



**DETERMINATION OF CHEMICAL COMPOSITION IN PM<sub>2.5</sub>  
SAMPLES COLLECTED IN URBAN AND SEMI-URBAN  
TWO STATIONS IN ANKARA**

**ANKARA'DA KENTSEL VE YARI-KENTSEL İKİ  
İSTASYONDA TOPLANAN PM<sub>2.5</sub> ÖRNEKLERİNİN  
KİMYASAL KOMPOZİSYONUNUN BELİRLENMESİ**

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*To my dear family,*

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PARISA FARAMARZI

## ÖZET

### **Ankara’da Kentsel ve Yarı-Kentsel İki İstasyonda Toplanan PM<sub>2.5</sub> Örneklerinin Kimyasal Kompozisyonunun Belirlenmesi**

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Son yıllarda yapılan çalışmalar hava kirliliğine bağlı olarak gerçekleşen ölümlerin azımsanmayacak kadar çok olduğunu göstermektedir. Durum bu kadar ciddi olmasına rağmen nüfusu yaklaşık olarak 5.5 milyon olan Ankara’da Çevre ve Şehircilik Bakanlığı tarafından işletilen hava kalitesi izleme istasyonlarında Partikül Madde (PM) için kütlece konsantrasyonlar belirlenmekte ancak PM’nin kimyasal kompozisyonunu ortaya koyacak çalışmalar birkaç araştırma grubu dışında yapılmamaktadır. Önerilen bu çalışmada analiz edilecek PM örnekleri Hacettepe Üniversitesi, Beytepe Kampüsü, B Nizamiye ve Türkiye Halk Sağlığı Kurumu bahçesi, Sıhhiye’de konuşlandırılan iki istasyonda günlük olarak kuvars filtreler üzerinde toplanmıştır. Toplanan örnekler 1.5 cm<sup>2</sup> büyüklüğünde parçalar alınacak ve alınan parçalar elementel karbon (EC), organik karbon (OC) ve toplam karbon (TC) içeriklerinin belirlenmesi amacıyla Sunset Lab (USA, Oregon) tarafından geliştirilen termal optik karbon analizörü kullanılarak analiz edilmiştir. Elde edilen veri seti istatistiksel olarak değerlendirilen ve analiz edilen

parametreler literatürde benzer çalışmalarda elde edilen değerlerle kıyaslanarak kentin hava kalitesi hakkında temel düzeyde bilgi edilmiştir. Örneklerde belirlenen EC ve OC değerleri kullanılarak primer ve sekonder organik karbon (sırasıyla POC ve SOC) değerleri de hesaplanmıştır. Bu çalışmanın bulguları, yaz ve kış aylarında, özellikle şehir merkezinde, PM<sub>2.5</sub> ve karbonlu kirliliğinin ciddi olduğunu gösterdi. PM<sub>2.5</sub> konsantrasyonları, kış ve yaz aylarında her iki noktada, DSÖ, AB ve EPA standart sınırlarının üzerindedir. Kentsel alanda PM<sub>2.5</sub> konsantrasyonlarında yaz-kış arası istatistiksel olarak önemli bir fark bulunmamaktadır. Bu, trafiğin egemen kirlenici kaynak olduğunu ve mevsime bağlı bir faktör olmadığını gösterir. Örnekleme dönemi boyunca OC, PM<sub>2.5</sub> kütlesine en fazla katkıda bulunan parametredir. OC konsantrasyonu kışın yaklaşık iki kat daha fazladır. EC ve OC konsantrasyonları hem kentsel alanda daha yüksek hem de bu alanın daha yoğun trafik ve emisyonların etkisi altında olduğunu göstermektedir. Organik karbon çoğunlukla birincil kaynaklardan şehrin atmosferine salınmaktadır.

Anahtar kelimeler: Ankara, PM, EC, OC, TC, POC, SOC

## **ABSTRACT**

# **DETERMINATION OF CHEMICAL COMPOSITION IN PM<sub>2.5</sub> SAMPLES COLLECTED IN URBAN AND SEMI-URBAN TWO STATIONS IN ANKARA**

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Studies carried out in recent years have shown considerable number of deaths due to air pollution. In spite of this serious situation, studies on chemical composition of particulate matter are conducted only by a few research groups at air quality monitoring stations operated by the Ministry of Environment and Urbanization in Ankara with about 4.6 million residents. PM samples recommended to be studied in this research are collected daily at Gate B, Beytepe campus of Hacettepe University and garden of General Directorate of Public Health of Turkey located in Sıhhiye on quartz filters. The collected filter samples are cut into 1.5 cm<sup>2</sup> pieces and these pieces will be analyzed in order to determine the contents of organic carbon (OC), elemental carbon (EC) and total carbon (TC) by thermal optic carbon analyzer developed by Sunset Lab (USA, Oregon). Obtained dataset were statistically evaluated and the analyzed parameters have been compared with similar previous studies in order to be able to provide basic information about urban air quality. The primary and secondary organic carbon (POC and SOC,

respectively) were calculated using the EC and OC values. The results of this study revealed that PM<sub>2.5</sub> and carbonaceous species pollution were serious during summer and winter especially at city center. PM<sub>2.5</sub> mean concentrations at both locations in winter and summer are above the WHO, EU and EPA standard limits. There is not a big statistically difference between PM<sub>2.5</sub> concentration at urban site between summer and winter. This shows that traffic is the dominant pollutant source and is not a season dependent factor. During the sampling period, OC was the parameter with the highest contribution to PM<sub>2.5</sub> mass at all the samples. The OC concentration is approximately two times higher in winter. EC and OC concentrations are both higher at urban site indicating that this area is exposed to more intensive traffic and emissions. Organic carbon is emitted mostly from primary sources to the atmosphere of the city.

Keywords: Ankara, PM, EC, OC, TC, POC, SOC

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## SYMBOLS AND ABBRIVIATIONS

### Symbols

M	: Meter
Mm	: Millimeter
$\mu\text{m}$	: Micrometer
$\mu\text{l}$	: Microliter
ppm	: Parts per million
$^{\circ}\text{C}$	: Centigrade degree

### Abbreviations

ANOVA	: Analysis of Variance
AOD	: Aerosol Optical Depth
Ar	: Argon
BC	: Black Carbon
$\text{CaCO}_3$	: Calcium Carbonate
CO	: Carbon Monoxide
$\text{CO}_2$	: Carbon Dioxide
$\text{CO}_3^{2-}$	: Carbonate
$\text{CH}_4$	: Methane
EC	: Elemental Carbon

EU	: European Union
FID	: Flame Ionization Detector
HCl	: Hydrochloric Acid
He	: Helium
H <sub>2</sub>	: Hydrogen
Cr	: Chrome
N	: Nitrogen
NO <sub>2</sub>	: Nitrogen Dioxide
NO <sub>x</sub>	: Nitrogen Oxides
NAAQS	: National Ambient Air Quality Standards
Ne	: Neon
Ni	: Nickel
NIOSH	: National Institute of Occupational Safety and Health
OC	: Organic Carbon
OH	: Hydroxyl
O <sub>2</sub>	: Oxygen
O <sub>3</sub>	: Ozone
PAH	: Polycyclic Aromatic Hydrocarbons
PM	: Particulate Matter
PM <sub>1</sub>	: Particulate Matter with Diameter < 1 μm
PM <sub>10</sub>	: Particulate Matter with Diameter < 10 μm

PM <sub>2.5</sub>	: Particulate Matter with Diameter < 2.5 μm
POC	: Primary Organic Carbon
POM	: Primary Organic Matter
SOC	: Secondary Organic Carbon
SO <sub>2</sub>	: Sulfur Dioxide
TC	: Total Carbon
USA	: United States of America
VOC	: Volatile Organic Carbon
WHO	: World Health Organization
Xe	: Xenon

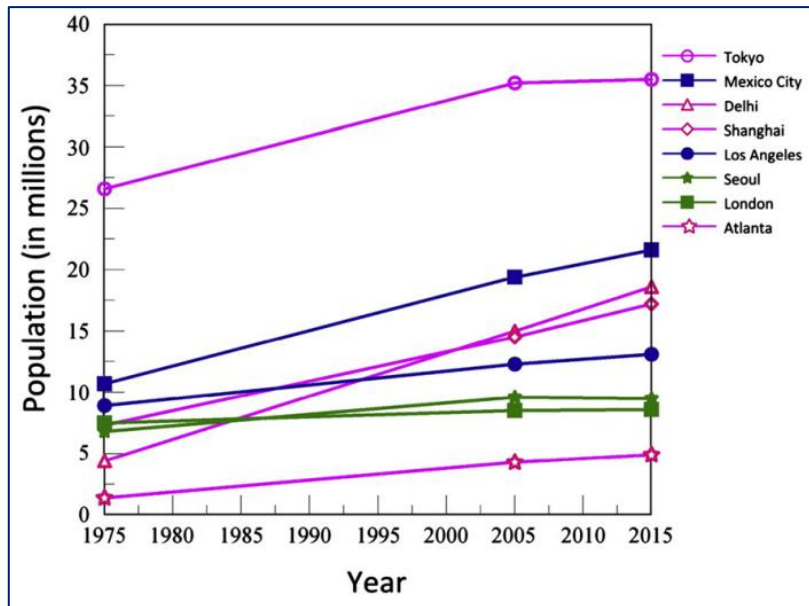
## 1. Introduction

The presence of any pollutant in the air at a concentration that will have an undesirable effect on the environment is simply called air pollution which is considered to affect both developed and developing countries as an important problem. Atmospheric pollutants originate naturally from forest fires, volcanic emissions and wind erosion or may result from domestic and industrial anthropogenic activities [1]. A five time increase is expected in air pollutant emissions in the world by 2030 by developing industrial regions and energy consumption increase [2].

By the year 1980's, 1.3 billion people have been reported to live in cities with pollution above air quality standards. Metropolitan cities in the world such as New York, Hong Kong etc. as well as Istanbul, Ankara, Izmir etc. in Turkey suffer from rapid urbanization and pollution because they are highly populated, industrially developed and receive immigrants. Urbanization and increasing anthropogenic activities influence the air quality adversely. This effect is especially notable in cities with intensive population and its negative impact is seen on regional climate and economy. Primary air pollutants (criteria pollutants) can be detected in high amounts in big cities which results in various environmental and detrimental health effects [3].

According to World Health Organization (WHO), urban air pollution is estimated to cause 800,000 premature death and 4.6 lost-life years in the world every year. PM pollution contributes to 22,000-52,000 premature deaths every year in the U.S and 200,000 premature deaths in Europe [5].

Figure 1.1 is showing the population growth trend in urban sites in some countries from 1975 to 2015. For some of these megacities the growth is more than 3 times such as Delhi and Mexico city, but for some of them such as Seoul and London the growth is not considerable [4].



**Figure 1.1.** Population growth trend in urban cluster

Atmospheric pollutants can be categorized as gas and particulate. Gaseous pollutants are formed from gaseous materials under normal pressure and temperature or from vapors of solid and liquid substances. The important gaseous pollutants are CO, HC, H<sub>2</sub>S, NO<sub>x</sub>, ozone, SO<sub>x</sub> and oxidants [1].

Aerosols are produced biologically, chemically and physically in oceans and on earth and anthropogenic activities play a great role in these processes. During the last decade, by increasing agricultural and industrial activities, urbanization, deforestation and fossil fuel consumption, more pollutants have been emitting into the atmosphere, and it is seen that the concentrations of carbon compounds increased in atmospheric composition [5]. Carbon compounds are extremely important substances in the atmosphere. They are very active against sunlight in the atmosphere and affect the heating balance of the earth by either cooling or heating effect.

Particulate matter has an important place among other atmospheric pollutants considering its effects on climate change, visibility degradation and human health. Its toxicity is affected by physical characteristics such as number, size and surface of particles in addition particle's chemical composition. Due to its chemical structure, PM consists of elemental and organic carbon compounds, sea salt, road dust, silicon oxides, metals, sulfates, nitrate compounds and ammonium [3]. Only

particles smaller than 10  $\mu\text{m}$  in diameter can be trapped by the respiratory tract. However, mostly particles smaller than 2.5  $\mu\text{m}$  in diameter can get to the alveolar region in lungs. These particles adversely affect human health by clinging to the alveolar region and considered to be important in scientific researches [3].

### **1.1 Content (scope) and objective of the study**

The main objective of this proposed study is to determine chemical compositions of particulate matter collected samples with aerodynamic diameter smaller than 2.5  $\mu\text{m}$  ( $\text{PM}_{2.5}$ ) in terms of EC, OC and TC in two different locations in Ankara. Some sub-main objectives of the study are listed below:

- Evaluation of the temporal variation of the measured parameters in the  $\text{PM}_{2.5}$  samples
- Determination of correlations between the parameters determined in the  $\text{PM}_{2.5}$  composition
- Investigation of the relationship between parameters determined in  $\text{PM}_{2.5}$  composition and meteorological parameters
- Determination of primary and secondary OC measured in  $\text{PM}_{2.5}$  samples

## 2. General Information

### 2.1 Air Pollution

Air pollution is determined as the outdoor and indoor environment contaminated by release of any gaseous or particulate materials from natural and anthropogenic resources that alters the natural characteristics of the atmosphere in exceeding levels and can show negative impact on living and non-living assets [6]. The amount of contribution from these sources change with time, season, location and climate [7]. Air pollution is due to combination of high amounts of emissions with improper air conditions. Air pollution is formed by frequent interaction between gaseous and particulate matter.[8] Urbanization and human activities have affected the air quality in negative way, especially the areas which urbanization is intensively grown suffer from negative regional climate and ecosystem [9].

### 2.2 Composition of Clean Air

Although there is not a clear description for clean air, researchers have found the composition of clean dry air as shown in Table 2.1 [10].

**Table 2.1.** Composition of clean air

<b>Component</b>	<b>Concentration (ppm)</b>
N <sub>2</sub>	780800
O <sub>2</sub>	209546
Ar	9340
CO <sub>2</sub>	330
Ne	18
He	5.2
CH <sub>4</sub>	1.2
Kr	0.5
H <sub>2</sub>	0.5
Xe	0.08
NO <sub>2</sub>	0.02
O <sub>3</sub>	0.01-0.04

## 2.3 Pollutants Causing Air Pollution

Apart from gases in the atmosphere, there are also particles formed by combination of liquid or solid particles in the gas environment. Briefly, air pollutants are chemical substances in the gas, liquid and solid state that changes the natural composition of air.

Pollutants are classified in four groups:

- 1) Primary and secondary pollutants
  - (i) Primary pollutants are directly emitted from the sources (e.g.  $\text{SO}_2$ , some  $\text{NO}_x$  species, CO, PM)
  - (ii) Secondary pollutants result from chemical reactions with other gases or pollutants (e.g., ozone,  $\text{NO}_x$ , and some particulates)
- 2) Gaseous pollutants (e.g.,  $\text{NO}_x$ , ozone, CO, SVOC)
- 3) Indoor and outdoor pollutants
- 4) Particulate Matter [11].

EPA has established NAAQS for primary pollutants, which are also known as “criteria” pollutants including carbon monoxide (CO), lead (Pb), nitrogen dioxide ( $\text{NO}_2$ ), ozone ( $\text{O}_3$ ), particulate matter (PM), and sulfur dioxide ( $\text{SO}_2$ ).

### 2.3.1 Carbon Monoxide

Carbon monoxide (CO) is a scentless, non-irritating, colorless and tasteless gas found in outdoor and indoor air. It is made when carbon in fuel burns incompletely. It is a product from both human-made sources and natural sources. The main human-made source of carbon monoxide comes from the exhaust of automobiles. Not properly adjusted heating appliances such as furnaces, wood burning stoves are main sources of carbon monoxide indoors. Carbon monoxide is also released from volcanoes and forest fires in huge amounts [8]. At the beginning of the combustion, particulate matters are dominant (elemental carbon and organic carbon) but CO dominates at the end [9].

Carbon monoxide remains in the atmosphere for about two months after releasing and reacts with other chemicals in the atmosphere and changes to carbon dioxide. It is slightly soluble in water [8].

People are exposed to carbon monoxide in many ways specially tobacco smoking and traffic. Breathing high levels of this gas can harm heart and brain. Lower levels of carbon monoxide might harm the mental development of the child during pregnancy [8]. Some other health effects are exhaustion, headache, dizziness, irritation, memory impairment, tinnitus and nausea [9].

### **2.3.2 Ozone**

Ozone ( $O_3$ ), composed of three atoms of oxygen is a strong oxidant gas produced naturally in the atmosphere. It is found both in stratosphere and troposphere. Depending on where it is found, it can be called good or bad. Good ozone or stratospheric ozone is found in the upper parts of atmosphere and plays a role as a layer to screen harmful solar ultraviolet rays. In troposphere it is created by photochemical reactions with precursor pollutants like nitrogen oxides and volatile organic compounds involving the action of sunlight. Ozone is destroyed in reaction with anthropogenically emitted chemicals which leads to ozone depletion in stratosphere. Anthropogenic emissions may elevate ozone concentration in troposphere which causes breathing problems in human [10]. Ozone concentrations of troposphere from both anthropogenic and biogenic resources changes in time and space reaching 8-hours average levels of around  $80 \mu\text{g}/\text{m}^3$  [10]. Removing ozone with the use of nitric acid from traffic reduces the ozone concentration downtown comparing with suburban [11]. Some studies in California have shown some asthma cases related to ozone but no other pollutants [11].

### **2.3.3 Nitrogen Oxides**

Molecular nitrogen ( $N_2$ ) forms 80% of the atmospheric air. Nitrogen can form different oxides. Nitrogen oxides ( $NO_x$ ) are important air pollutant chemicals in a group of seven compounds:  $N_2O$ ,  $NO$ ,  $N_2O_2$ ,  $N_2O_3$ ,  $NO_2$ ,  $N_2O_5$ .  $NO_x$  can get into reaction with different ozone concentrations depending on the number of the oxygen ions.

Half of the  $NO_x$  that is emitted come from vehicle exhaust. Electric power plant boilers produce about 40% of the  $NO_x$ . The remaining is emitted by other anthropogenic sources such as industrial boilers, gas turbines, metal and steel factories, petroleum refineries, glass factories and nitric acid production process.

According to EPA,  $N_2O$ ,  $NO$ , and  $NO_2$  are the most dominant nitrogen oxides in the atmosphere.  $N_2O$  has long-life of 100 to 150 years, which is produced by biogenic sources such as plants can react with ozone in both troposphere and stratosphere and it is an ozone depleting chemical.  $N_2O$  with almost 0.3 ppm worldwide abundance is also a greenhouse gas that absorbs long wave length infrared light which leads to global warming.

$NO_x$  combustion emissions usually are in form of  $NO$ . Rather than soil, natural fires and lightening,  $NO$  is generated from anthropogenic activities in a large amount. It is slightly soluble in water. It is not a big threat except very sensitive children and infants.  $NO_2$  is one of the important air pollutants. According to EPA,  $NO_2$  is the most predominant among other  $NO_x$  and is produced by anthropogenic activities. It produces nitric acid in water, which causes acid rains. It reacts in the atmosphere in the presence of oxygen and UV to form ozone and  $NO$ . Then  $NO$  oxidizes to  $NO_2$  by radicals from photo reaction of VOC [12] [9].

#### **2.3.4 Sulfur Oxides**

Sulfur dioxide is the dominant anthropogenic sulfur-containing air pollutant. It is a combustion product of sulfur containing fuels. Fossil fuels contain 1% to 5% sulfur according to source of sulfur in the fuel. Much of sulfur is removed from fuels in most of the developed countries [9]. In the high temperature combustion, sulfur can change to and  $SO_3$ .  $SO_2$  is toxic, dissolves in water and form sulfurous acid.  $SO_3$  is also toxic and changes to sulfuric acid by absorbing moisture in the air.  $SO_2$  and  $SO_3$  form sulfites and sulfates during acid neutralization. These acids can react with ammonia in the air and make solid particles.  $SO_2$  and  $SO_3$  can change acidity of water, so both  $NO_x$  and  $SO_x$  can kill plants and animals [12]. Studies have revealed that short-term contact with  $SO_2$  can lead to pulmonary malfunction and respiratory system [9].

Toxic sulfuric substances in the atmosphere are  $SO_x$  and  $H_2S$  gas. Among  $SO_x$  the most important gas is  $SO_2$ . This is a non-burning, colorless substance and in exceeding concentrations ( $> 3$  ppm) it shows stifling effects. It oxidizes very rapidly in the atmosphere and changes to  $SO_3$  and sulfates. The formed sulfates are precipitated and reduce visibility by interacting with visible light.  $SO_3$  combines with

rain or condensed droplets to form  $\text{H}_2\text{SO}_4$  in the air [1]. Sulfurous gases are harmful for human health especially  $\text{SO}_2$  which causes respiratory tract disorders and lung failure and thought to be lethal for respiratory system diseases [1].

### **2.3.5 Polycyclic Aromatic Hydrocarbons (PAHs)**

Polycyclic organic matter (POM) is a wide group of compounds including organic compounds with two or more combined aromatic (benzene) rings containing the elements hydrogen, carbon, nitrogen, oxygen and sulfur. The main suborder of POM is the polycyclic aromatic hydrocarbons [9]. They are originated from anthropogenic sources and fossil fuel combustion. PAHs are product of incomplete burning of fossil fuels or organic substances. They are found in air, water and soil and show a great tendency to attach to aerosol particulate matter. PAHs enter the air mainly from forest fires, volcanoes, traffic and smoking. They are mobile and are carried long distances before they reach earth by precipitation. They enter surface waters from waste water treatment plants and discharges. Their mobility depends of their solubility in water [17]. PAHs are highly lipophilic and lowly hydrophilic but soluble in most organic solvents [9]. PAHs might be influenced by direct photolysis and break down. Some microorganisms can decompose PAHs in soil. PAHs can also get into reaction with pollutants such as ozone, hydroxyl radicals, nitrogen dioxide and sulfur dioxide, producing diones, nitro- and dinitro-PAHs, and sulfonic acids, relatively. There are more than one hundred various PAHs generally occurring as complex mixtures, not single compounds. Following PAHs are classified in one group because these identified at high concentrations at National Priorities List (NPL) dangerous waste, there is more information available and they show more harmful effect than other PAHs [17].

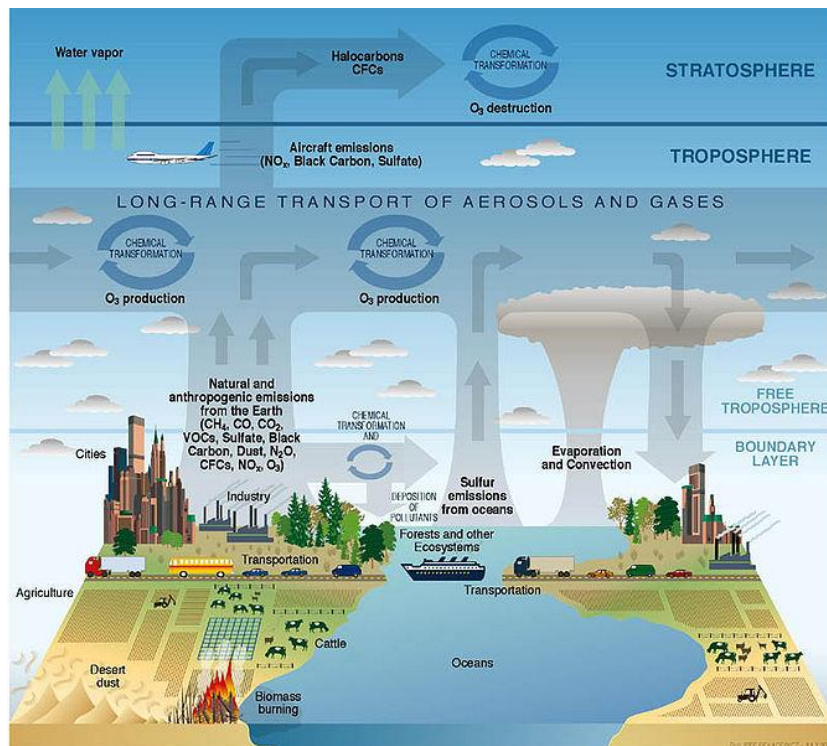
### **2.3.6 Particulate Matter**

Particulate matter (PM) or called particle pollution is a heterogeneous compound of suspended solid and liquid particles changing in physiochemical properties emitted from different number of sources depending on meteorological conditions. The size of these particles varies between  $10^{-9}$  -  $10^{-4}$  m. The most famous example of aerosols in the atmosphere are clouds but they are more known as suspended particulate matter [9].

Aerosols are produced biologically, chemically and physically in oceans and on earth and human activities play a great role in these processes. During the last decade, by increasing agricultural and industrial activities, urbanization, deforestation and fossil fuel consumption, more pollutants have been emitting into the atmosphere, and it is seen that the concentrations of carbon compounds increased in atmospheric composition [5]. Carbon compounds are extremely important substances in the atmosphere. They are very active against sunlight in the atmosphere and affect the heating balance by either cooling or heating effect.

Particles are divided as primary and secondary particles. Primary ones emit straightly from the sources (natural or anthropogenic) but secondary particles form from chemical reaction of gases and pollutants in the atmosphere

Figure 2.1 is showing atmospheric aerosol and gas pollutant sources and transport. As it is seen particulates are mostly emitted from anthropogenic sources such as industrial activities, transportation and biomass burning, while volcanic eruption, sea salt, desert dust and forest fire are natural sources of particulates [12]. In addition to anthropogenic and natural sources, conversion of gas molecules to particles in the atmosphere can lead to new particle formation [13]. These are formed in a result of condensation and nucleation reactions [10].



