzet Baysal University and industrial zone in 2010. Since 2009 allocation of natural gas to residence has been performed. It is expected that whole city will use natural gas by the end of 2014. For this reason, the study about the air quality of city center before 2014 is very crucial in order to evaluate the contribution of old fashioned heating process to the air pollution.

The sampling point of this study was located on the roof of Presidency building in Abant İzzet Baysal University Campus in $40^{\circ} 42.864'$ north latitude and $31^{\circ} 31.035'$ east longitude (Figure 2.1). The altitude of the sampling point is 15 m from ground level and 874 m from sea level. The distance between the university and D-100 or TEM highways and city center is 1.5 km and 8 km, respectively. Potential pollution sources around the sampling point are domestic heating, traffic and the asphalt production industry which is 2 km away.

In the selection of sampling point, safety of sampling instruments, the facility of electric generation and nonexistence of any buildings around the sampling point that restrict the wind flow are considered.

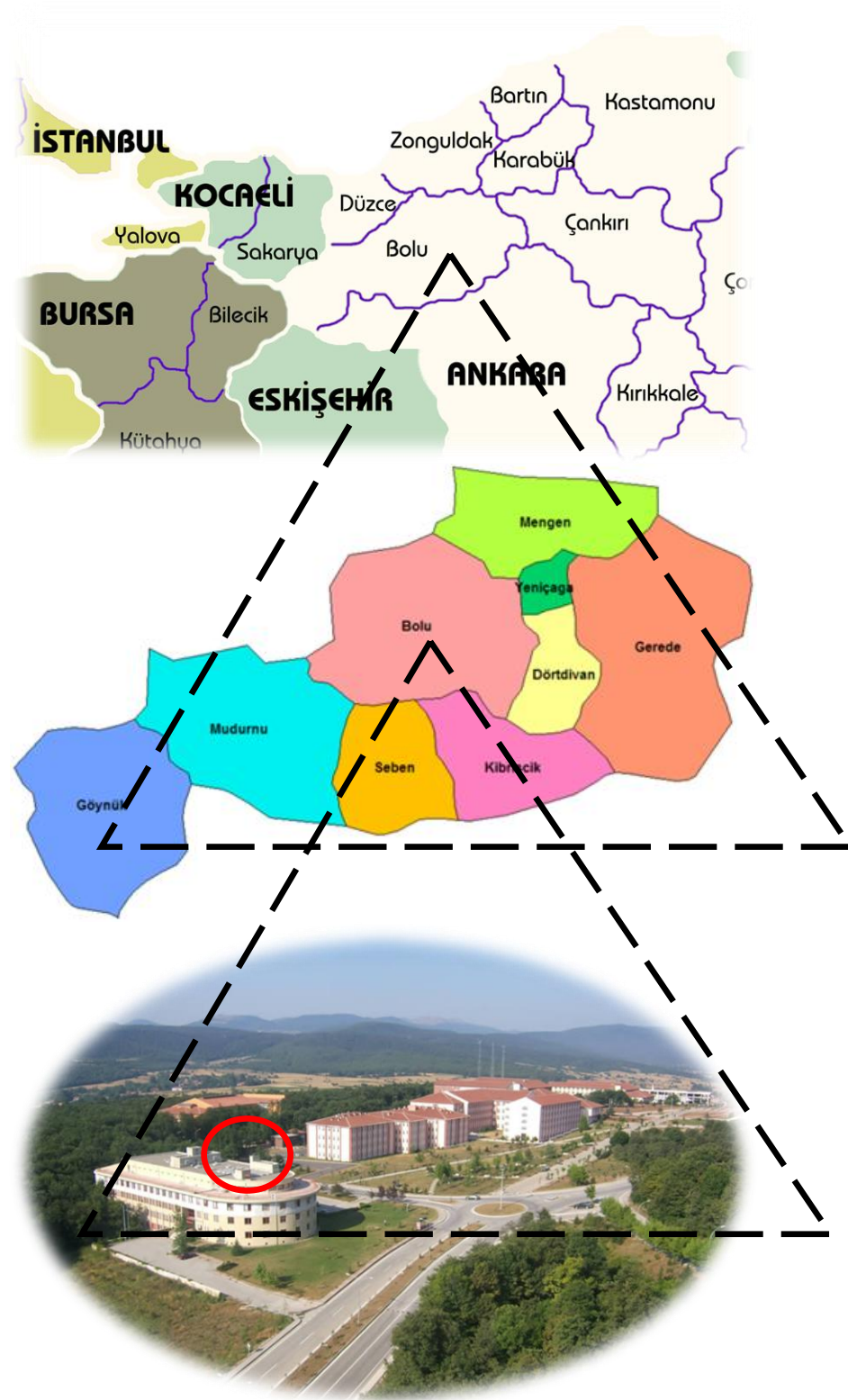


Figure 2.1. The map of Bolu and the sampling point (highlighted with red circle)

2.1.2. Sampling instruments

In sampling point one dichotomous sampler (collecting PM_{2.5} and PM_{2.5-10} samples separately), two particulate matter samplers (one PM₁₀ and one PM_{2.5}), one meteorology station and one O₃ analyzer were installed. Ozone monitoring was started in March 2009 and completed in March 2012. Daily aerosol samples were collected by the PM samplers and the dichotomous sampler between March 2009 and March 2010. Throughout the sampling period meteorology station provided hourly data.

2.1.2.1. Dichotomous

Thermo rp PARTISOL® 2000-D model Dichotomous sampler (Figure 2.2) is an instrument which collects both PM_{2.5} and PM_{2.5-10} on Teflon filter (Whatman PTFE-47 mm) simultaneously. Totally 16.7 l/min air is introduced to the head of the instrument then it is separated with flow controllers to maintain the fine particle stream at 15.0 l/min and the course particle stream at 1.67 l/min. The detailed schematic diagram of the instrument is shown in Figure 2.3.



Figure 2.2. Thermo rp Partisol 2000-D dichotomous sampler

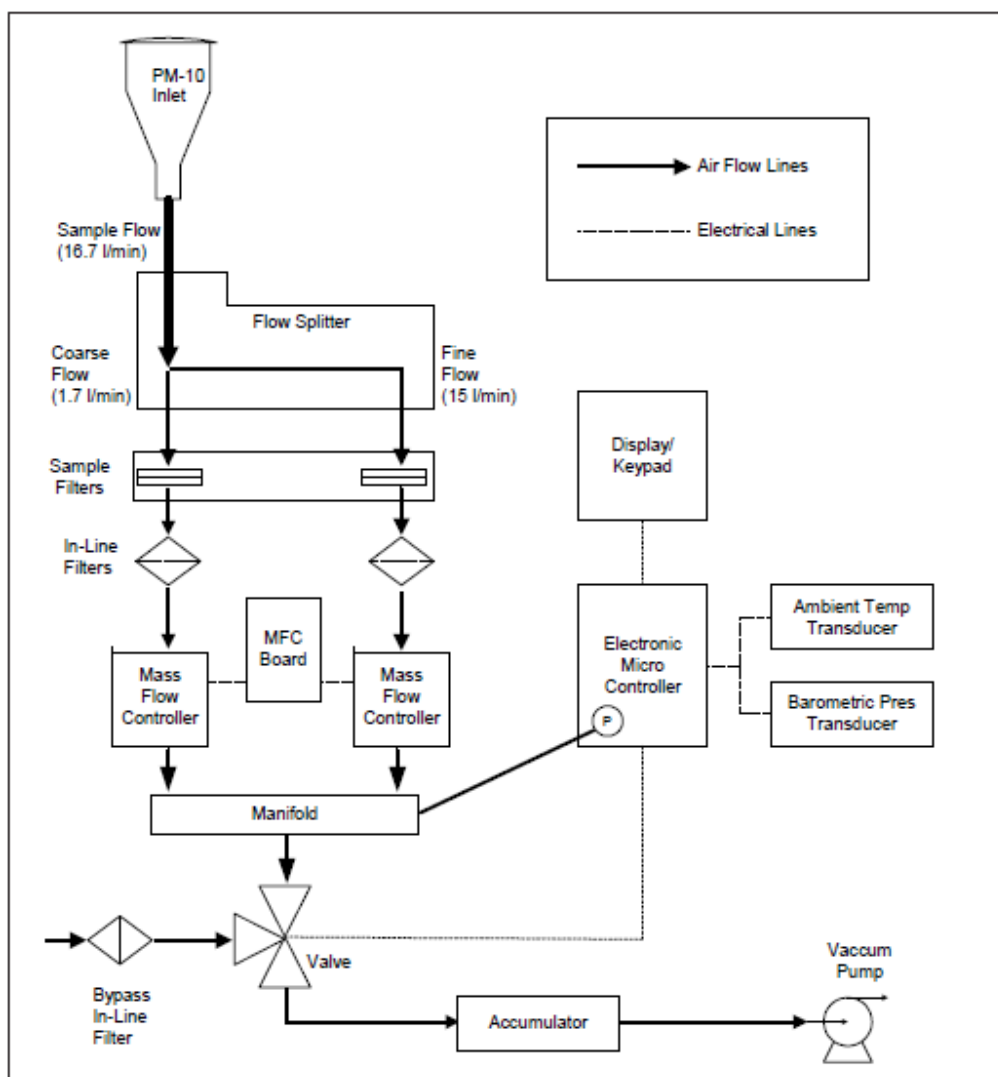


Figure 2.3. Schematic diagram of dichotomous sampler

The daily particulate matter samples were collected on 47 mm (diameter) Whatman PTFE (polytetrafluoroethylene) filters. Filter holders were designed in order to avoid filter contamination and safe carriage (Figure 2.4). These holders were introduced to the instrument as seen in Figure 2.5.

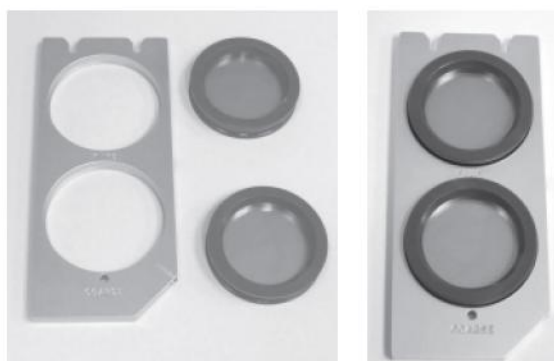


Figure 2.4. Filter holders



Figure 2.5. The placement of filters with filter holders to the instrument.

2.1.2.2. $PM_{2.5}$ and PM_{10} samplers

Atmospheric particulate matter samplers, the brand mark of Tecora Echo PM (Italy), consist of a sampling PM_{10} head, an impactor for only $PM_{2.5}$, sample filter holders, temperature and pressure sensors, a pump and a control panel in the body part. The only difference of the instrument from dichotomous sampler is that it does not separate the introduced air flow. Each fraction size of particles will be collected individually with an air flow rate of 16.7 l/min. The instrument on the right side in Figure 2.6 is that has an impactor below the sampling head is used for $PM_{2.5}$ samples. The main role of the impactor is to prevent filter samples from large size particles ($> 2.5 \mu m$). The instrument on left side is used for PM_{10} samples. The samples will be collected daily as in dichotomous sampler.

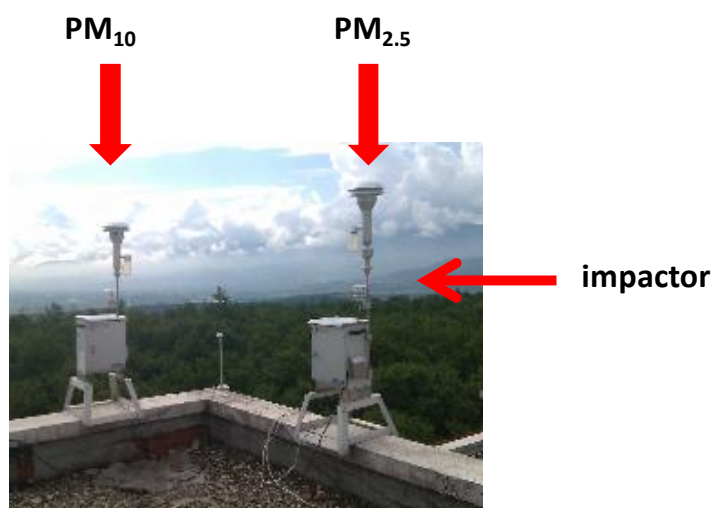


Figure 2.6. Atmospheric particulate matter samplers for $PM_{2.5}$ and PM_{10}

In this instrument particulate matters were collected on 47 mm Micro-glass fiber filters (brand mark Munktell). In this filter, total carbon, elemental carbon and organic carbon were determined

2.1.2.3. Ozone analyzer

Thermo 49i ozone analyzer is composed of filter, a scrubber, two solenoid valves, a UV absorption cell, a UV source lamp, a flow meter, a pump, a detector and a monitor. Air sucked by pump reach to the instrument by two ways at the same time. When some of them directly reach to the UV absorption cell (sample solenoid), the others reach to the other UV absorption cell (reference solenoid) to form reference gas after going through the scrubber (Figure 2.7). The solenoid valves alternate the sample and reference gases between the two UV cells every 10 seconds. This exchange is very fast then the change of the intensity of each cell can be ignored.

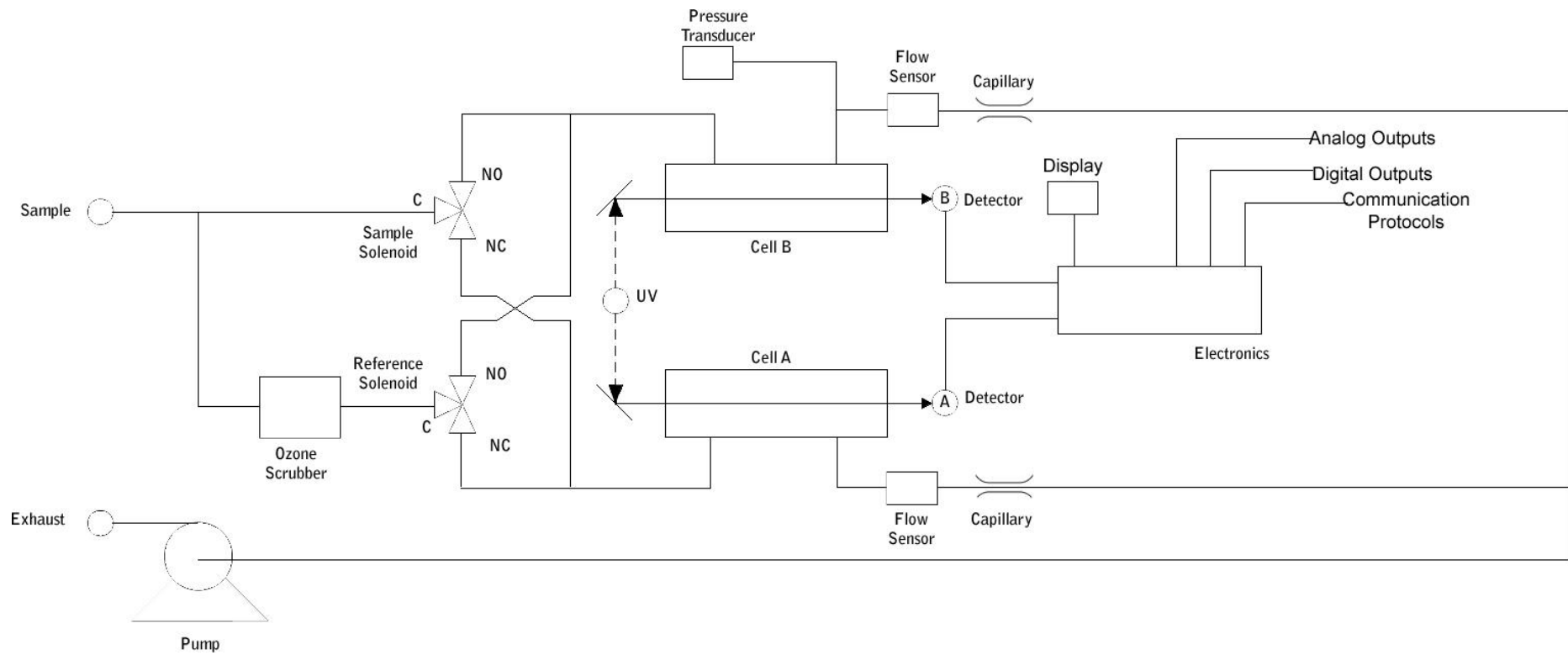


Figure 2.7. Schematic diagram of O₃ analyzer operation

The specifications and the operation conditions of the instrument are tabulated in Table 2.1. The instrument operates on the principle that O₃ molecules absorb UV radiation at a wavelength of 254 nm. The degree to which the UV light is absorbed is directly related to the O₃ concentration as in the Beer-Lambert Law in Equation 2.1:

$$\frac{I}{I_0} = e^{-KLC} \quad Eq (2.1)$$

I = UV light intensity of sample with ozone (sample gas)

I_0 = UV light intensity of sample without ozone (reference gas)

K = molecular absorption coefficient, 308 cm⁻¹ (at 0°C and 1 atm)

L = length of cell (38 cm)

C = ozone concentration (ppm)

Table 2.1. Thermo 49i Ozone analyzer specifications.

Parameters	Values
Present ranges	0-0.5, 0.1, 0.2, 0.5, 1, 2, 5, 10, 20, 50, 100, 200 ppm 0-0.1, 0.2, 0.5, 1, 2, 5, 10, 20, 50, 100, 200, 400 mg/m ³
Custom ranges	0-0.5 to 200 ppm 0.01 to 400 mg/m ³
Zero noise	0.25 ppb RMS (60 seconds averaging time)
Lower detectable limit	1.0 ppb
Zero drift	< 1 ppb / 24 hour < 2 ppb / 7 day
Span drift	Less than 1 % per month (including drift of transducers)
Response time	20 seconds (10 seconds lag time)
Linearity	± 1 % of full scale
Sample flow rate	1-3 LPM
Operating temperature	20-30°C

2.1.2.4. Meteorology station

WeatherLink meteorology station (Figure 2.8) is composed of integrated sensors (including wind rose and rain cup) and the console placed interior medium. Though 30 parameters are measured by means of this instrument, frequently used ones in atmospheric studies are listed in Table 2.2.



Figure 2.8. WeatherLink Meteorology Station

Table 2.2. Parameters measured in WeatherLink meteorology station.

Parameters	
1.	Barometric pressure
2.	Evapotranspiration
3.	Humidity -high and low
4.	Dew point
5.	Rain
6.	Rain rate
7.	Outside temperature-high and low
8.	Inside temperature-high and low
9.	Solar index
10.	Solar radiation-high
11.	Solar energy
12.	Heat index
13.	Wind speed-high
14.	Wind direction-high
15.	UV Radiation index
16.	UV Dose

2.1.3. Preparation of filter samples

2.1.3.1. Pretreatment

Filters were conditioned before sampling in the clean room at 25 °C and 25-30 % relative humidity. In sampling day, filters were weighed and placed in filter holders. With the help of special briefcase it was transported to the sampling point. The same procedure was applied to the blank filters and they were transported with sample filters to the sampling point. During the sampling, blank samples were retained in the sampling point and air was drawn on them for only one minute then, they were brought to the laboratory. All filters used in this study for both sampling and analyzing were listed in Table 2.3.

Table 2.3. Filters used in the study.

Brand name	Filter type	Grade	Diameter (mm)	Pore size (um)	Material	Usage
Whatman	Teflon filter	-	46.2	2	Polytetrafluoroethylene (PTFE)	sampling in dichotomous
Whatman	Quartz fiber filter	QM-A	47	-	High-purity quartz (SiO ₂)	analyzing for OC/EC
Whatman	Membrane filter	OE66	47	0.2	Cellulose acetate	filtering
Munktell	Micro-glass fiber filter	MGG	47	-	High-purity borosilicate	sampling in PM analyzers

2.1.3.2. Storage

The sampled filters and the blank samples were kept in petri dishes and labeled with sample ID and date. All samples were kept in the clean room at constant temperature and pressure.

2.1.3.3. Post treatment for analysis

Filters were kept one day at 25°C and 25-30 % relative humidity prior to analysis. Then they were weighed again to check the loss of particulate mass. Sampled Whatman PTFE filters (both fine and coarse fractions) were divided into two equal parts for the determination of metals and ions, separately in the laminar flow cabinet where the air was filtered twice with HEPA filter in the clean room. Small punches as 1.5 cm² for OC/EC analyzer and 0.30 cm² for elemental analyzer were taken from Micro-glass fiber filter in the same conditions for total carbon (TC), organic carbon (OC) and elemental carbon (EC) determinations.

2.2. Laboratory studies

2.2.1. Analytical methodology for PM samples

The general methodology of metal and ion determinations in aerosol samples is summarized in Figure 2.9. The determination of TC, OC and EC was illustrated in Figure 3.10. All these procedures were applied for both fine and coarse fractions.

The determination of metals and ions in filter samples were converted to solution phase by acid digestion and extraction, respectively. Then ions were detected by ion chromatography and the metals were detected by atomic absorption spectroscopy (AAS) and inductively coupled plasma mass spectrometry (ICP-MS) techniques. Sodium, K^+ , NH_4^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- and SO_4^{2-} were the determined ions in water extracted part. At the beginning of the study initially, the summer and winter samples were analyzed by AAS, AES and GFAAS techniques and Ca, Mg, K, Al, Fe, Cd, Cu, Cr, Co, Pb, V, Mn and Ni were determined. However, due to technical problems the rest of the samples were analyzed by ICP-MS. Additionally, As, Bi, Cs, Eu, Hf, Hg, La, Lu, Mo, Nd, P, Sb, Sc, Sm, Sn, Th, Ti, U, W, Y, Yb and Zn were determined by ICP-MS technique. In order to check the accuracy of the techniques (AAS and ICP-MS), the obtained results in the same samples in winter and summer time were compared. The results were discussed in Chapter 3.

Micro-glass fiber filter samples were introduced to the instruments without any pretreatment in the determination of TC, OC and EC. Again at the beginning of the study, summer and winter samples were analyzed in Eurovector CNHS analyzer. However, differentiation of carbon composition as OC and EC was very difficult in this instrument due to the lack of temperature ramp program. Only percent composition of carbon, nitrogen, hydrogen and sulfur in a given sample can be detected in the analyzer. We tried to determine EC by subtraction of OC from TC. The organic fraction (OC) was expelled in the oven at 350°C for 1 hour. Then this sample was analyzed in Eurovector CNHS analyzer. This application had some drawbacks then whole samples were analyzed by a specific instrument (Sunset OC/EC analyzer). Moreover, determination of carbonate carbon (CC) was also validated with this instrument.

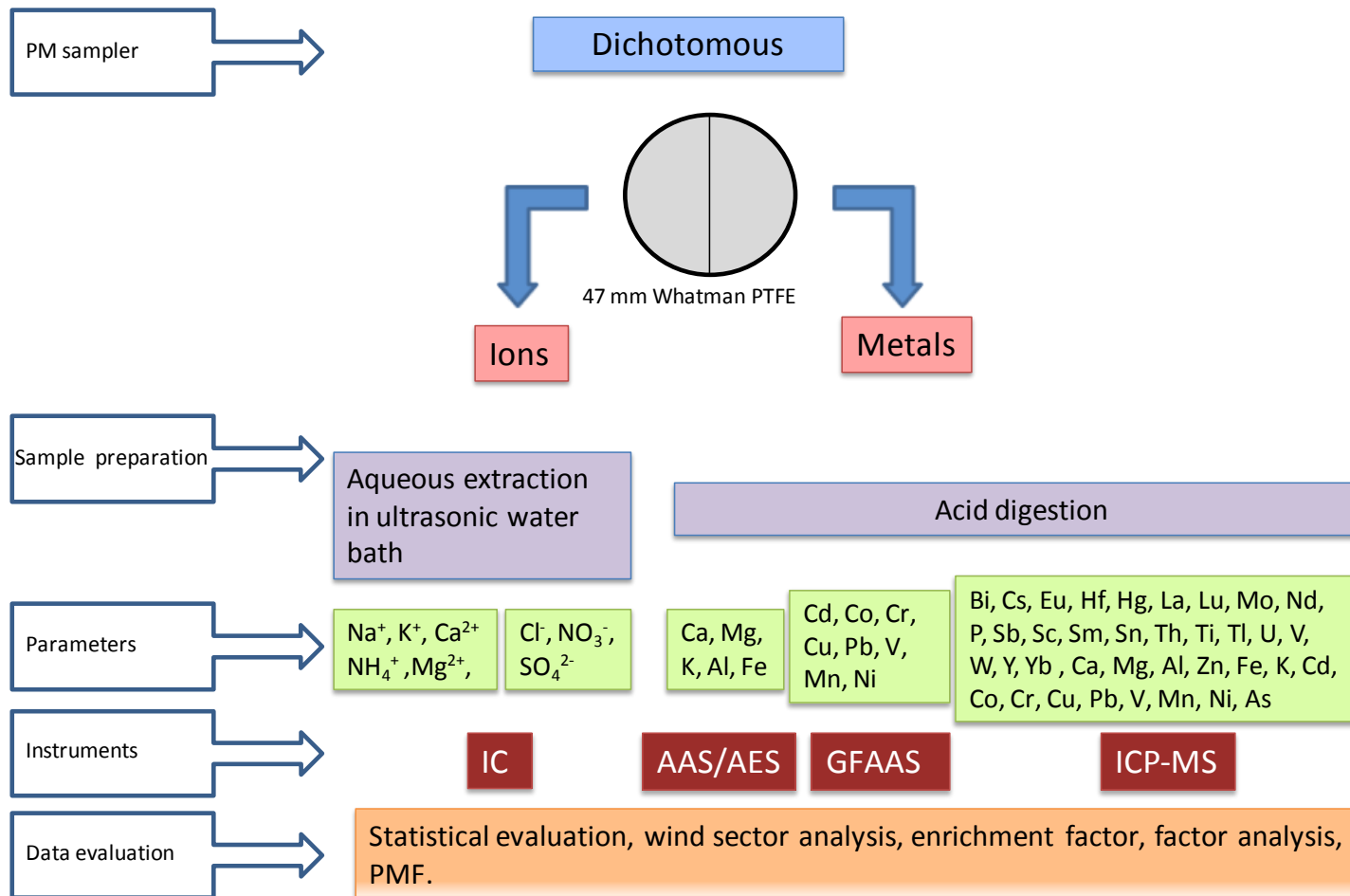


Figure 2.9. Methodology for ion and metal parameters in aerosol samples collected by dichotomous sampler

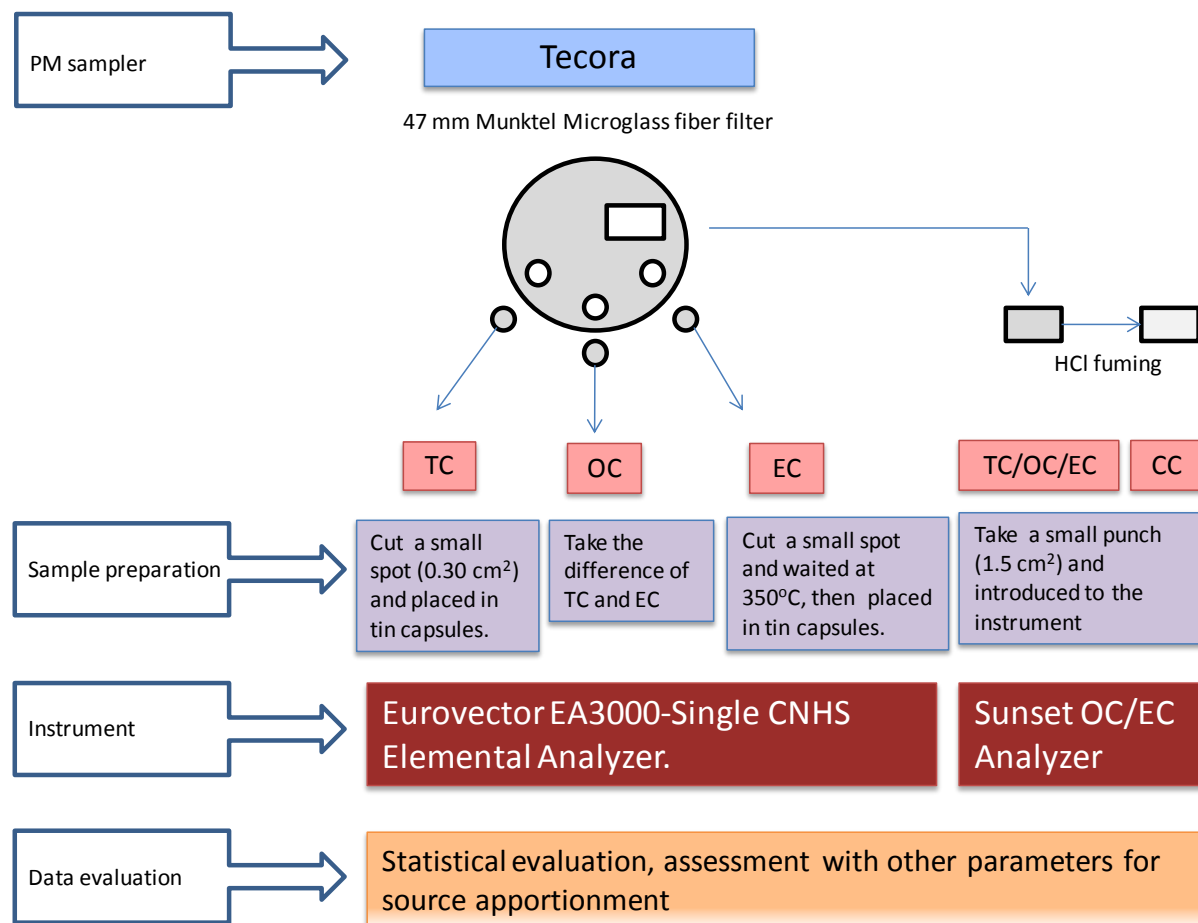


Figure 2.10. Methodology for TC/OC/EC in aerosol samples

2.2.1.1. Determination of metals

2.2.1.1.1. Reagents and chemicals

Suprapur HNO₃ (65%) (Merck):

Suprapur HF (40%) (Merck):

Ultrapur H₂O₂ (31%) (Merck): Suprapur and ultrapur grades are suitable for sensitive instrumental methods. Trace metals in low ppb range, frequently less than detection limits are found in these acids. These acids were used in the procedure of acid digestion for the analysis of metal content in particulate matters.

SRM 1648a-UPM (Urban Particulate Matter - NIST): is an atmospheric particulate matter collected in an urban area. A unit of SRM consists of one bottle containing 2 g of atmospheric particulate matter.

SRM 1633b-CFA (Constituent Elements in Coal Fly Ash - NIST): is intended for use in the evaluation of analytical methods for the determination of constituent elements in coal fly ash or materials with a similar matrix. A unit of SRM consists of 75 g of powdered material.

SRM 2783-APFM (Air Particulate on Filter Media - NIST): is an air particulate sample reduced in particle size to simulate PM_{2.5} air particulate matter and deposited on a polycarbonate filter media. A unit of SRM includes two loaded filters and two blank filters.

These standard reference materials were used for the validation of metal contents in particulate matter and analyzed in Flame AAS, Flame AES and GF-AAS. The validation calculations in ICP-MS were achieved by using only SRM 1648a-UPM. Moreover, SRM 1648a-UPM was also used for the validation of total carbon in Sunset OC/EC Analyzer.

ICP multi-element standard solution IV (Merck): contains 23 elements (Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Tl, Zn Certipur®) in diluted nitric acid solution (1000 mg/l). It is used as calibration standard for the analysis in Flame AAS, Flame AES and GF-AAS.

2.2.1.1.2. Gravimetric analysis

Filter samples were weighed before and after the sampling with a microbalance (AND GH-202) 0.001 mg sensitivity. The difference between two weighs gave the mass of particulate matter. In order to obtain the correct weight measurements storage conditions must be constant.

2.2.1.1.3. Sample preparation for elemental analysis

The filter samples of PM_{2.5} and PM_{2.5-10} in 47 mm Whatman PTFE were collected by dichotomous sampler and they were divided into two equal parts with a clean stainless steel bistoury. Half of the filter is used for metal determination. All glassware (volumetric flasks, forceps and beakers) was waited in 30% HNO₃ for 24 h before the analysis. Filter samples were taken into solution by an acid digestion in microwave oven. Microwave assistant digestion system have many advantages such

as reduction in time for sample dissolution, usage of less chemicals and lower losses of volatile metals (Swami et al., 2001).

At the beginning of the analysis, filters were digested in CEM-MARS 5XP-1500 microwave oven with 5 mL 65 % Suprapur HNO₃, 0.5 mL 40 % Suprapur HF and 4 mL Suprapur H₂O₂. All acids were purchased from Merck® (Germany).

The microwave oven program is composed of two steps. In the first step, temperature was increased from room temperature to 220°C in 20 minutes with a maximum power (800 W). In the second step, temperature was held constant at 180°C throughout 30 minutes. In the digestion system 40 samples in PFA® (Perfloro alkoksi) vessels can be digested simultaneously. Moreover, in each digestion set, there was always a reagent blank (the acids used for digestion). After digestion, digestion tubes were taken out from the oven and ventilated about 30 minutes.

After digestion, filter samples were transferred into 25 mL volumetric flasks and diluted to this volume with deionized water (DI) (18.1 MΩ, Ultrapure water). In order to not loose any sample adhered to the walls of vessels, volumetric flasks were rinsed with DI water many times and the washings were transferred to the volumetric flasks.

After aerosol samples were taken into solution phase, they were analyzed in Varian® SpectrAA 240 Atomic Absorption Spectroscopy and Perkin Elmer ICP-MS DRC-e in Environmental Engineering Department of Fatih University. The AAS instrument was used for the analysis of filter samples collected for two fractions in summer (92 days) and in winter (90 days) months. After that 762 fine fraction and 381 coarse fraction samples were analyzed by ICP-MS.

Quality control and quality assurance (QC/QA) of the method have been checked by reference substances of SRM 1648a-Urban Particulate Matter (NIST), SRM 2783-Air Particulate on Filter Media (NIST) and SRM 1633b-Constituent Elements in Coal Fly Ash (NIST).

2.2.1.1.4. Atomic Absorption and Emission Spectrometers (Flame AAS, Flame AES, GFAAS)

Atomic spectroscopy technique is based on the measurement of absorption/emission of light by atoms in gas phase. In this method sample can be liquid or solid and the atoms or ions of the analyte are vaporized by flame or furnace. Vaporized atoms absorb the UV and VIS radiation or emit the light then go into transition between higher energy states. The emission or absorption of energy then are measured after these transitions. Different configurations of atomic spectroscopy were used in the analysis of aerosols in terms of metals. Potassium was determined by Flame Atomic Emission Spectroscopy (AES) (Figure 2.11). Calcium, Mg, Al and Fe were determined by Flame Atomic Absorption Spectroscopy (AAS) (Figure 2.12) and finally, Cd, Co, Cr, Cu, Pb, V, As, Mn and Ni were determined by means of Graphite Furnace Atomic Absorption Spectroscopy (GF-AAS) (Figure 2.13). All these three systems have four main parts; atomizer, wavelength selector, detector and readout.

In AAS, the radiation source for absorption is hollow cathode lamp and except for Ca and Mg, own lamps are used for each parameter. Hollow cathode lamp consists of a tungsten anode and a cylindrical cathode that concentrate the radiation in a limited region of the desired metal placed in a glass tube that filled with an inert gas (neon or

argon) at a pressure of 1 to 5 torr (Skoog et al., 2007; Eblon et al., 1998). Presence of radiation source is the only difference between AAS and AES. Generally, flame is used as an atomizer where the sample solution is nebulized by a flow of gaseous oxidant and fuel. Air/acetylene or nitrous oxide/acetylene are the most common types of oxidant/fuel pair used in this system (Table 2.4).

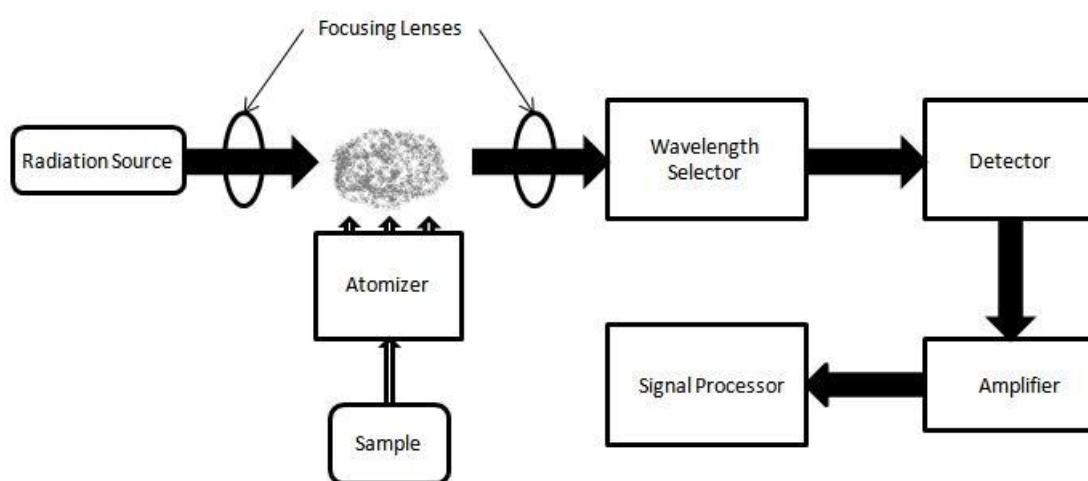


Figure 2.11. Block diagram of Flame AAS

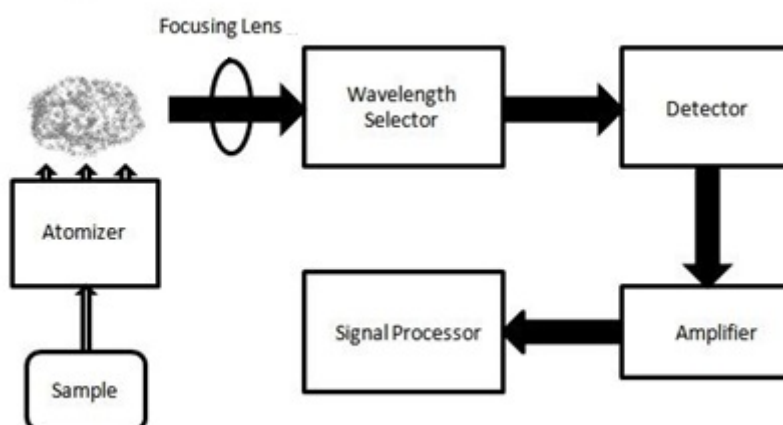


Figure 2.12. Block diagram of Flame AES

Table 2.4. Operation conditions for flame AAS and AES.

Parameters	Flame Type	Lamp current (mA)	Wavelength, λ (nm)	Slit width (nm)
K	O ₂ /C ₂ H ₂	*	766.5	0.2
Ca	N ₂ O/C ₂ H ₂	7	422.7	0.5
Mg	O ₂ /C ₂ H ₂	7	285.2	0.5
Al	N ₂ O/C ₂ H ₂	10	309.3	0.5
Fe	O ₂ /C ₂ H ₂	10	248.3	0.2

* The method is based on the emission technique.

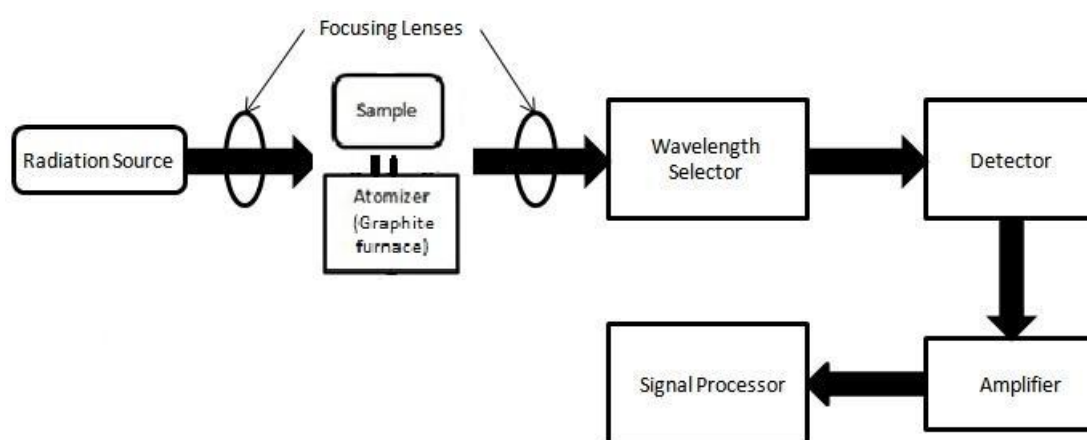


Figure 2.13. Block diagram of GFAAS

Instead of flame atomization, electrothermal atomization is used in GFAAS. Sample is directly injected to the cylindrical pyrolytic graphite tube by micropipette. After the injection, sample is dried, ashed, atomized, consequently. The operation conditions for GFAAS were given in Table 2.5.

Table 2.5. Operation conditions for GFAAS.

Parameter	Lamp current (mA)	Wavelength, λ (nm)	Slit width (nm)	Injection volume (μ L)
Cd	6	228.8	0.5	12
Co	12	240.7	0.2	12
Cr	10	357.9	0.2	12
Cu	10	324.8	0.5	12
Pb	10	217.0	1.0	12
V	20	318.5	0.2	16
Mn	10	279.5	0.2	12
Ni	12	232.0	0.2	12

In GFAAS, the concentrations are determined in four steps that are drying, ashing, atomizing and cleaning. Oven temperature program for each parameter is given in Table 2.6. Argon gas was used as mobile gas and D₂ lamp is used to correct the background signal. Except atomizing, argon gas is passed through the pyrolyzed graphite tube in other three steps with the flow rate of 300 mL/min.

Table 2.6. The oven temperature program for GF-AAS.

		Dry 1	Dry 2	Dry 3	Ashing	Atomizing	Cleaning
Time Oven temperature (°C) (sn)	Cd	85	95	120	250	1800	1800
	Co	85	95	120	750	2300	2300
	Cr	85	95	120	100	2600	2600
	Cu	85	95	120	800	2300	2300
	Pb	85	95	120	400	1200	1200
	V	85	95	120	1000	2700	2700
	Mn	85	95	120	700	2400	2400
	Ni	85	95	120	800	2400	2400
		5	40	10	8	2.8	2

Calibration curves of the metals (Ca, Mg, K, Fe, Cd, Cu, Co, Mn, Ni, V, Pb, and Cr) were given in Figure 2.14. All dilution processes and the preparation of calibration standards (from 1000 mg L⁻¹ standard metal mixture) were performed with 2 % Suprapur HNO₃ solution.

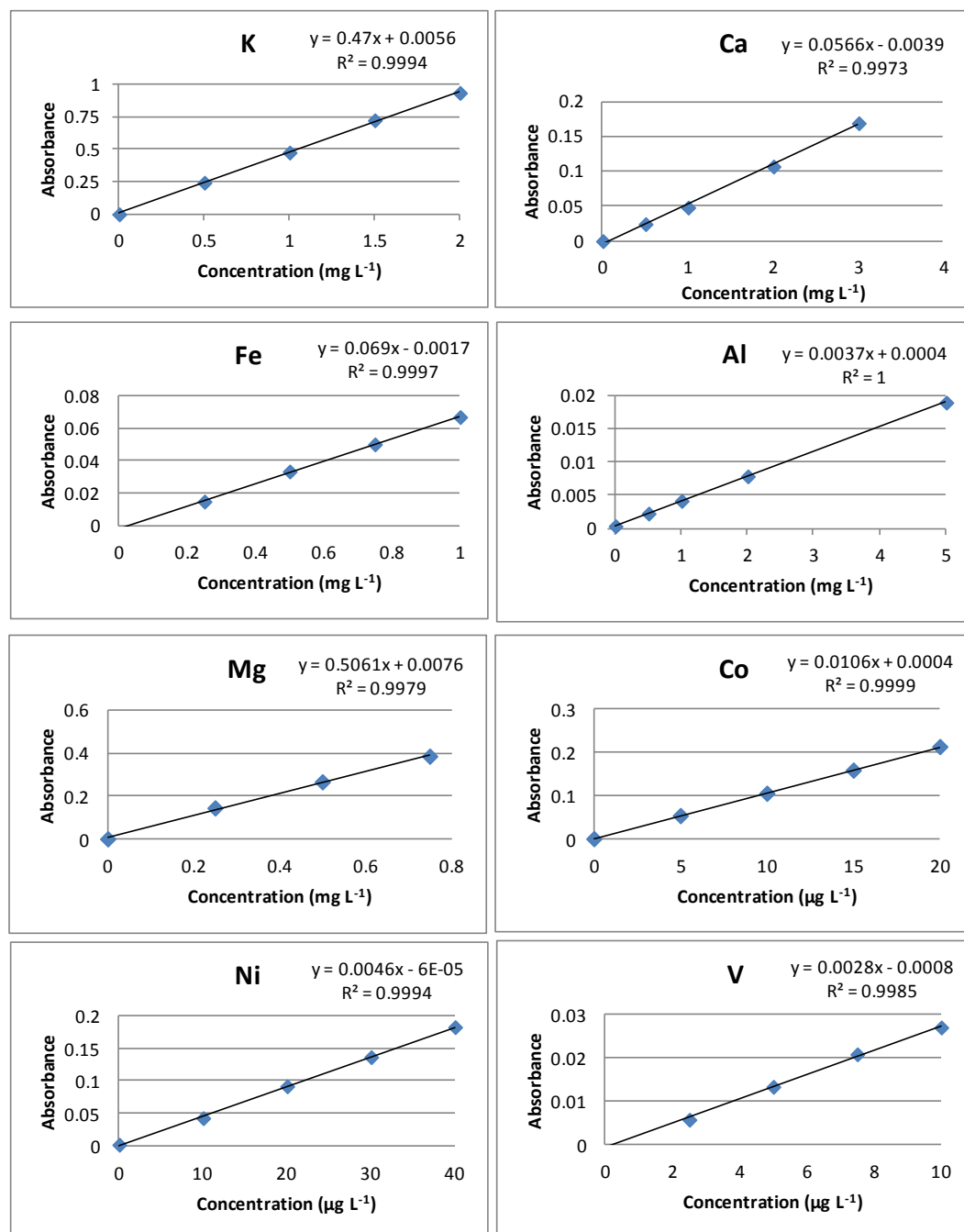


Figure 2.14. The calibration curves of metals in atomic spectrometry

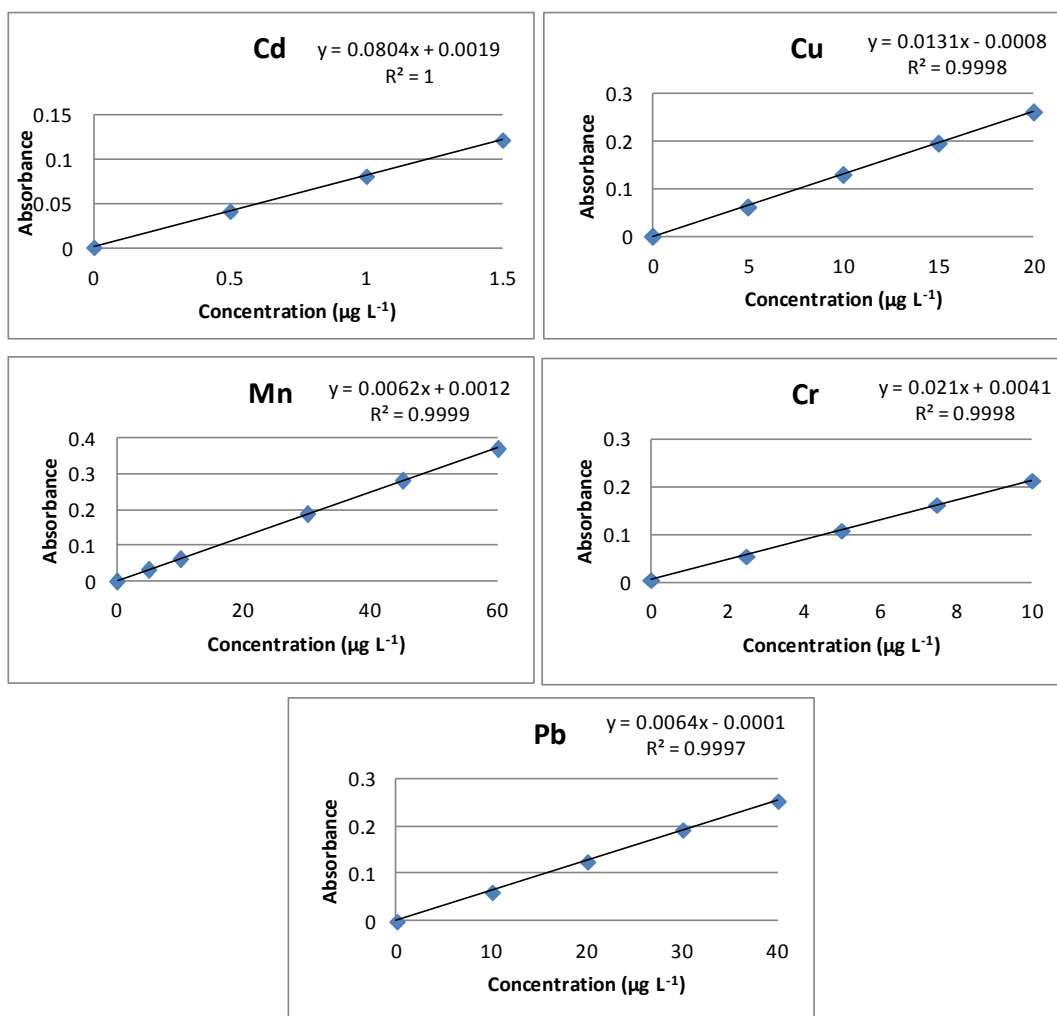


Figure 2.14. The calibration curves of metals in atomic spectrometry (cont.)

2.2.1.1.5. Inductively Coupled Plasma- Mass Spectrometry

Inductively coupled plasma is energized by inductively heating the gas with an electrical coil and contains sufficient concentration of ions and electrons to make the gas electrically conductive. An ICP-MS can be thought of as four main processes, including sample introduction and aerosol generation, ionization by an argon plasma source, mass discrimination, and the detection system.

In this technique, sample –generally in liquid form- is introduced by way of a nebulizer which aspirates the sample with high velocity argon, forming a fine mist. The aerosol then passes into a spray chamber where larger droplets are removed via a drain. Typically, only 2% of the original mist passes through the spray chamber. This process is necessary to produce droplets small enough to be vaporized in the plasma torch. Once the sample passes through the nebulizer and is partially desolvated, the aerosol moves into the torch body and is mixed with more argon gas. A coupling coil is used to transmit radio frequency to the heated argon gas, producing an argon plasma "flame" located at the torch. The hot plasma removes any remaining solvent and causes sample atomization followed by ionization. In addition to being ionized, sample atoms are excited in the hot plasma, a phenomenon which is used in ICP-atomic emission spectroscopy. The aerosol moves into the bottom of the torch body. Because atomization/ionization occurs at atmospheric pressure, the interface between the ICP and MS components become crucial in creating a vacuum environment for the MS system. Ions are removed from the plasma by a pumped extraction system in the first stage of the mass spectrometer. An ion beam is produced and focused further

into the actual unit. Ions are separated, based on their mass to charge ratio and measured by detector. The components of the instrument are shown in Figure 2.15.

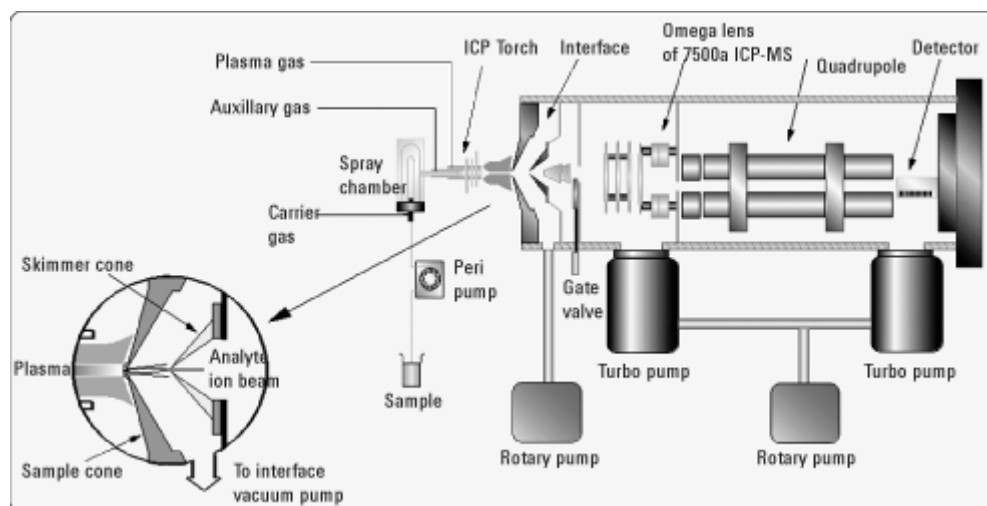


Figure 2.15. The components of ICP-MS system

Proper selection for analysis requires a basic understanding of each technique since each one has its individual strengths and limitations. The advantages and the disadvantages of ICP-MS technique are listed as below.

Advantages of ICP-MS technique;

- Fast quantitative and semi-quantitative trace element analysis
- Multi-element capability
- Solid and liquid samples can be analyzed

- Only small sample quantities required (typically ~3-5 mL for solution ICP-MS)
- Extensive analytical range (ppt to ppm)
- High sensitivity
- Good precision and accuracy
- Isotope measurements are possible
- Large linear dynamic working range
- Detection limits are 10-100 times superior to those of ICP-AES

Disadvantages of ICP-MS technique;

- The lower-cost ICP-MS systems utilize single-quadrupole mass analyzer systems, which are inherently sequential systems, and have relatively low mass resolution.
- The higher cost than ICP-AES, with a much lower body of knowledge and understanding available than the other technique.
- Elements such as Ca and Fe are difficult to determine by conventional Ar ICP-MS because of mass spectral interferences by argides.
- If Ni cones are used, can have as much as 5 ppt of nickel being detected as orifice ions. This can be alleviated by switching to more expensive Pt cones.
- Generally requires a clean room environment for ultra-low detection limits.

Although ICP-MS is a the most sensitive technique and has lower detection limits in ng L⁻¹, determination of As and Se is very problematic because both elements have high ionization potentials (Swami et al., 2001). Selenium has three most abundant isotopes (⁸⁰Se, ⁷⁸Se, ⁷⁶Se). Because of the isobaric interferences from Ar, analysis of Se becomes difficult. On the other hand, As is monoisotopic, ⁷⁵As, but there is a spectral interference from ⁴⁰Ar³⁵Cl, then, the analysis of samples containing low concentration of As and high concentration of Cl again becomes difficult (Swami et al., 2001).

The whole filter samples were analyzed with Perkin Elmer Elan DRC-e model ICP-MS (Inductively Coupled Plasma Mass Spectrometry) in Environment Hydrogeochemistry and Hydrogeology Laboratory in Geological Engineering Department at Kocaeli University. The operating conditions of the ICP-MS instrument are given in Table 2.7.

Table 2.7. Operating parameters of ICP-MS.

Parameter	Value
RF power (W)	1100
Plasma gas flow (L min ⁻¹)	15
Auxiliary gas flow (L min ⁻¹)	1.2
Nebulizer	Gemtip crossflow
Nebulizer gas flow (L min ⁻¹)	0.96
Sampling cone (orifice dia., mm)	Platinum (1.1)
Skimmer cone (orifice dia., mm)	Platinum (0.9)
Injector	Alumina
Peristaltic pump flow (rpm)	20
Spray chamber	Ryton Scott
Scanning mode	Both (analog and pulse)
Number of Scans (sweeps/reading) for each isotope	20
Ion lens setting	Adjusted to obtain maximum signal/noise ratio (CeO/Ce < %3, Ba ⁺⁺ /Ba < % 3), Background 220: 1.2, Background 8.5: 2.1
Auto sampler	CETAC ADX-500
Rinse time (s)	45
Sample Uptake time (flush) (s)	35

2.2.1.1.6. Method validation for metal determination

The trueness parameters in method validations in atomic spectrometry were realized by using the standard reference materials (SRM) 1648a-UPM (Urban Particulate Matter) (NIST), 1663b-CFA (Coal Fly Ash (NIST) and 2783-APFM (Air Particulate on Filter Media) (NIST). The same digestion and the analysis procedure were applied to certified reference materials like samples. The calculated values, the certified values and the percent error for each element in the certified reference materials analyzed in Flame AAS, Flame AES and GFAAS techniques are given in Table 2.8. The maximum percent error belonged to Mn and its values in UPM and CFA were

21.5 and 19.6, respectively. Iron had the high percent error value (18.5) in UPM. All other elements had the percent error values less than 10 %. The percent error values in APFM were all below 1.1 %.

Tablo 2.8. The trueness results for selected elements in SRM 1648a (UPM), SRM 1663b (CFA) and SRM 2783 (APFM).

SRM		Measured value $\pm$	Certified value	% error
(N)		Std	$\pm U (k=2)$	
UPM (2)	K (%)	1.039 ± 1	1.056 ± 0.049	-1.6
	Ca (%)	5.77 ± 0.020	5.84 ± 0.19	-1.2
	Mg (%)	0.800 ± 0.010	0.813 ± 0.012	-1.6
	Fe (%)	3.20 ± 0.14	3.92 ± 0.21	-18.4
	Al (%)	3.48 ± 0.13	3.43 ± 0.13	1.4
	Cd (mg kg ⁻¹)	72.1 ± 0.1	73.7 ± 2.3	-2.2
	Cu (mg kg ⁻¹)	609 ± 0.02	610 ± 70	-0.2
	Pb (%)	0.653 ± 0.006	0.655 ± 0.033	-0.3
	Mn (mg kg ⁻¹)	620 ± 54	790 ± 44	-21.5
	V (mg kg ⁻¹)	121.7 ± 5.5	127 ± 11	-4.2
CFA (2)	K (%)	1.942 ± 0.009	1.95 ± 0.03	-0.4
	Ca (%)	1.46 ± 0.02	1.51 ± 0.06	-3.3
	Mg (%)	0.4822 ± 0.0002	0.482 ± 0.008	-0.04
	Fe (%)	8.40 ± 1.12	7.78 ± 0.23	8.0
	Cd (mg kg ⁻¹)	0.778 ± 0.002	0.784 ± 0.006	0.8
	Cu (mg kg ⁻¹)	112.82 ± 0.01	112.8 ± 2.6	0.02
	Pb (mg kg ⁻¹)	68.0 ± 0.2	68.2 ± 1.1	0.3
	Mn (mg kg ⁻¹)	106.0 ± 2.6	131.8 ± 1.7	-19.6
	V (mg kg ⁻¹)	323.7 ± 5.4	295.7 ± 3.6	9.5
APFM (1)	K [*]	12975	13200 ± 1700	1.1
	Ca [*]	402	404 ± 42	0.5
	Mg [*]	5225	5280 ± 520	1.0
	Cu [*]	8575	8620 ± 520	0.5
	Pb [*]	1875	1860 ± 100	0.8

Std: standard deviation

U:expanded uncertainty (k=2, 95 % CL)

N: number of analysis

* mass loading on filter in ng

The trueness results of UPM analysis in ICP-MS was given in Table 2.9. All elements except for Cr (33 %), Na (19 %) and La (18 %) had the percent error value less than 10%.

Table 2.9. Analysis result of SRM 1648a-Urban Particulate Matter (NIST) (number of analysis=10).

	Calculated value (Mean conc. $\pm$ Std) (mg kg ⁻¹)	Certified value (Mean conc $\pm$ U k=2) (mg kg ⁻¹)	% error
Al	3.54 $\pm$ 0.74 (%)	3.43 $\pm$ 0.13	3.1
As	115.1 $\pm$ 4.2	115.5 $\pm$ 3.9	-0.3
Ca	5.56 $\pm$ 0.17 (%)	5.84 $\pm$ 0.19	-4.9
Cd	71.9 $\pm$ 1.9	73.7 $\pm$ 2.3	-2.4
Co	17.62 $\pm$ 0.94	17.93 $\pm$ 0.68	-1.7
Cr	270 $\pm$ 21	402 $\pm$ 13	-33
Cu	570 $\pm$ 18	610 $\pm$ 70	-6.5
Fe	3.90 $\pm$ 0.20 (%)	3.92 $\pm$ 0.21	-0.6
K	1.05 $\pm$ 0.10 (%)	1.06 $\pm$ 0.05	-0.8
Mg	0.82 $\pm$ 0.09 (%)	0.81 $\pm$ 0.01	0.9
Mn	775 $\pm$ 33	790 $\pm$ 44	-1.8
Na	3455 $\pm$ 905	4240 $\pm$ 60	-19
Ni	81.0 $\pm$ 1.5	81.1 $\pm$ 6.8	-0.1
Pb	0.62 $\pm$ 0.006	0.66 $\pm$ 0.033	-5.9
Sb	41.9 $\pm$ 0.7	45.4 $\pm$ 1.4	-7.7
Ti	3678 $\pm$ 235	4021 $\pm$ 86	-8.5
V	125 $\pm$ 2	127 $\pm$ 11	-1.6
Zn	4647 $\pm$ 107	4800 $\pm$ 270	-3.2
Cs	3.3 $\pm$ 0.1	3.4 $\pm$ 0.2	-4.3
La	32 $\pm$ 1	39 $\pm$ 3	-18
Sm	3.8 $\pm$ 0.2	4.3 $\pm$ 0.3	-9.4
W	4.6 $\pm$ 0.3	4.6 $\pm$ 0.3	-0.2
Hf	5.1 $\pm$ 2.0	5.2	-2.2

Std: standard deviation

U:expanded uncertainty (k=2, 95 % CL)

Method validation parameters; repeatability (% RSD), recovery, linearity, limit of detection (LOD) and limit of quantification (LOQ) for the elements determined in Flame AAS and Flame AES were given in Table 2.10 and for the elements determined in GFAAS were given in Table 2.11. Except for K and Ni, ten replications were made for the assessment of validation.

Repeatability describes the variation in data generated with a single sample and applying same procedure by a single analyst or instrument (Chairman et al., 1983). Then, precision or dispersion in generated data can be observed and reported as the percent relative standard deviation. The percent relative standard deviation of the whole elements were below 10 % except for K (14.6 %) and Cd (10.9). The highest LOD value was obtained for Al as 389 $\mu\text{g L}^{-1}$.

Trueness of the data which is the main parameter of the method validation. Although it is crucial, the exact result can not be obtained during the evaluation of it. Only bias can be estimated by analyzing standard or certified reference materials (Chairman et al, 1983). Different applications as spiking SRM on to the sample matrix, standard addition methods are used in order to eliminate the matrix effect on analyte concentration. In this study, the recovery was calculated as the following equation by analyzing SRM 1648a as a sample. Two different amount of SRM (0.05 and 0.1 g) was taken and analyzed. The lowest recovery had been obtained for Mn (78.5) and higher recovery values (>90 %) of the elements were obtained.

$$\% \text{ Recovery} = \frac{|\text{calculated value} - \text{certified value}|}{\text{certified value}} \times 100 \quad (\text{Eq 2.2})$$

Limit of detection (LOD) can be defined as the lowest concentration of an analyte that can be detected with reasonable certainty for a given analytical method (Long and Winefordner, 1983). Traditionally, limit of quantification (LOQ) can be defined as the lowest concentration on the standard curve which associated with a coefficient of variation of less than 20% (Bergstrand and Karlsson, 2009; Armbruster and Pry, 2008). Different calculation values were indicated in literature (Currie, 1968; Huber, 2003; Armbruster and Pry, 2008) but mostly used one is the application of a signal-

to-noise ratio established at 3 and 10 for LOD and LOQ, respectively (Ribes et al., 2007). Long and Winefordner, 1983, defined the region of detection as $3s_b \leq x \leq 10s_b$, where x is the measured signal and s_b is the standard deviation of blank. In this study, LOD and LOQ were calculated by the analysis of 10 replicates of reagent blank samples as in the Long and Winefordner study.

Tablo 2.10. Validation parameters for Flame AAS and Flame AES methods.

	% RSD (N)	Recovery (%) ^a	Linear-range (mg L ⁻¹)	R ²	LOD (µg m ⁻³)	LOQ (µg m ⁻³)
K	14.6 (8)	98.4	0.5-25	0.9895	0.008	0.028
Ca	1.8 (10)	98.8	0.5-3	0.9977	0.017	0.055
Mg	1.8 (10)	98.9	0.25-0.75	0.9979	0.003	0.011
Fe	2.2 (10)	81.5	0.25-1	0.9999	0.013	0.042
Al	8.9 (10)	98.8	0.1-5	0.9999	0.454	1.513

^a SRM 1648a (Urban Particulate Matter), N: number of analysis

Tablo 2.11. Validation parameters for GFAAS method.

	% RSD (N)	Recovery (%) ^a	Linearity (mg L ⁻¹)	R ²	LOD (ng m ⁻³)	LOQ (ng m ⁻³)
Cd	10.9 (10)	97.3	0.5-1.5	1.0000	0.014	0.045
Pb	6.3 (10)	99.7	10-40	0.9997	0.041	0.136
Cr	2.4 (10)	98.7	2.5-10	0.9998	2.67	8.89
Mn	8.4 (10)	78.5	5-60	0.9999	0.37	1.22
Ni	3.6 (3)	-	10-40	0.9994	2.90	9.66
Cu	3.3 (10)	99.8	5-20	0.9998	0.022	0.073
Co	3.8 (10)	-	5-20	0.9999	0.312	1.04
As	1.7 (10)	-	10-50	0.9996	1.00	3.35
V	4.2 (10)	95.8	2.5-10	0.9999	0.685	2.28

^a SRM 1648a (Urban Particulate Matter), N: number of analysis

Validation of ICP-MS method was carried out by SRM 1648a-UPM for ICP-MS method. Recovery and repeatability calculations could not be applied to whole elements, because some of the elements (P, Y, Mo, Sn, Nd, Eu, Yb, Bi, Tl, Th and U) are absent in the SRM. The lowest recovery was observed for Cr (67 %), for the other calculated elements recovery was above 80 % (Table 2.12). Except for Al, Na and Hf, RSD % values were below 10 %. Due to the high sensitivity of the instrument, LOD values were all very low for each element when the values compared to absorption techniques. The highest LOD value was observed in Ca determination (13 ng m^{-3}). The reason can be the interferences of Ar plasma which has the atomic weight of 39.9 g mol^{-1} that is near to Ca (40.1 g mol^{-1}).

Table 2.12. Validation of ICP-MS method for selected metals.

	Repeatability	Recovery	Linearity	R ²	LOD	LOQ
	% RSD	(%) ^a	(µg L ⁻¹)		(ng m ⁻³)	(ng m ⁻³)
Al	21	103	0.01-200	0.9999	4.81	16.04
As	4	100	0.01-200	1.0000	0.043	0.144
Ca	3	95	0.01-2000	1.0000	13	43.33
Cd	3	98	0.01-200	1.0000	0.150	0.502
Co	5	98	0.01-200	1.0000	0.050	0.168
Cr	8	67	0.01-200	1.0000	1.93	6.46
Cu	3	93	0.01-200	1.0000	0.928	3.09
Fe	5	99	0.01-2000	1.0000	6.40	21.3
K	10	99	0.01-2000	1.0000	1.07	3.56
Mg	10	101	0.01-2000	1.0000	2.42	8.07
Mn	4	98	0.01-200	0.9999	0.198	0.660
Na	26	81	0.01-2000	1.0000	23.8	79.2
Ni	2	100	0.01-200	1.0000	0.468	1.56
Pb	1	94	0.01-200	1.0000	0.279	0.930
Sb	2	92	0.01-40	1.0000	0.060	0.202
Ti	6	91	0.01-200	1.0000	2.98	9.92
V	1	98	0.01-200	1.0000	0.065	0.217
Zn	2	97	0.01-200	1.0000	2.38	7.94
Cs	3	96	0.01-200	1.0000	0.003	0.010
La	3	82	0.01-40	1.0000	0.044	0.149
Sm	6	91	0.01-40	1.0000	0.005	0.016
W	7	100	0.01-200	1.0000	0.205	0.682
Hf	38	98	0.01-40	1.0000	0.322	1.08
Y	-	-	0.01-40	1.0000	0.064	0.215
Mo	-	-	0.01-200	1.0000	0.096	0.321
Sn	-	-	0.01-40	1.0000	0.050	0.168
Nd	-	-	0.01-40	1.0000	0.008	0.025
Eu	-	-	0.01-40	1.0000	0.002	0.006
Yb	-	-	0.01-40	1.0000	0.004	0.013
Bi	-	-	0.01-200	1.0000	0.026	0.087
Tl	-	-	0.01-200	1.0000	0.004	0.012
Th	-	-	0.01-200	1.0000	0.020	0.068
U	-	-	0.01-200	1.0000	0.004	0.015

^a SRM 1648a (Urban Particulate Matter)

2.2.1.1.7. Comparison of analytical techniques for metal determination

At the beginning of the study 2 months in summer and 2 months in winter period filter samples in both $PM_{2.5}$ and $PM_{2.5-10}$ were analyzed with AAS and AES techniques. All of the fine samples and the half of coarse samples were analyzed with ICP-MS technique. In addition to SRM analysis the quality check of method was performed by comparing these two techniques. Figure 2.16 summarized the ratio of ICP-MS and AAS, AES techniques for both fine and coarse fraction PM samples for common parameters. Except for Ca, the ratio for all other parameters in $PM_{2.5-10}$ were below 1.5 and except for K, Mg, Ca and Cu, the ratio for the other elements in $PM_{2.5}$ were below 1.5. The ratio for Zn in both fractions and Ni in coarse fraction were below 1. Due to the closeness of ratio to 1, the missing values for the summer period samples in coarse fractions were filled with the results of AAS and AES techniques.

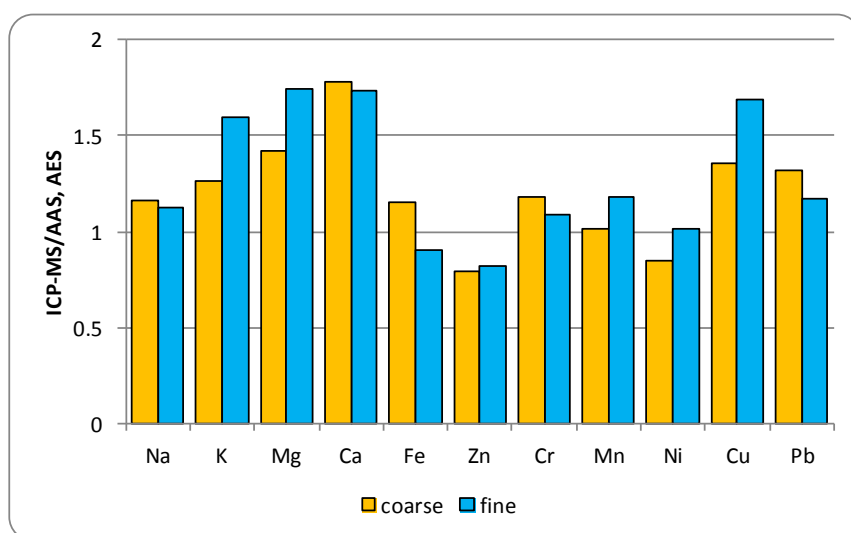


Figure 2.16. Comparison of ICP-MS and AAS, AES techniques for common elements

2.2.1.2. Determination of ions

2.2.1.2.1. Reagents and chemicals

Sodium carbonate (Dionex):

Molecular formula: Na_2CO_3

Molar mass: 105.99 mol^{-1}

Sodium carbonate was used as the mobile phase for anion determination in Dionex ICS 1100 Ion Chromatography. The concentration of stock solution is 0.5 M and it includes 94.7 % (w/v) water and 5.3 % (w/v) Na_2CO_3 .

Methanesulfonic acid (Dionex):

Molecular formula: $\text{CH}_3\text{SO}_3\text{H}$

Molar mass: 96.11 g mol^{-1}

Methanesulfonic acid was used as the mobile phase for cation determination in Dionex ICS 1100 Ion Chromatography. The concentration of stock solution is 1 M.

Standard Cations Mixture (Absolute Standards): has 6 components; LiNO_3 (Li^+), NaCl (Na^+), NH_4Cl (NH_4^+), KCl (K^+), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (Mg^{2+}), $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (Ca^{2+}). The concentrations of each component are $1000 \mu\text{g mL}^{-1}$ and the purity of each one is above 99.00 %.

Standard Anion Mixture (Absolute Standards): has 7 components; NaBr (Br⁻), NaCl (Cl⁻), NaF (F⁻), NaNO₂ (NO₂⁻), NaNO₃ (NO₃⁻), K₃PO₄ (PO₄³⁻), K₂SO₄ (SO₄²⁻). The concentrations of each component are 1000 µg mL⁻¹ and the purity of each one is above 99.00 %.

Individual standards for both anions and cations (High Purity Standards):

NaCl (Cl⁻): The certified value is 100 µg mL⁻¹ ± 0.5 µg mL⁻¹, the purity is 99.999 %.

NaNO₃ (NO₃⁻): The certified value is 100 µg mL⁻¹ ± 0.6 µg mL⁻¹, the purity is 99.999 %.

Na₂SO₄ (SO₄²⁻): The certified value is 100 µg mL⁻¹ ± 0.5 µg mL⁻¹, the purity is 99.999 %.

NaCl (Na⁺): The certified value is 100 µg mL⁻¹ ± 0.5 µg mL⁻¹, the purity is 99.999 %.

KCl (K⁺): The certified value is 100 µg mL⁻¹ ± 1 µg mL⁻¹, the purity is 99.999 %.

NH₄Cl (NH₄⁺): The certified value is 100 µg mL⁻¹ ± 1 µg mL⁻¹, the purity is 99.999 %.

CaCl₂ (Ca²⁺): The certified value is 100 µg mL⁻¹ ± 0.5 µg mL⁻¹, the purity is 99.99+ %.

MaCl₂·6H₂O (Mg²⁺): The certified value is 100 µg mL⁻¹ ± 0.5 µg mL⁻¹, the purity is 99.999 %.

Both mixture and individual standards were used as calibration standards.

BCR 409 Simulated Rainwater (IRMM): consists of artificial rainwater with a relatively high level of electrolytes (Cl^- , Ca^{2+} , H_3O^+ , K^+ , Mg^{2+} , Na^+ , HN_4^+ , NO_3^- , SO_4^{2-}). It is stored in sealed quartz ampoule containing approximately 100 mL of the material. This certified material is used to validate the accuracy of the method that was applied to determine the ion content in particulate matter.

2.2.1.2.2. Sample preparation

Second half of the 47 mm Whatman PTFE filter was used for ion determination. Filter samples were extracted in 12 mL deionized water in ultrasonic water bath during 1 hour. Then, the extracts were filtered with 0.22 μm cellulose acetate filter to remove the residuals prior to analysis. Total volume of the filtrate was approximately 10 mL after the filtration.

2.2.1.2.3. Ion Chromatography

Ion chromatography (IC) is an efficient method to identify ions qualitatively and quantitatively through columns. The main principle is the ion-exchange capacity in the column. Although ion-exchange separations have been applied since ion-exchange resins were developed (mid-1930s), ion change chromatography was first developed in the mid 1970s (Skoog et al., 2007). During that time, detection was performed by conductivity measurements however, they were not met the need due to the high electrolyte concentrations in both sample and mobile phases (eluent). Then low-exchange capacity columns were used to allow high sensitivity of conductivity (Skoog et al., 2007).

Generally, ion analysis in IC has six main stages as indicated in Figure 2.17. Eluent delivery systems are the first stage. Mobile phase or eluent contains a liquid that helps to separate the ions in sample and go through the system without any decomposition. Isocratic mobile phase delivery systems are more common in IC analysis in which the composition and the concentration of mobile phases are constant. An eluent introduced to the system by pumps and reached to the injection valves. A liquid sample is loaded to the system with these valves manually or automatically. Separation is achieved by a guard column and an analytical column. The guard column removes the impurities that might plug the analytical (separator) column. Ions in the sample are separated in the analytical column according to the ion-exchange principle. This means different ions migrate through the column at different rates depending on their interaction with the stationary phase in the column. Then, the eluent and the sample ions leave the column and reached the suppression system. The suppressor reduces the eluent conductivity and enhances the conductivity of the sample ions, thereby increase the detection sensitivity. For the detection, conductivity cell is used. It measures the electrical conductance of sample ions and produces a signal based on chemical and physical properties of the analyte. Finally, these signals are transmitted to the data collection system. Data is quantified by comparing the sample peaks in chromatogram that produced from standard solutions.

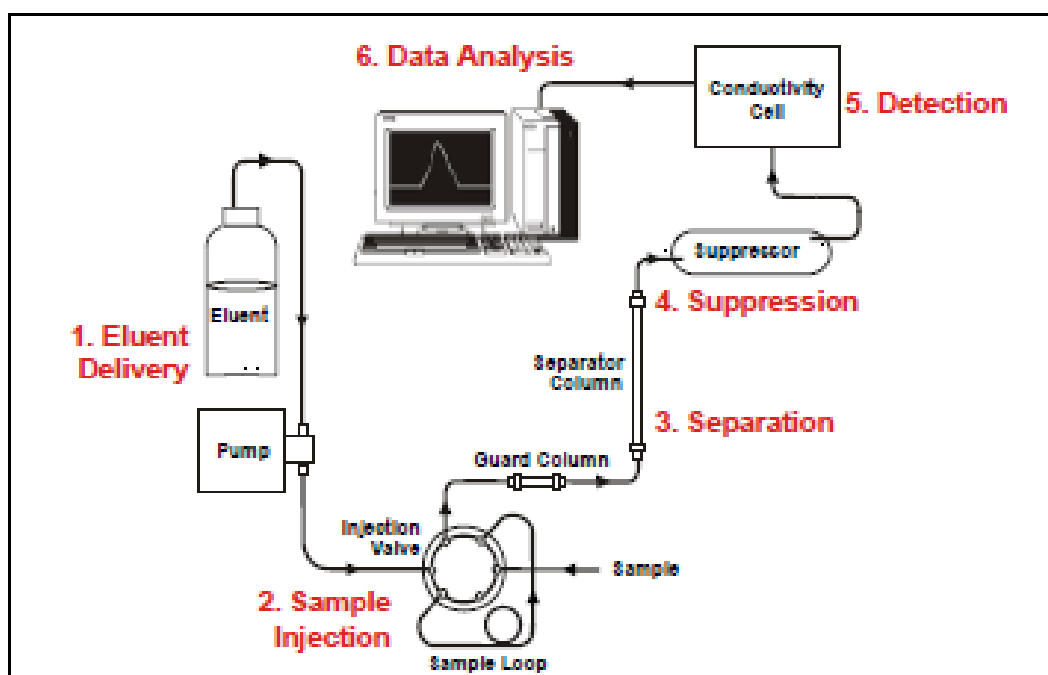


Figure 2.17. Sample ion analysis process

In this study anions (Cl^- , NO_3^- , SO_4^{2-}) and cations (Na^+ , K^+ , NH_4^+ , Mg^{2+} , Ca^{2+}) were determined by Dionex ICS 1100 Series Ion Chromatography. The operation conditions of the instrument are given in Table 2.13. Absolute Standard Anion Mix A (1000 mg/L) and Absolute Standard Cation Mix (1000 mg/L) were used for the calibration of the instrument before the analysis. In addition, the calibration results were checked by using individual standards (High-purity Standards®) of each ion.

Table 2.13. Optimum operation conditions for Dionex ICS 1100 Ion Chromatography.

	Anion	Cation
Mobile phase	9 mM Na ₂ CO ₃	20 mM CH ₃ SO ₃ H
Column	Ionpac AS9-HC (250 x 4 mm)	Ionpac CS12-A (250 x 4 mm)
Guard column	Ionpac AG9-HC (50 x 4 mm)	Ionpac CG12-A (50 x 4 mm)
Supressor	ASRS-4 mm	CSRS-4mm
Supressor current	45 mA	65 mA
Detector	Conductance detector	Conductance detector
Pressure (psi)	2000-3000	2000-3000
Oven temperature	30 °C	30 °C
Background conductance	< 30 µS	0.5-2 µS
Flow rate	1.00 mL/min	1.00 mL/min
Injection volume	500 µL	1000 µL
Rate of data transfer	5.0 Hz	5.0 Hz
Duration	30 min	15 min

The eluents were freshly prepared nearly every day. Both eluents, Na₂CO₃ (sodium carbonate) and CH₃SO₃H (metansulfonic acid) were diluted from stock solutions to obtain the concentrations of 0.5 M and 1 M, respectively. In order to remove the bubbles in the mobile phases, the solutions were agitated in ultrasonic water bath approximtely 1 hour. An automatic sampler was used for the anion analysis whereas, the samples were introduced to the instrument manually for cations due to the lack of enough sample volume.

The calibration graphs for each ion are given in Figure 2.18. The sample chromatograms for both anions and cations prepared from Absolute Standard Anion Mix A (7 components) and Absolute Standard Cation Mix (6 components) solutions were given in Figure 3.19 and in Figure 2.20.

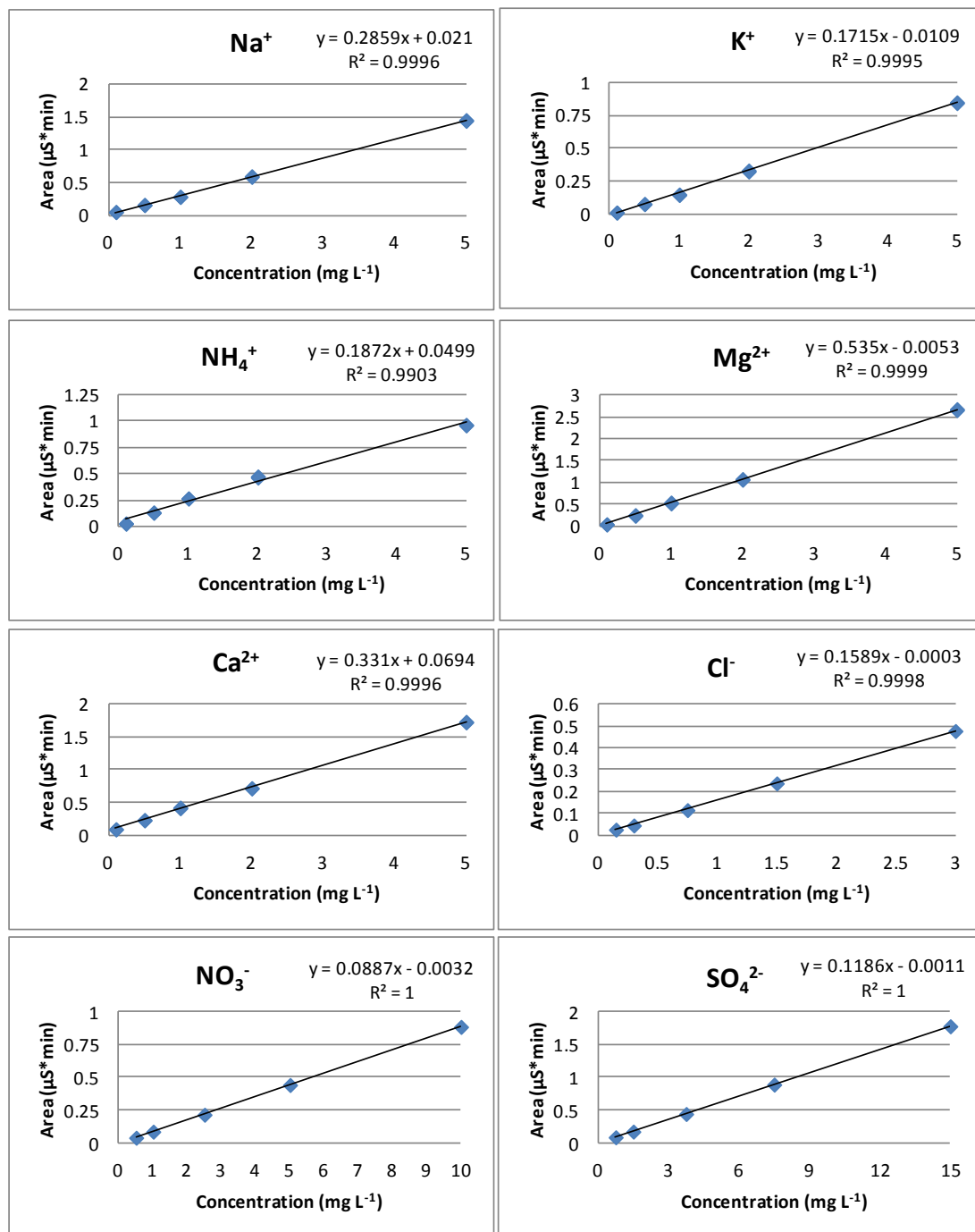


Figure 2.18. Calibration curves for each ion

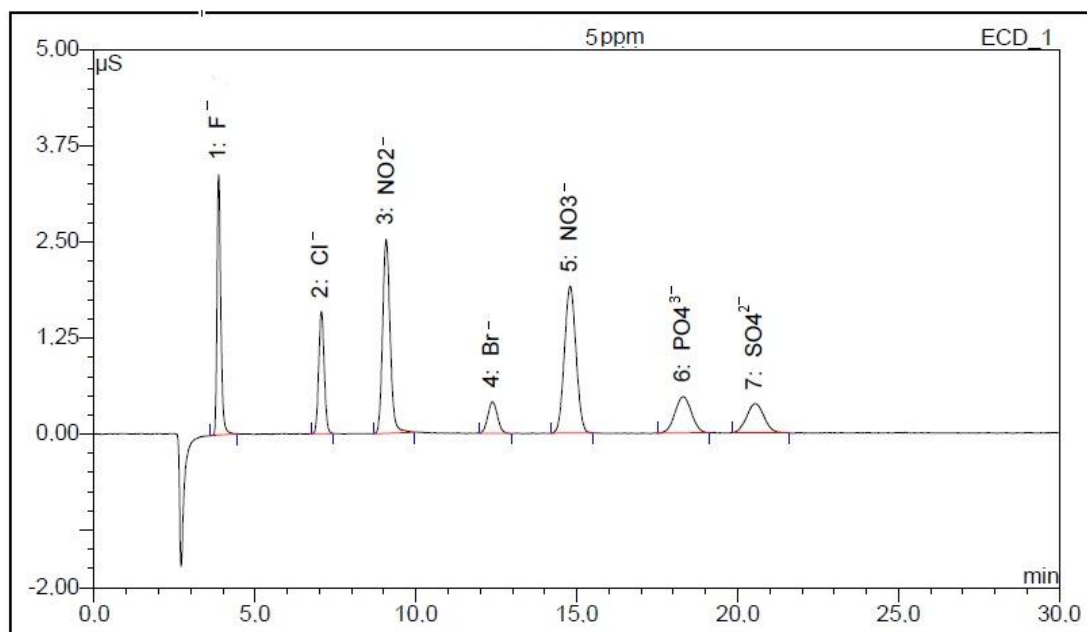


Figure 2.19. The chromatogram for 5 ppm Absolute Standard Anion Mix A solution

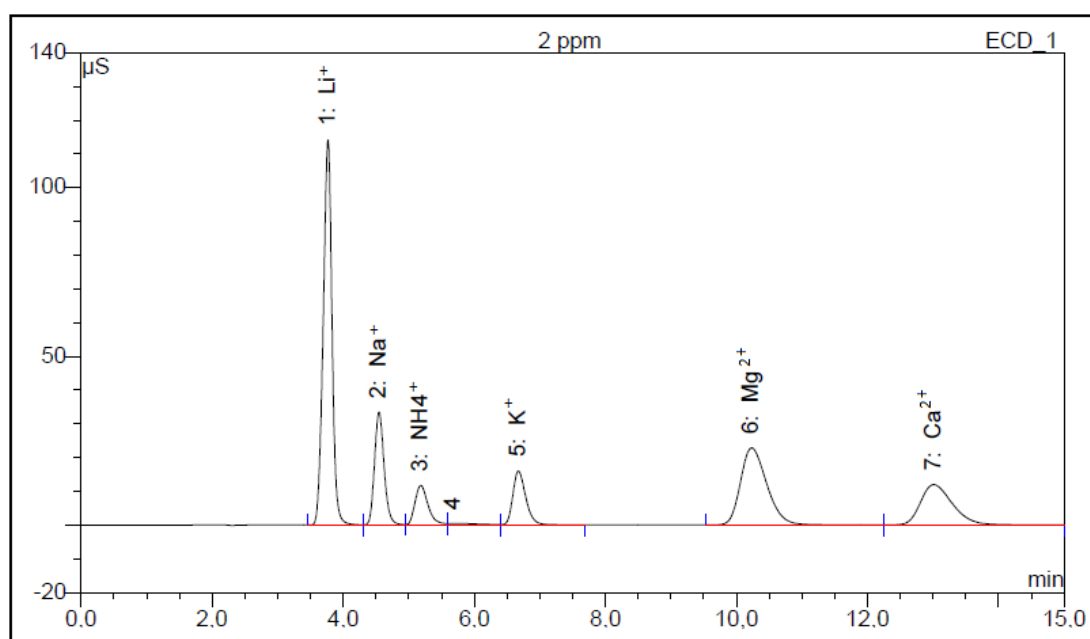


Figure 2.20. The chromatogram for 2 ppm Absolute Standard Cation Mix solution

2.2.1.2.4. Method validation for ion determination

The accuracy of the method was obtained by using the standard reference materials namely BCR 409 Simulated Rainwater (high content) and the results are given in Table 2.14. The percent error for anions and cations were less than 7 % and 17 %, respectively.

Tablo 2.14. BCR 409 results for anions and cations (number of analysis=10).

	Calculated value (Mean conc. $\pm$ Stdev) (mg L ⁻¹)	Certified value (Mean conc $\pm$ U k=2) (mg L ⁻¹)	% error
Na ⁺	1.884 $\pm$ 0.171	1.906 $\pm$ 0.0275	-1.2
NH ₄ ⁺	2.117 $\pm$ 0.124	1.909 $\pm$ 0.0360	10.9
K ⁺	0.191 $\pm$ 0.020	0.166 $\pm$ 0.008	15.1
Mg ²⁺	0.321 $\pm$ 0.022	0.299 $\pm$ 0.00486	7.4
Ca ²⁺	0.520 $\pm$ 0.106	0.6212 $\pm$ 0.0120	-16.3
Cl ⁻	0.805 $\pm$ 0.034	0.801 $\pm$ 0.0142	0.5
NO ₃ ⁻	1.034 $\pm$ 0.032	0.968 $\pm$ 0.012	6.8
SO ₄ ²⁻	1.070 $\pm$ 0.109	1.022 $\pm$ 0.0134	4.7

Other validation parameters for anions and cations are tabulated in Table 2.15 and Table 2.16, respectively. The linear calibration range is from 0.1 to 5 ppm for all cations however, this range is different for each anions. For Cl⁻, NO₃⁻ and SO₄²⁻ linear calibration ranges were 0.3-3, 1-10, 1.5-15 ppm, respectively. The recovery was calculated by using BCR 409 (Simulated Rain Water) certified reference material. After making the proper dilution (1:5), it was analyzed as the samples. The results show that all anions have 90 % recovery whereas the recoveries of cations

have higher than 85 %. Moreover, the long term and the short term repeatability was calculated for anions and cations. In long term repeatability, the same sample is analyzed in different days and in short term repeatability, the analysis of the same sample is repeated many times in a day. Two different standard concentrations (0.5 and 4 ppm) that were in the range of sample concentrations were used for both the long and the short term repeatability for anions however, for cations one standard concentration (1 ppm) was used. Maximum percent relative standard deviation was obtained for SO_4^{2-} in the short term repeatability (12%) and for Na^+ in the long term repeatability (16%). Finally, LOD and LOQ values were calculated by using field blank samples. LOD values for whole ions were in the range of $0.010 \mu\text{g m}^{-3}$ to $0.503 \mu\text{g m}^{-3}$ and for LOQ this range was between $0.033 \mu\text{g m}^{-3}$ to $1.678 \mu\text{g m}^{-3}$.

Table 2.15. Validation parameters for anions in ion chromatography.

Repeatability									
% RSD (N)					%	Linear	R ²	LOD (µg m ⁻³)	LOQ (µg m ⁻³)
Short term		Long term		Recovery [*] (N)	range (ppm)				
(a)	(b)								
0.5 ppm	4 ppm	0.5 ppm	4 ppm						
Cl ⁻	3.5	1.1	1.9	0.6	96.1	0.3-3	0.9993	0.503	1.678
	(20)	(20)	(5)	(5)	(15)				
NO ₃ ⁻	2.8	0.7	1.9	0.6	93.2	1-10	0.9992	0.062	0.206
	(20)	(20)	(5)	(5)	(15)				
SO ₄ ²⁻	12	2.2	4.5	0.7	95.3	1.5-15	0.9992	0.164	0.547
	(20)	(20)	(5)	(5)	(15)				

*BCR 409 Simulated Rainwater (high content)

N: total number of analysis

(a) number of analysis in a day, (b) number of total days for analysis

Table 2.16. Validation parameters for cations in ion chromatography.

	Repeatability		% Recovery [*] (N)	Linear range (ppm)	R ²	LOD (µg m ⁻³)	LOQ (µg m ⁻³)
	% RSD (N)						
	Short	Long term					
	term (a)	(b)					
Na ⁺	4.0 (10)	16 (5)	96 (6)	0.1-5	0.9998	0.129	0.431
NH ₄ ⁺	3.5 (10)	4.3 (5)	89.1 (8)	0.1-5	0.9905	0.089	0.296
K ⁺	3.6 (10)	9.0 (5)	84.9 (8)	0.1-5	0.9997	0.010	0.033
Mg ²⁺	1.4 (10)	8.1 (5)	92.6 (8)	0.1-5	0.9999	0.032	0.108
Ca ²⁺	5.4 (10)	8.1 (5)	85.8 (8)	0.1-5	0.9993	0.189	0.631

*BCR 409 Simulated Rainwater (high content)

N: total number of analysis, (a) number of analysis in a day, (b) number of total days for analysis

2.2.1.3. Determination of TC/OC/EC

2.2.1.3.1. Reagents and chemicals

Acetanalide (Merck):

Molecular formula: C₆H₅NHCOCH₃

Molar mass: 135.16 g mol⁻¹

Melting point: 114.3°C

Solubility in water: <1 g L⁻¹ (22 °C)

Acetanilide consists of 71.09 % carbon atom and it was used as a standard material for the determination of total carbon and organic carbon. In elemental analyzer calibration standards (2, 6, 10, 12, 14 mg L⁻¹) were prepared from 2000 mg L⁻¹ acetanilide solution. For the analysis in Sunset OC/EC Analyzer, 10 µL (contains 6.81 µg carbon) of the solution was impregnated to the filter surface.

Sucrose:

Molecular formula: C₁₂H₂₂O₁₁

Molar mass: 342.30 g mol⁻¹

Decomposing point: 186°C

Solubility in water: 2000 g L⁻¹ (25°C)

Sucrose was used as a calibration standard for the analysis in the Sunset OC/EC Analyzer. Maximum 10 µL (contains 35.04 µg carbon) of the solution was impregnated to the filter surface.

Calcium carbonate (Alfa Aesar):

Molecular formula: CaCO₃

Molar mass: 100.09 g mol⁻¹

Melting point: 825°C (aragonite), 1339 °C (calcite)

Solubility in water: 13 mg L⁻¹ (25°C)

Calcium oxalate (Alfa Aesar®):

Molecular formula: CaC_2O_4

Molar mass: 128.1 g mol^{-1}

Decomposing point: 200°C

Solubility in water: 6.7 mg L^{-1} (25°C)

Calcium carbonate and calcium oxalate were used to determine the carbonate carbon and oxalate carbon content in $\text{PM}_{2.5}$. Small amount of these chemicals were weighted and placed onto the filter samples and analyzed in the Sunset OC/EC analyzer.

Suprapur HCl 30 % (Merck): is used for the determination of CaCO_3 in particulate matter. Carbonate gives reaction with acids by producing CO_2 . After exposing the sample filters to the vapor of concentrated HCl, it was analyzed in Sunset OC/EC analyzer. The difference between the untreated and acid treated sample filter gives the carbonate amount.

Sodium carbonate solution (Dionex):

Molecular formula: Na_2CO_3

Molar mass: 105.99 mol^{-1}

Sodium carbonate was used as a standard to validate the determination of carbonate by fuming method. The concentration of stock solution is 0.5 M and it includes 94.7 % (w/v) water and 5.3 % (w/v) Na_2CO_3 .

2.2.1.3.2. CNHS (Carbon, Nitrogen, Hydrogen, Sulphur)

Elemental Analyzer

Samples collected on micro glass fiber filters by Tecora PM samplers were analyzed in order to find the concentration of total, elemental and organic carbon. After keeping at constant conditions ($\sim 25^{\circ}\text{C}$ and 20-25% humidity), filters were weighed and punched in 6.2 mm diameter as in Figure 2.21. One part of the filter was used for total carbon determination and the other part was used for elemental (black) carbon determination. Organic carbon was calculated by subtracting the elemental carbon from total carbon content of the samples.

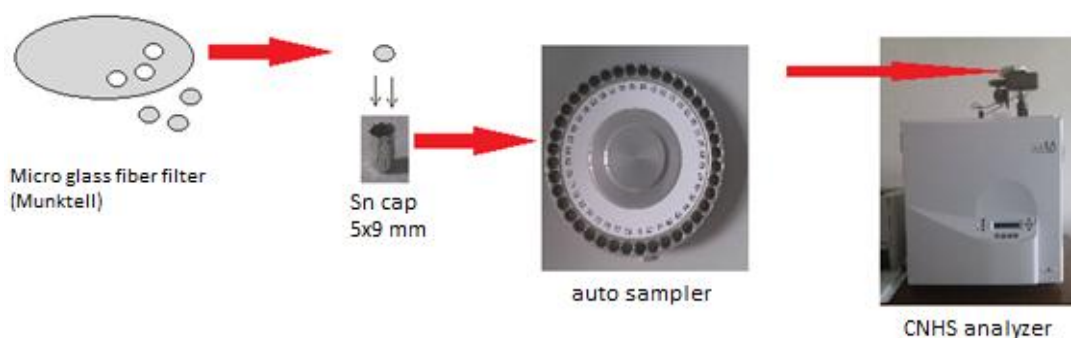


Figure 2.21. Summary of total carbon determination methodology

The procedure of determination of total carbon is summarized in Figure 2.22. As explained previously, one spot of the filter is placed in 5 x 9 mm tin caps and packed tightly with forceps. Then these caps were placed in auto sampler and introduced to the instrument (Eurovector EA3000-Single CNHS Elemental Analyzer).

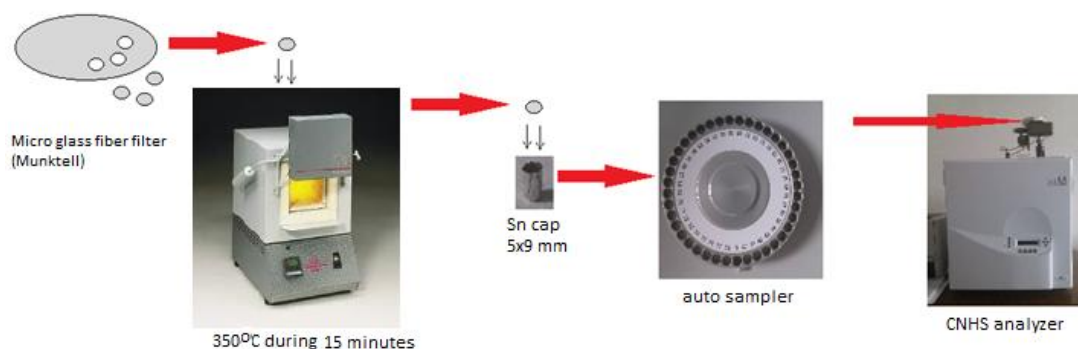


Figure 2.22. The summary of the Elemental carbon determination methodology

Beside carbon, this instrument can be also used for nitrogen, hydrogen and sulfur determination. Operation conditions of the instrument were given in Table 2.17. Helium was the mobile phase. In the first step of the analysis, the sample in auto sampler fell into the front furnace. The sample was combusted with oxygen and CO_2 was produced. The reducing agents in reactor (tungsten oxides and copper wire) reduced CO_2 to CH_4 and with the mobile phase it was reached to the thermal conductivity detector (TCD).

Table 2.17. Operation conditions for EuroEA3000.

Instrument parameters	
Mobile gas flux (mL/min)	120 ± 5
Mobile gas pressure (kPa)	80
Purge rate (mL/min)	80
O_2 (mL) for 5 x 9 mm tin caps	20
ΔPO_2 basinc1 (kPa)	35
Oxidation time (sec)	$\sim 8,7$
Sampling delay (sec)	~ 6
Run time (sec)	320
Front furnace temperature ($^{\circ}\text{C}$)	980
GC oven temperature ($^{\circ}\text{C}$)	115

For the determination of elemental carbon, the other spot is first kept at 350°C for 15 minutes in an oven in order to remove all organic composition on the filter. After that, the same procedure as in total carbon determination was applied for this portion. Organic carbon is then calculated by subtracting the elemental carbon concentration from total carbon concentration.

Acetanilide which includes 71.1 % carbon was used as calibration standard. 2000 mg L⁻¹ standard solution was prepared and impregnated onto the filters which were conditioned (25°C and 25% relative humidity) as sample filters. The maximum amount of injected volume that the filter absorbed was 7 µL (contains 14 µg C). The calibration standards were 1 µL (2 µg C), 3 µL (6 µg C), 5 µL (10 µg C), 6 µL (12 µg C) and 7 µL (14 µg C). Then, these standards were analyzed and the following calibration curve was obtained (Figure 2.23).

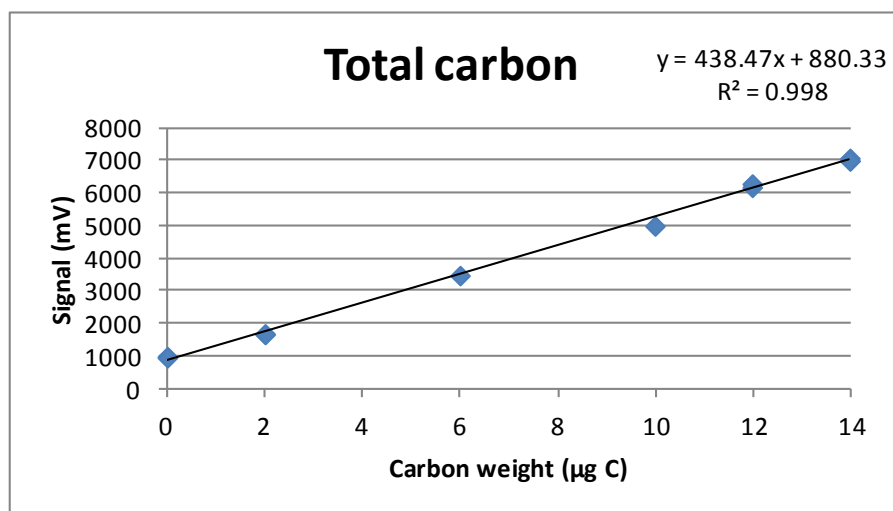


Figure 2.23. Calibration graph for total carbon determination in EuroVector CNHS Elemental Analyzer

2.2.1.3.3. OC/EC analyzer

The Sunset OC/EC Thermal Analyzer is an instrument utilized for the determination of organic and elemental carbon on particles collected on quartz fiber filters. The simplified schematic diagram of OC/EC system is shown in Figure 2.24.

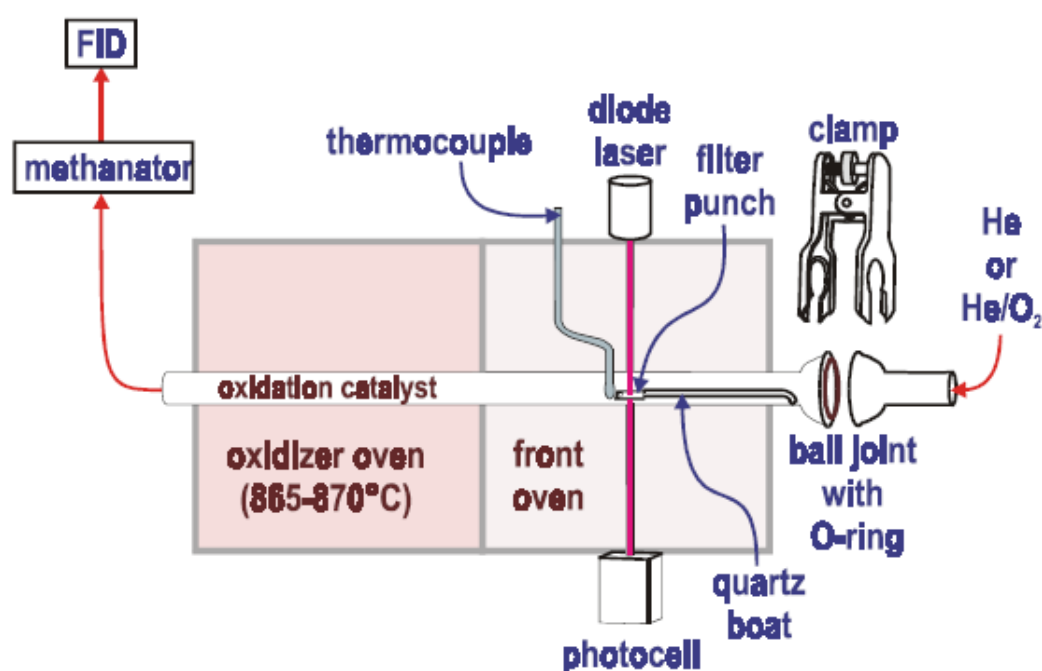


Figure 2.24. The schematic diagram of Sunset OC/EC Thermal Analyzer

The working principle of the instrument is the combination of thermal desorption and thermal optical transmission (TOT) of laser light through to the aerosol on a quartz filter. In this instrument, different analysis protocols can be applied according to the filter matrix (glass or quartz) and the carbon compositions. As indicated before, the main difference between protocols in this instrument is the temperature profiles. The temperature profiles of NIOSH 870 protocol for quartz filters which is commonly

used in literature and Glass protocol for glass filters that was used in this study were summarized in Table 2.18. The composition of sample and the type of sample filter are the main factors to determine the proper temperature profiles.

Table 2.18. Temperature profiles of NIOSH 870 and GLASS protocols.

Mobile phase	NIOSH 870		GLASS	
	Time (s)	Temperature (°C)	Time (s)	Temperature (°C)
Helium	10	1	10	1
Helium	80	310	80	310
Helium	80	475	80	475
Helium	80	615	80	575
Helium	110	870	110	650
Helium	45	550	45	550
Oxygen	45	550	45	550
Oxygen	45	625	45	625
Oxygen	45	700	45	700
Oxygen	45	775	45	775
Oxygen	45	850	45	850
Oxygen	110	870	110	870
Calibration gas (CH ₄)	120	1	110	1
Offline	1	0	1	0

The sample filters used in this study was micro-glass fiber filter, so NIOSH 870 method could not be applied because the melting of glass filter is starting at around 550°C. If NIOSH protocol was applied to the sample matrix was melted and the possible organic fractions that have resistance at high temperature (> 550°C) and EC could not be obtained because molten matrix could prevent the transmission of light. Therefore, Glass protocol was applied to the samples.

According to the mobile phases, both methods have three main steps. In the first step, quartz oven is purged with helium during 10 seconds. Then, temperature of the oven increases gradually (each step lasts within 80 seconds) until reaching to 870°C for NIOSH 870 and to 650 °C for Glass protocol. Oven temperature becomes constant at these maximum values during 110 seconds. Desorbed organic compounds and pyrolytic products are introduced into MnO₂ oxidizing oven. As the carbon fragments flow through into the MnO₂ oven, they are quantitatively converted to CO₂ gas. The CO₂ is swept out of the oxidizing oven in the helium stream and mixed with hydrogen gas. This mixture then flows through a heated nickel catalyst where it is quantitatively converted to CH₄. Finally, CH₄ is measured by using a flame ionization detector (FID).

The second step is same for both methods. The oven is cooled to 550°C and flow stream is switched to an oxidizing He/O₂ carrier gas mixture. The second temperature ramp is initiated in the oxidizing gas stream and any elemental carbon is oxidized off the filter and introduced to the oxidizing oven. Most of the organic species are transparent whereas the EC has dark color, then there is an initial transmittance signal when the analysis is started. After the first step, most of the OC are removed however, due to the high oven temperature some of them are pyrolyzed and make the filter darkness. Then, the transmittance signal decreases. When all OC fractions are removed the transmittance signal reaches its initial value. This point is called as split point that is used to differentiate OC and EC (Karanasiou et al., 2011; Na et al., 2004; Watson et al., 2005). Finally, oven temperature decreases immediately and calibration gas, CH₄, flows approximately during 2 minutes through the system.

Sample thermogram is given in Figure 2.25. Green and pink peaks are the signals of FID1 and FID2, respectively. Blue line shows the temperature profile, the red line shows the laser transmittance signal and the black line shows the absorbance signals. As indicated above paragraph vertical blue line indicates the split point. Peaks on the left side of this line assumed to be OC fractions and the peaks on the right side are EC fractions. The last peak belongs to calibration gas, CH₄.

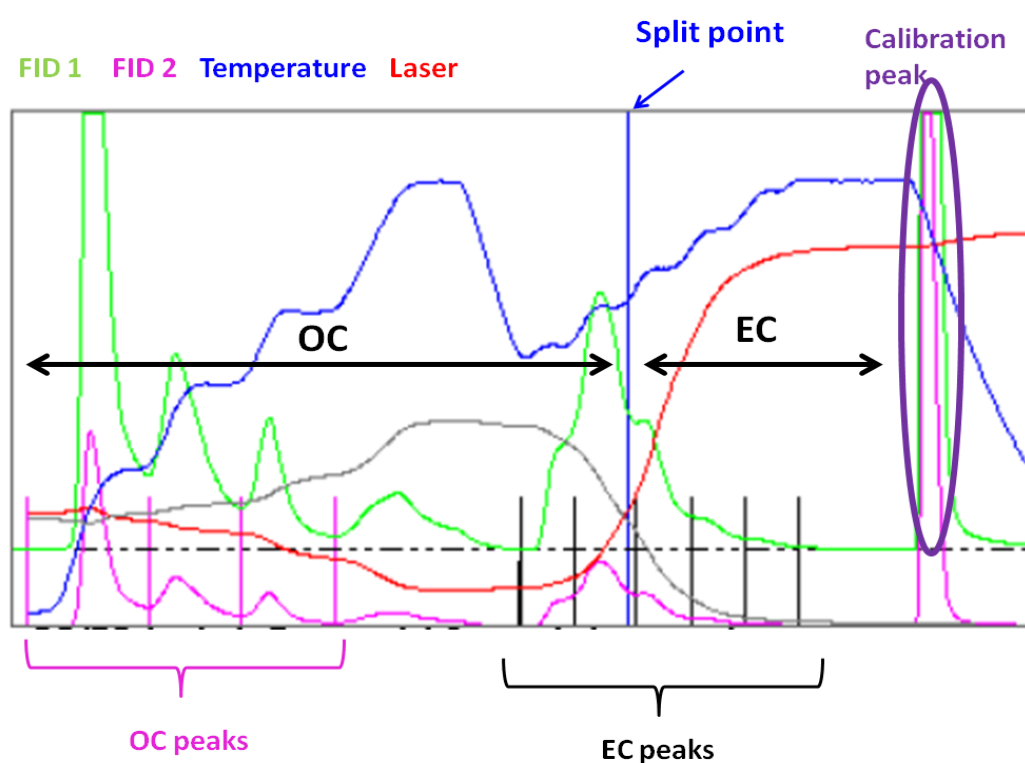


Figure 2.25. A sample thermogram in NIOSH 870 protocol

The interaction between filter sample and the laser is summarized in Figure 2.26. Incident radiation reaches to the surface of the filter to where the particulate matters covered as a layer. Great amount of the light back scattered whereas some of them reflected or forward scattered to the filter matrix. Finally, the total amount of light

reaches the detector and give the signal as transmission. During this process some artifacts may occur due to filter matrix. Multiple scattering of light by filter and light scattering due to aerosol particles tends to overestimate the absorption coefficient. In addition, shadowing of particles inside the filter matrix tends to underestimate the absorption coefficient (Kuhlbusch et al., 2009).

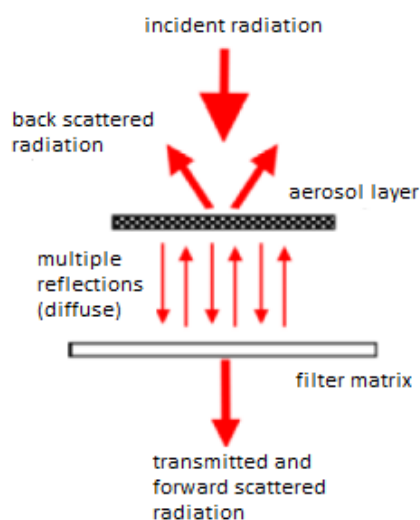


Figure 2.26. Light transmission through filter sample (Kuhlbusch et al., 2009)

The calibration of the method was achieved by standard addition method in order to minimize the matrix effect. In the standard addition method, a sample filter is spiked with known amounts of standard sucrose solution as 2, 4, 6, 10 μL from the concentration of $3.504 \mu\text{gC } \mu\text{L}^{-1}$. Figure 2.27 shows the calibration curve of the method. The intercept gives the amount of carbon in the sample.

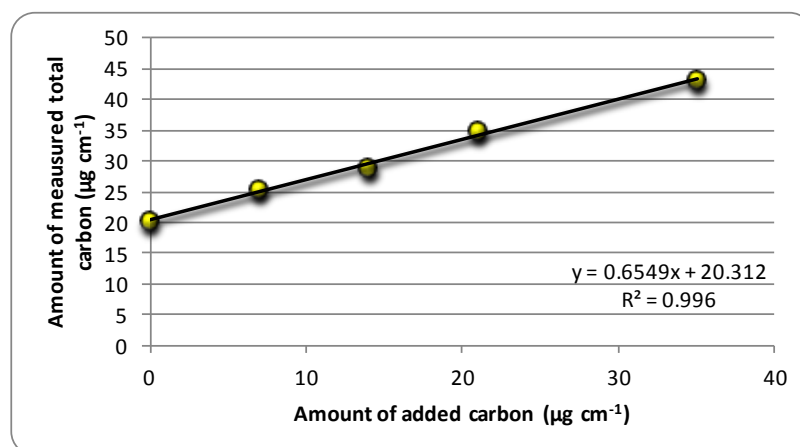


Figure 2.27. Calibration graph for total carbon determination in Sunset OC/EC Analyzer

2.2.1.3.4. Method validation for TC/OC/EC determination

Some of the method validation parameters were obtained using SRM 1648a Urban Particulate Matter in both EuroVector CNHS analyzer and Sunset OC/EC analyzer. The validation table for total carbon was given in Table 2.19 for CNHS analyzer. The repeatability of the method was checked by 5 replicates of a sample and the percent relative standard deviation was calculated as 23.2 %. Overall 38 analysis of SRM 1648a was made for the recovery calculation and the percent recovery of the method for total carbon was 96.0%. Acetanilide was used as a calibration standard and the range of calibration curve was between 2 and 14 $\mu\text{g C}$. Finally, the limit of detection and the limit of quantification was evaluated by field blanks and calculated as $0.024 \mu\text{g m}^{-3}$ and $0.080 \mu\text{g m}^{-3}$, respectively after 10 runs.

Table 2.19. Validation parameters for elemental and organic carbon in EuroVector CNHS analyzer.

	Repeatability (RSD %)	Recovery ^a (%)	Linear range ($\mu\text{g C}$)	R^2	LOD ($\mu\text{g m}^{-3}$)	LOQ ($\mu\text{g m}^{-3}$)
TC	23.2 (5)	96.0 $\pm$ 9.4 (38)	2-14	0.9996	0.024	0.080

^a SRM 1648a Urban Particulate Matter, number of analysis are given in parenthesis

Validation parameters (repeatability, percent recovery, limit of detection (LOD) and limit of quantification (LOQ) for the method used in Sunset OC/EC analyzer was given in Table 2.20. Validation was achieved by standards contain OC (standard sucrose and acetanilide solutions, SRM 1648a (Urban Particulate Matter-NIST) and randomly selected samples.

Table 2.20. Validation parameters for elemental and organic carbon in Sunset OC/EC analyzer.

	Repeatability		% Recovery		LOD	LOQ
	% RSD (N)		(N)			
	Short	Long	Sucrose	Acetanilide	($\mu\text{g m}^{-3}$)	($\mu\text{g m}^{-3}$)
	term (5)	term (5)	(82)	(10)		
OC	2.88	3.79	105.1 $\pm$ 2.40	97.8 $\pm$ 1.31	1.99	6.63
EC	3.52	12.7	-	-	0.113	0.376
TC	2.51	3.38	105.8 $\pm$ 2.28	97.8 $\pm$ 1.32	1.98	6.62

N=number of analysis

Long term and short term repeatability were designated by randomly selected two samples. Maximum 5 punches can be obtained from each sample then the number of analysis became limited for repeatability calculations. In short term repeatability, samples (5 punches in one sample) were analyzed in a day and in long term repeatability, daily analyses were performed during five days for the same sample. Percent RSD (relative standard deviation) in short term was 2.88, 3.52 and 2.51 % for OC, EC and TC, respectively. In long term the % RSD was 3.79, 12.7 and 3.38 for OC, EC and TC, respectively.

Standard sucrose and acetanilide solutions were used for the percent recovery calculations. The thermograms of sucrose and acetanilide for both Glass and NIOSH 870 protocol were given in Figure 2.28 and Figure 2.29, respectively. The concentration of sucrose solution was $3.504 \mu\text{g C } \mu\text{L}^{-1}$ and the concentration of acetanilide solution was $0.6810 \mu\text{g C } \mu\text{L}^{-1}$. From each standard solution $10 \mu\text{L}$ was impregnated onto the quartz filters that had 1.5 cm^2 area. This impregnation volume should be maximum $10 \mu\text{L}$, otherwise the excess amount of solution could pass to the other side of the filter. In the next step, these loaded filters were retained at constant temperature ($\sim 25^\circ\text{C}$) and humidity (20-25 %) in order to remove the moisture and then, they were analyzed like filter samples. Average percent recovery for 82 sucrose samples were 105.1 % and 105.8 % for OC and TC, respectively. For analyzed 10 acetanilide samples for both carbon species the average percent recovery was 97.8 %.

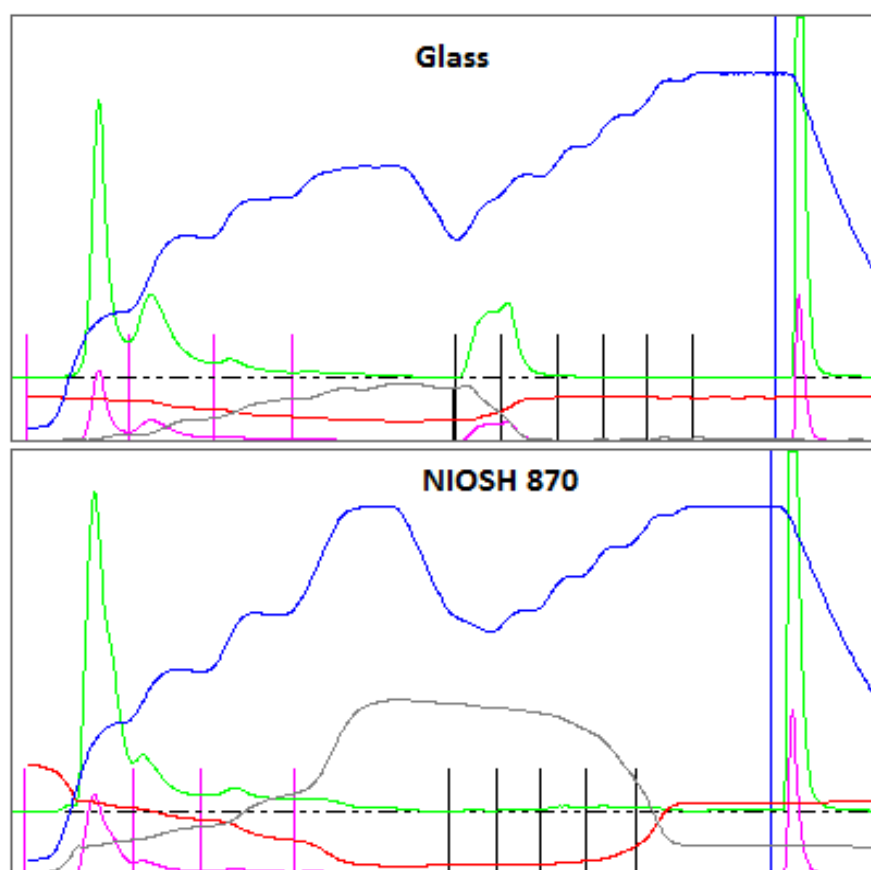


Figure 2.28. The thermograms of standard sucrose solution in Glass and NIO SH 870 protocol

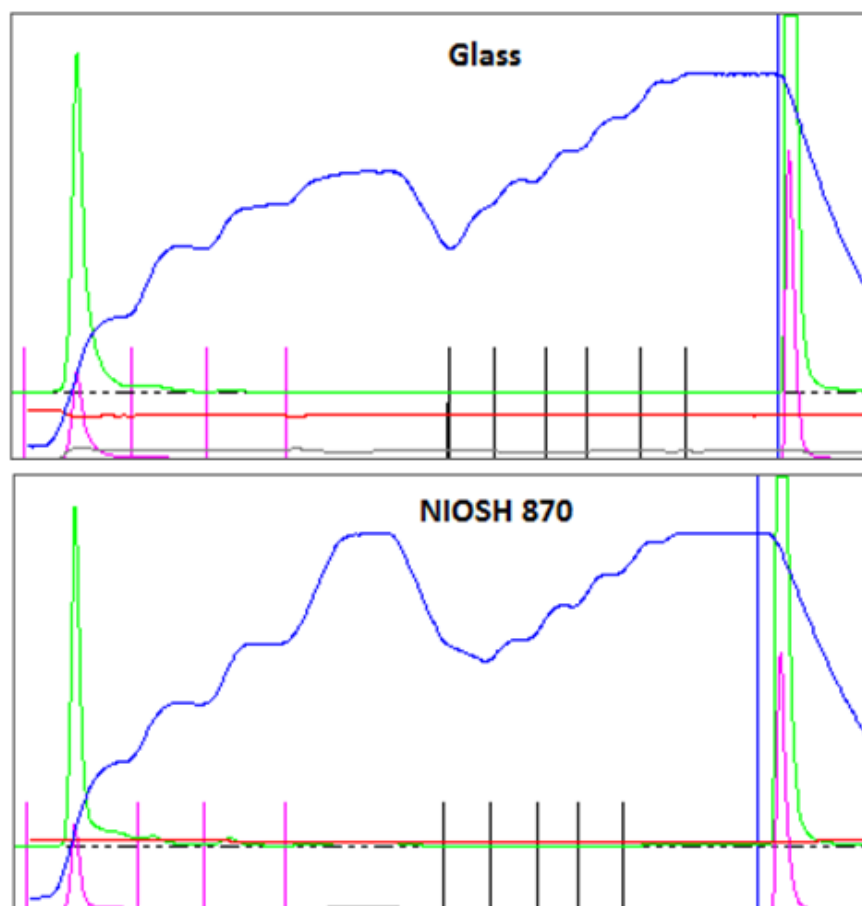


Figure 2.29. The thermograms of standard acetanilide solution in Glass and NIOSH 870 protocol

Limit of detection (LOD) and limit of quantification (LOQ) were determined by field blank samples (N=10). Range for LOD was between 0.113 and 1.98 $\mu\text{g cm}^{-3}$ and for LOQ the range was 0.376 and 6.63, for OC, EC and TC.

Moreover, the average percent recovery results were obtained with SRM 1648a for TC by applying two different analysis protocols. For the analysis 0.5-1.0 mg of SRM was weighted with a micro-balance with 0.001 mg sensitivity. Then, it was put onto a quartz filter and analyzed like filter samples. In NIOSH 870 protocol the maximum temperature was 870°C. The average percent recovery for this method was 97.7 %

and for the glass protocol in which the maximum temperature was 650°C, the average percent recovery of TC was 99.8 % (Table 2.21).

Table 2.21. The average percent recovery results for SRM 1648a for two different analysis protocols.

	NIOSH 870 (4) [†]		GLASS (5) [†]		Information value* (%)
	% Recovery	Found values %	% Recovery	Found values %	
TC	97.6 ± 7.18	12.4 ± 0.888	99.8 ± 3.24	12.6 ± 0.404	12.7

* Information values are based on results that did not allow complete assessment of all sources of uncertainty, hence, only estimated means without uncertainties are given.

[†] Number of samples are given in parenthesis.

Finally, NIOSH 870 and Glass protocol was compared by using the same samples. Due to the temperature profiles TC, OC and EC results were different between these two methods. Approximately TC results in Glass protocol was 1.2 times higher than in NIOSH 870 protocol. The correlation between these two methods for TC results was given in Figure 2.30.

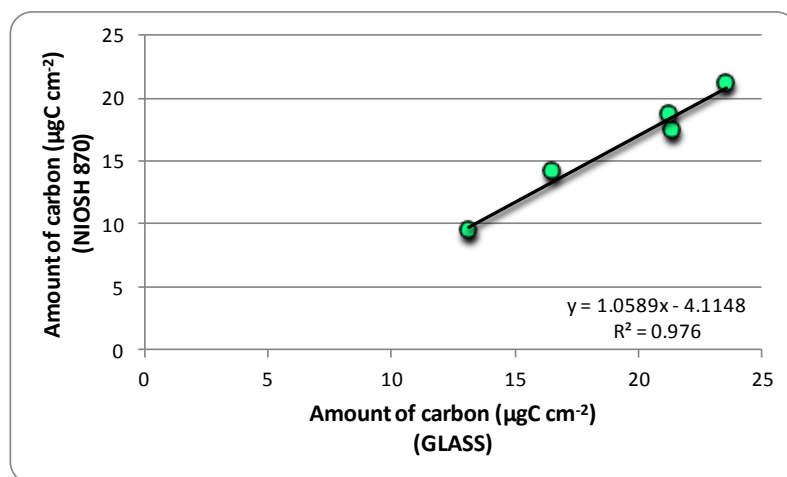


Figure 2.30. Correlation between NIOSH 870 and Glass protocols for TC results

Moreover, for the determination of carbonate carbon (CC) and oxalate carbon (OxC) with thermal optical method (Sunset OC/EC analyzer) was also validated in this study. Before starting to CaCO_3 analysis, thermal degradation of CaCO_3 was determined by thermal gravimetric analysis (TGA 4000-Perkin Elmer). Thermogram of the analysis was given in Figure 2.31. Dashed line gives the remain weight of the sample with respect to temperature. The tangent of the step gives the infection of degradation temperature. Degradation started at 757.85°C and end up at 860.10°C .

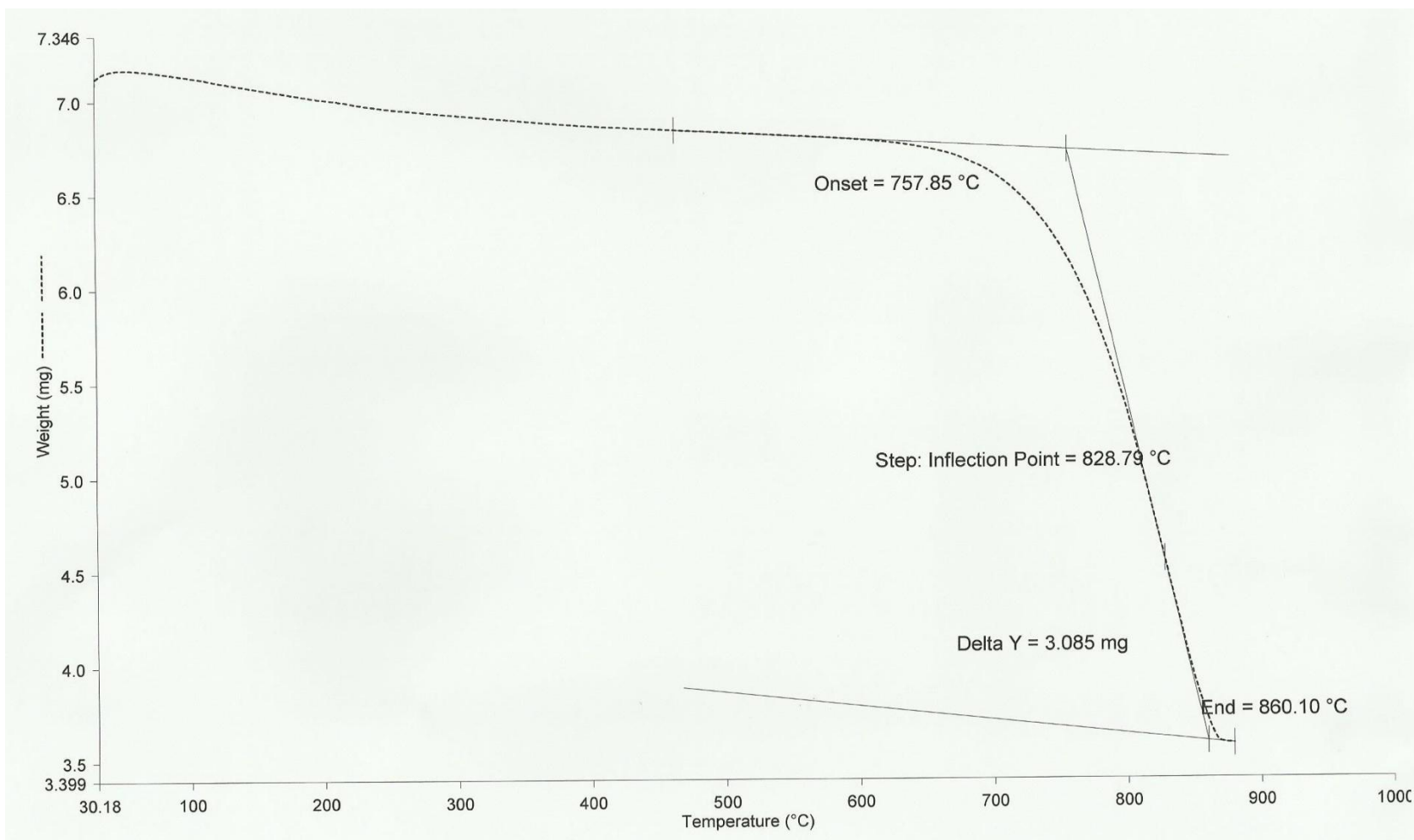


Figure 2.31. Sample thermogram of CaCO_3 in TGA

According to the TGA results, the inflection of the average temperature for degradation was found as 828.79°C and the maximum temperature was 860.10 °C. Chow and Watson (2002) mentioned that for carbonate analysis in thermal methods the system temperature should be above 800°C.

Figure 2.32 shows the thermogram of CaCO₃ (Alfa Aesar®) with NIOSH 870 method in OC/EC analyzer. The first peak belongs to CC which reaches its maximum signal at 863.82 °C. Sample was introduced to the system in powder form on quartz fiber filter with an area of 1.5 cm².

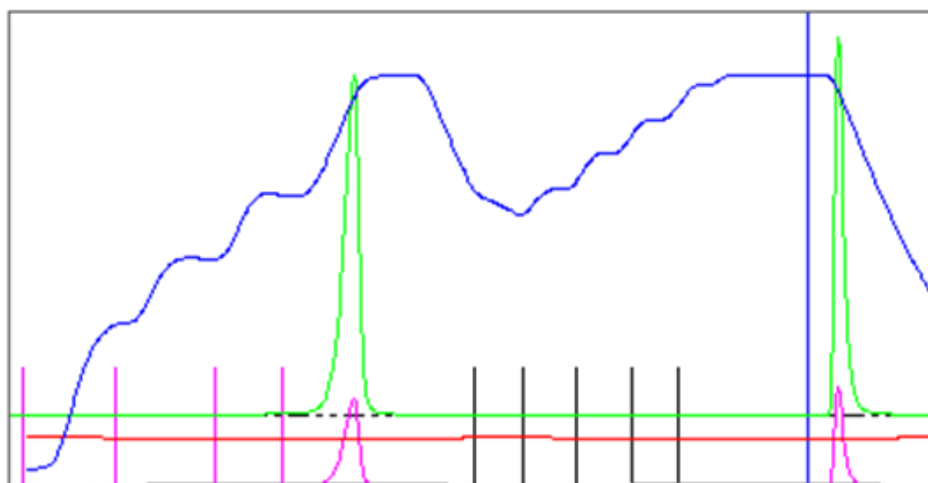


Figure 2.32. Thermogram for CaCO₃ in NIOSH 870 protocol

The amount of sample CaCO₃ was changed between 0.5 to 1.0 mg. Weighing and placement of these small amounts of samples were very difficult due to the static electricity and the underestimated results were obtained. In order to prevent this difficulty, Zerostat® anti-static gun was used. The correlation between weighted

amount and measured amount of CC was shown with the graph in Figure 2.33. Square of correlation coefficient was 0.9487 which indicates the reliability of results.

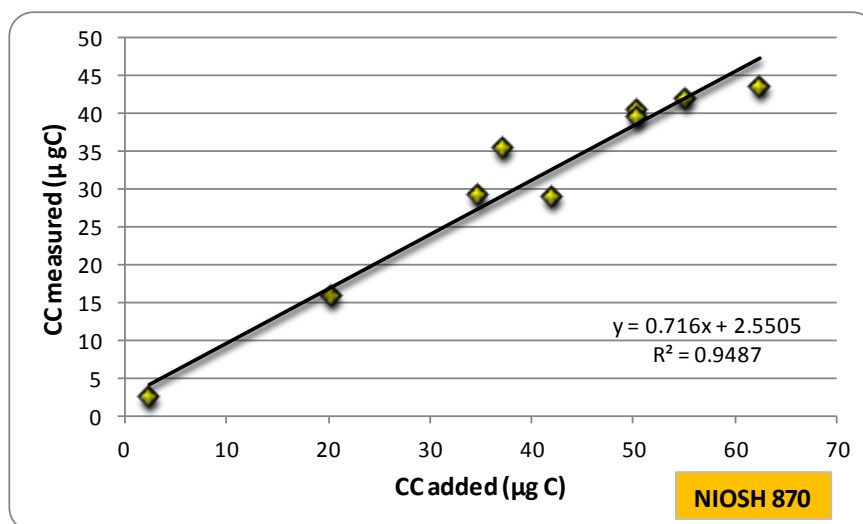


Figure 2.33. Correlation graph of measured and added CaCO_3 (CC) in NIOSH 870 protocol

Moreover, quantification of carbonate carbon was validated by acid fuming method as mentioned in literature (Karansiou et al., 2011; Fisseha et al., 2009; Chow and Watson, 2002; Jankowski et al., 2008) with some modifications in duration. In first step, 1 cm^2 punch of quartz filter was impregnated with 10 µL standard Na_2CO_3 solution (Dionex) (Figure 2.34). Then, this filter was exposed to concentrated HCl acid (Merck) vapor for about one hour (Figure 2.35) and two hours (Figure 2.36), separately. The remained CC peaks are indicated in red circles in figures. At the end of two hours, a negligible amount of Na_2CO_3 was remained onto the filter. Then, filter was placed in a clean petri dish and under the hood for an hour in order to remove the residual acids. Incomplete volatilization of acid vapor may cause serious

damages in the combustion oven of the analyzer (Karanasiou et al., 2011; Jankowski et al., 2008).

The difference between untreated impregnated filter and HCl fumigated filter was accounted for carbonate fraction in the sample. However, any evidence was not obtained for the presence of carbonate carbon in fine $PM_{2.5}$ samples in this sample.

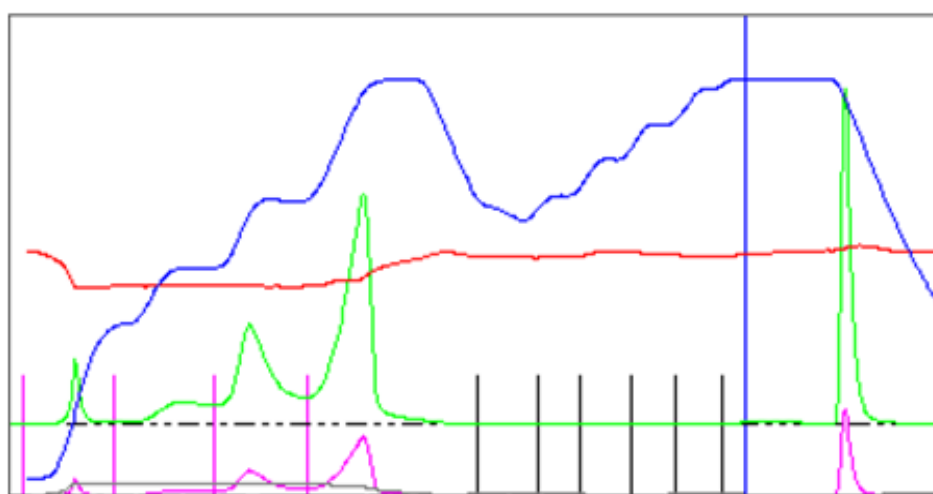


Figure 2.34. Impregnation of Na_2CO_3 solution onto quartz fiber filter.

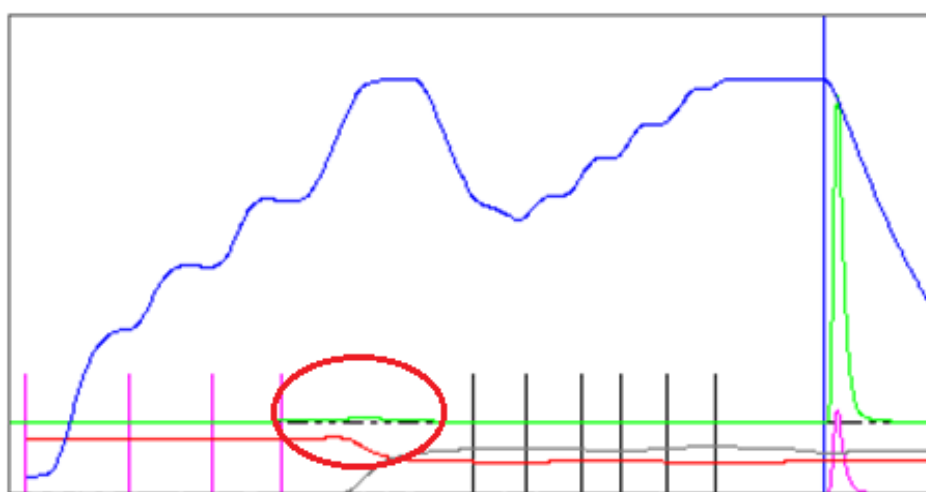


Figure 2.35. Exposure to HCl acid vapor for one hour.

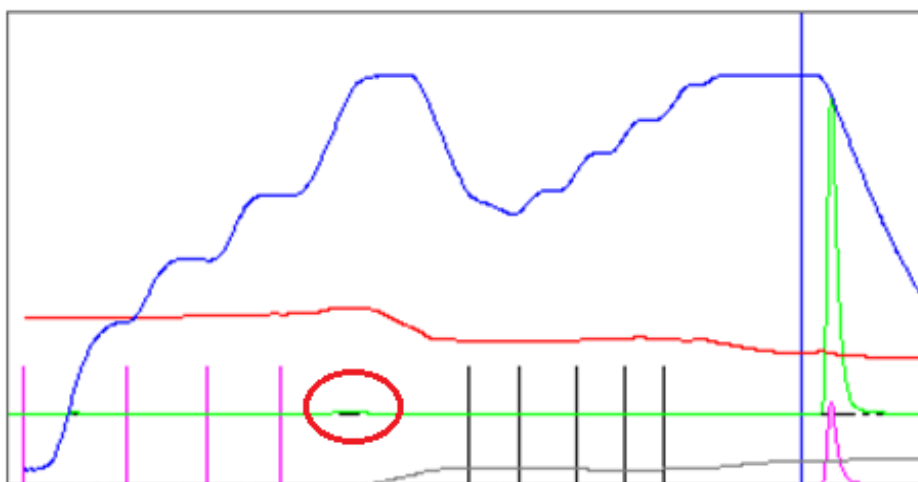


Figure 2.36. Exposure to HCl acid vapor for two hours.

Thermogram of CC in Glass protocol was given in Figure 2.37. Maximum degradation temperature was observed around at 770°C which is lower than NIOSH 870 protocol.

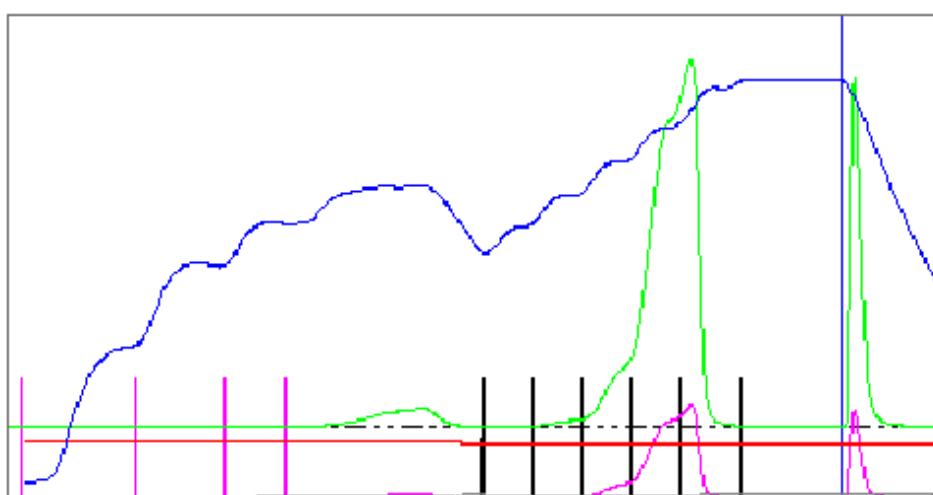


Figure 2.37. Thermogram for CaCO_3 in Glass protocol

The same correlation calculation was also done for Glass protocol. The correlation between weighted and measured amount of CaCO_3 in this method was given in Figure 2.38 ($R^2=0.9454$).

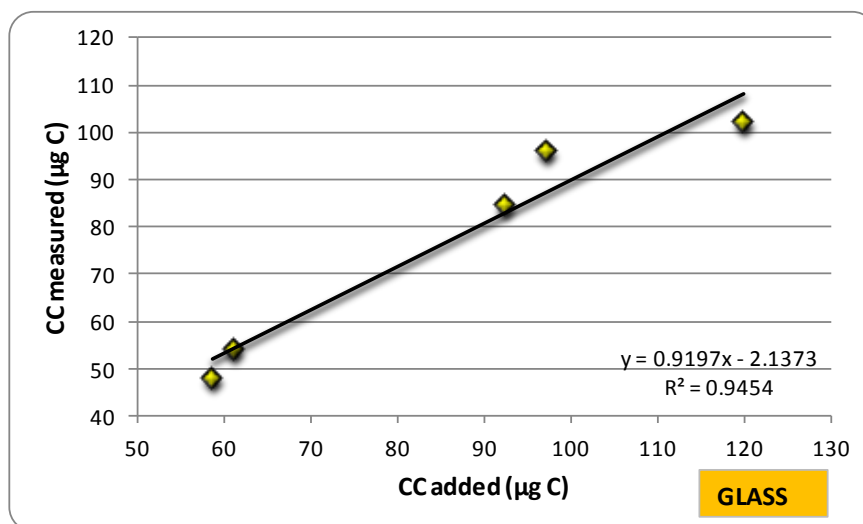


Figure 2.38. Correlation graph of measured and added CaCO_3 (CC) in Glass protocol

In order to determine the degradation of pure CaC_2O_4 (Alfa Aesar®) as in CaCO_3 analysis thermal gravimetric analysis was performed (Figure 2.39). Dashed red lines gives the remain weight of the sample with respect to temperature and the yellow line is the derivative of the weights. In the first step (141.35-179.23°C) water content of sample ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) was evaporated and unhydrated CaC_2O_4 was formed. In the second step (475.67-505.67°C), CaC_2O_4 was decomposed to CaCO_3 . Finally, in the last step (776.36-697.34°C), all CaCO_3 was decomposed to CaO . Thermal degradation reactions for CaC_2O_4 were summarized in Table 2.22.

Table 2.22. Theoretical results of degradation of CaC_2O_4 in TGA.

Step	Reaction	Removed species	Theoretical mass loss (%)
1	$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} \rightarrow \text{CaC}_2\text{O}_4 + \text{H}_2\text{O}$	H_2O	12.33
2	$\text{CaC}_2\text{O}_4 \rightarrow \text{CaCO}_3 + \text{CO}$	CO	19.17
3	$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$	CO_2	30.14

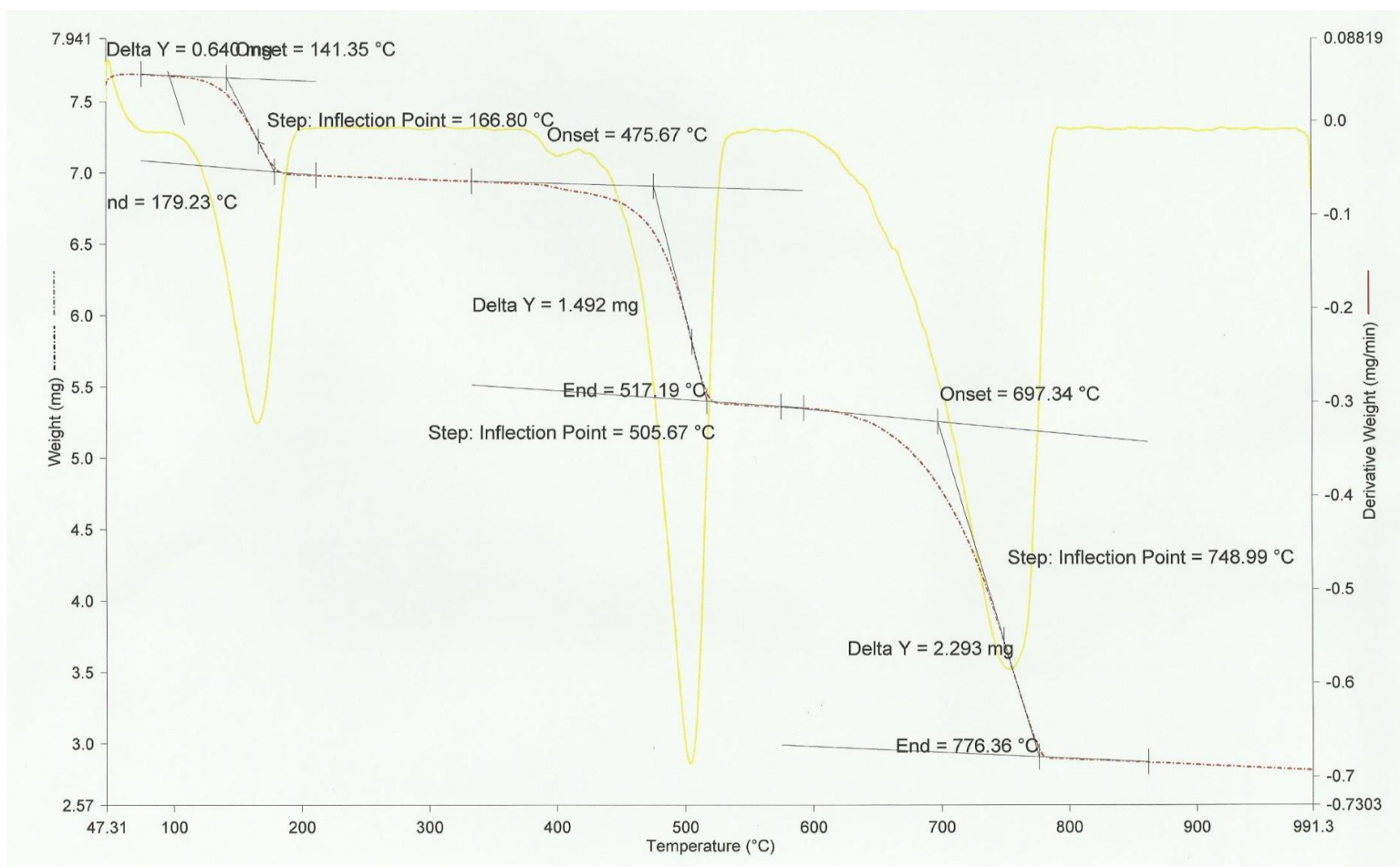


Figure 2.39. Thermogram of CaC_2O_4 in TGA

After the determination of degradation conditions, CaC_2O_4 was analyzed in Sunset OCEC analyzer by using both NIOSH 870 and Glass protocol and the thermograms were given in Figure 2.40. and Figure 2.41, respectively. In NIOSH 870 the first peak (at 615.25°C) belongs to carbon monoxide carbon that arose in the second step of the degradation (Table 2.21). Released CO was oxidized in the oven where MnO_2 is present and reduced to CH_4 in Ni/firebrick methanator and quantified as CH_4 by flame ionization detector (FID). The second peak was observed at 816.46°C in which the decomposition of carbonate was occurred. The same quantification procedure was applied for this peak.

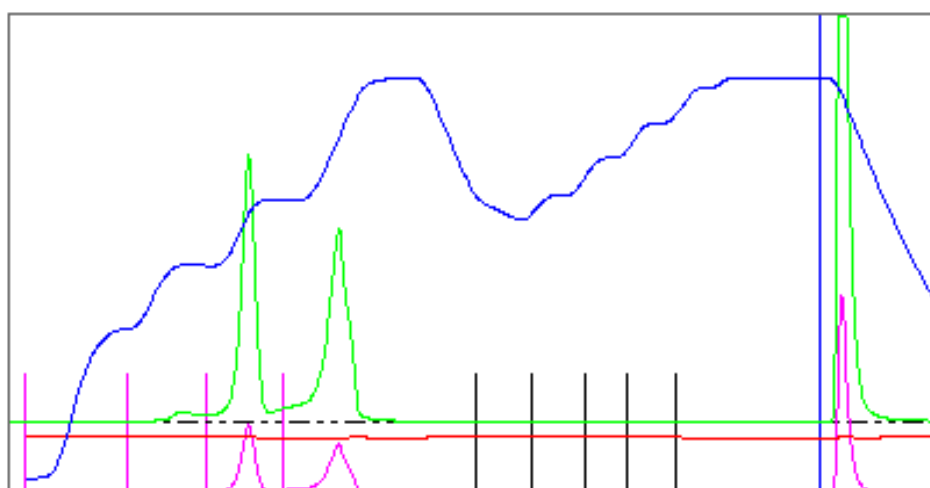


Figure 2.40. Thermogram for CaC_2O_4 in NIOSH 870 protocol

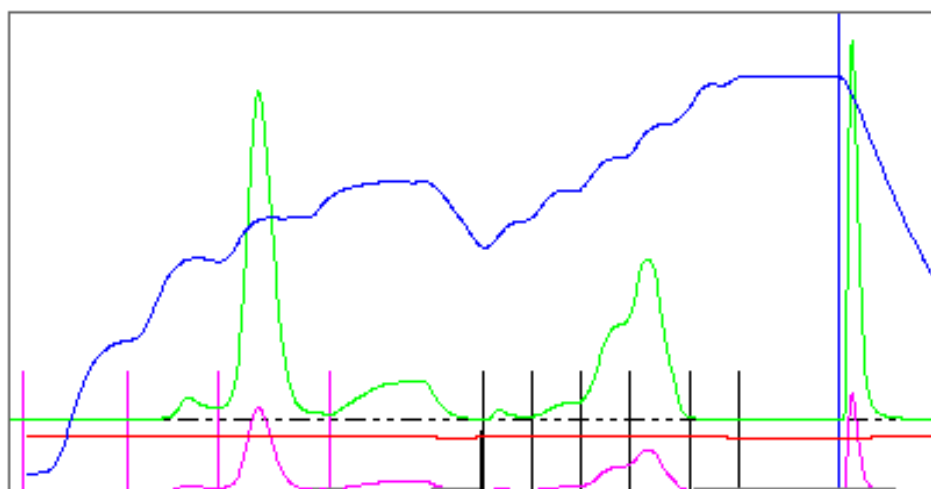


Figure 2.41. Thermogram for CaC_2O_4 in Glass protocol

Regression between added CaC_2O_4 and measured quantity by Glass protocol had high correlation ($R^2=0.9964$) as shown in Figure 2.42. The amount of carbon that measured in thermal protocol is the total carbon.

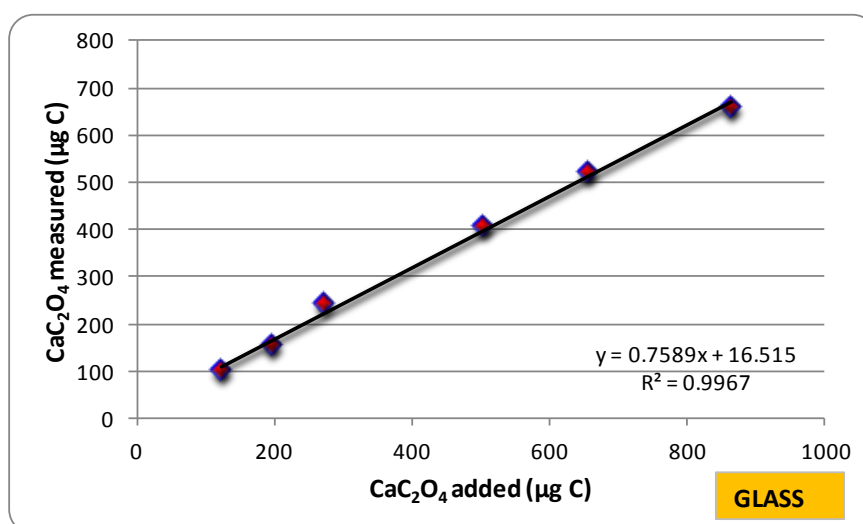


Figure 2.42. Correlation graph of measured and added CaC_2O_4 in Glass protocol

Although the compounds of carbonate and oxalate are the common parameters in environmental studies, in this study there was no samples that included these compounds.

2.2.1.3.5. Comparison of Eurovector CNHS and Sunset OC/EC analyzer

Eurovector CNHS analyzer and Sunset OC/EC analyzer were both used to determine the carbon fractions especially, TC in PM samples. Due to lack of temperature ramp program and the lack of arrangement of oven medium (ratio of He/O₂) determination of Oc and EC was impossible in CNHS analyzer. However, the regression results in Figure 2.43 shows there is a meaningful comparison of these two techniques. Total carbon was determined in the summer and the winter period samples. The agreement between the techniques for TC is within 80 % ($R^2=0.7977$).

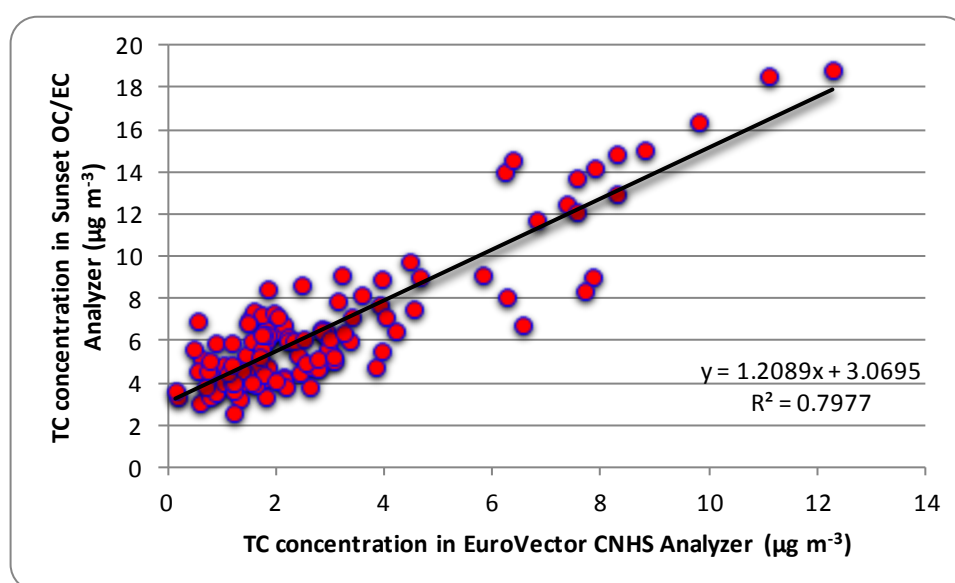


Figure 2.43. Comparison of CNHS and OC/EC analyzers for TC determination

CHAPTER 3

3. RESULTS AND DISCUSSION

3.1. General Characteristics of O₃ data

Diurnal ozone concentrations and meteorological parameters (temperature, wind speed, wind direction, rain, solar radiation, relative humidity) monitored through three-years sampling period were differentiated as daytime and night time in order to understand the reaction mechanism of photochemical O₃ production. Table 3.1 gives the statistical summary of O₃ and meteorological parameters during daytime, night time and diurnal throughout the sampling period. Diurnal average concentration of O₃ was 24.9 ppb and the average O₃ concentration of daytime and night time were 30.0 ppb and 17.5 ppb, respectively.

Table 3.1. Summary of statistical results of diurnal (daily), daytime and night time (nocturnal) O₃ concentration and meteorological parameters for three-years sampling.

	N	Mean	Stdev.	Max.	Min.	Median
<i>Diurnal</i>						
Ozone (ppb)	26599	24.9	14.9	125.5	0.0	23.8
Temperature (°C)	24606	10.0	8.0	35.3	-15.9	10.3
Wind speed (m s ⁻¹)	20033	2.1	1.5	8.5	0.4	1.8
Wind direction (°)	22218	210.8	73.8	337.5	0.0	247.5
Rain (mm)	1830	0.9	1.5	18.5	0.2	0.5
Solar rad. (W m ⁻²)	13033	309	282	1078	1.0	222
Relative humidity (%)	24606	75	21	100	0.2	82
<i>Daytime (06:00-19:00)</i>						
Ozone (ppb)	15586	30.0	14.9	125.5	0.0	29.7
T (°C)	14272	11.5	8.4	35.3	-13.1	11.6
Wind speed (m s ⁻¹)	12028	2.4	1.7	8.5	0.4	1.8
Wind direction (°)	12299	197.0	79.8	337.5	0.0	247.5
Rain (mm)	1174	0.9	1.3	18.5	0.2	0.5
Solar rad. (W m ⁻²)	12395	324	282	1078	1.0	244
Rel. humid. (%)	14272	71	22	100	0.2	74
<i>Night time (19:00-06:00)</i>						
Ozone (ppb)	11013	17.5	11.4	95.8	0.0	16.1
T (°C)	10247	8.2	7.0	26.2	-15.4	8.6
Wind speed (m s ⁻¹)	7937	1.7	1.1	8.5	0.4	1.3
Wind direction (°)	9921	228.0	61.2	337.5	0.0	247.5
Rain (mm)	652	1.0	1.7	16.8	0.2	0.5
Solar rad. (W m ⁻²)	591	20.8	24.6	135	1.0	10.0
Rel. humid. (%)	10247	82	18	100	0.4	89

3.1.1. Comparison of O₃ data with literature

Temporal variation of O₃ concentration in this study was compared with the literature values of the last 10-year studies observed in different sampling sites. Table 3.2 gives the information about the compared sampling sites with their average and maximum concentration values. Especially, different site types were selected in order to emphasize the effect of site variation on O₃ concentration.

Table 3.2. Comparison of average O₃ data with literature

Sampling site	Site type	Sampling period	Avg. conc. (ppb)	Max. conc. (ppb)	References
Bursa, Turkey ^a	urban	May 2001-April 2002	28.1	61.2	Esen et al., 2005
Udine, Italy	suburban		26	127	
Milan, Italy	rural	2001-2004	26	128	Paoletti, 2006
Perugia, Italy	suburban		27	113	
Erreterria, Spain	urban	January 1997-December 2000	30.5	-	Barrero et al., 2006
Nanjing, China ^b	urban	January 2000-February 2003	20.4	-	Tu et al., 2007
Castelporziano, Italy	sea-side	6 June-8 December 2004	35.7	-	Gerosa et al., 2009
Kocaeli, Turkey ^{a, c}	industrial region	September 2008-August 2009	9.1	22	Özbay et al., 2011
Santa Clara, Cuba ^a	suburban	February-April, 2010	26.5	-	Alejo et al., 2011
		August-October, 2010	12.2	-	
Seoul, Korea	urban traffic and background	1989-2010	15	33	Susaya et al., 2013
Agia Marina, Cyprus	rural inland	1997-2012	47.5	76.7	Keanthous et al., 2014
Bolu, Turkey	semi-rural	March 2009-March 2012	26	125	This study

^a the reported concentration was in $\mu\text{g m}^{-3}$ and it was converted in to ppb by the division with the coefficient of 1.96 ($1\text{ppb O}_3=1.96 \mu\text{g m}^{-3}$, Paoletti, 2006)

^b hourly average concentration results

^c monthly average concentration results (in this study avg: 24.8 ppb, average max:60.0 ppb)

a) Bursa, TURKEY (Esen et al., 2005)

Atmospheric O₃ was measured by Horriba APOA-360 which used a cross flow modulated infrared absorption method in Bursa city center between May 2001 and April 2002. The sampling station was densely populated and had heavy traffic load. Moreover, NO_x, NO₂ and NO were measured in the sampling site. Negative correlations were observed between O₃ and NO_x in all seasons. Although the sampling site type of the study was different from our study, the average O₃ concentration was 28.1 ppb however, the maximum O₃ concentration value was 61.2 ppb observed in summer.

b) Udine, Milan, Perugia, ITALY (Paoletti, 2006)

The aim of the study is to determine the possible effects of O₃ on Mediterranean forests and vegetation and to suggest prospects for future developments. Totally, the O₃ concentrations obtained from 14 monitoring stations throughout Italy during 2001-2004 were evaluated. However, only three of them (one rural and two suburban stations) whose average and maximum values were similar with our study were used for the comparison. Udine is a suburban station placed in Friuli Venezia Giulia region had the average and the maximum O₃ concentrations of 26 ppb and 127 ppb, respectively. Another suburban region, Perugia in Umbria had the average and the maximum O₃ concentration of 27 ppb and 113 ppb, respectively. Finally, a rural station, Milan in Lombardy region had the average O₃ concentration of 26 and the maximum value of 128 ppb. Although the last station was rural the concentration values were nearly same with our study.

c) Errenteria, SPAIN (Barrero et al., 2006)

Ozone concentration data were collected at an urban residential area in Errenteria by a continuous UV photometer O₃ analyzer (Model 1008-RS) from January 1997 to December 2000. Daily average concentrations of CO, SO₂, NO, NO₂ and SP (suspended particles) were also computed. The oceanic climatic conditions were dominant in the sampling area. The maximum and minimum temperatures were 21°C and 12°C, respectively and the winds were moderate and marine origin. The annual mean of O₃ concentration was 30.5 ppb which was 1.2 times higher than our results. Winter to summer ratio of O₃ and NO were 0.5 and 0.8, respectively whereas the ratios for the rest of pollutants (primary ones, CO, SO₂ and NO) were greater than 1. In our study the ratio of winter to summer for O₃ concentration was approximately 0.7.

d) Nanjing, CHINA (Tu et al., 2007)

Ozone and its precursors were collected at an urban site in Nanjing in China. Ozone concentration data were gathered from UV photometric API 400 Ozone Analyzer from January 2000 and February 2003. The hourly average concentration of O₃ throughout the sampling period was 20.4 ppb.

e) Castelporziano, ITALY (Gerosa et al., 2009)

The study was conducted in Castelporziano near Rome from June to December 2004. The aim of the study was to compare the effects of O₃ exposure and fluxes on Mediterranean oak forests. During sampling a fast-response chemiluminescence O₃ sensor (OS-G-2, GFAS) and for reference a slow-response O₃ analyzer (Advanced

Pollution Instrument mod.400) were used. The average O₃ concentration at the top of the canopy throughout the sampling period was 35.7 ppb.

f) Kocaeli, TURKEY (Özbay et al., 2011)

The sampling site, Dilovası was located in north west of Kocaeli and the O₃ data used in the study was collected from September 2008 to August 2009 by Thermo Environmental model photometric O₃ analyzer. In addition to O₃, PM₁₀, SO₂, NO, NO₂ and CO were also measured in the sampling point. Due to the presence of five main industrial areas in addition to two motorways, a railway and many seaports in the sampling region then, the sampling point was in the category of industrial region. The monthly average and the maximum O₃ concentrations were 9.1 ppb and 22 ppb, respectively.

g) Santa Clara, CUBA (Alejo et al., 2011)

The study was conducted in Cuba with two sampling periods. The first one was cold season, from February 21st to April 25th, 2004 and the second one was warm season from August 8th to September 5th and in October from 10th to 31th. Sampling was carried out by Radiello O₃ passive samplers. The average O₃ concentration in cold season was 26.5 ppb and in cold season O₃ concentration was 12.2 ppb.

h) Seoul, KOREA (Susaya et al., 2013)

In the study, tropospheric O₃ concentration was monitored in seven cities over 22-year period (1989-2010) by UV photometric O₃ analyzers (Monitor Lab model 8810 and DASIBI Model 1008-AH). The whole sampling situations were a mixture of urban background and urban traffic. Only the concentration results obtained in Seoul,

the capital of South Korea, was used for the comparison. The average and the maximum O₃ concentrations were 15.0 ppb and 33, respectively.

i) Agia Marina, CYPRUS (Kleanthous et al., 2014)

The sampling was conducted from 1997 to 2012 at four monitoring stations in Cyprus. Agia Maria is the rural inland station, Inia is the rural marine station, Cavo Greco is the lower altitude rural station and Stavrovouni is the rural station. Agia Maria is the part of the European Monitoring and Evaluation Programme (EMEP) then, the result of it was used for the comparison. Ozone concentrations were measured by continuous surface UV photometric O₃ analyzer (Ecotech 9810). The average concentration throughout the sampling period was 47.5 ppb which is nearly 2 times greater than our results and the maximum concentration was 76.7 ppb.