**Figure 2.1.** Atmospheric aerosol and gas pollutant sources and transport [14]

Particles are mostly found in troposphere ranging between 0.1 and 100  $\mu\text{m}$ . Particles  $>10 \mu\text{m}$  in effect of gravity and  $< 10 \mu\text{m}$  stay suspended in the air. Suspended particulate matter descends to the earth by rain or snow [15, 16]. Referring to EPA air quality standards for PM which uses the mass concentration of PM [PM with aerodynamic diameters  $\leq 10 \mu\text{m}$  ( $\text{PM}_{10}$ ) and  $\leq 2.5 \mu\text{m}$  ( $\text{PM}_{2.5}$ )] as a metric [6]. Generally, particles with diameter 2.5-10  $\mu\text{m}$  are called “coarse”, less than 2.5  $\mu\text{m}$  “fine” and less than 0.1  $\mu\text{m}$  “ultra-fine”.

Coarse particles are primarily related to suspended dusts, soils, and crustal materials from construction processes and to biogenic sources such as wind born particles and salt particles from the sea. Fine particles are emitted from combustion processes, industrial and motor vehicle sources [10].

Particles affect air quality, climate change, atmospheric composition and human health [17]. PM is one of the distinctive indexes of air pollution and must be observed regularly [18]. They absorb the sunlight and cool the earth. They also affect cloud formation and precipitation [19].

Chemical composition of particulate matter include sulfate, nitrate, ammonium, sea salt, Sahara dust, organic components and elemental or black carbon [10, 17, 20]. Nitrate, sulfate and ammonium are secondary pollutants and are serious air pollutants [21]. They also affect human health and visibility [22].

Carbonaceous aerosols are also important components and are highly active against sunlight, so they change heat balance by heating or cooling. These are main components of  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  in city centers [23].

#### **2.3.6.1 Limit Standards of PM**

Since 1999, limit values of air pollutants were introduced in many parts of Europe. First in 1999 air quality regulation (1999/30/EC) was introduced. The last regulation (2008/30/EC) was at 2008 and according to that daily  $\text{PM}_{10}$  limit value has been determined  $50 \mu\text{g m}^{-3}$ . However, studies have shown that in order to reduce PM levels only the particle mass of the particulate matter measuring is not sufficient and composition and sources of pollution must also be identified. Therefore, according to (2008/30/EC) regulation in the rural parts of Europe

measurement has started for water-soluble ions and EC/OC specially in PM<sub>2.5</sub> samples [24]. High concentrations of PM<sub>2.5</sub> result in human health difficulties in short and long term presence as well as a major component to urban smog and decreases visibility [6]. National Ambient Air Quality Standards (NAAQS) was founded by the United States Environmental Protection Agency (USEPA) to regulate the amount of airborne contaminants in order to reduce negative and harmful effects on health and visibility.

In the 1970s, heavy air pollution occurred in most of the big cities, especially in Ankara Province. After these incidents of air pollution after 1980s, some legal arrangements have been started. The procedures and principles related to air quality management in Turkey have been specified by the "Air Quality Assessment and Management Regulation" (HKDYY), fully compliant with the European Union (EU) environmental legislation. According to the legislation number 26898 daily and yearly limit values of PM<sub>10</sub> for the year 2009 was 300 and 150 µg/m<sup>3</sup> respectively. Accordingly on the date 09.09.2013 regulation number (2013/37) was regulated by Turkish ministry of Environment and urbanization, General directorate of environmental management air quality assessment and management in order to ensure air quality determination, a full air quality assessment based on defined methods and criteria determined in the Directive to ensure coexistence in ongoing applications and also to take necessary provisions to prevent the increase of limit values and to ensure that the public is informed and informed about the prevention of air quality and air pollution[25]. Table 2.2 is showing PM<sub>10</sub> and PM<sub>2.5</sub> limit values in some countries. Table 2.3 is showing Turkish air quality limit values according to General Directorate of environmental management air quality assessment and management regulation number (2013/37).

**Table 2.2.** PM<sub>10</sub> and PM<sub>2.5</sub> limit values in some countries (µg/m<sup>3</sup>)

	EU	USA	Japan	WHO	India	China	Turkey
<b>PM<sub>2.5</sub></b>	25	65 7 per year	-	25	-	50	-
<b>PM<sub>10</sub></b>	50 35 per year	150 1 per year	100	50	100	50	50* 35 per year

Sources:

EU — <http://ec.europa.eu/environment/air/quality.htm>.

USA — <http://epa.gov/air/criteria.html>.

WHO — [http://whqlibdoc.who.int/hq/2006/WHO\\_SDE\\_PHE\\_OEH\\_06.02\\_eng.pdf](http://whqlibdoc.who.int/hq/2006/WHO_SDE_PHE_OEH_06.02_eng.pdf).

Japan — <http://www.env.go.jp/en/air/aq/aq.html>.

India — <http://cpcbenvs.nic.in/airpollution/standard.htm>.

China — [http://www.epa.gov/oia/airandclimate/byregion/us\\_china\\_aqm\\_report.pdf](http://www.epa.gov/oia/airandclimate/byregion/us_china_aqm_report.pdf).

**Table 2.3.** Turkish air quality limit values (AQAMR, 2013) for PM<sub>10</sub> [25]

PM <sub>10</sub> (µg/m <sup>3</sup> )	2009	2013	2014	2015	2016	2017	2018	2019
<b>24 hours</b>	300	100	100	90	80	70	60	50
<b>Annual</b>	150	60	60	56	52	48	44	40

Table 2.4 is showing PM<sub>2.5</sub> standard according to WHO, EU and EPA. According to the table PM<sub>2.5</sub> limit values (24 hours) are 25, 25 and 65 µg/m<sup>3</sup> according to WHO, EU and EPA respectively. Annual limit values are 10 for WHO and 35 µg/m<sup>3</sup> for EPA [6].

**Table 2.4.** Comparison of PM<sub>2.5</sub> standard of WHO, EU and EPA

PM <sub>2.5</sub> (µg/m <sup>3</sup> )	WHO	EU	EPA
<b>24 hours average</b>	25	25	65
<b>Annual</b>	10	-	35

### 2.3.6.2 PM Health Effects

Particle can be inhaled and cause health problems. Toxicity of particles depend on both size and particle chemistry [16]. PM less than 10  $\mu\text{m}$  can be more harmful because they can penetrate deeper in the lungs [15]. Epidemiologic researches have shown a significant relation between cardiorespiratory illnesses and even mortality with ambient  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  levels [15].

Although there are considerable data and evidence which prove harmful health effects of coarse and fine particulate matter, a little is known about harmful effects of ultrafine particles that are more numerous and more poisonous. Studies have shown that ultrafine particles can affect circulation system and show toxic effects due to higher amount of transition metals and redox cycling chemicals [1].

PM has found to have many adverse effects on human health, especially  $\text{PM}_{10}$  was found to be toxic. The chemical compositions especially in  $\text{PM}_{10}$  has an important role in progress of cancer and allergic reactions. Also respiratory illnesses such as asthma and chronic lung diseases has been reported [26].

EPA standards for PM reflects health concerns because epidemiologic studies reveal an increase for cardiorespiratory diseases and death in atmospheric  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$ .  $\text{PM}_{2.5}$  has less mass but more inhalable and toxic. Chemistry and size of the particles determine the health effects of PM. Ultrafine particles penetrate into the lungs and enter the circulation system and lead to premature death, tissue damage of lungs and respiratory diseases [27]. Table 2.6 is showing levels of  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  ( $\mu\text{g}/\text{m}^3$ ) categorized according their health effects. According to this table since  $\text{PM}_{2.5}$  mean concentrations calculated in this study are in range of 40.5-65.4  $\mu\text{g}/\text{m}^3$ , they are considered to be known as unhealthy for sensitive groups according to USEPA standards.

**Table 2.5.** Levels of fine and coarse particulate air pollution ( $\mu\text{g}/\text{m}^3$ ) categorized according their health effects (USEPA, 1999)

Classification	Good	Moderate	Unhealthy for sensitive groups	Unhealthy	Very Unhealthy	Hazardous	
						Index value	Index value
	0-50	51-100	101-150	151-200	201-300	301-400	401-500
<b>PM<sub>2.5</sub></b>	0-15.4	15.5-40.4	40.5-65.4	65.5-150.4	150.5-250.4	250.5-350.4	350.5-500.4
<b>PM<sub>10</sub></b>	0-54	55-154	155-254	255-354	355-424	425-504	505-604

## 2.4 Carbonaceous Aerosols

Carbonaceous compounds are principal ubiquitous matters in ambient aerosols compounds with considerable fraction carbon responsible for about 10 to 20 percent of aerosol mass mainly from fossil fuels and biomass combustion. Carbonaceous aerosols are sorted as Organic Carbon (OC), Elemental Carbon (EC) or Black Carbon (BC), Equivalent Black Carbon (eBC), Refractory Black Carbon (rBC), Light Absorbing Carbon (LAC) and Brown Carbon (BrC) [28]. They are mainly classified as BC (Elemental Carbon) and OC and Carbonate ( $\text{CO}_3^{2-}$ ) Carbon (CC) but the distinction among complex carbonaceous mixtures is ambiguous. For the amount of carbonate carbon in total carbon is less than 5 %, aerosol carbon is mainly EC and OC. Carbonaceous matters are considered to be important because of their effects on atmospheric environment and human health and these are related to carbonaceous matter's chemistry, size distribution and sources [29, 30]. In recent years, increase in fossil fuel combustion, industrial activities, biomass burning and urbanization has led to an increase in concentration of carbonaceous aerosols [31].

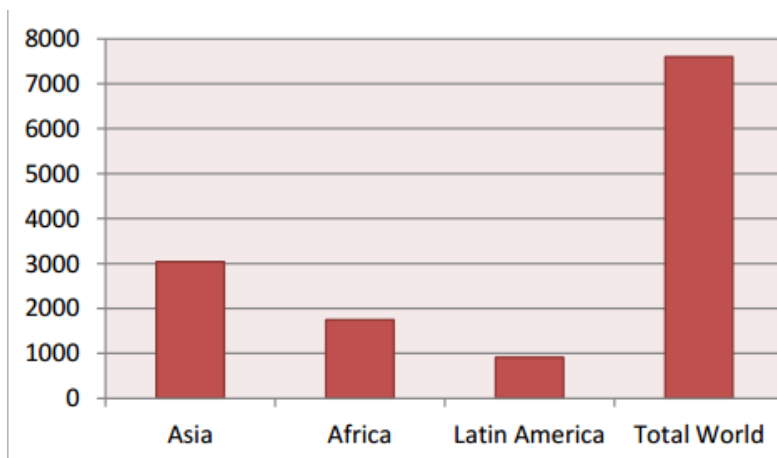
Organic carbon is a mixture of particulate organic compounds especially PAH, Polychlorinated Dibenzene-p-oxidase and Dibenzofuran (PCDD/Fs) and other toxic compounds [17, 32]. These harmful compounds threaten human health and cause death.[33] Organic carbon scatters sunlight and affects cloud formation properties with elemental carbon and directly or indirectly it affects world's thermal balance [34].

EC which is the most prominent kind of carbonaceous aerosols is an inert nonvolatile substance with high molecular weight [35, 36]. It is not soluble in water and any other solvent and can bear  $400^\circ\text{C}$ . It remains in the atmosphere from two days to one week and can be transported up to several thousand kilometers [37]. Its duration and light absorption in the atmosphere can change depending on its interaction with other aerosols. Elemental carbon with other aerosols' interaction increase the ability of sunlight absorption and the formation of liquid-cloud droplets [38].

Black carbon or elemental carbon is discharged from different combustion processes and usually is emitted with other gases such as  $\text{SO}_2$ ,  $\text{NO}_x$  and OC [39] and is found

almost everywhere in Earth system. A big part of atmospheric black carbon is formed in result of anthropogenic activities and is the absorbing part of carbonaceous aerosols and it might result in humic substances or other organic matter contributing to estimated black carbon absorption. After CO<sub>2</sub>, EC is the second contributor of global warming. It shows its effect on climate system by influencing cloud formation processes and absorbing sun light and scattering solar radiation and consequently changing snow melting the ice cover. It has a considerable effect on reducing visibility due to light absorption properties. It can interfere with some chemical reactions in the atmosphere including SO<sub>2</sub>, NO<sub>x</sub> and O<sub>3</sub> because of its catalytic properties. It is considered to be important because it contributes to soiling, has an effect on atmospheric radioactive budget and might cause degradation of stone buildings. It acts as a carrier of toxins into human respiratory system. Black carbon can be quickly removed from atmosphere by deposition, so global climate forcing reduction is possible in short term by mitigation strategies to slow the rate of climate change [38] [40].

An accurate global BC table was introduced by Lamarqua et al. (2010) for the year 2000. According to this report, global BC emission was 7,600 Giga grams in 2000. Figure 2.2.is showing the distribution of BC emission in selected regions of the world.



**Figure 2.2.** BC Emission(Gg) by Selected World Region, 2000 [41]

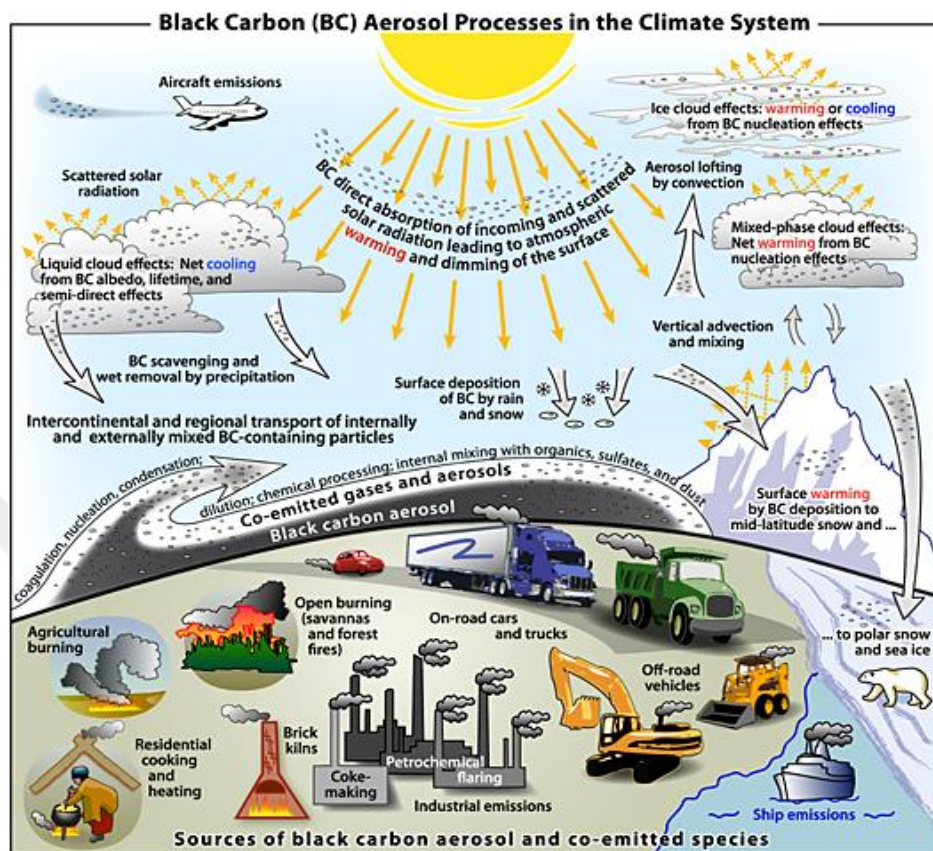
Table 2.6 is showing average yearly emissions of BC and OC from 1960s to 1990s. According to this table both OC and BC had rising trend and from 1960s to 1990s the increase rate is 1.6 times approximately for both pollutants

**Table 2.6.** Average yearly Emissions, Tg/a [42]

Species	1960s	1970s	1980s	1990s
BC	1.69	2.00	2.29	2.72
OC	13.3	15.7	18.5	22.4

#### 2.4.1 Black Carbon vs. Soot

Soot is in result of incomplete combustion of carbonaceous materials especially biomass and fossil fuels and it is determined either chemically or optically. Optical method is based on light absorption. The chemical (thermal or thermo optical) method shows the mass concentration of total carbon, in which the persistent component that does not evaporate under 400 degree in air is called Elemental Carbon [43]. The distinction between EC and BC is due to different fraction of light absorbing carbon [44]. Figure 2.3 describes the sources and effects of carbon on earth. As it is shown in the picture, EC is discharged to the atmosphere from both human activities and natural sources. The majority of these sources are mainly fossil fuels, domestic heating, forest fires and industrial activities. EC in the atmosphere is carried in regional scale and among continents and Descended to the earth by precipitation.[38]



**Figure 2.3.** Schematic picture of primary elemental carbon sources and their effects on process and climate change in the atmosphere [38]

## 2.4.2 Primary and Secondary Organic Carbon

Although big part of atmospheric aerosols include organic carbon, the significance of primary (POC) and secondary organic carbon (SOC) has always been discussed. Organic carbon is divided in two groups, primary and secondary organic carbons (POC and SOC, respectively) according to the source emitted. Primary ones are discharged to the atmosphere directly from the sources (natural or anthropogenic) in form of particulate and generally result from fossil fuel combustion, biomass burning, heating (especially coal), traffic and biogenic sources such as pollen and Terpenes. Secondary organic compounds are produced by the interaction of particulate matter with volatile organic compounds (VOC) by photochemical reactions of precursor gaseous compounds [33], [45], [46], [47]. Emission ratios of OC/EC change considerably from one source to another source, and therefore the primary ratio will be affected by meteorology, daily

and seasonal changes, and the effect of local origins.[48] Since elemental carbon (EC), also known as black carbon or graphitic carbon mainly results from fuel burning, it is considered as a tracer for primary organic carbon. So OC and EC correlation can show the source of carbon containing aerosols. Therefore, poor correlation of OC-EC and ratios of OC/EC exceeding the expected ratio of OC/EC for the primary aerosol is indicator of secondary organic aerosol. The existence of SOC is distinguished by OC/EC ratio when it is more than 2.0 [49].

#### **2.4.2.1 Environmental Effects of Carbonaceous Aerosols**

OC and EC both reduce visibility, have adverse health effects, affect climate regime and radioactive forcing of the earth, whereas EC shows a warming effect but OC has a cooling effect [50]. OC reflects the light and EC absorbs, so they both affect climate change this way. EC can directly affect the climate by attracting solar radiation and indirectly by cloud formation, brightness and lifetime [51]. Therefore determination of PM composition is essential because it is an important factor to identify both global scale of climate change and human health. In 1850s OC and EC emissions were more than SO<sub>2</sub> and was resulted from type of fuel used for heating and cooking [52, 53]. Amount of SO<sub>2</sub> started to increase by beginning of industrial era in 1850s especially from industrial and electric plant power. In the twentieth century, there was a considerable increase in amount of EC due to an increase in industrial activities and transportation [54]. Decreasing and removing of these matters are essential for human health and environment, therefore the fractional distribution of carbonaceous matter from different sources needs to be estimated. It is necessary to determine the source apportionment of the carbonaceous matters natural or anthropogenic in order to be able to prevent and control because the latter can be controlled by human activities [29, 30].

Recent studies show the influence of EC in the Eastern Mediterranean with negative radiative forcing in surface and big positive atmospheric forcing amounts almost identical to the highly absorbing south Asian haze observed over Arabian Sea. The role of these light absorbents is important especially during the summer when air flows mostly come from the Eastern Mediterranean, Balkans, Turkey and Central and Eastern Europe and

during this period anthropogenic aerosols, which are mainly comprised of sulfate and carbon containing aerosols causing 2/3 of the Aerosol Optical Depth (AOD) over the Greek-Turkish coastal area. Wild fires from southern Europe and Saharan dust originating from North Africa might considerably contribute to large amount of aerosol emissions in the Mediterranean atmosphere. Since these aerosols are solar radiation absorbents and have iron and phosphorus, they can control the atmospheric physics and chemistry, and also chemistry of the Mediterranean Sea [44].

Most of studies demonstrate the great impact of carbonaceous material on aerosol optical properties in the Mediterranean region but not many are supported by field observations which are especially rare and time dependent. The few of them done in the Eastern part of Mediterranean have indicated that a good analytical designation of their concentrations is a hard job principally because of the complexity of the aerosol compounds [44].

#### **2.4.2.2 Health Effects of Carbonaceous Aerosols**

The International Agency for Research on Cancer (IARC) put diesel emissions to its list of carcinogens in 2012 based on historical studies of occupational exposure .Some studies have shown a relation between exposure to exhaust and mortality, asthma improvement in children, breathing signs in adults, decrease in lung operation and cardiovascular problems [55].Toxicity of different component of PM may be different and which component of PM is more toxic is still being studied. The relative risk of EC is ten times higher than PM<sub>2.5</sub>.

Carbon in PM has shown an adverse effect on health. For example, lung malfunction has been reported in the women who were exposed to urban black carbon PM. In a similar study an adverse association has been observed between black carbon amount in airway and lung function in youngsters. A positive correlation has been reported between black carbon content PM<sub>2.5</sub> and blood pressure [50].

Toxicological studies have reported that pure BC may not be toxic but it can be toxin transporter to defense cells, lungs and blood circulation system [55]. There is a

significant correlation between  $PM_{2.5}$  content of elemental carbon and hypertension, and in children, lung function [56]. OC influences visibility reduction and has carcinogenic compounds which affect human health.

## **2.5 EC and OC Sources**

Carbonaceous aerosols are sent to the atmosphere from various anthropogenic and biogenic sources. EC is originated from combustion processes of carbon containing fuels only and is a primary pollutant from primary sources such as coal burning, exhaust emissions, biomass burning and dust from soil. OC is a composed of hydrocarbons and oxygenates which is not only emitted directly from primary sources such as combustion processes, soil dust and biogenic secondary carbon, but also it is made from heterogeneous atmospheric reactions of organic precursors. Concentration of carbonaceous aerosols and their ratios are source indicators, for example, OC/EC ratio bigger than 2.0 is secondary aerosol emission indicator. Emission ratio of OC/EC changes from one source to another source and it is influenced by local sources, meteorological and seasonal changes. Although organic matter of aerosols decreases quickly in long-range transport, EC has a long life-time (longer than 2 days) and can be transported farther [30].

## **2.6 Meteorological Factors**

Meteorological events have a major impact on air pollution. It has an effect on movement and transport of pollutants. Periodic winds, region properties and other meteorological conditions indicate a great role in the transport of pollutants in the atmosphere [1]. Meteorological conditions affect physical and chemical size distribution of PM by transport (wind direction, precipitation), dilution (mixing height and wind velocity), the distribution between gas and condensed phase (temperature and humidity) and chemistry resulting from chemical transformations (including gas phase, multiphase and heterogeneous reactions) so physical and chemical characteristics of atmospheric aerosols vary in urban and rural areas due to different aerodynamic sizes. Temperature, proportional humidity, fog formation, inversion, precipitation, pressure, wind direction and speed, the duration of sunshine and the severity of the sun's radiation has an important

role in air pollution. These factors are effective in increasing and decreasing the quantities of pollutants, accumulating and transporting, and chemical form of the pollutants.

### **2.6.1 Pressure Conditions and Wind**

In an area where high pressure conditions are present, air tends to sink continuously, so there is no chance of rising and dispersing for polluted air. At lower pressure (Cyclones), air movement is elevated. It has a turbulence motion. By transporting the polluted air to the upper levels of atmosphere, causes it to be dispersed by higher winds. Wind transports the polluted air and in its absence, it remains still. Therefore, enclosed (wind closed) areas are the most polluted ones [1].

### **2.6.2 Humidity**

Humidity in the air has negative aspects in terms of pollution. More water vapor existence in lower atmosphere increases solar energy absorption and increases the warmth. In high concentrations of SO<sub>2</sub> and humidity sulfuric acid can be produced [1].

### **2.6.3 Temperature Inversion**

At the normal course of the atmosphere, temperature decreases moving vertically upwards. Sometimes contrary of this situation is possible which is overturn of normal behavior of temperature in troposphere and a layer of cool air is covered by a layer of warmer air. It is called "temperature inversion". The most dangerous in terms of air pollution is the days when the temperature is reversed [1].

## **2.7 Saharan Dust Events and Carbon Compounds**

Dust can react with different species such as anthropogenic origin species. These reactions can influence the size distribution of the aerosol, optical properties and also chemical composition. It is little known about the interaction of dust with organic compounds, though. According to Sahara dust Experiment framework (SHADE) no carbon aerosols were found in dust samples while ACE ASIA study results show that air pollution affects dust aerosols with toxic materials, minerals and carbon compounds such

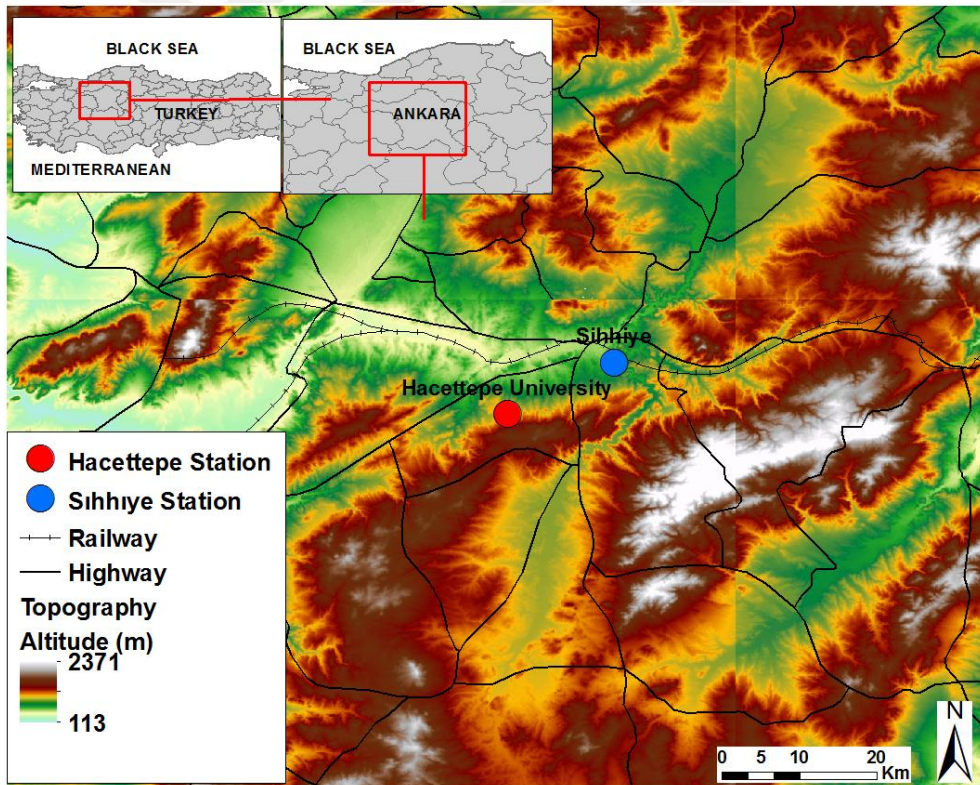
as elemental carbon which has an effect on climate human health. The studies and information about interaction of dust and anthropogenic source pollutants are imperfect especially with organic compounds [57]



### 3. Material and Method

#### 3.1 Sampling Site Description

Samplings were carried out at two different locations simultaneously in the city of Ankara (39°57'N, 32°53'E, 891 m). One is considered to be semi-rural and the other urban site. Ankara has a population of 5.346.518 (2016) and located in middle Anatolian region. Climate of Ankara is considered to be semi-arid according to the Köppen-Geiger climate classification characterized by 11.7°C annual temperature and 377.6 mm rainfall. The sampling duration between June to mid-August fell within the hot and dry period, and during winter fell within cold and wet period. Figure 3.1 shows locations of the sampling period on the map.



**Figure 3.1.** Location of the sampling points

Beytepe campus of Hacettepe University is located 39° 53′ 48.0156" and 32° 44′ 1.3884" in Ankara, lies about 16 km away from city center, between urban and country region about 918 meters above the sea level. The other sampling site at General

Directorate of Public Health of Turkey located 39°55'38.4"N 32°51'33.9" downtown in Sihhiye area on the corner of a crowded street at business district with heavy traffic and is mainly surrounded official buildings.

### 3.2 Sample Collection

Daily samples were collected between June 19<sup>th</sup> 2016 to August 11<sup>th</sup> 2016 and December 29<sup>th</sup> 2016 to 27<sup>th</sup> of January 2017. Sampling was disrupted for 10 days (3-10 July) due to power outage (technical problems). A TCRTECORA SKYPOST PM HV sampler (Certified by TÜV in accordance with EN12341 and DM60 norms) was used to collect PM<sub>2.5</sub> at the flow rate of 16.67 L/min. Figure 3.2 is showing PM samplers installed in sampling sites.



**Figure 3.2.** Samplers installed in sampling sites

The summary of the sampling methodology followed in this study was shown in Table 3.1.

**Table 3.1.** Summary of sampling followed in the study

Sampling site	Sampling period	Sampling period	N
Sihyye(urban)	19 June-11 August 2016 (Interrupted between 3-13 July)	24 hours	45
	29 Dec 2016-27 Jan 2017	24 hours	45
Hacettepe University(semi- rural)	19 June-15 August 2016	24 hours	45

### 3.3 Determination of PM<sub>2.5</sub> Concentration

In this study, Whatman 47 mm pre-fired quartz filters were used to collect PM<sub>2.5</sub> at both stations. The quartz filters were weighed after humidity equilibrium(25°C and 50% humidity) (>24h) in the desiccator and placed into sterilized petri dishes and kept in -18 degree until being used in the sampler. When sampling period is over the filters were reweighed after reaching humidity equilibrium (>24 h) on an analytical balance with a reading precision of 0.0000 g in order to calculate the PM<sub>2.5</sub>, concentration on the sampling site. Background contamination was regularly controlled by using operational blank (unexposed filters), which were prepared with the field sample at the same time.

The sampling duration was almost 24 hours for each sampling filter. The total number of samples was 90 PM<sub>2.5</sub>, forty five for each sampling site. Sensitive analytical balance is shown in the Figure 3.3.



**Figure 3.3.** Sensitive analytical balance

It is known that quartz filter can absorb organic gases and an equilibrium change between organic components, filter and gaseous organic materials can result in positive and negative artifacts during sampling. Positive one results from gaseous compound absorption on filters and negative artifacts comes from gaseous organic materials evaporation out of filters [58].

### **3.4 EC/OC Analysis of Collected PM<sub>2.5</sub> Samples**

Collected PM<sub>2.5</sub> samples were analyzed for EC, OC and TC (OC+EC) by thermal-optical transmittance (TOT) method using thermal optical carbon analyzer made by Sunset Laboratory, Oregon, USA. A photograph of the analyzer was illustrated in Figure 3.4. Analysis of EC and OC was performed on the basis of the modified protocol by NIOSH-870 (National Institute of Occupational Safety and Health). NIOSH 870 (National Institute for Occupational Safety and Health) was chosen as the most suitable protocol for this study from protocols based on different temperature programs [46]. The analysis phase starts after all the options required for analysis have been selected. The analysis has two steps, analyzer EC and OC analyzes are made by using thermal, optical and chemical properties.

In this analysis method, sampled filters were cut into standard pieces of 1.5 cm<sup>2</sup> and placed into quartz furnace as illustrated in Figure 3.5. The helium gas sent into the furnace raises the temperature of the furnace to 870°C. With rising the temperature the

organic compounds which are desorbed from the sample are transformed into pyrolysis products and move to manganese dioxide ( $\text{MnO}_2$ ) oxidizing furnace. Here, carbon fragments moving in the  $\text{MnO}_2$  furnace are transformed into  $\text{CO}_2$  gas. The  $\text{CO}_2$  swept by the helium gas from oxidizing environment is mixed with the hydrogen gas. This mixture is then changed to  $\text{CH}_4$  gas by heated nickel catalysis and the carbon type is determined by the flame ionization detector (FID). After the first step in the quartz sampling furnace is completed, the temperature in the furnace is reduced to  $550\text{ }^\circ\text{C}$  and the helium / oxygen carrier gas mixture flows through the furnace. With oxidizing gas mixture and second temperature spike elemental carbon in the filter oxidized in the filter and moves to  $\text{MnO}_2$  furnace. Then elemental carbon is determined by FID detector similar to organic carbon. The results of the analysis are taken both as a text file and as a thermogram. In a typical thermogram four organic carbon peaks ( $\text{OC}_1$ ,  $\text{OC}_2$ ,  $\text{OC}_3$  and  $\text{OC}_4$ ) and six elemental carbon peaks ( $\text{EC}_1$ ,  $\text{EC}_2$ ,  $\text{EC}_3$ ,  $\text{EC}_4$ ,  $\text{EC}_5$  and  $\text{EC}_6$ ) are expected. A typical thermogram obtained during the analysis of one sample was illustrated in Figure 3.6.



Figure 3.4. EC/OC analyzer (SUNSET LAB)

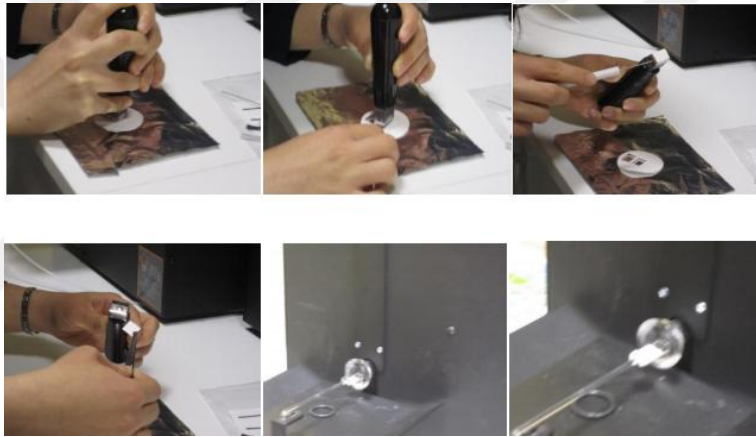


Figure 3.5. Filter punching and insertion into the analyzer

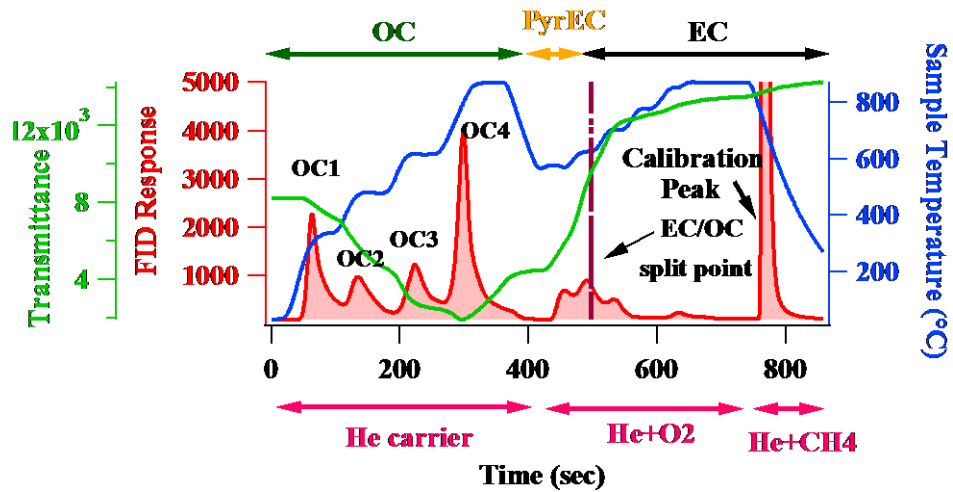


Figure 3.6. Thermogram of one of the samples

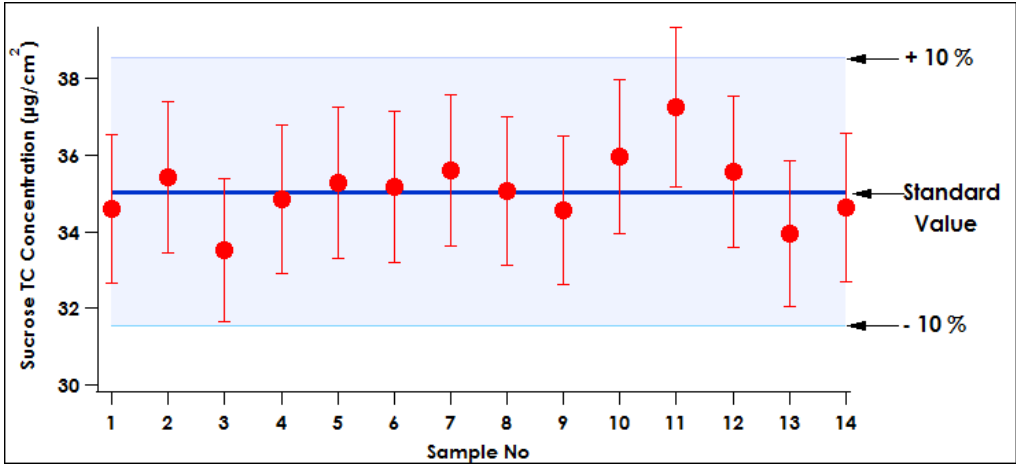
The thermogram obtained from EC/OC is presented in Figure 3.6 shows that the first phase of analysis begins with He gas (100%) flow. The temperature rises to 870°C in 4 steps and OC is desorbed by the effect of on the filter. With increasing temperature, the carbon compounds on the filter are converted into CO<sub>2</sub>. In the thermogram, four peaks belong to the OC, which are shown as OC<sub>1</sub>, OC<sub>2</sub>, OC<sub>3</sub> and OC<sub>4</sub>. During the first stage of the analysis in which the organic carbon is determined, the light permeability decreases during pyrolysis of the filtrate. As you can see there is PC between OC and EC. At the end of this phase, the section where the filter is placed slowly starts to cool down. Second phase of analysis starts with He+ O<sub>2</sub> gas flow (10% O<sub>2</sub> + 90% He). In four steps the temperature reaches 870°C again. Table 3.2 shows the analysis steps in the NIOSH 870 protocol including the type of gas used and duration of the analysis in each step. EC<sub>1</sub>, EC<sub>2</sub>, EC<sub>3</sub> and EC<sub>4</sub> are shown on the four-peak thermogram of the EC analysis. This stage of analysis is similar to the first stage. Here, PC and EC, which are formed in the first stage, are burned with heat effect. In the second phase of the analysis, carbon compounds are changed to CO<sub>2</sub>.

**Table 3.2.** The temperature of the formed peaks during EC / OC analysis time

Analysis Step	Gas	Analyze Time (s)	Analyze Temperature (°C)
OC <sub>1</sub>	He	60	310
OC <sub>2</sub>	He	60	475
OC <sub>3</sub>	He	60	615
OC <sub>4</sub>	He	60	870
	He	Cooling 50	
EC <sub>1</sub>	He/O <sub>2</sub>	45	550
EC <sub>2</sub>	He/O <sub>2</sub>	45	625
EC <sub>3</sub>	He/O <sub>2</sub>	45	700
EC <sub>4</sub>	He/O <sub>2</sub>	45	775
EC <sub>5</sub>	He/O <sub>2</sub>	45	850
EC <sub>6</sub>	He/O <sub>2</sub>	45	870

Throughout the analysis while permeability of OC decreases, the permeability of EC and PC increases. The point where EC and OC are separated from each other is determined automatically by the software and is expressed as "Split Point". The last peak on the thermogram is calibration peak and is formed by addition of CH<sub>4</sub> to He/O gas flow. Before analyzing the samples collected in the EC/OC analyzer, analysis of clean pre-fired blank quartz filters (blanks) used in the sampling was performed in terms of control and quality assurance. Mean TC concentration was found as approximately 3.16 µgcm<sup>-2</sup> (n=16) in the blank quartz filters.

For quality control and assurance of analysis, in addition to blank filter and sucrose solution was spiked on the clean pre-fired filters and analyzed in the same conditions with the sample. Figure 3.7 shows the variation of TC concentration in the sucrose spiked filter samples. The blue line in Figure 3.8 stands for the TC value in the sucrose spiked quartz filter. The expected TC concentration in the sucrose spiked quartz filter is 35.04 µg C/cm<sup>2</sup>. The red points and error bars are to show the mean and standard deviation of TC concentrations measured in different sucrose standards, correspondingly. After 30 samples analyzed and at the beginning of each analysis day instrument was run empty.



**Figure 3.7.**TC concentrations measured in sucrose standards

In addition to daily analyzed sucrose and blank filter samples, standard reference materials (SRM) and performance evaluation standard (PES) samples supplied by

Sunset Lab were analyzed regular intervals based on the NIOSH protocol. Therefore, the precision of the analysis was checked out regularly. The precision for OC, EC and TC were found as 2.34, 25.14 and 5.50 %, correspondingly, based on the SRM 1648a measurements which is given in Table 3.3. The accuracy values based on the analysis of PES standard was found as  $20.16 \pm 1.32$ ,  $8.13 \pm 0.93$  and  $18.83 \pm 1.33$  %, respectively, for OC, EC and TC as shown in Table 3.4.

**Table 3.3.** Accuracy of SRM 1648a

	<b>Accuracy (%)</b>			
<b>Protocol</b>	N	OC	EC	TC
<b>NIOSH</b>	5	2.34	25.14	5.50

\* As the SRM 1648a's sheet of certificate reports average values, only average accuracy values were calculated in the results

**Table 3.4.** The accuracy of results from analysis with EC / OC analyzer performance with evaluation standard from Sunset Lab

	<b>OC</b>		<b>EC</b>		<b>TC</b>	
	<b>Average</b> ( $\mu\text{g}/\text{m}^3$ )	<b>SD*</b>	<b>Average</b> ( $\mu\text{g}/\text{m}^3$ )	<b>SD*</b>	<b>Average</b> ( $\mu\text{g}/\text{m}^3$ )	<b>SD*</b>
<b>Observed Value</b>	13.37	1.33	1.88	0.34	15.26	1.67
<b>Certified Value</b>	16.75	0.94	2.05	0.2	18.8	1.14
<b>Accuracy (%)</b>	20.16	1.32	8.13	0.93	18.83	1.33

\*Shows standard deviation

Detection limit (DL) of the instrument was also calculated in this study. To end this, pre-fired blank quartz filters were analyzed and standard deviation of the measurement results was plugged into the following equation. In addition, the relative standard

deviation (RSD) that is also known as the precision of the measurements, was also computed in this study by dividing the relative standard deviation to the mean of the repeated measurements of blank filters. Both RSD and DL values computed in this study was provided in Table 3.5. The obtained precision value for EC, OC and TC was all less than 5 %. The DL for OC, EC and TC was found as 0.31, 0.06 and 0.34  $\mu\text{g}/\text{cm}^2$ , correspondingly, as provided in Table 3.5.

$$TS=3 \times S$$

**Table 3.5.**The limit of determination (TS) of the EC/OC analyzer and the measurement results repeatability

	<b>N</b>	<b>OC</b>	<b>EC</b>	<b>TC</b>
<b>*RSD (%)</b>	3	4.60	5.02	4.65
<b>**DL (<math>\mu\text{gcm}^{-2}</math>)</b>	7	0.31	0.06	0.34

\* Calculated with the results of performance evaluated standard analysis provided by Sunset lab

\*\* Calculated by the analysis results of pre-lit filter witnesses

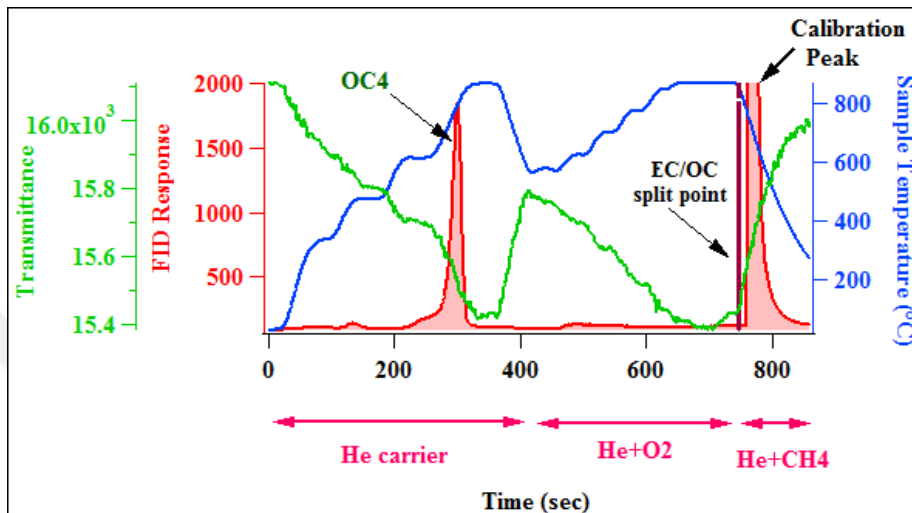
### 3.5 Carbonate Correction in EC/OC Analyses

In the EC/OC analyzes, the peak from the thermogram for OC<sub>4</sub> is observed higher on some days. It is known that this increase is due to the increase of CO<sub>3</sub><sup>2-</sup> containing compounds and dust events [59, 60].

The concentration of carbonate carbon (CC) in the PM content is determined by the thermal-optical analyzer in the inert atmosphere and at the maximum temperature. To determine the amount of CC in the analyzes, peaks are manually integrated using a software available in the analyzer [43].

In order to see whether OC<sub>4</sub> is really associated with the CO<sub>3</sub><sup>2-</sup> or not, pure CaCO<sub>3</sub> was put in the powder form on a piece of quartz filter and this was analyzed under the same conditions with the samples and obtained thermogram was shown in Figure 3.8. It is

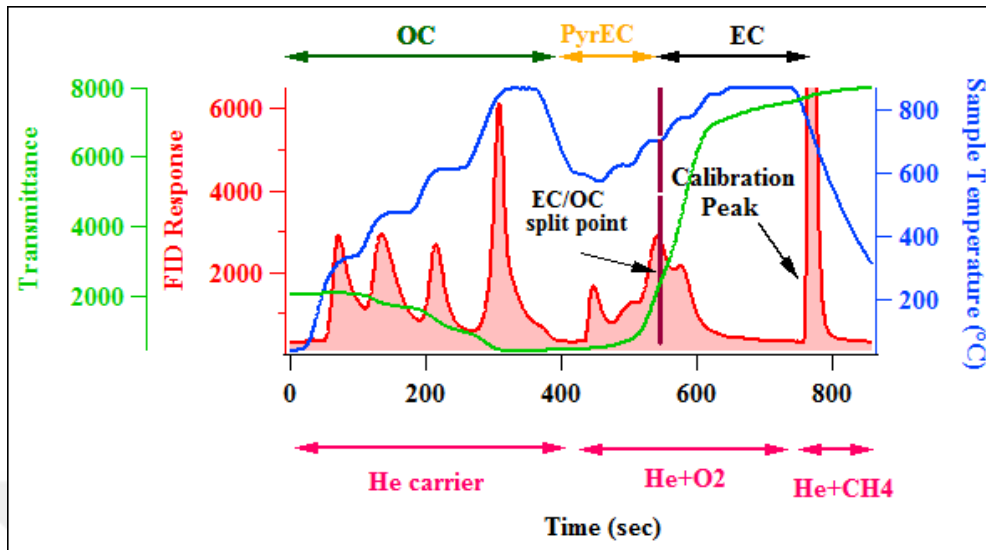
seen in Figure 3.8 that other peaks indicating OC and EC fractions were disappeared and OC<sub>4</sub> peaked in the thermograms indicating that elevated OC<sub>4</sub> is associated with the existence of CC in the sample.



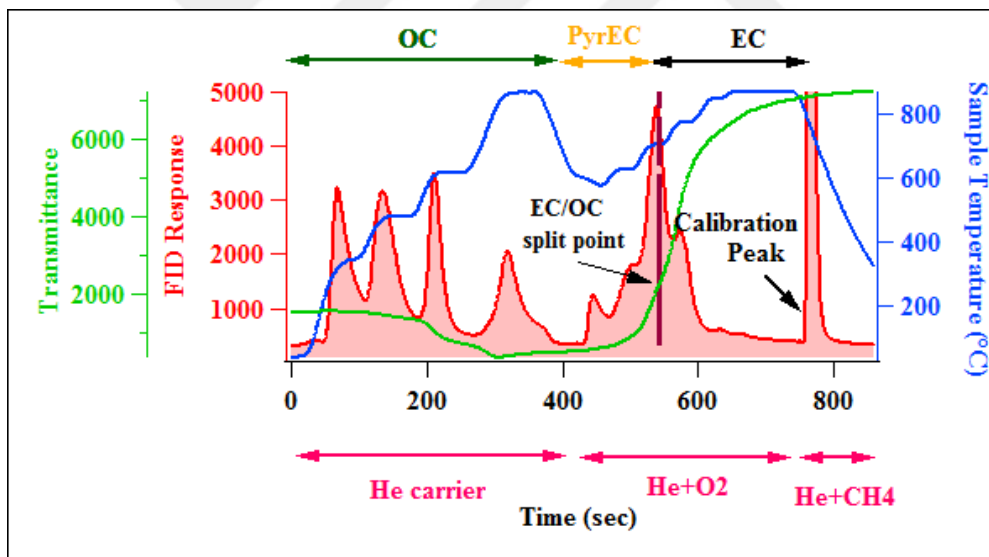
**Figure 3.8.** Thermogram of pure CaCO<sub>3</sub> in powder form, only OC<sub>4</sub> peak appears

Many related methods have been used to determine carbonate amount (CO<sub>3</sub><sup>2-</sup>) in different studies. The most common of these are the exposure of the filter samples to acid vapors before being analyzed and determine the released amount of CO<sub>2</sub> during the analyze [61, 62].

In this study the filter samples with high OC<sub>4</sub> peaks were detected and exposed to HCl to determine if it contains CC and analyzed again [63]. In this process, 1.5 cm<sup>2</sup> of filter punch was taken and placed into petri dishes and two drops of HCl were added away from the filter and lid of the petri dishes was closed and waited for three hours. Filter samples exposed to HCl vapors were analyzed again after this acid treatment. Thermograms of the sample collected on campus on 25/06/2016 before and after fumigation with HCl were depicted in Figures 3.9 and 3.10, correspondingly. The results evaluated in this study were carbonate carbon corrected.



**Figure 3.9.** Thermogram of sample collected on 26/06/2016 on campus before fumigation



**Figure 3.10.** Thermogram of sample collected on 26/06/2016 on campus after fumigation

### **3.6 Air Mass back Trajectory**

In the present study, the OC and EC data were collected in field campaigns conducted in an urban and semi urban area in Ankara, Turkey from in summer and winter seasons. Our objective is to run a 5-day back trajectory ending in Ankara to examine the compositions and sources of carbonaceous aerosols in  $PM_{2.5}$  and to evaluate the OC and EC fractions during Sahara dust storm events and non-dust storm time to specify the pathway and possible sources of carbonaceous aerosols. Since trace elements are not investigated and measured in this study, we are to take biomass burning, OC and EC concentrations into consideration more, in order to trace the possible sources.

#### **3.6.1 Back Trajectory Technique**

Back trajectories can be explained as the successive locations of an air mass before reaching a receptor at a specified height, location and time. In this study, the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) on the basis of National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory was applied with “Final Run” meteorological data achieves (FNL) to compute 120-hour isentropic back trajectories [64]. The resulting back trajectory data consisted of time, latitude, and longitude and altitude information for every hour of the 5 days of calculations. Each of the hourly location of the puff is called a “segment” or “endpoint”.

Each back trajectory was created at three starting point altitudes to average the possibility of transport at different levels. The starting levels of calculations were 500, 1500 and 3000 m above ground level (AGL).