3.2. Temporal variation of O₃ concentration and local meteorology

3.2.1. Annual variation

Through the whole sampling period (3 years (or 37 months)), ozone concentration and some meteorological parameters showed cyclic behavior in each year (Figure 3.1). Variation of O₃, temperature, wind speed, rain, solar radiation and relative humidity data were given in Table 3.3. The results in 2012 were not used for the comparison because it included only three months. The results obtained in 2010 and 2011 were similar except for the relative humidity. In 2011, the percent relative humidity (80 %) was a little bit higher than that in 2010 (69 %). The maximum O₃ concentration (125 ppb) was obtained in the 16th of July in 2009 which was the

highest value in the last three years when the maximum solar radiation (336 W m^{-2}) was lower than in 2010 (1078 W m^{-2}). This situation showed that although solar radiation is one of the basic parameters that affect the production of O_3 , it is not enough to explain the variation of O_3 individually. For better understanding of the effects of each meteorological parameter on O_3 concentration, statistical methods such as factor analysis and regression analysis were applied.

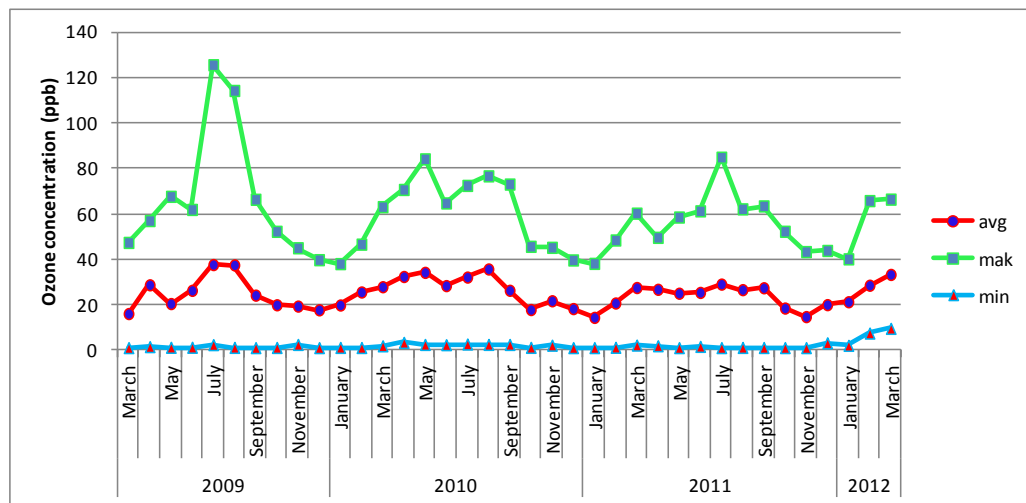


Figure 3.1. Ozone concentration through whole sampling period.

Table 3.3. Statistical summary of ozone concentrations (ppb) and meteorological parameters in each year.

		O ₃	Temperature	Wind Speed	Rain	Solar Radiation	Relative Humidity
2009	N	7126	7338	6814	594	4045	7338
	avg	25	11	2	1	336	77
	std	17	7	2	1	297	17
	mak	125	31	9	17	1018	100
	min	0.03	-5	0.4	0.2	1	19
2010	N	8727	8690	6563	554	4479	8690
	avg	27	11	2	1	299	69
	std	15	8	2	1	276	25
	mak	84	35	9	19	1078	100
	min	0.09	-13	0.4	0.2	1	0.3
2011	N	8564	7641	5864	588	4054	7641
	avg	23	9	2	1	301	80
	std	14	8	2	2	278	18
	mak	85	32	7	18	1069	100
	min	0.01	-11	0.4	0.2	1	0.3
2012	N	2182	937	792	94	455	937
	avg	28	-1	2	1	248	86
	std	11	5	1	0	230	13
	mak	66	14	8	2	863	100
	min	2	-16	0.4	0.2	1	36

Wind speed and wind directions are important factors for the estimation of the source of pollutants in local scale. These factors are also important for the dispersion of ozone precursors and for intrusion from stratosphere (Duenas et al., 2002). For that purpose, the dominant wind direction and average wind speed through whole sampling period were determined. As shown in Figure 3.2, dominant wind direction was WSW (West-South-West) with the percentage of 57 % and the highest average wind speed ($\sim 2.5 \text{ m s}^{-1}$) was observed in this direction. However, the highest average O₃ concentration ($\sim 30 \text{ ppb}$) was obtained in the southern direction (Figure 3.3). This shows that the sources of O₃ were variable and the back trajectory analysis was applied.

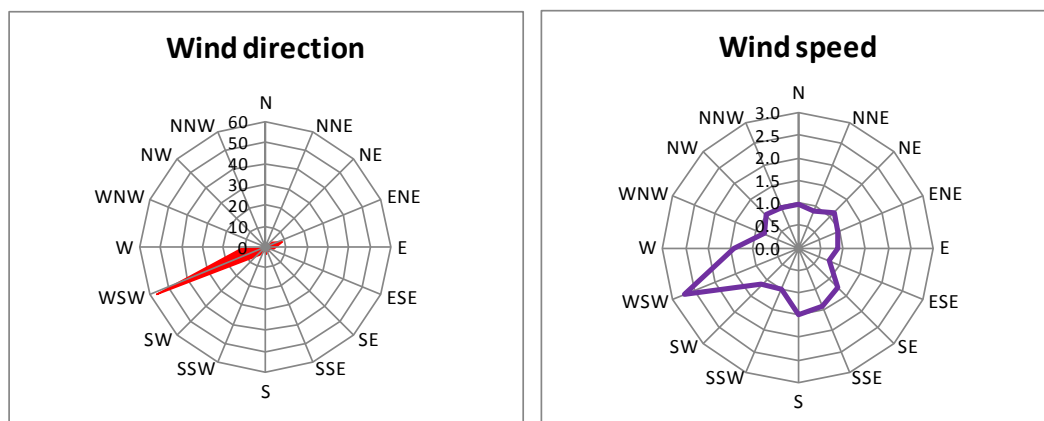


Figure 3.2. Dominant wind direction and the average wind speed in each wind direction through whole sampling period.

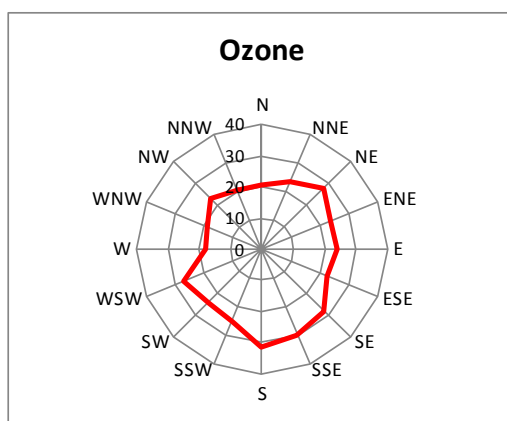


Figure 3.3. Diurnal average O_3 concentration through whole sampling period in each wind direction

The variation of average O_3 concentration and wind speed was given in Figure 3.4. The behaviors of O_3 concentration and wind speed were similar except for in WSW direction where the value of wind speed was the highest. The sharp increase of wind speed in this direction did not affect the concentration of O_3 directly. Although air parcels that contained O_3 moved with local winds in each direction, strong winds from WSW might cause the dilution of air.

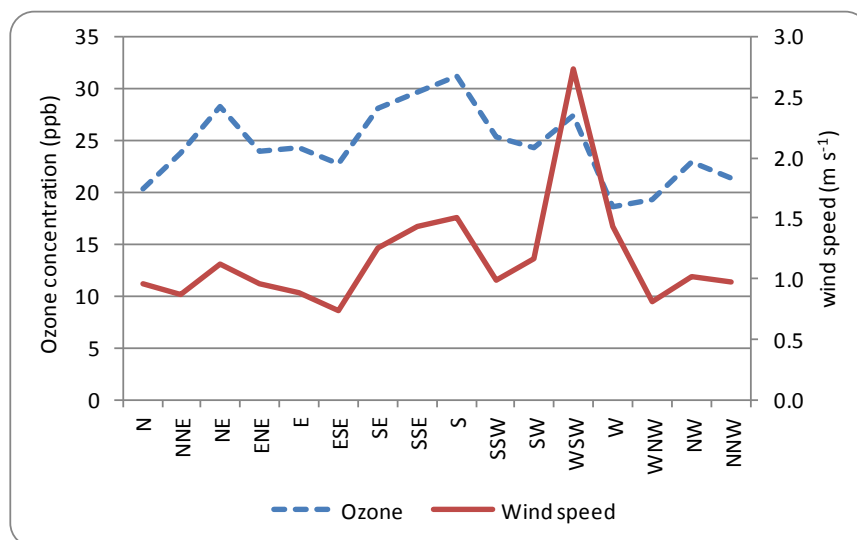


Figure 3.4. Relationship between diurnal ozone and wind speed in each wind direction.

High wind speed often implies high speed transport of air parcel, which is resulted in rapid dilution of primary pollutants, but this fact is much more complex for ozone (Shan et al., 2008). Duenas and his friends (Duenas et al., 2002) categorized the wind speeds as calm ($< 0.2 \text{ m s}^{-1}$), soft ($0.2\text{-}2 \text{ m s}^{-1}$), moderate ($2\text{-}4 \text{ m s}^{-1}$) and finally strong ($>4 \text{ m s}^{-1}$). In this study, throughout the sampling period, three of these winds; soft, moderate and strong winds were observed. The percentages of each wind were given in Figure 3.5. The dominant wind was soft wind which comprises 85 % of the total winds. Moreover, in Figure 3.6, the percentages of each wind in each wind direction were given. In WSW direction, moderate and strong winds reached their maximum percentage values whereas, soft winds had their lowest percent value in this direction.

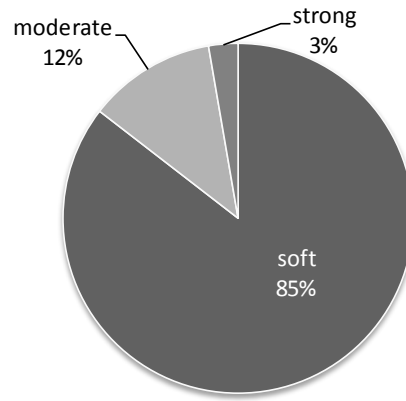


Figure 3.5. Percentage of each wind through the sampling period.

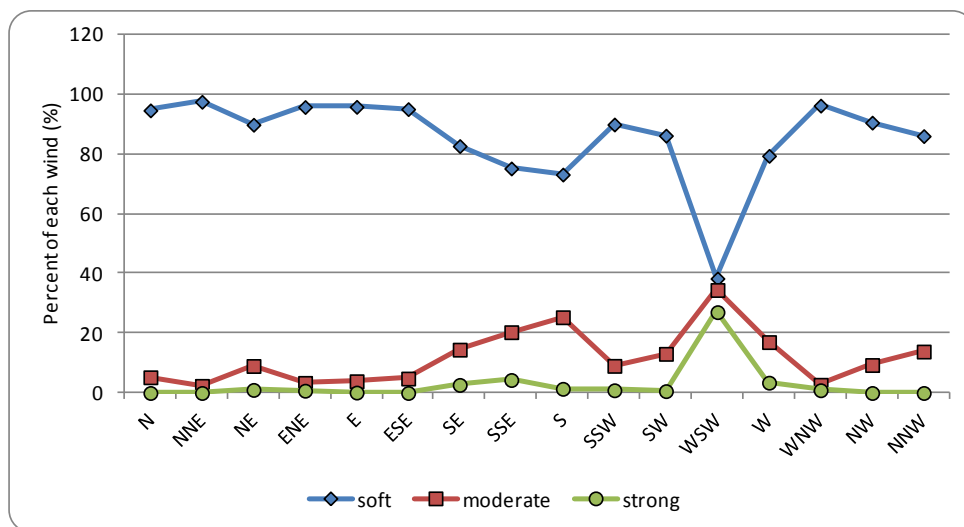


Figure 3.6. Percent of each wind speed category in each wind direction.

The maximum diurnal O_3 concentration was obtained with strong winds and minimum values were obtained with soft winds. However, the highest average O_3 concentrations were obtained when strong winds were blowing (Figure 3.7). We know that solar radiation influences O_3 production then, a new relationship between daytime O_3 and wind speed should be established.

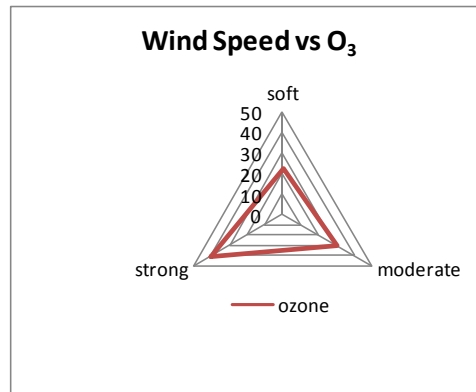


Figure 3.7. Relationship between diurnal O₃ and wind speed type.

Seasonal prevailing wind directions in each season was given in Figure 3.8. In all seasons the dominant wind direction was WSW and the percent of it was around 41 % to 65 %. Only in cold seasons (autumn and winter), wind direction of ENE was observed with 10 to 15 %.

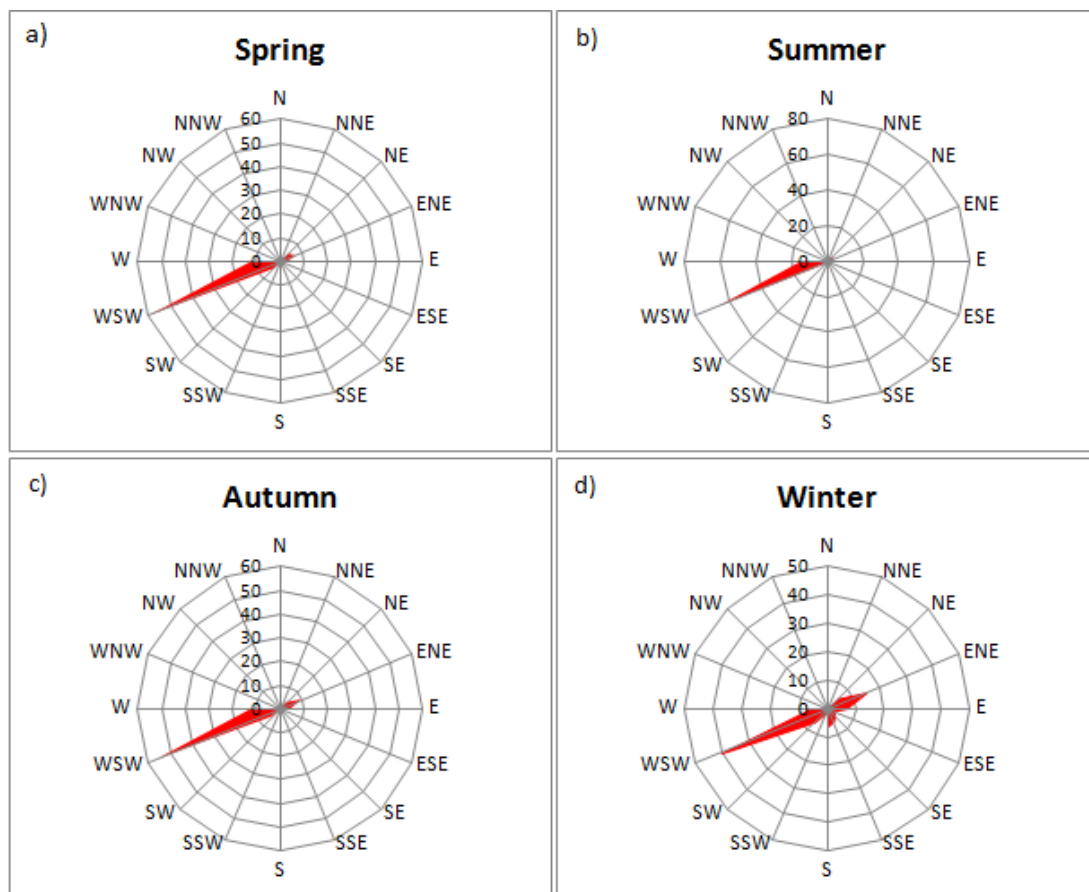


Figure 3.8. Seasonal variation of prevailing wind directions.

Ozone concentrations in each direction for each season were shown in Figure 3.9. The highest average O_3 concentrations which were higher than 35 ppb were seen in summer in the direction of NE, E and SSE. In spring and autumn the highest average O_3 concentration (>30 ppb) was observed in south direction, in winter in this direction O_3 concentration was around 28 ppb.

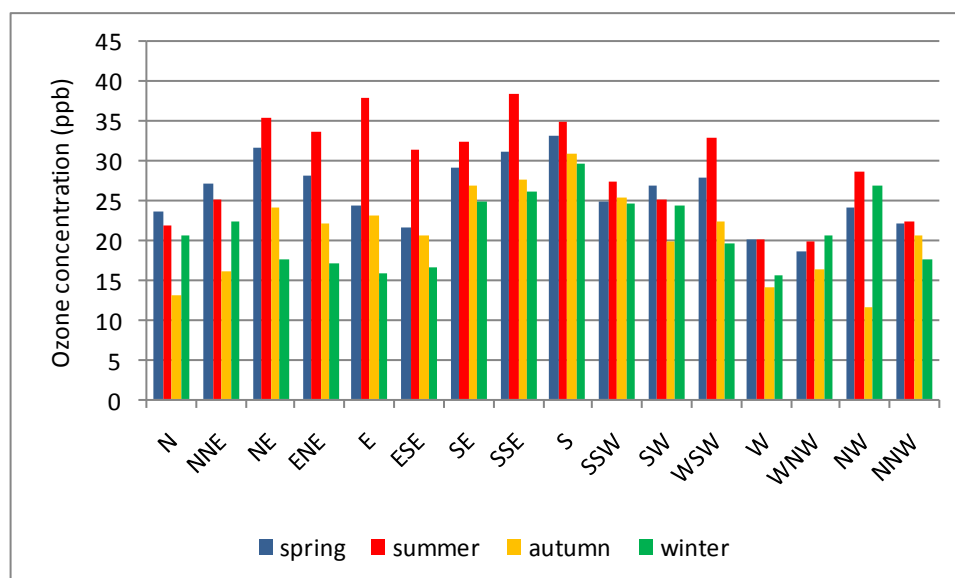


Figure 3.9. Diurnal average O₃ concentrations in each direction for each season.

Variations of wind speed in each season were given in Figure 3.10. As in annual variation, the strongest wind speed was obtained in WSW direction. In autumn and in winter, average wind speed was decreased. Except for in summer, in southern directions, wind speed was higher than 1.5 m s^{-1} . When the wind speed was related with ozone concentration it was seen that the behavior of O₃ concentration was similar to wind speed in all directions except for WSW direction in winter (Figure 3.11). When the wind speed started to change from SW to WSW direction, the concentration of O₃ became lower. In autumn the inverse relation between O₃ and wind speed was obtained in WNW direction.

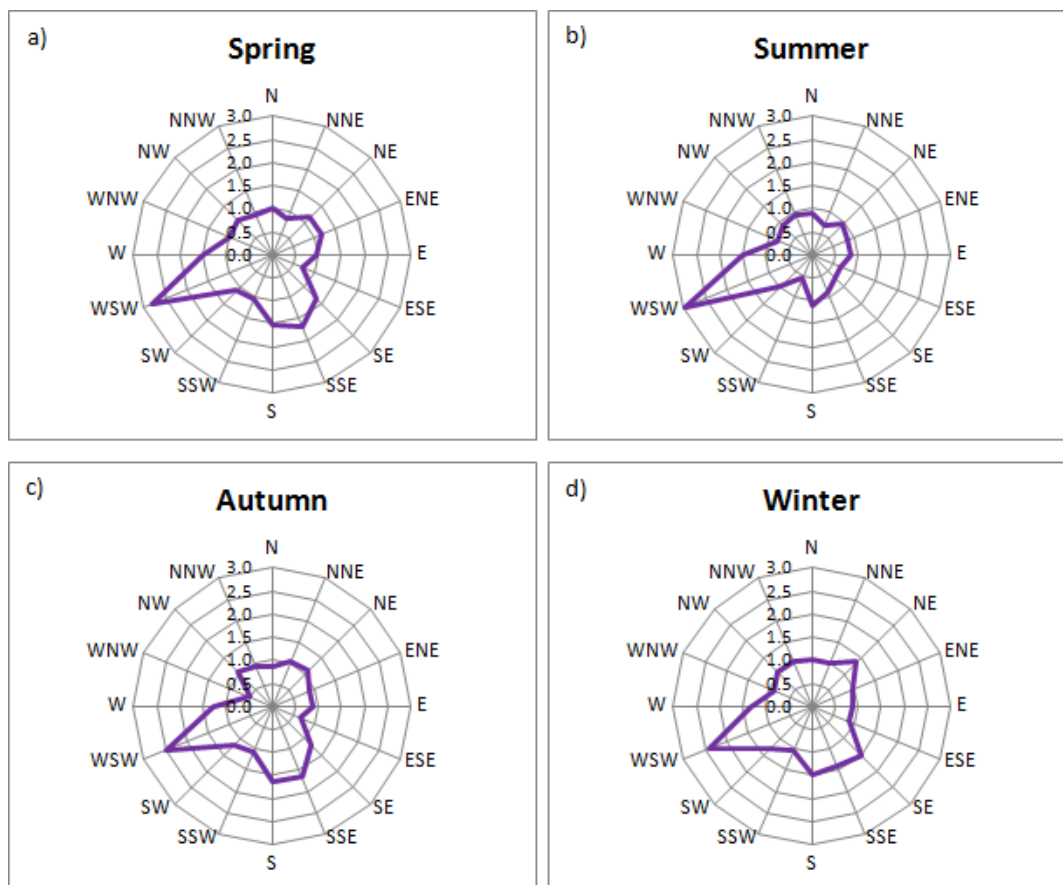


Figure 3.10. Seasonal variation of wind speed.

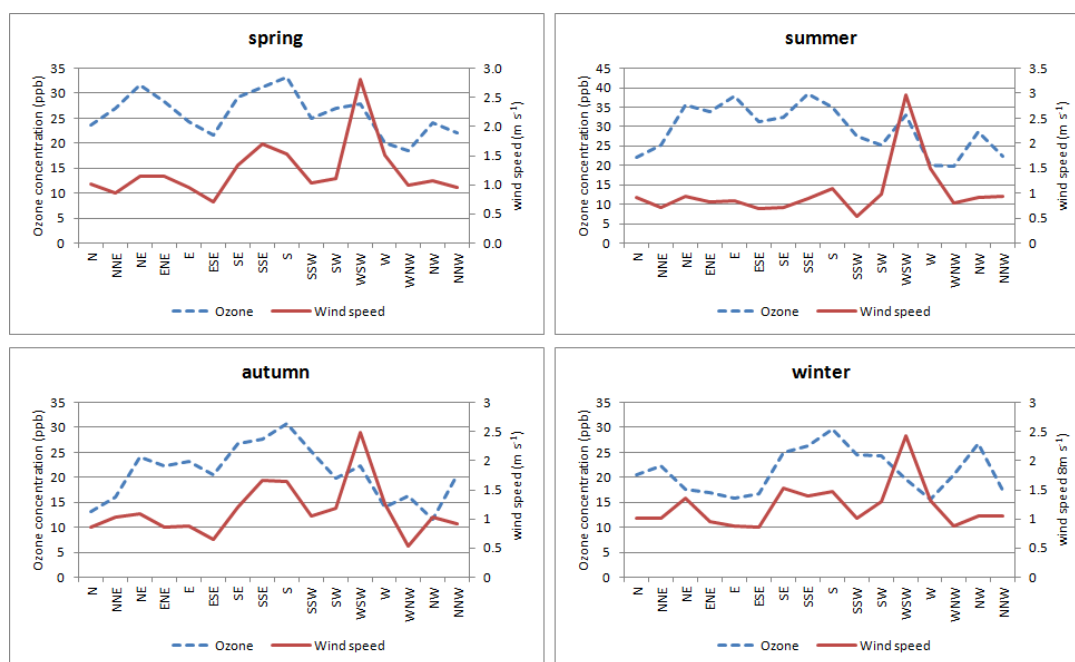


Figure 3.11. Relationship between ozone and wind speeds in each wind direction for each season.

3.2.2. Monthly variation

Diurnal variations of O₃ and meteorological parameters for each month in each year were discussed from Table 3.3 to Table 3.6. As indicated before, the maximum O₃ concentration was obtained in 2009. If monthly average values of all parameters in Table 3.4 were analyzed, it would be seen that maximum daily O₃ concentrations were obtained in July (125.5 ppb) and in August (114.2 ppb) and the highest average O₃ concentrations were again obtained in these months as 37.5 ppb and 37.4 ppb, respectively. Also in the summer period average temperature ($> 15^{\circ}\text{C}$), wind speed ($> 2.5 \text{ m s}^{-1}$) and solar radiation ($> 400 \text{ W m}^{-2}$) had maximum average values over other seasons. Finally minimum average relative humidity ($< 75 \%$) was obtained in spring.

In 2010 (Table 3.5), average O₃ concentration did not show a sharp increase in summer as in 2009. In summer the highest average O₃ concentrations ($> 30 \text{ ppb}$) were seen from April to September and the maximum O₃ concentration (84.1 ppb) was obtained in May. In this month and in June, solar radiation reached its maximum values as 1015.0 and 1078.0 W m^{-2} , respectively, whereas the highest average value of it (460.9 W m^{-2}) was seen in August. In summer, the average temperature was higher than 15°C and average wind speed was higher than 2.5 m s^{-1} . The percent relative humidity had its lowest value ($\sim 25\text{-}50 \%$) in autumn.

In 2011 (Table 3.6), the trends of each parameter except for relative humidity were similar as in the previous years. The maximum O₃ concentration (84.8 ppb) was observed in July and the maximum solar radiation (1069.0 W m^{-2}) was in June.

Again in summer the average temperature was higher than 15°C and the average solar radiation was around 400-450 W m⁻².

The first three months of 2012 were included in the sampling period and the evaluation of these months were given in Table 3.7. Each month in 2012 was compared with the same months in other years. In January, the maximum average O₃ (21.2 ppb) concentration was obtained in 2012, when the maximum average solar radiation was 185.8 W m⁻². Among the last three years (2010, 2011 and 2012), the maximum temperature in January was obtained in 2010. Although the average solar radiation in February in 2012 was the lowest (88.2 W m⁻²) the highest average O₃ concentration was obtained. Moreover, in February the highest average rainfall was observed in 2011 whereas there was no rain event in 2012. Finally, the rest of the parameters in January, in February and in March were similar in each year.

Table 3.4. Diurnal O₃ and meteorological parameters for each month in 2009.

		O ₃	Temperature	Wind Speed	Rain	Solar Radiation	Relative Humidity
MAR	avg	15.6	3.0	2.1	0.7	239.5	79.8
	std	9.8	4.9	1.3	0.7	220.2	17.2
	max	47.3	18.4	8.5	5.2	864.0	100.0
	min	0.0	-5.3	0.4	0.2	1.0	33.0
APR	avg	28.3	7.6	2.4	0.9	348.9	72.7
	std	13.9	4.8	1.7	0.9	302.5	19.8
	max	56.9	20.1	6.7	3.2	952.0	96.0
	min	0.1	-1.8	0.4	0.2	1.0	19.0
MAY	avg	20.1	12.0	2.3	1.2	388.2	74.7
	std	13.5	5.4	1.5	1.9	320.3	18.2
	max	67.6	29.3	7.2	10.4	1011.0	98.0
	min	0.0	1.1	0.4	0.2	1.0	20.0
JUN	avg	25.5	17.1	2.3	1.8	452.0	71.7
	std	15.1	5.1	1.6	3.3	332.4	17.9
	max	61.8	31.3	6.7	16.8	1018.0	97.0
	min	0.0	5.3	0.4	0.2	1.0	25.0
JUL	avg	37.5	18.2	2.6	1.1	412.5	78.9
	std	21.3	4.0	1.6	1.7	335.4	14.2
	max	125.5	27.8	6.7	11.0	1002.0	98.0
	min	2.3	9.5	0.4	0.2	1.0	31.0
AUG	avg	37.4	17.0	2.6	0.4	455.6	77.9
	std	22.2	4.3	1.8	0.3	309.8	13.9
	max	114.2	30.3	7.2	1.0	957.0	96.0
	min	1.1	7.3	0.4	0.2	1.0	27.0
SEP	avg	23.6	13.9	2.0	0.6	325.5	81.6
	std	14.6	4.2	1.4	0.8	268.7	15.6
	max	66.3	26.6	6.7	4.6	853.0	100.0
	min	0.2	3.1	0.4	0.2	1.0	29.0
OCT	avg	19.7	13.2	1.8	0.6	279.5	75.6
	std	11.6	4.8	1.3	0.9	226.9	18.9
	max	52.2	25.7	7.6	4.8	740.0	99.0
	min	0.4	5.1	0.4	0.2	1.0	23.0
NOV	avg	19.3	6.5	1.4	0.5	186.0	78.0
	std	9.7	4.5	0.9	0.4	176.3	16.0
	max	44.9	21.2	6.3	2.8	587.0	97.0
	min	2.4	-1.4	0.4	0.2	1.0	26.0
DEC	avg	17.4	4.9	1.6	0.8	124.9	78.9
	std	10.4	4.3	1.3	1.1	122.9	16.3
	max	39.7	15.8	7.2	8.9	473.6	97.0
	min	0.6	-4.2	0.4	0.3	1.1	22.0

Table 3.5. Diurnal O₃ and meteorological parameters for each month in 2010.

		O ₃	Temperature	Wind Speed	Rain	Solar Radiation	Relative Humidity
JAN	avg	19.6	1.9	1.7	0.6	129.1	82.2
	std	10.7	5.9	1.2	0.7	121.3	16.4
	max	38.0	16.9	6.7	3.8	558.1	100.0
	min	0.4	-13.1	0.4	0.3	1.2	28.0
FEB	avg	25.3	4.4	2.2	0.9	166.5	80.7
	std	11.6	5.3	1.5	1.0	156.0	15.4
	max	46.5	16.7	8.5	5.1	597.5	98.0
	min	0.4	-8.4	0.4	0.3	1.0	37.0
MAR	avg	27.8	4.6	2.3	0.9	266.8	79.3
	std	12.0	5.2	1.6	1.1	240.9	18.5
	max	63.0	20.7	7.6	7.6	829.6	98.0
	min	0.8	-6.8	0.4	0.3	1.0	25.0
APR	avg	32.3	8.5	2.1	1.2	295.7	78.1
	std	14.1	5.0	1.6	1.4	258.4	17.9
	max	70.6	22.4	7.6	7.1	913.8	98.0
	min	3.3	-1.6	0.4	0.3	1.5	24.0
MAY	avg	34.1	13.4	2.3	1.1	412.3	72.7
	std	16.2	5.6	1.5	1.4	311.9	17.6
	max	84.1	28.9	6.3	5.3	1015.0	97.0
	min	2.4	1.9	0.4	0.3	1.0	27.0
JUN	avg	28.3	16.6	2.2	1.6	365.9	82.9
	std	14.5	4.0	1.5	2.9	313.5	13.7
	max	64.7	28.7	6.3	18.5	1078.0	98.0
	min	2.3	9.5	0.4	0.3	1.0	34.0
JUL	avg	32.0	19.6	2.3	2.3	407.6	82.1
	std	16.3	3.9	1.6	3.5	322.5	13.4
	max	72.4	35.3	6.3	13.2	972.0	98.0
	min	2.6	11.2	0.4	0.3	1.0	26.0
AUG	avg	35.6	21.6	2.6	1.8	460.9	75.1
	std	17.9	4.8	1.8	0.4	295.5	17.3
	max	76.6	33.0	7.2	2.0	951.0	98.0
	min	2.4	11.4	0.4	1.5	1.0	22.0
SEP	avg	26.2	15.9	2.5	0.7	319.3	82.9
	std	14.4	4.0	1.7	1.1	266.5	15.2
	max	73.0	28.1	7.6	6.6	830.0	99.0
	min	2.4	6.5	0.4	0.3	1.0	29.0
OCT	avg	17.8	10.6	1.7	0.8	182.2	47.1
	std	11.3	4.6	1.2	0.7	176.3	22.3
	max	45.6	21.9	5.4	1.8	727.5	96.0
	min	1.1	-0.7	0.4	0.3	1.0	0.3
NOV	avg	21.6	11.6	1.7	0.0	232.4	26.1
	std	11.2	5.8	1.2	0.0	183.7	9.6
	max	45.1	25.2	5.4	0.0	595.6	57.2
	min	2.1	-0.7	0.4	0.0	1.1	0.4
DEC	avg	17.5	6.6	1.4	1.1	132.4	44.5
	std	11.7	6.3	1.1	0.8	128.3	21.7
	max	39.6	22.2	6.3	2.5	525.5	80.6
	min	0.1	-7.0	0.4	0.3	1.1	4.8

Table 3.6. Diurnal O₃ and meteorological parameters for each month in 2011.

		O ₃	Temperature	Wind Speed	Rain	Solar Radiation	Relative Humidity
JAN	avg	14.1	1.1	1.4	0.7	149.3	61.7
	std	9.6	3.4	1.1	1.1	132.1	22.3
	max	38.1	10.2	5.4	8.4	517.0	97.0
	min	0.5	-7.3	0.4	0.3	1.5	0.2
FEB	avg	20.5	1.1	1.9	2.5	237.1	68.2
	std	11.1	4.5	1.3	4.1	199.5	25.0
	max	48.4	13.1	5.8	18.3	777.0	98.0
	min	0.5	-11.0	0.4	0.3	1.0	18.3
MAR	avg	27.4	4.0	2.0	1.1	269.3	79.2
	std	12.0	5.5	1.4	2.6	246.7	18.6
	max	60.2	18.2	6.3	16.3	875.0	99.0
	min	2.1	-5.7	0.4	0.3	1.0	23.0
APR	avg	26.7	5.6	2.5	1.1	245.2	87.4
	std	12.6	3.9	1.6	1.1	244.8	12.8
	max	49.5	19.5	6.7	5.3	956.0	99.0
	min	1.8	-2.7	0.4	0.3	1.0	35.0
MAY	avg	24.7	14.6	2.0	1.7	375.6	86.1
	std	13.7	3.8	1.5	2.7	320.6	12.1
	max	58.5	23.7	5.8	13.2	1000.0	99.0
	min	0.1	3.7	0.4	0.3	1.0	36.0
JUN	avg	24.8	15.6	2.0	1.2	378.7	84.5
	std	14.8	4.2	1.5	1.5	319.1	12.9
	max	61.2	29.7	6.7	7.6	1069.0	99.0
	min	0.0	5.9	0.4	0.3	1.0	36.0
JUL	avg	28.7	19.7	2.4	1.3	442.9	80.4
	std	16.3	4.2	1.8	2.2	325.5	13.5
	max	84.8	32.1	6.3	4.6	994.0	100.0
	min	0.0	11.3	0.4	0.3	1.0	31.0
AUG	avg	26.1	16.4	2.5	1.0	409.3	83.3
	std	15.3	4.0	1.8	1.1	309.5	13.8
	max	62.1	25.9	6.3	4.1	925.0	99.0
	min	0.2	8.6	0.4	0.3	1.0	35.0
SEP	avg	26.9	15.1	2.2	0.5	369.0	77.0
	std	16.5	5.0	1.6	0.5	280.6	17.3
	max	63.4	30.1	6.3	1.8	856.0	99.0
	min	0.4	5.6	0.4	0.3	1.0	23.0
OCT	avg	18.0	8.4	1.8	1.0	215.6	85.1
	std	11.3	5.1	1.3	1.2	206.5	14.8
	max	52.2	22.2	5.8	6.9	708.0	99.0
	min	0.2	-2.6	0.4	0.3	1.0	36.0
NOV	avg	14.6	1.1	1.5	0.3	194.5	84.7
	std	9.0	3.4	1.2	0.1	175.2	12.9
	max	43.2	13.2	5.8	0.5	557.0	98.0
	min	0.5	-6.3	0.4	0.3	1.0	23.0
DEC	avg	19.9	2.2	1.2	0.6	167.3	80.5
	std	9.8	5.0	1.0	0.6	142.1	15.4
	max	43.7	13.8	5.4	3.6	465.0	98.0
	min	3.1	-8.5	0.4	0.3	1.0	22.0

Table 3.7. Diurnal O₃ and meteorological parameters for each month in 2012.

		O ₃	Temperature	Wind Speed	Rain	Solar Radiation	Relative Humidity
JAN	avg	21.2	-1.5	1.7	0.4	185.8	85.7
	std	9.1	5.1	1.4	0.3	176.7	11.7
	max	40.1	8.4	6.7	1.3	596.0	97.0
	min	2.0	-15.9	0.4	0.3	1.0	43.0
FEB	avg	28.5	-4.7	2.4	0.0	88.2	95.4
	std	9.8	0.5	1.1	0.0	79.7	0.9
	max	65.7	-3.7	4.5	0.0	238.0	96.0
	min	7.4	-5.4	0.9	0.0	2.0	93.0
MAR	avg	33.2	0.2	2.0	0.6	298.9	85.4
	std	9.5	4.3	1.4	0.5	253.0	14.7
	max	66.3	14.4	7.6	2.0	863.0	100.0
	min	9.5	-9.2	0.4	0.3	1.0	36.0

If the whole data were combined in Table 3.8, the highest average O₃ concentration was seen around 30 ppb to 35 ppb and the highest maximum O₃ concentration was observed as 125.5 ppb and 114.2 ppb in July and in August, respectively. This high values were expected due to high temperature and intense solar radiation in these months. However, beside these months, the high O₃ concentration was seen (84.1 ppb) in May. This spring time, the maximum value can be explained by regional photochemical reaction, the stratospheric intrusion and the long-range transportation (Latif et al., 2012). From June to September, the average temperature was higher than 15°C and the maximum temperature was higher than 30°C. In all months, the average wind speed was around 2.0 m s⁻¹ and rain was between 0.5 and 1.5 mm. Average solar radiation which was higher than 400 W m⁻² was obtained in July and in August. Finally, the relative humidity was 60 to 75 % in cooler season whereas in warmer and hotter seasons this value reached to 87 %.

Table 3.8. Diurnal O₃ and meteorological parameters for each month in three-years sampling period.

		O ₃	Temperature	Wind Speed	Rain	Solar Radiation	Relative Humidity
JAN	avg	18.3	0.9	1.6	0.6	149.9	74.8
	std	10.3	5.0	1.3	0.8	141.2	21.1
	max	40.1	16.9	6.7	8.4	596.0	100.0
	min	0.4	-15.9	0.4	0.3	1.0	0.2
FEB	avg	24.8	2.7	2.1	1.2	196.3	75.6
	std	11.3	5.3	1.5	2.1	179.5	21.2
	max	65.7	16.7	8.5	18.3	777.0	98.0
	min	0.4	-11.0	0.4	0.3	1.0	18.3
MAR	avg	26.3	3.2	2.1	0.8	265.9	80.6
	std	12.6	5.3	1.4	1.4	239.7	17.6
	max	66.3	20.7	8.5	16.3	875.0	100.0
	min	0.0	-9.2	0.4	0.2	1.0	23.0
APR	avg	29.1	5.6	2.5	1.1	245.2	87.4
	std	13.8	3.9	1.6	1.1	244.8	12.8
	max	70.6	19.5	6.7	5.3	956.0	99.0
	min	0.1	-2.7	0.4	0.3	1.0	35.0
MAY	avg	26.6	13.2	2.2	1.4	393.8	76.9
	std	15.8	5.2	1.5	2.1	317.4	17.5
	max	84.1	29.3	7.2	13.2	1015.0	99.0
	min	0.0	1.1	0.4	0.2	1.0	20.0
JUN	avg	26.2	16.4	2.2	1.5	399.0	79.7
	std	14.9	4.5	1.6	2.4	323.8	16.0
	max	64.7	31.3	6.7	18.5	1078.0	99.0
	min	0.0	5.3	0.4	0.2	1.0	25.0
JUL	avg	32.8	19.2	2.4	1.4	420.7	80.4
	std	18.5	4.1	1.7	2.2	328.0	13.8
	max	125.5	35.3	6.7	13.2	1002.0	100.0
	min	0.0	9.5	0.4	0.2	1.0	26.0
AUG	avg	33.0	18.6	2.6	0.8	447.0	78.1
	std	19.3	5.0	1.8	0.9	304.7	15.5
	max	114.2	33.0	7.2	4.1	957.0	99.0
	min	0.2	7.3	0.4	0.2	1.0	22.0
SEP	avg	25.6	15.0	2.3	0.6	338.0	80.5
	std	15.2	4.5	1.6	0.9	272.7	16.3
	max	73.0	30.1	7.6	6.6	856.0	100.0
	min	0.2	3.1	0.4	0.2	1.0	23.0
OCT	avg	18.5	11.0	1.8	0.9	227.6	67.5
	std	11.4	5.1	1.3	1.1	208.5	25.1
	max	52.2	25.7	7.6	6.9	740.0	99.0
	min	0.2	-2.6	0.4	0.2	1.0	0.3
NOV	avg	18.5	6.4	1.5	0.5	204.5	62.7
	std	10.4	6.3	1.1	0.4	179.5	29.3
	max	45.1	25.2	6.3	2.8	595.6	98.0
	min	0.5	-6.3	0.4	0.2	1.0	0.4
DEC	avg	18.3	4.7	1.4	0.7	140.0	67.1
	std	10.7	5.6	1.2	0.9	131.7	24.8
	max	43.7	22.2	7.2	8.9	525.5	98.0
	min	0.1	-8.5	0.4	0.3	1.0	4.8

The daily maximum and the average O₃ concentrations in each month throughout whole sampling period were summarized in Figure 3.12. From this figure, we can clearly see that in warmer seasons, O₃ concentration started to increase and reached its maximum value in summer season. Then, in order to understand the mechanism of O₃ production we should focus on the growing season (April to September in our study).

In Figure 3.13, the daily average O₃ concentrations for each month were given. The maximum deviation of the concentration values ($> \pm 15$ ppb) were obtained in the growing season, especially in May, in July, in August and in September.

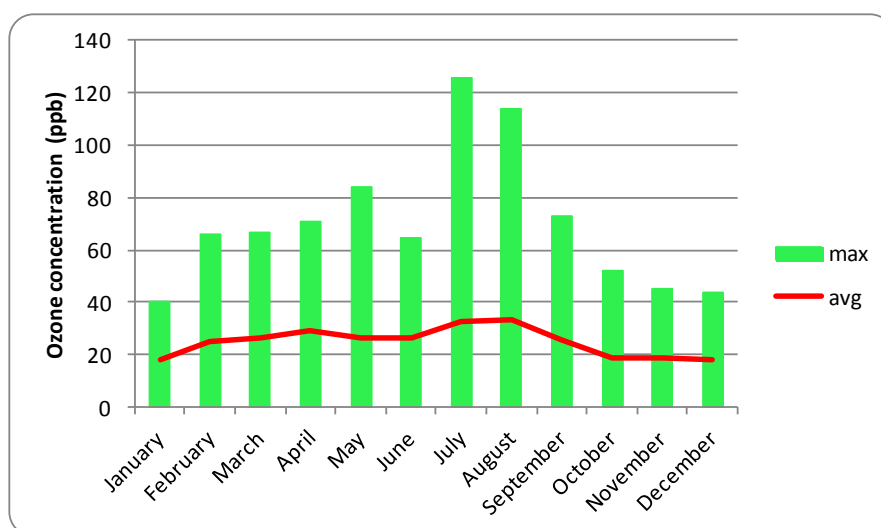


Figure 3.12. The maximum and the average ozone concentration in each month.

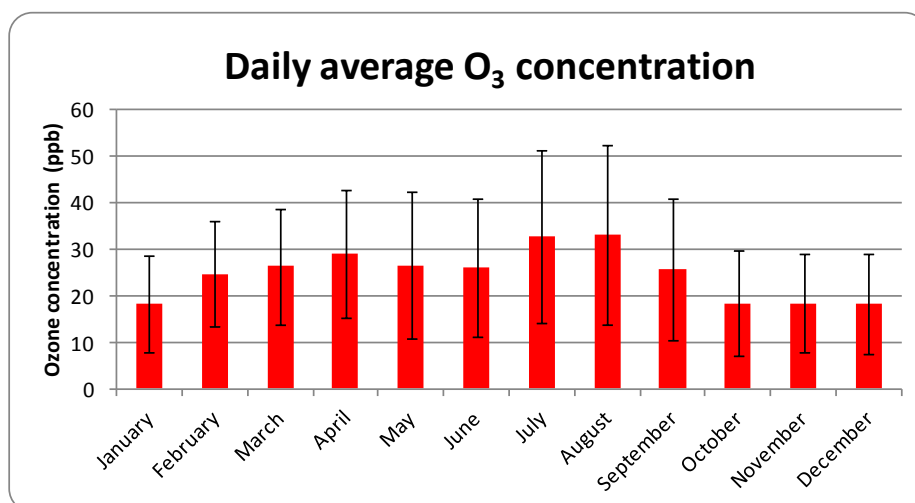


Figure 3.13. Average O₃ concentration with standard deviation for each month.

The monthly average of hourly O₃ concentration was strongly depended on the local meteorology (Figure 3.14). The episodic ozone behavior was observed both in the spring and in the summer. The highest monthly average (33 ppb) and the maximum (125 ppb) O₃ concentration was seen in the middle of dry season (July-August) when the highest average temperature (19 °C), the solar radiation (421-447 W m⁻²) and the wind speed (2.5 m s⁻¹) were reached. The prevailing winds were from west-south-west (225-247°) direction in these months. The direct relationship between the relative humidity and O₃ was seen only at the end of the winter and in the spring period whereas the meteorological parameters other than the relative humidity were much more effective in the dry season.

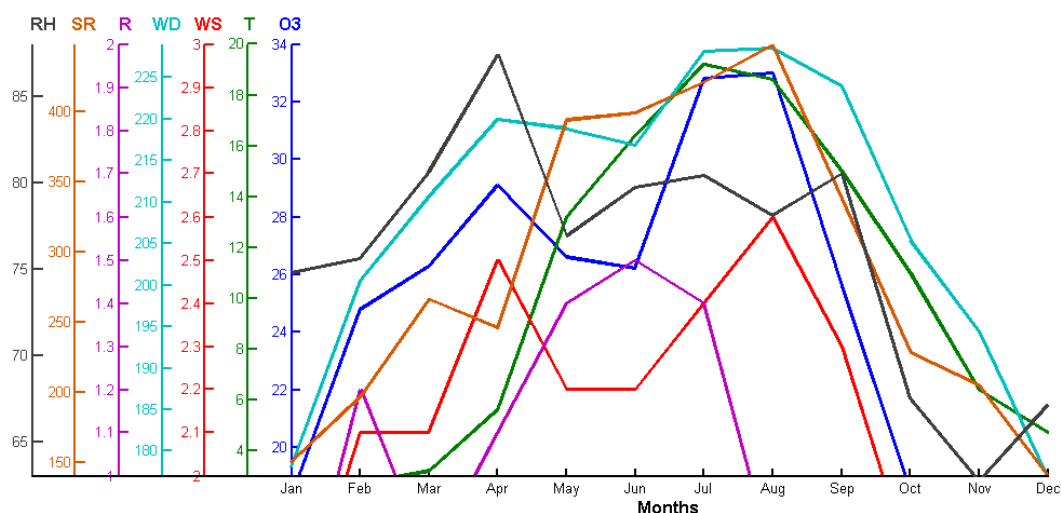


Figure 3.14. Monthly variations of each meteorological parameters and O₃ concentration.

3.2.3. Hourly variation

It was considered that solar radiation is one of the crucial parameters that influence the O₃ production. Then the behavior of O₃ variation at each hour of the day should be analyzed. Figure 3.15 shows the maximum and the average concentrations of O₃ at each hour. During the whole sampling period (26,395 hours), the maxima of O₃ concentration was higher than the threshold value of 90 ppb ($\sim 180 \mu\text{g m}^{-3}$) which is reported as hazardous to human health by United States of Environmental Protection Agency (USEPA NAAQS, 2006) and by European Union Council Directive (EU Council Directive 2002/3/EC) and it was observed between 06:00 and 19:00 (daytime hours). In June 17 (O₃ episode), at 03:00 and 04:00 high O₃ concentrations (90-96 ppb) were also observed. The increase in O₃ concentration before early morning may be due to intrusion from stratosphere or may be due to lower height of mixing layer or the transport of air masses that has high concentration of O₃ (Shan et

al., 2008). The stratospheric intrusion requires a systematic monitoring of the tracers of stratospheric ozone and the other precursors. The mass transfer from the stratosphere to troposphere at mid-altitudes is controlled non-locally by dynamic processes of global scale circulation in the middle atmosphere (Stohl et al., 2000). In this study the increase of O_3 concentration can be explained with the mixing height or the transportation of air mass including O_3 . In section 3.4.8. the O_3 episodes were discussed. Figure 3.47 shows the backtrajectory in July 17 and Figure 3.39 gives the diurnal variation of both mixing height and wind speed. There was not an obvious change in the mixing height whereas the wind speed was reached its maximum value at 03:00-04:00 in July 17. Then it can be considered that the increase of O_3 concentration at night may be due to the transportation of O_3 riched air mass from the north side of the sampling point.

Moreover, meteorological parameters also play important roles in diurnal variation of O_3 (Tu et al., 2007). However, these instant maxima did not affect the average O_3 concentration. The sharp decrease of O_3 concentration during 18:00-21:00 might be due to the O_3 depletion by reaction with NO emitted from the late rush-hour traffic (Shan et al., 2008).

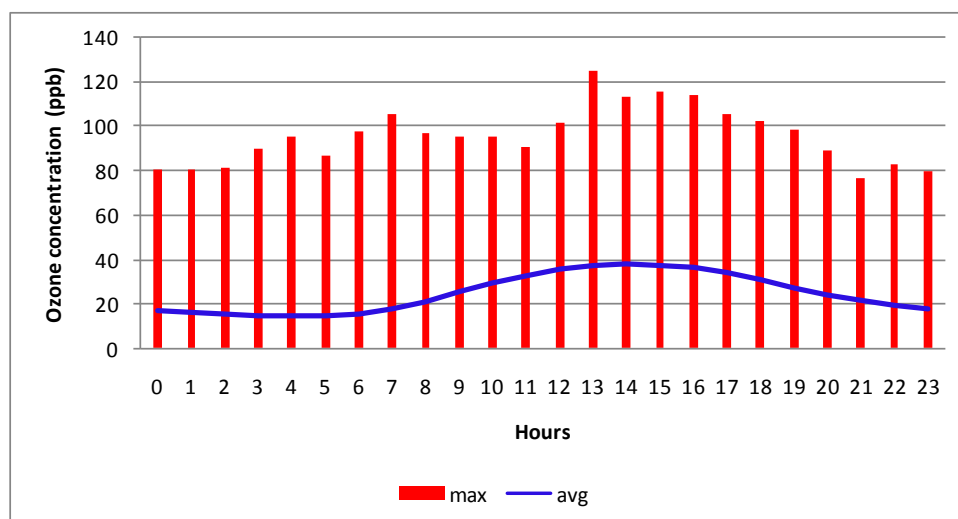


Figure 3.15. The maximum and the average diurnal O₃ concentration with respect to each hour.

As a matter of the fact, the solar radiation is required for O₃ production; consequently daylight hours become crucial for the assessment of ozone production (Markovic and Markovic, 2005). Camalier et al., (2007) define daylight hours as 07:00-16:00, Duenas and his friends (Duenas et al., 2002) used day time and night time as 07:00-19:00 and 20:00-06:00, respectively. Hourly ozone concentration and the meteorological parameters in daylight hours (06:00-19:00) in our study were given in Table 3.9.

Table 3.9. Daytime O₃ concentration and meteorological parameters in whole sampling period.

Hour		O ₃	Temperature	Wind Speed	Rain	Solar Radiation	Relative Humidity
06:00	avg	15.6	6.7	1.3	0.6	16.8	85.2
	std	10.2	6.4	1.0	1.1	21.2	17.5
	max	97.4	21.1	5.8	6.6	136.0	100.0
	min	0.2	-13.1	0.4	0.2	1.0	0.3
07:00	avg	17.4	7.0	1.2	0.7	51.5	84.7
	std	10.1	6.6	1.0	1.1	59.8	17.8
	max	105.9	21.7	6.3	7.6	365.0	100.0
	min	0.9	-12.9	0.4	0.2	1.0	0.4
08:00	avg	20.9	7.9	1.2	0.6	120.9	82.5
	std	10.7	6.9	1.0	0.6	113.3	18.5
	max	97.4	21.8	6.3	3.1	549.0	99.0
	min	0.0	-11.9	0.4	0.2	1.1	0.2
09:00	avg	25.3	9.3	1.2	0.6	246.9	78.3
	std	11.8	7.3	1.0	0.8	168.0	19.0
	max	95.4	24.8	6.7	5.8	699.0	99.0
	min	1.1	-11.1	0.4	0.2	6.8	1.3
10:00	avg	29.6	10.9	1.3	0.8	383.4	72.7
	std	12.6	7.7	1.1	0.9	217.5	19.4
	max	95.2	27.5	6.3	4.3	832.0	99.0
	min	0.3	-10.4	0.4	0.2	17.0	1.0
11:00	avg	32.8	12.2	1.6	1.0	482.0	66.7
	std	13.1	8.3	1.2	2.0	257.4	20.4
	max	91.1	30.2	6.3	18.3	979.0	99.0
	min	0.5	-10.5	0.4	0.2	20.7	1.0
12:00	avg	35.5	13.4	2.1	0.8	534.2	62.6
	std	13.6	8.5	1.4	0.7	283.4	21.3
	max	101.9	32.1	7.2	3.6	1028.0	100.0
	min	3.9	-8.1	0.4	0.2	18.2	0.8
13:00	avg	37.5	14.0	2.7	0.8	533.1	61.5
	std	14.2	8.5	1.5	0.8	295.0	22.0
	max	125.5	32.9	7.6	3.8	1078.0	98.0
	min	4.4	-8.1	0.4	0.2	24.0	0.8
14:00	avg	38.3	14.2	3.2	0.8	491.8	61.8
	std	14.3	8.5	1.7	1.2	301.1	22.0
	max	113.4	35.3	7.6	7.1	1029.0	99.0
	min	4.4	-7.6	0.4	0.2	21.0	1.1
15:00	avg	37.8	14.1	3.5	1.0	420.7	62.6
	std	14.2	8.5	1.7	1.7	289.8	21.8
	max	116.1	35.1	7.6	13.2	1025.0	99.0
	min	3.3	-7.6	0.4	0.2	4.0	2.2
16:00	avg	36.6	13.8	3.6	1.0	314.0	63.9
	std	14.2	8.5	1.7	1.7	265.5	21.6
	max	114.2	32.5	7.6	13.2	987.0	99.0
	min	1.4	-7.5	0.4	0.2	6.4	1.5
17:00	avg	34.5	13.1	3.5	0.9	219.6	66.1
	std	14.4	8.5	1.7	1.0	218.2	21.2
	max	105.7	31.2	7.6	5.3	725.0	99.0
	min	0.5	-7.8	0.4	0.2	1.0	1.9
18:00	avg	31.2	12.3	3.2	1.2	182.4	69.1
	std	14.0	8.4	1.7	2.5	151.6	20.2
	max	102.7	29.8	8.5	18.5	606.0	99.0
	min	0.2	-8.1	0.4	0.2	1.0	0.8
19:00	avg	27.3	11.4	2.8	1.0	106.4	72.5
	std	12.7	8.1	1.5	1.1	78.1	19.1
	max	98.4	28.0	7.6	5.1	355.0	100.0
	min	0.1	-8.2	0.4	0.2	1.0	0.6

Diurnal cycle of O₃ concentration and meteorological parameters were given in Figure 3.16. Apart from the relative humidity and rain, other meteorological parameters and O₃ had similar behavior throughout the day. In early hours (02:00-05:00), the air was stagnant, the temperature was at minimum, the humidity was at maximum and the absence of radiation resulted with the minimum O₃ concentration (13 ppb). When the solar radiation and the temperature increased, O₃ concentration began to increase and reach its maximum at noon hours. The daily highest average O₃ (38 ppb) and temperature (14 °C) was observed from 13:00-15:00. This increase in O₃ concentration during the daylight was attributed to the combined effects of photochemical process. At the beginning of the sunset (at 16:00), the descent of O₃ concentration began and the lower night-time O₃ was the result of destruction by the reaction with O₃ and NO (Duenas et al., 2002).

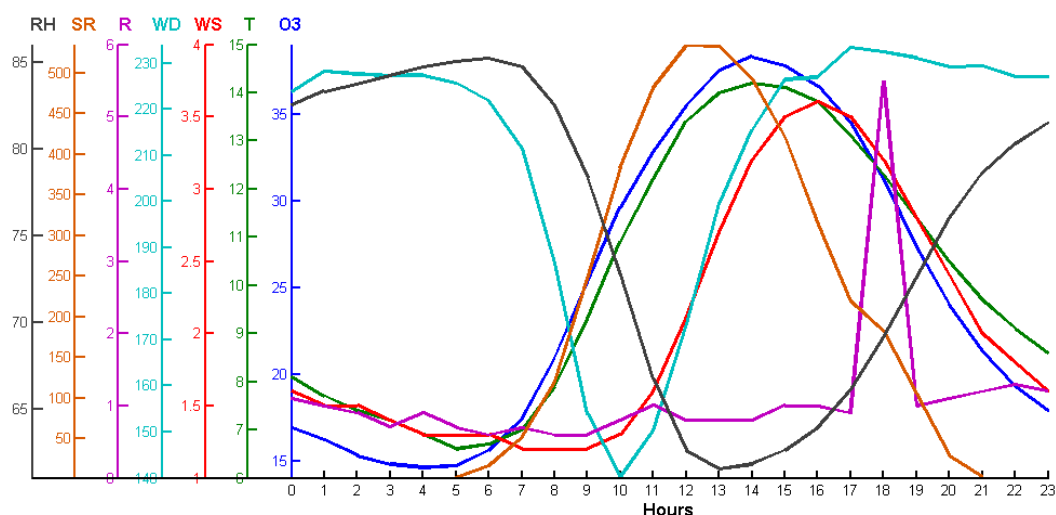


Figure 3.16. Hourly variations of each meteorological parameters and O₃ concentration.

3.2.4. Variation in the growing season

The harmful effects of O₃ on vegetation, forests and human health are generally seen during the growing season (Lengyel et al., 2004). The main reason is the effective photochemical reaction in this season (Dawson et al., 2007). Time interval of growing season can be ranged according to the location on Earth surface. The solar flux is different in each latitude because the incoming lights from sun reach to the surface in different latitudes with different angle.

Gvozdic et al., (2011) conducted their study in order to determine the influences of meteorological parameters on O₃ concentration between June to October. Moreover, Duenas et al., (2002) concluded that summer season is much more suitable to study the behaviour of photochemical origin of O₃ production.

In this study the growing season was defined from April to September. The average diurnal O₃ concentration and the temperature were given in Figure 3.17. Ozon concentration values in the growing season was same as throughout the whole sampling period (~25 ppb), the only difference was the minimum average concentration. It was 20 ppb in the former and 14 ppb in the latter. In summer months, O₃ concentration and temperature showed similar behaviors (as one of them increased the other one also increased). In these months beside the temperature, the effect of solar radiation on O₃ concentration was also observed. However, in the spring months, O₃ concentration decreased when temperature increased. This situation was observed three times; in May 2009, in June 2010 and in May 2011. Although the temperature and solar radiation in May 2009 was higher than in April the O₃ concentration was lower. The main reason may be the increase in relative

humidity in May. In the second date; June 2010, although the maximum solar radiation (1078 W m^{-2}) and the high average temperature (16.6°C) was obtained, O_3 concentration was low. The main reason may be the maximum rain fall (18.5 mm) and high relative humidity (89.2 %) in this month. In the last event; May 2011, the same situation observed in May 2009 was seen. The negative effect of relative humidity was dominant on O_3 concentration beside the temperature and the solar radiation.

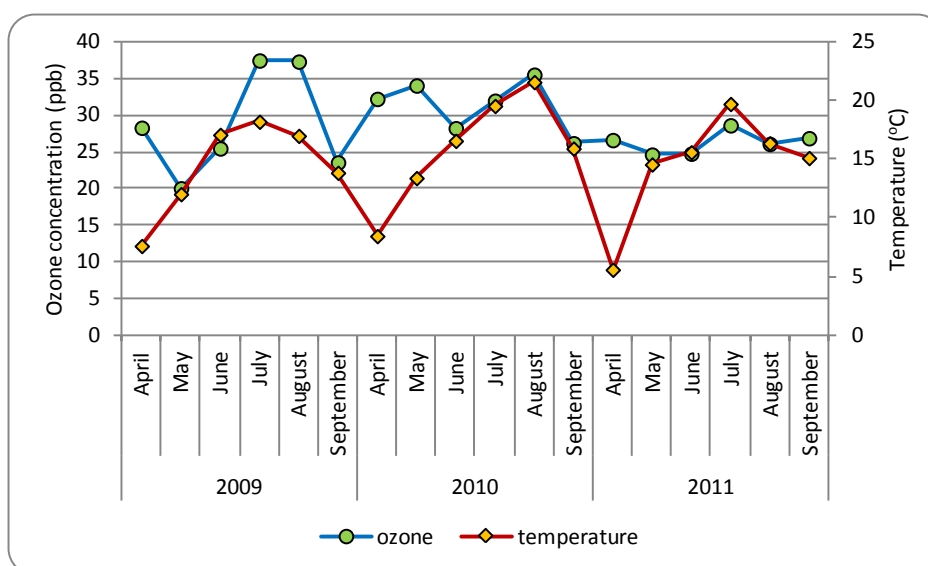


Figure 3.17. Average diurnal O_3 concentration and temperature in growing season.

The variation of wind direction and wind speed in the growing season should be analyzed in whole sampling period. The dominant wind direction was WSW with 64 % and the maximum average wind speed (2.9 m s^{-1}) was obtained in this direction (Figure 3.18).

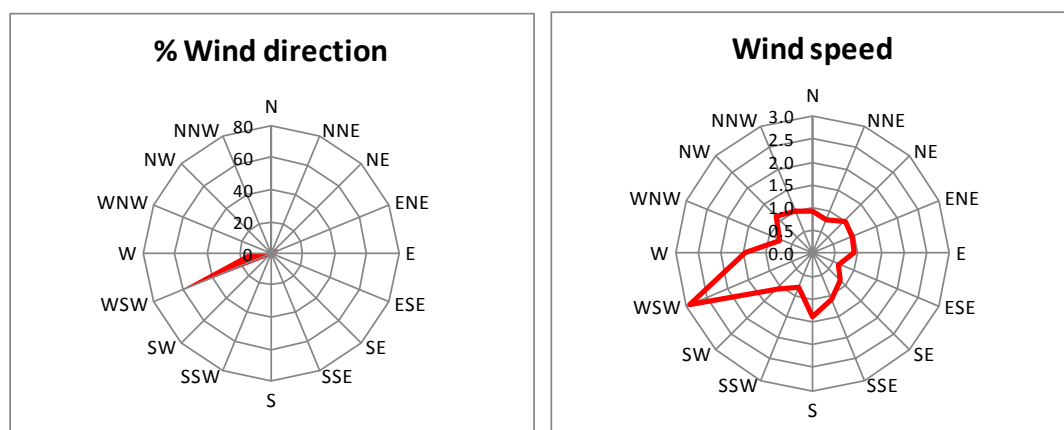


Figure 3.18. The dominant wind direction and the average wind speed in each direction throughout the growing season.

In Figure 3.19, the distribution of wind types in the growing season was shown. The values were very different when compared with the whole sampling period (Figure 3.5). The percentage of soft, moderate and strong winds in the growing season was 40 %, 32 % and 28 %, respectively whereas these values in whole sampling period were 85 %, 12 % and 3 %.

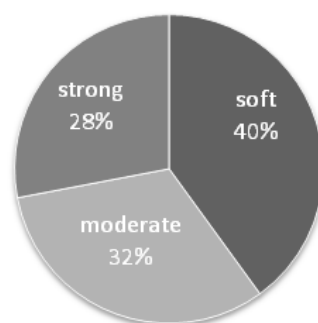


Figure 3.19. Types of wind speed and their percent distributions in the growing season.

Figure 3.20 gives the variation of diurnal O_3 concentration in each direction with the classification of each wind type. The highest maximum diurnal O_3 concentration (125 ppb) was seen in WSW direction when the strong winds were blowing and the lowest maximum diurnal O_3 concentrations (~ 40 ppb) were seen in SW and WNW where the strong and the moderate winds were dominant. In all directions, soft winds were detected and the average maximum diurnal O_3 concentration was around 66 ppb.

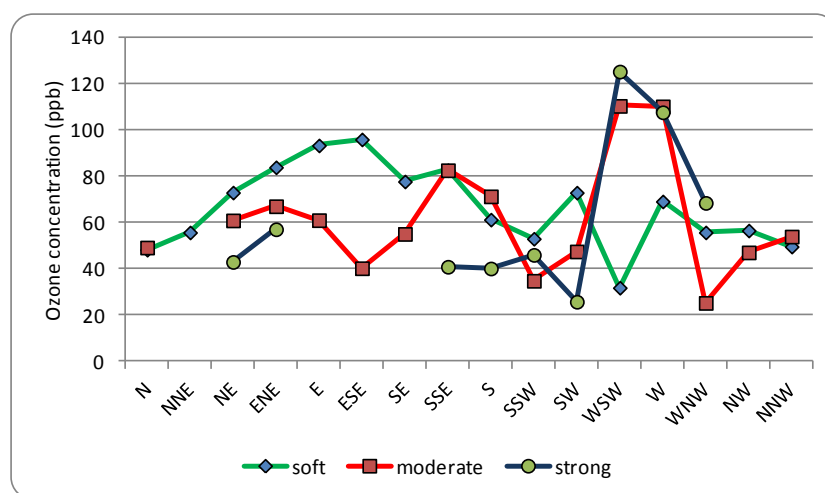


Figure 3.20. The maximum diurnal O_3 concentration in each wind direction with each wind type in the growing season.

In the growing season, the average diurnal O_3 concentrations in each wind direction were indicated in Figure 3.21. The maximum average O_3 concentration was around 35.5 ppb and was seen in SSE and S directions, however in the dominant wind direction (WSW), the average concentration value was 31 ppb.

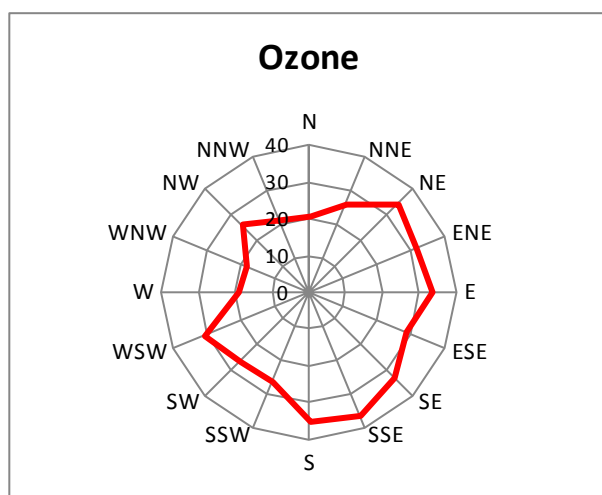


Figure 3.21. The average O₃ concentration in the growing season with respect to each wind direction.

The Box-Whisker plot in Figure 3.22 shows a graphical summary of variation of O₃ concentrations in daytime hours. In Box-Whisker graphs, the horizontal lines in the boxes are the median of the data, upper and lower boxes are the quartiles, the lines in the top and the bottom of the boxes are the whiskers which show the extent of data, stars are the outliers and finally circles are the extreme values in data set. The maximum average O₃ concentration was around 47 ppb at 14:00 and the minimum average O₃ concentration was 15 ppb at 06:00.

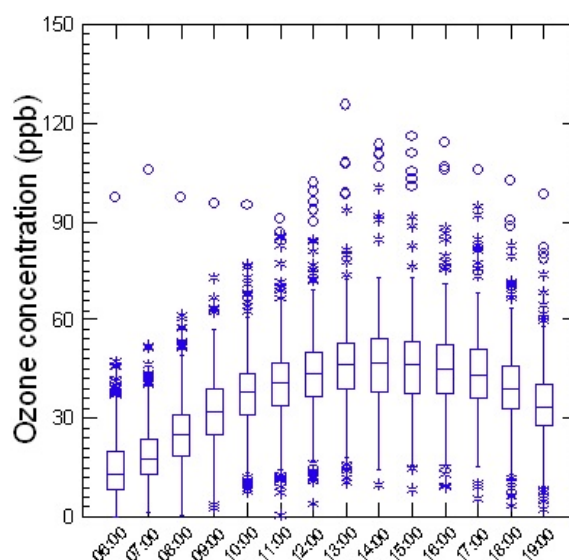


Figure 3.22. The daytime O₃ variation in the growing season

In order to determine the possible effects of meteorological parameters (temperature, solar radiation, relative humidity, rain and wind speed) on the concentration of O₃ concentration, each parameter was assessed during daylight time and the results were summarized in Figure 3.23. The variation of the amount of rain was discrepant in each hour because rain is season-dependent parameter. Then to discuss the effect of rain on O₃ production or destruction during daytime is not rational. Solar radiation and temperature had their maximum average value around at 13:00-14:00 and wind speed reached its maximum value at 16:00 as discussed before.

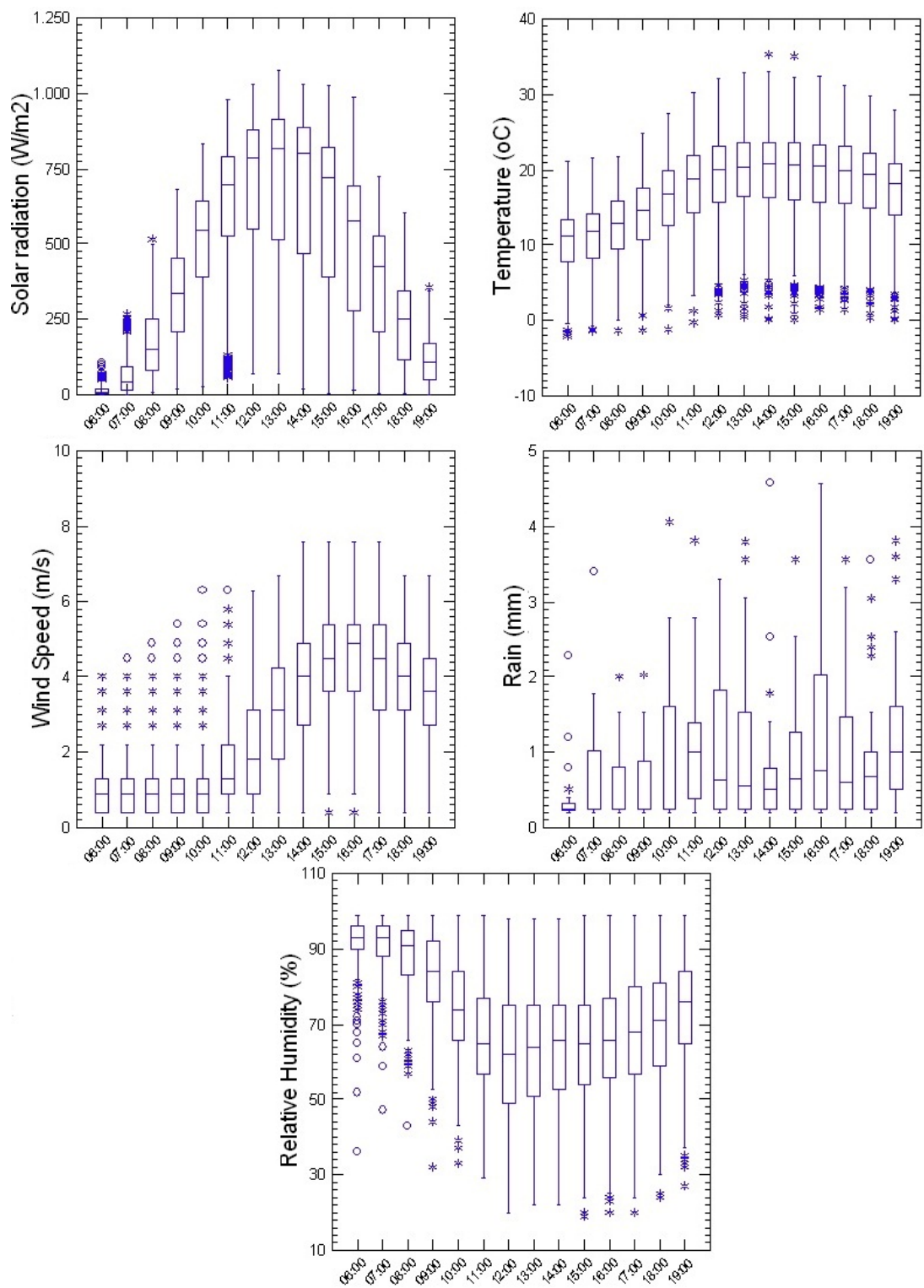


Figure 3.23. Variation of average daytime meteorological parameters in the growing season.

3.3. Assessment of O₃ variation with meteorology

Meteorological conditions have strong influences on the efficiency of photochemical process leading to O₃ formation and destruction (Bröniman and Neu, 1997). Also it is obvious that the meteorology plays an important role in the pollutant dispersion, dilution and transportation. The variation in meteorological parameters can affect the temporal variation in O₃ concentration and its precursors. Therefore, determination of the influences of meteorological parameters on O₃ at a specific site can contribute to a better understanding of local and regional sources of O₃ pollution (Tu et al., 2007). Apart from exceptions many studies show that the most effective meteorological parameters are temperature and solar radiation that enhanced the O₃ production whereas relative humidity, rain and wind speed which reduced the O₃ concentration (Kovac-Andric et al., 2009; Shan et al., 2009; Permadi and Oanh, 2008; Duenas et al., 2002; Gvozdic V. et al., 2011; Camalier et al., 2007).

In order to identify the major factors that affect O₃ concentration, several investigations have been applied. Multivariate methods frequently used for handling of monitoring data to model the air quality (Lengyel et al., 2004). These methods used in this study were binary correlations, multiple linear regression and factor analysis. During the whole statistical analysis, the hourly daytime (06:00-19:00) O₃ concentration in the growing season (April-September) was used as an input. All of the analysis was performed at 95 % confidence level ($p < 0.05$).

3.3.1. Binary correlation

Concentration variation of O₃ in daytime hours can be explained by correlation of it with meteorological parameters. The results of binary correlations were given in Table 3.10. The first row gives the correlation coefficients and the second row gives the p-values of each correlation in paranthesis. The pair(s) of variables with positive correlation coefficients and p-values below 0.050 tend to increase together. For the pairs with negative correlation coefficients and p-values below 0.050, one variable tends to decrease while the other increases. For pairs with p-values greater than 0.050, there is no significant relationship between the two variables.

Table 3.10. Binary correlation table of daytime O₃ concentration and meteorological parameters (p<0.05).

	Temperature	Wind speed	Wind direction	Rain	Solar radiation	Relative humidity
Ozone	0.541 (0.000)	0.488 (0.000)	-0.071 (0.000)	0.0101 (0.369)	0.664 (0.000)	-0.602 (0.000)
Temperature		0.322 (0.000)	-0.047 (0.000)	-0.088 (0.000)	0.559 (0.000)	-0.532 (0.000)
Wind speed			0.330 (0.000)	0.059 (0.000)	0.367 (0.000)	-0.317 (0.000)
Wind direction				0.0115 (0.287)	-0.193 (0.000)	0.169 (0.000)
Rain					-0.076 (0.000)	0.107 (0.000)
Solar radiation						-0.669 (0.000)

Ozone had correlations with all parameters except for the rain. The correlation coefficients of ozone and the temperature, the wind speed and the solar radiation were around 0.48 to 0.54 and the correlation coefficients of ozone with relative humidity and wind direction were -0.602 and -0.07, relatively. Ozone is positively correlated with variables such as the temperature (T), the solar radiation (SR) and the wind speed (WS) as it has been reported by other studies (Özbay et al., 2011; Abdul-Wahab, et al., 2005; Tu et al., 2007) with coefficients of 0.541, 0.664 and 0.488, respectively. Moreover, O_3 was negatively correlated with the wind direction (-0.071) and the relative humidity (-0.602). The temperature showed a significant positive correlation with the solar radiation (0.559) and the wind speed (0.322). The relative humidity showed high negative correlations with the temperature. This observation was also reported by other researchers as in the study of Abdul-Wahab, et al., (2005). The relative humidity, the wind speed and the solar radiation showed a significant negative correlation with the coefficients of -0.602, -0.317 and -0.669, respectively. The wind direction and the solar radiation showed positive correlation with the wind speed. The correlation coefficients of 0.330 and 0.367, were obtained respectively. The highest correlation between the temperature and O_3 was expected. Ozone concentration was influenced by the temperature because of temperature dependences of many reactions like VOC, PAN (peroxyacetyl nitrate) and NO_x decompositions (Özbay et al., 2011, Dawson et al., 2007; Kovac-Andric et al., 2009). The ozone precursors are generally emitted from the motor vehicles. In this study, the heavy traffic from the highways (TEM and D-100) and the forest were thought to be effective emitters of biogenic VOCs and NO.

3.3.2. Multiple Linear regression

Multiple linear regression (MLR) is one of the most frequent method used for predicting ozone concentration in dependence of meteorological parameters (Kovac-Andric et al., 2009; Shan et al., 2008; Gvozdic et al., 2011; Lengyel et al., 2004). Hourly daytime O₃ concentration was taken as dependent and meteorological parameters were taken as independent variables as indicated in the following equation (Eq 3.1). At 95 % confidence level, the results of MLR was given in Table 3.11.

$$C_{O_3} = 44.517 + 0.146T + 2.682WS - 0.0102WD + 2.041R + 0.0175SR - 0.313 RH \quad (R^2 = 0.630) \quad \text{Eq (3.1)}$$

Table 3.11. Multiple linear regression results in 95 % confidence level.

Variables	Coefficients	Std. Error	t	P
Constant	44.517	0.942	47.253	<0.001
Temperature (T)	0.146	0.022	6.807	<0.001
Wind Speed (WS)	2.682	0.076	35.279	<0.001
Wind direction (WD)	-0.010	0.002	-5.870	<0.001
Rain (R)	2.041	0.199	10.245	<0.001
Solar Radiation (SR)	0.018	0.0005	34.053	<0.001
Relative Humidity (RH)	-0.313	0.009	-34.614	<0.001

Rain was included in MLR analysis. However, daily rain data composed of 19.7 % of the whole growing season in three years and hourly rain data composed of only 5.4

% of the whole data set. In order to evaluate the relationship between rain and O₃ concentration only rainy days should be considered. The MLR equation in rainy days was given in Equation 3.2.

$$C_{O_3} = 74.729 + 0.043T + 2.456WS + 0.486R - 0.585 RH (R^2 = 0.214) \text{ Eq (3.2)}$$

Moreover, temperature is the indicator of solar radiation (Tu et al., 2007) and solar radiation comprises 50 % of the diurnal data set, then in the MLR analysis, solar radiation was not included (Eq 3.3).

$$C_{O_3} = 45.558 + 0.647T + 3.448WS - 0.031WD - 0.338RH (R^2 = 0.517) \text{ Eq(3.3)}$$

The percent contribution of each dependent variable to the independent variable can be calculated by the formulas given in Equation 3.4 to Equation 3.6.

$$Y = \sum_{D_i=1}^n X_{D_i} \quad \text{Eq (3.4)}$$

$$\% \text{ contribution of } D_i = \frac{X_i}{ID} \times 100 \quad \text{Eq (3.5)}$$

$$X = \frac{Coef_{MLR} D_i \times CC_{Pearson} (ID \text{ vs } D_i) \times Stdev D_i}{Stdev \text{ of } ID} \quad \text{Eq (3.6)}$$

ID = independent variable (O₃)

D_i = the dependent variable (i =temperature)

Y = total contribution of independent variables

X_i = contribution of i dependent variable

$\text{Coeff}_{\text{MLR}} D_i$ = multiple linear coefficient of i dependent variable

$\text{CC}_{\text{Pearson}} (\text{ID vs } D_i)$ = pearson product correlation coefficient between independent and i dependent variable

$\text{Stdev } D_i$ = standard deviation of i dependent variable

Stdev ID = standard deviation of independent variable

The percent contribution of the temperature, the wind speed, the wind direction and the relative humidity are 25.8 %, 31.4 %, 2.0 % and 40.8 %, respectively. The most dominant factor was the relative humidity. Although the prevailing wind direction was from the west-south west through the whole sampling period, O_3 concentration was not high from that direction. Negative sign of WD indicates the dilution of O_3 concentration. Daytime and night time multiple linear regression results and the percent contribution of each parameter for each equation were given in Table 3.12. At daytime the contributions of temperature and solar radiation were high (photochemical reactions) however, at night time, the most dominant factor was wind speed. The possible effects of wind speed on O_3 concentration might be dilution or transportation of O_3 rich air to the sampling site (Tu et al., 2007; Shan et al., 2008). Here, the contribution of wind speed on high O_3 concentration can be explained by the second effect.