Back trajectory technique is performed in order to determine dust period during sampling period. First the PM concentrations with elevated levels were detected and checked with satellite visible imagery on NASA earth data website backed up by HYSPLIT back trajectory for possible Sahara dust events. Satellite data gives a wider perspective of the dust transport event. These two data show the origin of the air mass. When air mass is from south west it clearly shows that it is originated from North Africa [65].

## 4. Result and Discussion

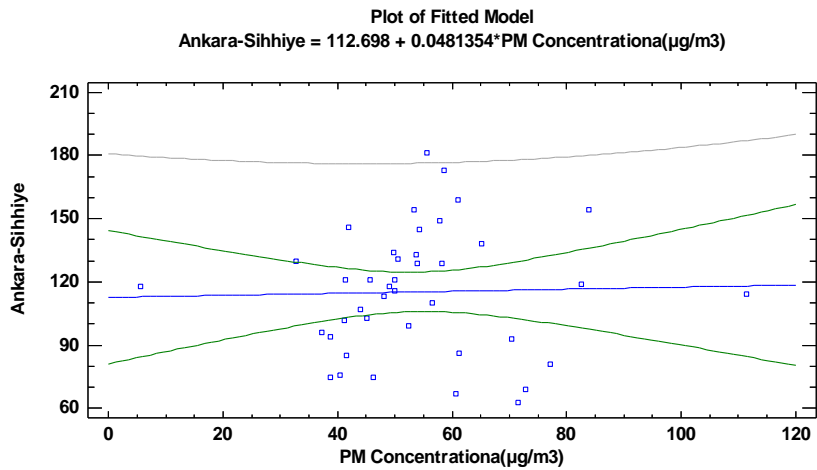
In this study, PM<sub>2.5</sub> samples are collected daily at Gate B, Beytepe campus of Hacettepe University (semi-rural) from 19 June-11 August and garden of General Directorate of Public Health of Turkey located in Sıhhiye (semi-rural) (19 June-11 August) and (29 December-27 January) on quartz filters (sampling interrupted between 3-13 of July due to power outage) in order to be analyzed for EC and OC with EC/OC analyzer and the generated data set was evaluated using various statistical methods. In addition, the real-time measurement obtained from the stations operated by the general directorate of meteorology was used and evaluated together with the PM<sub>2.5</sub> composition data produced in this study.

### 4.1 General Characteristics of Pollutant Concentrations

The concentrations of atmospheric pollutants usually change accidentally and vary with the amount of emissions and meteorological conditions. The frequency distribution of air pollutants is applied to study the statistical characteristics of data set and to assess how often an acute concentration level is exceeded during air pollution control plans development [66]. Distribution characteristics also help us choose the type of statistics that represent the data best.

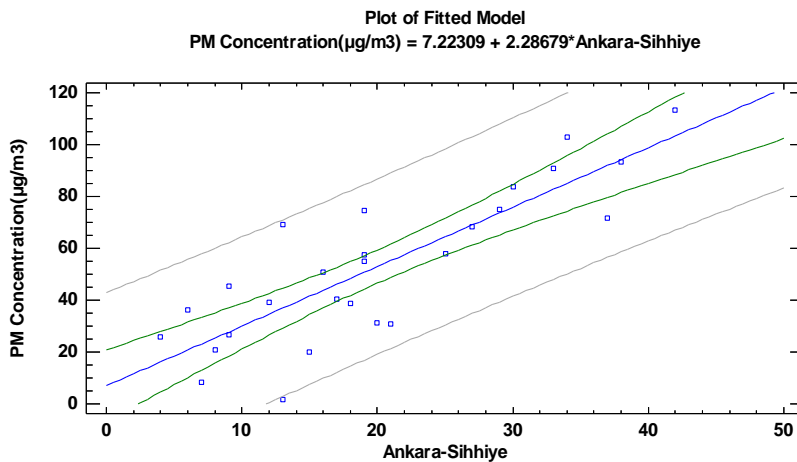
In this study PM<sub>2.5</sub> samples were collected during summer and winter and were compared with the gathered samples from stations of Çaldağ and TBMM during the same sampling period.

Figure 4.1 is showing simple regression plot for PM<sub>2.5</sub> concentrations collected at urban site during summer and PM<sub>2.5</sub> concentration measured by TBMM station at the same sampling period. Correlation coefficient  $R=0.02$  demonstrates that there is a relatively weak correlation between the variables.



**Figure 4.1.** Simple regression plot between collected PM<sub>2.5</sub> samples at urban site (summer) and TBMM station

Figure 4.2 is showing the simple regression plot performed between PM<sub>2.5</sub> concentrations collected at urban site during winter and PM<sub>2.5</sub> concentration measured by TBMM station at the same sampling period. Correlation coefficient R=0.83 indicates a moderately strong relation between the variables.



**Figure 4.2.** Simple regression plot between collected PM<sub>2.5</sub> samples at urban site (winter) and TBMM station

## 4.2 Statistical Summary of Pollutant Concentrations

In this study statistical description of measured concentrations are available in Table 4.1 and 4.2, such as average concentration with plus or minus standard deviation, median, geometric mean, maximum and minimum concentration ranges and number of detections. The values given in the Tables 4.1 and 4.2 are the daily average values.

During summer period at Sihhiye (urban) site, the mean concentration of  $PM_{2.5}$  was computed to be  $53.32 \pm 16.59 \mu\text{g m}^{-3}$  with maximum and minimum 111 and  $5.6 \mu\text{g m}^{-3}$  respectively. OC concentration  $7.63 \pm 1.87 \mu\text{g m}^{-3}$  with maximum and minimum 12.75 and  $4.86 \mu\text{g m}^{-3}$  respectively. EC mean concentration  $3.69 \pm 0.67 \mu\text{g m}^{-3}$  with maximum and minimum 8.88 and  $2.28 \mu\text{g m}^{-3}$  respectively. CC concentration  $0.98 \pm 0.56 \mu\text{g m}^{-3}$  with maximum and minimum 3.25 and  $0.37 \mu\text{g m}^{-3}$  respectively and TC  $12.27 \pm 2.65 \mu\text{g m}^{-3}$  with maximum and minimum 20.08 and  $7.96 \mu\text{g m}^{-3}$ .

During summer period at Beytepe campus (semi-urban) site these concentrations were estimated as following,  $PM_{2.5}$  was estimated  $46.34 \pm 15.43 \mu\text{g m}^{-3}$  with maximum and minimum 84.26 and  $13.99 \mu\text{g m}^{-3}$  respectively. OC concentration  $5.8 \pm 1.35 \mu\text{g m}^{-3}$  with maximum and minimum 8.89 and  $3.27 \mu\text{g m}^{-3}$  correspondingly. EC concentration  $1.26 \pm 0.35 \mu\text{g m}^{-3}$  with maximum and minimum 2.09 and  $0.53 \mu\text{g m}^{-3}$  correspondingly. CC concentration  $0.85 \pm 0.33 \mu\text{g m}^{-3}$  with maximum and minimum 1.73 and  $0.34 \mu\text{g m}^{-3}$  correspondingly and TC  $7.92 \pm 1.84 \mu\text{g m}^{-3}$  with maximum and minimum 11.59 and  $4.85 \mu\text{g m}^{-3}$  respectively.

During winter period at Sihhiye (urban) site the results are as following, the mean concentration of  $PM_{2.5}$  was estimated  $51.27 \pm 27.96 \mu\text{g m}^{-3}$  with maximum and minimum 113.28 and  $2.01 \mu\text{g m}^{-3}$  respectively. OC concentration  $14.21 \pm 8.46 \mu\text{g m}^{-3}$  with 39.25 and  $4.91 \mu\text{g m}^{-3}$  respectively. EC concentration  $3.65 \pm 1.48 \mu\text{g m}^{-3}$  with maximum and minimum 7.84 and  $1.60 \mu\text{g m}^{-3}$  respectively and TC  $17.86 \pm 9.59 \mu\text{g m}^{-3}$  with maximum and minimum 45.81 and  $7.03 \mu\text{g m}^{-3}$  respectively. It needs to be mentioned that in summer due to wet weather, precipitation and floor dust raise, no CC was emitted and sampled. Although the emissions from sources may be almost fixed, the consecutive mixing and dilution of pollutants as they are carried from source to receiver cause a log-

normal distribution of the ambient concentrations[67]. As displayed in Tables 4.1 and 4.2, arithmetic means differ from median values, suggest a deviation from symmetric Gaussian distribution.

Skewness defines the asymmetry degree of a distribution around its average. Zero shows. A symmetric Gaussian distribution Positive skewness shows a distribution with an asymmetric tail extending toward more positive values. In comparison, negative skewness shows a distribution with an asymmetric tail extending toward more negative values.

#### **4.2.1 Frequency Distributions of Measured Data**

In this study, Statgraphics was employed as a software to show if the log-normal distribution fits the data appropriately by using Kolmogorov-Smirnov test. This test computes the maximum difference between the accumulative distribution of the variable and the accumulative distribution role of the fitted log-normal distribution and accordingly  $p < 0.05$  shows data are normally distributed and  $P > 0.05$  shows non-normal distribution. For majority of data we see lognormal distribution. Data showed significant skewness for OC, EC, CC and TC except for EC summer period.

Table 4.1 and 4.2 are showing the statistical summary of the sampling data in  $PM_{2.5}$  aerosols during summer and winter sampling period.

**Table 4.1.** Summary statistics of elemental concentrations in PM<sub>2.5</sub> aerosols (Sihhiye) (Concentration unit:  $\mu\text{g m}^{-3}$ )

Parameter		N	Mean	Mean $\pm$ SD	Geo. Mean	Median	Max	Skewness	Kurtosis	Kolmogorov-Smirnov Test (lognormality)	Distribution
PM <sub>2.5</sub>	sum	45	53.32	53.32 $\pm$ 16.59	50.17	50.48	111	1.98	4.75	Log 0.1 Nor 0.3	Not lognormal Not normal
	win	30	51.27	51.27 $\pm$ 27.96	41.31	43.5	113.2	1.001	-0.48	0.42 0.62	Not lognormal Not normal
	total	75	52.5	52.5 $\pm$ 21.7		50.1	113.2	1.68	1.55	0.01	lognormal
OC	sum	45	7.63	7.63 $\pm$ 1.87	7.41	7.24	12.75	2.12	0.38	0.8 0.5	Not lognormal Not normal
	win	30	14.21	14.21 $\pm$ 8.46	12.10	10.81	39.24	2.49	1.06	0.62 0.26	Not lognormal Not normal
	total	75	10.26	10.26 $\pm$ 6.38		8.14	39.24	8.12	10.41		normal
EC	sum	45	3.69	3.69 $\pm$ 0.67	4.40	5.59	8.88	-0.35	-0.78	0.94 0.87	Not lognormal Not normal
	win	30	3.65	3.65 $\pm$ 1.48	3.48	3.36	7.83	2.36	1.05	0.94 0.35	Not lognormal Not normal
	total	75	3.67	3.67 $\pm$ 1.06		3.59	7.83	3.62	4.65		lognormal
CC	sum	45	0.98	0.98 $\pm$ 0.56	0.88	0.85	3.25	7.06	10.88	0.59 0.06	not lognormal not normal
	win	-	-	-	-	-	-	-	-	-	
	total	45	0.98	0.98 $\pm$ 0.56		0.85	3.25	7.06	10.88		lognormal
TC	sum	45	12.27	12.27 $\pm$ 2.65	12	12.07	20.08	2.12	1.08	0.96 0.83	Not lognormal Not normal
	Win	30	17.86	17.86 $\pm$ 9.59	15.92	14.96	45.81	2.46	0.97	0.57 0.28	Not lognormal Not normal
	total	75	14.51	14.51 $\pm$ 6.92		12.3	45.81	7.77	10.21		normal

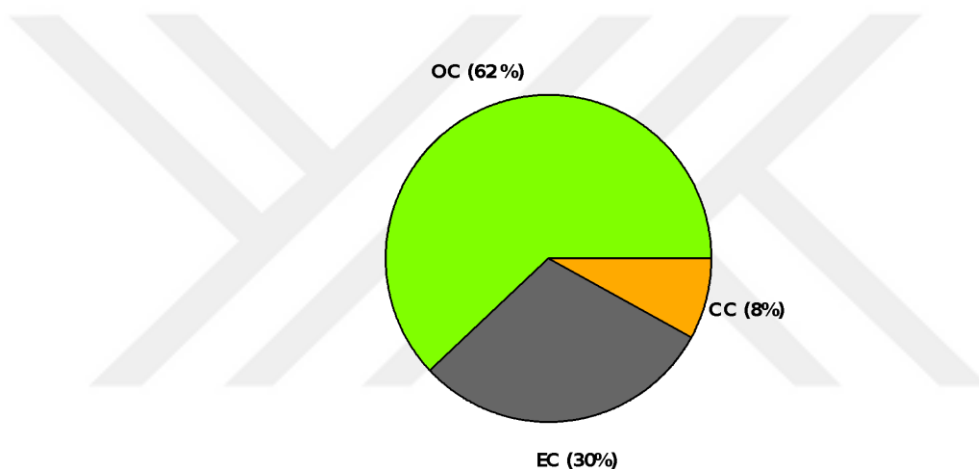
**Table 4.2.** Summary statistics of elemental concentrations in PM<sub>2.5</sub> aerosols (Beytepe) (Concentration unit:  $\mu\text{g m}^{-3}$ )

Parameter	N	Season	Mean	Mean $\pm$ SD	Median	Geo. Mean	Max	Skewness	Kurtosis	Kolmogorov-Smirnov test	Distribution
<b>PM<sub>2.5</sub></b>	45	sum	46.34	46.34 $\pm$ 15.43	44.34	43.67	84.26	1.002	-0.08	0.95 0.94	Not lognormal Not normal
<b>OC</b>	45	sum	5.8	5.8 $\pm$ 1.35	5.59	5.59	8.89	0.99	-0.89	0.93 0.72	Not lognormal Not normal
<b>EC</b>	45	sum	1.26	1.26 $\pm$ 0.35	1.27	1.27	2.09	0.28	-0.70	0.94 0.97	Not lognormal Not normal
<b>CC</b>	45	sum	0.85	0.85 $\pm$ 0.33	0.86	0.86	1.73	1.50	0.27	0.7 0.88	Not lognormal Not normal
<b>TC</b>	45	sum	7.92	7.92 $\pm$ 1.84	7.89	7.89	11.59	0.48	-1.3	0.87 0.96	Not lognormal Not normal

The European Air Quality Directive 1999/30/EC set a yearly mean limit value of  $40 \mu\text{g m}^{-3}$  for  $\text{PM}_{10}$  and lately, the limit on  $\text{PM}_{2.5}$  concentrations recommended by the European Commission is  $25 \mu\text{g m}^{-3}$ , averaged during a year. The values shown in the tables for  $\text{PM}_{2.5}$  are quiet higher than this limit value.

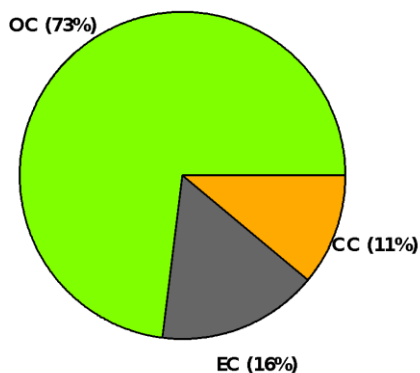
### 4.3 Contribution of OC, EC and CC to TC

Contributions of OC, EC and CC to total carbon at two stations are calculated and are shown in figures 4.3, 4.4 and 4.5.



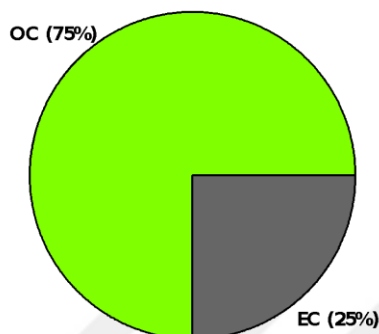
**Figure 4.3.**Contribution of OC, EC and CC at urban site in summer

At urban site during summer, OC with 62% has the largest contribution to  $\text{PM}_{2.5}$  mass concentration. Then EC and CC respectively with 30 % and 8 %.



**Figure 4.4.**Contribution of OC, EC and CC at semi-rural area in summer

Similarly at the semi-urban site during summer, contribution of OC, EC and CC to PM<sub>2.5</sub> were 73 %, 16 % and 11 % respectively.



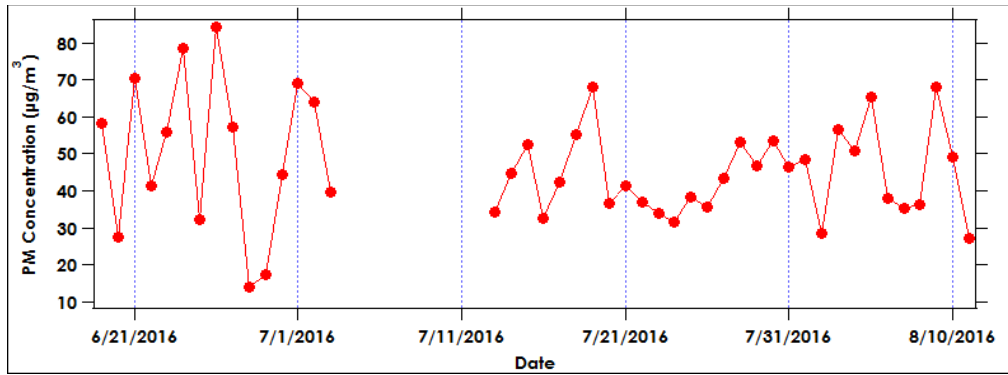
**Figure 4.5.**Contribution of OC and EC at urban site in winter

In winter period at urban site the contribution of OC and EC were 75% and 25% respectively.

#### **4.4 Temporal Variation of the PM<sub>2.5</sub>, OC, EC, CC and TC Concentration**

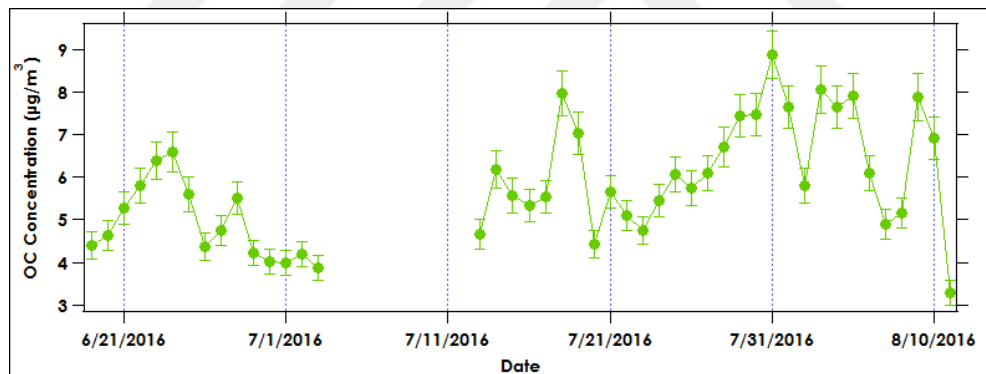
Time-depending variation of PM<sub>2.5</sub>, OC, EC, CC and TC at Beytepe in summer period are shown in the figures 4.4. to 4.9.The dots are showing daily average concentrations. July 3-13 sampling was interrupted so there is no data available.

Figure 4.6 is showing temporal variation of PM<sub>2.5</sub> concentration during summer in Beytepe. Average PM<sub>2.5</sub> concentration in this period is 46.35  $\mu\text{g m}^{-3}$  .Maximum concentration is 84.26  $\mu\text{g m}^{-3}$  which belongs to June 26<sup>th</sup> and minimum concentration is 13.99  $\mu\text{g m}^{-3}$  which belongs to June 28<sup>th</sup>.On the 26<sup>th</sup> June there is an increase in PM<sub>2.5</sub> concentration and a Sahara storm event is seen on that date. On 28<sup>th</sup> and 29<sup>th</sup> of June the decrease on PM<sub>2.5</sub> concentration is due to precipitation. The decrease of PM concentration on 20<sup>th</sup> of July is due to precipitation. On August 6<sup>th</sup>, 7<sup>th</sup> and 10<sup>th</sup> also the decrease is due to precipitation.



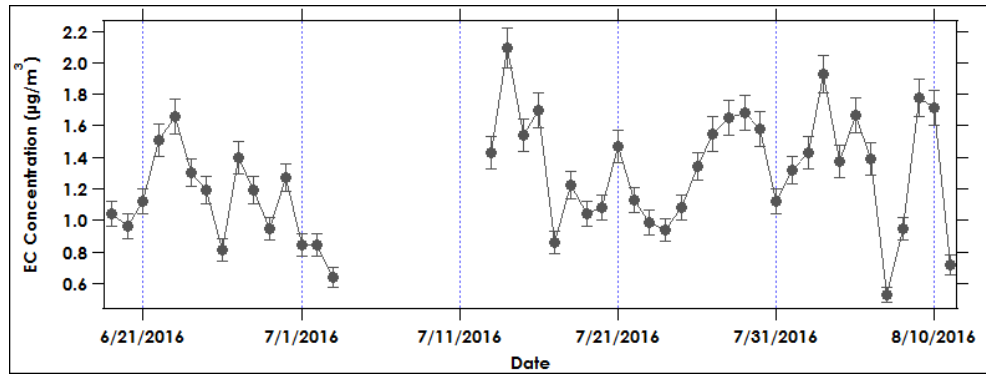
**Figure 4.6.**Temporal variation of the PM<sub>2.5</sub> concentration determined during summer sampling period at Beytepe

Figure 4.7 is showing the time-depending variation of OC concentration in Beytepe during summer sampling period. Average concentration of OC is  $5.80 \mu\text{g m}^{-3}$ . Maximum OC concentration is  $8.99$  and minimum is  $3.27 \mu\text{g m}^{-3}$ .



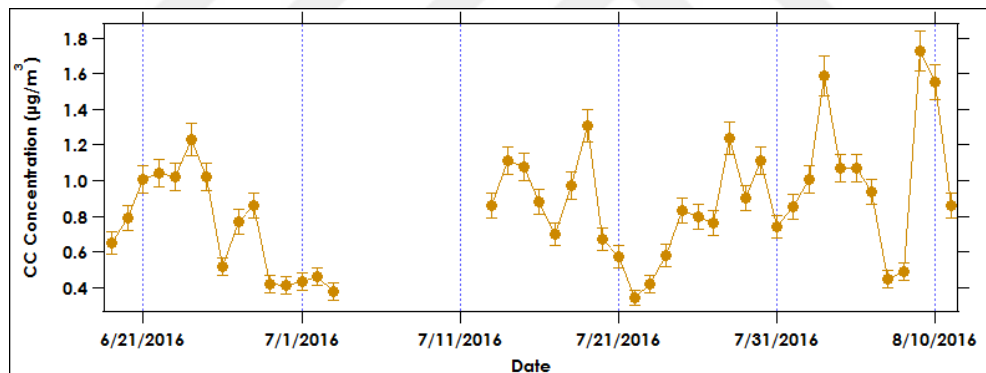
**Figure 4.7.**Temporal variation of the OC concentration determined during summer sampling period at Beytepe

Figure 4.8 shows the temporal variation of EC concentration in summer sampling period in Beytepe. Average concentration of EC is  $1.27 \mu\text{g m}^{-3}$ . Maximum concentration is  $2.09$  and minimum is  $0.53 \mu\text{g m}^{-3}$



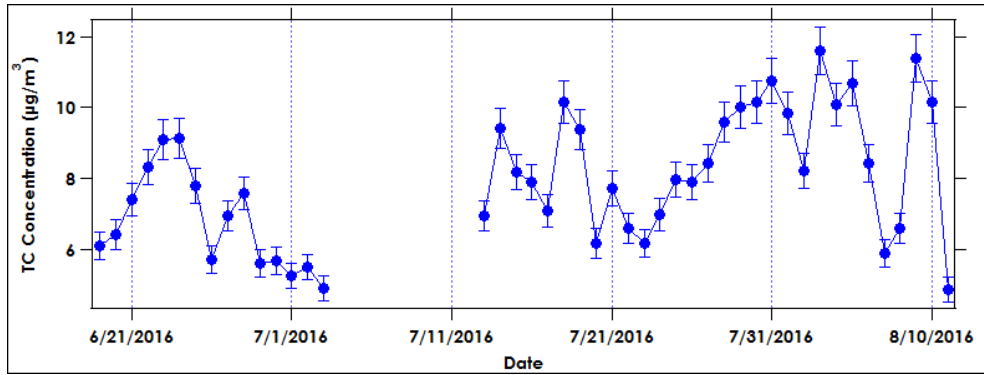
**Figure 4.8.**Temporal variation of the EC concentration determined during summer sampling period at Beytepe

Figure 4.9 shows time-dependent variation of CC in Beytepe in summer sampling period. Mean concentration of CC in this period is  $0.86 \mu\text{g m}^{-3}$ . Maximum and minimum concentrations are  $1.73$  and  $0.34 \mu\text{g m}^{-3}$  respectively.