Table 3.12. Multiple linear regression and the percent contribution results for each meteorological parameters in the growing season at daytime and at night time.

	R^2	T	WS	WD	SR	RH
<i>Daytime (06:00-19:00)</i>						
$C_{O_3} = 17.51 + 0.58T + 1.55WS + 0.01WD + 0.02SR - 0.05RH$	0.490	41.4	14.2	1.23	38.5	4.73
$C_{O_3} = 25.31 + 0.83T + 2.19WS - 0.12RH$	0.446	65.0	22.4	-	-	12.6
$C_{O_3} = 24.74 + 1.79WS + 0.02WD + 0.02SR - 0.11RH$	0.424	-	19.2	2.64	65.1	13.0
<i>Night time (20:00-05:00)</i>						
$C_{O_3} = 36.44 + 0.08T + 3.94WS - 0.01WD - 0.26RH$	0.223	4.13	64.7	0.18	-	31.1

If we elaborate the diurnal period with respect to time intervals, the percent contribution of each parameter will be changed. Twenty four hour can be classified in to 6 different period as early morning (05:00-07:00), morning (08:00-10:00), midday (11:00-14:00), afternoon (15:00-18:00), evening (19:00-21:00) and night (22:00-04:00). Multiple linear regression results and the percent contribution of parameters that appear to contribute to predict O_3 variation at 95% confidence level are given in Table 3.13. The contribution of wind speed in the early morning, in the evening and at night were the highest as 75.1 %, 51.6 % and 68.0 %, respectively. In the morning, the effects of the wind speed became lower and the contributions were shared between the temperature and the relative humidity as 46.1 % and 45.0 %, respectively. Through the midday contribution of the temperature and the solar radiation was investigated separately. The results show that the effect of solar radiation on the variation of O_3 concentration was not as high as expected. The temperature was dominant (65.2 %) in this period of the day. In the afternoon the dominant contributor was relative humidity and the percent contribution ranges from 56.9 % to 77.8 %.

Table 3.13. Multiple linear regression and the percent contribution results for each meteorological parameters in each part of the day in the growing season ($p < 0.05$).

	Equation	R^2	T	WS	WD	SR	RH
Early morning	$O_3 = 31.407 + 0.247 T + 4.439 WS - 0.245 RH$	0.144	5.70	75.2	-	-	19.5
Morning	$O_3 = 41.726 + 0.701 T + 2.748 WS - 0.273 RH$	0.265	46.1	8.92	-	-	45.0
Midday	$O_3 = 34.111 + 0.834 T + 1.517 WS - 0.154 RH$	0.278	65.2	8.51	-	-	26.2
	$O_3 = 48.612 + 1.387 WS + 0.009 SR - 0.224 RH$	0.192	-	11.2	-	34.5	54.3
	$O_3 = 32.897 + 0.645 T + 1.056 WS + 0.007 SR - 0.138 RH$	0.301	26.8	5.29	-	11.0	56.9
Afternoon	$O_3 = 36.468 + 0.701 T + 1.392 WS - 0.183 RH$	0.287	26.2	6.25	-	-	67.6
	$O_3 = 47.866 + 1.086 WS + 0.012 SR - 0.217 RH$	0.249	-	4.74	-	17.5	77.8
Evening	$O_3 = 27.769 + 0.365 T + 2.643 WS - 0.155 RH$	0.190	24.0	51.6	-	-	24.5
Night	$O_3 = 34.489 + 0.182 T + 4.151 WS + 0.024 WD - 0.228 RH$	0.176	3.79	68.0	2.22	-	25.7

3.3.3. Factor analysis

Factor analysis (FA) can be used for the classification of data to find connections between variables, finding similarities and detecting outliers in a data set (Lengyel et al., 2004; Gvozdic et al., 2011). FA construct a relationship among variables to minimize the number of variables (Wang et al., 2006). Factor analysis is also a variance analysis because it focuses on the common sources of components that have similar variance. Then the classification is based on the variance of the components.

In spite of the utility of FA, it also has some drawbacks. One of them is the requirement of a dense and meaningful data set. The other one is that factors that are considered as sources should be certain (Harrison, 1996).

In our study we obtained three factors that have eigen values greater than 1 after the varimax rotation (Figure 3.24) and these three factors explained approximately 64.4 % of the total variance.

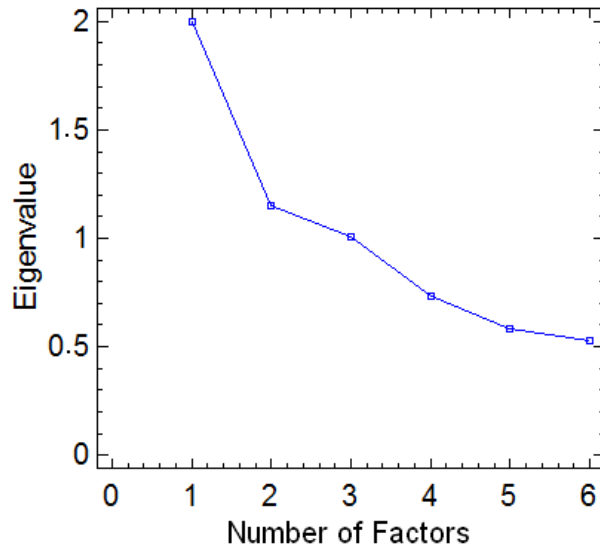


Figure 3.24. Number of factors that have eigen values greater than 1

Loadings of each factor were given in Table 3.14 and the graphical representation was shown in Figure 3.25. The first factor explained 28.6 % of the total variance and the hourly ozone concentration, the temperature, the wind speed, the wind direction and the relative humidity are the components in this factor. Apart from the relative humidity, the positive relation was obtained among the other parameters as in the binary correlation and MLR analysis. The second factor included the wind speed and the wind direction that explained 20.2 % of the total variance. The rain is the unique component of the third factor which explained the 15.6 % of the total variance.

Table 3.14. Loadings of each component in factor analysis.

	1	2	3
Ozone	0.641	0.344	0.126
Temperature	0.669	-0.202	0.278
Wind speed	0.114	0.802	0.120
Wind direction	-0.059	0.808	-0.087
Rain	-0.012	0.060	0.912
Solar radiation	0.658	0.097	-0.381
Relative Humidity	-0.791	0.016	0.130
Variance	2.000	1.417	1.095
% of total variance	28.576	20.246	15.643

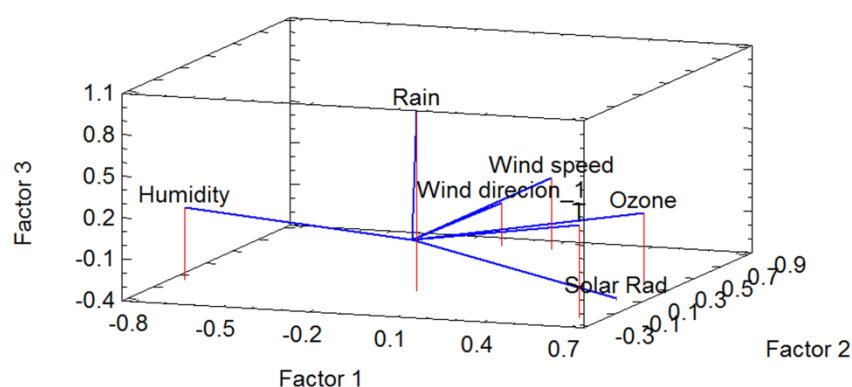


Figure 3.25. Graphical representation of factor analysis results

3.4. Estimation of O₃ exposures

3.4.1. AOT₄₀ modeling

The calculations of AOT₄₀ and exceeding of the critical level in Bolu semi-rural forest receptor area during the growing season between March 2009 and March 2012 were performed in this study. During the sampling period (549 days, 13176 hours) the percent exceeding of AOT₄₀ values was 26.0 % which means the critical value

was exceeded for 3421 hours. AOT₄₀ results in each month during sample period is given in Figure 3.26. The rapid increase of AOT₄₀ values were obtained in July and in August.

AOT₄₀ was calculated in daytime hours from May to July for O₃ exposure on vegetation and for forests it was calculated from April to September. The critical AOT₄₀ level for crops and forests are 3000 ppbh and 10000 ppbh, respectively (Hunova et al., 2003; Fuhrer et al., 1997).

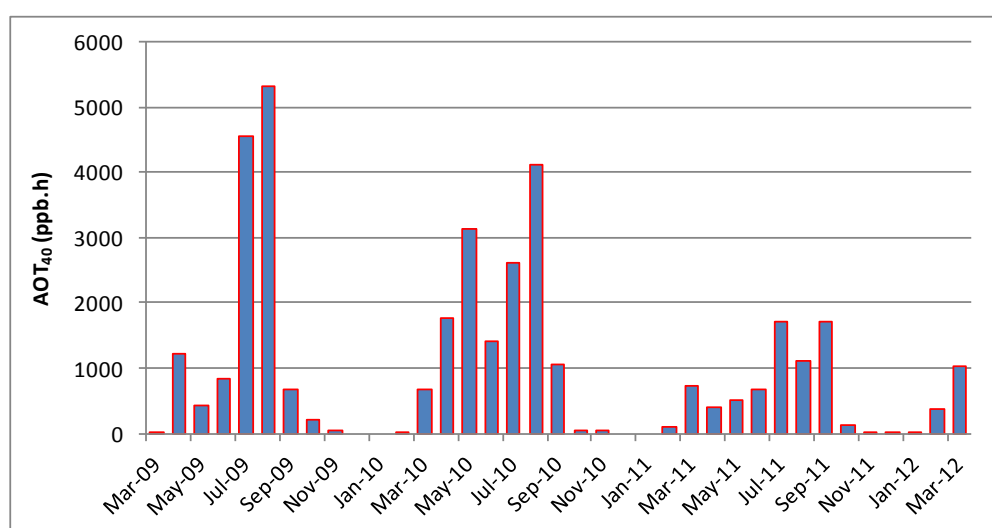


Figure 3.26. Monthly AOT₄₀ values during the sampling period

The frequency histogram of the AOT₄₀ model output in Figure 3.27 shows that most of the values are skewed to the right which means that the values are in the lowest quartile and show log-normal distribution.

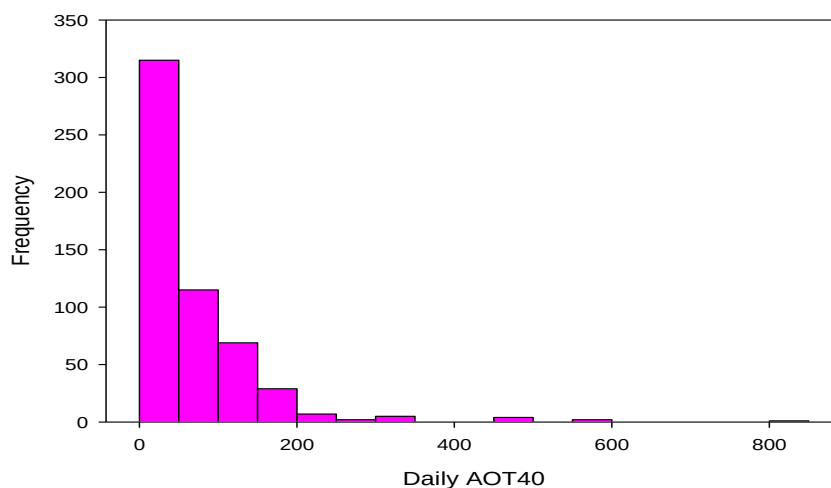


Figure 3.27. Daily AOT₄₀ frequency distribution

Figure 3.28 summarizes the AOT₄₀ results for crops and forests in each year during the sampling period. Especially in 2009 and 2010 the critical level exceeded for both the agricultural crops and the forests. The cumulative exposure for forests were 12997 ppbh and 14074 ppbh and for crops 5804 ppbh and 7145 ppbh, respectively.

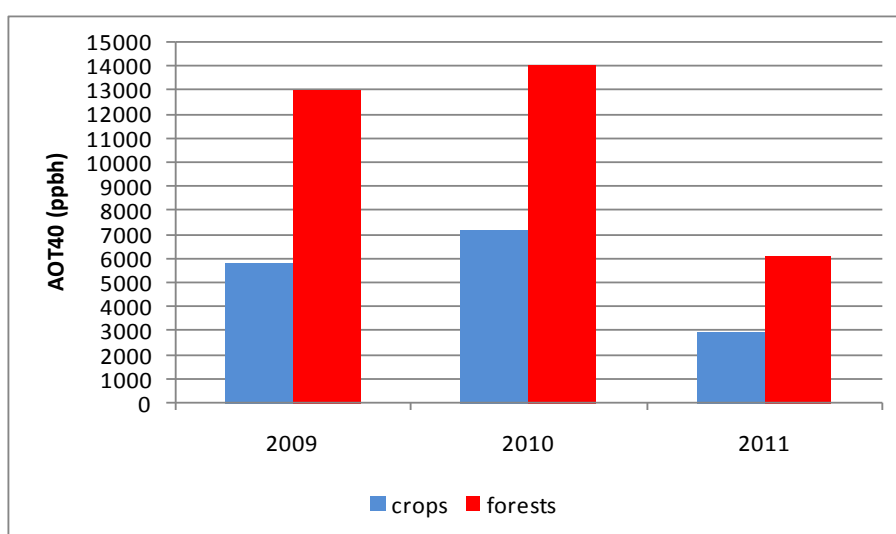


Figure 3.28. AOT₄₀ levels for crops and forests in each year during the sampling period

AOT₄₀ critical levels for some selected crops are given in Table 3.15. According to the table the most sensitive crop is the water melon whose critical level is 1.56 ppm.h and the most resistant one is the barley with the critical level of 83.33 ppm.h (Mills et al., 2003). According to the results of this study it is clear that all the sensitive group members were encountered with the risk of O₃ exposure. However, the use of critical levels should not imply that all crops are in safe if the critical levels are not exceeded. There may be some other factors like other pollutants, pests or pathogens that affect the yield of crops.

Table 3.15. AOT₄₀ levels for some selected crops (Mills et al., 2003).

Sensitive (≤ 5.0 ppm.h)		Moderately sensitive (5.0-10.0 ppm.h)		Moderately resistant (10.2-20.0 ppm.h)		Insensitive (> 20 ppm.h)	
Crop	CL	Crop	CL	Crop	CL	Crop	CL
Water melon	1.56	Sugarbeet	8.62	Rice	12.82	Fruit (plum& strawberry)	62.0
Wheat	2.96	Potato	8.93	Maize	13.89	Barley	83.33
Pulses	3.03	Rapessed	8.93	Grape	16.66		
Cotton	3.13	Tobacco	9.90	Brocoli	20.0		
Turnip	3.47						
Tomato	3.62						
Onion	4.13						
Soya	4.31						
Lettuce	4.63						

CL: critical level

3.4.2. Daily 8-h O₃ concentration

In 1997 EPA set the National Ambient Air Quality Standard level for O₃ based on daily maximum 8-h average concentration and for moderate health concern it should be 80 ppb (Table 2.2). During the calculation hourly O₃ concentrations are used and for each 8 hours an average is taken (totally 24 averages are obtained). For the meaningful data set 75% of the data should be available (18 of the 24 averages). Finally the daily maximum is the highest of the 24 possible 8-h averages.

In this study 8-h averages were taken for three years sampling (March 2009-March 2012). The average of daily maximum 8-h average O₃ concentration through whole sampling was 37.2 ppb (Figure 3.29). Only in 7 days, the threshold level (80 ppb) was exceeded. These days are 17, 18, 19 July 2009 and 4, 5, 6, 7 August 2009.

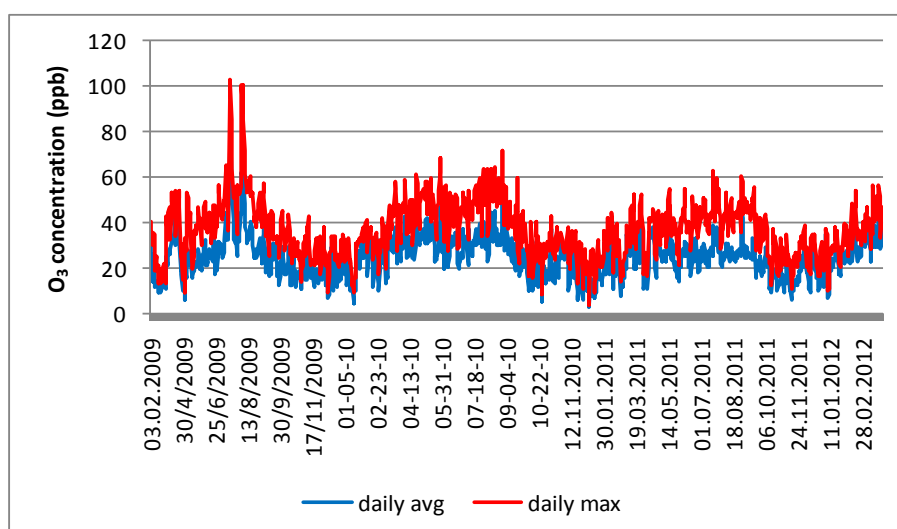


Figure 3.29. Daily average and daily maximum 8-h average O₃ concentrations (March 2009-March 2012)

3.4.3. Mixing height and ventilation coefficient in the sampling period

3.4.3.1. Mixing height

The mixing height (MH) is a key parameter in the evaluation of the dispersion potential of the atmosphere and the transport of pollutants in the atmosphere over a given location (Seibert et al., 1997; Norton and Hoidale, 1976).

In literature, there are many definitions for mixing height (MH) and some of them are given as;

- The mixing height is the height of the layer adjacent to the ground over which pollutants or any constituents emitted within this layer or entrained into it become vertically dispersed by convection or mechanical turbulence within a time scale of about an hour (Seibert et al., 1997).
- The MH refers to the height above the ground of the layer of the atmosphere adjacent to the surface where vigorous mixing occurs as a result of thermal and mechanical turbulence (Norton and Hoidale, 1976).
- The MH is defined as the height above the earth's surface up to which released pollutants will disperse primarily through the action of atmospheric turbulence (Goyal and Chalapati, 2007).

Accurate quantification of the mixing height depends on several factors such as prevailing meteorological conditions, strength of atmospheric convection, local time of the observation and geographical location of the experiment. The mixing layer

variations over a site are largely driven by the diurnal and seasonal changes in these parameters (Srivastava et al., 2010).

Temporal variation in the mixing layer affects the concentration level of the pollutants from natural and anthropogenic activities within the atmosphere and their mixing in the free troposphere.

The mixing height primarily depends on the initial vertical temperature structure and the heat input at the surface. Neglecting the temperature advection, the maximum surface temperature is observed from 12:00 to 16:00 (Holzworth, 1967), then the highest value of the mixing heights are expected to be seen in these time intervals. In Figure 3.30, the graph on the left side belongs to the change in mixing height in each month through the whole sampling period. As indicated above the highest mixing height levels were seen between 12:00 and 16:00. However, in July 2011, there was a decrease in the mixing height. The enlarged graph in the middle shows the variation of the mixing height for and we obtained that the lowest values in 2011. Finally the graph on the right side shows variation of mixing height in July 2011. The maximum mixing height was observed between 20-25 July, 2011.

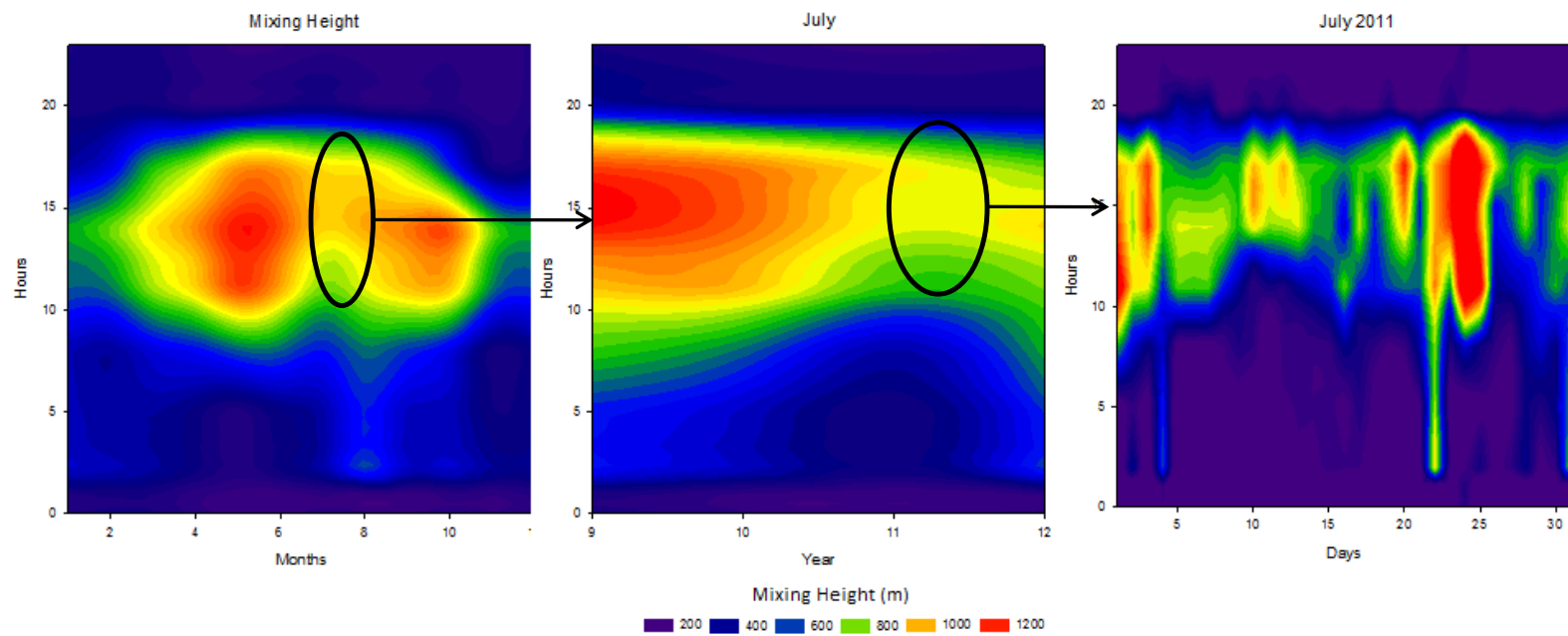


Figure 3.30. Variation of mixing height through the whole sampling

In this study the calculation of hourly mixing height was achieved by Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) from National Oceanic and Atmospheric Administration (NOAA). (http://www.arl.noaa.gov/HYSPLIT_info.php). As an input the coordinates of the sampling site (40.42°E and 31.31°N), the height above ground level (15 m) and the desired date were used.

3.4.3.2. Daytime and night time variations of O₃ with the mixing height

In general, tropospheric O₃ exhibits strong diurnal variation with a maximum value in midday and a minimum value in early morning. Concentrations in daytime are much larger than those at night time as seen in Figure 3.31. In addition to the photochemical O₃ production, the temporal variation of ground-level ozone concentration is strongly controlled by the change in the mixing height during the day (Kim et al., 2007).

At night time, the presence of the temperature inversion isolates the surface level O₃ from the upper layer, as there is little or no vertical mixing between surface layer and nocturnal boundary layer (Aneja et al., 2000). Surface O₃ is partly removed by some deposition processes and reactions with other pollutants such as NO. Since there is no production of O₃ in the absence of sunlight, O₃ concentrations begin to decrease after sunset and reach minimum in the early morning hours until the sunrise.

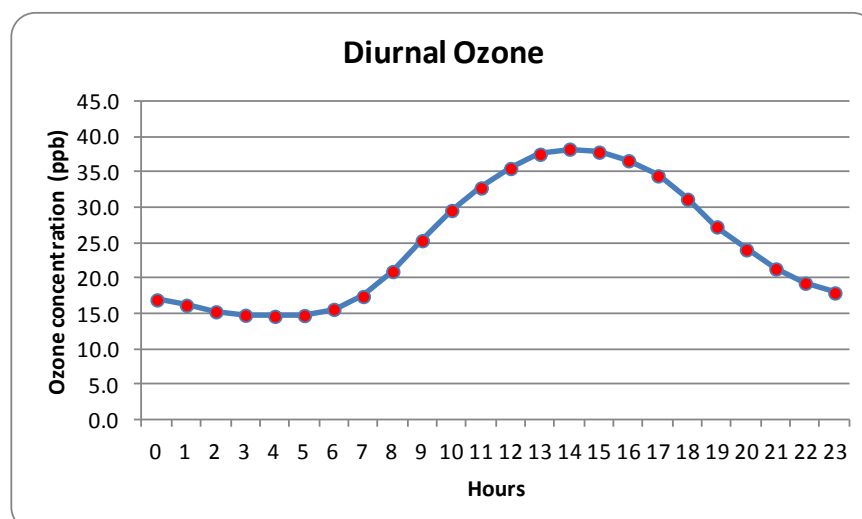


Figure 3.31. Average diurnal O₃ concentration variation

After sunrise, the height of unstable boundary layer begins to increase as the surface is heated and the nocturnal inversion is destroyed (Aneja et al., 2000) and this results in downward mixing of O₃ from stratosphere (Aneja et al, 2000; Zhang and Rao, 1999). Moreover with the increase in the intensity of sunlight O₃ is produced by reactions of NO_x and VOCs.

Strong photochemical production and strong convection in the midday cause the highest level in O₃ concentration. At noon, the mixing height also exceeds 1000 m and O₃ is well mixed within the mixing layer.

Change in O₃ concentrations with the mixing height in daytime and in night time are given in Figure 3.32.

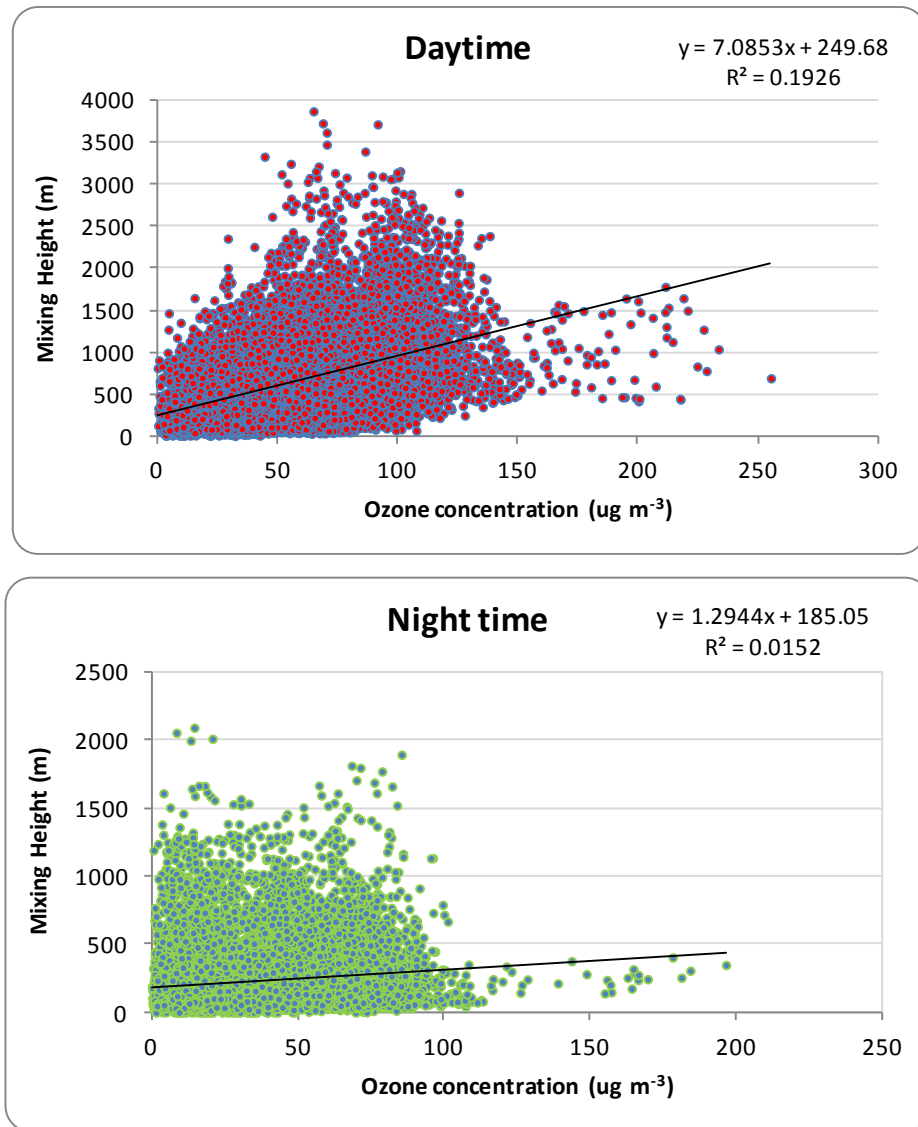


Figure 3.32. The correlation graphs between O_3 and the mixing height in daytime and in night time

The relation between O_3 and the mixing height was seen in daytime. As mentioned before at night the production of O_3 decreases due to lack of sunlight and also the mixing layer at night gets lower due to nocturnal inversion. However, the rate of change in O_3 concentration is much higher than in the mixing layer. On the other hand, in daytime, sunlight both increases the O_3 concentration (photochemical reaction) and also the mixing height (heating).

3.4.3.3. Warm and cold season variation of O₃ with the mixing height

As indicated above the mixing height depends on the ambient temperature. Then, the temporal variation of the mixing height was investigated with respect to warm (March-August) and cold seasons (September-February) as shown in Figure 3.33. After the half of September, the mixing height level started to decrease and reached its minimum values from the beginning of December to the end of January.

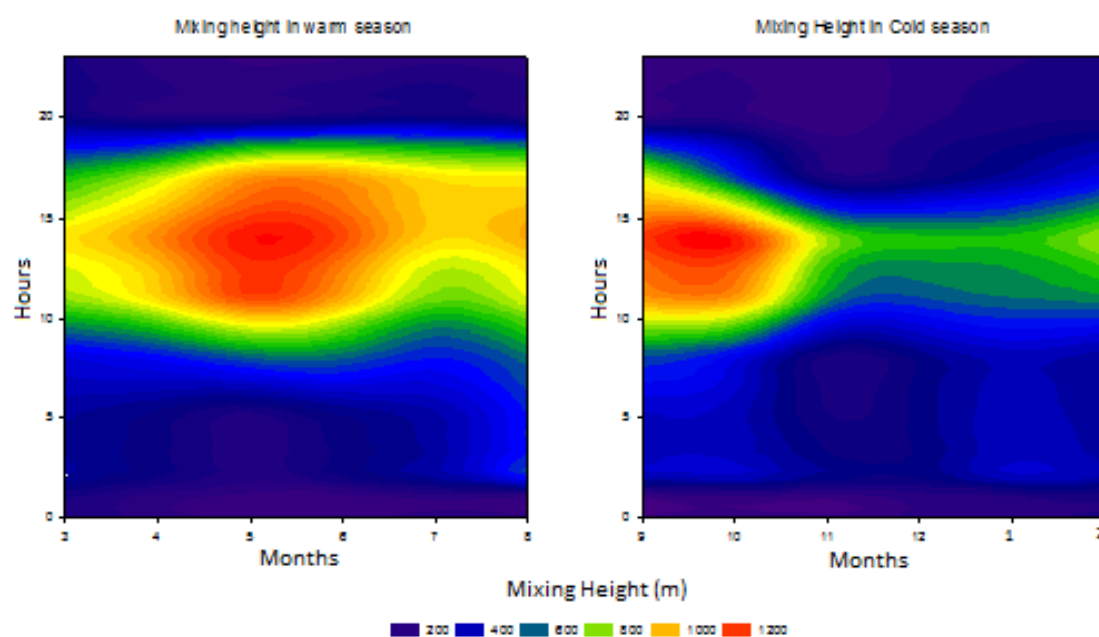


Figure 3.33. Variation of the mixing height in warm and cold seasons

3.4.3.4. Ventilation coefficient

Ventilation coefficient represents the rate at which the air within the convective boundary layer is transported. It plays an important role in the dispersion of air pollutants and is one of the factors that determine the dispersal potential of pollutants over a region of interest (Goyal and Chalapari, 2007). The ventilation coefficient is the product of two meteorological parameters; mixing height and the wind speed through the mixing layer as in Equation 4.

$$VC = MH_i \times WS \quad Eq (4)$$

where, MH_i is the atmospheric boundary layer height in meter (mixing height) and WS is the average wind speed in the mixed layer in $m s^{-1}$. This equation is illustrated graphically in Figure 3.34. Inverse relation between the wind speed and the mixing height is observed from this figure. This also indicated that the flow of wind was in horizontal direction. When wind speed increased the mixing height level decreased because the air mass in the boundary layer was swept.

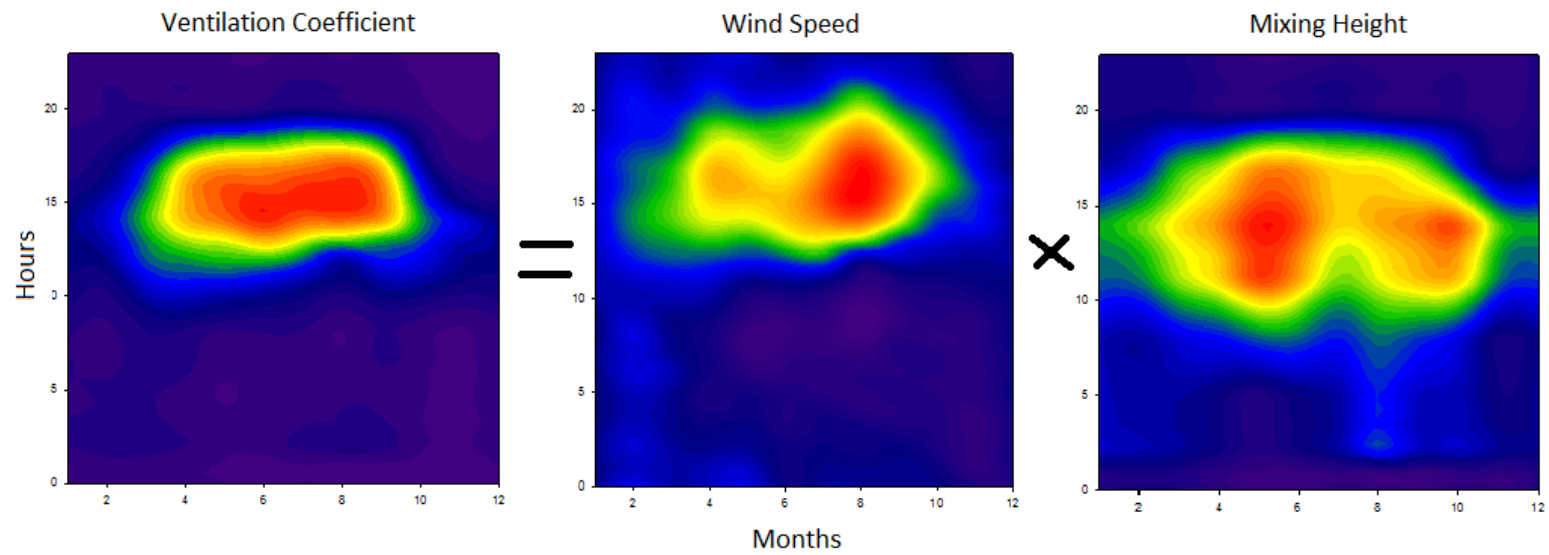


Figure 3.34. Calculation of ventilation coefficient in graphical representation

Diurnal variation of the mixing height and the ventilation coefficient are given in Figure 3.35. The highest values of each parameter was observed in the afternoon (13:00-15:00) and the minimum values were obtained when the ambient temperature decreased.

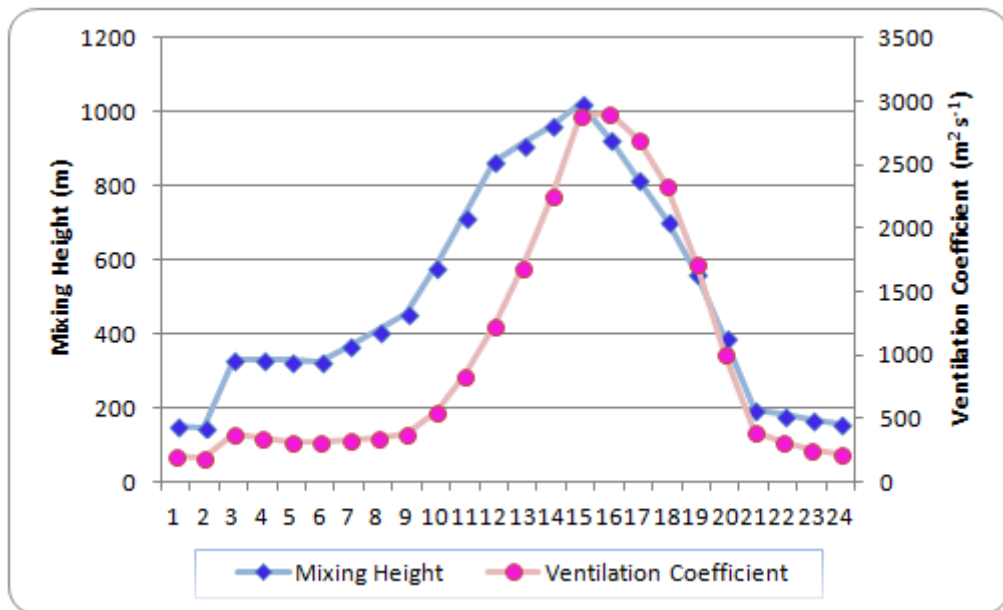


Figure 3.35. Mixing height and ventilation coefficients with respect to hours

The similar result was obtained in the variation of these two parameters with respect to months (Figure 3.36). In the summer months especially in June and in July, the ventilation coefficient reached its maximum value.

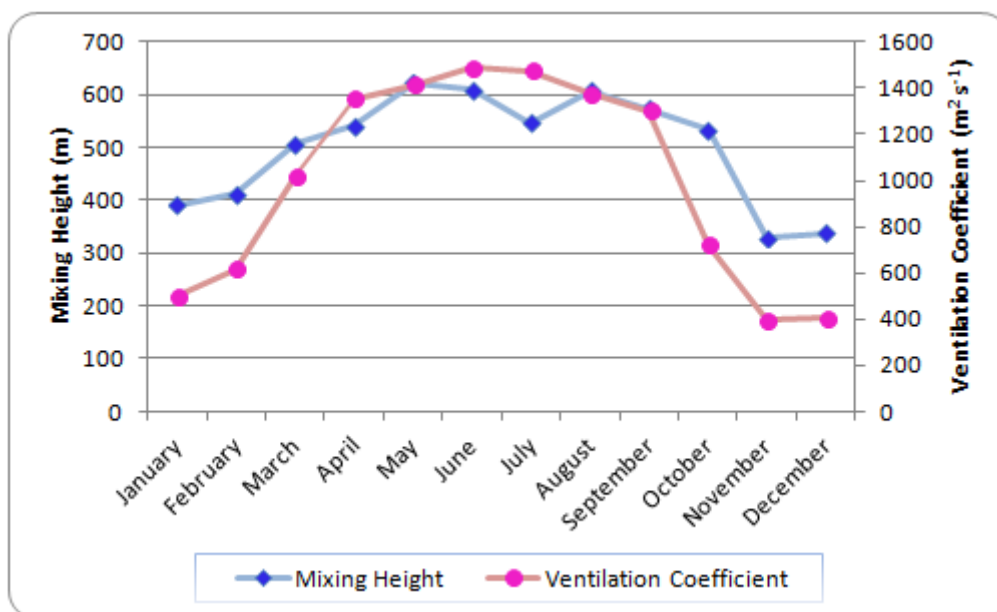


Figure 3.36. The mixing height and the ventilation coefficients with respect to months

Lower values of the ventilation coefficient indicate less (pollution) dispersion potential of pollutants in the atmosphere. The higher the coefficient, the greater is the ability of the atmosphere to disperse the pollutants and hence less pollution hazard or good air quality (Goyal and Chalapati, 2007; Eagleman, 1991). The atmospheric pollution potential is given in Table 3.16. In this table, the situation of the atmosphere is evaluated by the distribution of the range of ventilation coefficients. According to the table 76 % of the whole sampling was very polluted, 14 % was polluted, 7 % is moderate and finally only 3 % was good. These results show that Bolu is under the risk of air pollution due to the trapped pollutants in the air.

Table 3.16. Evaluation of air pollution with respect to ventilation coefficient.

Ventilation Coefficient ($\text{m}^2 \text{s}^{-1}$)	# of case	% of case	Situation
0-2000	15,234	76	Very polluted
2001-4000	2,812	14	Polluted
4001-6000	1,360	7	Moderate
>6000	602	3	Good
TOTAL	20,008	100	

3.4.4. Ozone episodes

Backward trajectory is a useful tool to monitor the long-range transport of air mass. HYSPLIT model was also used for the backward trajectory analysis. The archive in Global Data Assimilation System (GDAS) was used. In this archive there is a latitude/longitude global grid with a resolution of 1 degree. The vertical motion of the air mass was selected as isentropic because it is considered to reflect more realistic motion of air than the isobaric type (Wang et al., 2006). Danielsen (1961) explained the main differences between these two vertical motions. He said "three dimensional motions of the air, or trajectories, can be computed from the conventional pressure analysis, but vertical motions add complexities and uncertainties not only in the vertical component of the trajectories but also in the horizontal components as well. Isentropic analysis offer an alternative procedure for trajectory computations. By directly incorporating the vertical motions and velocity shears, they eliminate the major sources of error of the isobaric method, but another source of error is introduced because it is necessary to evaluate the diabatic temperature change. This is difficult but usually the order of magnitude of the change

can be determined". Finally, due to the reactivity of O₃, the run time was 72 hours (3 days) and the height levels were selected as 100, 500 and 1500 m. Through the whole sampling period in 7 days in 2009 (three days in July and four days in August) the threshold level for population information (180 µg m⁻³ in 1-h) was exceeded.

July 2009

Between 16 and 18 July, the maximum ozone concentrations were 250 µg m⁻³, 229 µg m⁻³ and 207 µg m⁻³, respectively. The backward trajectories of these days are given in Figure 3.37. The entrance of the air mass to our sampling side was from the north of Turkey but the start point of the air mass was in the north eastern part. Diurnal variation of meteorological parameters, mixing height, ventilation coefficient and O₃ concentration are given in Figure 3.38 to Figure 3.40 for each date, respectively.

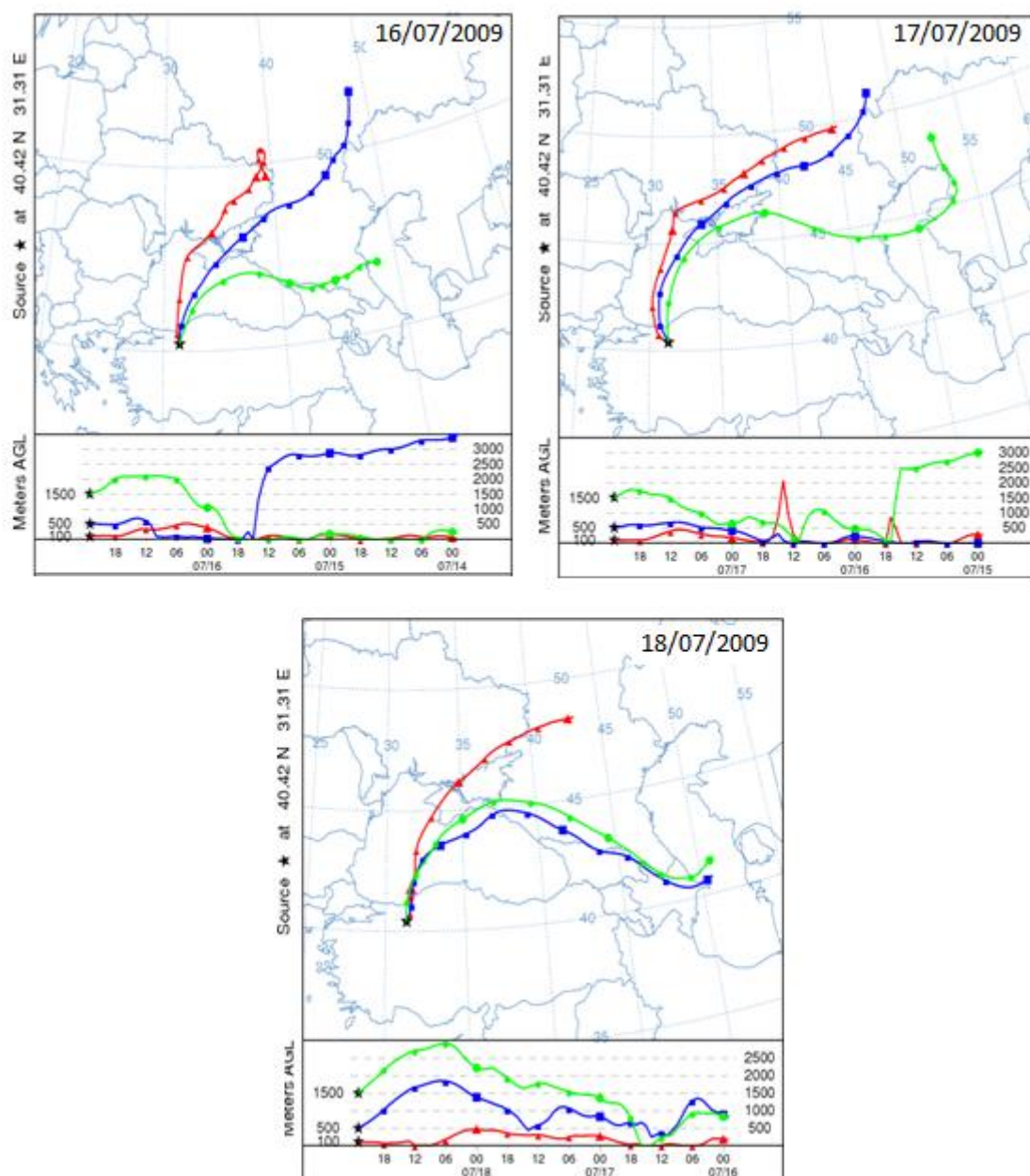


Figure 3.37. Backward trajectories of O_3 episodes in July 2009

The trends of O₃, the temperature, the solar radiation, the wind speed and the ventilation coefficient were similar at night time on 16 July 2009. All these parameters had their minimum value at 02:00 whereas the relative humidity had its maximum value. The low concentration of O₃ at that time can be explain by two ways. The first one is the lack of solar radiation and low temperature in addition to low wind speed that transfer the O₃ riched air mass in local scale. The second one is the increase in the relative humidity. The water content in air may cause a dilution of O₃ in air. The maximum O₃ concentration (250 µg m⁻³) was observed at 14:00 when solar radiation reached its maximum (376 W m⁻²). After 15:00, O₃ stays in a range of 150-210 µg m⁻³ until 17 July 2009 at 19:00. On 17 July 2009 the concentration of O₃ was between 119 µg m⁻³ and 229 µg m⁻³ during whole day. The mixing height values in July 17 were lower than in July 16 especially at night time and early morning hours. Then the concentration of O₃ was high at these hours.

Except on 16 July, the ventilation coefficient started to increase at 10:00, reached its maximum at 14:00-16:00 and after the sunset it decreased. However, on that day the rate of change in the ventilation coefficient (05:00-19:00) was very low and ranged from 1000 to 2500 m² s⁻¹.

In July 17, the dilution effect of wind speed was observed at 01:00 and 11:00. When it was decreased O₃ concentration was increased. High O₃ concentrations were observed when the temperature, the solar radiation, the wind speed, the ventilation coefficient and the mixing hight had high values and the relative humidity had low values (13:00-17:00). In the last day of July O₃ episode, 18 July 2009, showed similar trend like in July 17.

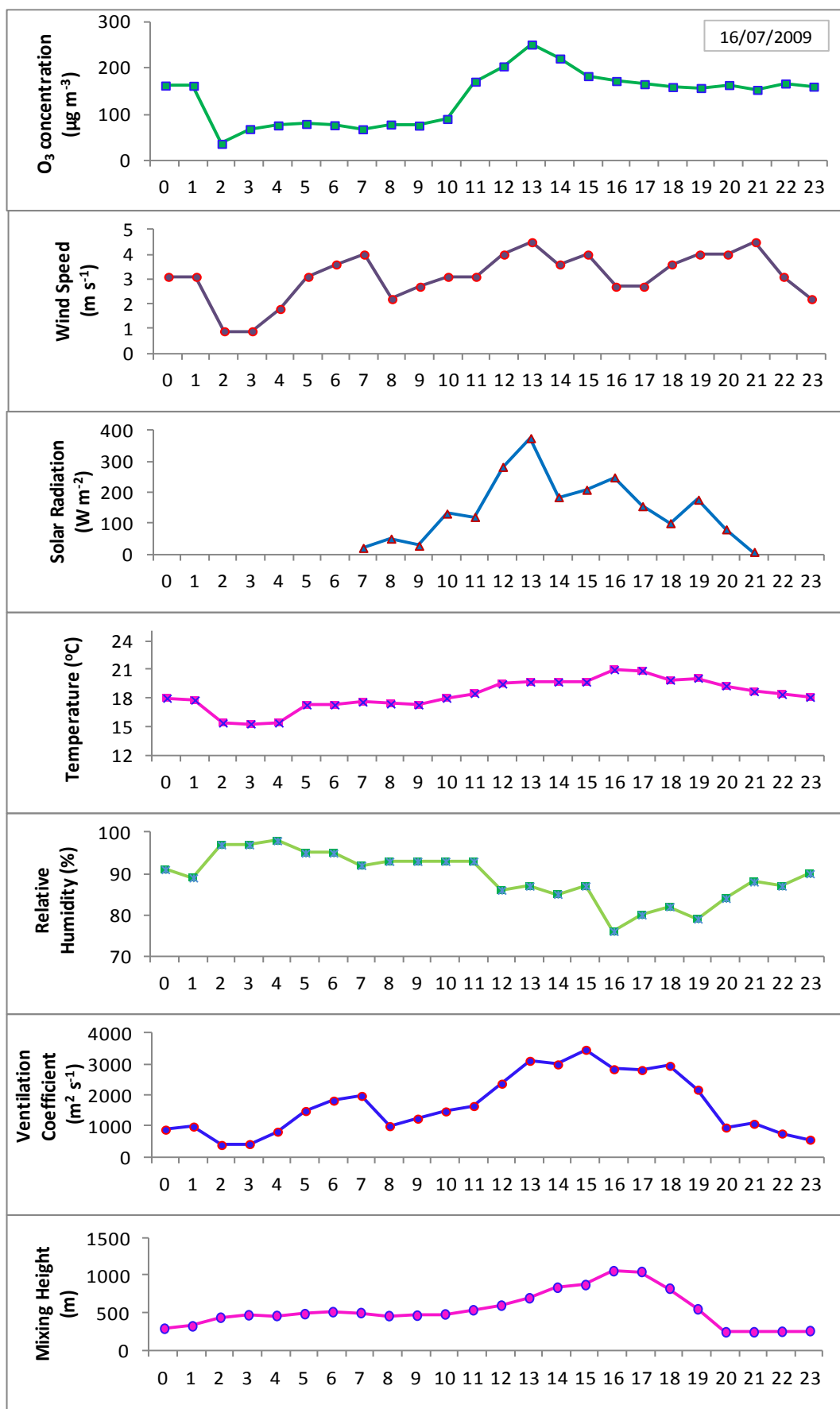


Figure 3.38. Hourly variation of parameters on 16 July 2009

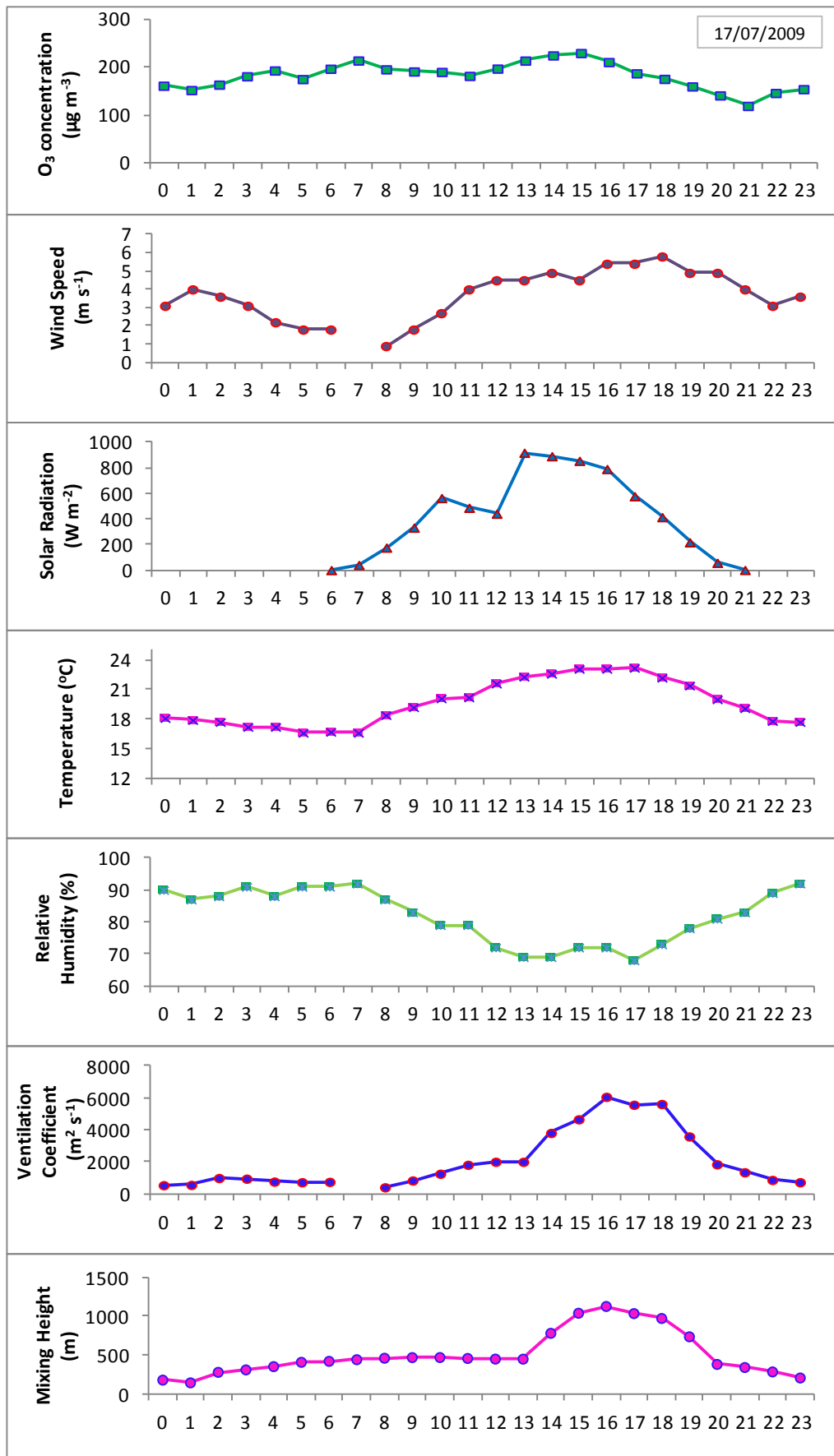


Figure 3.39. Hourly variation of parameters on 17 July 2009

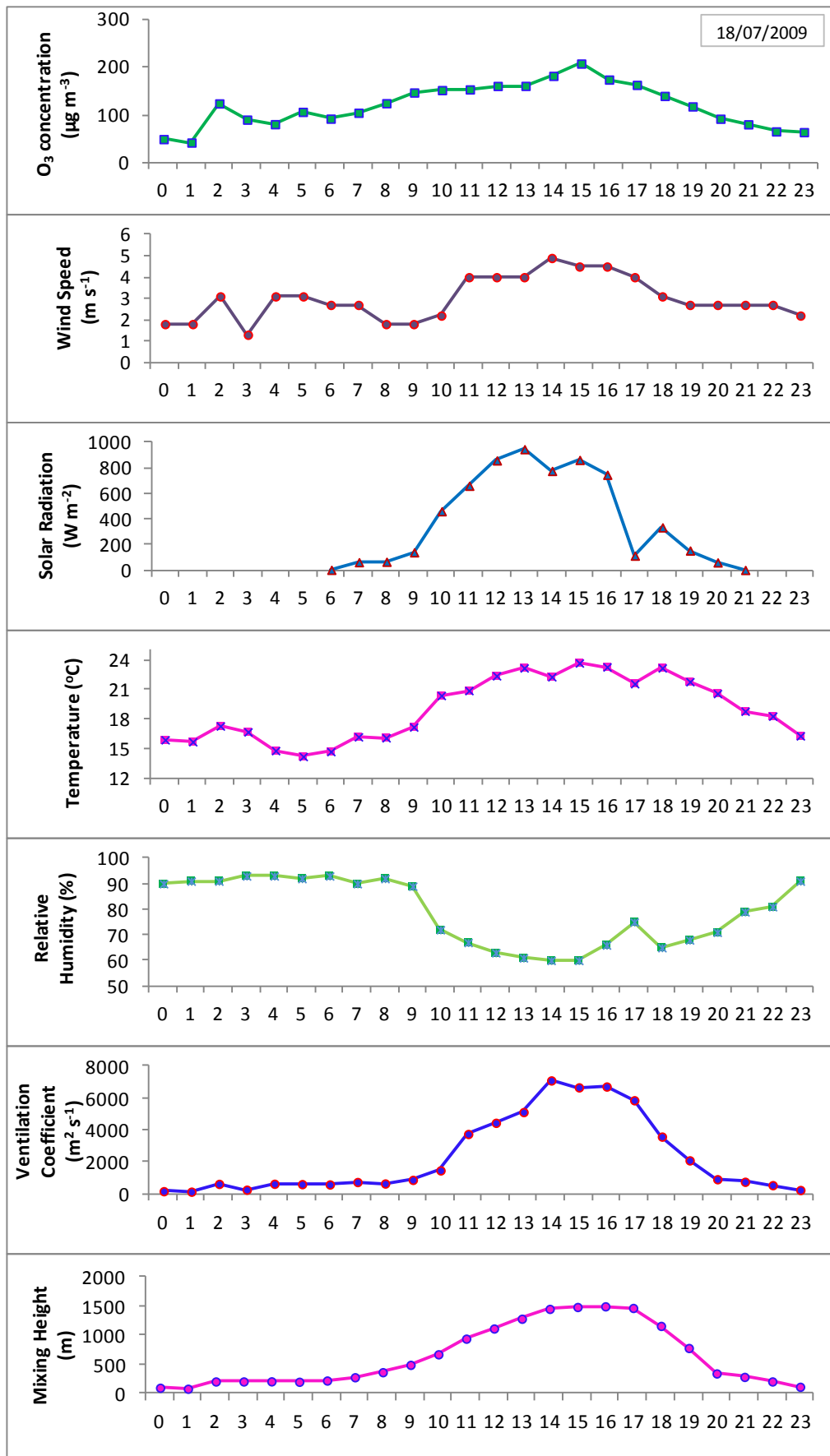


Figure 3.40. Hourly variation of parameters on 18 July 2009

August 2009

Four days in the first week of August 2009 (3-6 August) O₃ concentrations were 208 $\mu\text{g m}^{-3}$, 207 $\mu\text{g m}^{-3}$, 223 $\mu\text{g m}^{-3}$ and 185 $\mu\text{g m}^{-3}$, respectively. Backward trajectories of these days are given in Figure 3.41. On 3 August 2009 and 4 August, 2009 the origin of the air mass was from Russia and the transport direction was not changed and enter to our sampling side from the north. Although the entrance of air from the north, on 6 August the start point of the air mass is in the north eastern. On 5 August the air mass at high altitudes came from the west of sampling point and it travelled the west part of Turkey then reached the sampling point.

Diurnal variation of whole parameters belong to August episode are given in Figure 3.42 to Figure 3.45. The changes in the O₃ concentration and the mixing height through the day were in wide time interval and they were identical in August episode. The increase in the mixing height and the wind speed at the same time shows that the movement of air mass is vertical rather than horizontal. This may be the indicator of the stratospheric intrusion to troposphere in these days.

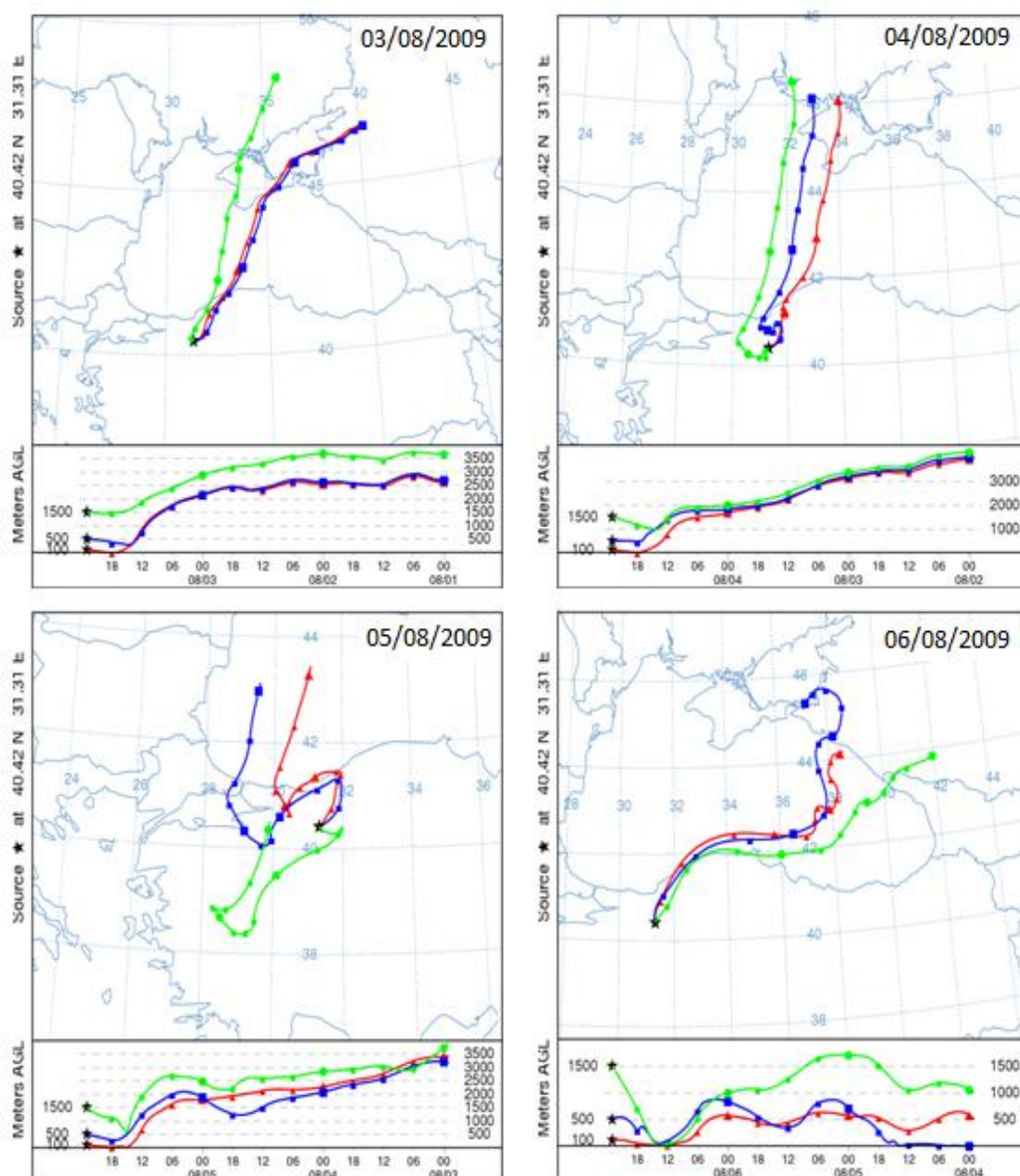


Figure 3.41. Backward trajectories of O_3 episodes in August 2009.

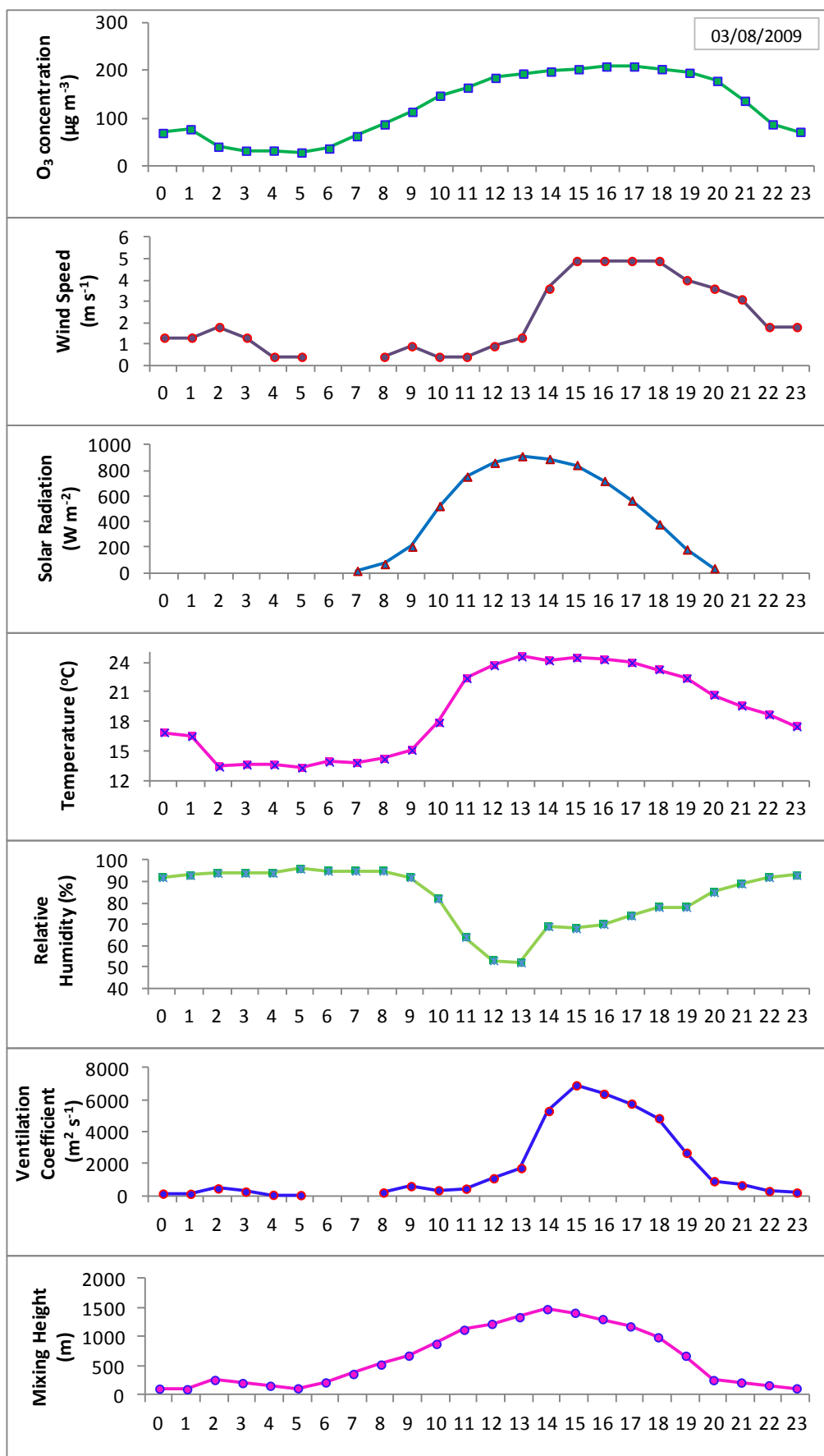


Figure 3.42. Hourly variation of parameters on 3 August 2009

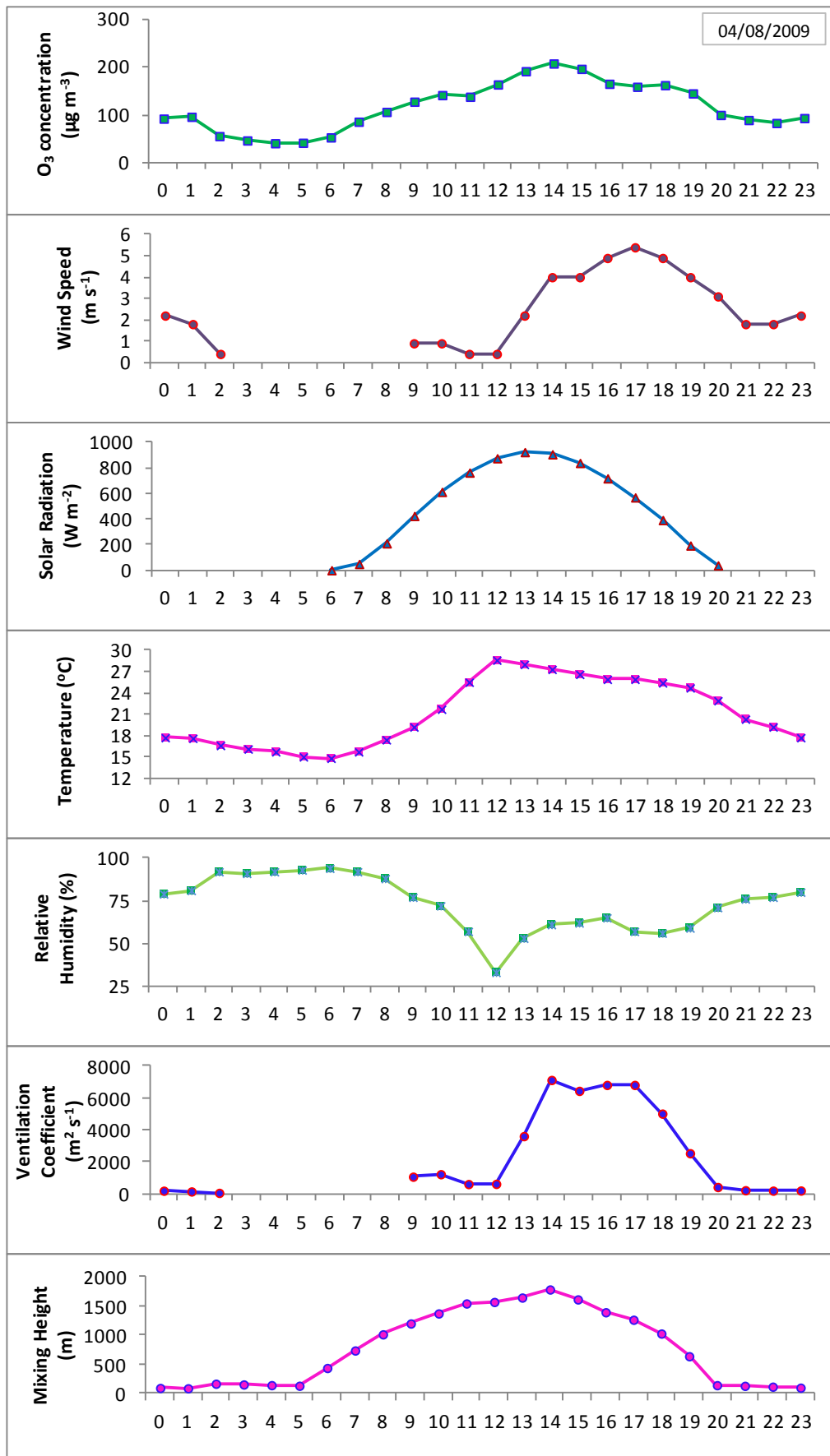


Figure 3.43. Hourly variation of parameters on 4 August 2009

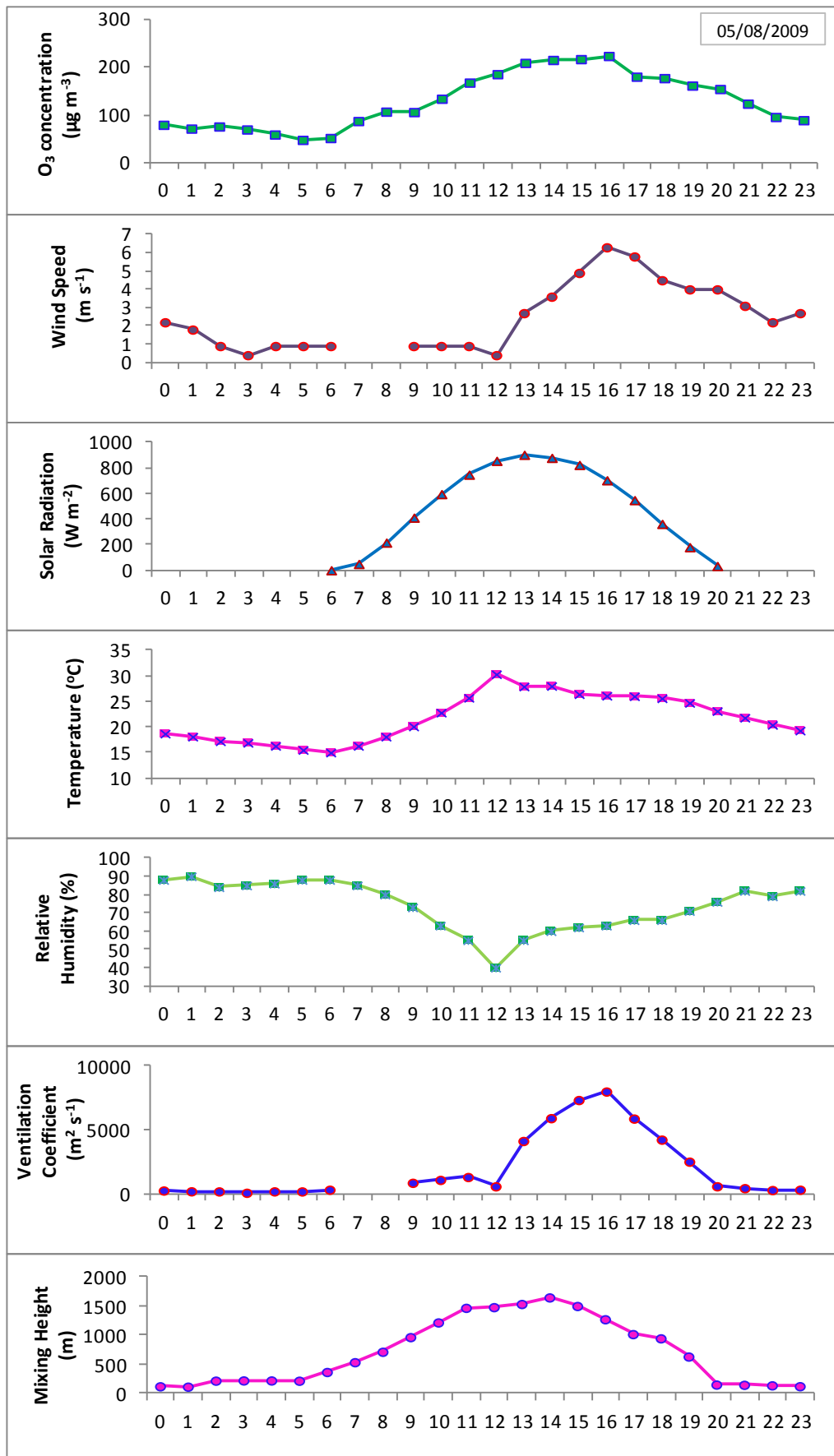


Figure 3.44. Hourly variation of parameters on 5 August 2009

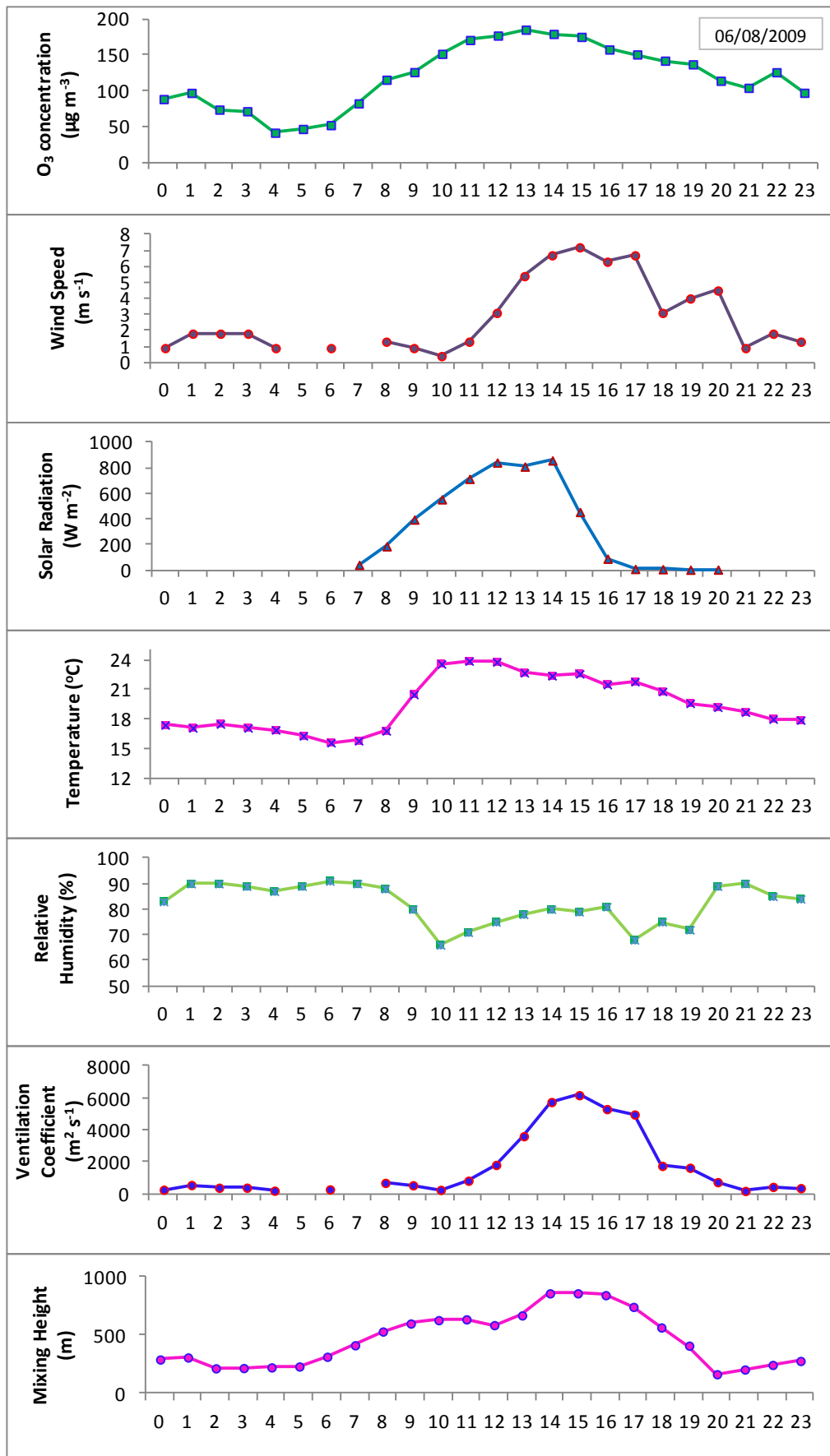


Figure 3.45. Hourly variation of parameters on 6 August 2009

3.5. Statistical evaluation of aerosol data

Composition of particulate matters can be investigated with respect to both temporal variations and relating with meteorological parameters. Then, aerosol concentrations should be evaluated by statistical methods. Statgraphics Centurion XV.II program has been used for the analysis. Summary of the results of statistical analysis are given in Table 3.17 and in Table 3.18 for $PM_{2.5}$ and $PM_{2.5-10}$, respectively.

The parameters used for statistical treatment were arithmetic mean, standard deviation, geometric mean, geometric standard deviation, median, mode, minimum and maximum. It is not surprising that the concentration values have high standard deviations. Pollutants are dynamic in the ambient atmosphere. The structure and the composition of pollutants can be changed by chemical and physical processes and also their residence time can differ due to the effects of meteorological parameters.

Both arithmetic and geometric mean are given in the statistical analysis. Generally arithmetic mean is used for the data set with normal distribution. In normal distribution, the values of arithmetic mean, geometric mean and median are close to each other. In the data set of this study these parameters differ from each other for most of the elements. This indicated that the distributions of data were log-normal. Generally in log-normal distribution geometric mean and geometric standard deviation are used. However, arithmetic mean was used in this study for the comparison with the literature. The main reason of the difference in values of arithmetic mean, geometric mean and the median can be the effects of pollution sources, meteorological and geological parameters on each element.

The statistical analysis results showed that the highest arithmetic mean of the elements for both fine and coarse particles were Na and Ca. In PM_{2.5} Na $5.2 \pm 2.4 \mu\text{g m}^{-3}$ and Ca $4.4 \pm 2.7 \mu\text{g m}^{-3}$, whereas in PM_{2.5-10} these values for Na and Ca are $4.4 \pm 1.9 \mu\text{g m}^{-3}$ and $4.2 \pm 3.9 \mu\text{g m}^{-3}$, respectively.

Anthropogenic elements had high concentrations in PM_{2.5} as expected. For instance, As was 1.4 ng m^{-3} in PM_{2.5-10} while it was 5.2 ng m^{-3} in PM_{2.5}.