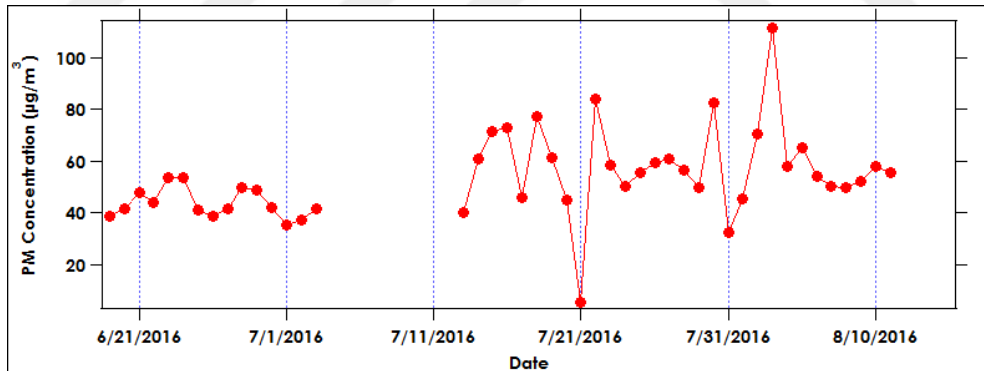
**Figure 4.9.**Temporal variation of the CC concentration determined during summer sampling period at Beytepe

Figure 4.10 shows temporal variation of TC in Beytepe in summer sampling period. Mean concentration is  $7.92 \mu\text{g m}^{-3}$ . Maximum and minimum concentrations are respectively  $11.59$  and  $4.85 \mu\text{g m}^{-3}$ .



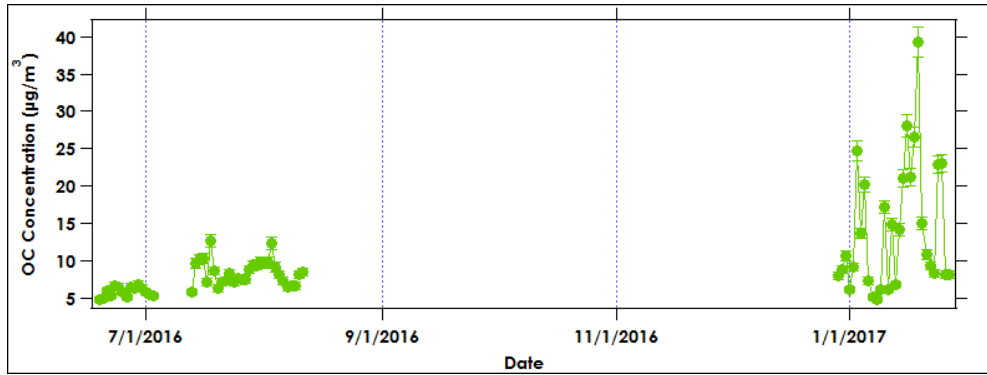
**Figure 4.10.** Temporal variation of the TC concentration determined during summer sampling period at Beytepe

Figures 4.11 to 4.15 are showing the temporal variation of summer and winter period at Sihhiye sampling site. Figure 4.11 is showing temporal variation of PM<sub>2.5</sub> concentration at Sihhiye during summer sampling period. The mean concentration of PM<sub>2.5</sub> was computed to be 53.32 µg m<sup>-3</sup> with maximum and minimum 111 µg m<sup>-3</sup> (3 August) and 5.6 µg m<sup>-3</sup> (21 July) respectively.



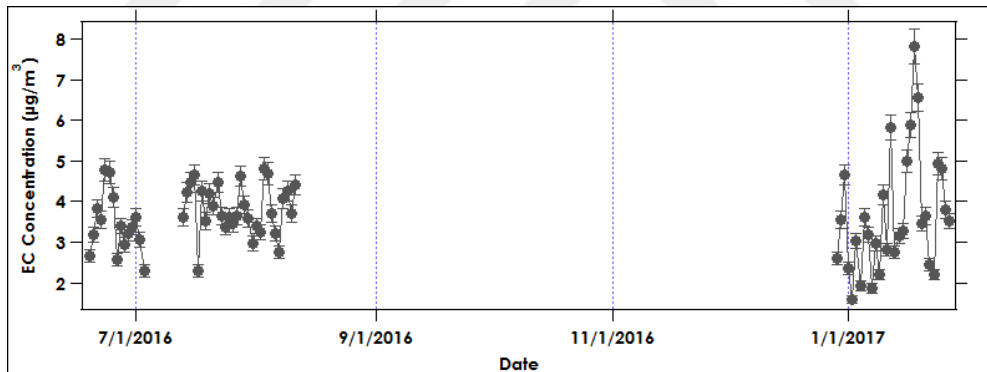
**Figure 4.11.** Temporal variation of the PM<sub>2.5</sub> concentration determined during summer sampling period at Sihhiye

Figure 4.12 is showing temporal variation of OC concentration during summer and winter sampling period at Sihhiye. OC concentrations vary in a big scale and higher in winter sampling period. Mean concentration of OC is 7.63 and 14.21 µg m<sup>-3</sup> in summer and winter respectively.



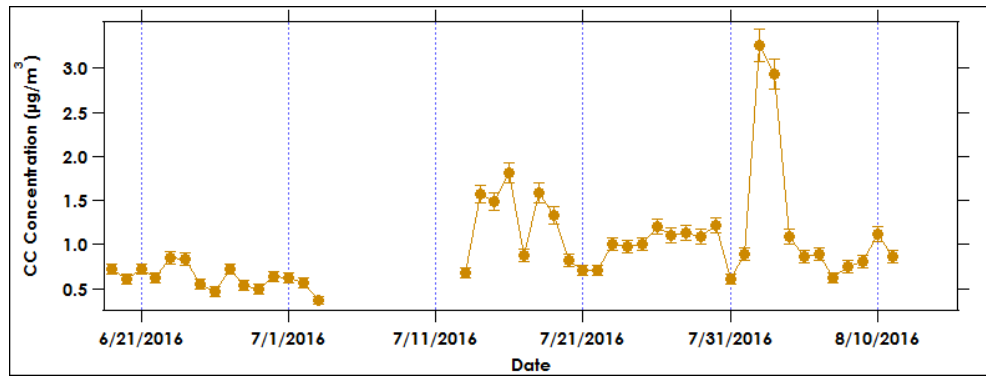
**Figure 4.12.**Temporal variation of the OC concentration determined during summer sampling period at Sihhiye

Figure 4.13 is showing time-depending variation of EC concentration during summer and winter sampling period at Sihhiye. Although EC concentrations change in a variable scale in winter, there is not a big difference between mean concentrations regarding the season. Mean concentration of EC in summer and winter are 3.69 and 3.65  $\mu\text{g m}^{-3}$  respectively.



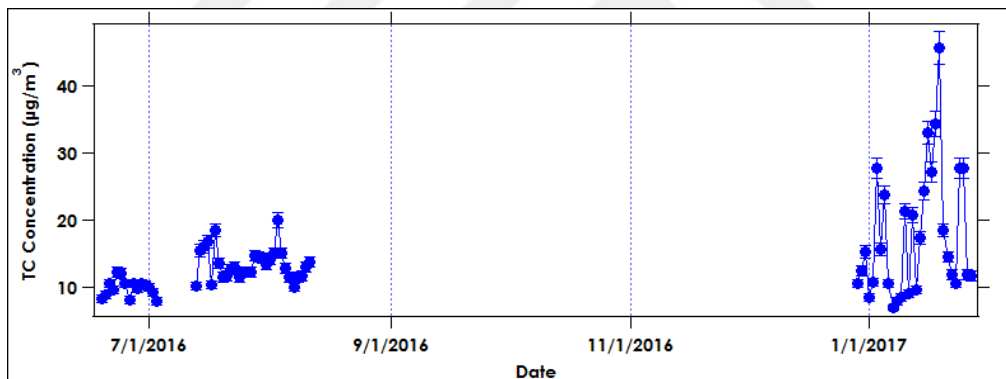
**Figure 4.13.**Temporal variation of the EC concentration determined during summer sampling period at Sihhiye

Figure 4.14 is showing time-depending variation of the CC concentration determined during summer sampling period at Sihhiye in summer. Mean concentration of CC is calculated 3.26  $\mu\text{g m}^{-3}$ .



**Figure 4.14.**Temporal variation of the CC concentration determined during summer sampling period at Sihhiye

Figure 4.15 is showing temporal variation of the TC concentration determined during summer and winter sampling period at Sihhiye. TC concentrations is higher in winter. 12.27 and 17.87  $\mu\text{g m}^{-3}$  in summer and winter correspondingly.

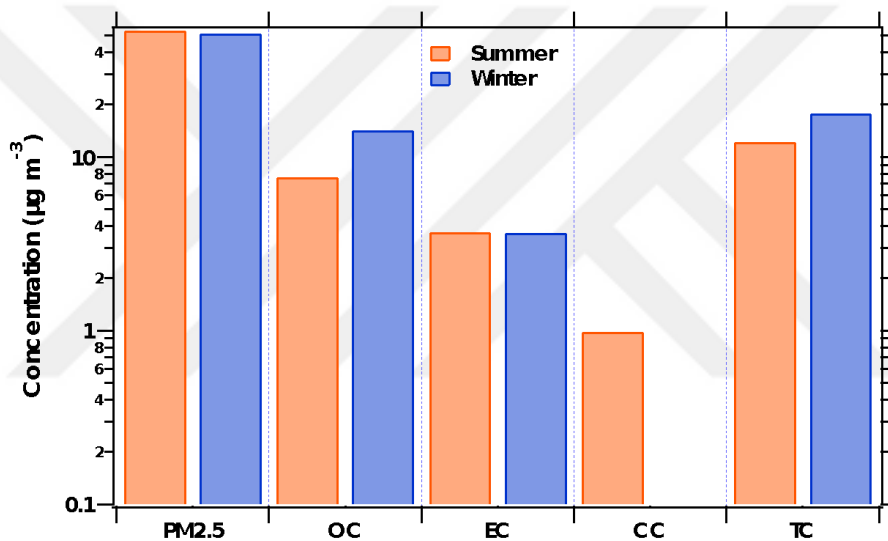


**Figure 4.15.**Temporal variation of the TC concentration determined during summer and winter sampling period at Sihhiye

#### 4.4.1 Seasonal Variation of Pollutant Concentrations

Since human-caused activities and natural processes that release atmospheric pollutants are changeable in different seasons, pollutants in the atmosphere are also linked to these seasonally activities. An examination of the seasonality of pollutants provides information about the predominant sources in the environment. For the parameters evaluated in this study, summer and winter data for Sihhiye station are shown in Figure 4.16.

Figure 4.16 is showing comparison of mean concentration of PM<sub>2.5</sub>, OC, EC, CC and TC between summer and winter period at semi-urban site. PM mean concentration during summer sampling period is 53.32  $\mu\text{g m}^{-3}$  and during winter sampling period is 51.27  $\mu\text{g m}^{-3}$ . OC mean concentration in summer and winter are 7.63 and 14.21  $\mu\text{g m}^{-3}$  correspondingly. EC mean concentration in summer and winter are 3.69 and 3.65  $\mu\text{g m}^{-3}$  relatively. CC mean concentration in summer is 0.98  $\mu\text{g m}^{-3}$ . In winter due to precipitation and wet land there is not any CC seen. TC mean concentration for summer and winter sampling period are 12.27 and 17.87  $\mu\text{g m}^{-3}$  correspondingly.



**Figure 4.16.** Comparing mean concentration of PM<sub>2.5</sub>, OC, EC, CC and TC between summer and winter period at urban site ( $\mu\text{g m}^{-3}$ )

#### 4.5 T-test

This test is performed to compare number of samples to check if there is a meaningful difference between their means. The p-value is the probability that 't' falls into a certain range. For our purposes, a p-value  $\leq 0.05$  shows a meaningful difference between the average value of sample population and null hypothesis would be rejected. A p-value  $> 0.05$  suggests no significant difference between the means of our sample populations and null hypothesis wouldn't be rejected. (If the p-value for the test is less than 0.05, the null hypothesis is rejected at the 95.0% confidence level). T-test was run

to compare the average concentration of  $PM_{2.5}$ , OC, EC, CC, TC between two sampling locations (Sihhiye and Beytepe campus) in summer and the results are given in the tables 4.3 and 4.4. According to the results, p-value for  $PM_{2.5}$  is calculated 0.04 and because it is less than 0.05, there is a statistical difference between mean concentrations of  $PM_{2.5}$  in two locations.



**Table 4.3.**T-test results in different locations ( $\mu\text{g m}^{-3}$ )

Summer	Sihhiye (location 1)	Beytepe Campus (location2)	T-test P- value		t-test result
<b>PM<sub>2.5</sub></b>	53.32±16.59	46.34±15.43	0.04	0.04<0.05	The means are different at CL 95%.
<b>OC</b>	7.63±1.87	5.8±1.35	7.72	7.72>0.05	The means are not different at CL 95%.
<b>EC</b>	5.80±0.66	1.26±0.35	0	0<0.05	The means are different at CL 95%.
<b>CC</b>	0.98±0.56	0.85±0.33	0.1	0.1>0.05	The means are not different at CL 95%.
<b>TC</b>	12.27±2.65	7.92±1.84	3.35	3.35>0.05	The means are not different at CL 95%.
<b>OC/EC</b>	2.12±0.5	4.76±1.22	0	0<0.05	The means are different at CL 95%.
<b>TC/EC</b>	3.35±0.55	6.46±1.31	0	0<0.05	The means are different at CL 95%.

**Table 4.4.**T-test results for Sihhiye in different seasons ( $\mu\text{g m}^{-3}$ )

	<b>Sihhiye summer</b>	<b>Sihhiye winter</b>	<b>t-test P-value</b>		<b>t-test result</b>
<b>PM<sub>2.5</sub></b>	53.32 ± 16.59	51.27 ± 27.96	0.69	0.69>0.05	The means are not different at CL 95%.
<b>OC</b>	7.63 ± 1.87	14.21 ± 8.46	0.000003	0.000003<0.05	The means are different at CL 95%.
<b>EC</b>	5.80 ± 0.66	3.65 ± 1.48	1.19	1.19 >0.05	The means are not different at CL 95%.
<b>CC</b>	0.98 ± 0.56	-	-	-	-
<b>TC</b>	12.27±2.65	17.86±9.59	0.0003	0.0003<0.05	The means are different at CL 95%.

#### **4.6 Meteorological Data**

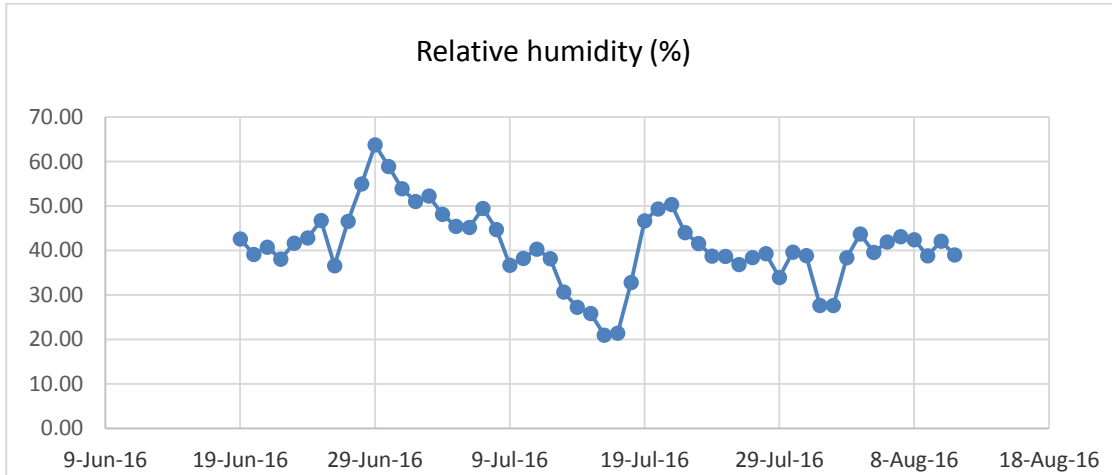
Meteorological variables influence physical, chemical and photochemical properties of particles [68]. Changes in local meteorology influence the transportation, dispersion and dilution of pollutants in the atmosphere [69]. Thus the meteorological variables obtained by General Directorate of Meteorology in Ankara from different stations were evaluated together with the data obtained in the study. In this study meteorological data was received from TBMM station for urban site and from Çaldağ station for semi-rural site.

The meteorological variables of Ankara (temperature(T), relative humidity(RH), wind speed(WS), wind direction(WD), precipitation, pressure(P) and mixing height) from 19 June-11 August 2016 and 29 December 2016 to 27 January 2017 were evaluated and results are shown in table 4.5.

**Table 4.5.** Meteorological variables obtained by General Directorate of Meteorology

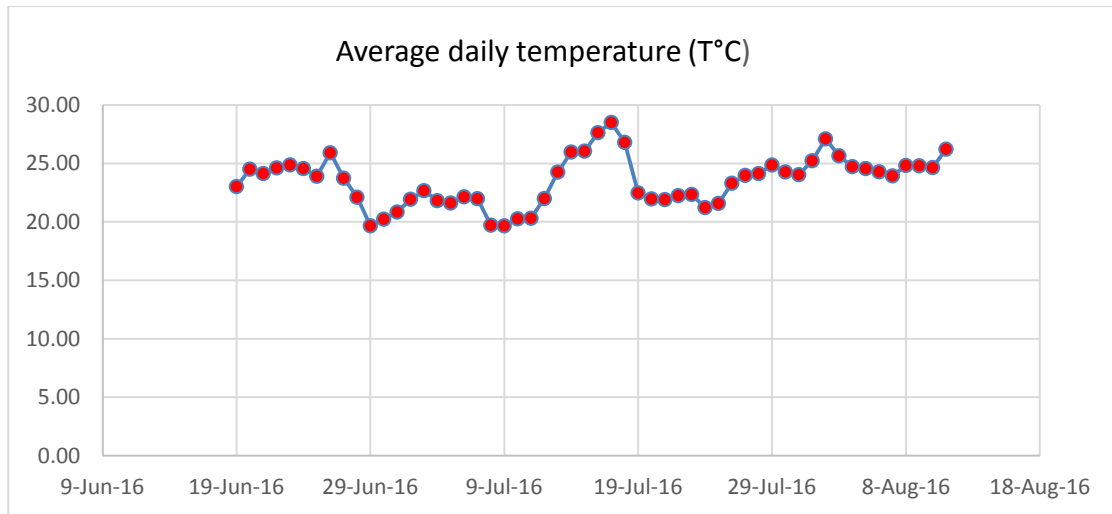
Site	Period	T(°C) Ave. ± SD	RH Ave.± SD	Min T(°C)	Max T(°C)	Total precipitation (mm)	Ave. WS(m/s)	Max WS (m/s)	Pressure (hpa)
Sihhiye (TBMM)	Summer	25.5 ± 4.8	41 ± 8.38	12.4	35.6	2.7	1.53	7.4	907.45
	Winter	-0.25 ± 5.25	68.44 ± 17	-19	16.8	58.6	1.25	9	910.7
Beytepe (Çaldağ)	Summer	21 ± 4.49	45.61 ± 18.36	10.1	33.3	7.4	3.48	9.7	-

Temporal variation of RH, T and Pressure for stations are depicted in following figures. Figure 4.17 is showing change of relative humidity at urban site during summer period. Average relative humidity for this sampling site is 41%.



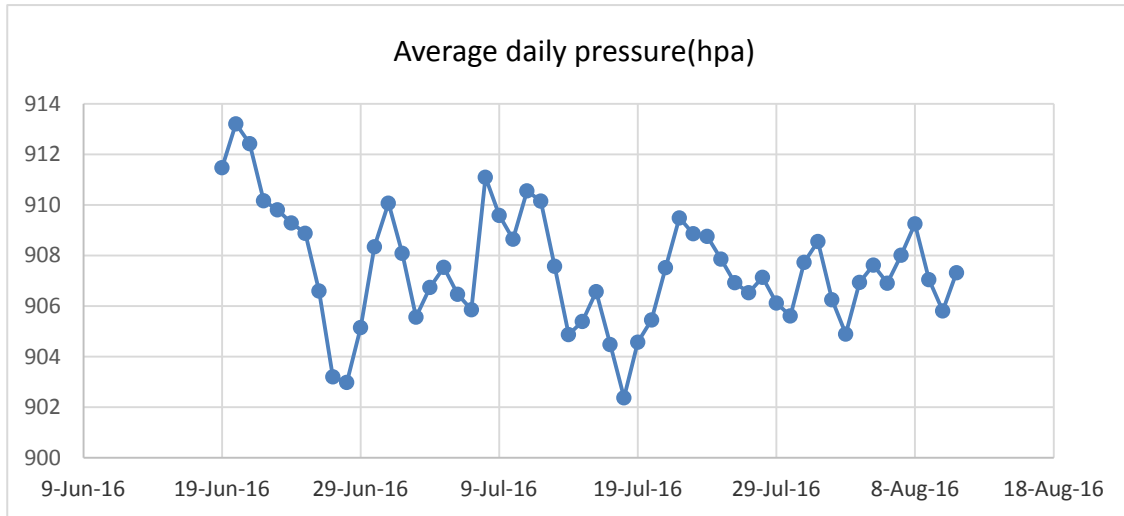
**Figure 4.17.** Time-dependent change of relative humidity at Sihhiye site in summer

Figure 4.18 is showing variation of temperature at Sihhiye site in summer. Average temperature in summer period at this site is calculated 25.5°C with minimum and maximum 12.4 and 35.6°C correspondingly.



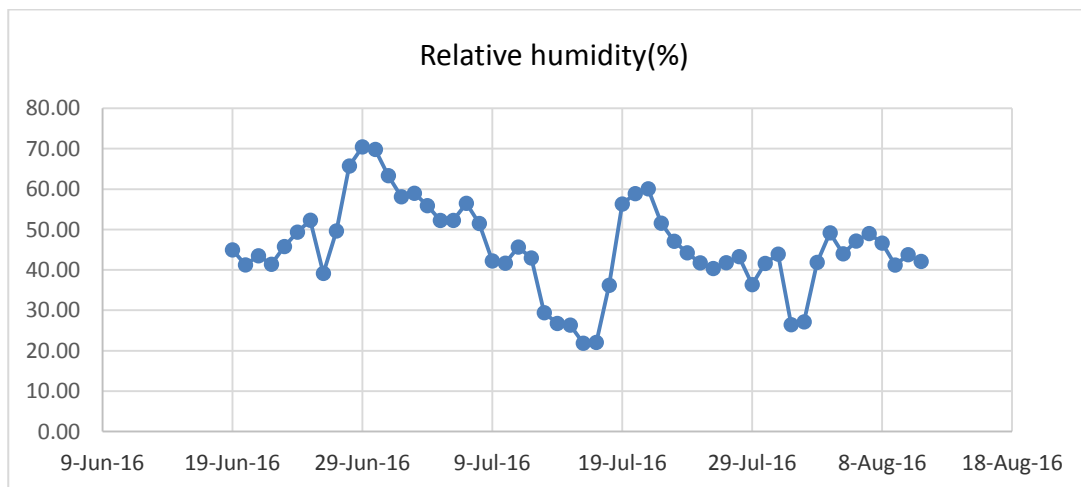
**Figure 4.18.** Time-dependent change of temperature at Sihhiye site in summer

Figure 4.19 is showing variation of daily pressure at urban site during summer. Average daily pressure is calculated 907.45 hpa in this sampling period.



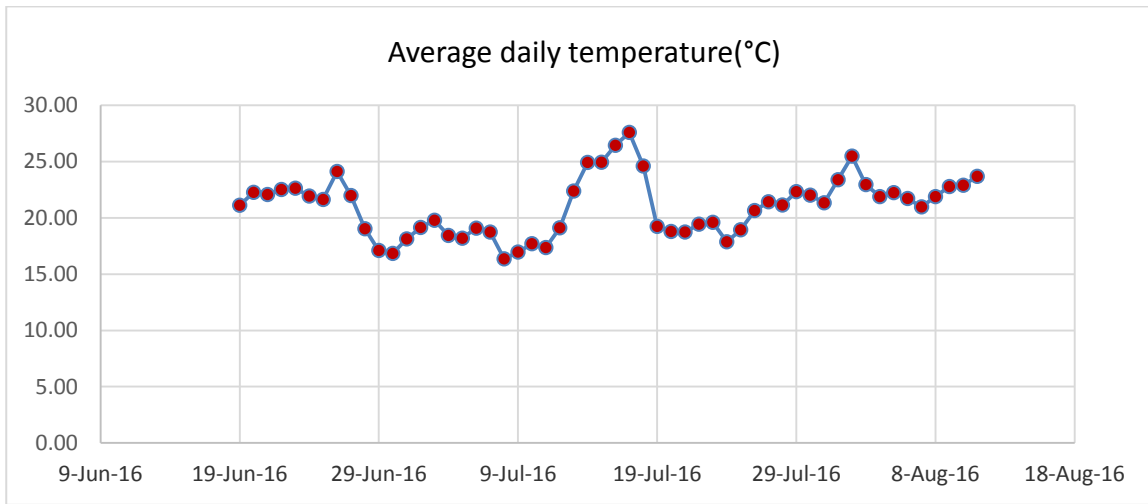
**Figure 4.19.** Time-dependent change of pressure at Sihhiye site in summer

Time-dependent change of meteorological data at Beytepe site in summer are shown in the following figures. Figure 4.20 shows variation of relative humidity during summer at sub-urban site. Average humidity in summer sampling period at Beytepe is calculated 45.61%.



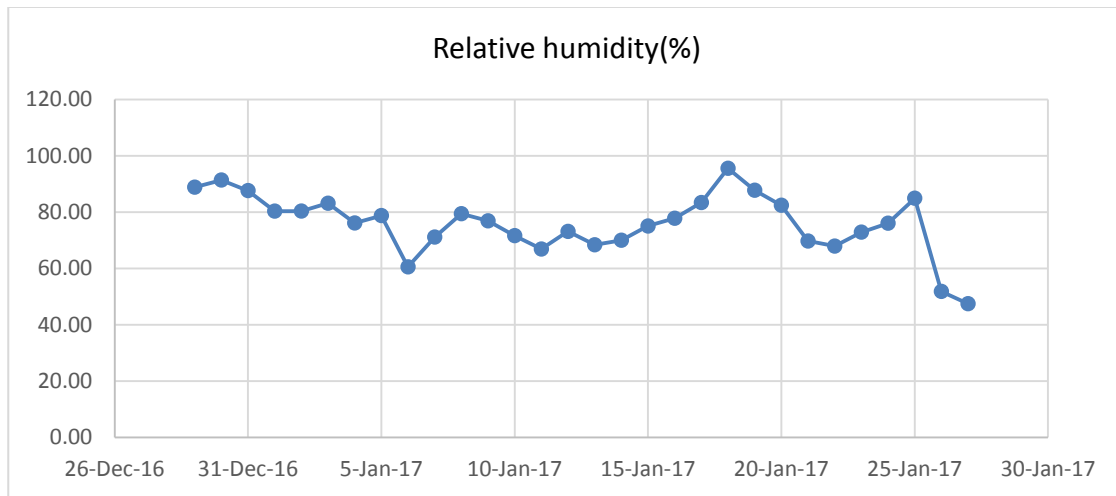
**Figure 4.20.** Time-dependent change of relative humidity at Beytepe in summer

Figure 4.21 is showing time-dependent change of meteorological data at Beytepe in summer. Average temperature is 21°C with minimum and maximum 10.1 and 33.3 °C.



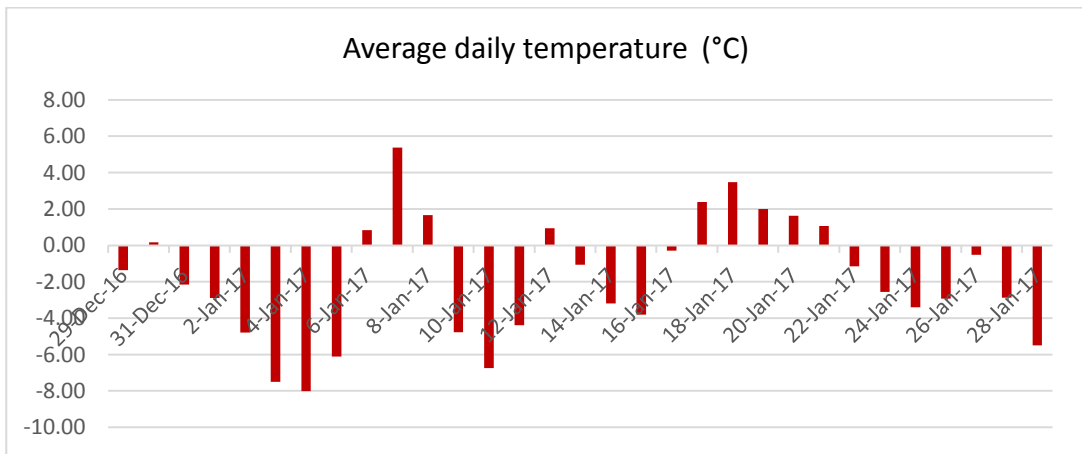
**Figure 4.21.** Time-dependent change of meteorological data at Beytepe site in summer

Time-dependent change of meteorological data at Sihhiye during winter are depicted in following figures. Figure 4.22 is showing variation of relative humidity at Sihhiye during winter sampling period. Average humidity is calculated 68.44 %.



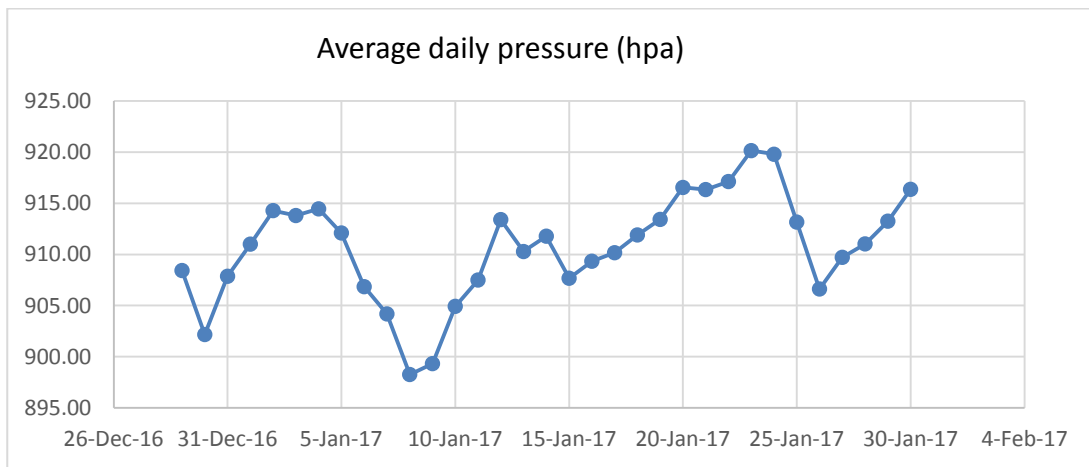
**Figure 4.22.** Time-dependent change of relative humidity at Sihhiye during winter

Figure 4.23 is showing time-dependent change of relative humidity at Sihhiye during winter sampling period. Average temperature in this period is  $-0.25^{\circ}\text{C}$  with minimum and maximum  $16.8$  and  $58.6^{\circ}\text{C}$ .



**Figure 4.23.** Time-dependent change of relative humidity at Sihhiye during winter

Figure 4.24 is showing Time-dependent change of pressure at Sihhiye during winter. Average pressure in this period is  $910.7$  hpa.



**Figure 4.24.** Time-dependent change of pressure at Sihhiye during winter

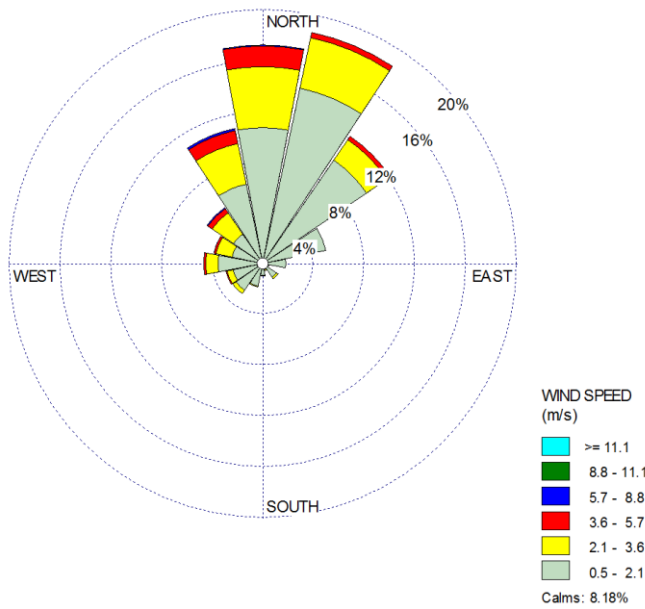
Temperature which is one of the most significant variables especially in determining the speed of photochemical reactions was determined  $-0.25 \pm 5.25$  °C and  $25.5 \pm 4.8$  °C in winter and summer period correspondingly in urban site (Sihhiye). In winter period  $-19^{\circ}\text{C}$  and  $16.8$  °C were minimum and maximum reported temperature and  $12.4$  °C and  $35.6$

°C were reported minimum and maximum temperature in summer period respectively. Average temperature in semi-rural site (Beytepe) was  $21 \pm 4.49$  °C in summer sampling period with reported minimum and maximum 10.1°C and 33.3°C correspondingly. In addition to temperature, the average relative humidity is  $41 \pm 8.38$  % and  $68.44 \pm 17$  % for summer and winter period in urban site (Sihhiye) respectively. Average humidity was  $45.61 \pm 18.36$  % for summer period in semi-rural (Beytepe) site. Total precipitation was 2.7 mm and 58.6 mm in urban site for summer and winter period correspondingly. Total precipitation was recorded 3.48 mm in summer period at semi-urban site.

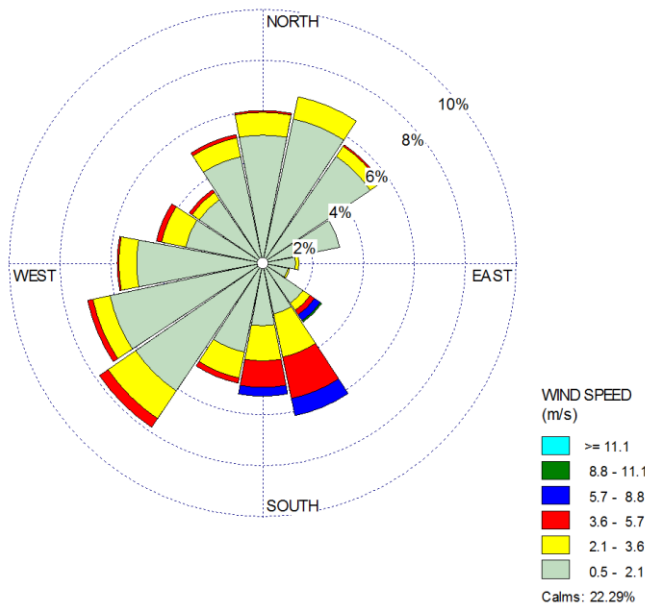
#### **4.6.1 Wind Roses at the Sampling Sites**

Wind observations during sampling are shown in figures 4.23, 4.24 and 4.25 to show the impact of local emission sources. Winds which are near to surface are an illustrative factor in local-scale transport, but upper air winds must be studied to determine regional-scale transport.

The changes in wind speed and direction at the sampling sites were investigated in this study and results were depicted in Figures 4.25 and 4.27 for Sihhiye station and 4.25 for Beytepe. The data is taken from General Directorate of Meterology in Ankara. For Sihhiye sampling site, data are used from TBMM station and for Beytepe sampling site, and data from Çaldağ station are used.



**Figure 4.25.**Wind rose of TBMM in summer sampling period

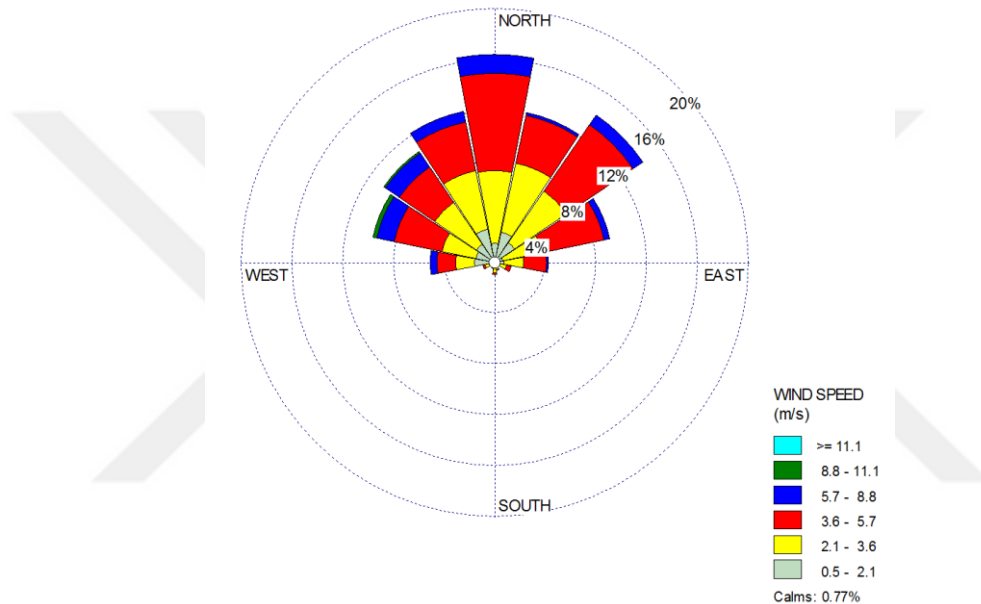


**Figure 4.26.**Wind rose of TBMM during winter sampling period

It has been shown that the prevailing wind is northeast in summer sampling period. In addition, it can be deduced that the north direction is secondary dominant direction

affecting the station in summer sampling period .Average wind speed in summer period is 1.53 m/s.

The dominant wind direction is southwest in winter sampling period, but northeast direction is a secondary dominant direction which is shown to be affecting the station. Average wind direction is 1.25 m/s in winter sampling period.



**Figure 4.27.**Wind rose for Çaldağ in summer sampling period

The prevailing wind direction is northern in summer sampling period at semi-rural site (Beytepe) but as it is shown in the figure, northeastern wind is secondary dominant wind direction affecting the station .Average wind speed is 3.48 m/s in summer sampling period at semi-rural site.

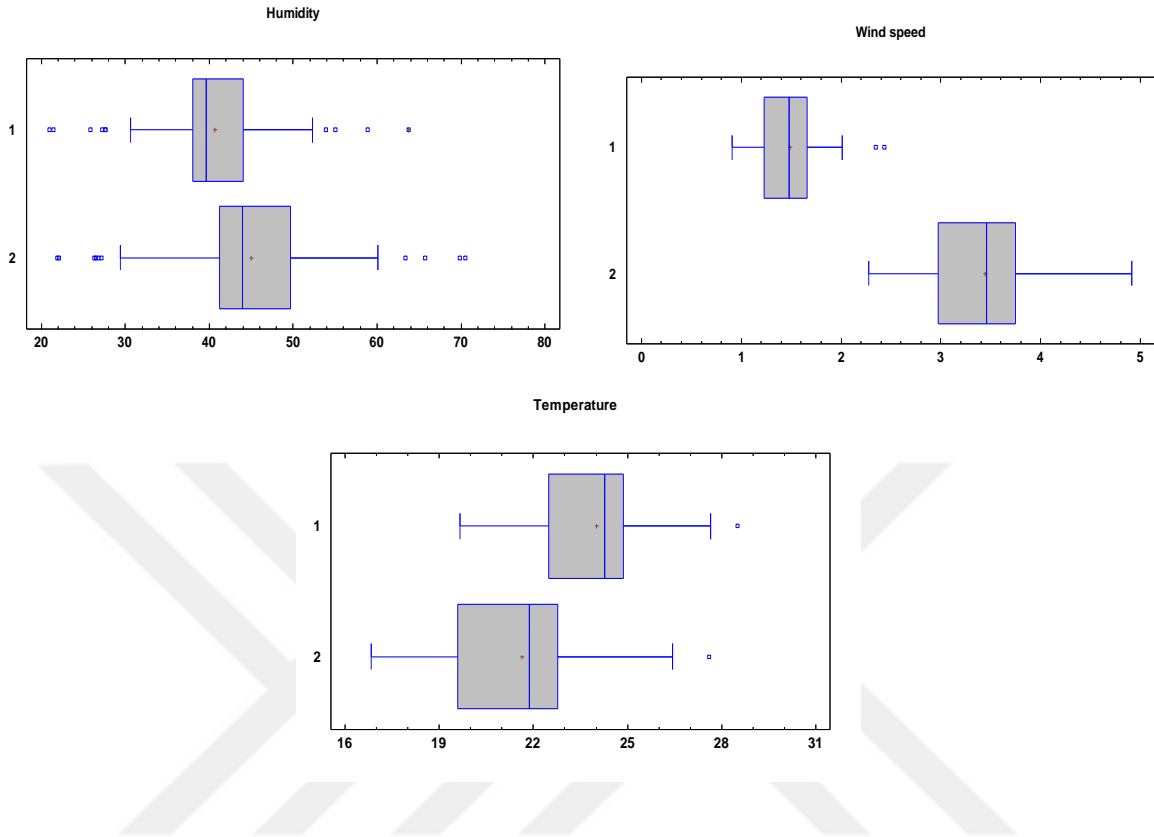
#### 4.7 Seasonal Variation of Meteorological Parameters

ANOVA test is performed to see if there is statistically difference between mean concentrations of meteorological data at two different sites (urban and semi-urban) during summer sampling period.

**Table 4.6.**One way ANOVA analysis result and P-values for different locations ( $\mu\text{g m}^{-3}$ )

<b>Parameter</b>	<b>Location</b>	<b>mean</b>	<b>P-value</b>
<b>Temperature</b>	Sihhiye 1	24	<b>0.0000</b>
	Beytepe 2	21.6	
<b>Humidity</b>	Sihhiye 1	9.02	<b>0.05</b>
	Beytepe 2	11.7	
<b>Wind speed</b>	Sihhiye 1	0.35	<b>0.0000</b>
	Beytepe 2	0.61	

Table 4.6 shows the result of one way ANOVA test and the P-values. This ANOVA test is performed to see whether there is statistically meaningful difference between mean concentrations of meteorological data at two different sites (urban and semi-urban) during summer sampling period. For the P-value is smaller than 0.05, there is a significant difference between the mean concentrations of temperature, humidity and wind speed from one level of location to another.



**Figure 4.28.** Distribution of temperature, humidity and wind speed depending on locations 1) Sihhiye 2) Beytepe

The box plot (box and whisker diagram) is a standardized way of determining the distribution of data on the basis of the five number summary: minimum, first quartile, median, third quartile, and maximum. These values are applied to compare how close other data values are to them. In order to create a box plot, we use a horizontal or vertical number line and a rectangular box. The smallest and largest data values label the endpoints of the axis. The first quartile denotes one end of the box and the third quartile shows the other end of the box. Nearly the middle 50 percent of the data fall inside the box. The “whiskers” extend from the ends of the box to the smallest and largest data values. The median or second quartile can be between the first and third quartiles, or it can be one, or the other, or both. The box plot shows a good, brief picture of the data.

## **4.8 Comparison with the Literature**

In order to reveal the air quality in Ankara from the point of the values we have determined in this study, the data were compared with the values obtained in similar studies in the literature.

### **4.8.1 Ankara, Turkey (this study)**

TCRTECORA sampler was used to sample  $PM_{2.5}$  on pre-fired quartz filters at two stations urban and semi-rural area in summer and winter in Ankara from 19/06/2016 to 11/08/2016 and 29/12/2016 to 27/01/2017. Samples were studied in terms of organic carbon and elemental carbon.

### **4.8.2 Bolu, Turkey**

Wintertime chemical compositions of  $PM_{2.5-10}$  and  $PM_{2.5}$  were studied between December 2014 and February 2015 at an urban site, situated at the Bolu plain, Turkey. Collected samples were studied regarding metals, elemental carbon (EC); and organic carbon (OC). Highest concentration measured was  $59.9 \pm 50.4 \mu\text{g}/\text{m}^3$  for OC in  $PM_{2.5}$ . The contributions of primary and secondary OC (POC and SOC) to total OC mass were 60 % and 40 %, respectively, while contribution of SOC to OC elevated to 74 % in steady atmospheric conditions. The remarkable high OC/EC ratio was about 10.1 calculated in this study relative to other winter period studies was because of elevated emissions from domestic heating and inversion during the study [56].

### **4.8.3 Istanbul, Turkey**

Black carbon was studied in  $PM_{2.5}$  samples collected in 4 sites in Istanbul. Annually average BC has  $38 \pm 14\%$  of  $PM_{2.5}$  levels (annual average BC:  $13 \mu\text{g m}^{-3}$  and  $PM_{2.5}$   $36 \mu\text{g m}^{-3}$ ) [70].

#### 4.8.4 Iskenderun, Turkey

Arı A. et al., have investigated  $PM_{2.5}$  and  $PM_{10}$  concentration in four different sites in Iskenderun and Payas between 06.05.2008 to 21.05.2008. According to the findings,  $PM_{2.5}$  concentrations are  $26.7 \mu\text{g m}^{-3}$  at city center of Iskenderun,  $21.3 \mu\text{g m}^{-3}$  at semi-urban site of Iskenderun,  $28.8 \mu\text{g m}^{-3}$  at Payas center and  $26.4 \mu\text{g m}^{-3}$  at Payas seaside sampling site. Mass concentrations of  $PM_{10}$  are found  $60 \mu\text{g m}^{-3}$ ,  $59.9 \mu\text{g m}^{-3}$ ,  $147.1 \mu\text{g m}^{-3}$  and  $125.7 \mu\text{g m}^{-3}$  correspondingly [71].

#### 4.8.5 Zonguldak, Turkey

In a study in Zonguldak, Turkey, mass and trace element concentrations of  $PM_{2.5}$ , and  $PM_{2.5-10}$  were investigated from December 2004 to October 2005. The average mass concentration of  $PM_{2.5}$ ,  $PM_{2.5-10}$  and  $PM_{10}$  were  $29.38 \mu\text{g m}^{-3}$ ,  $23.85 \mu\text{g m}^{-3}$  and  $53.72 \mu\text{g m}^{-3}$  correspondingly. Mean mass concentration of  $PM_{2.5}$  in winter and summer were  $34.17 \mu\text{g m}^{-3}$ ,  $25.03 \mu\text{g m}^{-3}$ . Mean mass concentration of  $PM_{10}$  in winter and summer were  $63.59 \mu\text{g m}^{-3}$ ,  $41.83 \mu\text{g m}^{-3}$ . In both particle groups, higher concentrations were observed during the warm-up season than in summer [72].

#### 4.8.6 Istanbul, Turkey

Cyclic changes of the monthly average concentrations of  $PM_{10}$  and  $PM_{2.5}$  data were studied in 86 aerosol samples (24hours) between July 2002 and July 2003. The  $PM_{10}$  annual mean value of  $47.1 \mu\text{g m}^{-3}$ , was lower than the Turkish air quality standard of  $60 \mu\text{g m}^{-3}$ . [3].

Theodosi. et al investigated aerosol chemical composition over Istanbul, Turkey over Bosphorus area (November 2007 to June 2009) in 325 collected  $PM_{10}$  samples. Samples were analyzed in terms of ions, trace metals, organic (OC) and elemental carbon (EC). The yearly mean concentrations of OC and EC were  $6.65 \mu\text{g m}^{-3}$  and  $2.92 \mu\text{g m}^{-3}$  accordingly. Referring to the results, there is a high correlation among all carbon compounds (EC, OC and WSOC) and show the highest during winter and the lowest during summer. This seasonal change shows the distribution of sources such as

household heating systems and TC amount is affected due to this in winter. OC/EC ratio shows that OC is mostly primary and EC is traffic related [73].

#### **4.8.7 Erdemli, Turkey**

In a study conducted in rural site (Erdemli) situated on the coast of the Eastern Mediterranean, PM<sub>2.5</sub> and PM<sub>10</sub> daily samples (April2001-April2002) were analyzed. Yearly mean concentration of PM<sub>10</sub> and PM<sub>2.5</sub> were  $36.4 \pm 27.8$  and  $9.7 \pm 5.9$   $\mu\text{gm}^{-3}$ . PM<sub>10</sub> and PM<sub>2.5</sub> concentrations showed orders of changes from day to day (PM<sub>2.5</sub> = 2-323  $\mu\text{gm}^{-3}$ ; PM<sub>2.5</sub> =0.5-28  $\mu\text{gm}^{-3}$ ). Highest amount of PM<sub>10</sub> was seen in March, April and May (transition period) when Saharan dust transported and during winter due to sea salt production. Highest amount was observed for PM<sub>2.5</sub> during summer in result of elevated secondary aerosols. PM<sub>2.5</sub>/PM<sub>10</sub> ratio (0.25) and categorization of air mass of 86 daily back trajectories showed that PM<sub>10</sub> is under control of primary aerosol emissions [74].

All of these conducted studies in Turkey were carried out based on daily samplings to specify the chemical compounds of particulate matter. Elemental and organic carbon content of PM<sub>2.5</sub> using EC/OC analyzer has done for the first time in Turkey. This was done for PM<sub>10</sub> in a study in Bolu by Fatma Öztürk ve Melek Keleş [56].

#### **4.8.8 Gangetic, India**

Black carbon (BC) aerosols were studied out of PM<sub>2.5</sub> samples from 16<sup>th</sup> of June to 15<sup>th</sup> of August (monsoon), 2014 in a rural sitet in the highly-polluted Indo-Gangetic, India. The mean mass concentration of BC was calculated to be  $4.03 \pm 0.8$   $\mu\text{gm}^{-3}$ , however, the mean mass PM<sub>2.5</sub> concentration was  $34.7 \pm 19.9$   $\mu\text{gm}^{-3}$ . The contribution of Black Carbon in PM<sub>2.5</sub> was almost 13% that is much higher than previous reports observed in the rural areas in India [44].

#### **4.8.9 Beijing, China**

OC and EC were measured in PM<sub>2.5</sub> in Beijing, China during four season November 2005-October 2006.Quartz filters were used. OC concentrations at urban site were  $20 \pm$

19 and  $10 \pm 5 \mu\text{g C/m}^3$  in winter and summer correspondingly. Obvious changes in OC concentrations were observed and were affected by seasonal and daily pattern changes in sources, meteorology and emission rates. High amount of OC in winter was greatly because of coal burning emission and domestic heating but in autumn it resulted from constant weather conditions. Summer precipitations influenced concentrations and resulted in lower amounts. EC and OC were strongly correlated in winter but not in summer showing the effect of SOC in that period. SOC concentrations were evaluated by using the EC-tracer method as about  $2.6 \pm 3.1$  and  $4.5 \pm 2.9 \mu\text{g C/m}^3$ , accounting for 19% and 45% of total organic carbon in winter and summer correspondingly [75].

#### **4.8.10 Shanghai, China**

In Shanghai, China, concentration and seasonal characteristics of  $\text{PM}_{2.5}$ , organic carbon (OC) and elemental carbon (EC) were evaluated at urban and semi-urban sites during four seasons in 2005–2006. Results revealed that the yearly average  $\text{PM}_{2.5}$  concentrations were  $90.3\text{--}95.5 \mu\text{g m}^{-3}$  at both sites, while OC and EC were  $14.7\text{--}17.4 \mu\text{g m}^{-3}$  and  $2.8\text{--}3.0 \mu\text{g m}^{-3}$ , respectively, with the OC/EC ratios of 5.0–5.6. The carbonaceous aerosol accounted for about 30% of  $\text{PM}_{2.5}$  mass. There was a strong correlations ( $r=0.79\text{--}0.93$ ) between OC and EC in the four seasons. Average level of secondary organic carbon (SOC) was  $5.7\text{--}7.2 \mu\text{g m}^{-3}$ , contributing for about 30% of the total OC [32].