Table 3.17. Statistical evaluation of PM_{2.5} aerosols

Parameter	N	Arithmetic mean $\pm$ STD	Geometric mean $\pm$ STD ¹	Median	Mode	Range
Na ($\mu\text{g m}^{-3}$)	289	5.2 $\pm$ 2.4	4.5 $\pm$ 1.8	5.3	5.9	0.37-10
K ($\mu\text{g m}^{-3}$)	323	0.56 $\pm$ 0.49	0.42 $\pm$ 2.1	0.35	0.25	0.057-2.0
Mg ($\mu\text{g m}^{-3}$)	321	0.88 $\pm$ 0.52	0.74 $\pm$ 1.9	0.82	1.1	0.058-4.5
Ca ($\mu\text{g m}^{-3}$)	318	4.4 $\pm$ 2.7	3.5 $\pm$ 2.0	3.5	2.8	0.28-11
Fe ($\mu\text{g m}^{-3}$)	320	0.254 $\pm$ 0.249	0.18 $\pm$ 2.4	0.18	0.10	2.2x10 ⁻³ -1.8
Al ($\mu\text{g m}^{-3}$)	287	1.8 $\pm$ 0.85	1.5 $\pm$ 2.0	1.8	0.39	0.1-3.5
Zn ($\mu\text{g m}^{-3}$)	321	0.087 $\pm$ 0.051	0.073 $\pm$ 1.8	0.078	0.040	7.1x10 ⁻³ -0.35
V (ng m ⁻³)	287	3.8 $\pm$ 1.8	3.3 $\pm$ 1.7	3.5	3.3	0.14-10
Cr ($\mu\text{g m}^{-3}$)	325	0.033 $\pm$ 0.019	0.029 $\pm$ 1.6	0.032	0.039	4.7x10 ⁻³ -0.19
Mn (ng m ⁻³)	318	8.99 $\pm$ 7.40	6.7 $\pm$ 2.4	7.0	8.9	0.018-47
Co (ng m ⁻³)	292	1.48 $\pm$ 1.47	0.89 $\pm$ 2.8	0.73	0.69	0.019-6.7
Ni ($\mu\text{g m}^{-3}$)	322	0.033 $\pm$ 0.026	0.025 $\pm$ 2.01	0.021	0.018	1.8x10 ⁻³ -0.20
Cu (ng m ⁻³)	320	8.89 $\pm$ 8.86	7.0 $\pm$ 2.0	7.0	5.3	0.19-88
As (ng m ⁻³)	322	5.2 $\pm$ 9.6	1.7 $\pm$ 3.7	1.5	0.92	0.060-56
Cd (ng m ⁻³)	308	1.6 $\pm$ 3.6	0.53 $\pm$ 3.9	0.38	0.22	0.025-35
Pb ($\mu\text{g m}^{-3}$)	322	0.019 $\pm$ 0.018	0.014 $\pm$ 2.1	0.013	0.012	2.4x10 ⁻³ -0.18
P ($\mu\text{g m}^{-3}$)	295	0.15 $\pm$ 0.67	0.086 $\pm$ 2.0	0.077	0.065	5.7x10 ⁻³ -11
Sc (ng m ⁻³)	283	7.35 $\pm$ 19.5	2.3 $\pm$ 3.3	2.1	0.98	0.14-158
Ti ($\mu\text{g m}^{-3}$)	293	0.079 $\pm$ 0.18	0.049 $\pm$ 2.2	0.043	0.047	2.7x10 ⁻³ -2.0
Se (ng m ⁻³)	137	0.19 $\pm$ 0.16	0.15 $\pm$ 2.1	0.14	0.10	0.030-1.1
Y (ng m ⁻³)	295	0.23 $\pm$ 0.48	0.11 $\pm$ 2.6	0.093	0.057	0.012-3.9
Mo (ng m ⁻³)	295	3.4 $\pm$ 1.6	3.2 $\pm$ 1.5	3.3	3.3	0.59-12
Sb (ng m ⁻³)	292	0.95 $\pm$ 0.30	0.90 $\pm$ 1.4	0.93	0.77	0.15-2.1
Cs (ng m ⁻³)	189	0.069 $\pm$ 0.038	0.057 $\pm$ 2.0	0.065	0.080	2.6x10 ⁻³ -0.25
La (ng m ⁻³)	294	0.22 $\pm$ 0.27	0.16 $\pm$ 2.1	0.13	0.066	0.037-2.6
Nd (ng m ⁻³)	295	0.18 $\pm$ 0.21	0.12 $\pm$ 2.3	0.10	0.066	0.012-1.5
Eu (ng m ⁻³)	285	0.011 $\pm$ 0.016	0.0070 $\pm$ 2.3	5.6x10 ⁻³	4.0x10 ⁻³	1.6x10 ⁻³ -0.12
U (ng m ⁻³)	214	0.14 $\pm$ 0.17	0.096 $\pm$ 2.3	0.085	0.070	5.6x10 ⁻³ -1.1
Tl (ng m ⁻³)	168	0.076 $\pm$ 0.10	0.046 $\pm$ 2.6	0.045	0.035	2.6x10 ⁻³ -0.67
Sm (ng m ⁻³)	291	0.028 $\pm$ 0.038	0.018 $\pm$ 2.3	0.016	9.0x10 ⁻³	2.6x10 ⁻³ -0.28

Table 3.17. Statistical evaluation of PM_{2.5} aerosols (cont.)

Parameter	N	Arithmetic mean $\pm$ STD	Geometric mean $\pm$ STD ¹	Median	Mode	Range
Yb (ng m ⁻³)	294	0.041 $\pm$ 0.10	0.015 $\pm$ 2.9	0.011	9.0x10 ⁻³	2.2x10 ⁻³ -0.83
Lu (ng m ⁻³)	127	0.015 $\pm$ 0.028	0.0060 $\pm$ 3.4	3.2x10 ⁻³	3.0x10 ⁻³	1.9x10 ⁻³ -0.15
Hf (ng m ⁻³)	295	1.05 $\pm$ 3.17	0.22 $\pm$ 3.9	0.19	0.074	0.018-23
W (ng m ⁻³)	276	0.24 $\pm$ 0.29	0.17 $\pm$ 2.1	0.15	0.10	0.01-2.8
Th (ng m ⁻³)	295	0.076 $\pm$ 0.13	0.043 $\pm$ 2.4	0.036	0.023	3.2x10 ⁻³ -1.0
Hg (ng m ⁻³)	229	1.8 $\pm$ 6.1	0.39 $\pm$ 4.8	0.35	0.055	0.012-53
Bi (ng m ⁻³)	225	0.16 $\pm$ 0.14	0.11 $\pm$ 2.6	0.12	0.054	2.3x10 ⁻³ -0.75
Cl ⁻ (μ g m ⁻³)	334	2.1 $\pm$ 0.57	2.0 $\pm$ 1.3	1.9	1.8	0.33-5.9
NO ₃ ⁻ (μ g m ⁻³)	331	0.81 $\pm$ 0.82	0.60 $\pm$ 2.1	0.57	0.56	0.038-7.1
SO ₄ ²⁻ (μ g m ⁻³)	332	3.6 $\pm$ 2.2	3.1 $\pm$ 1.8	3.2	3.3	0.072-21
Na ⁺ (μ g m ⁻³)	90	0.59 $\pm$ 1.00	0.20 $\pm$ 4.6	0.15	0.074	0.010-6.7
NH ₄ ⁺ (μ g m ⁻³)	314	1.6 $\pm$ 1.1	1.2 $\pm$ 2.1	1.4	0.31	0.073-8.1
K ⁺ (μ g m ⁻³)	307	0.10 $\pm$ 0.11	0.065 $\pm$ 2.8	0.077	9.0x10 ⁻³	2.7x10 ⁻³ -1.1
Mg ²⁺ (μ g m ⁻³)	99	0.046 $\pm$ 0.062	0.023 $\pm$ 3.8	0.027	4.0x10 ⁻³	1.4x10 ⁻⁴ -0.36
Ca ²⁺ (μ g m ⁻³)	143	0.40 $\pm$ 0.61	0.20 $\pm$ 3.4	0.21	0.13	7.0x10 ⁻³ -3.8
OC (μ g m ⁻³)	309	7.0 $\pm$ 4.6	6.0 $\pm$ 1.7	5.6	4.4	1.9-34
EC (μ g m ⁻³)	309	1.6 $\pm$ 1.1	1.3 $\pm$ 1.9	1.3	1.1	0.054-8.2
TC (μ g m ⁻³)	309	8.6 $\pm$ 5.6	7.3 $\pm$ 1.7	6.8	5.3	2.5-44
PM _{2.5} (μ g m ⁻³) ^a	311	18 $\pm$ 10	16 $\pm$ 1.7	16	9.3	1.0-73
PM _{2.5} (μ g m ⁻³) ^b	338	17.5 $\pm$ 18.4	14 $\pm$ 2.0	14	15	0.47-277

N: number of observations

¹ geometric standard deviation^a in micro-glass fiber filter^b in teflon filter

Table 3.18. Statistical evaluation of PM_{2.5-10} aerosols

Parameter	N	Arithmetic mean $\pm$ STD	Geometric mean $\pm$ STD ¹	Median	Mode	Range
Na ($\mu\text{g m}^{-3}$)	223	4.4 $\pm$ 1.9	4.0 $\pm$ 1.5	3.9	5	0.32-11
K ($\mu\text{g m}^{-3}$)	227	0.29 $\pm$ 0.41	0.19 $\pm$ 2.2	0.19	0.20	0.011-4.2
Mg ($\mu\text{g m}^{-3}$)	280	0.74 $\pm$ 0.58	0.58 $\pm$ 1.9	0.59	0.39	0.020-6.2
Ca ($\mu\text{g m}^{-3}$)	281	4.2 $\pm$ 3.9	3.2 $\pm$ 1.8	3.7	1.4	0.210-41
Fe ($\mu\text{g m}^{-3}$)	278	0.31 $\pm$ 0.28	0.24 $\pm$ 1.8	0.23	0.16	0.028-2.2
Al ($\mu\text{g m}^{-3}$)	256	1.6 $\pm$ 0.87	1.4 $\pm$ 1.8	1.5	1.1	0.046-5.6
Zn ($\mu\text{g m}^{-3}$)	261	0.081 $\pm$ 0.046	0.066 $\pm$ 1.8	0.073	0.10	2.9x10 ⁻³ -0.22
V (ng m ⁻³)	203	3.2 $\pm$ 5.6	2.0 $\pm$ 2.3	2.0	1.6	0.075-34
Cr ($\mu\text{g m}^{-3}$)	279	0.023 $\pm$ 0.010	0.021 $\pm$ 1.4	0.021	0.019	5.1x10 ⁻³ -0.11
Mn (ng m ⁻³)	273	10 $\pm$ 9.3	7.7 $\pm$ 1.9	7.8	6.4	0.61-67
Co (ng m ⁻³)	242	2.1 $\pm$ 3.2	1.0 $\pm$ 3.1	0.81	0.56	0.062-15
Ni ($\mu\text{g m}^{-3}$)	278	0.026 $\pm$ 0.019	0.021 $\pm$ 1.8	0.018	0.012	3.3x10 ⁻³ -0.097
Cu (ng m ⁻³)	272	6.1 $\pm$ 5.2	4.8 $\pm$ 1.7	4.5	3.4	0.53-48
As (ng m ⁻³)	169	1.4 $\pm$ 3.3	0.52 $\pm$ 3.9	0.59	0.49	6.3x10 ⁻³ -20
Cd (ng m ⁻³)	148	1.4 $\pm$ 3.8	0.31 $\pm$ 4.5	0.32	0.080	9.5x10 ⁻³ -24
Pb ($\mu\text{g m}^{-3}$)	281	0.020 $\pm$ 0.056	0.0080 $\pm$ 2.9	6.5x10 ⁻³	4.0x10 ⁻³	3.2x10 ⁻³ -0.66
P ($\mu\text{g m}^{-3}$)	169	0.11 $\pm$ 0.15	0.075 $\pm$ 2.2	0.073	0.090	7.7x10 ⁻³ -1.0
Sc (ng m ⁻³)	148	2.1 $\pm$ 3.4	1.2 $\pm$ 4.0	1.3	2.2	1.0x10 ⁻² -26
Ti ($\mu\text{g m}^{-3}$)	170	0.080 $\pm$ 0.14	0.049 $\pm$ 2.3	0.043	0.039	5.9x10 ⁻³ -1.2
Se (ng m ⁻³)	65	0.19 $\pm$ 0.24	0.12 $\pm$ 2.8	0.12	0.14	4.5x10 ⁻³ -1.2
Y (ng m ⁻³)	176	0.26 $\pm$ 0.50	0.14 $\pm$ 2.5	0.14	0.17	0.015-3.6
Mo (ng m ⁻³)	175	2.6 $\pm$ 1.5	2.3 $\pm$ 1.7	2.4	2.6	0.057-13
Sb (ng m ⁻³)	175	1.6 $\pm$ 3.0	0.96 $\pm$ 2.2	0.83	0.84	0.15-28
Cs (ng m ⁻³)	110	0.071 $\pm$ 0.046	0.057 $\pm$ 2.1	0.063	0.034	1.1x10 ⁻³ -0.30
La (ng m ⁻³)	176	0.28 $\pm$ 0.31	0.20 $\pm$ 2.2	0.19	0.15	0.017-1.9
Nd (ng m ⁻³)	176	0.24 $\pm$ 0.28	0.16 $\pm$ 2.2	0.15	0.14	0.032-1.9
Eu (ng m ⁻³)	173	0.023 $\pm$ 0.035	0.012 $\pm$ 2.9	9.2x10 ⁻³	8.0x10 ⁻³	1.1x10 ⁻³ -0.24
U (ng m ⁻³)	138	0.12 $\pm$ 0.19	0.068 $\pm$ 2.8	0.076	0.064	2.7x10 ⁻³ -1.18
Tl (ng m ⁻³)	108	0.068 $\pm$ 0.10	0.033 $\pm$ 3.4	0.033	0.024	9.1x10 ⁻⁴ -0.59
Sm (ng m ⁻³)	176	0.042 $\pm$ 0.055	0.028 $\pm$ 2.4	0.027	0.028	1.5x10 ⁻³ -0.35

Table 3.18. Statistical evaluation of PM_{2.5-10} aerosols (cont.)

Parameter	N	Arithmetic mean $\pm$ STD	Geometric		Mode	Range
			mean $\pm$ STD ¹	Median		
Yb (ng m ⁻³)	171	0.042 $\pm$ 0.11	0.017 $\pm$ 2.8	0.016	0.016	3.1x10 ⁻⁴ -0.78
Lu (ng m ⁻³)	134	0.0090 $\pm$ 0.024	0.0040 $\pm$ 2.6	3.2x10 ⁻³	2.0x10 ⁻³	3.7x10 ⁻⁴ -0.15
Hf (ng m ⁻³)	166	0.87 $\pm$ 3.3	0.19 $\pm$ 3.3	0.18	0.081	3.0x10 ⁻³ -23
W (ng m ⁻³)	157	0.26 $\pm$ 0.58	0.15 $\pm$ 2.4	0.12	0.094	9.6x10 ⁻⁴ -5.6
Th (ng m ⁻³)	176	0.094 $\pm$ 0.16	0.056 $\pm$ 2.4	0.053	0.034	4.6x10 ⁻³ -1.0
Hg (ng m ⁻³)	138	0.66 $\pm$ 1.1	0.26 $\pm$ 3.9	0.21	0.050	5.6x10 ⁻³ -7.6
Bi (ng m ⁻³)	118	0.18 $\pm$ 0.27	0.088 $\pm$ 3.7	0.098	0.045	3.8x10 ⁻³ -1.9
Cl ⁻ (μg m ⁻³)	96	0.72 $\pm$ 0.79	1.0 $\pm$ 6.5	0.32	0.034	1.0x10 ⁻³ -4.5
NO ₃ ⁻ (μg m ⁻³)	182	0.72 $\pm$ 2.0	0.32 $\pm$ 3.8	0.37	0.19	2.4x10 ⁻³ -26
SO ₄ ²⁻ (μg m ⁻³)	333	1.5 $\pm$ 3.4	0.81 $\pm$ 2.7	0.76	0.56	9.0x10 ⁻³ -39
Na ⁺ (μg m ⁻³)	58	0.46 $\pm$ 1.0	0.18 $\pm$ 3.8	0.20	0.051	0.016-7.6
NH ₄ ⁺ (μg m ⁻³)	180	0.58 $\pm$ 0.54	0.34 $\pm$ 3.6	0.46	7.0x10 ⁻³	2.2x10 ⁻³ -3.8
K ⁺ (μg m ⁻³)	154	0.043 $\pm$ 0.14	0.017 $\pm$ 3.5	0.018	0.010	2.4x10 ⁻⁴ -1.5
Mg ²⁺ (μg m ⁻³)	97	0.052 $\pm$ 0.10	0.023 $\pm$ 3.8	0.034	0.014	8.7x10 ⁻⁴ -0.91
Ca ²⁺ (μg m ⁻³)	202	0.81 $\pm$ 0.72	0.50 $\pm$ 3.3	0.59	0.55	2.4x10 ⁻³ -4.0
PM _{2.5-10} (μg m ⁻³)	328	13 $\pm$ 9.2	10 $\pm$ 2.2	12	10	0.23-71

N: number of observations

¹ geometric standard deviation^a in micro-glass fiber filter^b in teflon filter

In this study, Skewness, Kurtosis, K-S DN and p-values were given in order to determine the distribution types (Table 3.19 and Table 3.20). As indicated above in environmental studies distribution functions can be varied with respect to emission sources and meteorological parameters. In general normal, log-normal and weibull distribution functions were found in atmospheric studies. In general, if pollutants are emitted from one source, normal and weibull distributions may be observed. However, sometimes log-normal distributions may be more possible although pollutants emitted from one source, because meteorological and geological parameters can alter the composition and the concentration of the pollutants.

The symmetry of the distribution around the mean value can be determined by skewness. For example, symmetric Gaussian distribution gives the skewness value as zero. Positive skewness value shows that distribution has the non-symmetric tendency through the positive values and vice versa in negative skewness.

Kurtosis value determines the condensation in the center of distribution and K-S DN (Kolmogorov-Smirnov) value determines the convenience of the log-normal distribution to the data set.

Finally, p-value is used to select the most suitable distribution function. P-value of the function should be greater than 0.05 however, if it is smaller than 0.05 then the function that has the smallest K-S DN value will be selected. In $PM_{2.5}$, all parameters except for Na, Mg, Fe, Al, Zn, V, Mn, Sb, Cs, Lu, NH_4^+ , K^+ , Mg^{2+} , $PM_{2.5}$, the others showed log-normal distribution and in $PM_{2.5-10}$ except for Mg, Al, Zn, Sn, Cs, NH_4^+ , Mg^{2+} , Ca^{2+} and $PM_{2.5-10}$, the others showed log-normal distribution.

Table 3.19. Distribution fitting parameters for elements in fine mode

Parameter	Skewness	Kurtosis	K-S DN	p-value	Distribution type
Na	-0.040	-0.90	0.073	0.092	Normal
K	1.7	1.7	0.12	1.2×10^{-4}	Log-normal
Mg	2.1	9.4	0.087	0.015	Weibull
Ca	0.70	-0.5	0.091	0.010	Log-normal
Fe	2.9	10	0.12	2.2×10^{-4}	Weibull
Al	-0.14	-0.82	0.059	0.26	Normal
Zn	1.4	3.6	0.058	0.23	Weibull
V	0.94	1.4	0.055	0.35	Weibull
Cr	4.6	30	0.11	5.2×10^{-4}	Log-normal
Mn	2.3	6.9	0.099	0.004	Weibull
Co	1.2	0.54	0.13	1.1×10^{-4}	Log-normal
Ni	2.0	6.5	0.15	1.7×10^{-6}	Log-normal
Cu	5.4	40	0.046	0.53	Log-normal
As	2.6	6.1	0.094	7.0×10^{-3}	Log-normal
Cd	5.5	37	0.12	3.7×10^{-4}	Log-normal
Pb	3.6	21	0.050	0.40	Log-normal
P	15	264	0.14	1.4×10^{-5}	Log-normal
Sc	4.9	27	0.21	0.00	Log-normal
Ti	8.0	72	0.13	6.6×10^{-5}	Log-normal
Se	2.4	7.9	0.035	1.0	Log-normal
Y	4.8	27	0.18	0.00	Log-normal
Mo	2.9	12	0.10	5.0×10^{-3}	Log-normal
Sb	0.32	1.1	0.060	0.24	Normal
Cs	1.3	3.8	0.076	0.23	Weibull
La	4.7	30	0.11	2.0×10^{-3}	Log-normal
Nd	3.4	14	0.073	0.088	Log-normal
Eu	4.2	21	0.15	7.2×10^{-6}	Log-normal
U	3.6	15	0.091	0.057	Log-normal
Tl	3.8	16	0.045	0.89	Log-normal

Table 3.19. Distribution fitting parameters for elements in fine mode (cont.)

Parameter	Skewness	Kurtosis	K-S DN	p-value	Distribution type
Sm	3.8	17	0.10	0.004	Log-normal
Yb	4.8	26	0.22	0.00	Log-normal
Lu	2.9	8.8	0.27	1.8×10^{-8}	Weibull
Hf	4.7	24	0.26	0.00	Log-normal
W	5.5	40	0.088	0.027	Log-normal
Th	4.2	21	0.17	8.4×10^{-8}	Log-normal
Hg	6.5	46	0.078	0.12	Log-normal
Bi	1.9	4.5	0.061	0.38	Log-normal
F ⁻	4.2	19	0.16	0.041	Log-normal
Cl ⁻	1.8	6.2	0.15	2.7×10^{-7}	Log-normal
NO ₃ ⁻	3.9	20	0.062	0.15	Log-normal
SO ₄ ²⁻	2.7	16	0.051	0.36	Log-normal
Li ⁺	2.8	9.9	0.34	1.5×10^{-5}	Log-normal
Na ⁺	3.3	15	0.083	0.56	Log-normal
NH ₄ ⁺	1.5	4.3	0.033	0.88	Weibull
K ⁺	4.8	36	0.055	0.31	Weibull
Mg ²⁺	3.0	11	0.074	0.65	Weibull
Ca ²⁺	3.5	14	0.077	0.37	Log-normal
OC	2.6	9.7	0.073	0.076	Log-normal
EC	2.3	8.0	0.050	0.41	Log-normal
TC	2.5	9.2	0.071	0.085	Log-normal
PM _{2.5}	1.6	4.5	0.073	0.053	Weibull

Table 3.20. Distribution fitting parameters for elements in coarse mode

Parameter	Skewness	Kurtosis	K-S DN	p-value	Distribution type
Na	1.4	2.9	0.067	0.27	Log-normal
K	6.0	47	0.042	0.83	Log-normal
Mg	4.0	30	0.11	3.0×10^{-3}	Weibull
Ca	5.1	39	0.097	0.021	Log-normal
Fe	3.0	12	0.044	0.65	Log-normal
Al	1.1	2.2	0.10	0.011	Weibull
Zn	0.74	0.18	0.032	0.96	Weibull
V	4.5	2.	0.094	0.053	Log-normal
Cr	2.7	19	0.081	0.051	Log-normal
Mn	3.2	13	0.063	0.23	Log-normal
Co	2.4	5.3	0.097	0.021	Log-normal
Ni	1.4	1.3	0.091	0.020	Log-normal
Cu	3.7	20	0.072	0.12	Log-normal
As	4.3	18	0.10	0.049	Log-normal
Cd	4.5	21	0.092	0.16	Log-normal
Pb	8.7	88	0.12	1.0×10^{-3}	Log-normal
P	3.7	15	0.12	0.011	Log-normal
Sc	5.4	33	0.15	2.0×10^{-3}	Log-normal
Ti	5.6	37	0.14	4.0×10^{-3}	Log-normal
Se	3.4	12	0.11	0.42	Log-normal
Y	5.0	27	0.13	5.0×10^{-3}	Log-normal
Mo	3.8	20	0.15	1.0×10^{-3}	Log-normal
Sb	6.0	46	0.23	9.3×10^{-9}	Log-normal
Cs	2.1	6.1	0.11	0.12	Weibull
La	3.1	10	0.075	0.28	Log-normal
Nd	3.4	12	0.089	0.12	Log-normal
Eu	3.0	11	0.12	0.017	Log-normal
U	4.4	20	0.12	0.040	Log-normal
Tl	2.9	9.6	0.061	0.82	Log-normal

Table 3.20. Distribution fitting parameters for elements in coarse mode (cont.)

Parameter	Skewness	Kurtosis	K-S DN	p-value	Distribution type
Sm	3.4	12	0.094	0.090	Log-normal
Yb	5.3	29	0.15	1.0×10^{-3}	Log-normal
Lu	4.8	22	0.22	3.9×10^{-6}	Log-normal
Hf	5.4	28	0.19	8.7×10^{-6}	Log-normal
W	6.7	53	0.17	2.4×10^{-4}	Log-normal
Th	4.2	19	0.11	0.038	Log-normal
Hg	3.5	15	0.12	0.026	Log-normal
Bi	3.7	17	0.064	0.72	Log-normal
F ⁻	3.4	15	0.16	0.041	Log-normal
Cl ⁻	1.6	4.1	0.13	0.096	Log-normal
NO ₃ ⁻	11	145	0.067	0.39	Log-normal
SO ₄ ²⁻	8.4	81	0.084	0.019	Log-normal
Li ⁺	1.4	2.0	0.34	1.5×10^{-5}	Log-normal
Na ⁺	6.0	41	0.082	0.84	Log-normal
NH ₄ ⁺	2.2	8.5	0.051	0.74	Weibull
K ⁺	9.0	90	0.075	0.36	Log-normal
Mg ²⁺	6.9	57	0.095	0.35	Weibull
Ca ²⁺	1.4	2.4	0.040	0.91	Weibull
PM _{2.5-10}	2.1	8.4	0.071	0.073	Weibull

3.5.1. Comparison of aerosol data with literature

In order to evaluate the conducted study, the concentration results of metal contents (Table 3.21 and Table 3.22) the ion contents (Table 3.23) and carbonaceous constituents, OC and EC (Table 3.24) were compared with literature values. In addition to suburban sites which had similar to our sampling point, different types of

sampling stations were used for the comparison. The aim is to observe the effect of site variation in aerosol constituents. For the comparison, the average concentration of each parameters were used.

The selected sites in literature for metal contents comparison in both fine and coarse fractions were suburban and urban site in İzmir (Yatkin et al., 2007), suburban site in Ankara (Yatin et al., 2000), city center of Budapest, Hungary (Salma and Maenhaut, 2006), urban site of Al-Hashimya, Jordan (Al-Momani et al., 2005), suburban site of Basel in Switzerland (Hueglin et al., 2005), Suburban site in Venice, Italy (Masiol et al., 2010), both traffic and industrial urban site in Thessaloniki, Greece (Terzi et al., 2010) and the same sampling point with our study (Sağırlı, 2013).

The ion constituents in the conducted study for both fractions were compared with the results of suburban sites in Basel, Switzerland (Hueglin et al., 2005) and Venice, Italy (Masiol et al., 2010), rural site in Erdemli (Koçak et al., 2007), semi rural site in Patras, Greece (Glavas et al., 2008), urban site of Iasi in Romani (Arsene et al., 2011), the mixture of five situations (traffic; industrial, residential, rural and suburban sites) in Beijing, China (Wang et al., 2005), rural and coastal site in Yangtze River Delta region in China (Kong et al., 2014) and finally, the urban site of Kanbur, India (Ram and Sarin, 2011).

Organic and elemental carbon fractions were determined only in PM_{2.5} in this study. However, for the comparison the carbonaceous contents in different particulate sizes were also used. The selected sites for OC, EC comparison in TSP in different types of sites (suburban, urban, rural and high-altitude) were conducted in India (Satsangi et al., 2012; Ram and Sarin, 2010; Rengaranjan et al., 2007).

The average organic and elemental concentrations in $PM_{2.5}$ were compared with urban site of Kanbur, India (Ram and Sarin, 2011) and three different sites (suburban, urban and industrial) in Xiamen, China (Zang et al., 2011).

Finally, in coarse fraction, PM_{10} , urban site of Kanbur in India (Ram and Sarin, 2011), both traffic and industrial sites of Thessaloniki in Greece (Terzi et al., 2010) and coastal site of Gdynia in Poland (Lewandowska et al., 2010) were selected for the comparison.

Tablo 3.21. Comparison of metal contents in PM_{2.5} with literature values (ng m⁻³)

	Izmir, Turkey ¹		Ankara, Turkey ²	Budapest, Hungary ³	This study
	Suburban	Urban	Suburban	City center	Semi-rural
Na	614	336	61	77	5200
K	193	548	140		562
Mg	60	104	70	81	880
Ca	894	177	95	262	4400
Fe	263	398	100	427	254
Al	494	858	110		1800
Zn	110	180	16	30	87
V	7	13	4	0.93	4
Cr	10	24	3	BDL	33
Mn	10	16	5		9
Co			3	0.09	1.5
Ni	8	18	3		33
Cu	11	40		18	9
As			2	0.39	2
Cd	0.8	1.5	0.11		1.6
Pb	32	98	71	16	19
Ti					79
Se			0.48	0.31	0.19
Y					0.23
Mo					3
Sb			1.3	6	0.95
Cs			0.08		0.069
La			0.14		0.22
Nd					0.18
Eu			0.02		0.011
Tl					0.076
Sm			0.02		0.028
Fine				20050 ^b	17500 ^a

^aPM_{2.5}, ^bPM_{2.0}

¹Yatkın et al., 2007

²Yatin et al., 2000

³Salma and Maenhaut, 2006

Table 3.21. Comparison of metal contents in PM_{2.5} with literature values (ng m⁻³) (cont.)

	Al-Hashimya, Jordan ⁴ Urban	Basel, Switzerland ⁵ Suburban	Bolu, Turkey ⁶ Semi-rural	This study Semi-rural
Na	418	117	217	5200
K	128	224	184	562
Mg	1008	16	73	880
Ca	4239	64	756	4400
Fe	248	66	199	254
Al	569	37	1970	1800
Zn	324		27	87
V	2	1.2	1	4
Cr	2		20	33
Mn	3	3.1	4	9
Co	5		2	1.5
Ni	7	1.7	6	33
Cu	26	6	6	9
As	0.68	0.4	1	2
Cd	4	0.48	5	1.6
Pb	24	19	12	19
Ti	21		11	79
Se		0.4	0.4	0.19
Y		0.01	0.05	0.23
Mo		0.39	0.3	3
Sb	10		1	0.95
Cs			0.1	0.069
La		0.05	0.1	0.22
Nd		0.02	0.1	0.18
Eu			0.01	0.011
Tl		0.03	0.1	0.076
Sm			0.02	0.028
Fine		18900		17500

^aPM_{2.5}

⁴Al-Momani et al., 2005

⁵Hueglin et al., 2005

⁶Sağırlı, 2013

Tablo 3.22. Comparison of metal contents in PM_{2.5-10} with literature values (ng m⁻³)

	Izmir, Turkey ¹		Budapest, Hungary ²	Al-Hashimya, Jordan ³	Venice, Italy ⁴	This study
	Suburban	Urban	City center	Urban	Suburban	Semi-rural
Na	1204	1024	353	948	1058	4400
K	336	490		509	195	290
Mg	208	271	386	1363	178	740
Ca	3490	4307	2334	17319	573	4200
Fe	738	912	1504	1600	224	310
Al	1187	1332		2690	212	1600
Zn	182	290	60	212	30	81
V	10	15	2	13	7	3
Cr	14	27	7	10	3	23
Mn	20	29		50	8	10
Co			0.39	11		2
Ni	20	16		9	4	26
Cu	20	48	44	10	7	6
As			1	2		1
Cd	1.4	2		4		1
Pb	50	149	11	89		20
P					28	110
Ti				2099	16	80
Se			BDL			0.20
Y						0.26
Mo						3
Sb			10	179		2
La						0.28
Nd						0.24
Tl						0.06
Coarse			30360 ^c		19 ^b	13400 ^a

^aPM_{2.5-10}, ^bPM₁₀, ^cPM_{2.0-10},

BDL: Below Detection Limit,

¹Yatkin et al., 2007,

²Salma and Maenhaut, 2006,

³Al-Momani et al., 2005,

⁴Masiol et al., 2010,

Tablo 3.22. Comparison of metal contents in PM_{2.5-10} with literature values (ng m⁻³) (cont.)

	Thessaloniki, Greece ⁵		Basel, Switzerland ⁶	Bolu, Turkey ⁷	This study
	Urban, industrial	Urban, traffic	Suburban	Semi-rural	Semi-rural
Na	-		147	310	4400
K	1637	935	41	135	290
Mg	276	197	34	128	740
Ca	10972	5726	196	1494	4200
Fe	981	592	221	237	310
Al	692	438	51	1393	1600
Zn	119	68		28	81
V	12	11	0.3	1	3
Cr	14	6		11	23
Mn	38	24	5	5	10
Co	8	3		2	2
Ni	12	8	0.46	3	26
Cu	63	33	3	5	6
As	6	3	0.11	1	1
Cd	20	12	0.04	13	1
Pb	35	19	4	11	20
P				17	110
Ti	69	43		22	80
Se	3	2	0.05	0.3	0.20
Y			0.03		0.26
Mo			0.42	0.2	3
Sb	17	22	0.29	0.4	2
La			0.05	0.2	0.28
Nd			0.04		0.24
Tl			0.01	0.04	0.06
Coarse			6700		13400

^aPM_{2.5-10}, ^bPM₁₀, ^cPM_{2.0-10},
BDL: Below Detection Limit,
⁵Terzi et al., 2010
⁶Hueglin et al., 2005,
⁷Sağırlı, 2013

Tablo 3.23. Comparison of ion contents in PM_{2.5} and PM_{2.5-10} with literature values (ng m⁻³)

		Basel, Switzerland ¹ suburban	Venice, Italy ² suburban	Erdemli, Turkey ³ rural	Patras, Greece ⁴ semi rural	Iasi, Romania ⁵ urban	Beijing, China ⁶ mix	Yangtze, China ⁷ rural, coastal	Kanbur, India ⁸ urban	This study semi-rural
Cl ⁻	Fine	145		108	120	191	3070	1518	675	2108
	Coarse	111	326	5384		215		936	970	725
NO ₃ ⁻	Fine			268	400	211	11520	14290	5750	809
	Coarse		985	1589		431		4578	9150	720
SO ₄ ²⁻	Fine			3142	3200	492	17070	15270	13550	3643
	Coarse		4051	1541		506		2830	16250	1474
Na ⁺	Fine	111		339		36	550	727	250	591
	Coarse	128	694	3095		145		1052	550	464
NH ₄ ⁺	Fine			850	1600	126	8720	11530	5250	1581
	Coarse		1380	-		46		1202	5450	575
K ⁺	Fine	218		108		27	1550	958	2400	101
	Coarse	28		95		15		187	2800	43
Mg ²⁺	Fine	13		54		14	170	105	45	46
	Coarse	26	131	435		119		247	300	52
Ca ²⁺	Fine	71		162	330	78	1630	1517	300	398
	Coarse	279		1398		1276		2631	305	814

¹Hueglin et al., 2005, ²Masiol et al., 2010, ³Koçak et al., 2007, ⁴Glavas et al., 2008, ⁵Arsene et al., 2011, ⁶Wang et al., 2005, ⁷Kong et al., 2014, ⁸Ram and Sarin, 2011

Table 3.24. Comparison of OC and EC in this study with different size fractions in literature ($\mu\text{g m}^{-3}$).

	Sampling site/ Site type	Sampling period	OC	EC	Reference
TSP	Dayalbagh, India/suburban	Dec 2008-Feb 2009	37.4	6.3	Satsangi et al., 2012
	Allahabad, India/urban	Dec 2004	49	6.2	
	Kanbur, India/urban	Jan-Mar 2007	25	4.8	Ram and Sarin, 2010
	Jaduguda, India/rural	Dec 2004	35.3	11.6	
	Manora Peak, India/high-altitude	Dec 2007-Feb 2008	13	2.0	Rengarajan et al., 2007
	Hisar, India/agricultural	Dec 2004	33	3.8	
	Manora Peak, India/high-altitude		3.8	0.9	
PM _{2.5}	Kanbur, India/urban	19-30 Oct 2008	45.8	8.2	Ram and Sarin, 2011
	Xiamen, suburban China urban industrial	Apr 2009-Jan 2010	15.8	2.7	Zhang et al., 2011
			19.3	3.3	
			19.7	3.5	
	Bolu, Turkey/semi- rural	Mar 2009-Mar 2010	7.0	1.6	This study
PM ₁₀	Kanbur, India/urban	19-30 Oct 2008	60.3	10.6	Ram and Sarin, 2011
	Thessaloniki, Greece/urban- industrial	Dec 2006-Mar 2007	7.7	2.9	Terzi et al., 2010
	Thessaloniki, Greece/urban-traffic	Jun-Sep 2007	7.9	2.2	
	Gdynia, Poland/coastal	Sep-Oct 2007	5.0	0.5	Lewandowska et al., 2010

a) İzmir, TURKEY (Yatkin et al., 2007)

Aerosol samples were collected on cellulose acetate filters with dichotomous sampler every 6 days between June 2004-May 2005. Sampling was conducted in urban and suburban sites in summer and winter period. The annual average concentration values were used for the comparison. When the suburban results of fine fractions were compared with our study, Ca, Fe and Cu values were close to each other.

In coarse fraction, Al, K, Cr and Ca results in summer were close to the values obtained in Bolu. Concentration of other elements except for Mg, were higher than our study. For example, Cd, Fe and Mn were 2 times, Pb and Zn were 3 times and finally Cu was 5 times greater than the values found in Bolu.

b) Ankara, TURKEY (Yatin et al., 2000)

Particulate matters were collected on polycarbonate filters by "GENT" stacked filter unit (SFU) in Middle East Technical University campus between February 4 and June 8, 1993. Sampling point was 10 km far away from the city center then it was identified as suburban. In these two studies (Ankara and Bolu), concentration of some rare earth metals (Cs, La, and Sm), V, Sb and As in fine fraction were close to each other. The concentrations of Na and Mg in our study were 85 and 12.5 times greater than the study of Yatin et al. (2000), respectively. The main reason might be the closeness of Bolu to the sea-side. The concentrations of K was 4 times, Zn was 5 times, Cr and Ni were 11 times, Cd was 4 times and Mn was 2 times lower than in our study. The main crustal elements, Ca, Fe and Al were 46 times, 2.5 times and 16 times lower than in our study. On the other hand, Co and Eu were 2 times and Pb and Se were 4 times greater than our results.

c) Budapest, HUNGARY (Salma and Maenhaut, 2006)

Aerosol samples were collected with same procedure as discussed in the study that performed by Yatin et al. (2000). Except for Pb, differences in concentrations of other elements in this study and in our study are great. For instance, in fine fraction, Mg concentration in Bolu was 10 times, Ca was 20 and Zn was 30 times higher than the values in the study of Salma and Maenhaut, 2006. Although concentrations of As and V were close to the values obtained in Bolu, the concentration of Pb, Ca and Mg were 2 times, the concentration of Zn was 1.5 times, the concentration of Cr was 3 times and the concentration of Co was 5 times greater in Bolu in coarse fraction.

d) Al-Hashimya, JORDAN (Al-Momani et al., 2005)

Daily samples were collected with SFU in urban area between 2000 and 2001. In our study, the concentration values for the most of the elements were 2 to 15 times greater than that in this study. For example, Ti, As and K, 4 times; Mn, Al, 3 times; V, 2 times; Ni, 5 times and Cr was 15 times greater in Bolu than in Al-Hashimya. Except for these elements, concentrations values for Ca, Fe and Pb were comparable in both studies. In coarse fraction, our study results for, Cr was 2 times, for Ni was 3 times and Na was 5 times greater. However, other elements were 2 to 5 times greater in Jordon.

e) Basel, SWITZERLAND (Hueglin et al., 2005)

Samples were collected in suburban area between 1998 and 1999. Although sampling areas were similar in both studies, the concentration values obtained in Bolu were higher than in Basel. However, Pb concentrations were close to each other. The concentrations of most elements obtained in Bolu were 2 to 20 times (like

Ca and Sb) greater than in this study in coarse fraction. In addition to metal contents also ionic composition of aerosols were also investigated. The concentration results were all lower than our concentration values in both PM_{2.5} and PM_{2.5-10}.

f) Bolu, TURKEY (Sağırlı, 2013)

The main difference between this study and our study was the sampling instrument. In this study samples were collected on polycarbonate filter instead of Teflon filter with SFU. Sağırlı conducted this study between 2011 and 2012. Although the sampling point was the same, except for Al, Cr, Co, Sb, Cs, Eu, Tl and Sm the concentrations of other elements were 2 to 10 times lower than our study.

Like in fine fractions, the concentration of some elements in coarse fractions were higher than that obtained in the study of Sağırlı (2013). However, Al, Co, Cu, As, Se and Tl values were comparable in both studies.

g) Venice, ITALY (Masiol et al., 2010)

Sampling was carried out in the coastal site in a relatively remote area in the north-eastern part of Italy, located between Adriatic Sea and the Po Valley which is recognized as the most industrialized district of Italy. Daily samples were collected on polycarbonate filters with low volume Skypost PMHV (TCR Tecora) instrument. Although the sampling site was close to industrial zone metal concentration values were lower than in Bolu. One of the reasons may be the dilution of pollutants by the predominant winds (NNE). The concentration values of SO₄²⁻, NH₄⁺ and Mg²⁺ were approximately 2.5 times greater than our results.

h) Erdemli, TURKEY (Koçak et al., 2007)

Atmospheric particles in two fractions, PM_{2.5} and PM_{2.5-10} were collected by a gent-type PM10 SFU at a rural site in Erdemli which is located on the coast of eastern Mediterranean. Sampling was conducted from April 2001 to April 2002. Water soluble ions (Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺) were measured by IC. Ammonium ion was determined only in fine fraction. Except for SO₄²⁻, the rest of the ion concentrations were high in PM_{2.5-10}. Especially for Cl⁻, Na⁺ and Mg²⁺ this high concentration values can be explained by sea effect. However, in our study only Mg²⁺ and Ca²⁺ had higher concentrations in PM_{2.5-10} than in PM_{2.5}. The SO₄²⁻ concentrations in two fractions and K⁺ in fine fraction were nearly same with our study. Nitrat, NH₄⁺, Cl⁻, Na⁺ and Ca²⁺ concentrations in PM_{2.5} were 3.0, 2.0, 19.5, 1.7 and 2.5 times lower than in our study, respectively. On the other hand, Cl⁻ Mg²⁺, Na⁺, NO₃⁻ and Ca²⁺ in PM_{2.5-10} were 7.0, 8.0, 6.7, 2.0 and 1.7 times greater than in our study.

i) Patras, GREECE (Glavas et al., 2008)

Inonic composition in PM_{2.5} was investigated for one year period (November 2004-October 2005) in this study. The semi-rural sampling point was located at the campus of the University of Patras in Greece. Aerosol samples were collected by Patashnick Partisol FRM-2000 Air Sampler at a flow rate of 16.67 l min⁻¹. Sulfate, NH₄⁺ and Ca²⁺ concentrations were similar to our results. Chloride concentration was nearly 17.5 times and NO₃⁻ concentration was 2 times lower than our results.

j) Iasi, ROMANIA (Arsene et al., 2011)

The sampling point was located in an urban site, Iasi which is in the north-eastern Romania. Sampling was performed twice a week, on weekend and working days between January 2007 and March 2008. PM_{2.5} and PM₁₀ aerosol samples were collected daily with SFU on polycarbonate filters. Samples were analyzed with Dionex DX-500 ion chromatography. Sodium, NH₄⁺, Cl⁻, SO₄²⁻ and Ca²⁺ in PM_{2.5} in our study were 5 to 16 times, NO₃⁻ and K⁺ were 4 times, and Mg²⁺ was 3 times greater than the concentration results in this study. In coarse fraction, Mg²⁺ and Ca²⁺ in this study were nearly 2 times greater than our results whereas the concentrations of NH₄⁺ was 13 times, Cl⁻, SO₄²⁻, Na⁺ and K⁺ were 3 times and NO₃⁻ was 2 times lower than our results.

k) Beijing, CHINA (Wang et al., 2005)

The study was conducted at five stations (traffic, industrial, residential, rural and suburban sites) and the aerosol samples of PM_{2.5} were collected on Whatman 41 filters by Medium-Volume samplers at a flow rate of 77.59 L min⁻¹ throughout 2 years (2001-2003). The results were the average concentrations obtained in these five stations. The concentrations of K⁺, NO₃⁻, NH₄⁺ and SO₄²⁻ in this study were 15, 14, 6 and 5 times greater than our results. Moreover, Ca²⁺ and Mg²⁺ were 4 times and Cl⁻ was 1.5 times greater than our concentration values. Finally, the average concentration of Na⁺ was nearly same with our result.

l) Yangtze, CHINA (Kong et al., 2014)

Yangtze River Delta region is located at the south of Yellow Sea in China. The sampling site was a kind of rural coastal site. An FA-3 particle sampler was used to

collect the particles that had size ranges between 0.43 to 10 μm . Only two fractions were used for comparison (fine, $\text{PM}_{2.1}$ and coarse, $\text{PM}_{2.1-10}$). Except for Na^+ and Mg^{2+} , all ions had higher concentrations in coarse mode than in fine mode. Chloride ion concentration in $\text{PM}_{2.1}$ was 1.4 times lower whereas, the rest of the ions were 1.2 to 18 times greater than our results. Especially, the ratio of NO_3^- , K^+ , NH_4^+ concentration values for two studies were 18, 9 and 7, respectively.

m) Kanbur, INDIA (Ram and Sarin, 2011)

The sampling site, Kanbur is a typical urban site that was located in the center of Indo-Gangetic Plain. Aerosol samples (both $\text{PM}_{2.5}$ and PM_{10}) were collected as day and night sample by Thermo Andersen Hi-Volume samplers during two weeks (19-30 October 2008). In the comparison table, the average of day and night samples were used. The concentrations of all ions in coarse mode were higher than in fine mode. The concentration ratio between coarse and fine for NH_4^+ , K^+ and Ca^{2+} were near to 1. Magnesium concentration in $\text{PM}_{2.5}$ was same as in our study. Sulfate concentration in this study was 3 times greater than our study in fine mode and 11 times higher than in coarse mode. In $\text{PM}_{2.5}$, NH_4^+ , K^+ and NO_3^- were 3.3, 23, and 7.1 times higher and in PM_{10} , 9.5, 65 and 12 times higher, respectively than our results.

Moreover, OC and EC were also determined in this study. The concentration values of OC and EC in this study were 6.5 and 5.1 times greater than our values, respectively.

n) Dayalbagh, Agra, INDIA (Satsangi et al., 2012)

The sampling was conducted from December 2008 to February 2009 in a suburban region, Dayalbagh, in where there was no industrial activities and the agricultural

activities were dominant. The daily air samples were collected on quartz microfiber filters by using a Low-Volume sampler at a flow rate of 30 L min^{-1} . Organic carbon and EC concentrations were determined with Sunset OC/EC analyzer (Model 2000) using NIOSH 5040 method. Although there is an influence on sampling site in our study the concentration of OC and EC in this study was nearly 5 times and 4 times greater than our results, respectively. Moreover, both OC and EC concentrations were also higher than the studies conducted in urban site in India (Ram and Sarin, 2010; Ram and Sarin, 2011).

o) Allahabad and Kanbur, INDIA (Ram and Sarin, 2010)

Total suspended particulate matters (TSP) were collected during winter time in two urban sites (Allahabad and Kanbur), one rural site (Jaduguda) and one high-altitude site stations. The carbonaceous species, OC and EC, were measured with Sunset Lab EC-OC Analyzer. The minimum concentration values were obtained at high-altitude station. Especially, EC concentration at this site was nearly same with our result.

p) Hisar and Manora Peak, INDIA (Rengarajan et al., 2007)

The study was conducted in two sites (Hisar, an agricultural area and Manora Peak, high-altitude) during December 2004. Aerosol samples (TSP) were collected by Andersen Hi-Volume sampler at a flow rate of $1.2 \text{ m}^3 \text{ min}^{-1}$ on Whatman quartz filters and analyzed in Sunset EC/OC Analyzer to determine the OC and EC fractions. The concentration of OC in Hisar was nearly 5 times and EC was 2.5 times higher than in our study. At high-altitude station the concentrations of both fractions were lower than in Hisar and they were approximately 2 times lower than our results.

q) Thessaloniki, GREECE (Terzi et al., 2010)

The chemical composition (minerals, elements, water soluble ions and carbonaceous fractions) of PM₁₀ was investigated in this study. Sampling was carried out at two urban sites (traffic and industrial sites) in Thessaloniki during December 2006-March 2007 and June-September 2007). Aerosol samples were collected on quartz filters (ions, OC and EC) and teflon filters (elements) by Low-Volume PM₁₀ samplers at a flow rate of 2.3 m³ h⁻¹. Elemental constituents were determined by Energy Dispersive X-ray Fluorescence (ED-XRF) technique, ions were determined by IC and OC and EC content were determined by Sunset EC-OC Analyzer.

Cadmium, Se, Cu and Sb in industrialized urban site were 20, 15, 11 and 9 times greater than our study, respectively. Arsenic and K were 6 times, V, Co and Mn were 4 times, Fe and Ca were 3 times and finally, Pb was 2 times greater than our results. The concentrations of Zn, Cr and Ti were nearly same with our results.

Cadmium, Sb, Se, Cu and V in traffic site were 12, 11, 10, 6 and 4 times greater than our results. The concentrations of K and As were 3 times and Mn, Fe and Co were 2 times greater than in our study. Calcium, Pb, Zn and Ni concentrations were near to our concentration values. Finally, the OC and EC concentrations in each site were same. Moreover, these results were also similar to OC and EC concentrations in our study.

r) Gdynia, POLAND (Lewandowska et al., 2010)

The sampling was performed in a coastal site, Gdynia in Poland from September to October 2007. The aerosol samples were collected on quartz filters by Low-Volume Sampler. Filter samples were analyzed with Perkin Elmer CHNS/O analyzer (Model

2400). The OC concentration exceeded the concentration of EC by one order of magnitude. The concentration of OC in our study was 1.4 times and the EC concentration was 3.2 times greater than this study.

3.6. Temporal variations of particulate matters

Daily concentration values of PM_{2.5} and PM_{2.5-10} aerosol contents in the sampling period (March 2009-March 2010) were illustrated in Figure 3.46 to Figure 3.49. During the whole sampling period the concentrations of Na, Al, V, Zn, Se, Cs, Sb, Bi, Li⁺, K⁺, NH₄⁺, NO₃⁻ and SO₄²⁻ showed little or no variation in fine fraction. Emission sources for these elements might be constant and local. In summer period especially, K, Mo, Ca, Ca²⁺, Mg²⁺, Na⁺ and Cl⁻ and rare earth metals had high concentrations. Except for K and Mo, the others are crustal and marine origin elements. In summer time, wood is generally used for heating which is the main source of K. Iron and Cu, reached their high concentration values both in summer and winter months. Effect of crustal sources could be observed in summer however, sources of high concentrations of them in winter might be anthropogenic. Nickel, Mn and Cr had also high concentrations in winter.

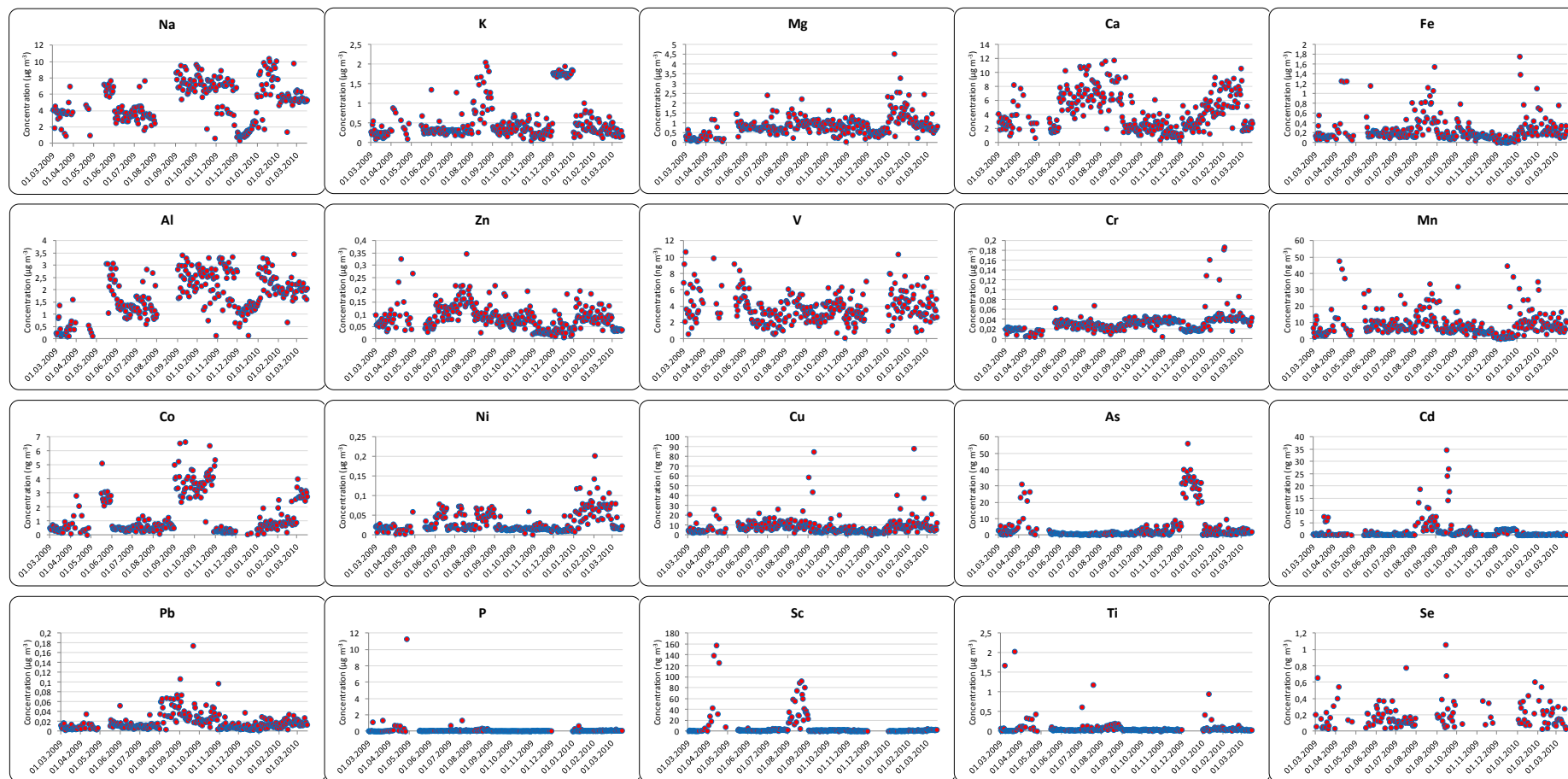


Figure 3.46. Daily concentrations of metals in fine fraction during the sampling period

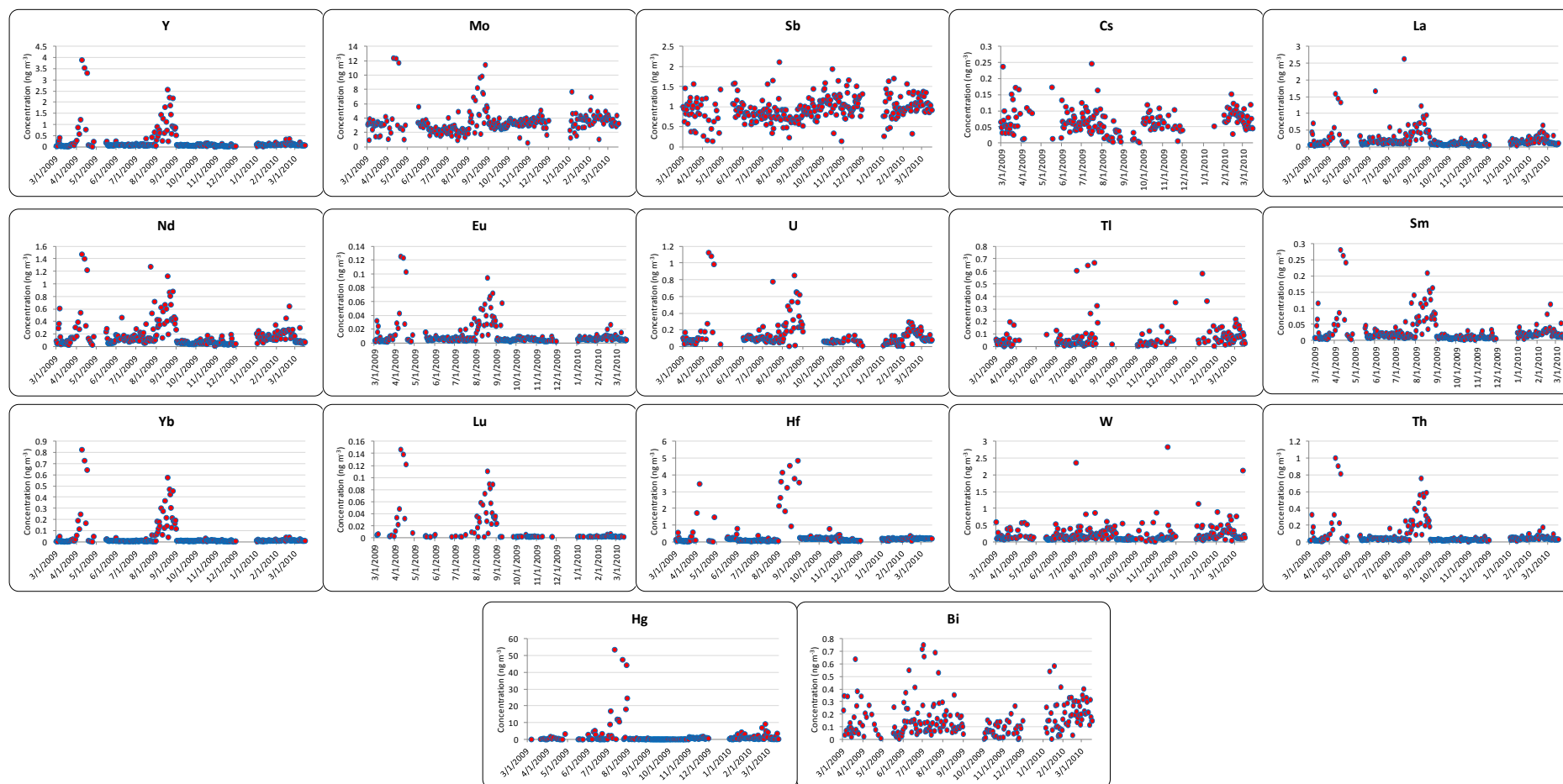


Figure 3.46. Daily concentrations of metals in fine fraction during the sampling period

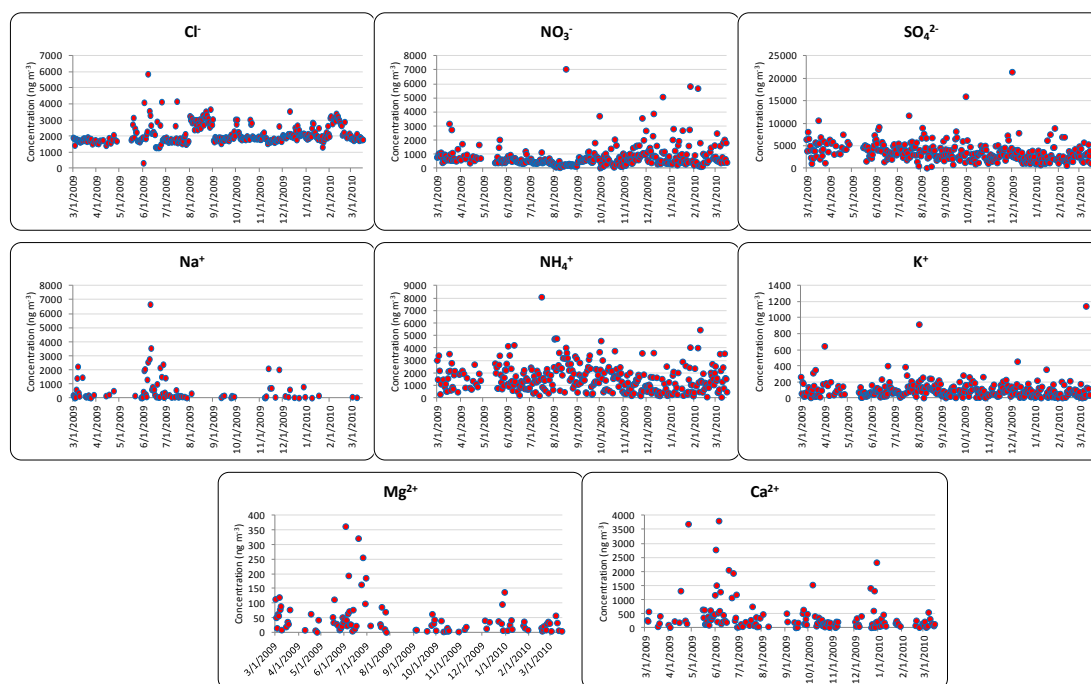


Figure 3.47. Daily concentrations of ions in fine fraction during the sampling period

In coarse fraction the concentration variations of each element during the sampling period are given in Figure 3.48 and ions in Figure 3.49. Sodium, Na^+ , Mg, Mg^{2+} , Al, Zn, NO_3^- , Ca^{2+} and except for few days Pb and Se concentrations were nearly the same during the whole sampling period. At the beginning of the growing season (April to June) K, Fe, V, Mn, As, P, Mo and some rare earth metals (Sc, Tl, Y, U, Nd, La, Sm, Th and Yb) had high concentrations. Similar trends between anthropogenic and crustal elements can be explained as the deposition of anthropogenic elements on crustal particles. Finally, in summer, Ca, W, Bi, Hg, NH_4^+ and K^+ had the highest concentrations.

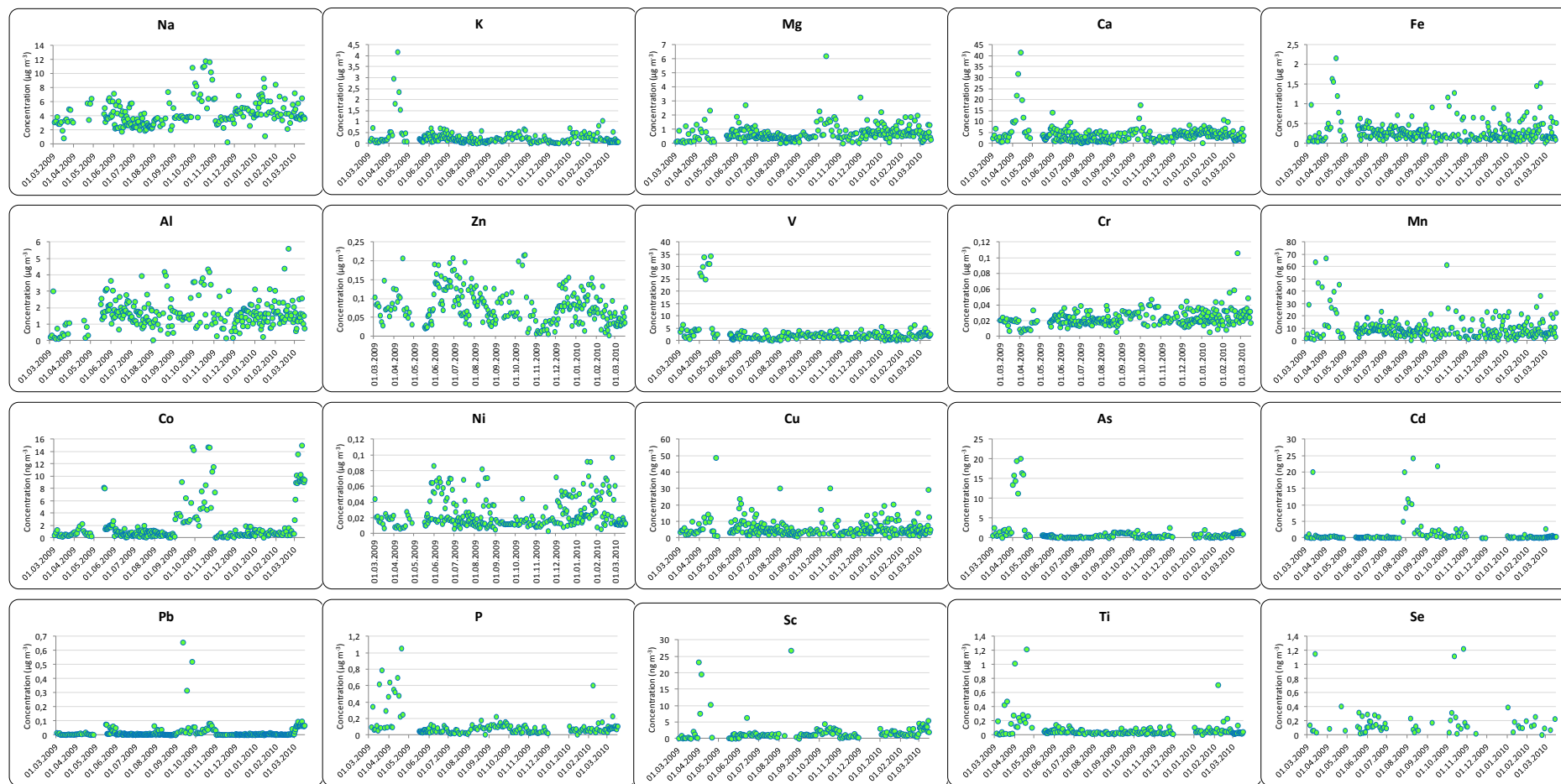


Figure 3.48. Daily Average concentrations of metals in coarse fraction during the sampling period

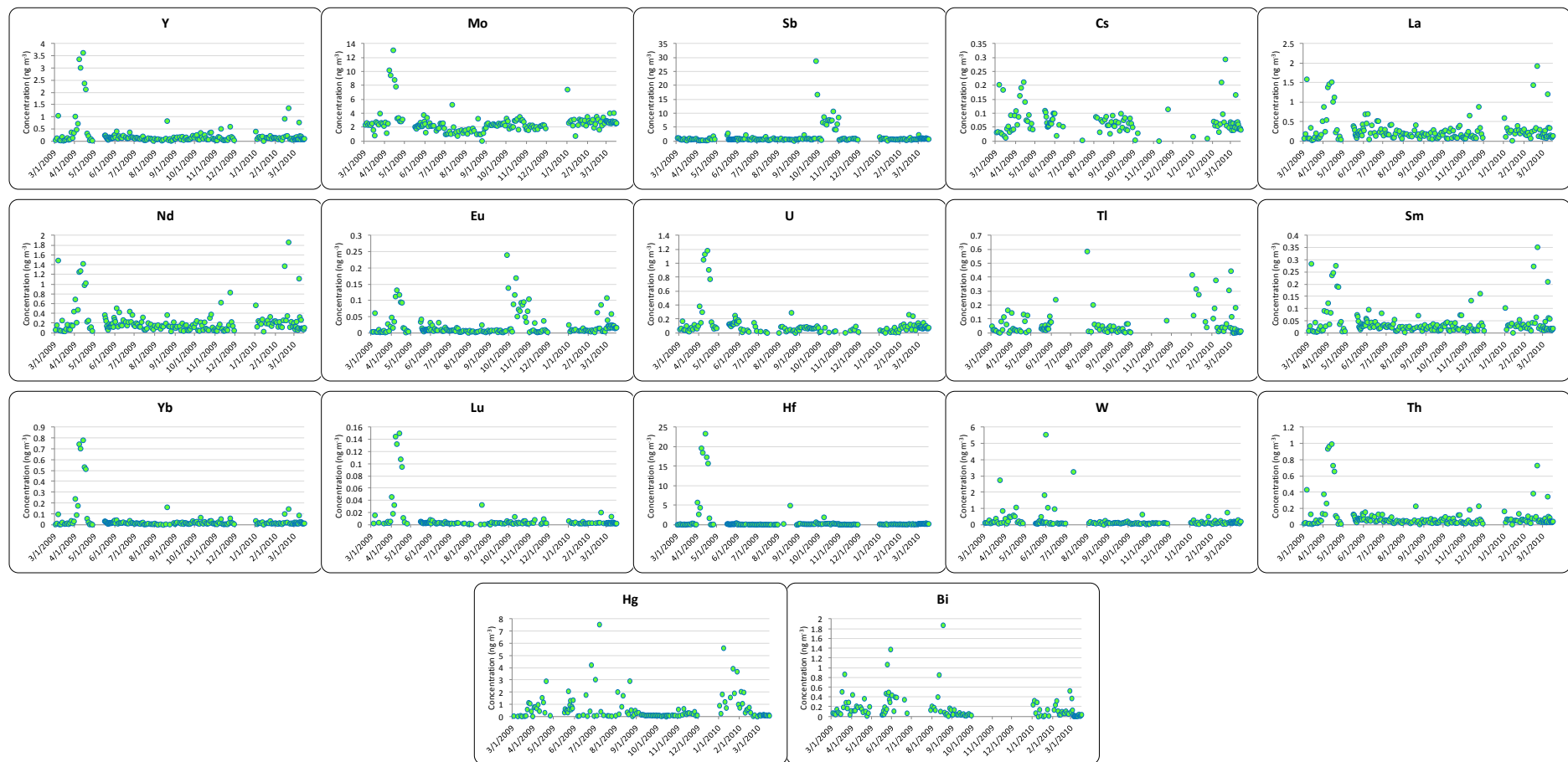


Figure 3.48. Daily Average concentrations of metals in coarse fraction during the sampling period (cont.)

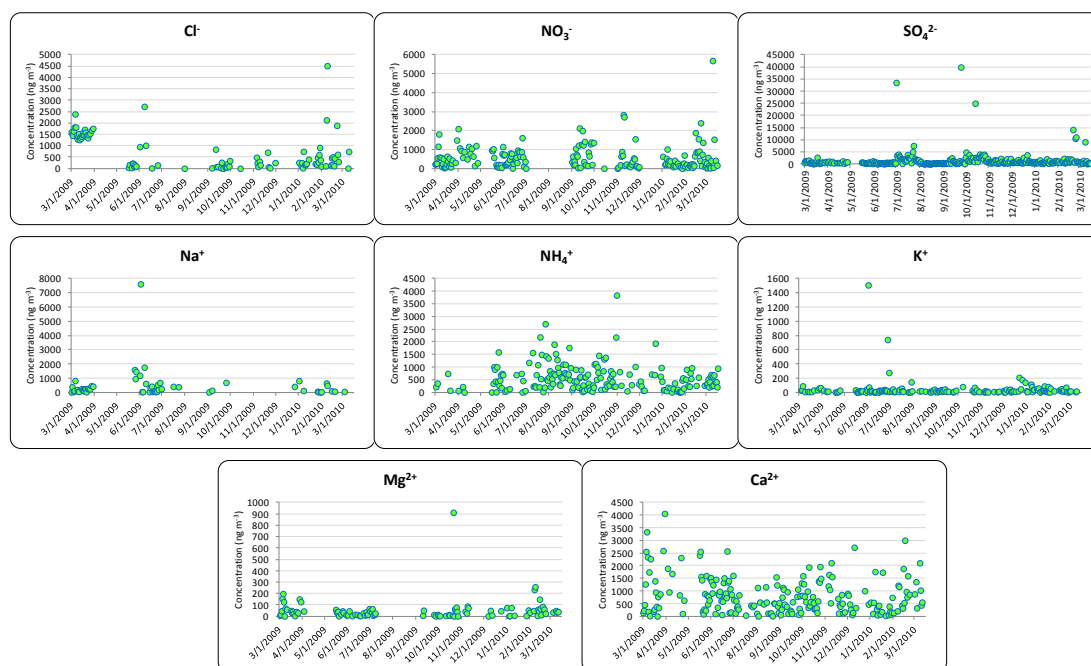


Figure 3.49. Daily concentrations of ions in coarse fraction during the sampling period

Elemental distribution in each fraction is given in Figure 3.50. Aluminum, Zn, Co, Na, Na^+ , W, NO_3^- , Y, Mg, Mn, V, Cd, Hf, Se, U, Tl, Ti, Cs, Th, Yb, Bi and Pb exist almost equally in both fractions. In $\text{PM}_{2.5}$ fraction the most of the anthropogenic elements Hg, As, Mo, Cu, Ni, Cr, K, P, K^+ , NH_4^+ , Cl^- , SO_4^{2-} and crustal elements Lu and Sc were found. Finally, the concentrations of Eu, Sm, Sb, Ca^{2+} , Fe, Nd, La and Mg^{2+} were generally observed in $\text{PM}_{2.5-10}$ fraction.

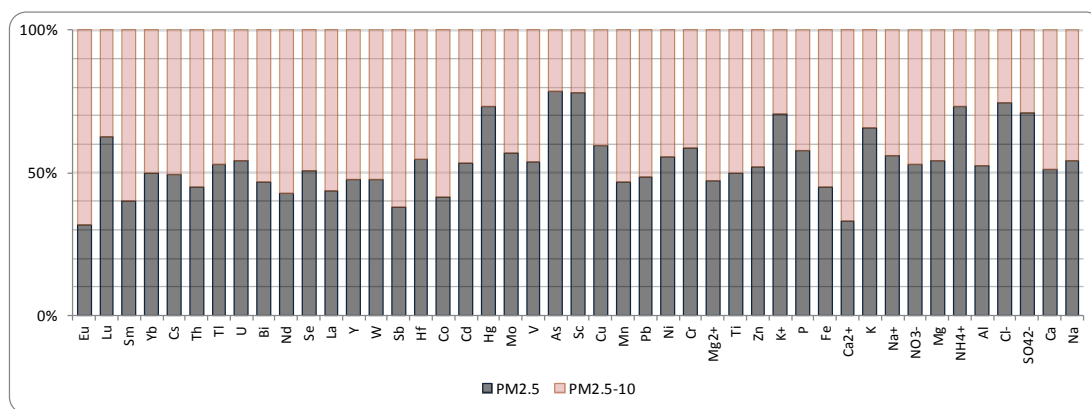


Figure 3.50. Percent distribution of fractions for each element

The mass concentration ratios of $PM_{2.5}$ and $PM_{2.5-10}$ are given in Figure 3.51. Except for June, the concentration of $PM_{2.5}$ was always greater than $PM_{2.5-10}$. The reason can be the scavenging of fine mode particulates in this month due to wet deposition. Rain events were obtained during April to August in the sampling period and the maximum rainfall was obtained in June (Figure 3.14). Especially, in winter months due to domestic heating and less dispersion, fine mode particulates are much more favorable then, the ratios were greater.

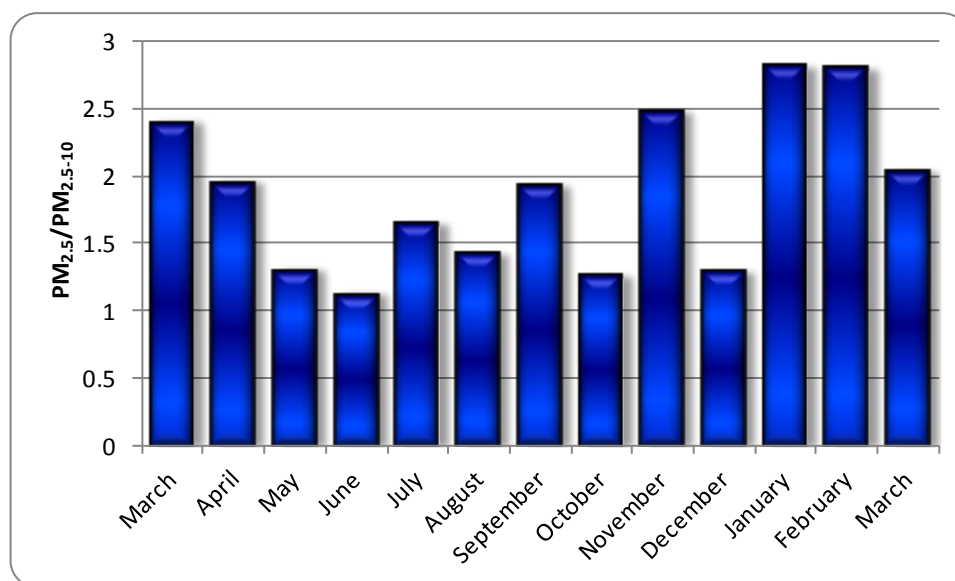


Figure 3.51. Monthly ratios of fine and coarse mode particulate matters

3.6.1. Seasonal variation

Investigation of seasonal variation of pollutants is one of the main tools for source apportionment. For example, some elements like As, Sb might have higher concentrations in winter than in summer. This indicates that these pollutants might be emitted from domestic heating. However, we cannot generalize that the seasonal differences are only due to source variation. Meteorological parameters also alter the residence time and formation/destruction mechanisms of the pollutants. Then, the related pollutants have different structure and concentration when reach to the receptor after the emission.

Seasonal variation of elements in PM_{2.5} and PM_{2.5-10} are given in Table 3.25. In this study seasons are identified as heating season (September to February) and non-heating season (March to August). In both fractions Na, Mg, Cr and Co have high concentrations in heating season.

Table 3.25. Average and median concentrations of elements in winter (heating) and in summer (non-heating) seasons with respect to fine and coarse mode (ng m⁻³).

	PM _{2.5}				PM _{2.5-10}			
	Winter (Heating)		Summer (Non-heating)		Winter (Heating)		Summer (Non-heating)	
	avg	med	avg	med	avg	med	avg	med
Na	5874	6484	4021	3763	5073	4372	3625	3300
K	605	388	488	324	239	192	332	192
Mg	981	903	739	728	885	754	585	466
Ca	3508	2705	5590	5857	4232	4050	4153	3102
Fe	217	164	303	195	300	198	327	265
Al	2128	2116	1229	1205	1672	1541	1608	1577
Zn	71	66	109	100	70	63	93	86
V	3.8	3.6	3.8	3.4	2.2	2.1	4.6	2.0
Cr	39	37	25	24	26	24	20	19
Mn	8.0	6.3	10	8.0	9.3	6.6	11	8.6
Co	2.0	1.3	0.84	0.54	3.4	1.2	0.95	0.66
Ni	33	19	31	23	27	18	25	19
Cu	8.6	5.9	9.3	8.3	6.0	4.6	6.2	4.3
As	7.3	2.2	2.3	0.96	0.81	0.80	2.0	0.47
Cd	1.6	0.45	1.6	0.32	0.88	0.36	1.8	0.21
Pb	20	15	18	12	28	7.1	11	6.3
P	88	71	223	86	85	78	141	67
Sc	1.8	1.8	14	2.5	1.9	1.5	2.3	0.98
Ti	56	44	105	42	58	41	105	45
Se	0.22	0.17	0.17	0.13	0.22	0.13	0.16	0.11
Y	0.095	0.088	0.39	0.10	0.18	0.14	0.34	0.14
Mo	3.5	3.5	3.4	2.9	2.6	2.6	2.6	2.2
Sb	1.0	1.0	0.85	0.82	2.3	0.95	0.82	0.74
Cs	0.070	0.067	0.068	0.060	0.066	0.056	0.075	0.067
La	0.14	0.12	0.31	0.17	0.25	0.18	0.32	0.21
Nd	0.11	0.081	0.25	0.14	0.21	0.14	0.26	0.16
Eu	0.0063	0.0053	0.016	0.0068	0.030	0.012	0.017	0.0086
U	0.093	0.072	0.18	0.095	0.072	0.073	0.16	0.091
Tl	0.081	0.055	0.072	0.034	0.078	0.032	0.060	0.033
Sm	0.017	0.014	0.041	0.019	0.038	0.025	0.047	0.028
Yb	0.013	0.012	0.073	0.011	0.021	0.016	0.064	0.016

Table 3.25. Average and median concentrations of elements in winter (heating) and in summer (non-heating) seasons with respect to fine and coarse mode (ng m^{-3}) (cont).

	PM _{2.5}				PM _{2.5-10}			
	Winter (Heating)		Summer (Non-heating)		Winter (Heating)		Summer (Non-heating)	
	avg	med	avg	med	avg	med	avg	med
Lu	0.0032	0.0027	0.032	0.020	0.0038	0.0031	0.015	0.0033
Hf	0.19	0.20	2.0	0.12	0.23	0.21	1.6	0.14
W	0.24	0.13	0.23	0.16	0.14	0.12	0.39	0.14
Th	0.037	0.031	0.12	0.043	0.070	0.049	0.12	0.059
Hg	0.83	0.39	3.5	0.32	0.52	0.14	0.83	0.45
Bi	0.16	0.14	0.16	0.11	0.087	0.043	0.27	0.15
Cl ⁻	2072	1933	2153	1848	407	210	1135	1409
NO ₃ ⁻	937	655	644	515	847	274	551	485
SO ₄ ²⁻	3201	2697	4206	4041	1691	873	1184	568
Na ⁺	328	93	698	201	243	94	541	242
NH ₄ ⁺	1396	1232	1819	1603	504	381	677	583
K ⁺	90	72	114	86	31	19	56	16
Mg ²⁺	24	15	65	42	61	37	41	31
Ca ²⁺	261	154	563	278	730	541	901	730

Summer/winter elemental concentration ratios for PM_{2.5} and PM_{2.5-10} are summarized in Figure 3.52 and Figure 3.53, respectively. Summer to winter ratios for Cu, Cl⁻, Bi, V, Cd, Cs, W, Mo and Ni were close to 1. This indicated that these elements showed no seasonal variation and they could have been emitted from local sources. A possible source for the anthropogenic elements (Hf, Hg, Th, U, Zn and Mn) could be long-range transportation in summer. On the other hand, other anthropogenic elements (Pb, Tl, Sb, K, Se, Cr, Co and As) had higher concentrations in winter months and this situation indicated that these elements could have been emitted from coal combustion.

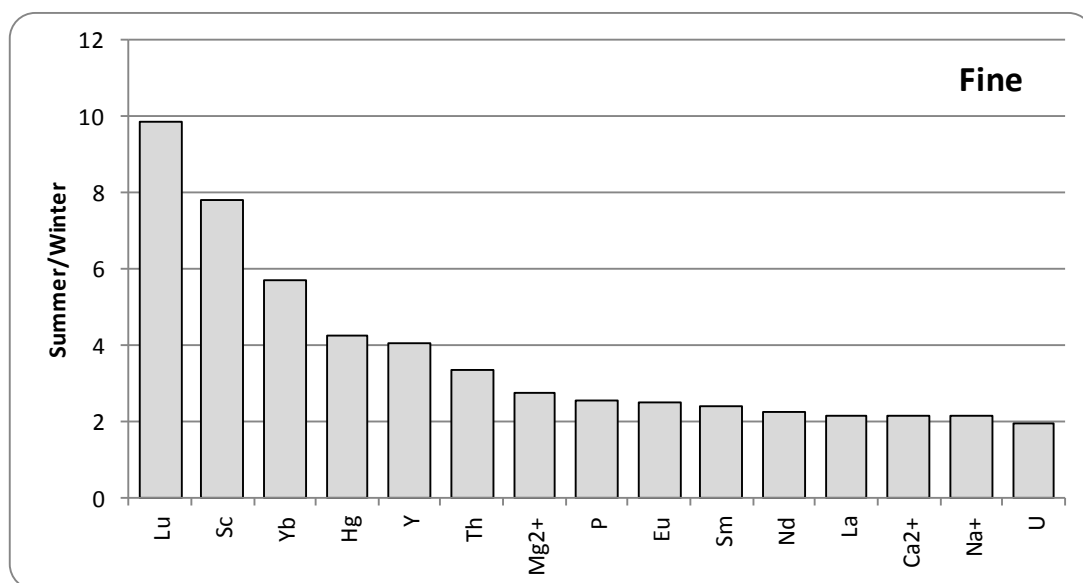


Figure 3.52. Summer to winter ratios of elements in fine fraction

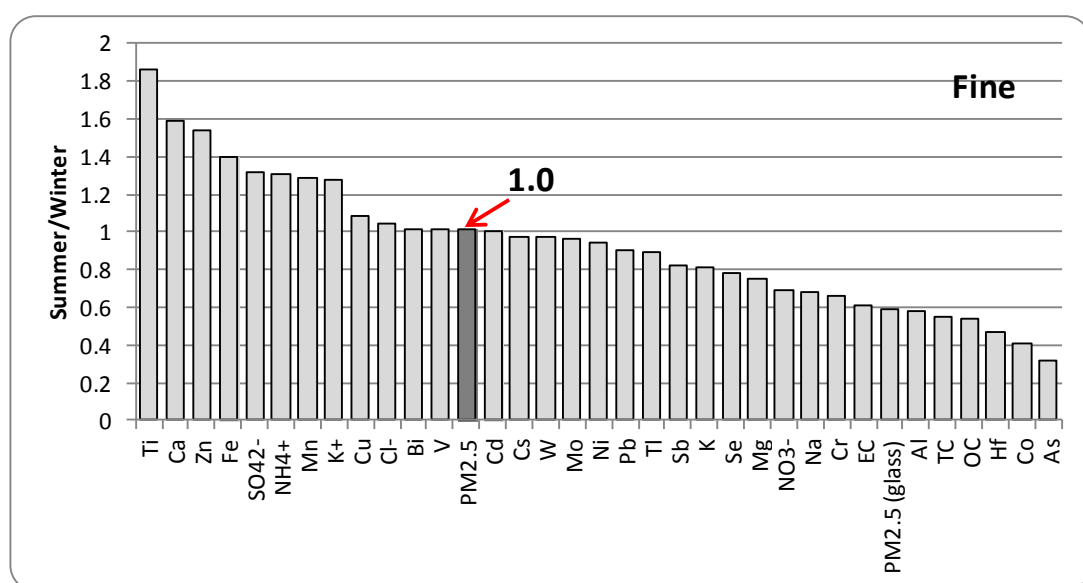


Figure 3.52. Summer to winter ratios of elements in fine fraction (cont.)

Summer to winter ratios for crustal elements in PM_{2.5-10} were higher like in PM_{2.5}. this ratio values for Ca, Mo, Al and Ni were close to 1. In coarse particles As was observed 2 times higher in summer than in winter. However, Se, Co and Sb had higher concentrations in winter.

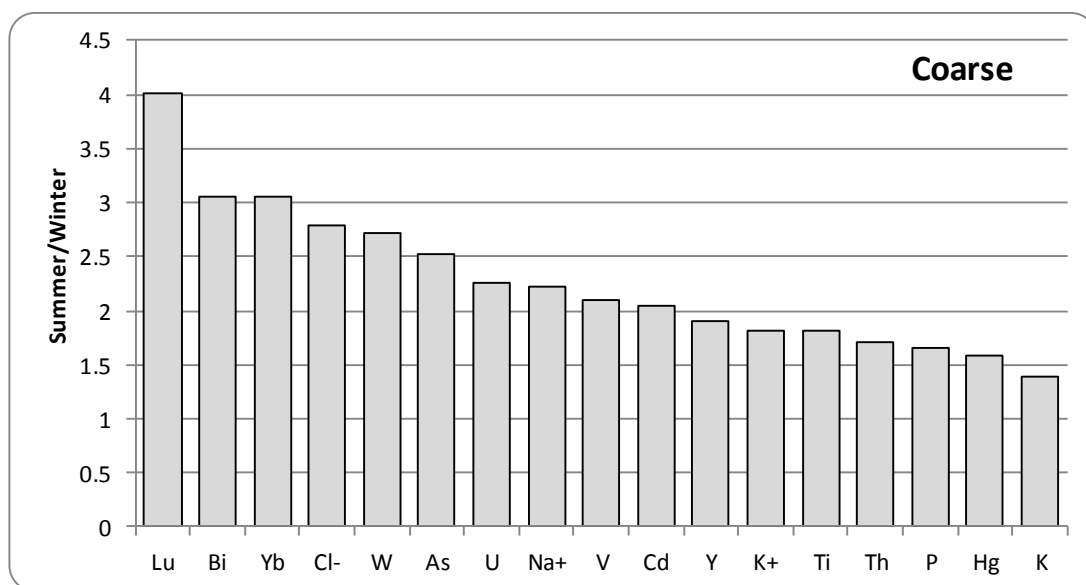


Figure 3.53. Summer to winter ratios of elements in coarse fraction

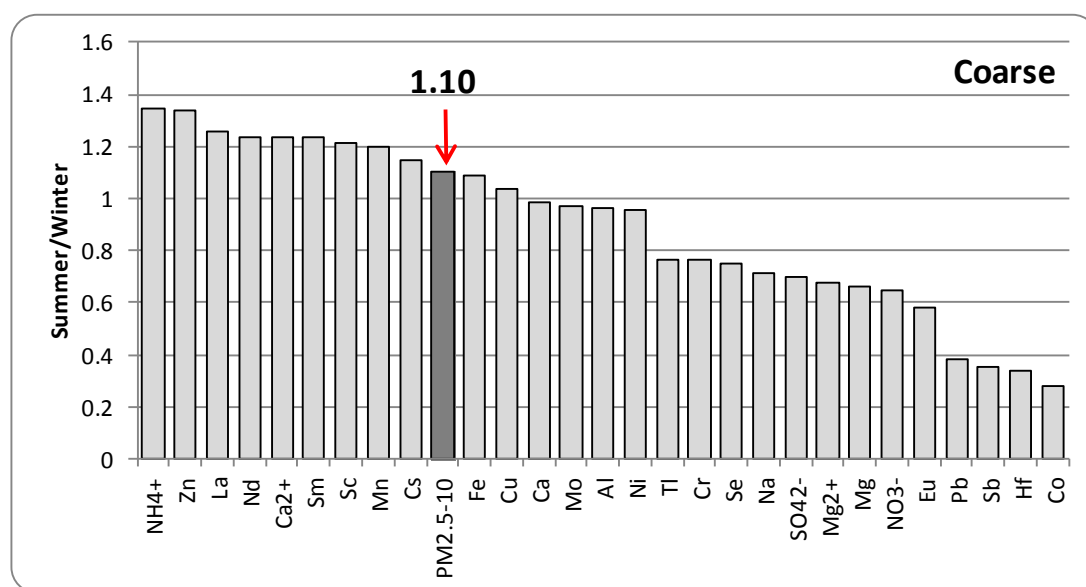


Figure 3.53. Summer to winter ratios of elements in coarse fraction (cont.)

3.7. Carbon contents in PM_{2.5}

Carbonaceous compositions (total carbon content) nearly composed of 30 % of fine mode aerosol samples. The regression results of OC, EC, TC and PM_{2.5} are given in Figure 3.54 with R² values as 0.692, 0.626 and 0.707, respectively.

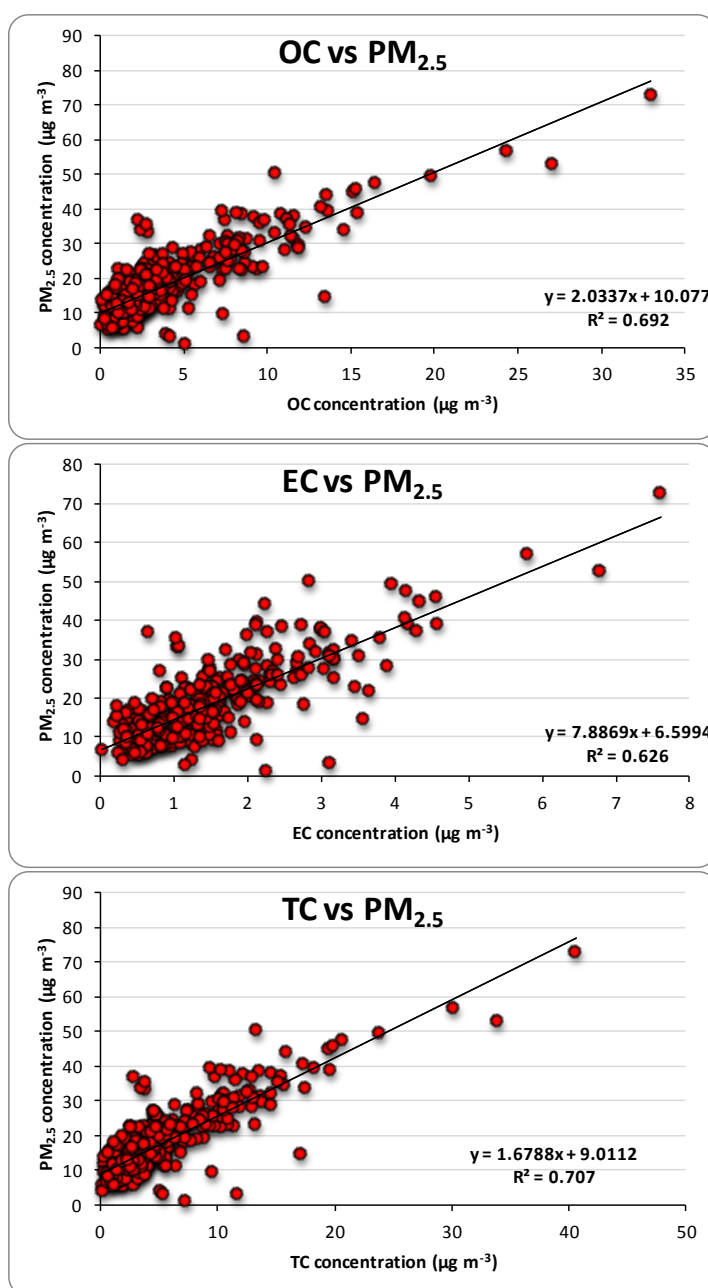


Figure 3.54. Correlations between carbonaceous compositions and PM_{2.5}

3.7.1. Secondary organic carbon

Secondary organic fraction of carbonaceous aerosols can be estimated by assuming that the lowest OC/EC ratio found for a location is representative for primary OC/EC ratio (Schaap, et al., 2007) because primary OC and EC have the same source (Salma, et al., 2004). This approach generally used for urban locations where the ratio of OC/EC is near to 1. However, it is difficult to conclude the presence of secondary OC from the absolute values of OC/EC alone (Na et al., 2004) and also the amount of secondary OC aerosol depends not only on the ratio, but also on ambient carbon concentrations (Turpin and Huntzicker, 1995). Hence, extrapolation of the minimum OC/EC value to the whole sampling period as a substitute for the primary OC/EC ratio can not be accepted for any locations other than heavily pollutant urban sides. In our sampling site one of the dominant source was found as traffic. Then the minimum OC/EC value was accepted to calculate primary OC. Secondary organic carbon (OC_{sec}) can be estimated from the following equations (Turpin and Huntzicker, 1995; Na et al., 2004; Satsangi et al., 2012; Salma et al., 2004; Zhou et al., 2012).

$$OC_{sec} = OC_{tot} - OC_{pri} \quad (\text{Eq 3.5})$$

$$OC_{pri} = EC \times (OC/EC)_{pri} \quad (\text{Eq 3.6})$$

These calculations can be used in fine fraction of aerosols because in coarse mode OC originates from other sources like pollen, spores, paved road dust, tyre rubber. One of the weakness of this approach is the variation of $(OC/EC)_{pri}$ emission rates. This ratio can be influenced by local sources and meteorology (Salma et al., 2004).

The amount of primary organic carbon (OC_{pri}) was calculated by taking the average of the minimum ratios of OC/EC and multiplying it with the average concentration of EC in each month.

The percent distribution of the primary OC and the secondary OC concentrations in each month is given in Figure 3.55. Throughout the growing season (April to September) the percent distribution of OC_{pri} was greater than 50%.

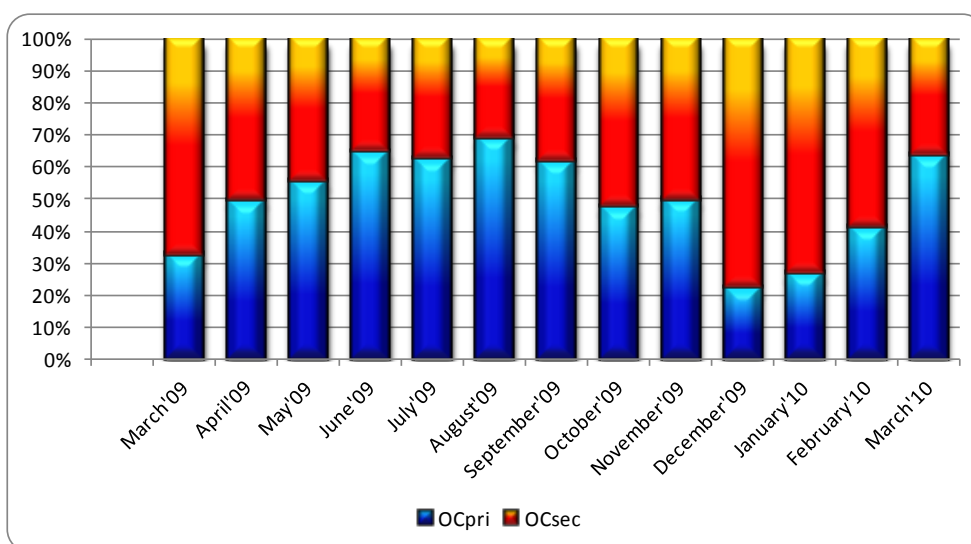


Figure 3.55. Percent distribution of OC_{pri} and OC_{sec}

The main source for OC_{pri} is the biomass burning. Some of the tracers for biomass burning are levoglucosan, mannosan (1,6-anhydro- β -D-mannopyranose), galactosan (1,6-anhydro- β -D-galactopyranose) and 1,6-anhydro- β -D-glucofuranose (1,6-AGF) (Kourtchev et al., 2011). There are two formation processes for the formation of OC_{sec} . The first one is the production of condensable organic compounds (i.e., isoprene, α -/ β -pinene and D-limonene) by oxidation reactions with radicals and

oxidizing agents like $\text{OH}\cdot$, NO_3 and O_3 and the second one is subsequent the nucleation and condensation processes (Na et al., 2004; Blanchard et al., 2008). The common markers of OC_{sec} are 2-methyltetrols (2-methylthreitol and 2-methylerythritol), C_5 -alkenetriols (i.e., cis- and trans-2-methyl-1,3,4-trihydroxy-1-butene and 3-methyl-2,3,4-trihydroxy-1-butene), -methyl-1,2,3-butanetricarboxylic acid (3-MBTCA) and 3-carboxyheptanedioic acid (Kourtchev et al., 2011).

Temporal variations of O_3 , OC_{pri} and OC_{sec} were illustrated in Figure 3.56. Except for April 2009, November 2009 and March 2010, the concentration of OC_{pri} was not changed too much and the value was around $1.3 \mu\text{g m}^{-3}$ and the overall annual average concentration was $1.5 \mu\text{g m}^{-3}$. Then, the source of OC_{pri} might be constant and local rather than biomass burning. In cold season (October to March) the concentrations of OC_{sec} were greater than OC_{pri} and the annual average concentration was $1.8 \mu\text{g m}^{-3}$. Due to the the presence of forest and agricultural areas around the sampling point the biogenic emissions by terrestrial vegetation as biogenic volatile organic compounds (BVOCs) were obtained throughout the year. However, in summer months when the photochemical activities are greater these is a much consumption of these compounds and OC_{sec} . In the general mechanism of catalytic formation of O_3 , VOCs and NO_x are oxidized in the presence of intense sunlight. The annual average of O_3 was 24.5 ppb whereas the summer average concentration value was 34.0 ppb.

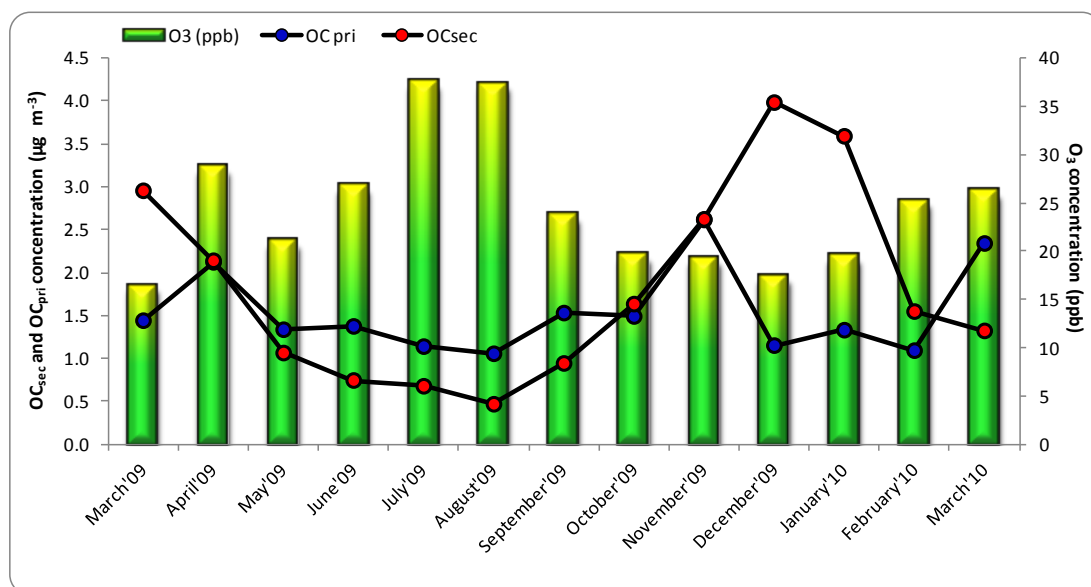


Figure 3.56. Temporal variations of O₃, primary and secondary organic carbon

The statistical relationship between organic carbon fractions (OC_{pri} and OC_{sec}, independent variables) and O₃ (dependent variable) was determined by regression analysis (Figure 3.57). Organics are used up during the formation of O₃ then the correlations between variables were negative as expected. The simple regression between O₃ and OC_{total} in Figure 3.57(a), between O₃ and OC_{pri} in Figure 3.57(b) and between O₃ and OC_{sec} in Figure 3.57(c) show that the models explained 41.7%, 4.1% and 51.2% of the variability in O₃ concentration, respectively. According to the results OC_{sec} is used more than OC_{pri} for the formation of O₃.

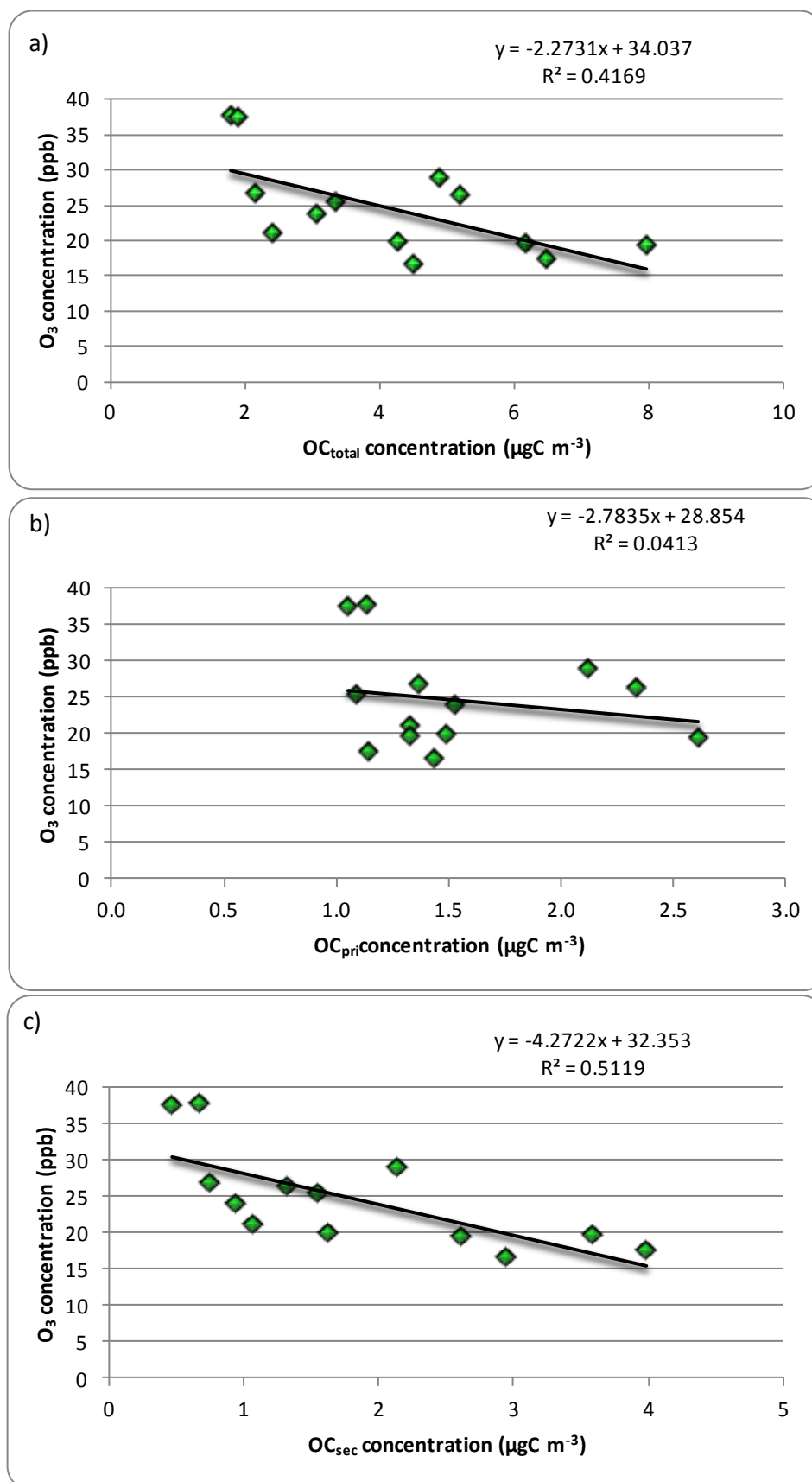


Figure 3.57. The regression graphs of O₃, OC_{total} (a) OC_{pri} (b) and (c) OC_{sec}

3.7.2. Relationship between OC and EC concentrations

The relationship between OC and EC concentrations can be used to identify the potential source of carbonaceous particles (Na et al., 2004; Turpin and Huntzicker, 1995). It is well known that EC arises as result of incomplete combustion sources, it is often used as a tracer of primary OC (Satsangi et al., 2012; Cao et al., 2004). Change of concentrations of OC and EC during the sampling period are given in Figure 3.58. It was observed that there was an obvious increase in the concentrations of both OC and EC during the heating season.

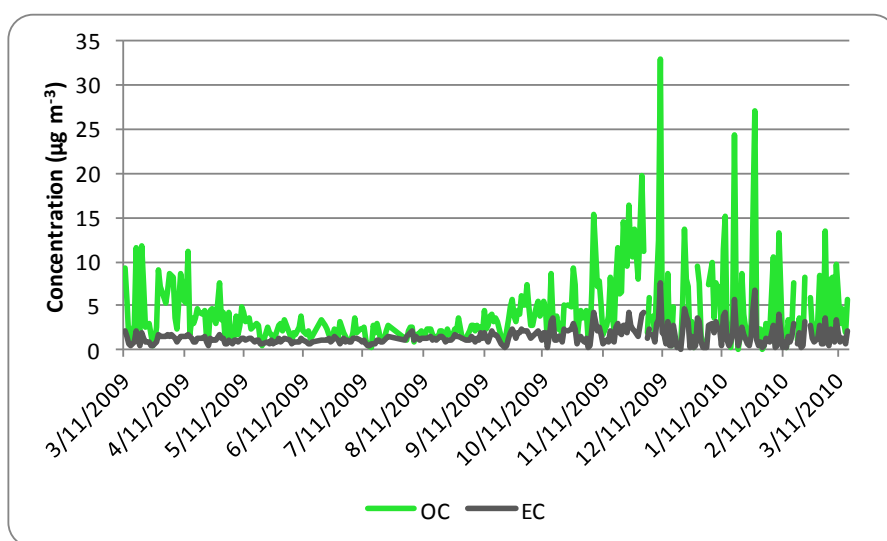


Figure 3.58. Temporal variations of OC and EC during the sampling period.

The regression between OC and EC concentrations (Figure 3.59) gives the relationship between these parameters. A good correlation was observed between OC and EC ($R^2=0.803$). This high correlation showed that OC and EC emissions were

proportional to each other and indicated the presence of common sources like coal combustion and traffic (Na et al., 2004; Satsangi et al., 2012).

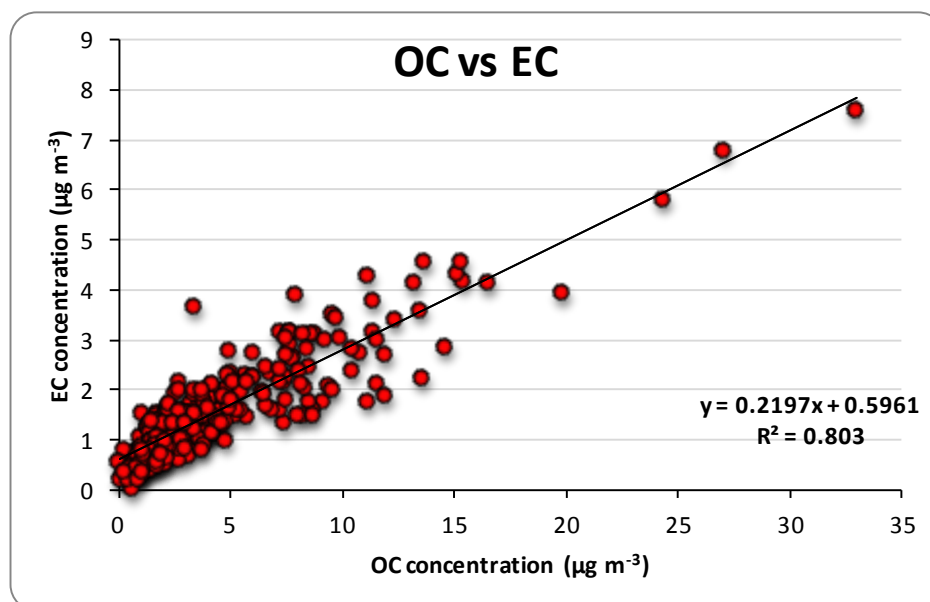


Figure 3.59. Correlation between OC and EC concentrations during the sampling period.

Relation between OC and EC during whole sampling period gives cumulative results. In order to determine the possible sources for both constituents the assessment of seasonal variations and correlations are required. Figure 3.60 gives the seasonal correlations between OC and EC. The correlation in summer ($R^2=0.3391$) was lower than in winter ($R^2=0.8364$). This weak correlation in summer can be the result of the consumption of OC in the formation of O_3 during high photochemical activities in this season (Na et al., 2004) or indicating the presence of other sources (Cao et al., 2004). High correlation in winter can be concluded in two ways. The sources of both OC and EC can be the same (Cao et al., 2004; Satsangi et al., 2012;

Na et al., 2004) or the increase in OC due to the formation of OC_{sec} is parallel to the increase in emission of EC due to coal combustion and traffic.

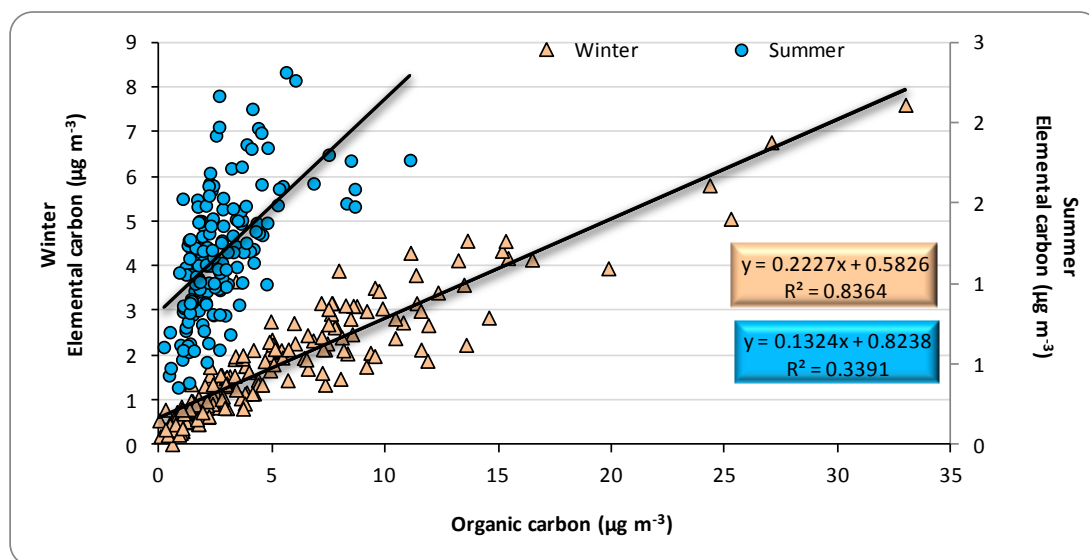


Figure 3.60. Regression between OC and EC concentrations in winter and in summer.

Monthly regressions of OC and EC are given in Figure 3.61. The correlation coefficients were between 0.35 and 0.95. As indicated above, the highest correlations were observed especially in winter months.

Monthly concentration variations of carbonaceous composition and fine fraction aerosol samples are also illustrated in Figure 3.62. Especially, in winter OC concentrations were very high and in November TC was composed of 30 % of PM_{2.5}.

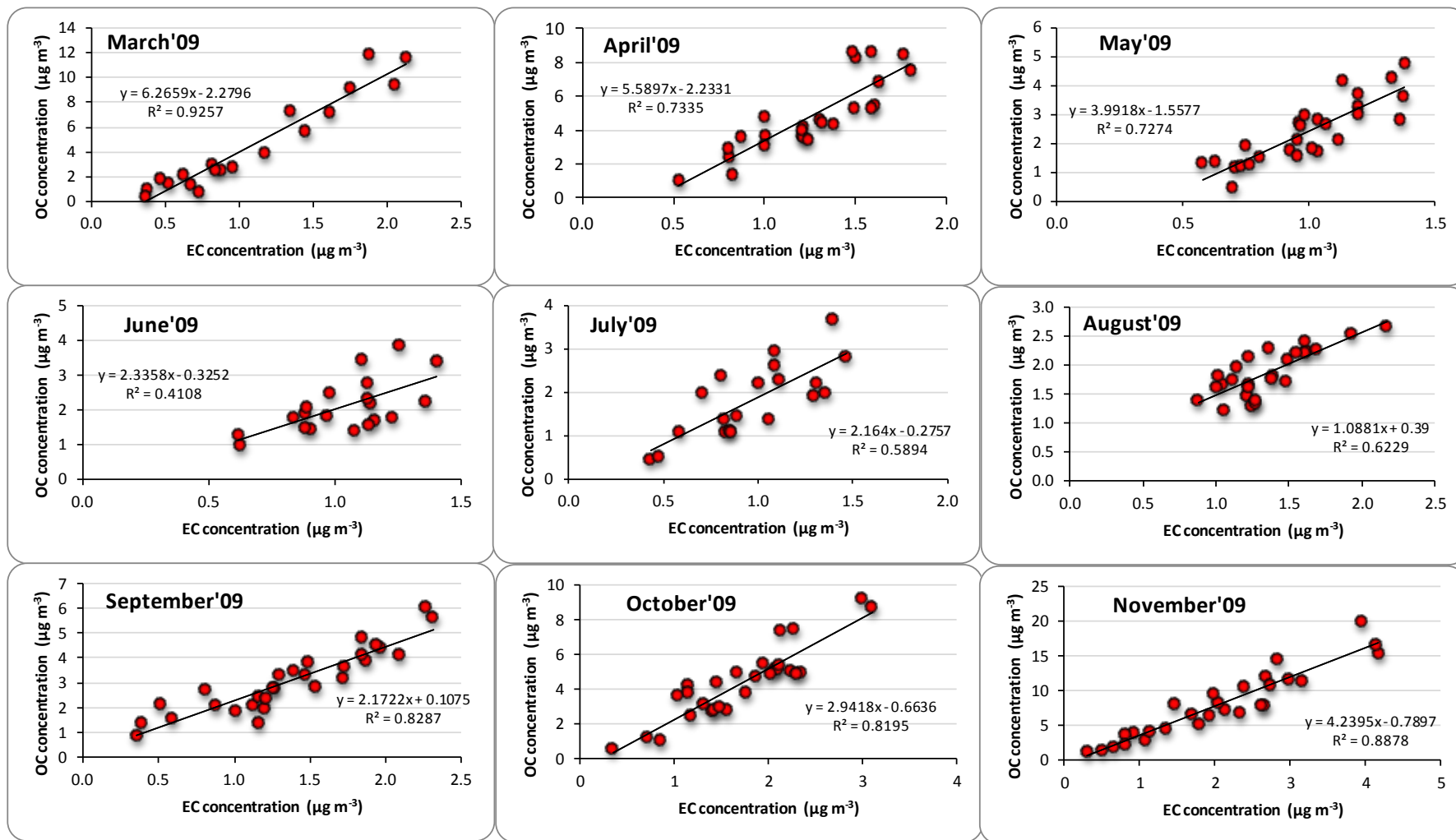


Figure 3.61. Regressions between OC and EC in each month.

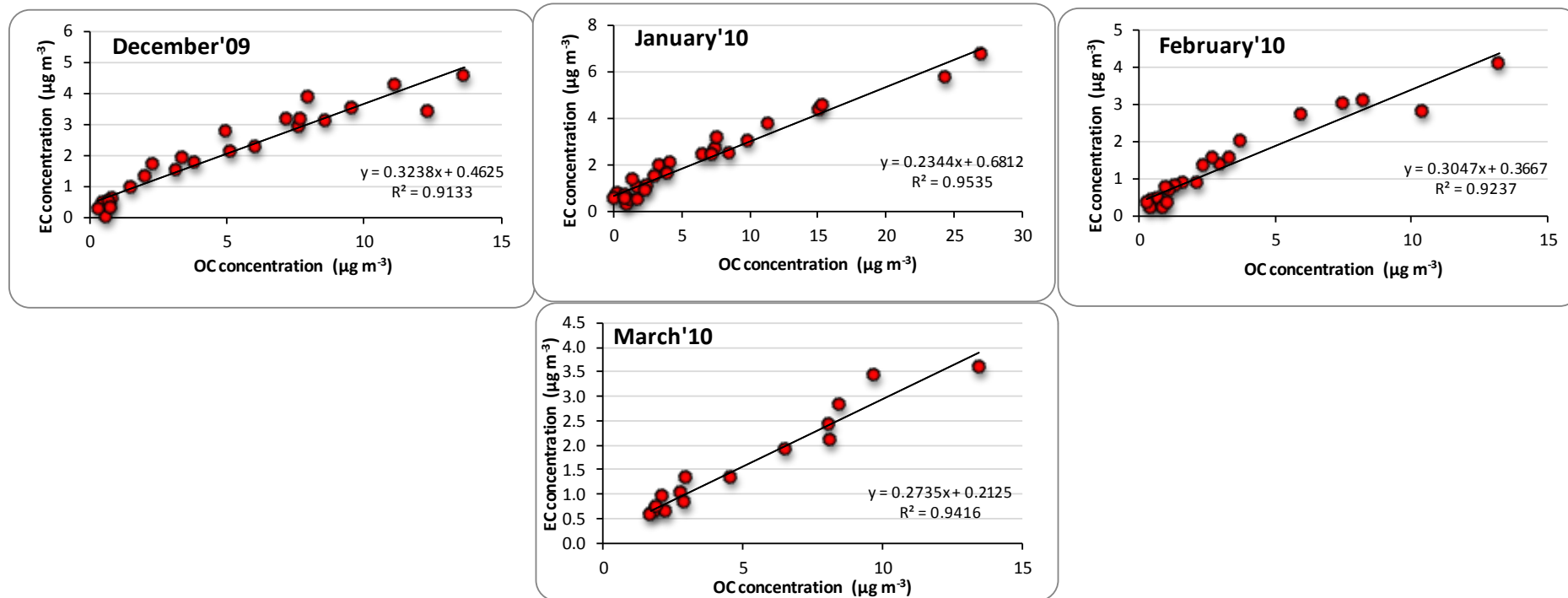


Figure 3.61. Regressions between OC and EC in each month (cont.).

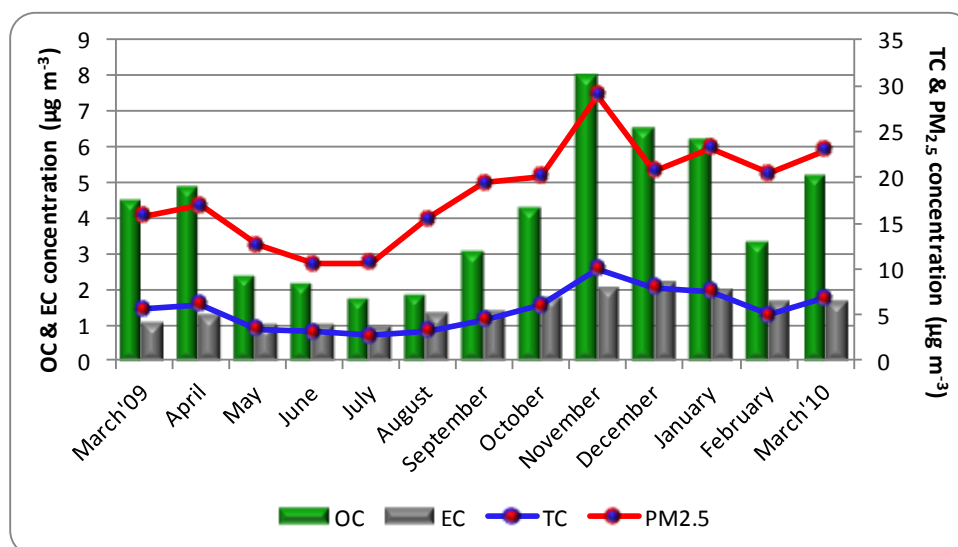


Figure 3.62. Temporal variation of OC, EC, TC and PM_{2.5}.

3.7.3. The ratios of OC/EC and possible sources of carbonaceous aerosols

In order to interpret the emission and transformation characteristics of carbonaceous aerosols OC/EC ratio is commonly used (Satsangi et al., 2012). According to the ratio of OC/EC, the sampling sites have been classified as rural background if the ratio is 5-6 and traffic dominated if the ratio is 2-3 (Schaap et al., 2007). Table 3.20 summarizes ratio of OC and EC from the possible sources in literature.

In this study, the range of OC/EC ratio was from 1.4 to 4.1 and the average ratio was found as 2.7. The traffic emission is one of the dominant source in the sampling site. Domestic heating may be the other source for carbonaceous aerosol according to the Table 3.26.

Table 3.26. Ratios of OC and EC emitted from different sources.

Emission source	OC/EC	References
Tunnel	0.76	Gillies et al. (2001)
Residential coal smoke	2.5-14	Chen et al. (2006)
Biomass burning	7.7	Feng et al. (2009)
Diesel and gasoline powered vehicles	1.0-4.2	Schauer et al. (1999)
Wood combustion	16.8-40.0	Schauer et al. (2001)
Residential wood combustion	4.15	Watson et al. (2001)
Light-duty gasoline vehicles	2.2	Hildemann et al. (1991)
Light-duty gasoline vehicles	2.2	Watson et al. (1994)
Heavy duty diesel vehicles	0.8	Hildemann et al. (1991)
Paved road dust	13.1	Watson et al. (1994)
Natural gas home appliances	12.7	Hildemann et al. (1991)
Forest fire	14.51	Watson et al. (2001)
Kitchen emissions	32.9-81.6	He et al. (2004)

Figure 3.63 gives the ratios of OC and EC for each month. Different ratios in each month indicated that concentrations of carbonaceous aerosols varied considerably from source to source due to different source emissions strengths of OC and EC (Na et al., 2004; Turpin and Huntzicker, 95).

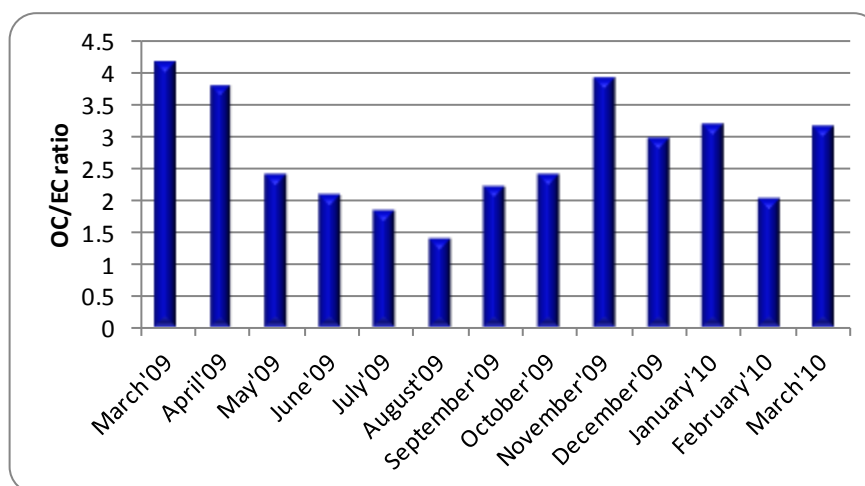


Figure 3.63. Ratios of OC/EC in each month.

3.8. Source apportionment and receptor models

3.8.1. Correlations between parameters

Preliminary information about pollution sources is gathered by binary correlation analysis. Correlation analysis was applied to elements in fine and coarse fraction by using STATGRAPHICS software program. Meaningful relations were obtained at 95 confidence level ($p < 0.05$) in this analysis. Correlation results for $PM_{2.5}$ and $PM_{2.5-10}$ are given in Table 3.27 and Table 3.28, respectively. Correlation coefficients between ± 0.25 are not given in the tables.

Crustal elements have high correlations in both fractions (some of them had correlation coefficients greater than 0.90). Furthermore, K had high correlations with other crustal elements in both $PM_{2.5}$ and $PM_{2.5-10}$ ($r > 0.70$).

Correlations are not very high in $PM_{2.5}$ except for P and Ti ($r=0.90$). Aluminum showed high correlation with the crustal elements like Na and Mg. Moreover, Al had moderate correlations with Hf, Cr, Co and Mo which indicated that contribution of anthropogenic sources were also dominant. Calcium had high correlations with both crustal (Sc, Y, La, Nd, Eu, U, Sm, Th, Lu) and anthropogenic elements (Zn, Ni, Mn, Bi and Cl). High correlations between Fe and crustal elements indicate that the main source of Fe can be crustal.

Manganese which is both crustal and anthropogenic element, had a close relationship with crustal elements rather than other anthropogenic ones. Correlations between Ni and Fe, Cr, Mn showed that these elements emitted from industrial sources. Copper was another element that had a relation with Ni. Zinc had correlation only with Ca and Cu. Lead was correlated with Co and Cd. The other element emitted from coal combustion, As showed high correlation with K and V. Relation between As and K indicated the presence of coal and wood burning together. Thallium was related with only P and Bi.

The strong relation was obtained between NH_4^+ and SO_4^{2-} , this implied the neutralization with ammonia. Moreover Cl^- had a relation between Na^+ and Mg^{2+} which showed the effects of sea salt in particulate matter. Calcium ion showed a correlation with Mg^{2+} . Correlation between Ca^{2+} and Mg^{2+} showed the effect of sea salt. Finally, NO_3^- had high correlations with OC, EC and TC. In nitrogen cycle, carbonaceous species have crucial role for the formation and destruction of nitrogen oxides.

Table 3.27. Binary correlation matrix of elements in fine mode ($p < 0.05$).

	K	Mg	Ca	Fe	Al	Zn	V	Cr	Mn	Co	Ni	Cu	As	Cd	Pb	P	Sc	Ti	Se	Y	Mo	Sb	Cs	La	Nd
Na	-0.33	0.61		0.37	0.78		0.37	0.48	0.29	0.50			-0.48		0.40				0.27		0.65	0.45			
K							0.34						0.78				0.82		0.41	0.82	0.69			0.48	0.66
Mg			0.37	0.41	0.59	0.26		0.57	0.45		0.52	0.36						0.30			0.33				
Ca				0.40		0.69			0.39	-0.27	0.53	0.43					0.39			0.43	0.25		0.15	0.48	0.57
Fe					0.28	0.27	0.27	0.26	0.71		0.35	0.27			0.25		0.62			0.66	0.70			0.53	0.67
Al								0.44		0.43					0.35						0.45	0.30			
Zn									0.34		0.27	0.32				0.28								0.29	0.31
V									0.33				0.50						0.27		0.40	0.46			
Cr									0.28		0.65											0.33			
Mn										0.38	0.32						0.63	0.29	0.25	0.65	0.70			0.52	0.63
Co															0.44							0.31			
Ni											0.34														
Cu																									
As																	0.49		0.30	0.50	0.42			0.30	0.38
Cd															0.59										
Pb																			0.26		0.25				
P																		0.92							
Sc																				0.99	0.80	-0.26		0.67	0.83
Ti																									
Se																						0.30	0.31		
Y																					0.80			0.71	0.88
Mo																								0.55	0.70
Sb																							0.38		
Cs																									
La																									0.92

[illegible]

Table 3.27. Binary correlation matrix of elements in fine mode (p<0.05) cont.

[illegible]

Binary correlations in $PM_{2.5-10}$ had higher correlation coefficients than that in $PM_{2.5}$ (Table 3.28). In this fraction, the crustal elements showed high correlations among each other ($r > 0.40$). The correlation coefficient between V and As was calculated as 0.98 in this fraction. Moreover, high correlations between these elements and among crustal ones showed the deposition of V and As in soil for many years due to coal combustion. Aluminum had high correlations with Cr and other crustal ones ($r > 0.50$). Then, Al might be originated from crustal in this fraction. Cobalt had correlations with Pb and Sb which implied the effects of traffic on the sampling site. Uranium had high correlation with As and Mo and the crustal elements. This might be related with the contribution of coal combustion to this element. Selenium was correlated only with Cs (0.63).

The correlation coefficient between NO_3^- and SO_4^{2-} was higher in coarse fraction (0.65) than in fine fraction (0.36) which implied that the emission source of these species might have been the same. In coarse mode, Cl^- was related only with Mg^{2+} (0.55). Finally, the correlation coefficient between Na^+ and K^+ was very high (0.85) then, the source of these ions might be sea salt.

Table 3.28. Binary correlation matrix of elements in coarse mode ($p < 0.05$).

[illegible]

Table 3.28. Binary correlation matrix of elements in coarse mode (p<0.05) (cont.).

	La	Nd	Eu	U	Tl	Sm	Yb	Lu	Hf	W	Th	Hg	Bi	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺
Na			0.55						0.43					-0.29							
K	0.72	0.73	0.48	0.87		0.72	0.91	0.91	0.89		0.88										0.29
Mg	0.26		0.43		0.31																
Ca	0.66	0.66	0.50	0.86		0.65	0.84	0.85	0.82		0.81										
Fe	0.81	0.82	0.48	0.70		0.82	0.72	0.72	0.64		0.82										0.37
Al	0.55	0.55	0.31	0.32		0.55	0.61	0.53	0.32		0.59			-0.33							0.25
Zn																					
V	0.62	0.62	0.40	0.83		0.61	0.87	0.87	0.87		0.81			0.27							0.28
Cr				-0.32			-0.26	-0.32	-0.29												
Mn	0.52	0.53	0.25	0.35		0.54	0.42	0.43	0.36		0.50										0.26
Co			0.48									-0.25	-0.25							0.32	
Ni																					
Cu																	0.54				
As	0.53	0.53	0.38	0.84		0.54	0.87	0.87	0.88		0.77										
Cd																				0.33	
Pb															0.58	0.39					
P	0.43	0.44		0.52		0.45	0.54	0.56	0.52		0.54										
Sc				0.59			0.79	0.84	0.93		0.39										
Ti	0.34	0.34		0.28		0.33	0.30	0.29	0.27		0.35										
Se	0.25		0.41			0.29					0.26					0.27					
Y	0.81	0.82	0.51	0.94		0.82	0.98	0.98	0.95		0.98										0.34
Mo	0.58	0.58	0.42	0.84		0.59	0.84	0.86	0.85		0.77										

Table 3.28. Binary correlation matrix of elements in coarse mode ($p < 0.05$) (cont.).

[illegible]

3.8.2. Multiple linear regression analysis for carbonaceous species in aerosol

The equation of multiple linear regression (Eq 3.7) for organic fractions of PM_{2.5} was conducted by one year daily concentration data ($\mu\text{g m}^{-3}$). Table 3.29 summarizes the results of the analysis and it was seen that there was a statistically significant relationship between the variables at the 95.0 % confidence level. The R-squared of the model indicated that the model explained 67.2 % of the variability in PM_{2.5}.

$$\text{PM}_{2.5} = 8.720 + 1.590 \text{ OC} + 2.129 \text{ EC} \quad (R^2=0.672) \quad (\text{Eq 3.7})$$

Table 3.29. Summary of multiple linear regression results.

	Coefficient	Std. error	t	p
Constant	8.720	0.601	14.50	<0.001
OC	1.590	0.171	9.302	<0.001
EC	2.129	0.682	3.123	0.002

Observed versus predicted scatter plot of the model (0.730) is given in Figure 3.64. The closeness of the points to the diagonal line in the plot showed the reasonable agreement between the variables.

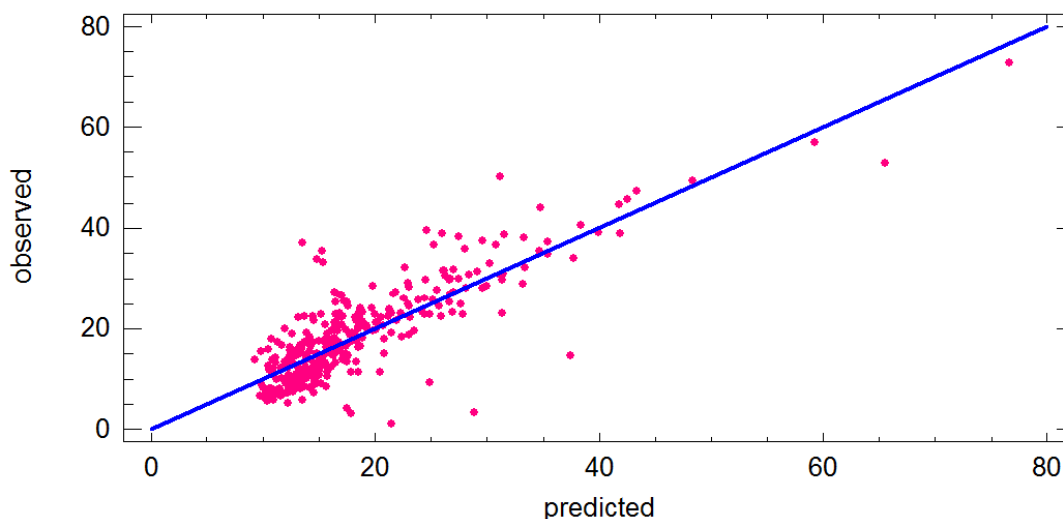


Figure 3.64. Observed versus predicted scatter plot for PM_{2.5} in micro glass fiber filter.

3.8.3. Crustal enrichment factors

Enrichment factor results for both fractions (PM_{2.5} ve PM_{2.5-10}) are shown in Figure 3.65 and in Figure 3.66. In PM_{2.5}, Sm, Fe, Y, Nd, Th, La, Eu, Yb, Mn, Ti, Lu, K, Cs, Al and V were identified as crustal elements. In PM_{2.5-10} besides these elements Mg and U were qualified as crustal elements. In both fractions Sb, Cd and Hg had the highest enrichment factors (>1000).

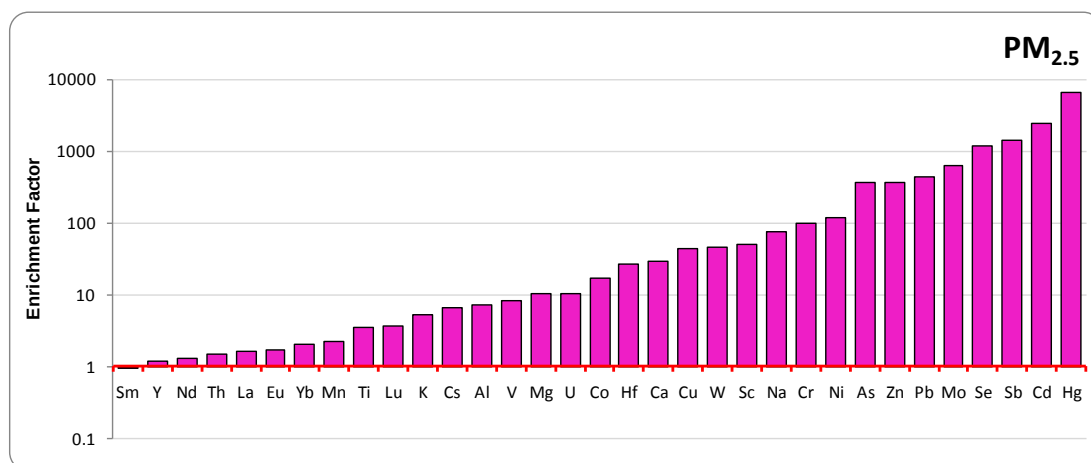


Figure 3.65. Crustal Enrichment factors of the elements in fine fraction aerosols.

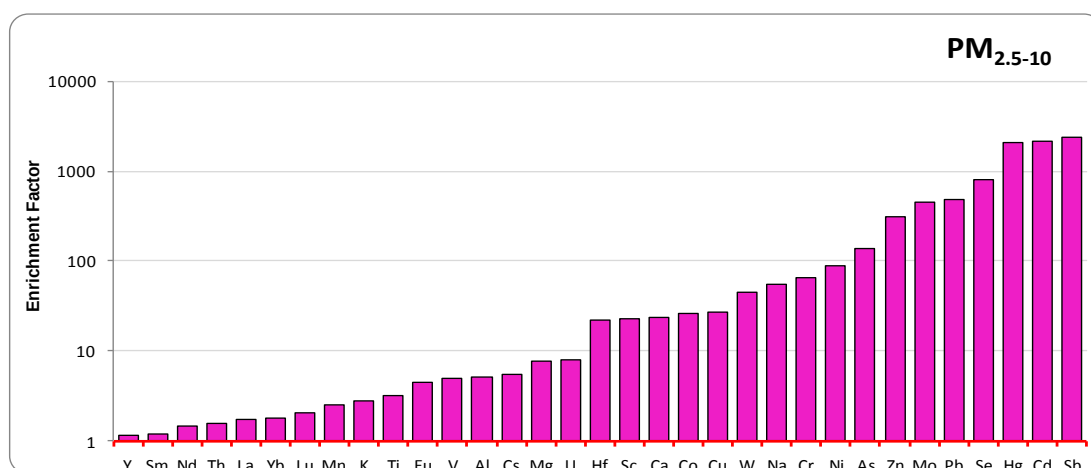


Figure 3.66. Crustal Enrichment factors of the elements in coarse fraction aerosols.

Seasonal variations of enrichment factors for each element are shown in Figure 3.67 and in Figure 3.68. Aluminium had EF values 2.5 times greater in winter than in summer in PM_{2.5}. This meant that the effect of anthropogenic sources like aluminum joinery and coal combustion on Al concentration were high in winter than in summer. Magnesium and Co which are moderately enriched had higher EF in winter than in summer. High EFs in winter for Pb, As and Cd indicated the possible

source for these elements was coal combustion. High EF for Hg in summer showed the effect of the long range transport.

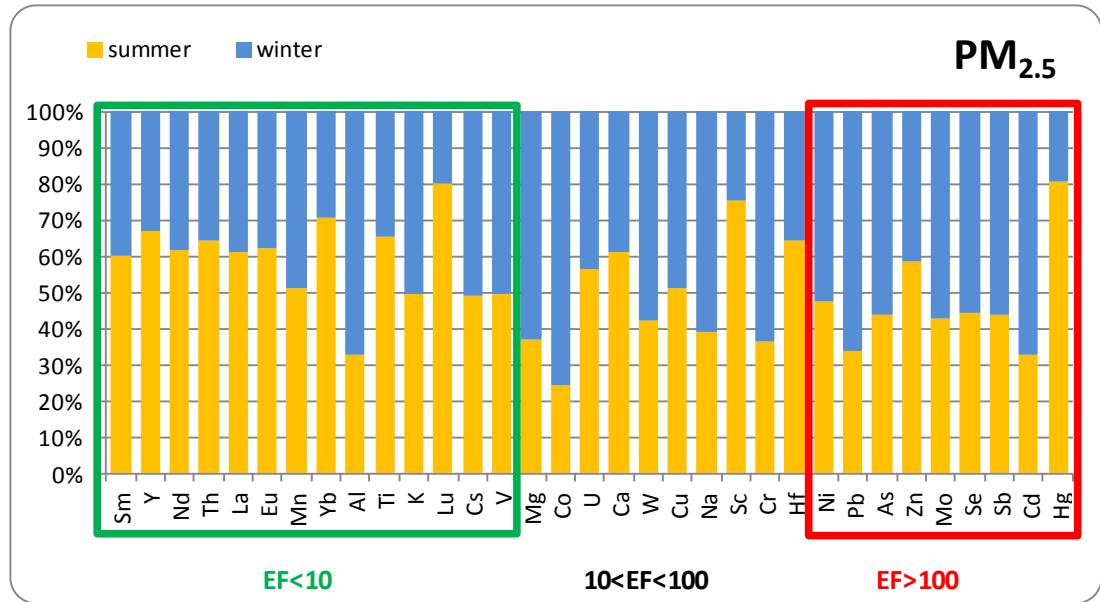


Figure 3.67. Seasonal variation of crustal enrichment factors of elements in PM_{2.5}.

In PM_{2.5-10} except for Eu and Mg, the seasonal EFs of crustal elements were close to 1. Then it was understood that in both seasons crustal elements were not affected from anthropogenic sources. Lead and Sb had high EF during the sampling period and also these elements had higher EFs in winter than in summer.

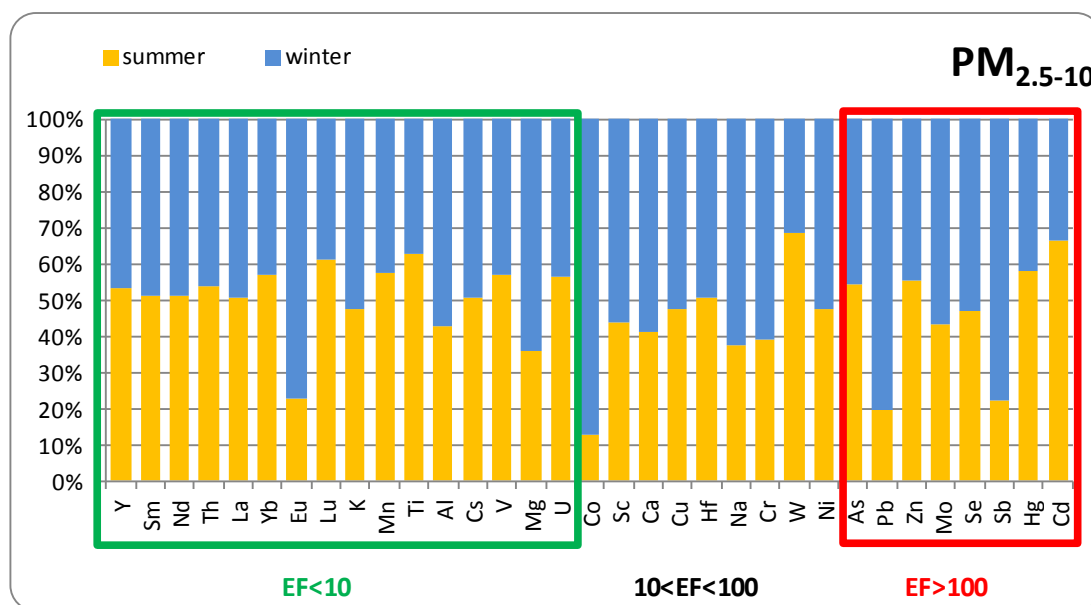


Figure 3.68. Seasonal variation of crustal enrichment factors of elements in PM_{2.5-10}.

3.8.4. Wind sector analysis

The wind sector analysis was another method that was used for determining the possible sources and transportations of local pollutants. The average concentrations of pollutants in each wind direction were used in this method. If there was a pollution source in the direction of high concentration, the pollutants would be emitted from that source and reached to the receptor with the winds in that direction. Possible sources that are 50 km far from the sampling point are given with the directions in Table 2.12.

The percent distribution of winds in selected sectors during the sampling period is given in Figure 3.69. According to the graph the prolonged wind directions was WSW (77.3 %). Wind rose for whole sampling period, in summer time and in winter

time are given in Figure 3.670 and Figure 3.71, respectively. Besides WSW, ENE and SSE directions were dominant in winter.

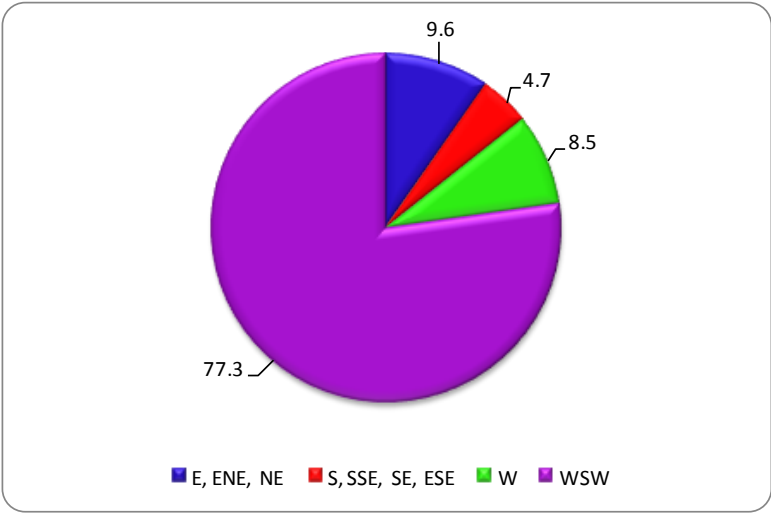


Figure 3.69. Percent distribution of each wind sector.

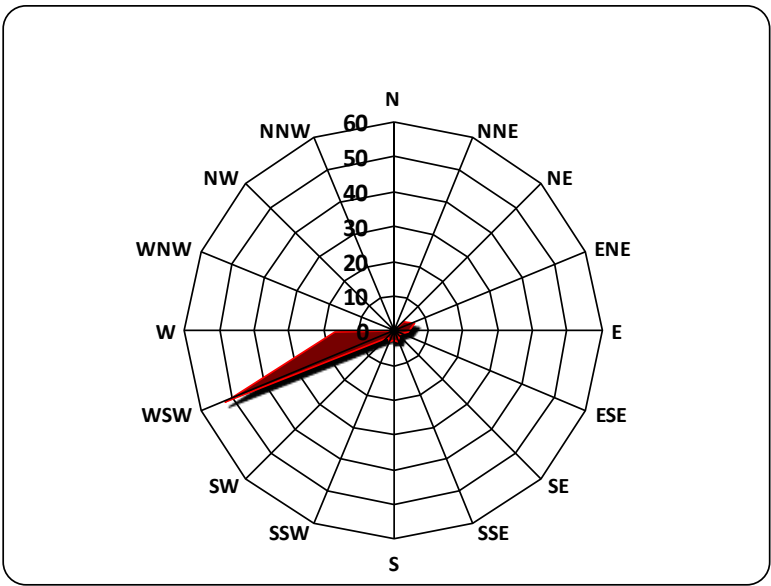


Figure 3.70. Wind rose of the sampling period.

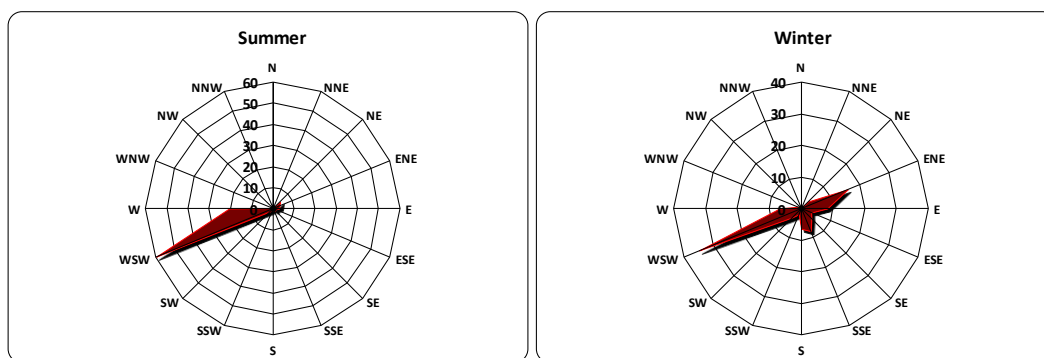


Figure 3.71. Wind roses for summer and winter period.

3.8.4.1. Wind sector analysis for the parameters in $PM_{2.5}$

The percent distribution of $PM_{2.5}$ compositions with respect to four main wind sectors is given in Figure 3.72. According to the figure, Mg, V, Cr, Co, Ni, Cu, As, Sc, Ti, Se, Y, Mo, Sb, Eu, Tl, Yb, Hf, Bi, NO_3^- , SO_4^{2-} and $PM_{2.5}$ were mostly seen in E-ENE-NE directions. Potassium, As, Zn, Mn, Pb, Cs, La, Nd, Sm, Th, Na^+ and Cl^- were seen in S-SSE-SE-ESE directions. Sodium, W and Ca^{2+} were seen in W direction and finally, Ca, Cd, P, U, Lu, Hg, NH_4^+ , K^+ , Mg^{2+} , OC, EC and TC were generally obtained in WSW-SW directions. Aluminum and Fe were equally distributed in these four wind sectors. Elemental concentrations of each parameter in each wind sector is given in Table 3.30. The highest concentrations were indicated as bold.

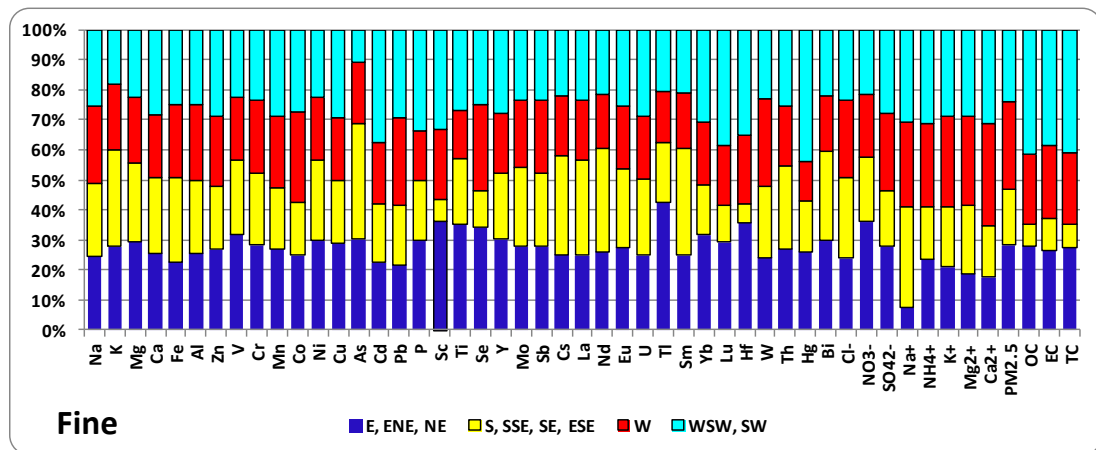


Figure 3.72. Distribution of fine mode elements in each wind sector.

Table 3.30. Average and median concentrations of fine mode elements in different wind sectors (ng m⁻³).

	E-ENE-NE (33)		S-SSE-SE-ESE (16)		W (29)		WSW-SW (265)	
	Avg	Med	Avg	Med	Avg	Med	Avg	Med
Na	5103	5767	4971	5334	5395	5494	5244	5267
K	771	497	884	395	608	436	502	335
Mg	1112	920	984	806	833	812	847	813
Ca	4115	3727	4015	3470	3381	2370	4530	3694
Fe	231	180	284	175	249	178	255	180
Al	1867	1836	1761	1789	1852	1706	1803	1862
Zn	84	87	65	64	74	63	90	81
V	5.2	4.9	4.0	3.7	3.4	3.1	3.6	3.4
Cr	39	38	33	38	33	32	32	31
Mn	8.8	6.0	6.6	4.9	7.8	6.8	9.3	7.1
Co	1.4	0.80	0.95	0.70	1.6	0.74	1.5	0.69
Ni	42	26	38	29	30	19	31	20
Cu	9.0	6.3	6.6	5.0	6.6	6.0	9.3	7.3
As	11	3.1	13.6	3.0	7.1	2.4	3.7	1.2
Cd	1.0	0.45	0.91	0.31	0.94	0.32	1.7	0.39
Pb	15	13	13	11	19	13	20	13
P	144	92	96	72	81	76	162	76
Sc	8.4	1.2	1.7	1.6	5.4	2.0	7.7	2.3
Ti	106	53	65	58	48	41	81	42
Se	0.26	0.20	0.091	0.041	0.22	0.20	0.19	0.14
Y	0.26	0.097	0.19	0.12	0.17	0.091	0.24	0.093
Mo	4.0	3.7	3.8	3.6	3.2	3.2	3.4	3.2
Sb	1.1	1.1	0.97	0.92	0.96	0.98	0.93	0.92
Cs	0.078	0.082	0.10	0.11	0.063	0.055	0.067	0.062
La	0.23	0.15	0.29	0.21	0.18	0.14	0.22	0.13
Nd	0.21	0.13	0.28	0.19	0.14	0.12	0.17	0.098
Eu	0.012	6.3x10 ⁻³	0.011	7.2 x10 ⁻³	8.9 x10 ⁻³	5.6 x10 ⁻³	0.011	5.6 x10 ⁻³
U	0.12	0.073	0.13	0.13	0.11	0.089	0.15	0.086
Tl	0.14	0.074	0.068	0.059	0.057	0.055	0.069	0.036
Sm	0.033	0.018	0.047	0.028	0.024	0.017	0.028	0.015
Yb	0.044	0.014	0.024	0.016	0.029	0.011	0.043	0.011
Lu	0.013	2.7 x10 ⁻³	5.5 x10 ⁻³	6.3 x10 ⁻³	8.7 x10 ⁻³	2.5 x10 ⁻³	0.017	3.3 x10 ⁻³
Hf	1.1	0.19	0.20	0.20	0.72	0.19	1.1	0.19
W	0.24	0.17	0.24	0.16	0.29	0.13	0.23	0.15
Th	0.082	0.039	0.083	0.059	0.059	0.039	0.077	0.035
Hg	1.2	0.70	0.81	0.65	0.62	0.24	2.1	0.27
Bi	0.21	0.15	0.21	0.19	0.13	0.12	0.16	0.12
Cl ⁻	2110	2000	2400	2150	2250	1900	2080	1900
NO ₃ ⁻	1289	667	764	554	750	672	762	564
SO ₄ ²⁻	3720	2600	2500	1950	3500	3350	3750	3400
Na ⁺	158	118	683	601	579	74	635	169
NH ₄ ⁺	1300	917	929	582	1500	1450	1700	1500
K ⁺	77	52	74	47	109	105	105	79
Mg ²⁺	31	29	37	20	49	35	48	26
Ca ²⁺	241	129	232	191	462	283	425	209

Table 3.30. Average and median concentrations of fine mode elements in different wind sectors (ng m⁻³) cont.

	E-ENE-NE (33)		S-SSE-SE-ESE (16)		W (29)		WSW-SW (265)	
	Avg	Med	Avg	Med	Avg	Med	Avg	Med
OC	6.42	3.98	1.62	1.17	5.37	3.83	9.40	8.93
EC	1.98	1.63	0.795	0.408	1.82	1.53	2.86	2.78
TC	8.26	5.61	2.30	1.13	7.19	5.59	12.2	11.7
PM _{2.5} ^a	24.1	21.2	13.6	12.4	21.8	20.2	30.8	29.9
PM _{2.5} ^b	18700	15400	12500	7250	19200	17750	15950	14950

^a PM_{2.5} in micro-glass fiber filter

^b PM_{2.5} in teflon filter

Pollution roses for each element are given in Figure 3.73 and possible local pollution sources can be explained by these graphs. The crustal elements were distributed among three main directions; NE, S-SSE-SE and ENE-E. Calcium, Fe, Mn, Ti, Cu and Al reached their maximum average concentration in NE direction. Residential, agricultural and industrial areas (isopoly, PVC, aluminum carpentry and petrochemical industry) were came together in this direction. Then, in addition to these crustal elements also anthropogenic ones like Zn, Cr, Ni, Mo, Sb, Bi and P were mostly seen in this direction. Sodium, Mg and Cl⁻ were the tracers of the sea salt and the high concentrations of these parameters in NE direction might be the effect of Black Sea. Then, the source of these elements in this direction might be the long range transportation.

Some rare earth metals like, Nd, Eu, U, Sm, La and Cs were seen in S-SSE-SE directions. Wood-pulp factory and agricultural areas are pesent in these directions. In addition to these crustal elements Mg²⁺, W, Th and the tracers of wood and coal combustion elements; K and As were obtained in these directions. The presence of As and U which are the tracers of local coal (Eğilli, 1999), indicated that coal combustion in this direction was much more dominant.

The high concentration of some rare earth elements; Sc, Se, Y, Lu and Yb, carbonaceous fractions; OC, EC and TC, the anthropogenic elements; V and Hf and the high mass concentration of $PM_{2.5}$ were obtained in ENE-E directions where the industrial areas (leather cement factories) and city center are present.

Finally, Co, Cd, Pb, Hg, Na^+ , NH_4^+ , K^+ and Ca^{2+} were seen in W-WSW and ENE directions where residential areas and highways are present. Especially, Cd and Pb are the tracers of traffic emission. The local traffic and the highways might be the source of the high concentration of these elements.

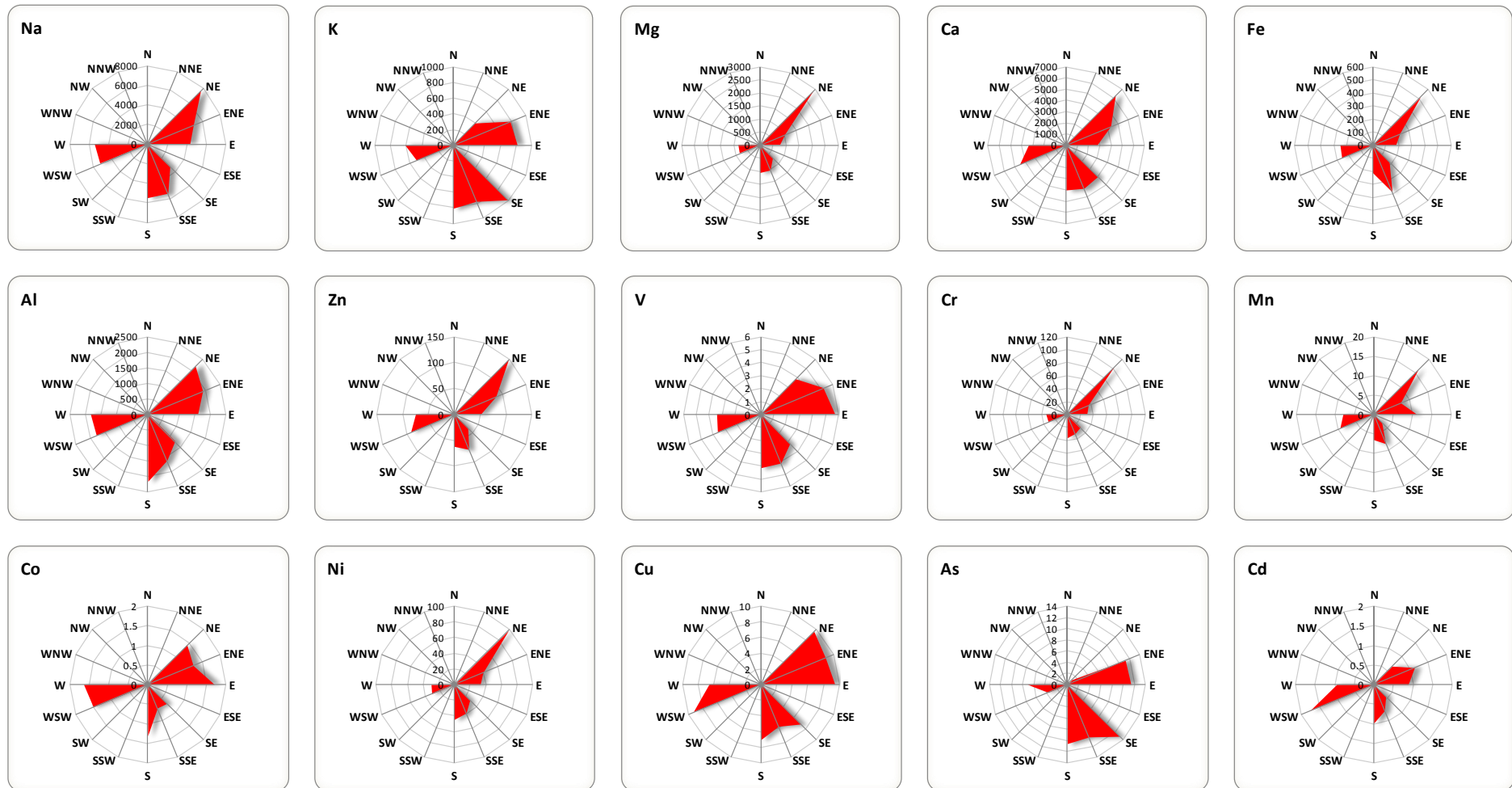


Figure 3.73. Pollution roses of each element in fine fraction.

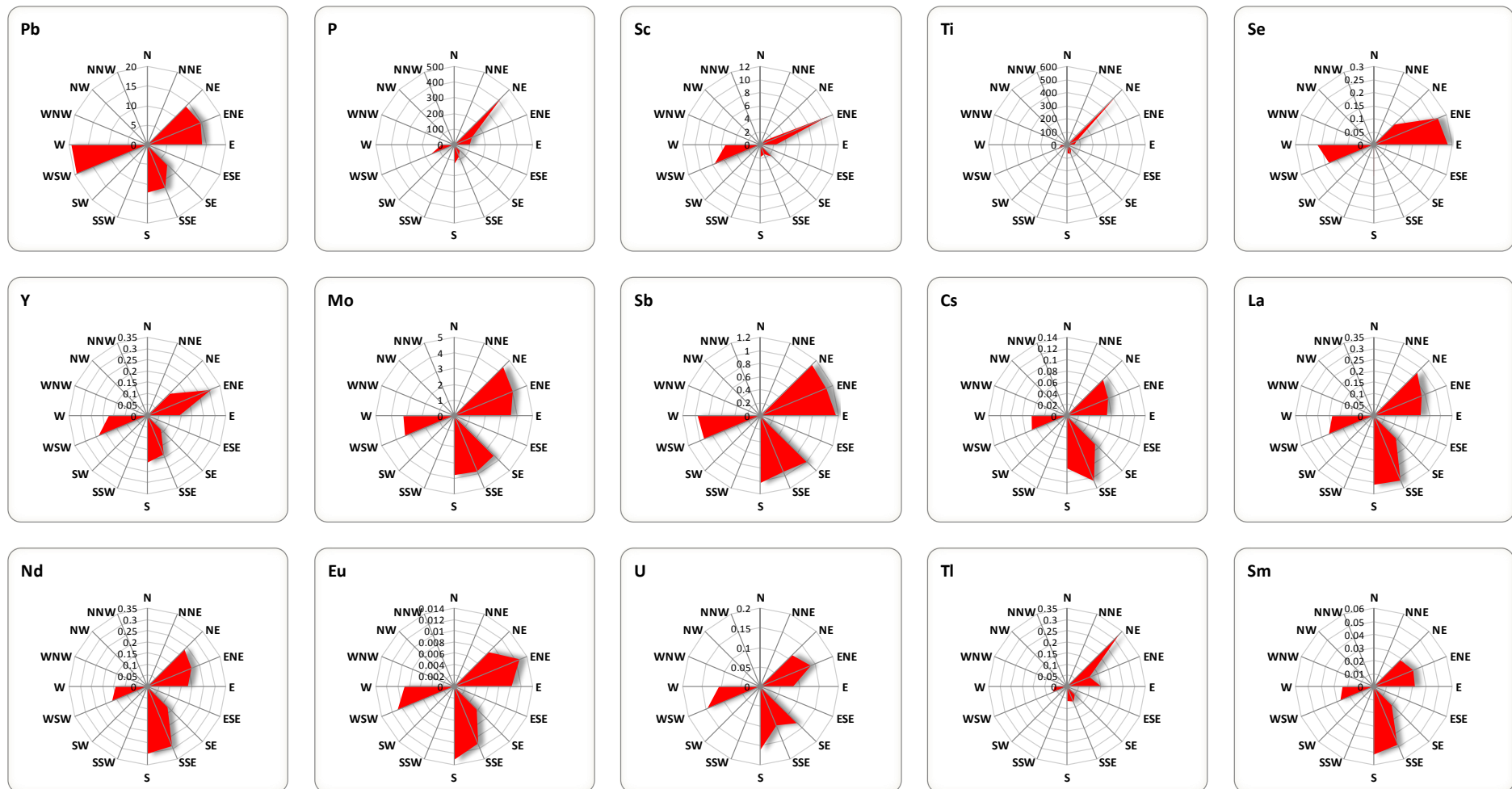


Figure 3.73. Pollution roses of each element in fine fraction (cont.).