#### **4.8.11 Amsterdam, Barcelona and Ghent, Europe**

$\text{PM}_{2.5}$  aerosol samples were collected and analyzed for OC and EC in three cities in Europe Amsterdam, Barcelona and Ghent. OC and EC mean concentrations were the highest in Amsterdam  $3.9\text{--}6.7$  and  $1.7\text{--}1.9 \mu\text{g m}^{-3}$  correspondingly, then in Barcelona with  $3.6\text{--}6.9$  and  $1.5\text{--}2.6 \mu\text{g m}^{-3}$  respectively and lowest in Ghent with  $2.7\text{--}5.4$  and  $0.8\text{--}1.2 \mu\text{g m}^{-3}$  correspondingly [76].

#### 4.8.12 Hong Kong, China

Chemical composition, EC and OC were studied in  $PM_{2.5}$  and  $PM_{10}$  in Hong-Kong at urban, industrial and non-urban locations from November 2000 to February 2001. According to the results  $PM_{2.5}$  mass concentrations in Hong-Kong are obviously higher than other Asian cities in urban site. The highest OC level in  $PM_{2.5}$  was observed at industrial site. Amount of TC in  $PM_{2.5}$  and  $PM_{10}$  was higher in industrial and urban than non-urban site. OC/EC ratios for  $PM_{10}$  and  $PM_{2.5}$  at urban and industrial area were less than 2.0 but this ratios were more than 3.0 at non-urban location for  $PM_{10}$  and  $PM_{2.5}$  showing the attendance of SOA and that SOC is probably from transport or transformation of anthropogenic organic sources. High correlation between EC and OC was seen in winter ( $r=0.93$  for  $PM_{2.5}$ ;  $r=0.96$  for  $PM_{10}$ ) at non-urban site showing that transportation/transformation of organic aerosols from northeastern area was major source in winter [77].

#### 4.8.13 Xi'an, China

Carbonaceous aerosols OC and EC were examined in  $PM_{2.5}$  samples during a study in Xi'an, China in fall and winter (September 2003 through February 2004). OC and EC concentrations are higher than many Asian cities. OC and EC correlation was strongly correlated ( $R>0.95$ ) in fall and moderately well-correlated in winter ( $R=0.81$ ). Carbonaceous aerosols accounted for  $48.8\% \pm 10.1\%$  of the  $PM_{2.5}$  mass during fall and  $45.9\% \pm 7.5\%$  during winter [78].

Table 4.7 is showing the comparison of measured concentration in this study with the literature.

**Table 4.7.** Comparison of measured concentration in this study with the literature ( $\mu\text{g m}^{-3}$ )

sample	location	Period	PM	OC	EC	OC/EC	Source
PM2.5	Ankara (urban) (Sihhiye)	19.6.2016 to 11.08.2016 (summer)	53.32 $\pm$ 16.59	7.63 $\pm$ 1.87	3.69 $\pm$ 0.67	1.43	This study
	Semi-rural (Beytepe)	19.06.2016 to 11.08.2016 (Summer)	46.34 $\pm$ 15.43	5.8 $\pm$ 1.35	1.26 $\pm$ 0.35	3.12	This study
	Urban (Sihhiye)	29.12.2016 to 27.01.2017 (winter)	51.27 $\pm$ 27.96	14.21 $\pm$ 8.46	3.65 $\pm$ 1.48	2.01	This study
PM2.5	Bolu	December 2014 and February 2015	20 $\pm$ 15	59.9 $\pm$ 50.4	5.92 $\pm$ 4.79	10.1	Öztürk F. et al. (2016)
PM2.5	Istanbul	July 2008-June 2009	36		13		
PM2.5	Istanbul	July 2002 and July 2003	20.8				
PM2.5	Iskenderun (urban)	06.05.2008 to 21.05.2008	26.7				Arı A. et al. (2008)
	Iskenderun (suburban)	06.05.2008 to 21.05.2008	21.3				
PM2.5	Zonguldag	December 2004 to October 2005 summer	25.03				
		winter	34.17				
PM2.5	Beijing, China (urban)	November 2005-October 2006 ( winter)		20 $\pm$ 19			
		summer		10 $\pm$ 5			
PM2.5	Erdemli	April 2001-April 2002	9.7 $\pm$ 5.9				
PM2.5	Gangetic, India	16 June to 15 August, 2014	34.7 $\pm$ 19.9		4.03 $\pm$ 0.85		J.Sciare et al. (2014)

PM2.5	Shanghai (Urban)	2005 to 2006	90.3	14.7	2.8	5.0	Feng Y. et al. 2006
	Suburban		95.5	17.4	3	5.6	
PM2.5	Beirut, Lebanon (semi-urban)	2012 winter		4.5	1.4	3.2	Waked et al. (2013)
PM2.5	Amsterdam (winter)	2007	34.4 ± 15.8	6.7 ± 3.8	1.7 ± 0.9	4.7	Viana et al. (2007)
	(summer)		17.8 ± 7.8	3.9 ± 1.6	1.9 ± 0.7	2.8	
PM2.5	Barcelona (winter)	2007	29.1 ± 15.3	6.9 ± 2.5	2.6 ± 1.4	3.1	Viana et al. (2007)
	(summer)		17.7 ± 6.0	3.6 ± 1.4	1.5 ± 0.7	2.6	
PM2.5	Ghent (winter)	2007	20.8 ± 18.3	5.4 ± 4.5	1.2 ± 0.6	4.4	Viana et al. (2007)
	(summer)		15.7 ± 4.9	2.7 ± 1.0	0.8 ± 0.3	3.5	
PM2.5	Xi'an, China	Fall 2003-2004		34.1 ± 18.0	11.3 ± 6.9	3.3	Cao J.J. Et al.(2005)
		Winter 2004		61.9 ± 33.2	12.3 ± 5.3	5.1	

In this study  $PM_{2.5}$  were samples and analyzed for OC and EC at two different stations (urban and sub-urban) during summer and winter in Ankara, Turkey. The results obtained by analyzing the samples collected from different stations were compared with the values obtained in this study and this comparison is discussed as following:

Comparison in terms of  $PM_{2.5}$  concentration,  $PM_{2.5}$  concentrations in this study are found to be higher than Istanbul (2008-2009). Among the cities in Turkey  $PM_{2.5}$  concentration in Ankara>Istanbul>Zonguldağ>Iskenderun>Bolu>Erdemli. OC and EC mean concentration measured in Bolu during winter ( $59.9 \mu\text{gm}^{-3}$  and  $5.92 \mu\text{gm}^{-3}$ ) is much higher than measured OC mean concentration during winter in Ankara ( $14.21 \mu\text{gm}^{-3}$  and  $3.65 \mu\text{gm}^{-3}$ ). The reason can be burning coal for heating in winter.

Shanghai has the highest  $PM_{2.5}$  mean concentration, urban and sub-urban  $90.3 \mu\text{gm}^{-3}$  and  $95.5 \mu\text{gm}^{-3}$  correspondingly. OC and EC mean concentrations at urban site are  $14.7$  and  $2.8 \mu\text{gm}^{-3}$  and at sub-urban site are  $17.4 \mu\text{gm}^{-3}$  and  $3 \mu\text{gm}^{-3}$  respectively.

Among European cities (Amsterdam, Barcelona and Ghent) Viana et al. (2007), Amsterdam has the highest  $PM_{2.5}$  mean concentration ( $34.4 \mu\text{gm}^{-3}$ ) which is observed in winter. In all of these cities  $PM_{2.5}$  concentration is found to be higher in winter than summer. On the other hand,  $PM_{2.5}$  mean concentrations in all of these European cities are lower than  $PM_{2.5}$  mean concentrations in Ankara. OC and EC mean concentrations are also higher in winter than summer months. Barcelona has the highest OC and EC in comparison with others. OC and EC mean concentrations in Ankara are much higher than all these cities in both seasons.

#### **4.9 Correlation of Measured Parameters with Gathered Data from Ambient Air Quality Network**

In order to see whether the gathered data are correlated with the data gathered at stations installed by Ministry of Environment and Urbanization during the same sampling period in this study, a multiple-Variable analysis (Correlation) was conducted which is a way to determine whether variables are related. The result is called the correlation

coefficient (or "r"). It changes between -1.0 to +1.0. If r is closer to +1 or -1, the two variables relativity gets higher.

Multiple-variable correlation among PM<sub>2.5</sub>, OC, and EC measured at urban site (Sihhiye) by TCRTECORA SKYPOST PM HV sampler in this study and the parameters (PM<sub>2.5</sub>, PM<sub>10</sub> SO<sub>2</sub>, NO, NO<sub>x</sub>, NO<sub>2</sub>) measured and reported by Ministry of Environment and Urbanization Ambient Air Quality Network.

Table 4.8 shows the correlation table of the gathered data in this study at Sihhiye station during summer sampling period with the gathered data reported by Ambient air Quality Network.

**Table 4.8.**Correlation table for Sihhiye station in summer

	PM10	PM2.5	SO2	NO	NO2	NOx	CO	PM <sub>2.5</sub> (t)	OC	EC
PM10										
PM2.5	<b>0.54</b> 0.002									
SO2	<b>0.51</b> 0.004	0.29 0.1								
NO	<b>0.48</b> 0.006	-0.1 0.3	<b>0.3</b> 0.03							
NO2	<b>0.79</b> 0.00	-0.04 0.7	<b>0.4</b> 0.008	<b>0.6</b> 0.00						
NOx	<b>0.65</b> 0.00	-0.1 0.5	<b>0.4</b> 0.008	<b>0.8</b> 0.00	<b>0.9</b> 0.00					
CO	0.02 0.89	0.2 0.2	0.1 0.4	-0.2 0.1	-0.2 0.1	-0.2 0.1				
PM2.5(t)	<b>0.6</b> 0.00	0.1 0.2	0.2 0.2	<b>0.3</b> 0.01	<b>0.4</b> 0.001	<b>0.4</b> 0.001	-0.08 0.6			
OC	<b>0.72</b> 0.00	<b>0.7</b> 0.00	0.2 0.1	<b>0.4</b> 0.004	<b>0.6</b> 0.00	<b>0.6</b> 0.00	-0.2 0.2	<b>0.6</b> 0.00		
EC	<b>0.43</b> 0.003	<b>0.4</b> 0.003	0.1 0.5	<b>0.7</b> 0.00	<b>0.3</b> 0.01	<b>0.5</b> 0.0002	-0.09 0.6	<b>0.4</b> 0.001	<b>0.4</b> 0.001	

\*R  
\*\*P-value

**Table 4.9.**Correlation table for Sihhiye station in winter

	PM10	PM2.5	SO2	NO	NO2	NOx	CO	PM2.5(t)	OC	EC
PM10										
PM2.5	<b>*0.9</b> <b>**0.00</b>									
SO2	0.01 <b>0.9</b>	-0.06 <b>0.7</b>								
NO	<b>0.4</b> <b>0.04</b>	<b>0.5</b> <b>0.01</b>	-0.2 <b>0.2</b>							
NO2	<b>0.5</b> <b>0.01</b>	<b>0.5</b> <b>0.01</b>	-0.09 <b>0.6</b>	<b>0.6</b> <b>0.0003</b>						
NOx	<b>0.5</b> <b>0.01</b>	<b>0.6</b> <b>0.005</b>	-0.2 <b>0.2</b>	<b>0.9</b> <b>0.00</b>	<b>0.8</b> <b>0.00</b>					
CO	<b>0.7</b> <b>0.00</b>	<b>0.8</b> <b>0.00</b>	-0.2 <b>0.1</b>	<b>0.8</b> <b>0.00</b>	<b>0.5</b> <b>0.003</b>	<b>0.7</b> <b>0.00</b>				
PM2.5(t)	<b>0.8</b> <b>0.00</b>	<b>0.8</b> <b>0.00</b>	-0.1 <b>0.4</b>	<b>0.4</b> <b>0.01</b>	<b>0.5</b> <b>0.006</b>	<b>0.5</b> <b>0.006</b>	<b>0.7</b> <b>0.00</b>			
OC	<b>0.8</b> <b>0.00</b>	<b>0.9</b> <b>0.00</b>	-0.2 <b>0.2</b>	<b>0.5</b> <b>0.007</b>	<b>0.5</b> <b>0.01</b>	<b>0.5</b> <b>0.003</b>	<b>0.8</b> <b>0.00</b>	<b>0.8</b> <b>0.00</b>		
EC	<b>0.5</b> <b>0.002</b>	<b>0.6</b> <b>0.003</b>	-0.2 <b>0.1</b>	<b>0.7</b> <b>0.0001</b>	0.3 <b>0.1</b>	<b>0.6</b> <b>0.001</b>	<b>0.8</b> <b>0.00</b>	<b>0.4</b> <b>0.01</b>	<b>0.7</b> <b>0.00</b>	

\*R\*\*  
P-value

#### **4.10 Correlation of Measured Parameters with Meteorological Parameters**

In correlation analysis, the correlation between two variables can be positive (i.e., higher levels of one variable are related with higher levels of the other) or negative (i.e., higher levels of one variable are associated with lower levels of the other). P-values are shown in the tables 4.10.



**Table 4.10.**Table of correlation Sihhiye during summer sampling period

	PM <sub>2.5</sub>	OC	EC	CC	TC	Temp	Press	Hum.	WS	Prec
PM <sub>2.5</sub>										
OC	<b>*0.67</b> <b>** (0.0)</b>									
EC	<b>0.45</b> <b>(0.00)</b>	<b>0.46</b> <b>(0.00)</b>								
CC	<b>0.69</b> <b>(0.00)</b>	<b>0.73</b> <b>(0.00)</b>	<b>0.35</b> <b>(0.01)</b>							
TC	<b>0.72</b> <b>(0.00)</b>	<b>0.94</b> <b>(0.00)</b>	<b>0.66</b> <b>(0.00)</b>	<b>0.77</b> <b>(0.00)</b>						
Temp.	<b>0.36</b> <b>(0.01)</b>	<b>0.46</b> <b>(0.00)</b>	<b>0.21</b> <b>(0.15)</b>	<b>-0.2</b> <b>(0.00)</b>	<b>0.46</b> <b>(0.00)</b>					
Press.	-0.13 <b>(0.37)</b>	<b>0.36</b> <b>(0.01)</b>	0.06 <b>(0.66)</b>	0.19 <b>(0.1)</b>	-0.28 <b>(0.06)</b>	<b>-0.32</b> <b>(0.02)</b>				
Hum.	<b>-0.34</b> <b>(0.01)</b>	<b>-0.49</b> <b>(0.00)</b>	0.17 <b>(0.26)</b>	<b>-0.49</b> <b>(0.00)</b>	<b>-0.4</b> <b>(0.00)</b>	<b>0.85</b> <b>(0.00)</b>	<b>0.37</b> <b>(0.0)</b>			
WS	0.05 <b>(0.85)</b>	<b>-0.18</b> <b>(0.01)</b>	-0.31 <b>(0.14)</b>	-0.28 <b>(0.97)</b>	0.074 <b>(0.6)</b>	<b>-0.3</b> <b>(0.04)</b>	0.2 <b>(0.1)</b>	<b>0.33</b> <b>(0.02)</b>		
Perci	-0.24 <b>(0.75)</b>	-0.33 <b>(0.66)</b>	-0.84 <b>(0.15)</b>	-0.85 <b>(0.1)</b>	-0.73 <b>(0.26)</b>	-0.85 <b>(0.1)</b>	0.24 <b>(0.7)</b>	0.91 <b>(0.2)</b>	-0.71 <b>(0.2)</b>	
MH	-0.1 <b>(0.2)</b>	-0.09 <b>(0.5)</b>	-0.0 <b>(0.8)</b>	-0.1 <b>(0.2)</b>	-0.1 <b>(0.2)</b>	-0.1 <b>(0.4)</b>	0.1 <b>(0.3)</b>	0.2 <b>(0.07)</b>	-0.03 <b>(0.8)</b>	-0.1 <b>(0.4)</b>

\*R

\*\* P-value

**Table 4.11.** Table of correlation Sihhiye during winter sampling period

	PM <sub>2.5</sub>	OC	EC	TC	Temp	Press	Hum.	WS	Prec.
PM <sub>2.5</sub>									
OC	<b>*0.84</b> <b>** (0.00)</b>								
EC	<b>0.42</b> <b>(0.01)</b>	<b>0.72</b> <b>(0.00)</b>							
TC	<b>0.8</b> <b>(0.00)</b>	<b>0.99</b> <b>(0.00)</b>	<b>0.79</b> <b>(0.00)</b>						
Temp	-0.2 <b>(0.28)</b>	0.008 <b>(0.96)</b>	<b>0.39</b> <b>(0.02)</b>	0.06 <b>(0.71)</b>					
Press	<b>0.4</b> <b>(0.02)</b>	0.35 <b>(0.056)</b>	0.13 <b>(0.49)</b>	0.33 <b>(0.07)</b>	-0.16 <b>(0.37)</b>				
Hum.	<b>0.38</b> <b>(0.03)</b>	<b>0.43</b> <b>(0.01)</b>	0.34 <b>(0.06)</b>	<b>0.43</b> <b>(0.01)</b>	0.1 <b>(0.57)</b>	0.03 <b>(0.86)</b>			
WS	<b>-0.5</b> <b>(0.00)</b>	<b>-0.4</b> <b>(0.00)</b>	-0.22 <b>(0.24)</b>	<b>0.46</b> <b>(0.009)</b>	<b>0.44</b> <b>(0.007)</b>	<b>-0.2</b> <b>(0.001)</b>	-0.2 <b>(0.14)</b>		
Prec.	-0.13 <b>(0.49)</b>	-0.02 <b>(0.89)</b>	0.1 <b>(0.39)</b>	0.003 <b>(0.98)</b>	0.25 <b>(0.1)</b>	0.54 <b>(0.27)</b>	<b>0.54</b> <b>0.003</b>	0.1 <b>(0.61)</b>	
MH	0.1 <b>(0.4)</b>	0.3 <b>(0.1)</b>	<b>0.3</b> <b>(0.05)</b>	0.3 <b>(0.08)</b>	<b>0.5</b> <b>(0.004)</b>	-0.1 <b>(0.5)</b>	0.05 <b>(0.7)</b>	0.2 <b>(0.1)</b>	0.2 <b>(0.1)</b>

\*R

\*\* P-value

**Table 4.12.**Table of correlation for Beytepe during summer sampling period

	PM <sub>2.5</sub>	OC	EC	CC	TC	Temp	Hum.	WS	Prec.
PM <sub>2.5</sub>									
OC	* <b>0.29</b> **(0.05)								
EC	0.1 (0.32)	<b>0.59</b> (0.00)							
CC	<b>0.31</b> (0.03)	<b>0.67</b> (0.00)	<b>0.69</b> (0.00)						
TC	<b>0.3</b> (0.04)	<b>0.96</b> (0.00)	<b>0.75</b> (0.00)	<b>0.8</b> (0.00)					
Temp	0.12 (0.4)	<b>0.3</b> (0.03)	<b>0.32</b> (0.02)	<b>0.42</b> (0.003)	<b>0.36</b> (0.01)				
Humi	- 0.04 (0.7)	<b>-0.3</b> (0.02)	<b>-0.3</b> (0.009)	<b>-0.3</b> (0.01)	<b>-0.3</b> (0.01)	<b>-0.08</b> (0.00)			
WS	0.06 (0.6)	0.07 (0.6)	- 0.04 (0.7)	0.09 (0.55)	0.06 (0.1)	- 0.2 (0.6)	<b>0.33</b> (0.02)		
Preci	<b>- 0.6</b> (0.07)	-0.2 (0.53)	-0.13 (0.7)	-0.2 (0.4)	-0.2 (0.5)	-0.5 (0.1)	<b>0.62</b> (0.009)	0.007 (0.9)	
MH	-0.1 (0.2)	-0.09 (0.5)	-0.0 (0.8)	-0.1 (0.2)	-0.1 (0.4)	0.1 (0.3)	-0.2 (0.07)	-0.03 (0.8)	-0.1 (0.4)

\*R

\*\* P-value

According to the results, during summer sampling period at Sihhiye, there is a meaningful correlation between  $PM_{2.5}$  and OC, EC, CC and TC concentrations with coefficient of  $R= 0.67, 0.45, 0.69$  and  $0.72$  correspondingly. There is also a correlation between temperature and  $PM_{2.5}$ , OC, EC, CC and TC with  $R= 0.36, 0.46, 0.21, - 0.2$  and  $0.46$  respectively. There is a negative correlation between humidity and  $PM_{2.5}$ , OC, CC and TC with  $R=-0.34, -0.49, -0.49, -0.4$  respectively, showing that as humidity increases the concentration of pollutants decreases. A negative correlation is shown between wind speed and EC with  $R=-0.18$  showing that stagnant air increases the pollution. There is no correlation between OC/EC and wind speed. There is a significantly strong correlation between OC/EC and temperature ( $R=0.46$ ). No correlation is observed between precipitation and concentration of parameters.

While in the same sampling period in semi-urban site, there is a weak correlation between  $PM_{2.5}$  and OC concentration ( $R=0.29$ ), there is a correlation between  $PM_{2.5}$  and CC and TC concentrations ( $R=0.31$  and  $0.3$ ) but there is not a meaningful correlation between  $PM_{2.5}$  and EC concentrations. OC and EC are significantly correlated ( $R=0.59$ ). Temperature is positively correlated with OC, EC, CC and TC ( $R=0.31, 0.32, 0.42, \text{ and } 0.36$  respectively). Humidity is negatively correlated with OC, EC, CC and TC ( $R=-0.3$ ) demonstrating that humidity and wet air washes out the carbon. Precipitation is correlated with  $PM_{2.5}$  negatively ( $R=-0.6$ ) showing that precipitation has scavenging effect. There has not been shown a correlation between OC/EC and wind speed.

At urban area in winter,  $PM_{2.5}$  is correlated with OC, EC and TC. Temperature only shows correlation with EC. Humidity is correlated with  $PM_{2.5}$ , OC, EC and TC. Wind speed is correlated with  $PM_{2.5}$ , OC and TC. Air pressure is correlated with  $PM_{2.5}$  and TC only. Precipitation does not show a significant correlation with parameters. There is strong correlation between OC/EC and wind speed.

#### **4.11 Comparing the Mean Concentrations between summer and winter sampling Period at Urban Site (Sihhiye) Performing One-way ANOVA**

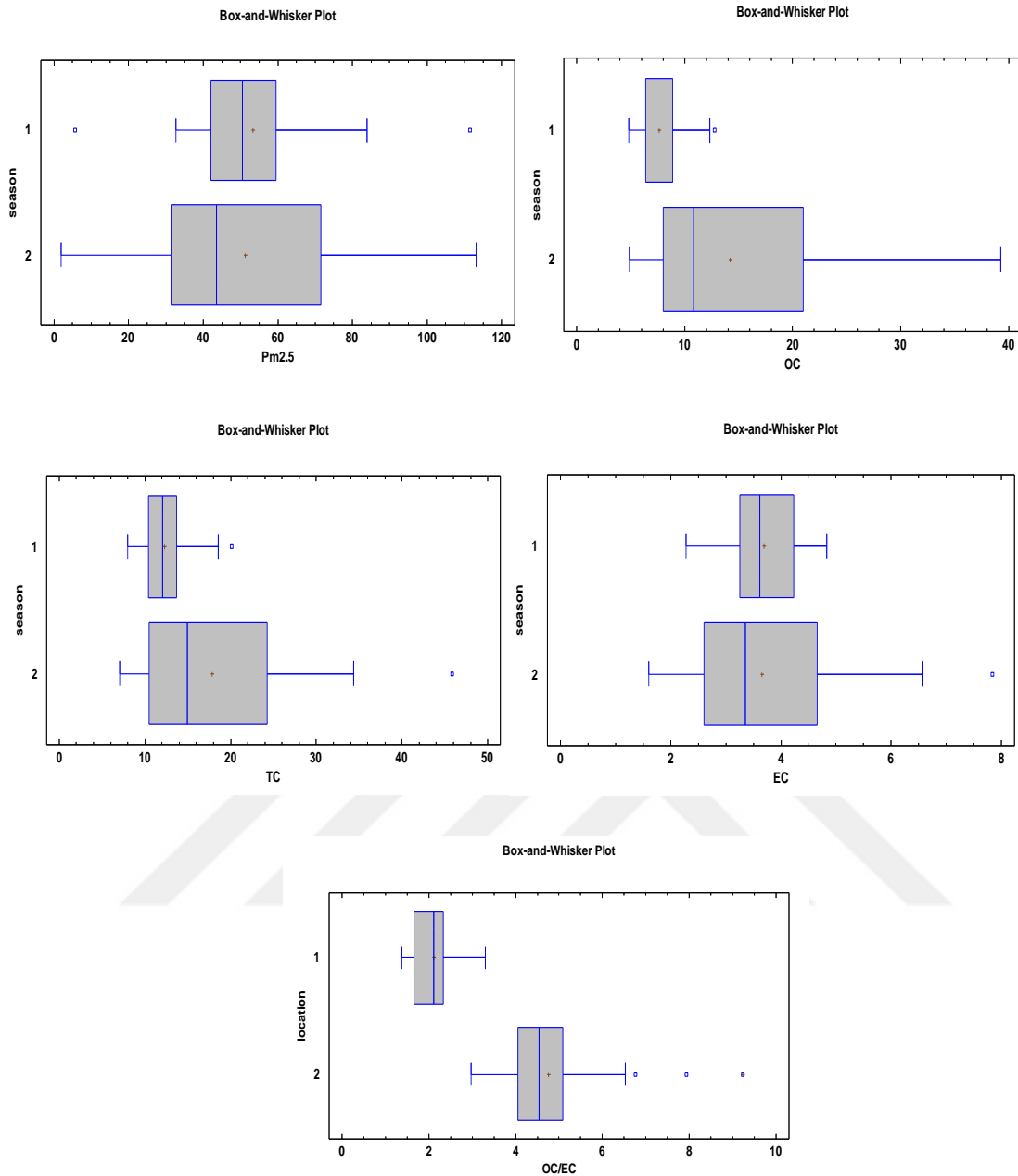
The one-way analysis of variance (ANOVA) is used to show whether there are any statistically meaningful differences between the means of three or more

independent (unrelated) groups using the F-distribution. The one-way ANOVA compares the means between the groups we are interested in and shows whether any of those means have statistically meaningful differences from each other. If the P-value is smaller than 0.05, there is a statistically significant difference between the averages from one level of location to another at the 95.0% confidence level.