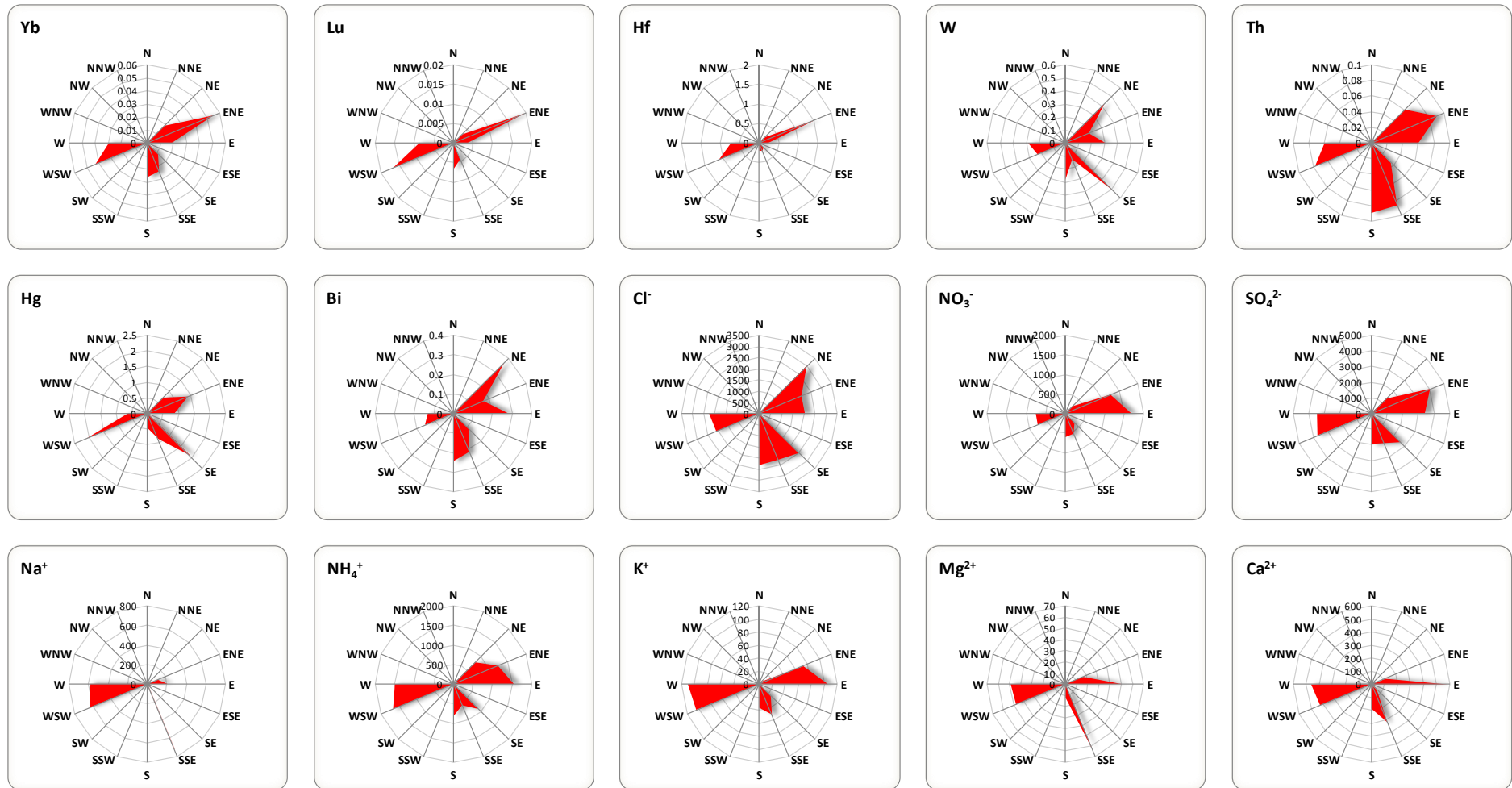


Figure 3.73. Pollution roses of each element in fine fraction (cont.).

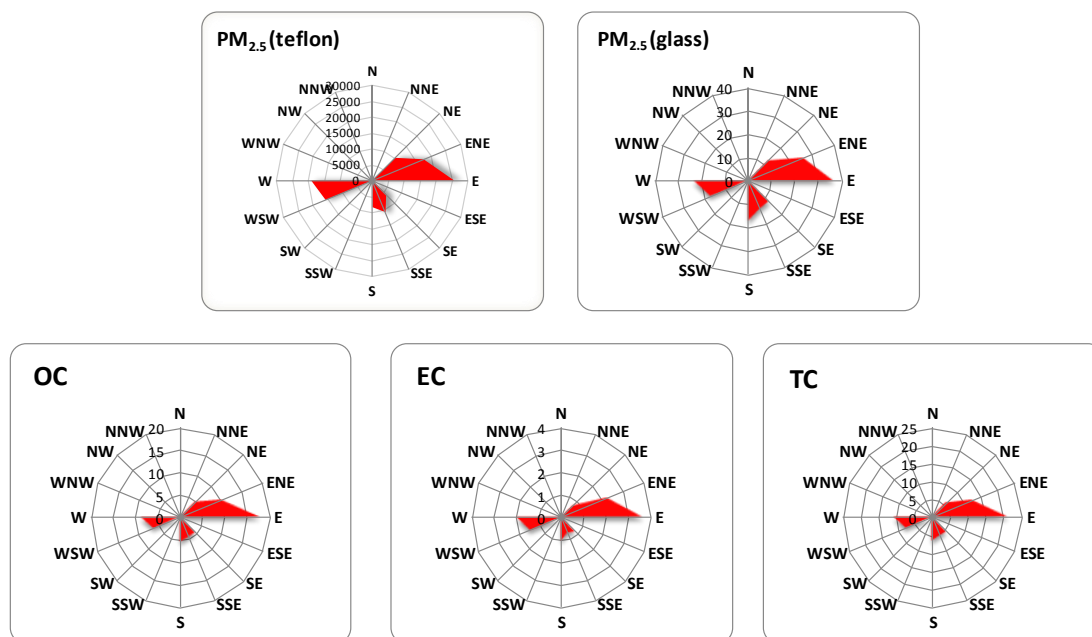


Figure 3.73. Pollution roses of each element in fine fraction (cont.).

3.8.4.2. Wind sector analysis for the parameters in $PM_{2.5-10}$

The percent distribution of each element in coarse fraction with respect to each wind sector is illustrated in Figure 3.74 and the elemental concentrations in these sectors are given in Table 3.31. Mostly Cd, W and Bi were obtained and their concentrations were 1.5, 0.16 and 0.29 $ng\ m^{-3}$ in the direction of WSW and W, respectively. Lead ($36\ ng\ m^{-3}$), Se ($0.55\ ng\ m^{-3}$) and Sb ($3.7\ ng\ m^{-3}$) came from W direction where the residential areas are present. Mostly crustal elements were transported in the direction of agricultural areas (ESE-S). Moreover, in NE-E direction where industrial zone is present, anthropogenic elements such as Ni ($35\ ng\ m^{-3}$), As ($2.5\ ng\ m^{-3}$), P ($187\ ng\ m^{-3}$), Mo ($3.3\ ng\ m^{-3}$) and Hg ($1.0\ ng\ m^{-3}$) and some crustal elements such as Ti ($136\ ng\ m^{-3}$), Tl ($0.17\ ng\ m^{-3}$), Yb ($0.077\ ng\ m^{-3}$), Lu ($0.018\ ng\ m^{-3}$) and Hf ($1.8\ ng\ m^{-3}$) were obtained.

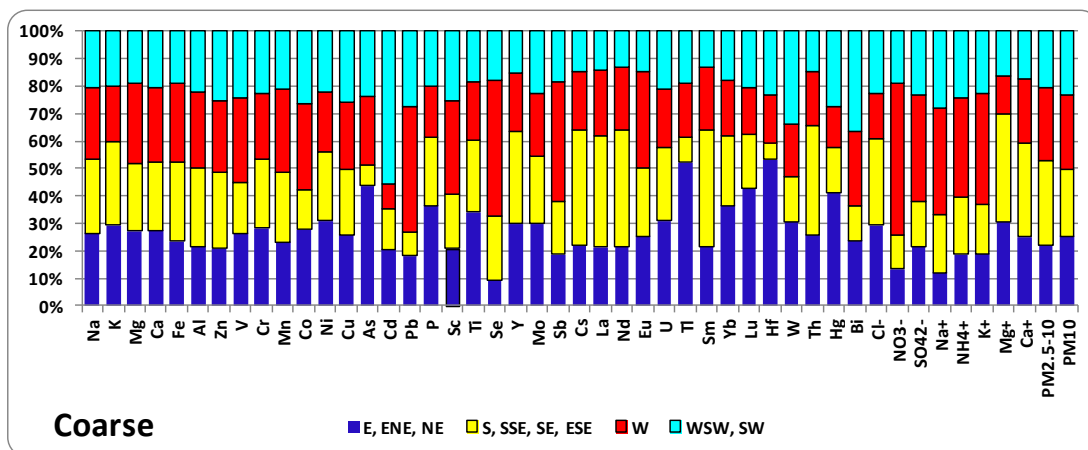


Figure 3.74. Distribution of fine mode elements in each wind sector.

Table 3.31. Average and median concentrations of coarse mode elements in different wind sectors (ng m⁻³).

	E-ENE-NE (33)		S-SSE-SE-ESE (16)		W (29)		WSW-SW (265)	
	Average	Median	Average	Median	Average	Median	Average	Median
Na	5370	4790	5560	4380	5285	5165	4230	3770
K	403	148	414	392	282	298	274	189
Mg	998	790	895	807	1070	556	702	570
Ca	5360	4280	4800	4275	5290	4085	4030	3350
Fe	370	219	451	297	451	341	298	212
Al	1590	1545	2075	1800	2040	1850	1620	1500
Zn	67	64	89	81	83	70	82	75
V	3.6	2.4	2.5	1.7	4.2	2.5	3.3	2.0
Cr	28	26	25	20	24	21	22	21
Mn	11	8.2	12	8.8	14	11	10	7.5
Co	2.3	0.83	1.16	0.79	2.6	0.91	2.1	0.80
Ni	35	25	28	25	25	17	25	18
Cu	6.1	5.0	5.7	4.6	5.8	4.2	6.1	4.4
As	2.5	1.0	0.44	0.24	1.4	0.49	1.4	0.60
Cd	0.53	0.34	0.39	0.18	0.23	0.14	1.5	0.34
Pb	14	7.4	6.9	5.1	36	6.1	21	6.5
P	187	74	128	78	96	86	104	72
Sc	1.7	1.2	1.7	1.5	2.9	1.5	2.1	1.3
Ti	136	62	104	61	84	51	74	40
Se	0.10	0.13	0.26	0.26	0.55	0.41	0.20	0.11
Y	0.44	0.15	0.50	0.18	0.31	0.23	0.23	0.12
Mo	3.3	2.8	2.7	2.6	2.5	2.5	2.5	2.4
Sb	1.6	0.87	1.6	0.80	3.7	0.96	1.6	0.81
Cs	0.10	0.068	0.19	0.20	0.096	0.085	0.066	0.057
La	0.38	0.23	0.73	0.28	0.43	0.29	0.26	0.17
Nd	0.34	0.21	0.68	0.26	0.36	0.22	0.21	0.14
Eu	0.038	9.2x10 ⁻³	0.038	3.2x10 ⁻²	5.3 x10 ⁻²	1.5 x10 ⁻²	0.022	8.7 x10 ⁻³
U	0.16	0.089	0.14	0.13	0.11	0.079	0.11	0.073
Tl	0.17	0.118	0.029	0.024	0.066	0.046	0.062	0.031
Sm	0.063	0.030	0.124	0.034	0.067	0.042	0.038	0.025
Yb	0.077	0.016	0.053	0.022	0.043	0.023	0.038	0.015
Lu	0.018	3.0 x10 ⁻³	8.0 x10 ⁻³	3.3 x10 ⁻³	7.1 x10 ⁻³	4.0 x10 ⁻³	0.008	3.0 x10 ⁻³
Hf	1.8	0.17	0.20	0.22	0.62	0.21	0.80	0.18
W	0.24	0.15	0.13	0.13	0.15	0.14	0.26	0.12
Th	0.15	0.059	0.23	0.070	0.12	0.077	0.084	0.049
Hg	1.0	0.46	0.37	0.36	0.35	0.11	0.64	0.23
Bi	0.12	0.12	0.07	0.05	0.14	0.09	0.19	0.10
Cl ⁻	863	250	938	427	475	181	677	441
NO ₃ ⁻	534	246	502	189	2188	545	765	360
SO ₄ ²⁻	1400	829	1070	968	2500	774	1505	743
Na ⁺	215	128	378	339	701	681	504	202
NH ₄ ⁺	453	363	508	429	863	735	591	458
K ⁺	37	27	36	25	79	18	44	16
Mg ²⁺	81	56	103	61	36	27	43	30
Ca ²⁺	1085	851	1470	1205	1020	858	758	541
PM _{2.5-10}	13790	11650	19550	13000	16450	15970	13050	11650

Pollution roses for each element in coarse fraction are given in Figure 3.75. Most of the elements in PM_{2.5-10} had high concentration values as in the case of PM_{2.5}. These elements and the directions in which they had high concentrations were; Na and Cu in NE direction; Co, Cd and Pb in W-WSW and ENE directions; K, Nd, Eu, U, Sm, La, Th and Mg²⁺ in S-SSE-SE directions and finally, V, Yb, Y, Lu and Hf in ENE-E directions.

Calcium, Mg, Ni, and Mo had high concentrations in ENE direction whereas in PM_{2.5}, the dominant wind direction was NE. The dominant direction for P and Ti was from NE. In addition to ENE, the high concentrations were also obtained in SSE and WSW directions for these two elements. The only direction for Tl emission in PM_{2.5-10} was the E direction where leather and cement factories are present.

The dominant direction for Cl⁻, Ca²⁺, Zn, Cr, Mn, Al, Fe and PM_{2.5-10} was S-SSE directions where the wood-pulp factory and agricultural areas are present. Most of the As emissions and high concentrations of W and Hg were obtained in ENE direction where asphalt manufacturing plant is located. Tungsten and Bi were also seen in WSW direction, however there is no possible source for these elements then, the long range transportation might be considered.

The high concentration of Sc, Se and Sb were seen in W direction. The source might be again the long range transportation. The only emission source for Cs was in S direction where agricultural areas are present and the only emission source for Tl was E direction.

Most of the ions, Na^+ , K^+ , NH_4^+ , NO_3^- and SO_4^{2-} had high concentrations in W direction. The same possible source for NH_4^+ and SO_4^{2-} indicates the secondary aerosol formation in that direction.

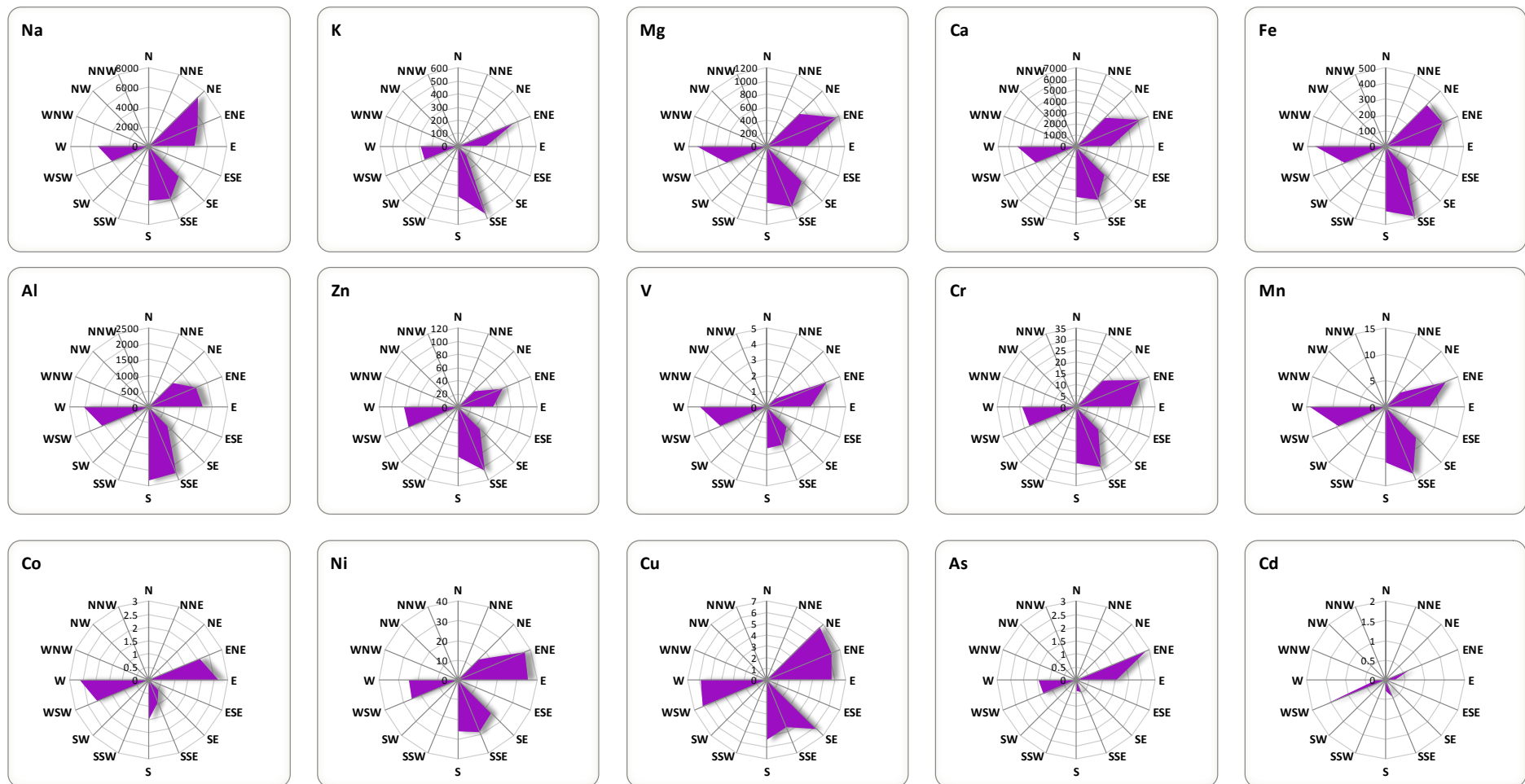


Figure 3.75. Pollution roses of each element in coarse fraction.

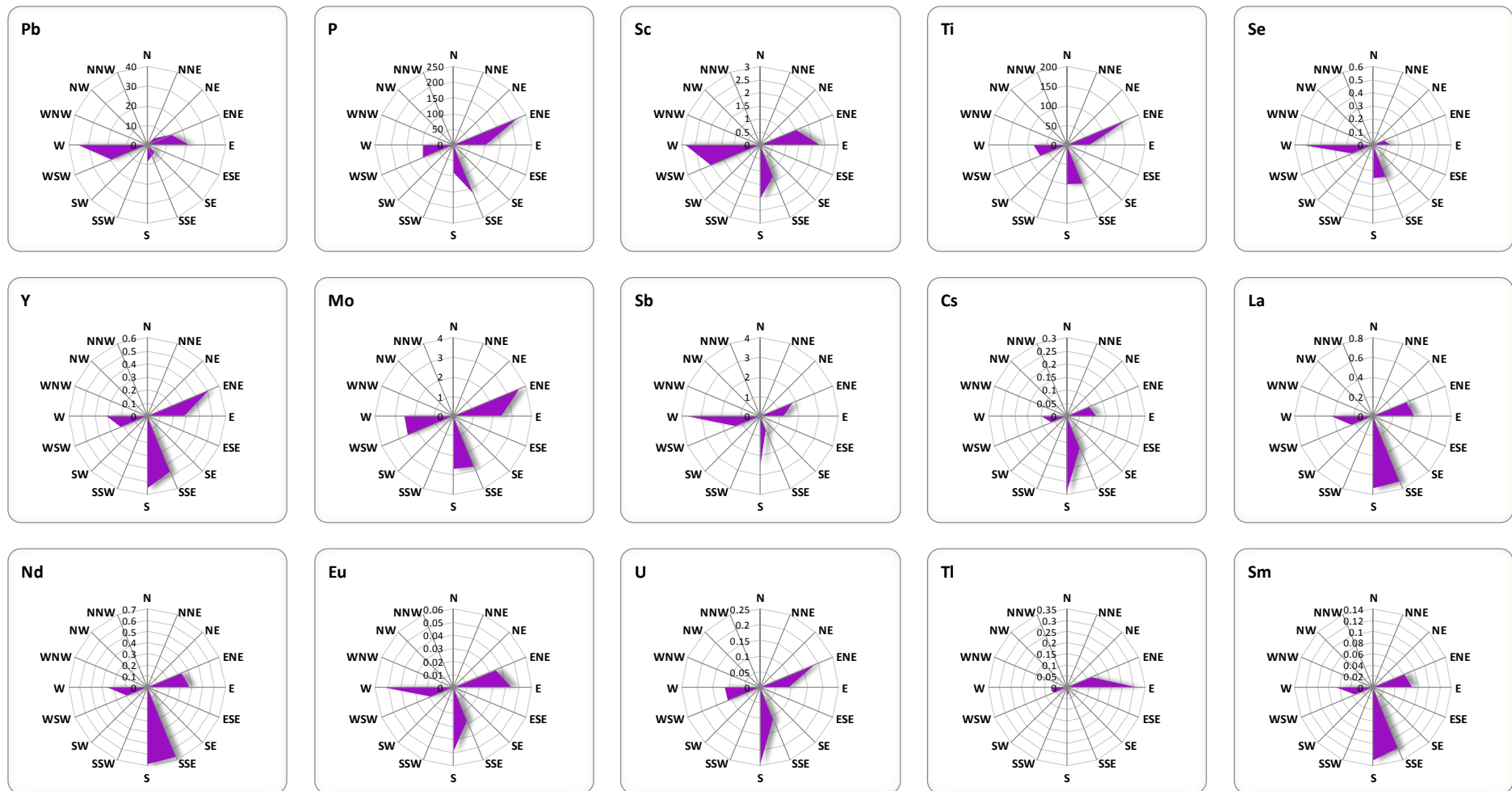


Figure 3.75. Pollution roses of each element in coarse fraction (cont.).

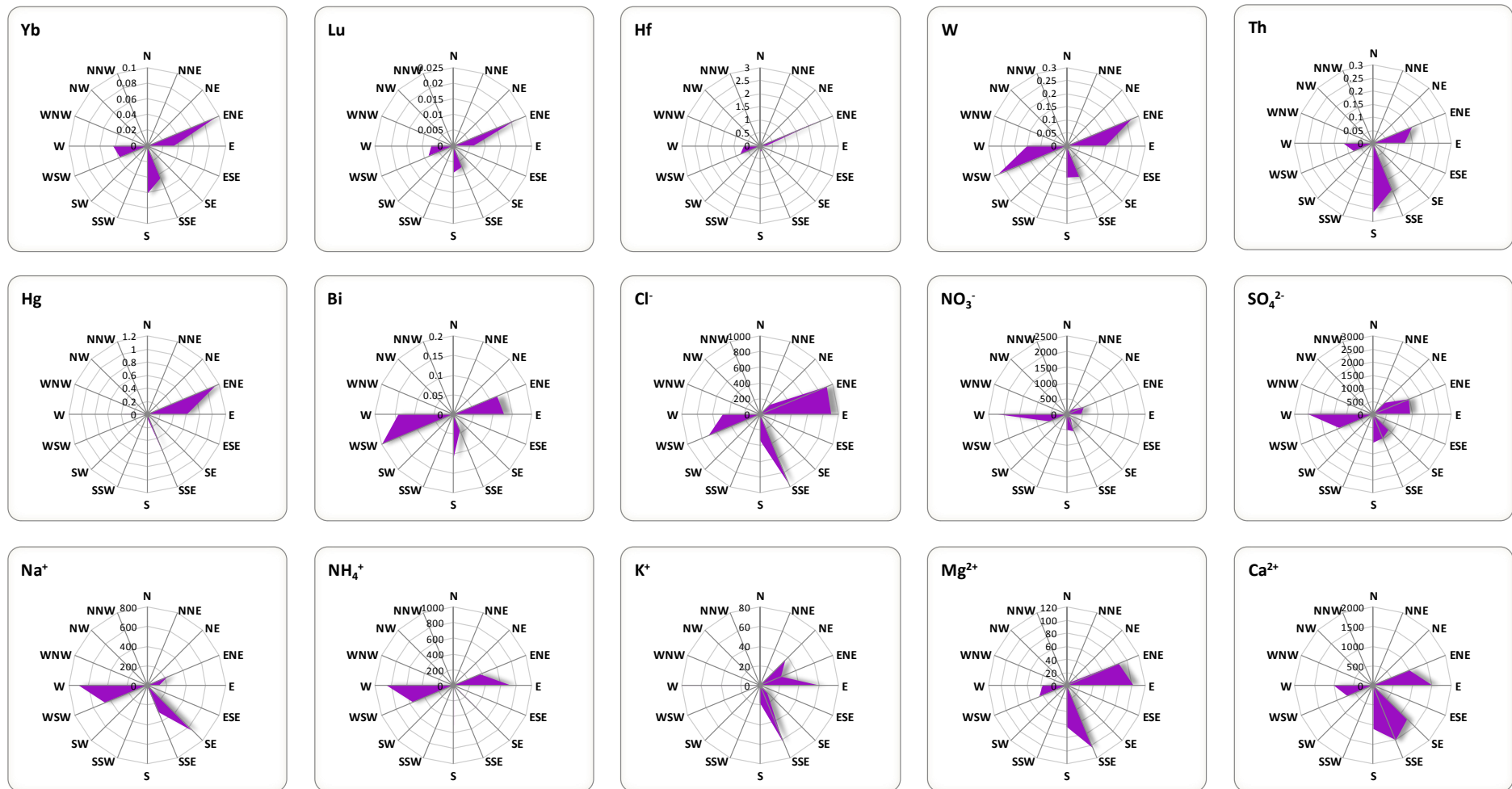


Figure 3.75. Pollution roses of each element in coarse fraction (cont.).

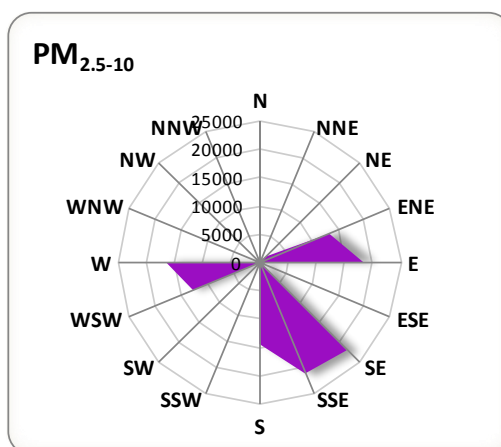


Figure 3.75. Pollution roses of each element in coarse fraction (cont.).

3.8.5. Factor analysis

In this study, the parameters that have values greater than 70%, have been used for the analysis. In order to obtain the complete data set, the missing days (not analyzed) were filled with the median values and the missing days due to being below the detection limit were filled with the half of detection limit values. In the factor analysis table, the factor loadings greater than 0.25 and the communalities greater than 0.50 have been included.

3.8.5.1. Factor analysis results for $PM_{2.5}$

Factor analysis results for fine fraction are given in Table 3.32. In the analysis six identifiable factors accounted for 79.07% of the total variance. In the first factor, rare earth elements (Y, La, Nd, Eu, Sm, Th, Lu, U and Yb) had factor loadings greater than 0.80, the other crustal elements, Fe and Mn had factor loadings 0.72 and Ca had factor loading of 0.28 and K had factor loading 0.53. Finally, although As is an

anthropogenic element it was included in this factor with the factor loading of 0.55. This implies the presence of the residues of coal burning in soil. This factor explains the 27.1% of the total variance and called as a contaminated soil.

Table 3.32. Factor analysis results for PM_{2.5}.

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Communality
Na			0.48	0.71			0.79
K	0.53			0.40	0.45		0.72
Mg			0.42	0.39	0.57		0.71
Ca	0.28				0.76		0.72
Fe	0.72						0.64
Al			0.34	0.70			0.70
Cr			0.75		0.38		0.74
Mn	0.72		0.32		0.25		0.70
Co			0.33	0.64			0.71
Ni			0.43		0.75		0.77
As	0.55	0.37					0.62
Pb				0.74			0.64
Y	0.98						0.98
Mo	0.84		0.31				0.86
Sb		0.35	0.63			0.27	0.64
La	0.76						0.63
Nd	0.91						0.88
Eu	0.96						0.94
U	0.92						0.86
Sm	0.95						0.93

Table 3.32. Factor analysis results for PM_{2.5} (cont.).

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Communality
Yb	0.97						0.98
Lu	0.96						0.96
Hf	0.96						0.96
Th	0.97						0.96
NO ₃ ⁻		0.57				0.44	0.54
SO ₄ ²⁻						0.88	0.80
NH ₄ ⁺						0.83	0.76
PM _{2.5} ^a		0.54				0.57	0.64
OC		0.97					0.96
EC		0.91					0.85
TC		0.97					0.96
PM _{2.5} ^b		0.89					0.82
Eigen values	11.76	5.59	3.64	2.14	1.76	1.20	
% variance	35.63	16.93	11.04	6.50	5.32	3.65	79.07
Source	contaminated soil	diesel/gasoline vehicles and coal combustion	metal works	traffic and road dust	industrial emission	secondary compounds from LRT	

^aPM_{2.5} in teflon filter^bPM_{2.5} in micro glass fiber filter

LRT: long range transport

Arsenic, Sb, NO_3^- , $\text{PM}_{2.5}$ (teflon), $\text{PM}_{2.5}$ (glass fiber), OC, EC, TC were present in the second factor which explained the 16.93 % of the total variance. Factor loadings of carbonaceous fractions were greater than 0.80. The ratio of OC/EC was 1.06 which implies the effect of diesel and gasoline powered vehicles (Schauer et al. 1999). Also the presence of NO_3^- with high factor loading of 0.57, supports the idea of traffic emission (Zhou et al., 2004). Moreover, As and Sb are the primary sources of coal combustion (Öztürk et al., 2012; Karakaş, 1999; Yenisoy-Karakaş, 2000; Salma and Maenhaut, 2006). Moreover, the concentration of As, U and Th are high in local coal (Eğilli, 1999). The highest factor scores in this factor were observed in winter months (Figure 3.76) as expected. This factor was called as the mixture of diesel and gasoline powered vehicles and coal combustion.

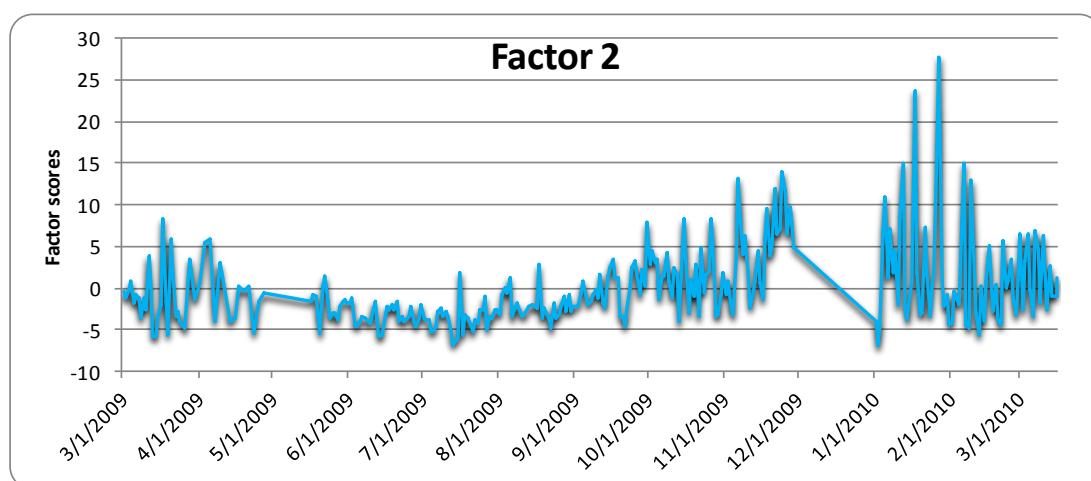


Figure 3.76. Variation of factor scores in Factor 2.

The third factor which includes Na, Mg, Al, Cr, Mn, Co, Ni, Mo and Sb explained the 11.04 % of the total variance. The elemental composition of this factor was

complicated due to the presence of both crustal (Al, Mn, Cr, Ni, Na and Mg) and anthropogenic elements (Ni, Cr, Mn, Mo and Sb). However, the factor loadings of anthropogenic elements were greater than the others. Then the factor can be explained as the effects of anthropogenic ones on crustal materials and called as a contaminated soil by non-ferrous metal works (Han et al., 2006). The variation of factor scores in the sampling period was given in Figure 3.77. Except for some days in winter months, the factor scores were constant throughout the sampling. This also implied that the emission source of pollutants did not show any seasonal variation and it might be local.

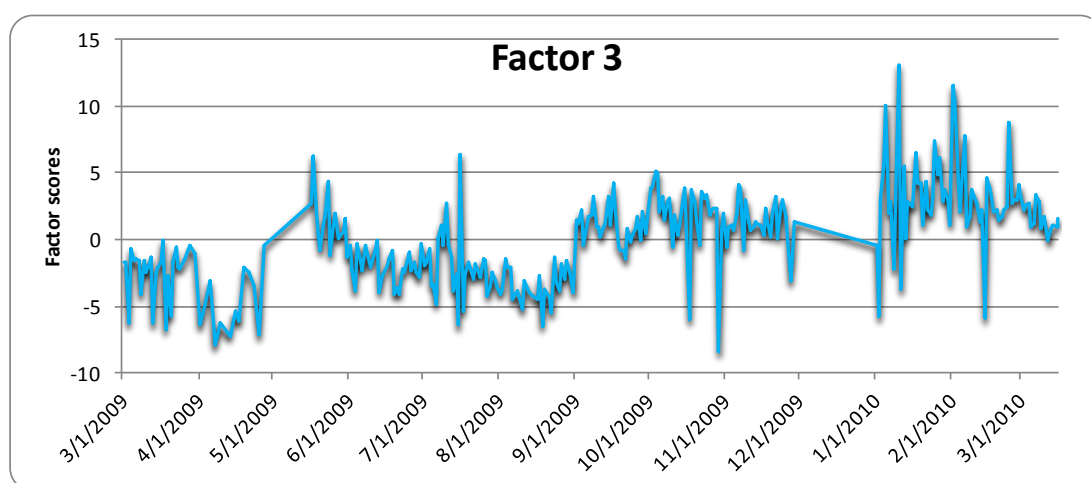


Figure 3.77. Variation of factor scores in Factor 3.

Factor four included Na, K, Mg, Al, Co and Pb and this factor explained the 6.50 % of the total variance. Lead and Co are the main pollutants emitted from traffic and their factor loadings in this factor were 0.74 and 0.64, respectively. Also one of the main crustal element, Al has higher factor loading (0.70). Karanasiou et al. (2009) explained that vehicle emissions, road abrasion and tire/break wear debris

contaminate the soil (includes Al) with metals (especially, Pb) in heavy traffic. Near the sampling point, there are two main arteries, D-100 road and TEM highway. Then, this factor can be labeled as a contaminated soil due to traffic emission. Although the wear products are emitted as coarse particles during the engine and break workings, the temperature becomes very high to evaporate these materials. Then these elements are obtained in the fine fraction (Karanasiou et al., 2009). The reason for the high factor loadings of Na, K and Mg might be the salt addition to the road to prevent from icing in winter.

The fifth factor explained the 5.32 % of the total variance. In this factor K, Mg, Ca, Cr, Mn and Ni were present. The source of this factor was mixed. The variation of factor loadings in the sampling period (Figure 3.78) showed two sharp peak regions. The increase in the warm season could be explained by the construction activities. One of the main source of Ca is the construction activities (Karanasiou et al., 2009) the factor loading of it was 0.76. In winter months, the increase might be due to wood burning that emits K and also the emission from industrial zone. Broadly the source of this factor can be labeled as anthropogenic.

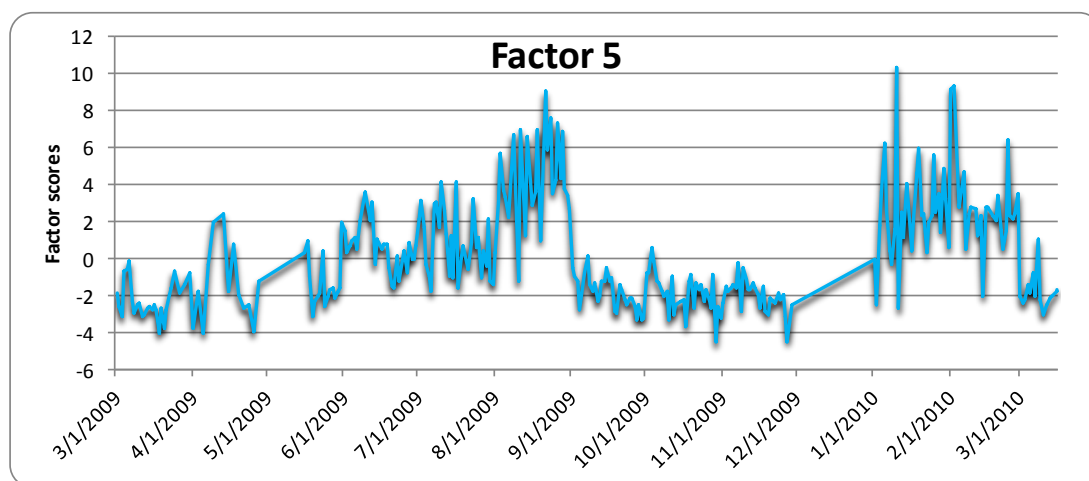


Figure 3.78. Variation of factor scores in Factor 5.

Finally, the six factor included Sb, NO_3^- , SO_4^{2-} , NH_4^+ and $\text{PM}_{2.5}$ (teflon) concentration in which the metal and ion contents were determined. This factor explained only 3.65% of the total variance. The source of this factor was the secondary compounds from the long range transport. Ammonium and SO_4^{2-} had higher factor loadings of 0.83 and 0.88, respectively. Kim et al. (2003 (a)) implied that NH_4^+ and SO_4^{2-} are the main contributors for secondary aerosol formation. The high factor loading of $\text{PM}_{2.5}$ (0.57) indicated the long range transport of the air mass. The lack of trend in the factor scores throughout the sampling period in Figure 3.79 denoted the source as continuous.

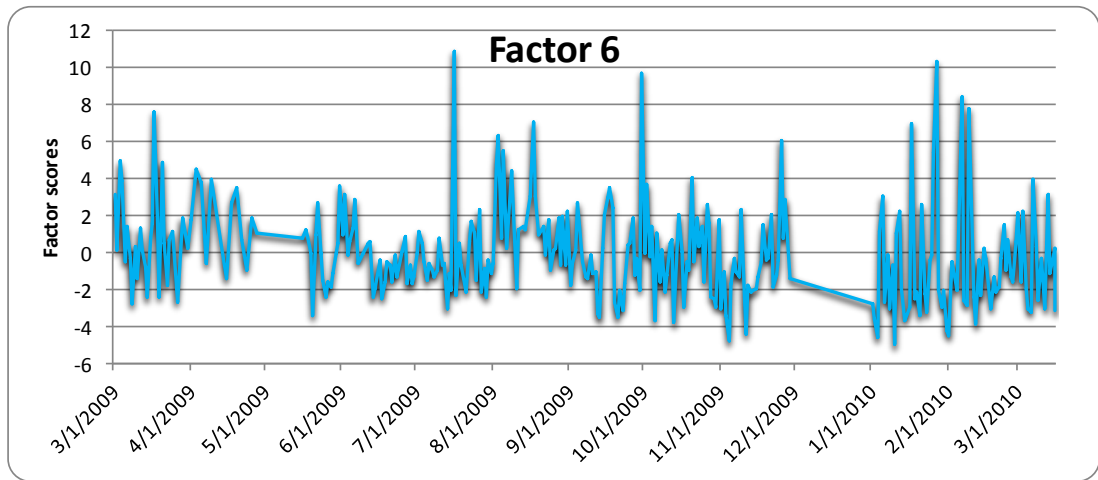


Figure 3.79. Variation of factor scores in Factor 6.

3.8.5.2. Factor analysis results for PM_{2.5-10}

Twenty seven parameters in 165 samples in coarse mode were analyzed in factor analysis. Six factors were identified in coarse fraction of particulate matter samples and explained 67% of the total variance (Table 3.33).

The first factor explained the 28.32 % of the total variance. In this factor Y, La, Nd, Sm, Yb and Th had high factor loadings greater than 0.70. These elements are crustal origin, so this factor was called as *crustal*.

The second factor explained the 11.95 % of the total variance. Sodium (0.73) and Mg (0.63) were the identifier of the sea salt, Eu (0.83), Yb and Lu (0.42), Al (0.48) and Ca (0.46) were the tracers of crustal source. Cobalt (0.56) was the anthropogenic element that was included in this factor. The back trajectories for the dates with the highest factor scores (15.6 and 15.4) were given in Figure 3.80. On the 13th of October the air mass was originated from Mediterranean and on the 15th of October, the air was originated from Atlantic Ocean and travelled throughout the Mediterranean Sea. Then the source of this factor was called as the *long range transportation*.

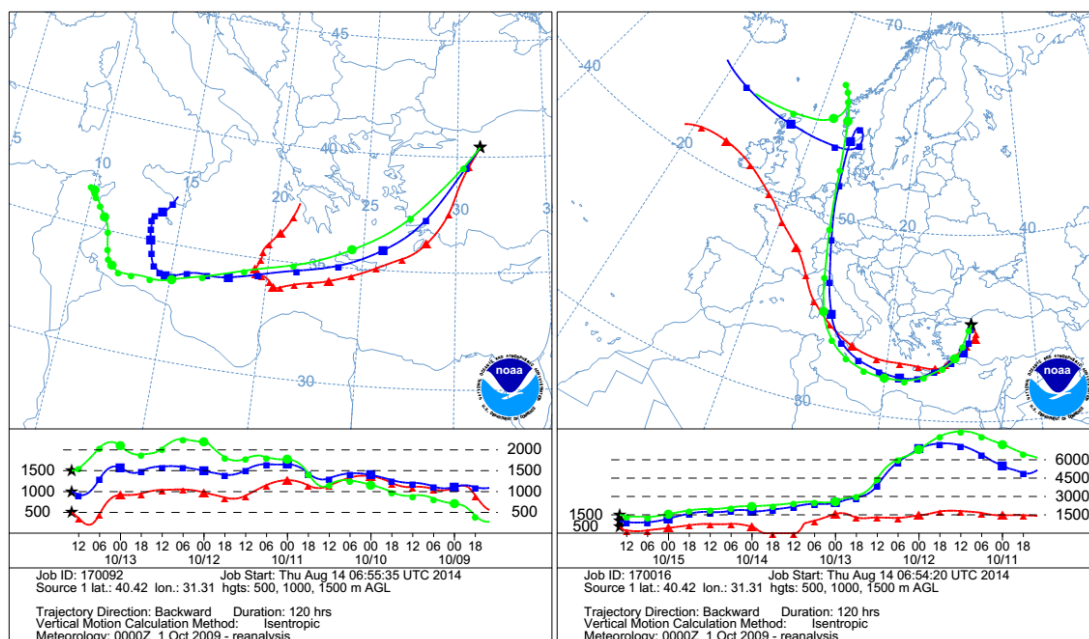


Figure 3.80. The back trajectories of the dates with the highest factor scores in coarse fraction (Factor 2)

The indicator of oil combustion, V (0.31) and the indicator of coal combustion, As (0.62) and Mo (0.85) are present in the third factor and then, called as *oil and coal combustion*. This factor explained the 9.05 % of the total variance.

The factor 4 was called as metal works and explained the 5.43 % of the total variance. The elements in this factor are K (0.58), Mg (0.43), Ca (0.57), Fe (0.37), Zn (0.78), Ni (0.39) and Cu (0.57). The possible source of these elements were *metal industries*.

In the factor 5, the combustion and traffic emission products like, V, As, Pb, Co were present. Moreover, PM_{2.5-10}, the identifier of soil was also included in this factor. Then, the effects of traffic emission on soil were seen and this factor was called as *road dust* for this factor.

Finally, Ti, Mn and Mg were present in the factor 6 with high factor loadings above 0.30. Chow (1995), mentioned that Mn and Ti in the coarse fraction can be originated from *paved road dust*. This factor explained only 5.14 % of the total variance.

Table 3.33. Factor analysis results for PM_{2.5-10}.

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Communality
Na		0.73	0.32				0.68
K	0.47	0.30		0.58			0.67
Mg		0.63		0.43		0.31	0.76
Ca	0.38	0.46		0.57			0.70
Fe	0.45	0.31		0.37			0.50
Al	0.42	0.48					0.56
Zn				0.78			0.66
V	0.31		0.61		0.37		0.62
Cr			0.64				0.62
Mn						0.84	0.81
Co		0.56	0.34		0.52		0.73
Ni	0.29			0.39			0.62
Cu				0.57			0.36
As			0.62		0.43		0.65
Pb					0.62		0.45
Ti						0.79	0.66
Y	0.86	0.29					0.90
Mo			0.85				0.79
La	0.80			0.28			0.73
Nd	0.91						0.91

Table 3.33. Factor analysis results for PM_{2.5-10} (cont.).

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Communality
Eu		0.83					0.76
Sm	0.91						0.88
Yb	0.74	0.42					0.83
Lu	0.47	0.42					0.55
Th	0.90						0.83
PM _{2.5-10}	0.44				0.53		0.57
Eigen values	7.93	3.34	2.53	2.08	1.52	1.44	
% variance	28.32	11.95	9.05	7.42	5.43	5.14	67.31
	crustal	LRT	oil and coal combustion	metal works	road dust	paved road dust	

3.8.6. Positive Matrix Factorization

EPA PMF 3.0 was applied to the aerosol data for the determination of source apportionment of the investigated parameters both qualitative and quantitatively. The flowchart of the application of PMF 3.0 is given in Figure 3.81. In the model, six main steps were included. First of all, the concentration and the uncertainty values of each species for each sample were calculated and prepared for input files. The missing values for the concentrations were filled with the median values and the values below detection limit were replaced by the half of the detection limits. The uncertainty values for the concentration values were 0.05 times the concentration value plus the detection limit. For missing data the uncertainty was the four times the median value. Finally the uncertainty values for the values below detection limit was calculated as 5/6 times the detection limit.

After the loading of input files the system calculated signal to noise ratio (S/N) in the second step (Analyze Input Data). The species were categorized according to their S/N values. The values less than 0.2 were identified as bad, the values between greater than 0.2 but less than 2.0 were identified as weak and finally, the values greater than 2 were categorized as strong (EPA PMF 3.0 User Guide, 2008). The model base run was started with a defined number of factors. When the base run was completed, Model Execution screen gives the Q_{robust} and Q_{true} (Eq 2.12) values which were used for the assessment of how well the model fit into the input data. Q_{robust} is the goodness-of-fit parameter calculated excluding outliers and Q_{true} is calculated by including outliers. The theoretical Q is not calculated by EPA PMF but can be approximated by the user as $nm - p$ ($n+m$), where n is the number of species, m is the

number of samples in the data set, and p is the number of factors fitted by the model. Solutions where Q_{true} is greater than 1.5 times Q_{robust} indicate that peak events may be disproportionately influencing the model (EPA PMF 3.0 User Guide, 2008). In base model results the factor profiles and source contributions were obtained.

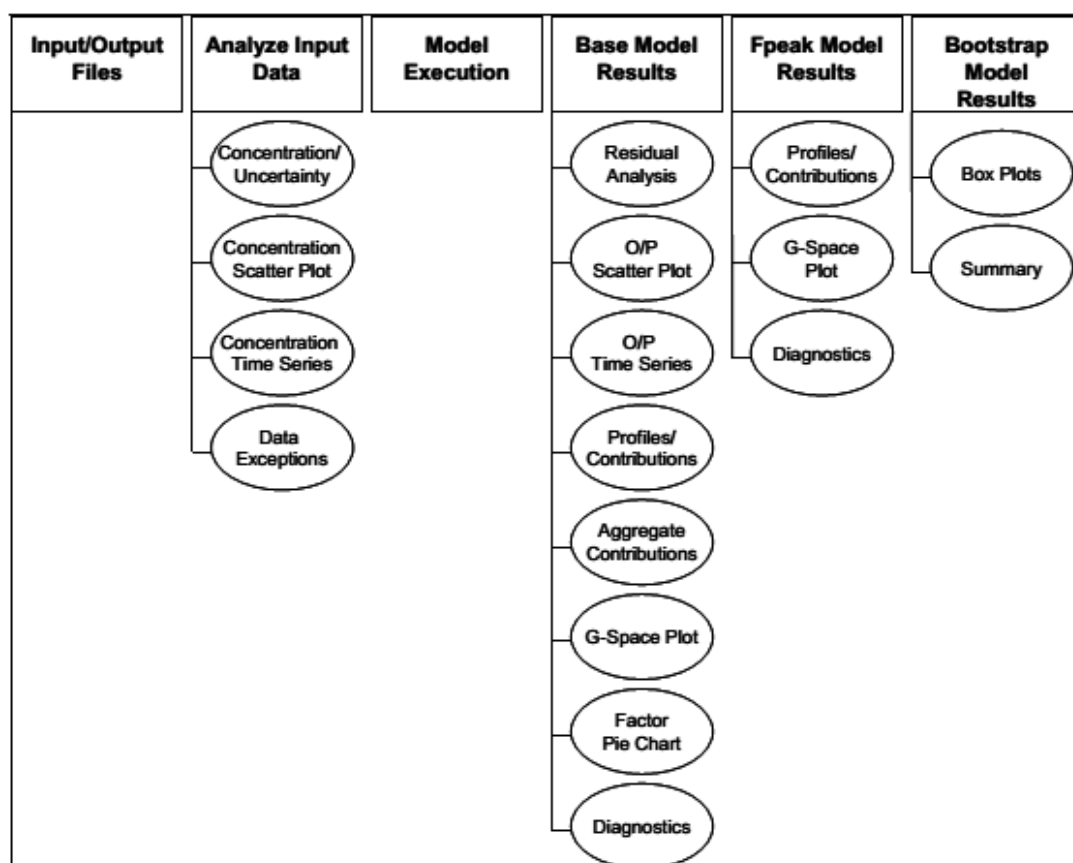


Figure 3.81. The flowchart of EPA PMF 3.0

The species with the percent of missing values above 30 % were excluded from the model as in factor analysis and labeled as "bad". In addition to this criterion, the species do not fit the model were also excluded from the application. The goodness of fit to the model can be evaluated by the scatter plot of observed and predicted

values of the species after the model run as in Figure 3.82. The correlation coefficient of the first graph belonged to Cd is very low that means this parameter was not fit the model. The main reason may be the high percentage of the values below detection limit. However, Nd in the second graph had high correlated coefficient between observed and predicted values. Then it was included in the model.

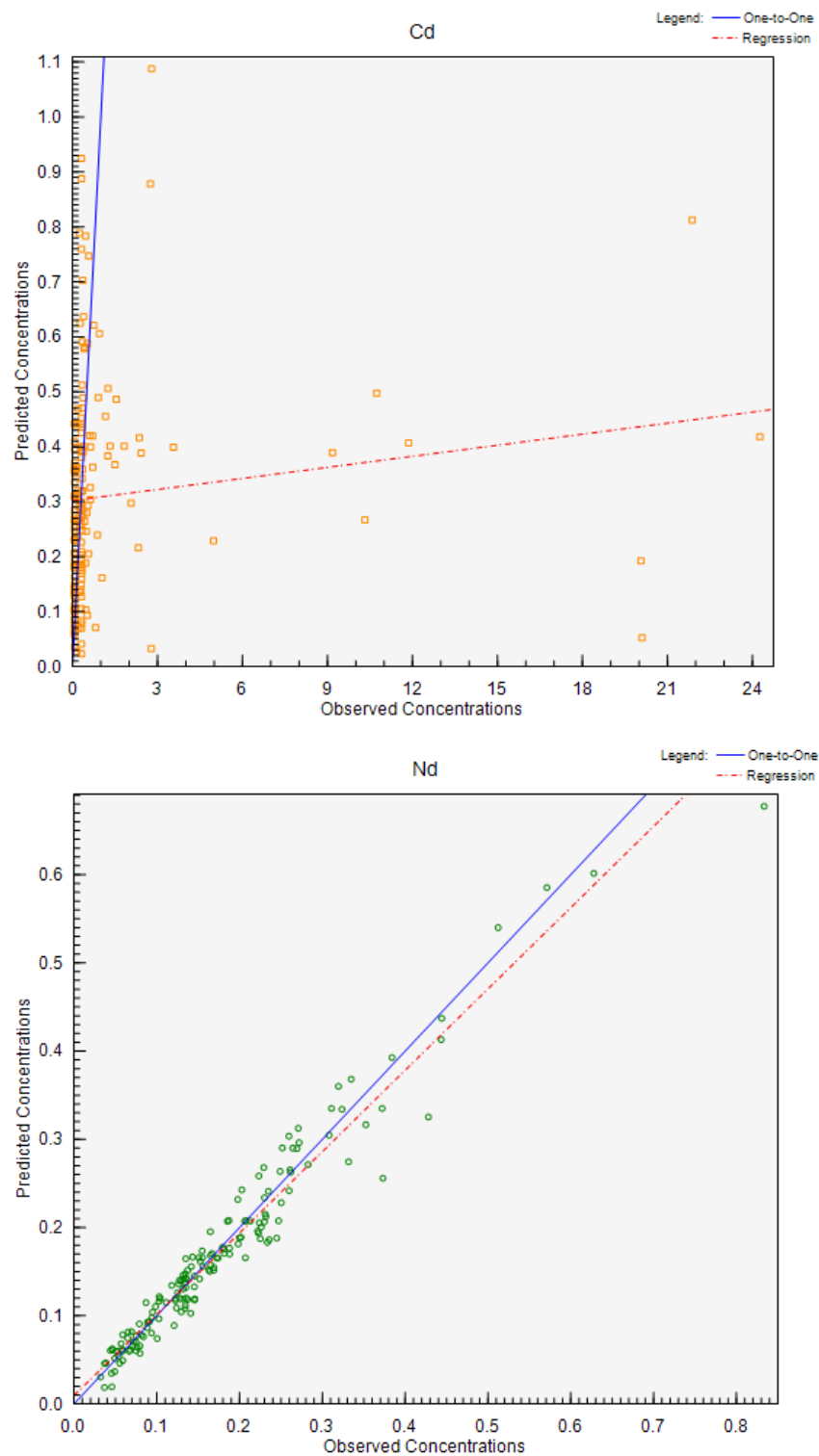


Figure 3.82. Sample of observed versus predicted scatter plot

3.8.6.1. Positive Matrix Factorization results for PM_{2.5}

The input data of PM_{2.5} samples for PMF analysis is summarized in Table 3.34. The species excluded from the model were Cs, Lu, Tl, Se, Na⁺, Mg²⁺ and Ca²⁺ and they were labelled as "bad".

After the model application, six factors were obtained to explain the possible sources of PM_{2.5} components. The concentration and the percent values of each species for each factor were determined in order to identify the tracer species for the corresponding factor. Then time series of each factor throughout the sampling period was plotted to observe the variations and finally, the crustal enrichment factors on the basis of Fe, were calculated for each factor.

Table 3.34. Input data of each parameter in PM_{2.5} for PMF analysis.

Species	Category	S/N	25th	75th	% of missing values	% of BDL values
Na	Weak	0.99	3940	7118	12.5	0.00
K	Weak	3.67	252	481	1.02	0.00
Mg	Strong	2.28	646	1083	1.69	0.00
Ca	Weak	2.33	2142	6618	2.71	0.00
Fe	Weak	3.51	138	295	1.69	0.00
Al	Weak	0.97	1378	2492	14.2	0.00
Zn	Strong	13.10	58	112	0.68	0.00
V	Weak	1.80	2.59	4.60	2.71	0.00
Cr	Weak	4.13	23.80	38.85	0.34	0.00
Mn	Weak	2.87	5.22	10.90	1.69	0.00
Co	Weak	5.24	0.44	2.69	1.69	0.34
Ni	Weak	5.52	16.58	48.58	0.68	0.00
Cu	Weak	3.54	4.81	10.87	1.02	0.00
As	Weak	6.31	0.69	2.56	1.36	0.00
Cd	Weak	9.22	0.20	0.89	6.10	14.24
Pb	Strong	3.72	8.93	23.80	1.36	0.00
P	Weak	16.81	62.59	106	0.34	0.00
Ti	Weak	10.34	33.90	60.77	0.68	0.34
Se	Bad	0.82	0.14	0.14	53.6	0.00
Y	Strong	6.30	0.07	0.14	0.00	20.68
Mo	Strong	12.54	2.63	3.83	0.00	0.00
Sb	Weak	2.36	0.77	1.10	1.02	0.00
Cs	Bad	0.83	0.05	0.07	35.9	0.34
La	Strong	4.60	0.09	0.22	0.34	1.02
Nd	Strong	12.87	0.06	0.18	0.00	0.00
Eu	Strong	3.59	0.00	0.01	3.39	1.36
U	Weak	1.20	0.07	0.11	27.5	0.00
Tl	Bad	1.08	0.04	0.05	43.0	0.34

Table 3.34. Input data of each parameter in PM_{2.5} for PMF analysis (cont.)

Species	Category	S/N	25th	75th	% of missing value	% of BDL values
Sm	Strong	4.29	0.01	0.02	1.36	3.05
Yb	Strong	12.46	0.01	0.02	0.34	3.05
Lu	Bad	2.12	0.00	0.00	57.0	0.00
Hf	Strong	8.39	0.16	0.16	0.00	3.39
W	Weak	1.19	0.10	0.24	6.44	61.69
Th	Strong	5.53	0.03	0.05	0.00	9.15
Hg	Weak	7.45	0.14	0.79	22.4	0.34
Bi	Weak	1.00	0.08	0.18	23.7	4.75
Cl ⁻	Weak	1.43	1755	2235	2.03	0.34
NO ₃ ⁻	Strong	2.68	407	866	2.71	0.34
SO ₄ ²⁻	Weak	1.84	2326	4589	2.71	0.00
Na ⁺	Bad	1.09	160	160	72.9	10.85
NH ₄ ⁺	Weak	1.30	859	2156	7.12	0.34
K ⁺	Weak	1.51	41.30	119.08	10.2	7.12
Mg ²⁺	Bad	0.83	25.53	25.53	70.2	17.29
Ca ²⁺	Bad	0.96	200	200	57.6	20.00
PM _{2.5} ^a	Strong	3.00	10261	20056	1.02	0.00
OC	Weak	1.04	4365	7631	10.8	0.34
EC	Weak	1.17	948	1785	10.8	0.00
TC	Weak	1.07	5214	9343	10.8	0.00
PM _{2.5} ^b	Weak	1.21	11831	22706	9.83	0.00

^a PM_{2.5} in teflon filter^b PM_{2.5} in micro glass fiber filter

BDL: below detection limit

The dominant species in Factor 1 were V, As, NO_3^- , SO_4^{2-} , NH_4^+ , K^+ , OC, EC, TC and $\text{PM}_{2.5}$ samples in both glass and teflon filters (Figure 3.83). This factor seems to be the combination of Factor 2 and Factor 6 in factor analysis. The presence of NH_4^+ and SO_4^{2-} indicated the secondary compounds and on the other hand the presence of carbonaceous species showed that the source of this factor might be the diesel and gasoline powered vehicles. This factor was named as "secondary compounds and combustion". Moreover As, and V which were the primary sources of coal and oil combustion, respectively have high percentage values. Then, the combustion effects can be also considered.

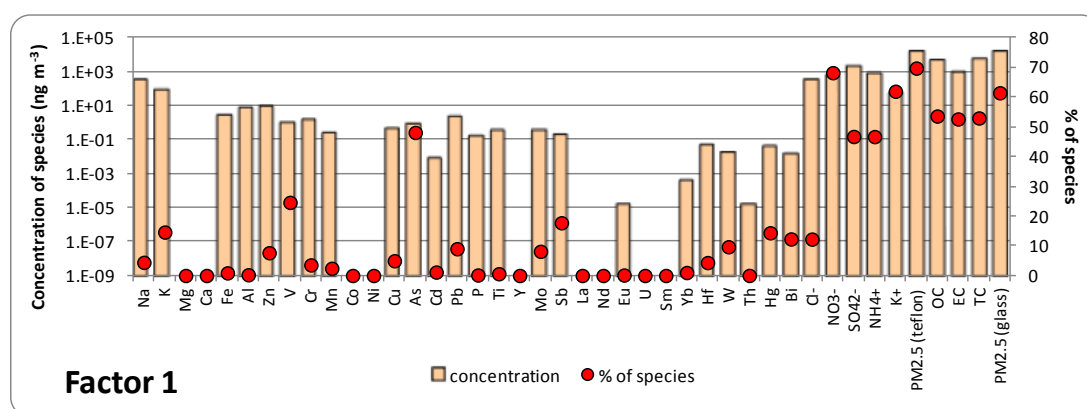


Figure 3.83. The concentration and percentage values of species for $\text{PM}_{2.5}$ (Factor 1).

The variation of this factor in Figure 3.84 showed that there was a considerable increase in winter months. Enrichment factors in Figure 3.85 denoted that this factor was highly enriched in V, Cu, Na, W, Cr, Hf, Cd, Zn, Pb, Mo, As, Hg and Sb.

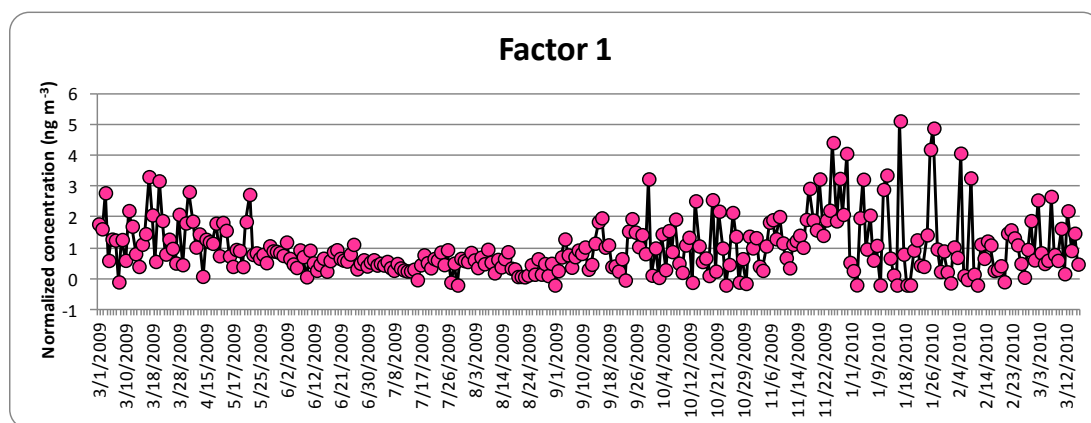


Figure 3.84. The variation of source contributions in Factor 1 for PM_{2.5}.

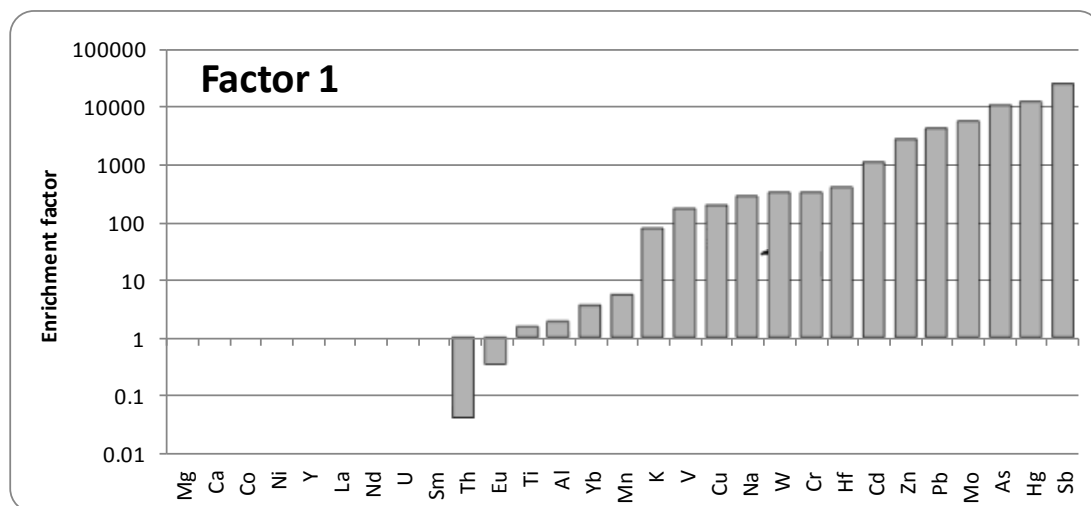


Figure 3.85. The enrichment factor values in Factor 1 for PM_{2.5}.

In the second factor Co, Cd and Pb which are the tracers of traffic emission were dominant (Figure 3.86) Then, this factor was called as *traffic*. Although the percent contribution of Cr, Na, Mo, Zn and Sb were low, they were highly enriched in this factor (Figure 3.87). Finally, the source contribution in this factor was high enough from August to the end of October as seen in Figure 3.88.

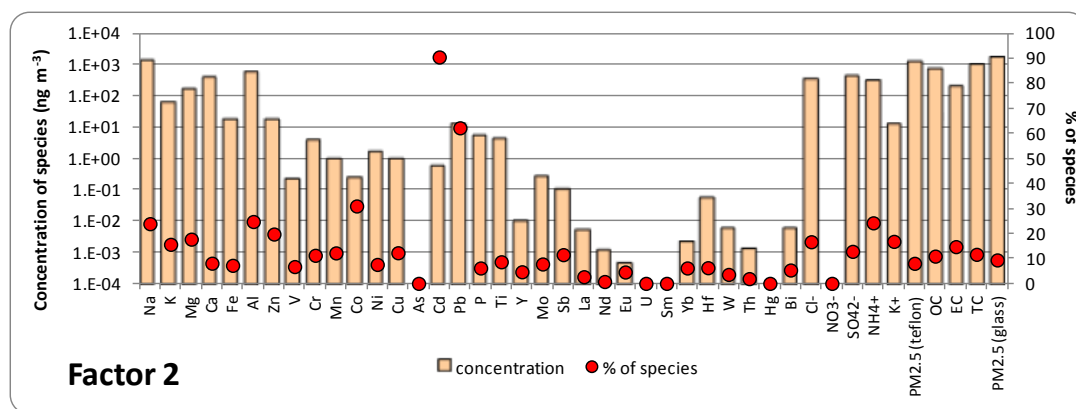


Figure 3.86. The concentration and percentage values of species for PM_{2.5} (Factor 2).

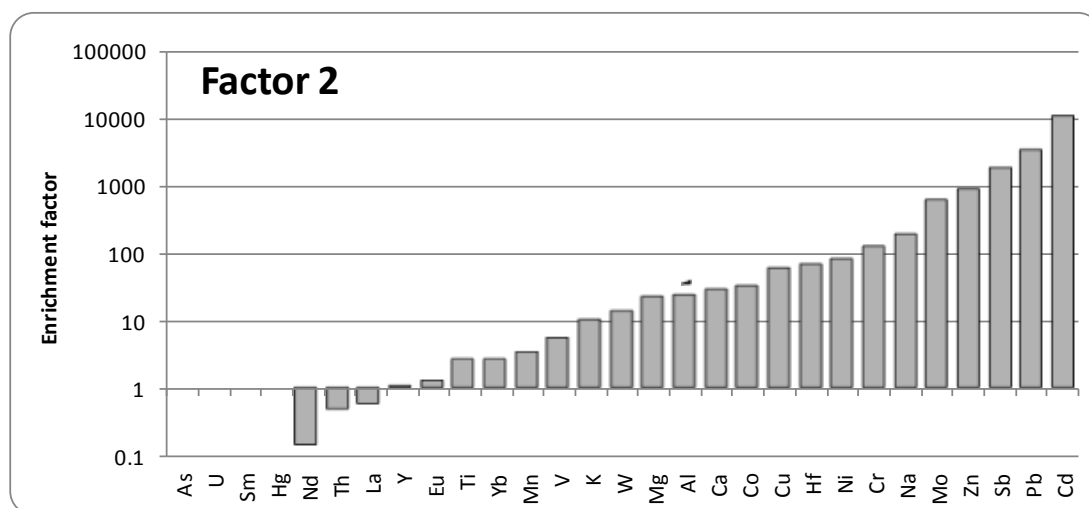


Figure 3.87. The enrichment factor values in Factor 2 for PM_{2.5}.

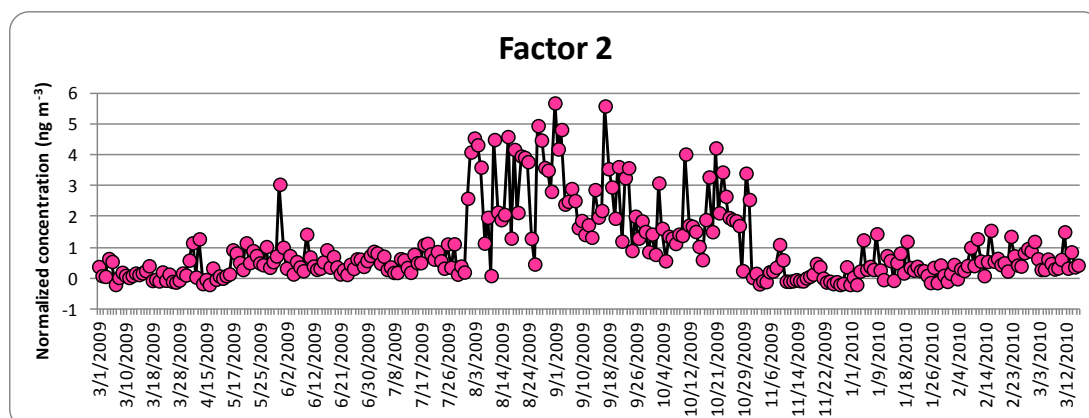


Figure 3.88. The variation of source contributions in Factor 2 for PM_{2.5}.

The crustal elements, Y, La, Nd, Eu, U, Sm, Yb, Hf and Th had high percent of explained variation around 60% in the third factor (Figure 3.89). In Figure 3.90 it was clearly seen that there are two increments during the sampling period. Especially in spring and summer months, the contribution of this source was very high as it was expected. Although the concentration and the percent explanation variation of the crustal elements were high as anthropogenic ones there might be a contributions due to local anthropogenic emissions. Then this factor called as *soil*.

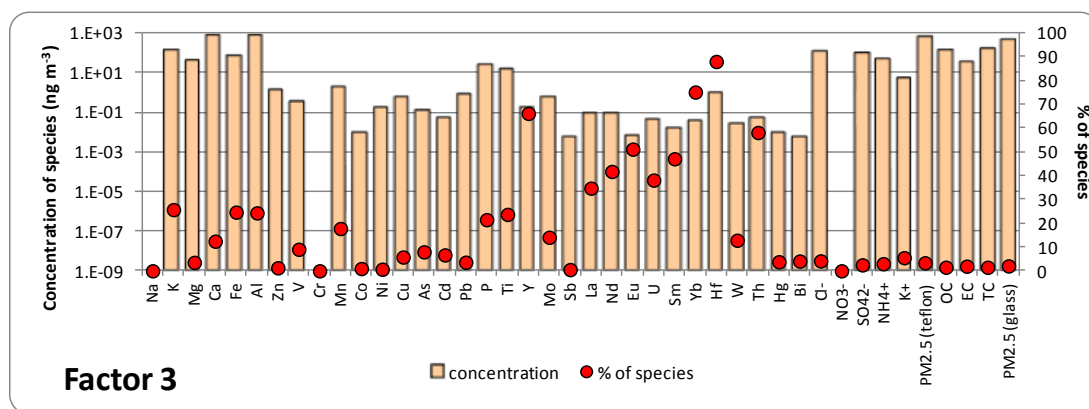


Figure 3.89. The concentration and percentage values of species for PM_{2.5} (Factor 3).

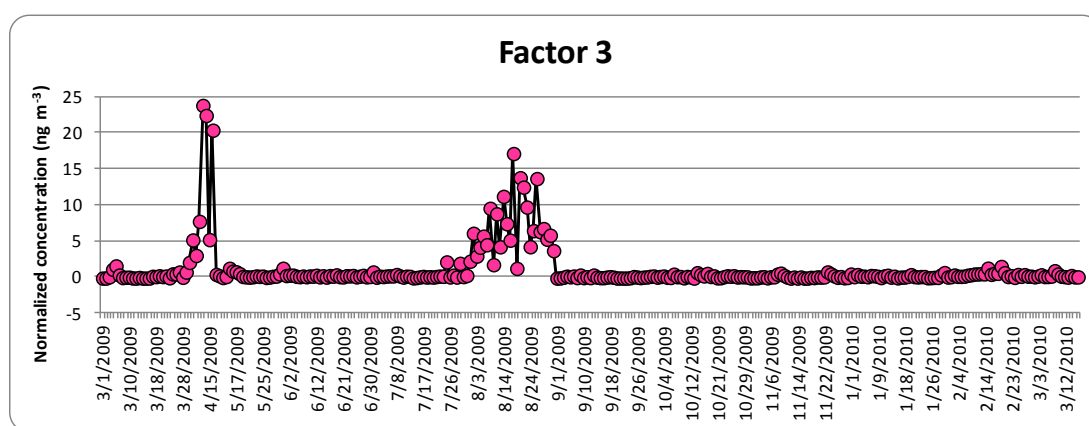


Figure 3.90. The variation of source contributions in Factor 3 for PM_{2.5}.

The fourth factor consisted of high percentages of Co (50 %), U (41 %), W (40 %), Mo, Sb (38 %), As (36 %), V (35 %), Cr (34 %), Bi (33 %) and Ni (32 %) (Figure 3.91). Vanadium is the main tracer of oil combustion (Chow, 1995; Karakaş, 1999; Öztürk et al., 2012) but it was not enriched in this factor. Highly enriched species in this factor were Zn, Pb, As, Mo and Sb which were generally emitted from coal combustion (Figure 3.92). However, Figure 3.93 did not show any seasonal variation of this factor throughout the sampling period and the emissions of these pollutants were continuous. Then, this factor was called as *regional background*.

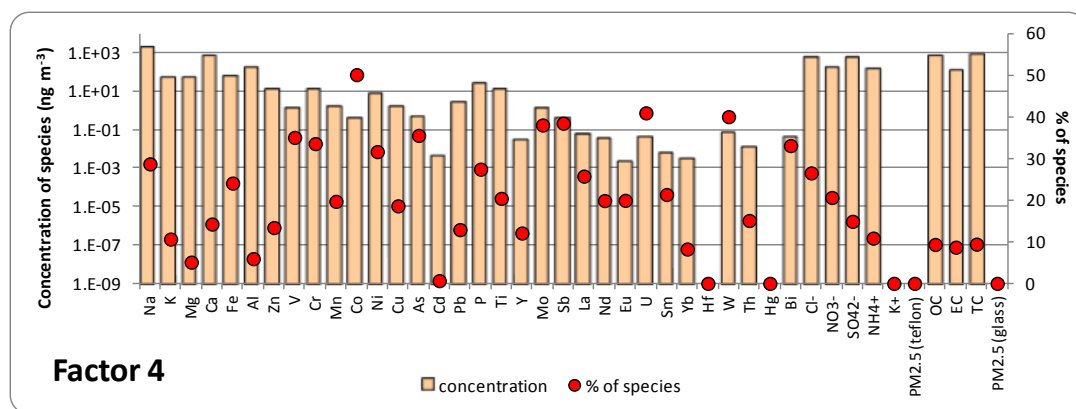


Figure 3.91. The concentration and percentage values of species for PM_{2.5} (Factor 4).

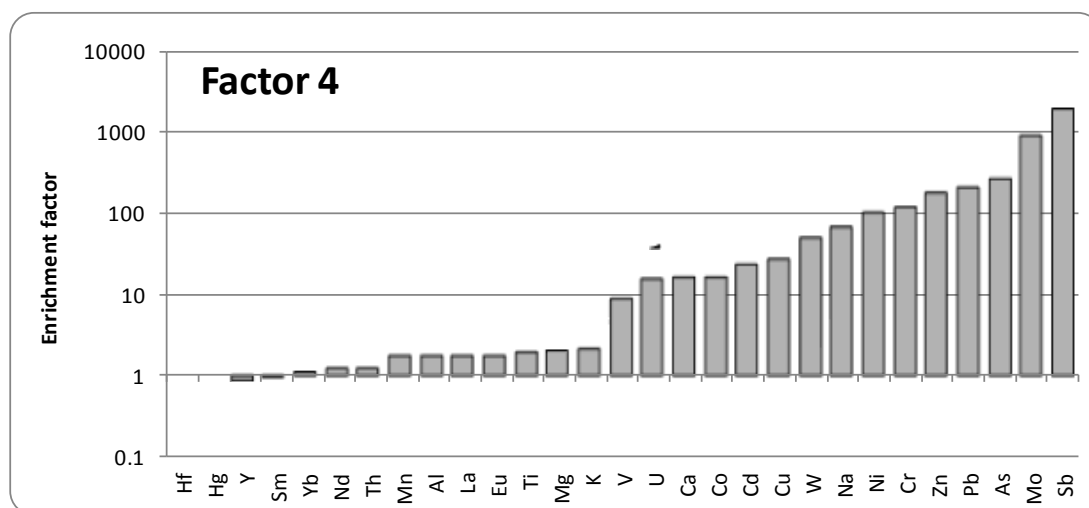


Figure 3.92. The enrichment factor values in Factor 4 for PM_{2.5}.

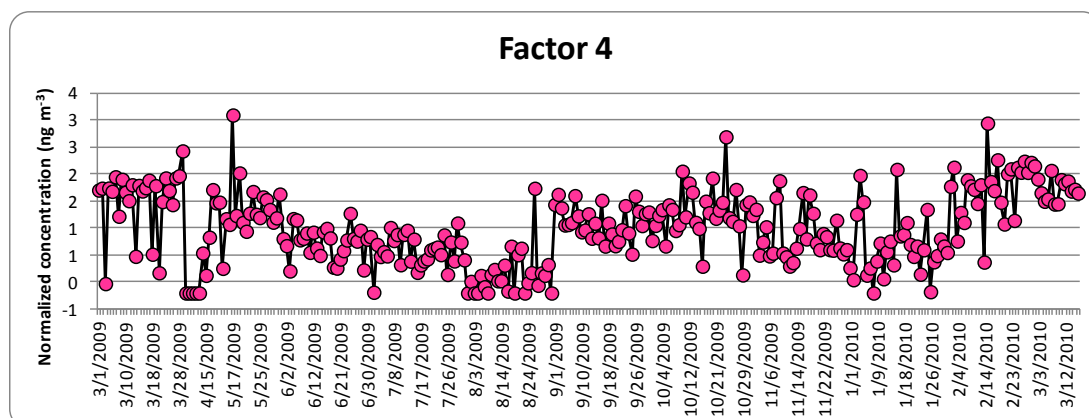


Figure 3.93. The variation of source contributions in Factor 4 for PM_{2.5}.

Magnesium (59 %), Hg (48 %), Al (45 %), Na (42 %), Cr (41 %), Ti (32 %), Ni (30 %) and P, Mo, Fe, Mn, Cl⁻, OC and TC around 25 % were included in the fifth factor (Figure 3.94). Most of these elements were emitted from industrial metal processes. Pollution roses of these elements (Figure 3.73) especially, Ni, Al, Cr, Fe, Mn, P and Ti were emitted from NE direction where the industrial areas (isopoly and PVC production, aluminum carpentry, petrochemical and motor oil) are located. The lack of variation in daily concentrations also indicated the emissions from continuous sources (Figure 3.95). Beside these metals also Na, Mg and Cl⁻ were present with high concentration in this factor then, the possible effect of sea salt might be considered. Enrichment factor of Na was around 100 (Figure 3.96). That means that it was moderately enriched. This element was originated from sea. The back trajectories of the highest source contribution dates (10/01/2010 and 24/02/2010) shows the sea salt effect obviously (Figure 3.97). On the 1st of January 2010, the air mass was travelled above the Aegean Sea and on the 24st of February 2010, the air mass was travelled along Mediterranean Sea. Consequently, this factor was called as the mixture of *metal works and sea salt*.

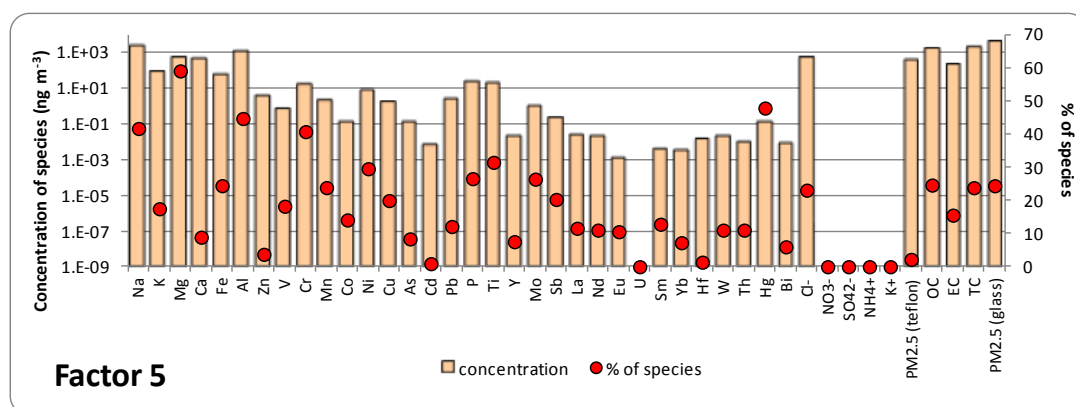


Figure 3.94. The concentration and percentage values of species for PM_{2.5} (Factor 5).

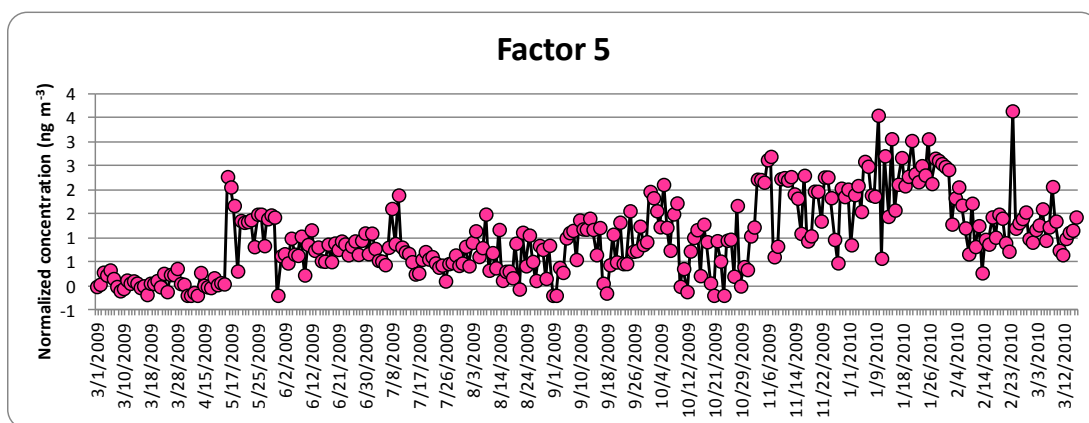


Figure 3.95. The variation of source contributions in Factor 5 for PM_{2.5}.

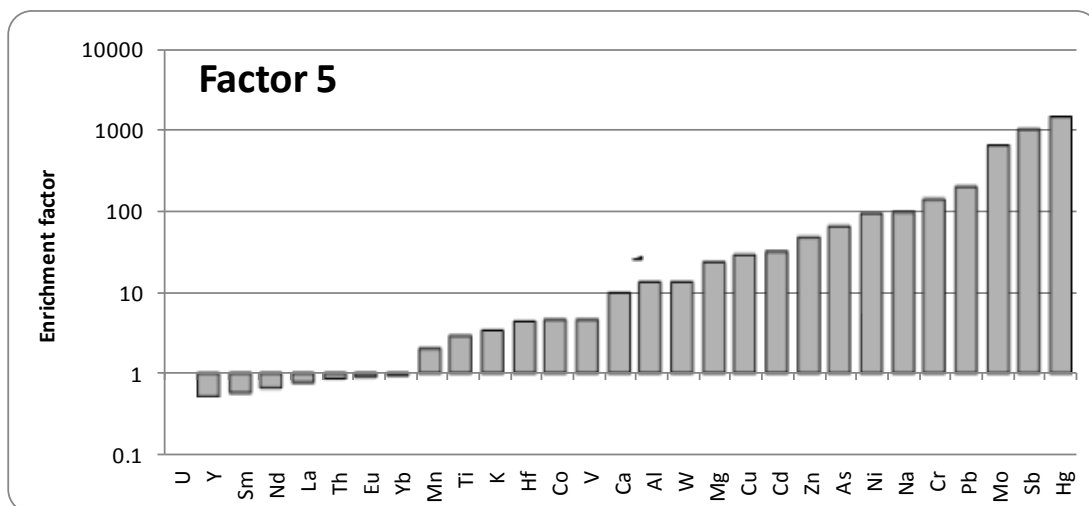


Figure 3.96. The enrichment factor values in Factor 5 for PM_{2.5}.

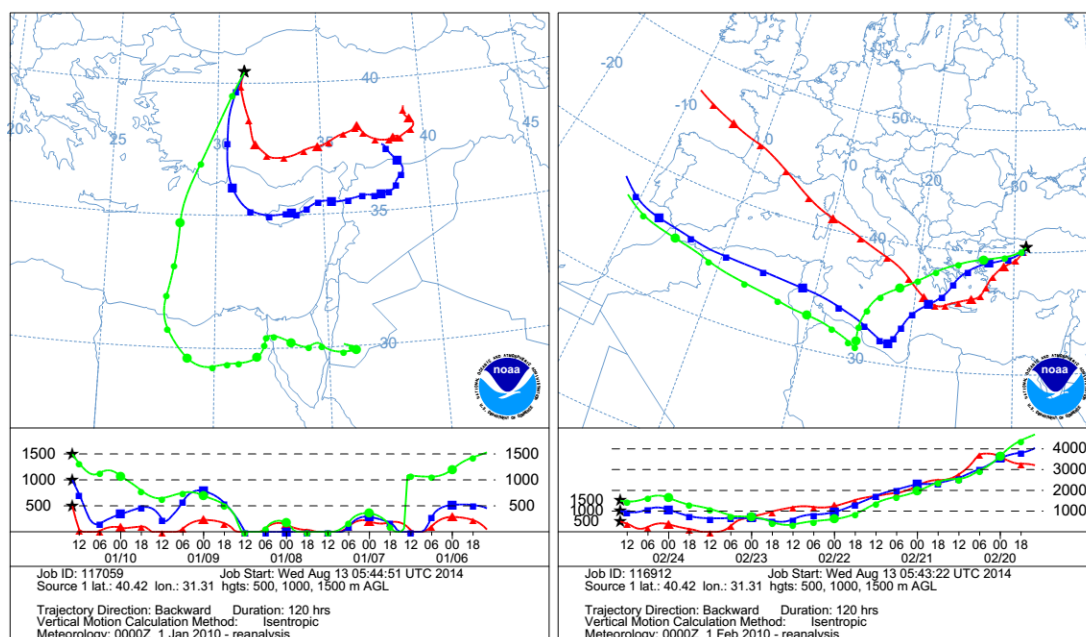


Figure 3.97. The back trajectories of the highest source contribution dates for PM_{2.5} (Factor 5)

The possible source of Factor 6 can be *industrial emission* due to the high percentage of Ca (56%), Zn (54%), Bi (39%), Cu (38%), Hg (34%) and Ni (31%) (Figure 3.98). The high concentration of Ca was due to the construction processes as mentioned in factor analysis. Then the rise in contribution in these months might be due to the high concentration of Ca. Especially, in summer and autumn months there was an increase in source contribution for this factor as seen in Figure 3.99. The back trajectories of the highest source contribution dates (02/07/2009 and 09/06/2009) were given in Figure 3.100. Although the origins of the air masses on both dates were different, the entrance of the air masses were from NE direction (the local industrial zone). The highly enriched parameters in this factor was Ni, Mo, Sb, Zn and Hg (Figure 3.101).

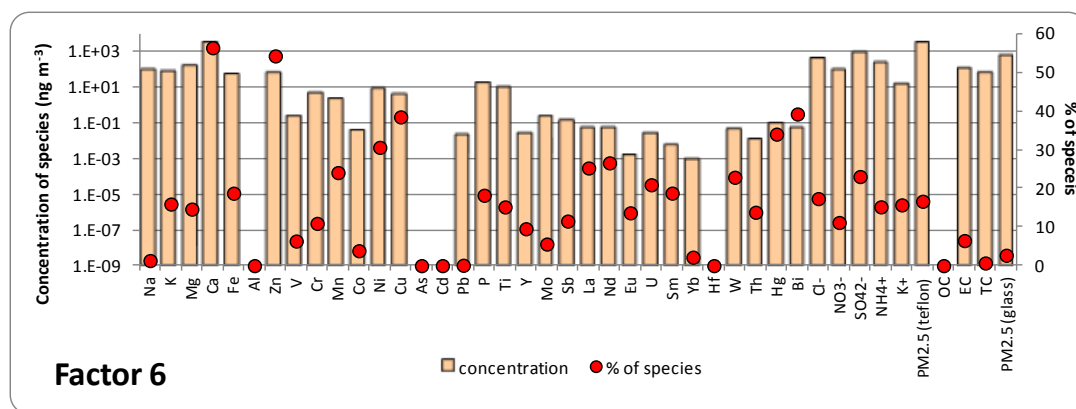


Figure 3.98. The concentration and percentage values of species for PM_{2.5} (Factor 6).

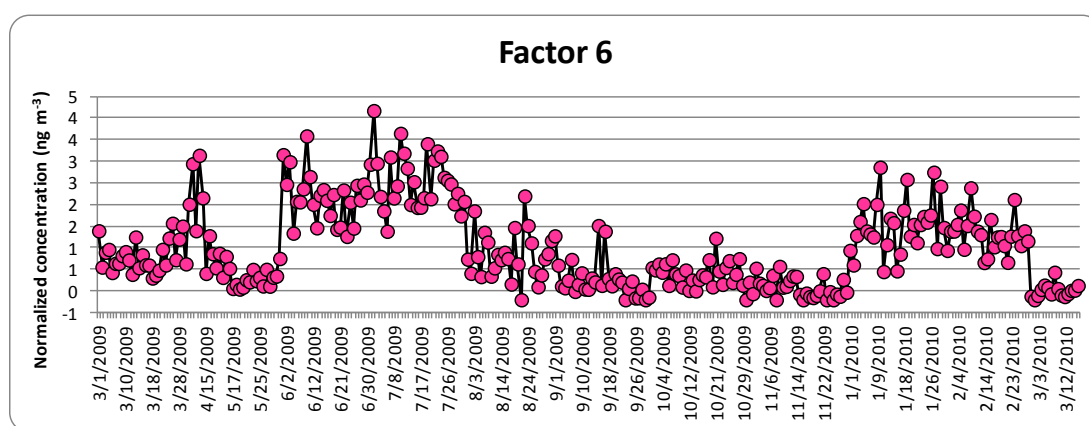


Figure 3.99. The variation of source contributions in Factor 6 for PM_{2.5}.

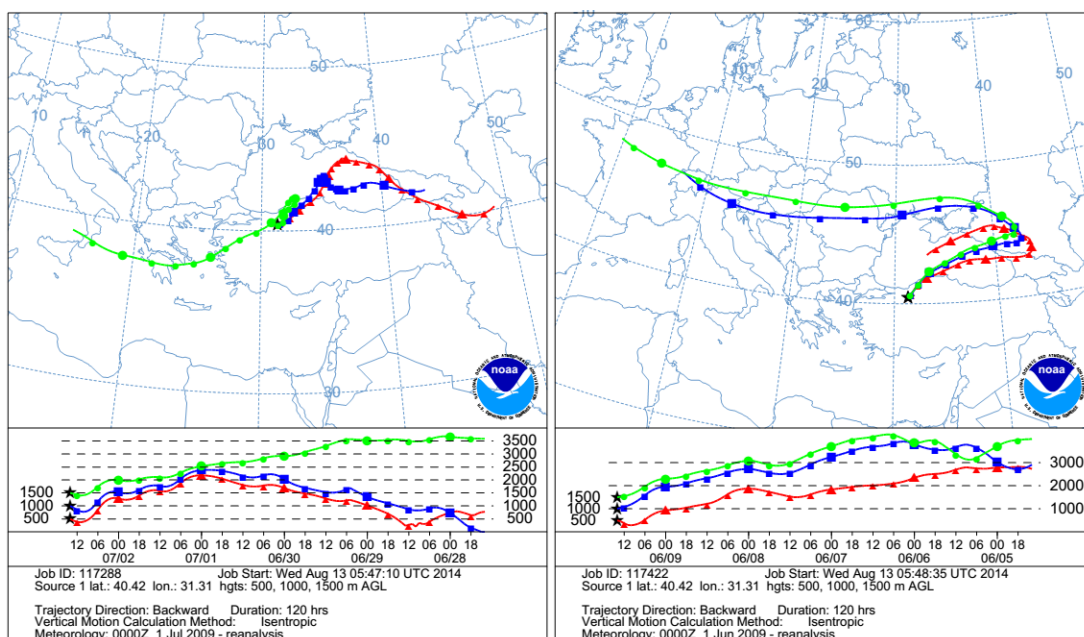


Figure 3.100. The back trajectories of the highest source contribution dates for PM_{2.5} (Factor 6)

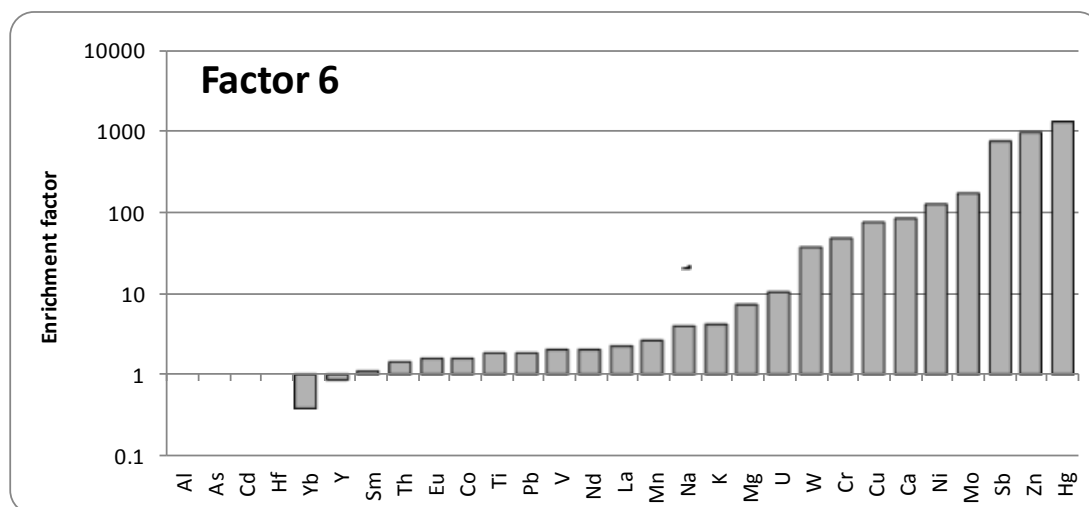


Figure 3.101. The enrichment factor values in Factor 6 for PM_{2.5}.

The contribution of each factor to each parameter was given in Figure 3.102. Arsenic, NO₃⁻, SO₄²⁻, NH₄⁺, K⁺, OC, EC, TC, and PM_{2.5} samples in both glass and teflon filters were high in Factor 1 which was called as *secondary compounds and combustion*. Factor 2 which was called as *traffic* mostly contributed to Co, Cd and

Pb. The factor 3 was labelled *soil* due to high contributions of crustal elements. Factor 4 was called as *regional background*, including high percent contribution of Na, Mg, V, Cr, Co, Ni, As, Mo, Sb, U, W, Bi and Cl⁻. The effect of *metal works and sea salt* were observed in Factor 5 which includes Na, Mg, Cl⁻, Al, Cr, Mn, Ni, P, Ti and Hg. Finally, Factor 6 was explained with the high contributions of Ca, Zn, Bi, Cu and Hg and called as *industrial emission*.

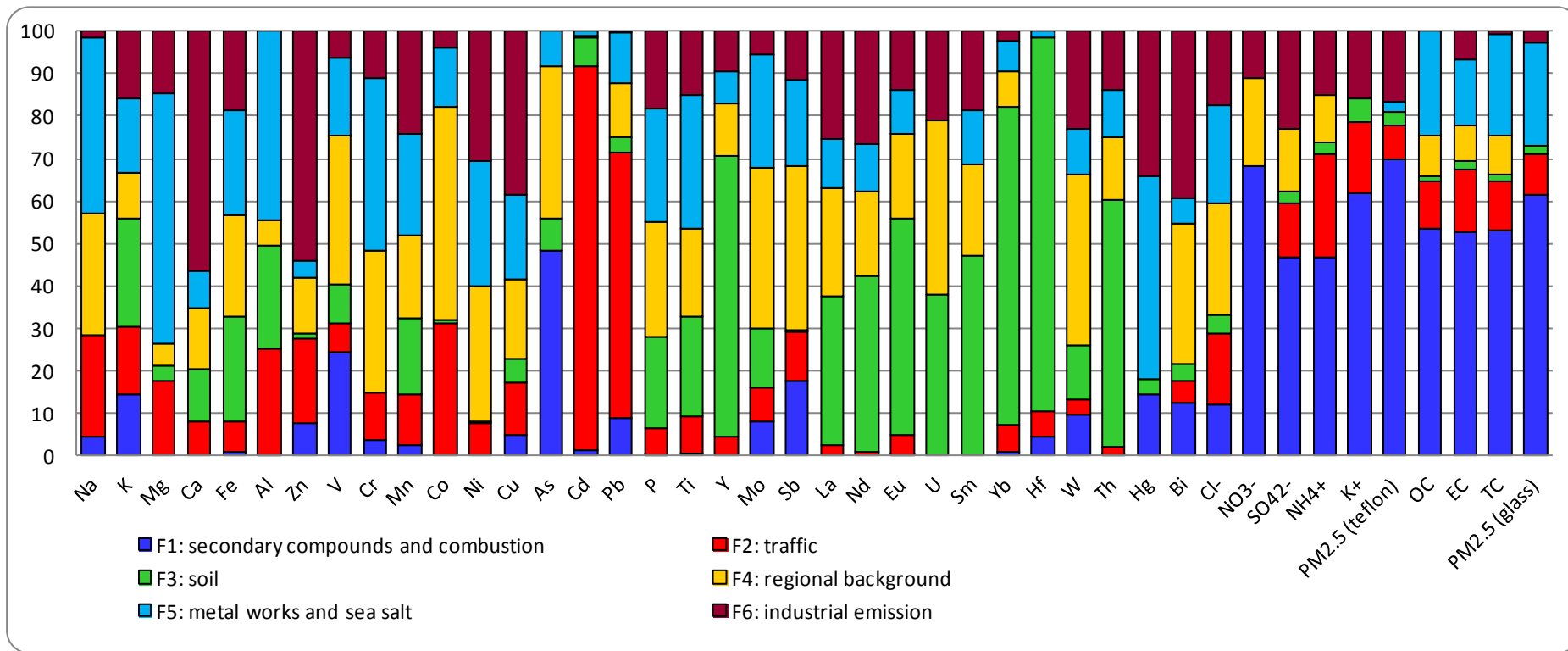


Figure 3.102. The percent contribution of each factor to each parameter in fine mode.

3.8.6.2. Positive Matrix Factorization results for PM_{2.5-10}

First of all, concentration and uncertainty files were constructed for the application of PMF 3.0 for the concentration of species in coarse particles. The analysis of input data of PM_{2.5-10} was given in Table 3.35. Bad categorized species which were excluded from the model were Cd, P, Se, Sb, Cs, Tl, Hf, W, Hg, Bi, Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺. As mentioned before, the species had the percentage of missing value above 30 were excluded and six factors were extracted from the model.

Table 3.35. Input data of each parameter in PM_{2.5-10} for PMF analysis.

Species	Category	S/N	25th	75th	% of missing values	% of BDL values
Na	Strong	17.39	3488	5713	5.68	0.00
K	Weak	4.26	130	370	1.14	38.74
Mg	Strong	18.30	452	975	0.00	9.49
Ca	Strong	18.10	2519	5412	0.00	0.00
Fe	Strong	14.75	148	359	0.00	39.92
Al	Strong	18.18	1072	2192	5.11	3.95
Zn	Weak	2.75	40.10	94.73	1.14	68.77
V	Strong	12.70	1.31	3.09	0.57	69.17
Cr	Strong	7.43	19.38	30.51	0.57	69.17
Mn	Weak	3.73	5.22	10.72	1.14	68.77
Co	Weak	11.74	0.47	2.97	0.57	69.17
Ni	Weak	5.46	13.17	41.39	0.57	69.17
Cu	Weak	2.22	3.46	7.51	2.84	67.59
As	Weak	1.88	0.25	1.05	3.98	66.80
Cd	Bad	6.30	0.08	0.52	15.9	58.50
Pb	Strong	18.42	4.33	33.68	0.57	67.98
P	Bad	2.37	42.61	99.72	3.98	62.06
Ti	Weak	2.91	28.02	60.52	3.41	64.03
Se	Bad	0.87	0.12	0.12	63.1	25.69
Y	Strong	2.58	0.08	0.17	0.00	69.57
Mo	Strong	10.51	1.90	2.80	0.57	69.17
Sb	Bad	15.61	0.69	1.06	0.57	69.17

Table 3.35. Input data of each parameter in PM_{2.5-10} for PMF analysis (cont.)

Species	Category	S/N	25th	75th	% of missing values	% of BDL values
Cs	Bad	0.83	0.05	0.07	37.5	43.48
La	Strong	5.18	0.12	0.28	0.00	69.57
Nd	Strong	13.38	0.09	0.23	0.00	69.57
Eu	Weak	5.87	0.01	0.02	1.70	68.38
U	Weak	0.91	0.05	0.09	22.2	54.15
Tl	Bad	1.31	0.03	0.04	38.6	42.69
Sm	Strong	7.28	0.02	0.04	0.00	69.57
Yb	Weak	1.93	0.01	0.02	2.84	67.59
Lu	Weak	0.88	0.00	0.00	24.4	52.57
Hf	Bad	0.64	0.16	0.16	5.68	65.61
W	Bad	2.22	0.10	0.12	10.8	62.06
Th	Strong	3.66	0.03	0.07	0.00	69.57
Hg	Bad	2.73	0.10	0.51	21.6	54.55
Bi	Bad	1.28	0.05	0.13	33.0	46.64
Cl ⁻	Bad	0.88	267	267	66.5	11.07
NO ₃ ⁻	Bad	2.44	206	419	35.8	18.18
SO ₄ ²⁻	Bad	8.12	453	1329	2.27	3.95
Na ⁺	Bad	0.78	324	324	83.0	5.53
NH ₄ ⁺	Bad	0.89	356	532	41.5	13.44
K ⁺	Bad	0.82	17.28	17.28	52.8	32.81
Mg ²⁺	Bad	0.99	32.84	32.84	65.9	22.92
Ca ²⁺	Bad	0.89	431	868	38.1	10.28
PM _{2.5-10}	Weak	1.49	7828	15751	5.11	0.40

BDL: below detection limit

The concentration and percent variation of each species in Factor 1 is given in Figure 3.103. This factor includes both natural and anthropogenic constituents like, Na, Mg, Al, Cr, Ti, Mo, Eu greater than 30 % and Ni and Cu greater than 20%. High concentration of sodium and magnesium indicated the presence of sea salt effect. However, beside these parameters metal constituents were also included. Then, the anthropogenic contribution to the transportation of sea salt might be possible for this factor. The maximum source contribution of this factor was in October, as shown in Figure 3.104 and the back trajectories of the highest contribution dates in this month were given in Figure 3.105. On the 1st of October, the origin of air parcel at high altitude (1500 m) was the Atlantic Ocean and it was travelled along the Europe and finally, entered the sampling from NW direction. However, on the 27th of October, the air mass was originated from Iraq (the opposite direction of the first one) and reached the sampling point in SE direction. The running time of the air mass on the second date was shorter than the first one. On the other dates (17/10/2009 and 23/10/2009) the air masses were come from North Africa and travelled along the Mediterranean Sea. The high concentrations of Al and Ti indicated the Saharan dust and the high concentration of Na and Mg indicated the sea salt transportation. Consequently, this factor was the composition of Saharan dust and sea salt and it was called as *long range transportation (LRT)*.

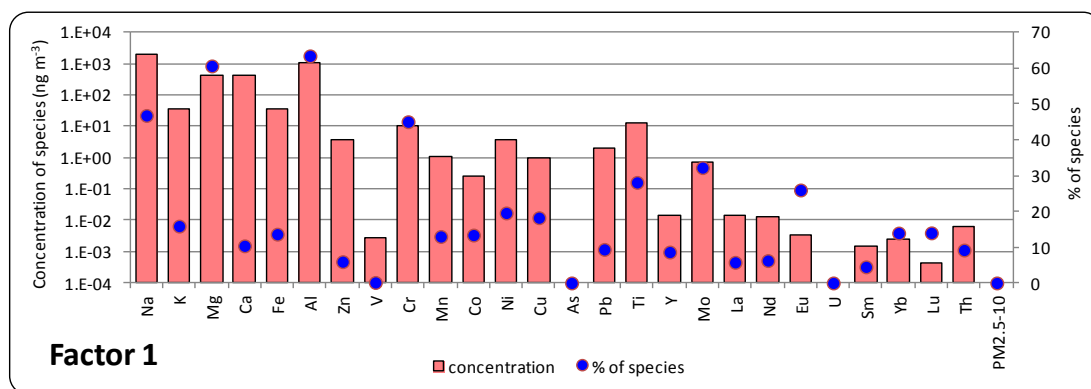


Figure 3.103. The concentration and percentage values of species for PM_{2.5-10} (Factor 1)

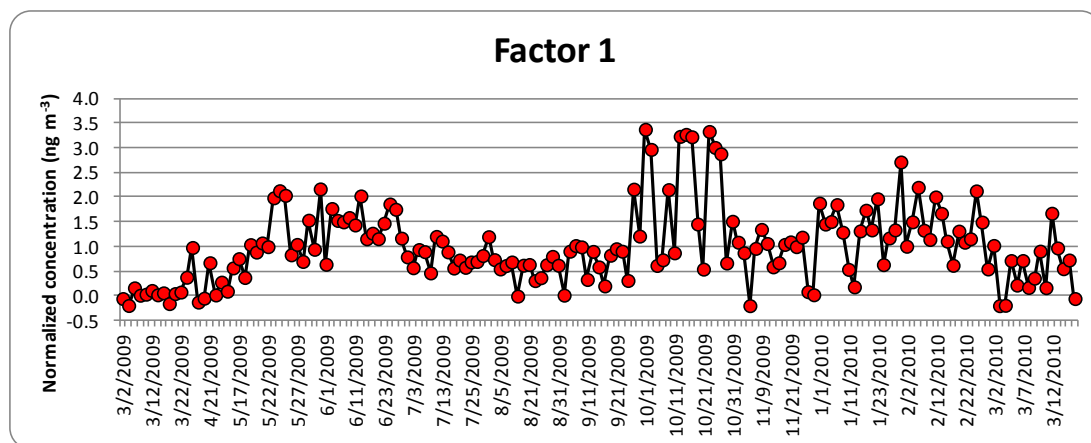


Figure 3.104. The variation of source contributions in Factor 1 for PM_{2.5-10}.

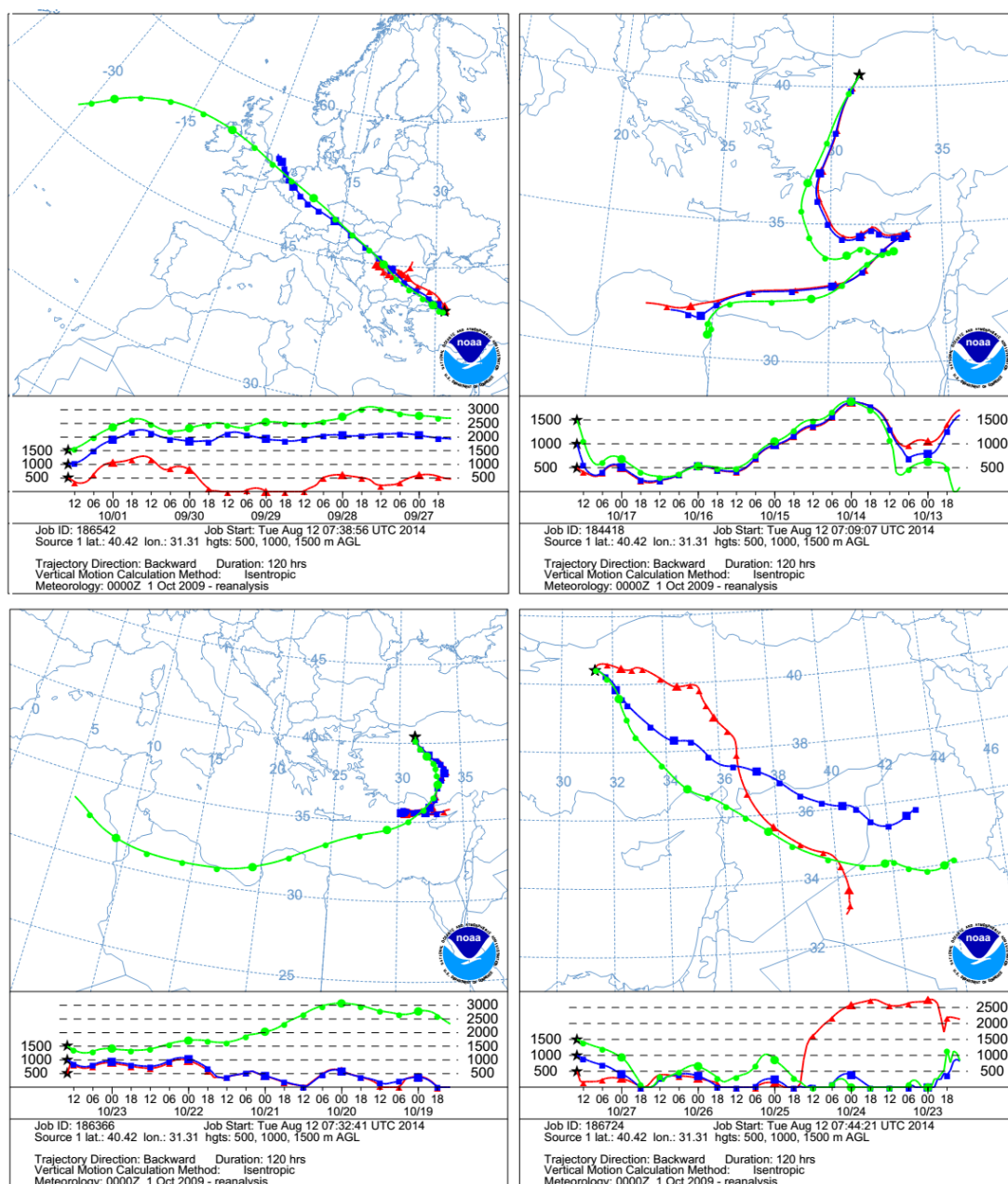


Figure 3.105. The back trajectories of the highest contribution dates for $PM_{2.5-10}$ (Factor 1).

Enrichment factor results are given in Figure 3.106 and it showed that the highly enriched species were Na, Cr, Mo and Pb and the moderately enriched ones were Ca, Co, Al, Cu, Mg, Y, Ni and Zn.

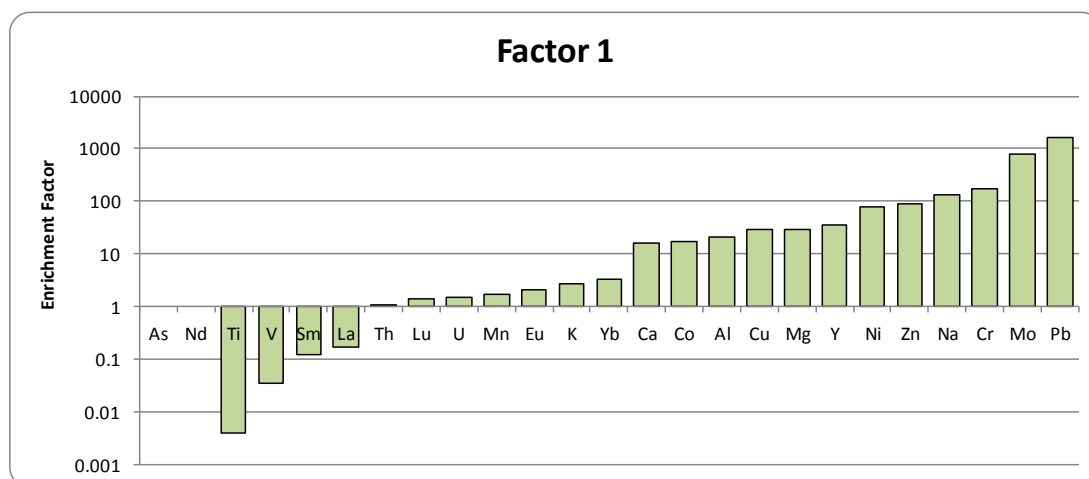


Figure 3.106. The enrichment factor values in Factor 1 for PM_{2.5-10}.

The second factor includes Pb (83 %), Co (80 %), As (27 %) and Eu (25 %) (Figure 3.107) and the source contribution variation of this factor was given in Figure 3.108. Especially, Pb and Co are the indicators of traffic emission and As is the indicator of coal burning. However, there is also a rare earth element, Eu, in this factor. The enrichment factor results in Figure 3.109 showed that crustal elements were included in this factor but Ti was enriched besides Pb, As, Co and Zn. Then, there was a contribution of traffic emission to the soil. This factor can be named as *road dust*.

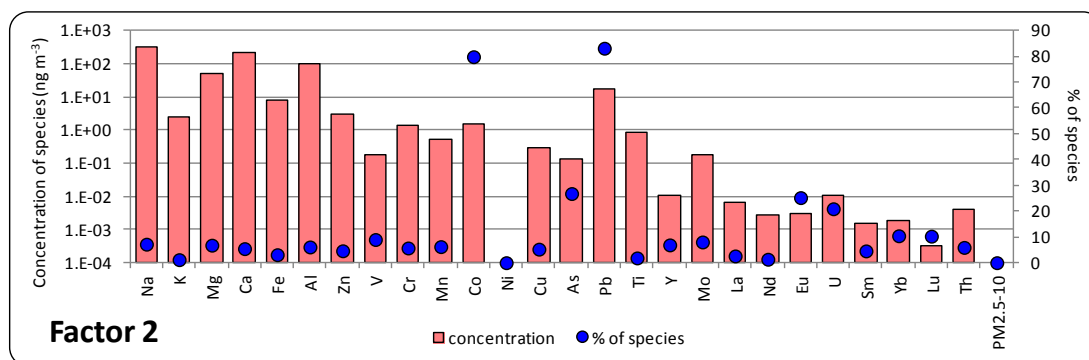


Figure 3.107. The concentration and percentage values of species in Factor 2 for PM_{2.5-10}.

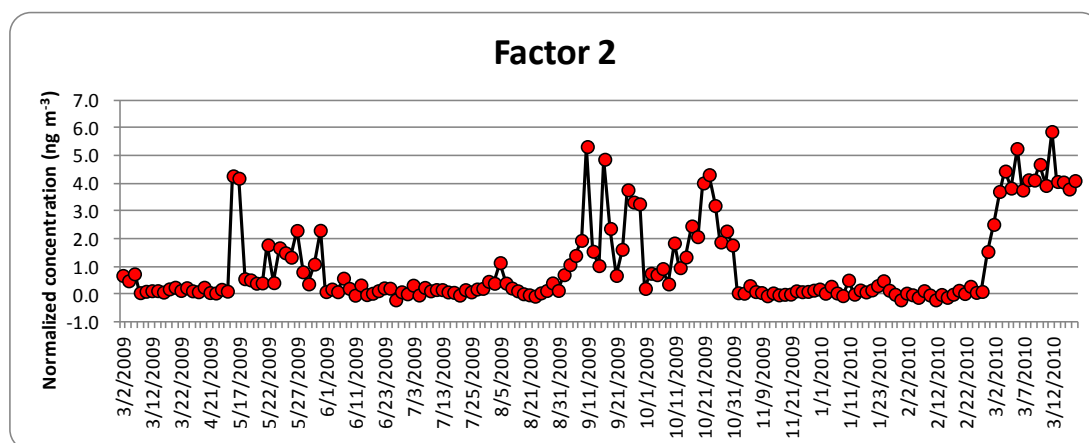


Figure 3.108. The variation of source contributions in Factor 2 for PM_{2.5-10}.

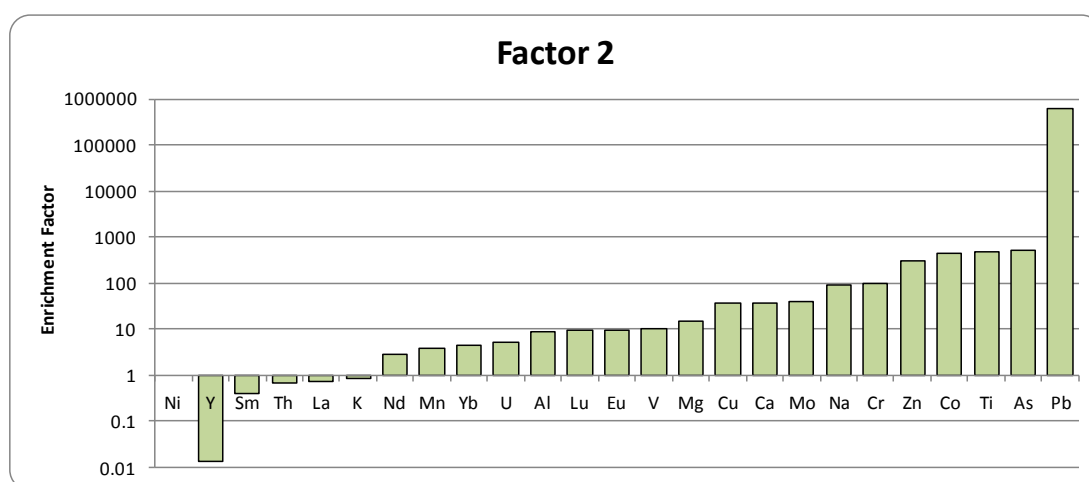


Figure 3.109. The enrichment factor values in Factor 2 for PM_{2.5-10}.

Figure 3.110 shows the composition of elements in Factor 3 as Mo (50 %), U (47 %), As (46 %), Cr (36 %), Ni (34 %) and Na (24 %). Most of these elements are the products of combustion processes. The times series of this factor in Figure 3.111 indicated that the possible source in this factor was continuous and negligible fluctuations were observed throughout the sampling period. Copper and U were moderately enriched and Zn, Na, Ni, Cr, As and Mo were highly enriched species

(Figure 3.112). High enrichment factors of As and Mo indicated that the possible source in this factor was *coal combustion*.

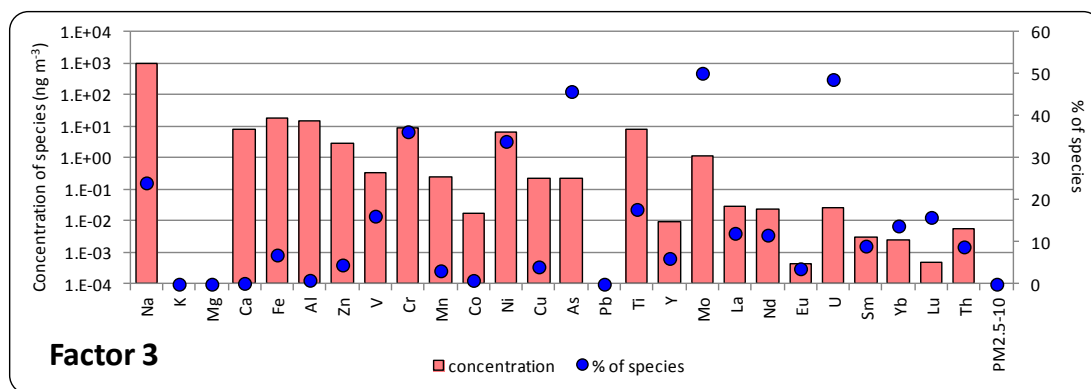


Figure 3.110. The concentration and percentage values of species in Factor 3 for PM_{2.5-10}.

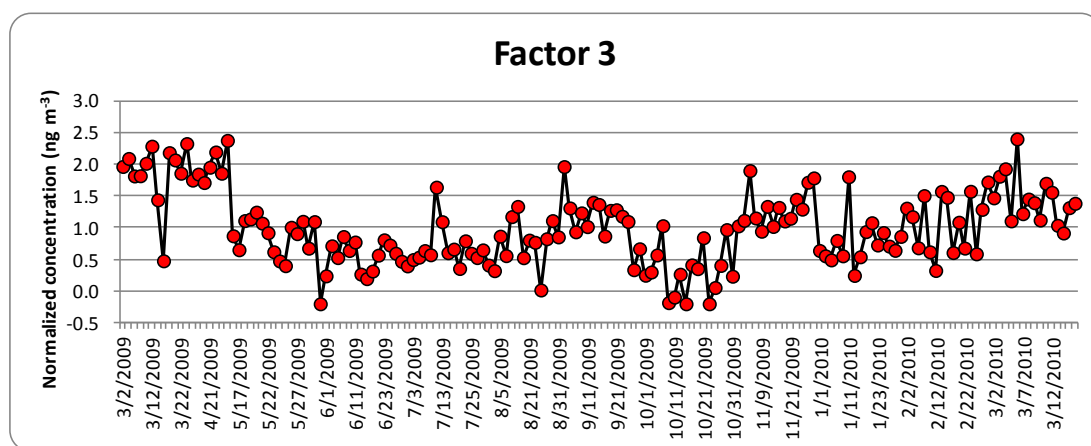


Figure 3.111. The variation of source contributions in Factor 3 for PM_{2.5-10}.

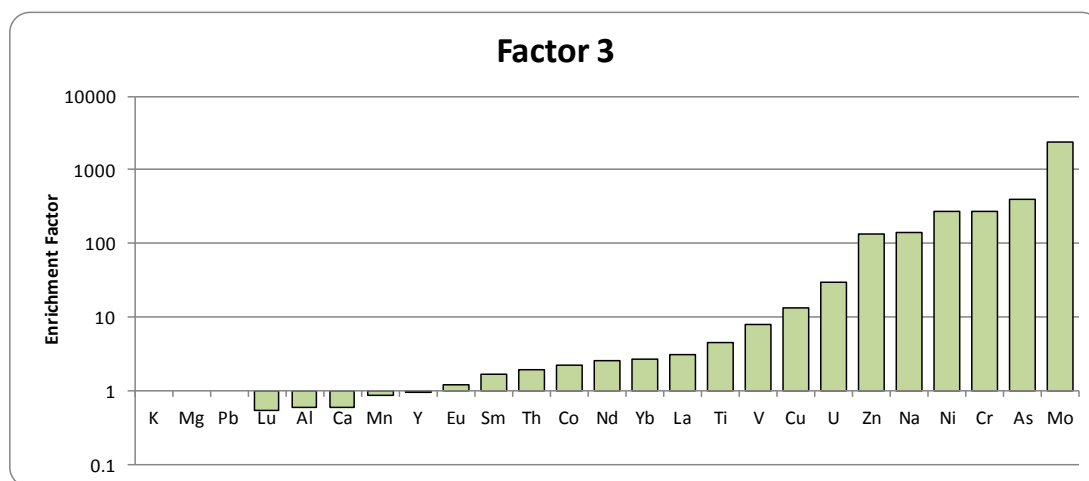


Figure 3.112. The enrichment factor values in Factor 3 for PM_{2.5-10}.

The constituents of Factor 4 were K, Mg, Ca, Zn, Mn, Ni, Cu and U with percent contribution above 20 % (Figure 3.113). Throughout the whole sampling period only two peaks were observed in 2 days (31/05/2009 and 11/10/2009) (Figure 3.114). the back-trajectories of these dates were given in Figure 3.115. On the 31st of May, the air mass at 1500 m came from the east and at 500 m and 1000 m altitudes, the air parcel originated from Russia and reached the sampling zone from north direction. In the other episode, on the 11th of October, at all altitudes the air mass came from the north-East (NE) direction and entered to the sampling point in south direction. The air parcel originated from north and north-east direction generally carries metal contents from Karabük and Ereğli. In this factor enriched species were Ni, Pb, Mo, Zn, Cr, Na, Cu and Ca (Figure 3.116). Then, this factor may be called as *metal works* due to the metal contents.

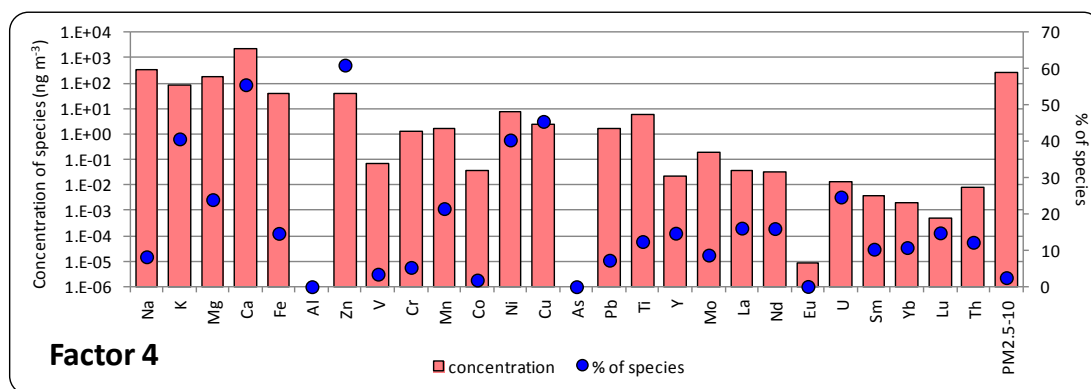


Figure 3.113. The concentration and percentage values of species in Factor 4 for PM_{2.5-10}.

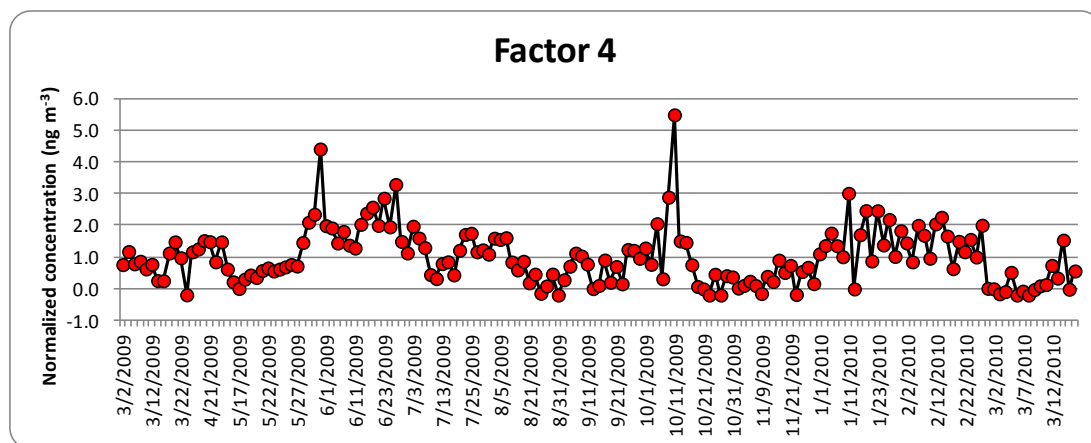


Figure 3.114. The variation of source contributions in Factor 4 for PM_{2.5-10}.

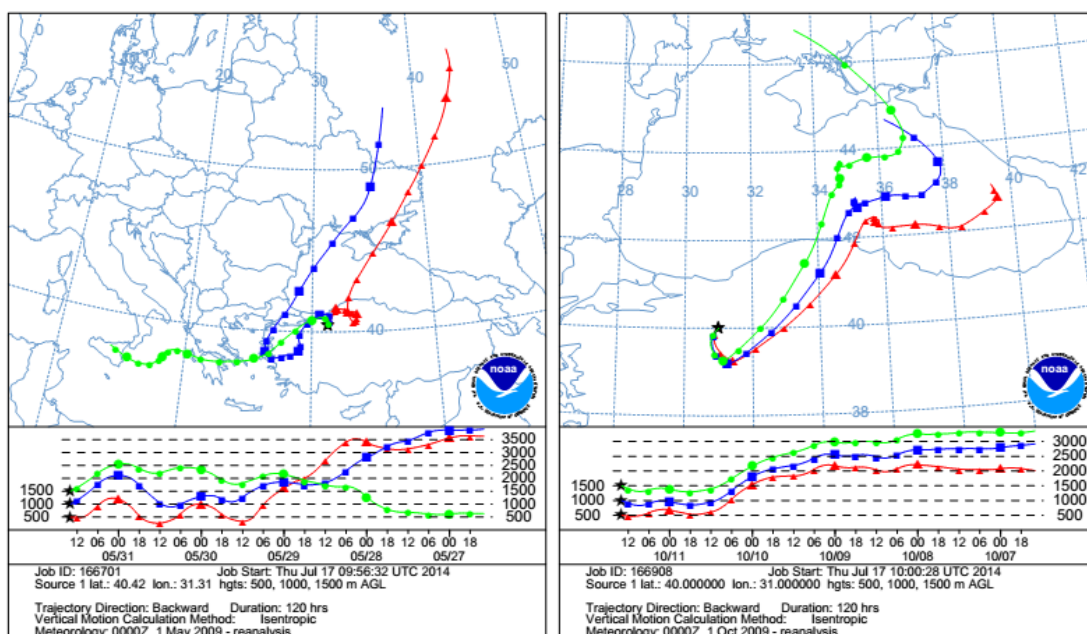


Figure 3.115. The trajectory of the highest contribution dates for PM_{2.5-10} (Factor 4).

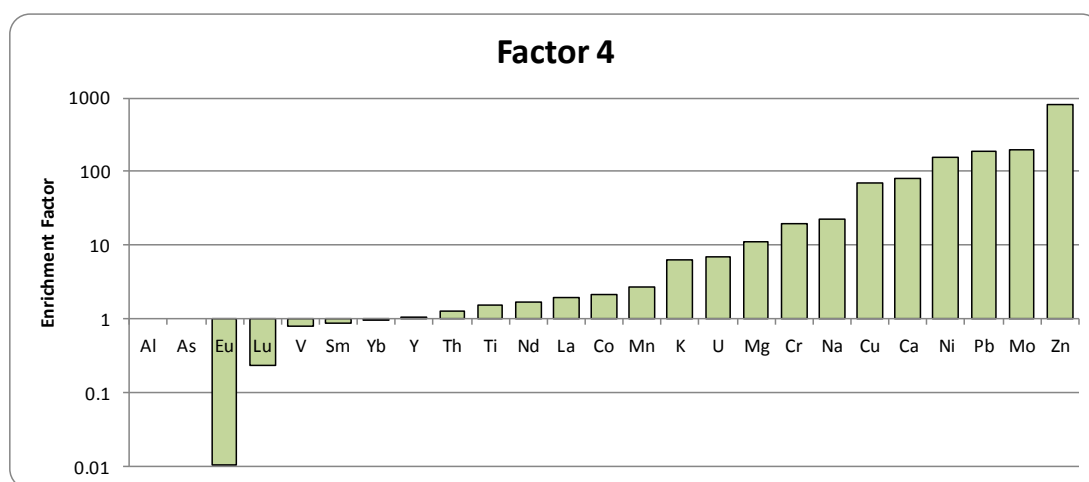


Figure 3.116. The enrichment factor values in Factor 4 for PM_{2.5-10}.

The fifth factor was composed of soil derived elements like, Fe, Mn, Ti, Y, La, Nd, Eu, Sm, Yb, Lu, Th and PM_{2.5-10} and the concentration and percentage of each species are given in Figure 3.117. The time series of the factor contribution is given in Figure 3.118. There were four days with high source contributions (06/03/2009, 14/02/2010, 20/02/2010 and 08/03/2010). The back-trajectories of these dates are

given in Figure 3.119. In all these dates the air parcel was transported from North Africa. Although the local soil contains the concentration of Fe, it was increased in these dates due to the Saharan dust. The comparison between Fe concentration and source contribution throughout the sampling period was given in Figure 3.120. General trend was similar between these two parameters however, in summer months there was an increase in Fe concentration (highlighted with a circle) in addition to the Saharan dust events. That means the high concentration of Fe was due to both Saharan dust and local soil.

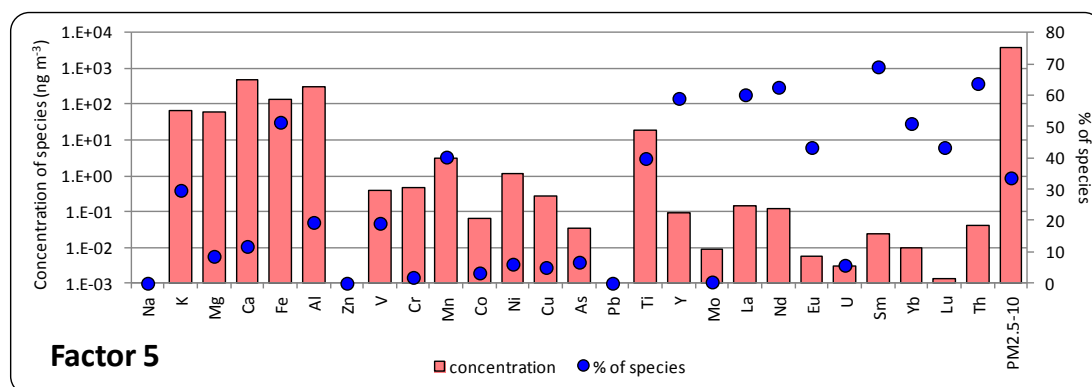


Figure 3.117. The concentration and percentage values of species for PM_{2.5-10} (Factor 5).

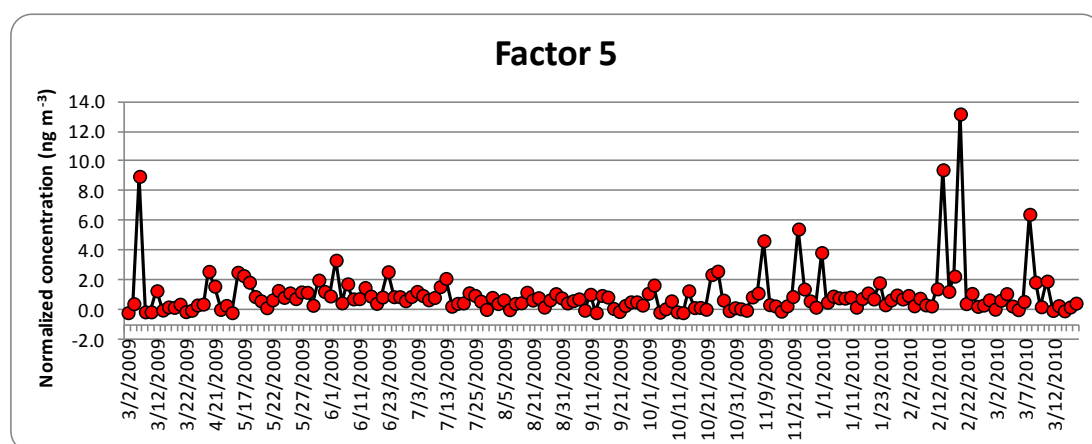


Figure 3.118. The variation of source contributions in Factor 5 for PM_{2.5-10}.

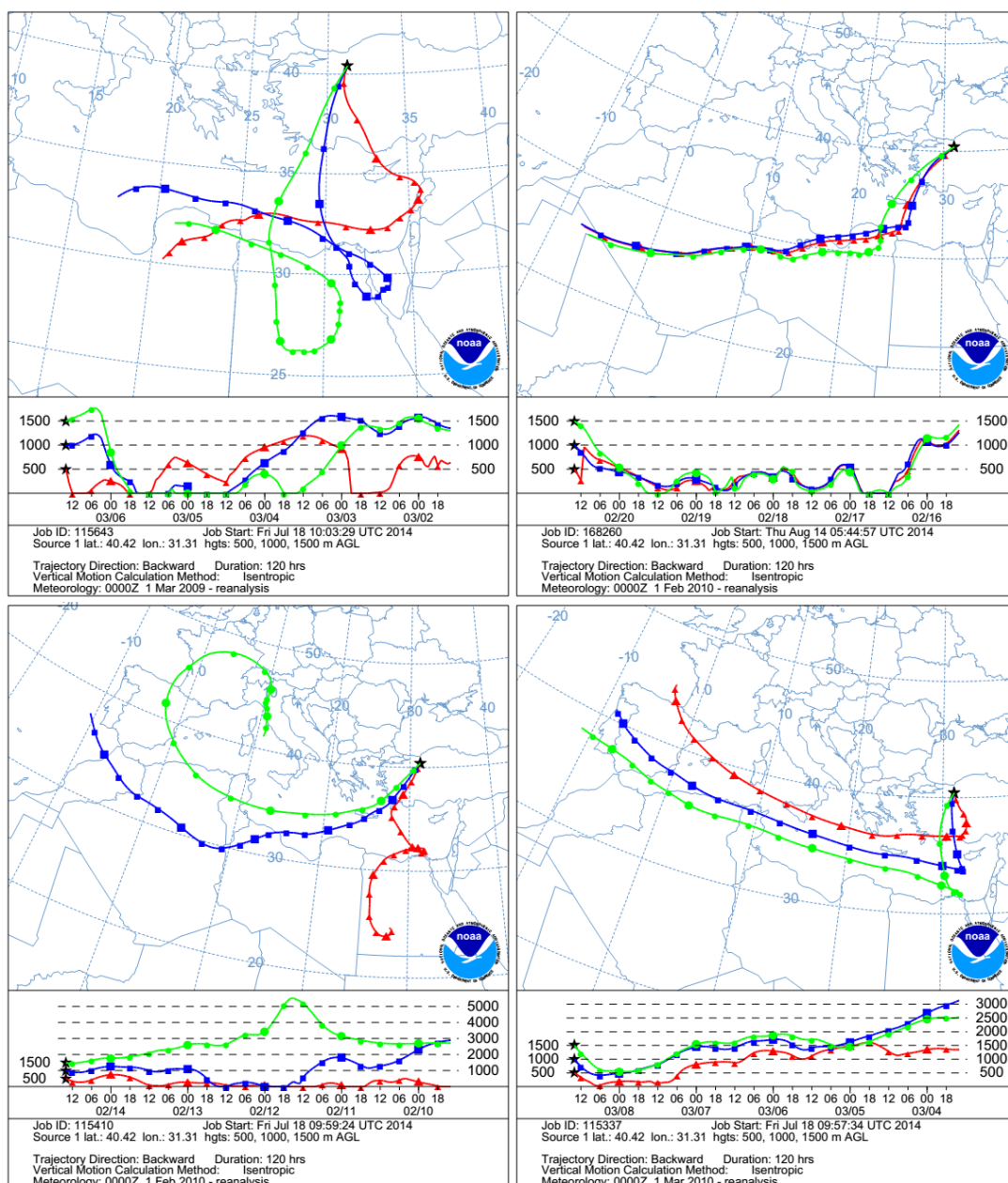


Figure 3.119. The trajectory of the highest contribution dates for PM_{2.5-10} (Factor 5)

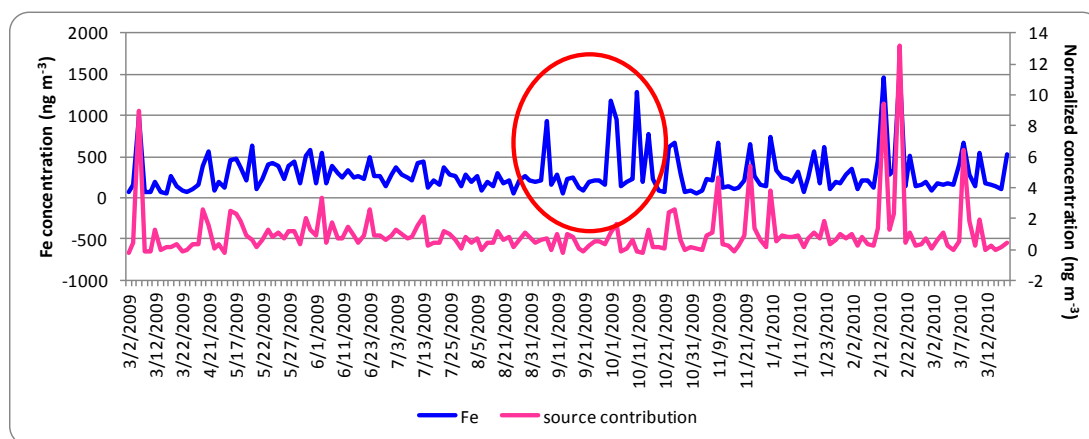


Figure 3.120. The comparison of Fe concentrations and source contributions in PM_{2.5-10} (Factor 5)

Finally, enrichment factor results in Figure 3.121 mentioned that none of the species were enriched in this factor. Then, this factor was called as *crustal*.

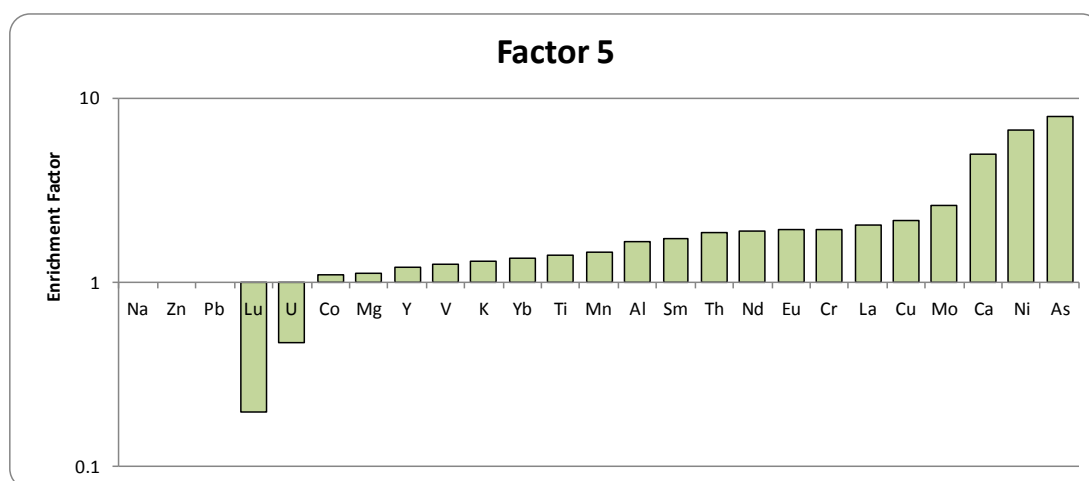


Figure 3.121. The enrichment factor values in Factor 5 for PM_{2.5-10}.

The only constituents with high percentage were V and PM_{2.5-10} in Factor 6 (Figure 3.122). Despite the high concentrations of Na, Ca, Fe, Al, Zn, Cr, Mn and Cu, their percent contributions to this factor were very low. The high concentration and high percent value of PM_{2.5-10} showed that this factor mainly related with soil. The time series of this factor in Figure 3.123 showed that there was a constant emission from the possible source. Moreover, most of the anthropogenic elements were enriched in this factor as seen in Figure 3.124. These elements are, Mo, V, Cr, Co, Cu, Na, As and Zn. Especially, V, As and Mn are the combustion products. The presence of high percentage of V gave an impression of pollution in soil. Then the source of this factor might be the *surface soil* due to the contribution of pollution derived elements.

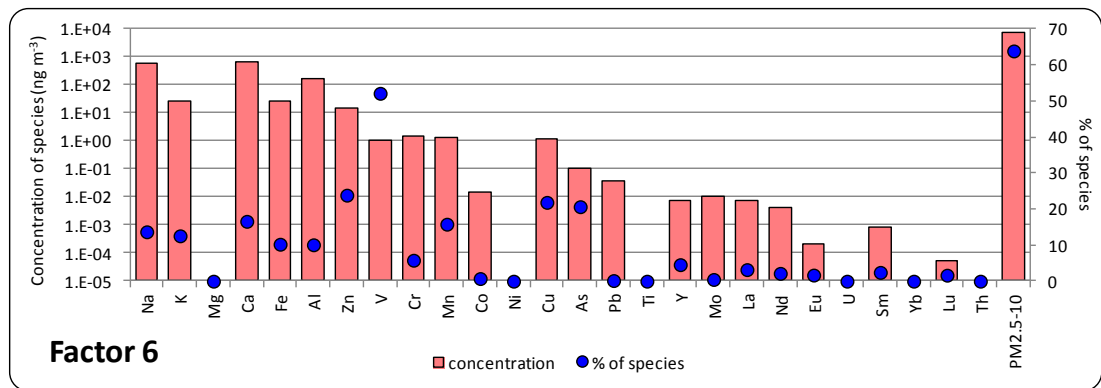


Figure 3.122. The concentration and percentage values of species for PM_{2.5-10} (Factor 6).

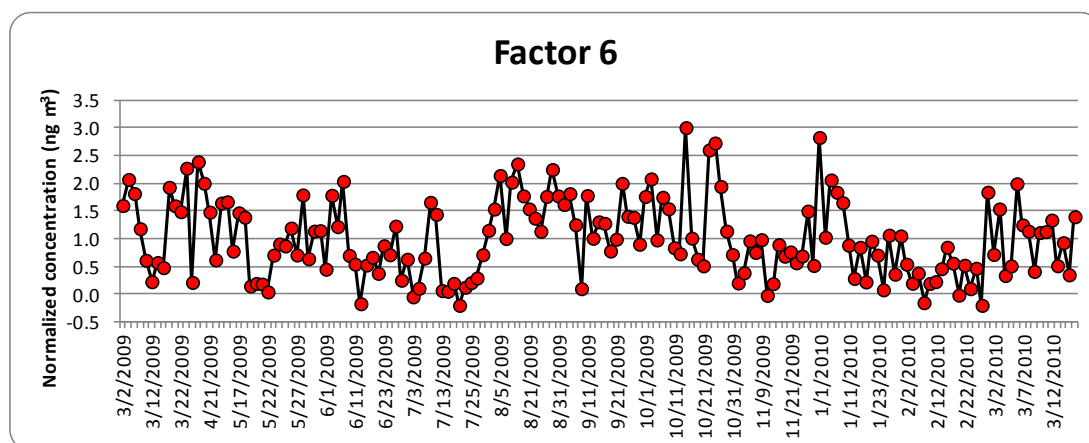


Figure 3.123. The variation of source contributions in Factor 6 for PM_{2.5-10}.

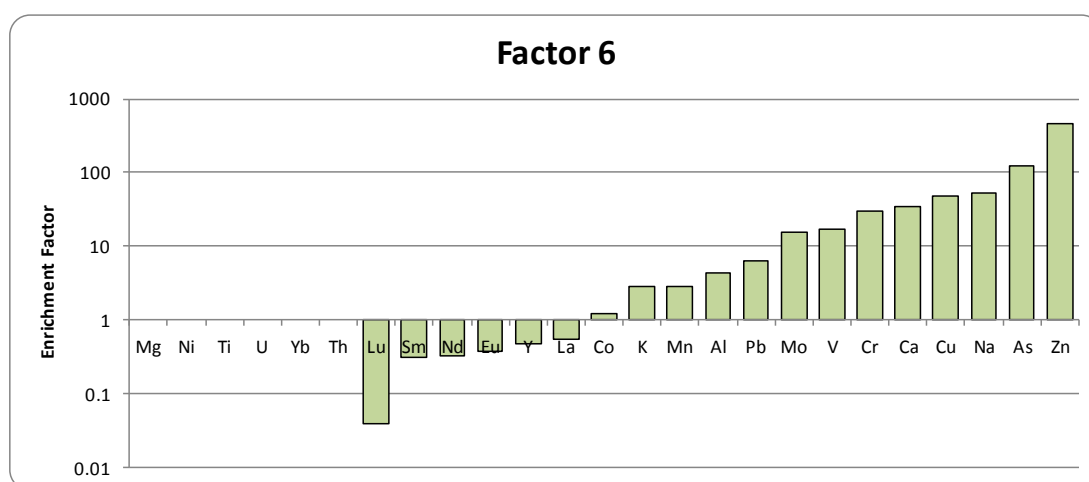


Figure 3.124. The enrichment factor values in Factor 6 for PM_{2.5-10}.

Figure 3.125 summarizes the percent contribution of each factor to each species in coarse mode particulate matter. High percentage of Factor 1 was seen in Na, Mg, Al, Ti, Cr and Mo which were originated from natural and anthropogenic sources. Na and Mg are the indicators of sea salt, Ti and Al are crustal (Saharan dust) and the rest of them are anthropogenic species. The back-trajectories of the highest source contribution dates showed that the air parcels were originated from Atlantic Ocean, Iraq and North Africa. This factor was named as *long range transportation (LRT)*.

The effects of Factor 2 was seen mostly in Co, As, Pb, Eu and U. Except for As, Eu and U, the other species were originated from traffic emission. However, the presence of crustal elements identifies this factor as *road dust*. The high percent contribution of Factor 3 was seen in Cr, Ni, As, Mo and U. Especially, As was the identifier of coal combustion. Then this factor was called as *coal combustion*. Potassium, Ca, Zn, Ni and Cu had high contributions to Factor 4 which was named as *metal works*. Rare earth elements, Fe, Mn and PM_{2.5-10} were mostly seen with the contributions of Saharan dust in Factor 5 which was called as *crustal*. Finally, Factor 6 included V and PM_{2.5-10} with high percent values. This factor was identified as *surface soil*.

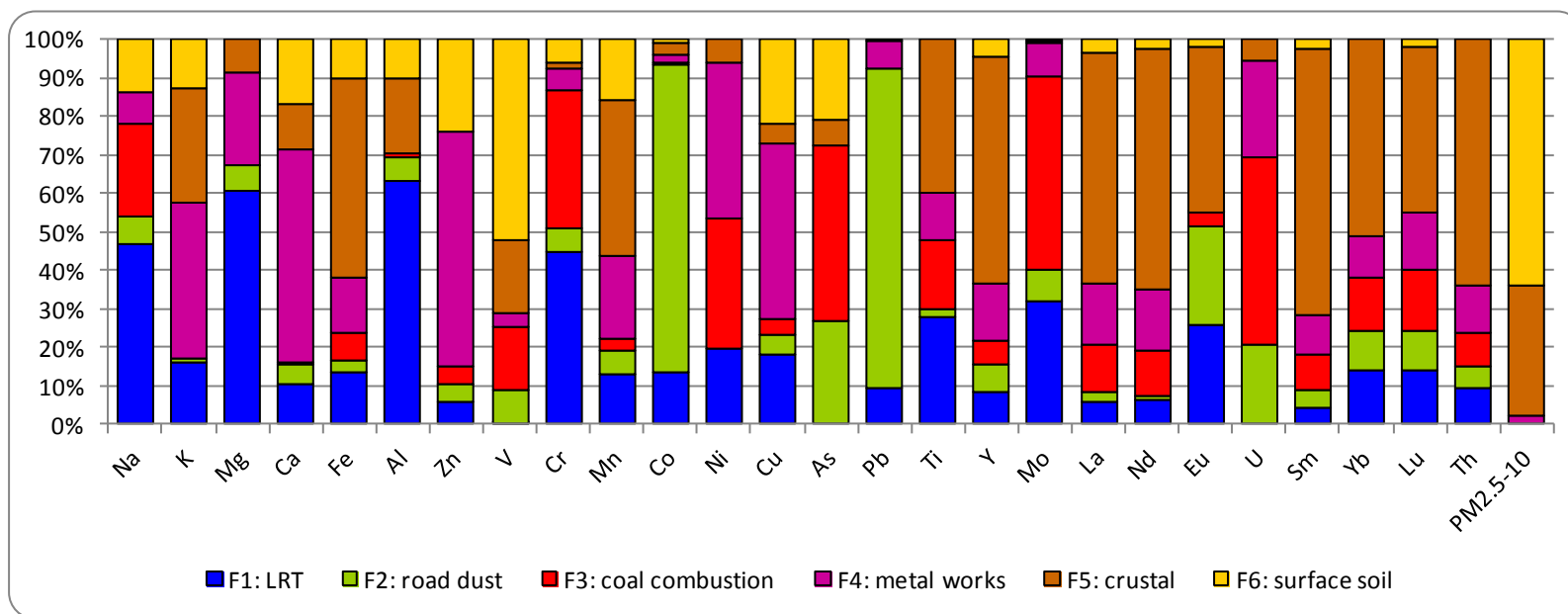


Figure 3.125. The percent contribution of each factor to each parameter in coarse mode.

CHAPTER 4

4. CONCLUSION

Fine and coarse mode particulate matters were collected during one year sampling period and ozone and meteorological parameters were monitored during three-years sampling in a station placed on the roof of the presidency building in the campus of Abant Izzet Baysal University. In filter samples 38 elements were determined by Perkin Elmer Elan DRC-e model ICP-MS, 8 ions were determined by in Dionex ICS 1100 Ion Chromatography system, organic and elemental carbons were determined Sunset OC/EC Analyzer. Finally, O₃ concentrations were continuously measured by Thermo 49i UV photometric O₃ analyzer.

The obtained data set from particulate matters were used to interpret the temporal variation of the compositions and to find the possible sources of the pollutants. Moreover, the temporal variation of O₃ concentration, the effects of local meteorology on O₃ and the possible effects of O₃ on crops and forest during growing season (April to September) were discussed in this study.

Daily O₃ concentration was differentiated as daytime (06:00-19:00) and night time (19:00-06:00) in order to understand the reaction mechanism of photochemical production. Diurnal, daytime and night time average concentration of O₃ were 24.9 ppb, 30.0 ppb and 17.5 ppb, respectively.

The average and the maximum O₃ concentrations were compared with literature values. The study conducted by Paoletti et al. (2006) in Italy in two different sites (suburban and rural), the study in the suburban site of Cuba (Alejo et al., 2011) and the study in the urban site of Bursa (Esen et al. 2005) had the similar average concentration values with our study.

The behavior of O₃ variation at each hour of the day should be analyzed due to the influence of solar radiation on O₃ production. When the solar radiation and the temperature increase, O₃ concentration begins to increase and reach its maximum at noon hours. The daily highest average O₃ (38 ppb) and temperature (14 °C) was observed from 13:00-15:00. This increase in O₃ level during the daylight is attributed to the combined effects of photochemical process. At the beginning of the sunset (at 16:00), the descent of O₃ concentration begins and the lower night-time O₃ is the result of destruction by the reaction with O₃ and NO.

The influences of meteorological parameters on O₃ were determined for a better understanding of local and regional sources of O₃ pollution. For statistical treatments the hourly daytime (06:00-19:00) O₃ concentration in the growing season (April-September) was used as an input. The correlation coefficients of ozone and the temperature, the wind speed and the solar radiation were around 0.48 to 0.54 and the correlation coefficients of ozone with relative humidity and wind direction were -0.602 and -0.07, relatively.

Three factors that has eigen values greater than 1 and explained the 64.4 % of the total variance were determined in factor analysis. The first factor explained 28.6 % of the total variance and the hourly ozone concentration, the temperature, the wind speed, the wind direction and the relative humidity are the components in this factor.

The second factor included the wind speed and the wind direction that explained 20.2 % of the total variance. Finally, the rain is the unique component of the third factor which explained the 15.6 % of the total variance.

During the sampling period (549 days, 13176 hours) the percent exceeding of AOT₄₀ values was 26.0 % which means the critical value was exceeded for 3421 hours. AOT₄₀ was calculated in daytime hours from May to July for O₃ exposure on vegetation and for forests it was calculated from April to September. The critical AOT₄₀ level for crops and forests are 3000 ppbh and 10000 ppbh, respectively. Especially in 2009 and 2010 the critical level exceeded for both the agricultural crops and the forests. The cumulative exposure for forests were 12997 ppbh and 14074 ppbh and for crops 5804 ppbh and 7145 ppbh, respectively.

Moreover, through the whole sampling period in 7 days in 2009 (three days in July and four days in August) the threshold level for population information ($180 \mu\text{g m}^{-3}$ in 1-h) was exceeded.

According to the statistical treatments the concentration of particulate matters were ranged from $0.011 \pm 0.016 \text{ ng m}^{-3}$ for Eu to $7.0 \pm 4.6 \mu\text{g m}^{-3}$ for OC in PM_{2.5} and this concentration range in PM_{2.5-10} from $0.0090 \pm 0.024 \text{ ng m}^{-3}$ for Lu to $4.4 \pm 1.9 \mu\text{g m}^{-3}$ for Na. In PM_{2.5}, all parameters except for Na, Mg, Fe, Al, Zn, V, Mn, Sn, Sb, Cs, Lu, NH₄⁺, K⁺ and Mg²⁺ showed log-normal distribution and in PM_{2.5-10} except for Mg, Al, Zn, Sn, Cs, NH₄⁺, Mg²⁺ and Ca²⁺ showed log-normal distribution.

The average concentration values for aerosol samples in this study were compared with other studies in literature conducted in both semi-rural and other types of sites. Comparison with different sites allowed us to observe the site variation in aerosol

composition. Twenty seven elements (Na, K, Mg, Ca, Fe, Al, Zn, V, Cr, Mn, Co, Ni, Cu, As, Cd, Pb, Ti, Se, Y, Mo, Sb, Cs, La, Nd, Eu, Tl and Sm) in both fine and coarse fractions, 8 ions (Cl^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}) and OC and EC in TSP, $\text{PM}_{2.5}$ and PM_{10} were used for the comparison. The concentration of crustal and rare earth elements in most of studies were nearly same. However, according to the closeness of the sampling point to pollution sources, the concentration of anthropogenic elements were varied.

Sodium, Al, V, Zn, Se, Sn, Cs, Sb, Bi, Li^+ , K^+ , NH_4^+ , NO_3^- and SO_4^{2-} showed little or no variation in fine fraction throughout the whole sampling period. Emission sources for these elements might be stationary and also near the sampling point. In summer period especially, K, Mo, Ca, Ca^{2+} , Mg^{2+} , Na^+ and Cl^- and rare earth metals had high concentrations and in winter period Ni, Mn, Cr had high concentrations. In coarse fraction Na, Na^+ , Mg, Mg^{2+} , Al, Zn, Sn, NO_2^- , NO_3^- , Li^+ , Ca^{2+} and except few days Pb and Se concentrations were nearly the same during the whole sampling period. At the beginning of growing season (April to June) K, Fe, V, Mn, As, P, Mo and some rare earth metals (Sc, Tl, Y, U, Nd, La, Sm, Th and Yb) had high concentrations.

Except for June, the concentration of $\text{PM}_{2.5}$ was always greater than $\text{PM}_{2.5-10}$. The reason can be the scavenging of fine mode particulates in this month due to wet deposition.

Organic and elemental carbon were determined only in $\text{PM}_{2.5}$ in this study. Total carbon composed of 30 % of fine mode aerosol samples. There was an obvious increase in the concentrations of both OC and EC during the heating season. A good correlation was observed between OC and EC ($R^2=0.803$) which indicates the presence of common source for both fraction like coal combustion and traffic.

To interpret the emission sources for carbonaceous species, OC/EC ratio is commonly used. In this study the range of OC/EC ratio was from 1.4 to 4.1 and the average ratio was found as 2.7. According to the literature values traffic emission and domestic heating may be the possible sources for OC and EC.

Moreover, OC was differentiated as secondary and primary in order to determine the possible emission sources more accurately. Throughout the growing season (April to September) the percent distribution of primary organic carbon (OC_{pri}) was greater than 50%. Main source for OC_{pri} is the biomass burning then, the high concentration of OC_{pri} in this season was expected. In cold season (October to March) the concentrations of OC_{sec} were greater than OC_{pri} and the annual average concentration was $1.8 \mu\text{g m}^{-3}$. Due to the presence of forest and agricultural areas around the sampling point the biogenic emissions by terrestrial vegetation as biogenic volatile organic compounds (BVOCs) were obtained throughout the year. However, in summer months when the photochemical activities are greater there is a much consumption of BVOCs and OC_{sec} . Then there is a negative correlation between O_3 and OC_{sec} .

In order to identify qualitatively and estimate quantitatively the possible pollution sources receptor models are used. The relations between the pollutants were determined by statistical treatments (binary correlation and multiple linear regression (MLR)) and the source apportionments were determined by crustal enrichment factor (EF), wind sector analysis, factor analysis (FA) and positive matrix factorization (PMF).

According to the crustal enrichment factors Sm, Fe, Y, Nd, Th, La, Eu, Yb, Mn, Ti, Lu, K, Cs, Al and V in $PM_{2.5}$ were identified as crustal and in $PM_{2.5-10}$ besides these

elements Mg and U were qualified as crustal elements. In both fractions Sb, Cd and Hg had the highest enrichment factors (>1000).

The average concentrations of pollutants in each wind direction were used for wind sector analysis. Throughout the sampling period the prolonged wind directions was WSW (77.3 %). In $PM_{2.5}$, Mg, V, Cr, Co, Ni, Cu, As, Sc, Ti, Se, Y, Mo, Sb, Eu, Tl, Yb, Hf, Bi, NO_3^- , SO_4^{2-} were mostly seen in E-ESE-NE directions (industrial zone). Potassium, As, Zn, Mn, Pb, Cs, La, Nd, Sm, Th, Na^+ and Cl^- were seen in S-SSE-SE-ESE directions (agricultural and industrial). Sodium, W and Ca^{2+} were seen in W direction (residential areas) and finally, Ca, Cd, P, U, Lu, Hg, NH_4^+ , K^+ , Mg^{2+} , OC, EC and TC were generally obtained in WSW-SW directions (agricultural and forest zone). Aluminum and Fe were equally distributed in these four wind sectors.

In coarse fraction Cd, W and Bi were obtained in the direction of WSW and W. Lead, Se and Sb came from W direction. Mostly crustal elements were transported in the direction of agricultural areas (ESE-S). Moreover, in NE-E direction where anthropogenic elements like Ni, As, P, Mo, Hg and some crustal elements like Ti, Tl, Yb, Lu and Hf were obtained.

For fine fraction six factors accounted for 79.07% of the total variance were identified in factor analysis. The possible sources for each factor were contaminated soil, combustion due to diesel/gasoline vehicles and coal, metal works, traffic and road dust, industrial emission and finally secondary compounds from long range transportation (LRT).

Like in $PM_{2.5}$, six factors were identified in coarse fraction which explained the 67% of the total variance. Crustal, LRT, oil and coal combustion, metal works, road dust and finally paved road dust.

The same data set in factor analysis were used in PMF. Six possible sources were identified for $PM_{2.5}$ and $PM_{2.5-10}$. Secondary compounds and combustion, traffic, soil, regional background, metal works and sea salt and finally, industrial emission were found as the sources in $PM_{2.5}$. For $PM_{2.5-10}$, LRT, road dust, coal combustion, metal works, crustal and surface soil were identified as the possible sources.

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