One-way ANOVA test was performed to find out whether there is statistically significant difference between concentration means of PM<sub>2.5</sub>, OC, EC, CC and TC between summer and winter sampling periods and the results and P-values are given in tables below.

**Table 4.13.**One way ANOVA table for different seasons ( $\mu\text{g m}^{-3}$ )

<b>Parameter</b>	<b>Season</b>	<b>Mean</b>	<b>P-value</b>
<b>PM<sub>2.5</sub></b>	Summer1	53.32	<b>0.6914</b>
	Winter2	51.27	
<b>OC</b>	Summer1	7.63	<b>0.0000</b>
	Winter2	14.21	
<b>EC</b>	Summer1	3.68	<b>0.8889</b>
	Winter2	3.65	
<b>TC</b>	Summer1	12.27	<b>0.0004</b>
	Winter2	17.86	
<b>OC/EC</b>	Summer1	2.11	<b>0.0000</b>
	Winter2	4.76	

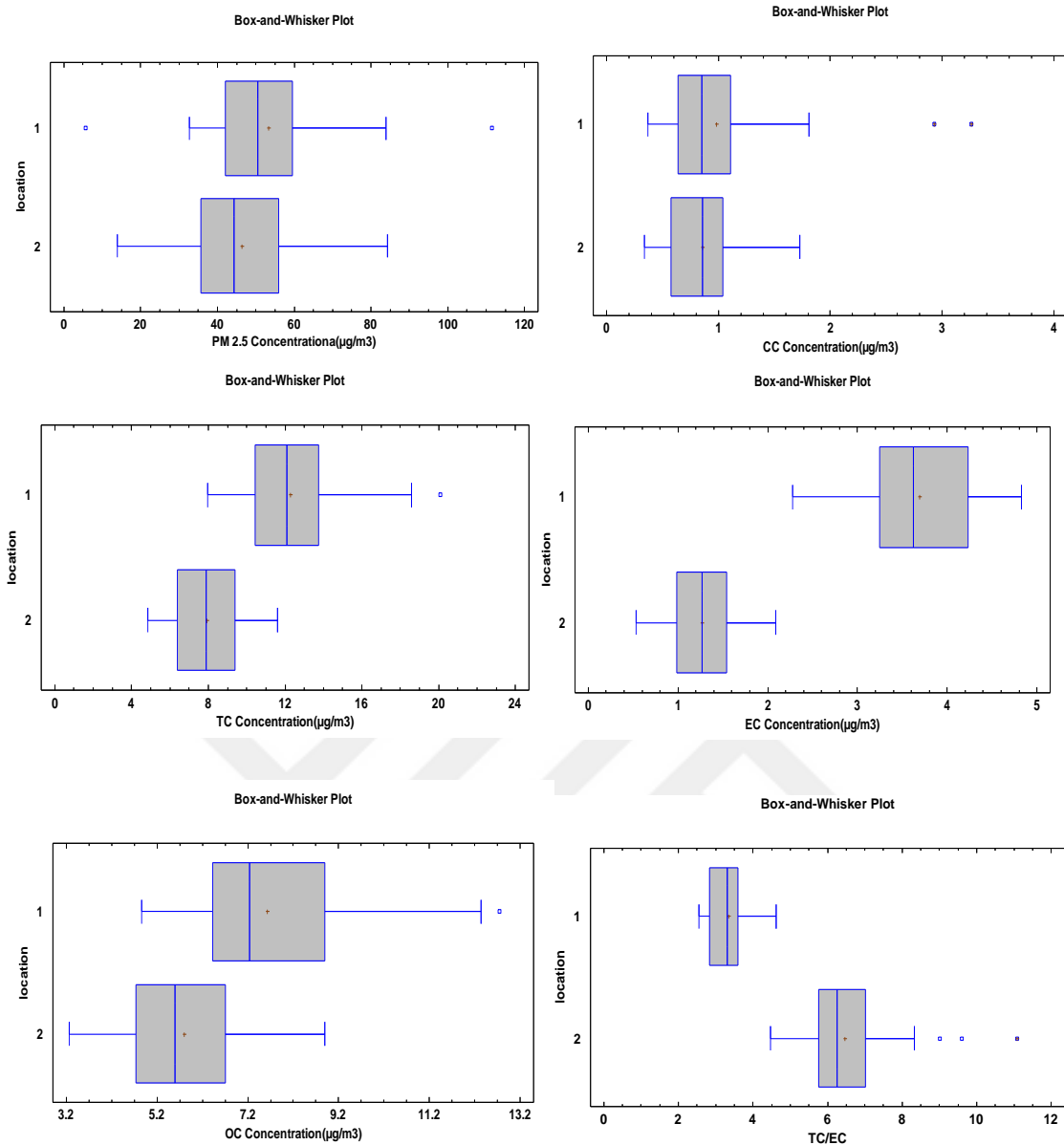


**Figure 4.29.** Distribution of PM<sub>2.5</sub>, OC, EC and TC depending on seasons 1) summer 2) winter

According to one-way ANOVA test table which analyzes the variance of parameters, since the result of F-test shows the P-value less than 0.05, there is a statistical meaningful difference between the mean concentrations of OC, CC and TC from one level of season to another at the 95.0% confidence level.

**Table 4.14.**One way ANOVA table for different locations in summer ( $\mu\text{g m}^{-3}$ )

<b>Parameter</b>	<b>Location</b>	<b>Mean</b>	<b>P-value</b>
<b>PM<sub>2.5</sub></b>	Sihhiye1	53.32	<b>0.0419</b>
	Campus 2	46.34	
<b>OC</b>	Sihhiye	7.63	<b>0.0000</b>
	Campus	5.80	
<b>EC</b>	Sihhiye	3.68	<b>0.0000</b>
	Campus	1.26	
<b>CC</b>	Sihhiye	0.98	<b>0.1885</b>
	Campus	0.85	
<b>TC</b>	Sihhiye	12.27	<b>0.0000</b>
	Campus	7.92	
<b>OC/EC</b>	Sihhiye	2.11	<b>0.0000</b>
	Campus	4.76	
<b>TC/EC</b>	Sihhiye	3.35	<b>0.0000</b>
	Campus	6.46	

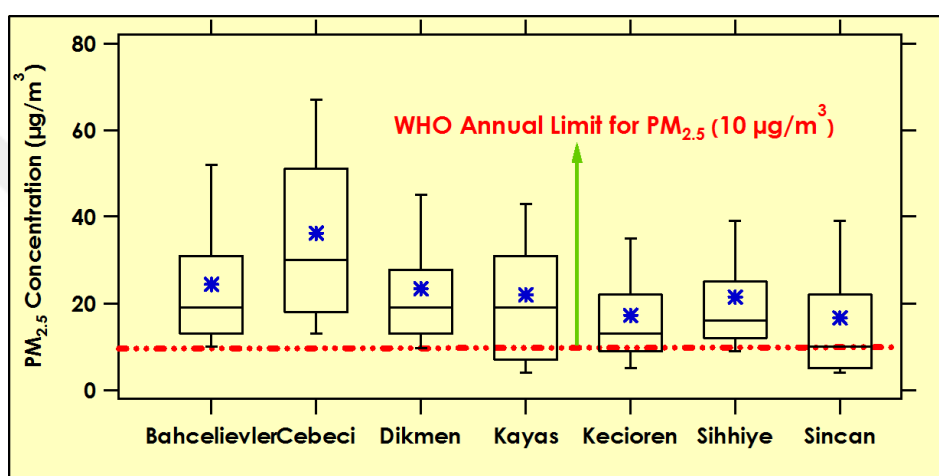


**Figure 4.30.** Distribution of PM<sub>2.5</sub>, OC, EC, CC, TC OC/EC and TC/EC depending on location 1) Sihhiye 2) Campus

Tables 4.12 and 4.13 show the result of one way ANOVA test and the P-values. This anova test is performed to see whether there is statistically difference between mean concentrations of PM<sub>2.5</sub>, OC, EC, CC and TC at two different sites (urban and sub-urban) during summer sampling period. Since the result of F-test shows the P-value less than 0.05, there is a statistical meaningful difference between the mean concentrations of PM<sub>2.5</sub>, OC, EC, CC and TC from one level of location to another at the 95.0% confidence level.

#### 4.12 PM<sub>2.5</sub> Concentrations at Quality Control Stations in Ankara

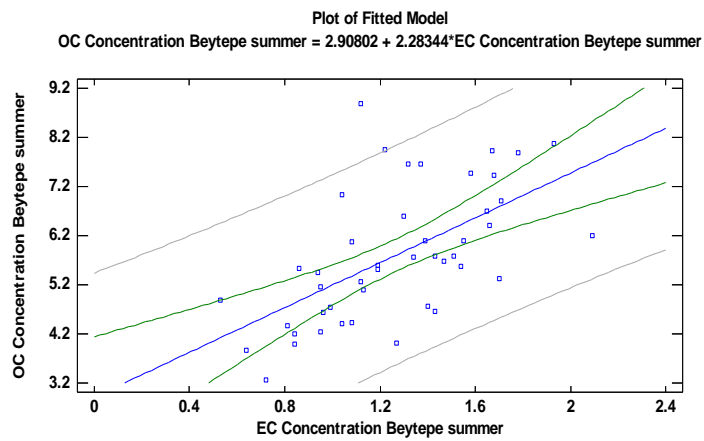
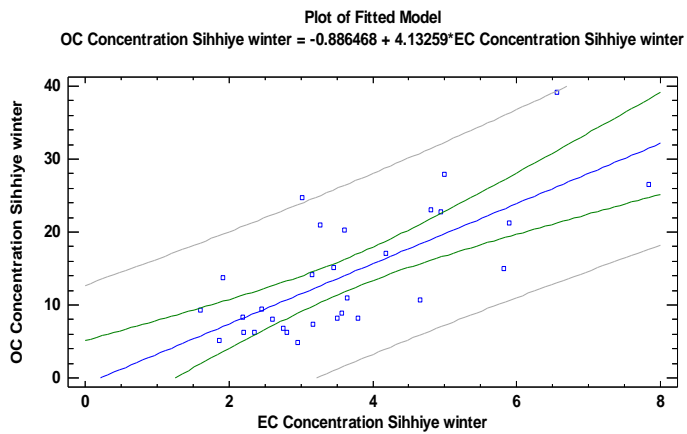
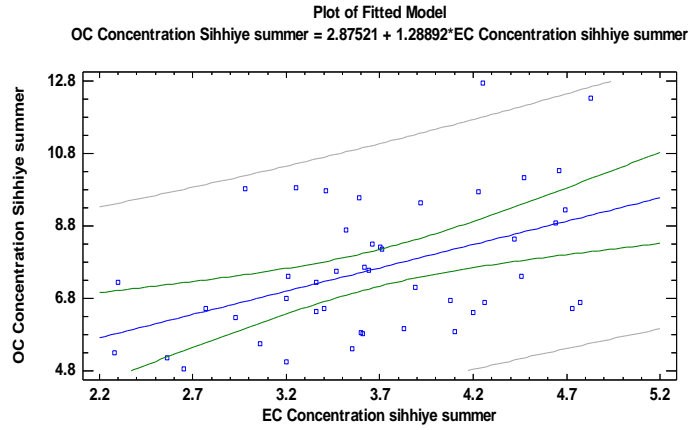
Figure 4.31 shows the variation of PM<sub>2.5</sub> concentration at 7 quality control stations in Ankara. Concentration of PM<sub>2.5</sub> is exceeding WHO and EPA standard values for PM<sub>2.5</sub> in all the stations. The length of the box is showing the frequency distribution. The highest change in distribution is seen for Cebeci station. According to this figure blue points show the mean concentrations of PM<sub>2.5</sub>. The highest concentration is seen at Cebeci station and the lowest belongs to Keçiören station.



**Figure 4.31.** Changes in concentrations in quality control stations in Ankara in 2016-2017

#### 4.13 EC/OC Correlation

In this study the correlation between OC and EC concentrations at both sampling sites during winter and summer was examined and the results are given in the figures 4.32 below. The correlation coefficient (R) between EC and OC at Sıhhiye in summer was calculated (R=0.46) indicating a relatively weak relation between the variables. The correlation coefficient (R) between EC and OC at Sıhhiye in winter was calculated (R=0.72) showing a moderately strong correlation between the variables. The correlation coefficient (R) between EC and OC at Beytepe in summer (R=0.59) indicate a moderately strong relationship between the variables.



**Figure 4.32.** OC/EC correlation at a) Sihhiye in summer sampling period b) Sihhiye in winter sampling period c) Beytepe in summer sampling period

#### 4.14 Primary and Secondary Organic Carbon Calculation

Although big part of atmosphere aerosol includes organic carbon, the significance of primary and secondary organic carbon has always been discussed. Primary one is sent directly to the atmosphere in form of particulate such as biomass and fossil fuel burning, while secondary OC is a particulate element which is formed from photochemical reactions. Since elemental carbon (EC), also known as black carbon mainly results from fuel burning, it is considered as a tracer for primary organic carbon. So OC and EC correlation can show the source of carbonaceous aerosols. Therefore, poor OC-EC correlations and ratios of OC/EC exceeding the expected ratio of OC/EC for the primary aerosol indicates the existence of secondary organic aerosol [48].

In this study primary organic carbon (POC) and secondary organic carbon (SOC) were calculated using EC tracer method. The calculation method is given in the "LITERATURE REVIEW" section of this work, so it will not be discussed further here. Using this method, POC and SOC are calculated in this study for both locations and seasons. SOA is considered to be important due to its effect on haze, climate, visibility and health. SOA is computed by multiplying SOC by 1.6.

The contributions of SOC and POC to total OC mass in terms of locations of stations are examined and are shown formed in figures 4.33 and 4.34.

Primary OC/EC was calculated for both stations in summer and winter sampling periods and the results are as following. Primary OC/EC for urban site in summer is 1.43 while this equation in winter is 2.01. Calculated primary OC/EC for suburban site in summer is 3.12. Inter-seasonal comparison of OC/EC shows a higher amount in winter than summer at urban site and the reasons could be that more semi-volatile organic compounds condensed into particles in low temperature so OC is higher in low temperatures. But OC/EC in at suburban site is higher than urban site in summer and this may result from biomass burning of agricultural waste in summer.

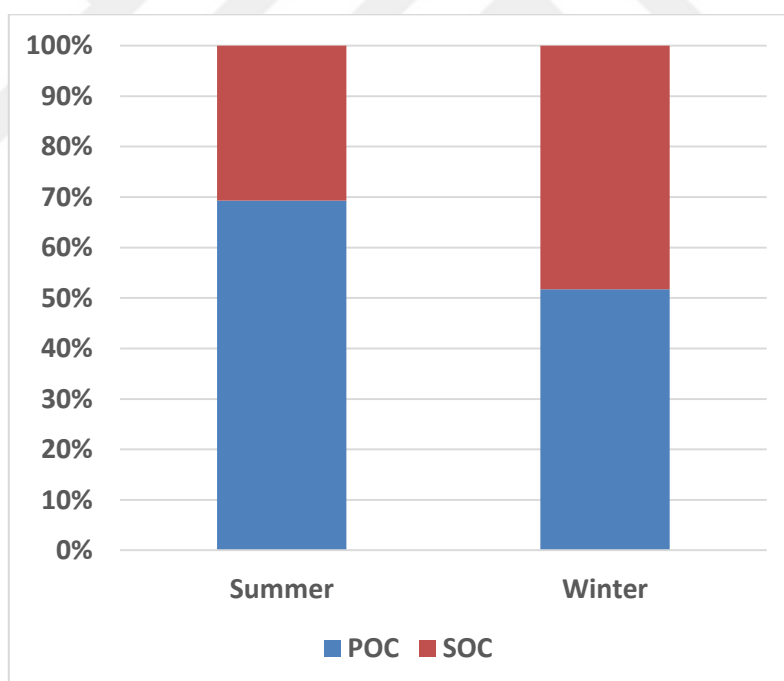
Calculated POC and SOC for urban site (Sihhiye) in summer are respectively  $5.29 \pm 0.96$  and  $2.34 \pm 1.67 \mu\text{gm}^{-3}$ . Contribution of POC and SOC to total OC mass is 72 % and 28 % respectively. SOA is calculated 3.74.

POC and SOC for semi-rural site (Beytepe campus) in summer are respectively  $3.91 \pm 1.11$  and  $1.84 \pm 1.12 \mu\text{gm}^{-3}$ . Contribution of POC and SOC to total OC mass is 68% and 32 % respectively. SOA is calculate to be 2.94.

Calculated POC and SOC for urban site (Sihhiye) in winter sampling period are respectively  $7.39 \pm 2.99$  and  $6.86 \pm 6.63 \mu\text{gm}^{-3}$ . Contribution of POC and SOC to total OC mass is 61 and 39  $\mu\text{gm}^{-3}$  respectively. SOA is calculated to be 10.97.

**Table 4.15.** Mean concentration of primary and secondary organic carbon in summer and winter at Sihhiye

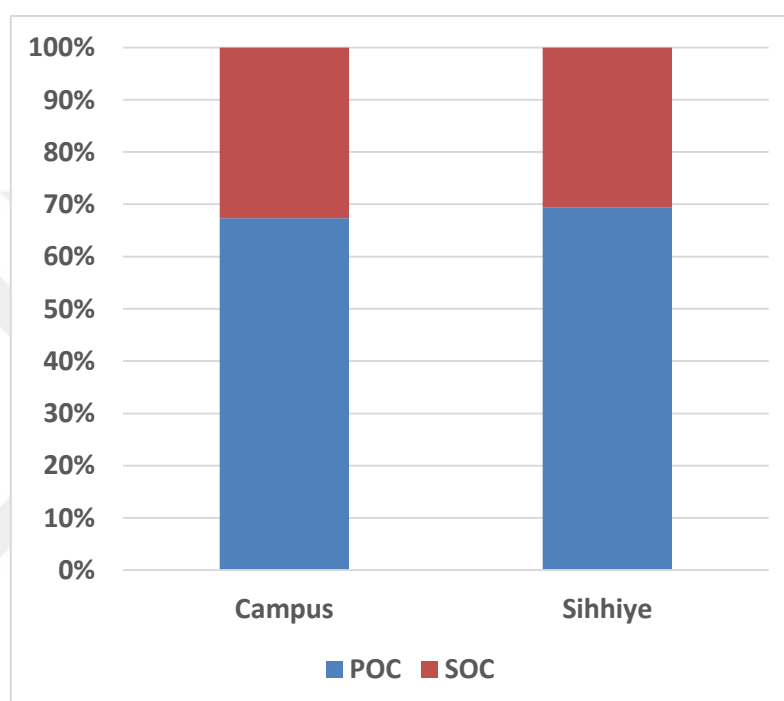
	Summer		Winter	
	Mean( $\mu\text{gm}^{-3}$ )	STD( $\mu\text{gm}^{-3}$ )	Mean( $\mu\text{gm}^{-3}$ )	STD( $\mu\text{gm}^{-3}$ )
<b>OC(primary)</b>	5.29	0.96	7.36	2.99
<b>SOC</b>	2.34	56	6.86	6.64



**Figure 4.33.** Seasonal variation of primary and secondary organic carbon at urban site

**Table 4.16.** Mean concentration of primary and secondary organic carbon at urban and sub-urban sites in summer

	Campus		Sihhiye	
	Mean( $\mu\text{gm}^{-3}$ )	STD( $\mu\text{gm}^{-3}$ )	Mean( $\mu\text{gm}^{-3}$ )	STD( $\mu\text{gm}^{-3}$ )
<b>OC(primary)</b>	3.91	1.11	5.29	0.96
<b>SOC</b>	1.84	1.12	2.34	1.67

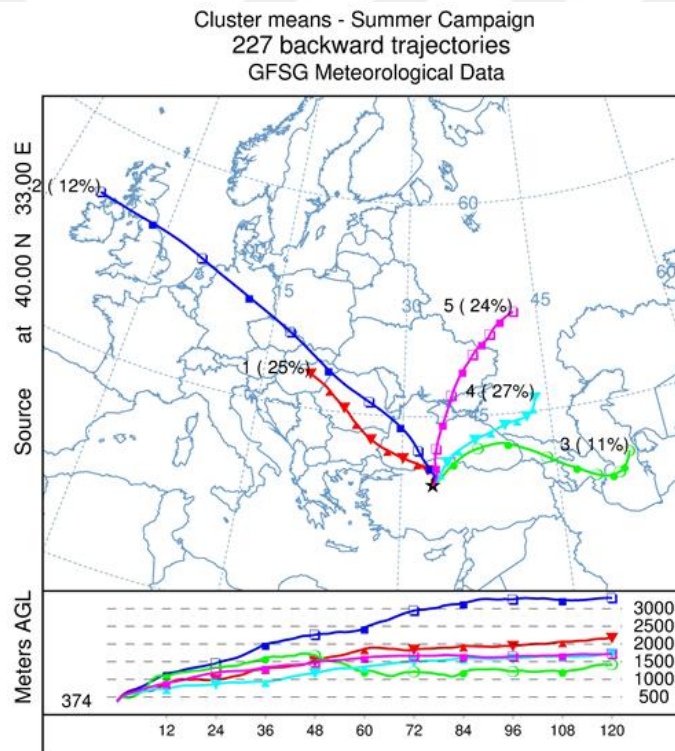


**Figure 4.34.** Variation of primary and secondary organic carbon at urban and sub-urban sites in summer

#### 4.15 Back Trajectory Cluster Mode for Summer and Winter Campaign

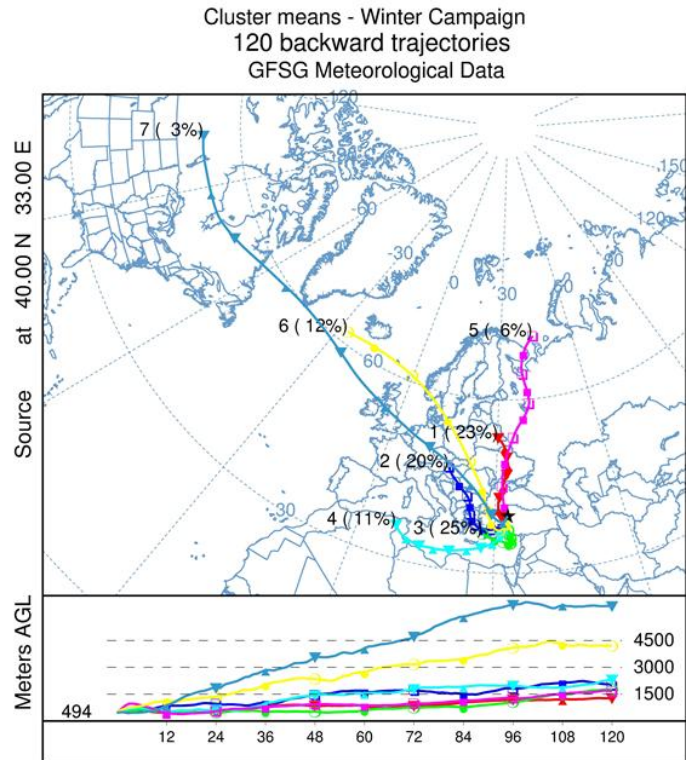
In order to understand the contribution of transported aerosols to Ankara's ambient air, trajectory analysis have been conducted for the summer and winter campaign periods. 120-hour back trajectories calculated with Hybrid Single-Particle Lagrangian Integrated Trajectory Version-4 (HYSPPLIT\_4) model as described by Draxler and Hess for 57 days between 16.06.2016 - 11.08.2016 and 30 days between 29.12.2016 - 27.01.2017 for 6-hours interval and 1-hour retention time in each grid cell. Model run by Global Data Assimilation System (GDAS)  $0.5^{\circ} \times 0.5^{\circ}$  gridded data obtained from US National Oceanic and Atmospheric Administration (NOAA), Air Sources Laboratory (ARL) READY meteorological data archive.

40.00° Latitude and 33.00° Longitude Ankara city center coordinates were used as start point to determine both stations. 1500 m above mean sea level (AMSL) elevation was used to eliminate the impact of Planetary Boundary Layer (PBL) seasonal changes above the land surface and to represent both PBL and lower Free Tropospheric air parcel transport. After the completion of each daily 0.5°x0.5° spatial and 1-hour temporal resolution trajectories, air parcels are clustered according to their end point spatial variances so as to determine main transport patterns which arrive at Ankara. Plots are depicted as above ground level (AGL) elevations and with mean path percentages of each cluster for both summer and winter campaign periods. Figures 4.35 and 4.36 are showing cluster 5-day back trajectories of summer and winter campaign.



**Figure 4.35.** Summer site 5-day back trajectories representing: (1) Central - Eastern Europe, (2) Atlantic Ocean - Ireland, (3) Caspian - Black Sea, (4) Caucasia - Black Sea, and (5) Russia - Ukraine - Black Sea

Figure 4.35 is showing cluster 5-day back trajectory of summer campaign. Cluster back trajectory flow pattern for summer campaign demonstrates that during summer sampling period 27% of air mass is originated from Caucasia - Black Sea, 25% from Central - Eastern Europe, 24% from Russia - Ukraine - Black Sea, 12% from Atlantic Ocean – Ireland and 11% from Caspian - Black Sea.

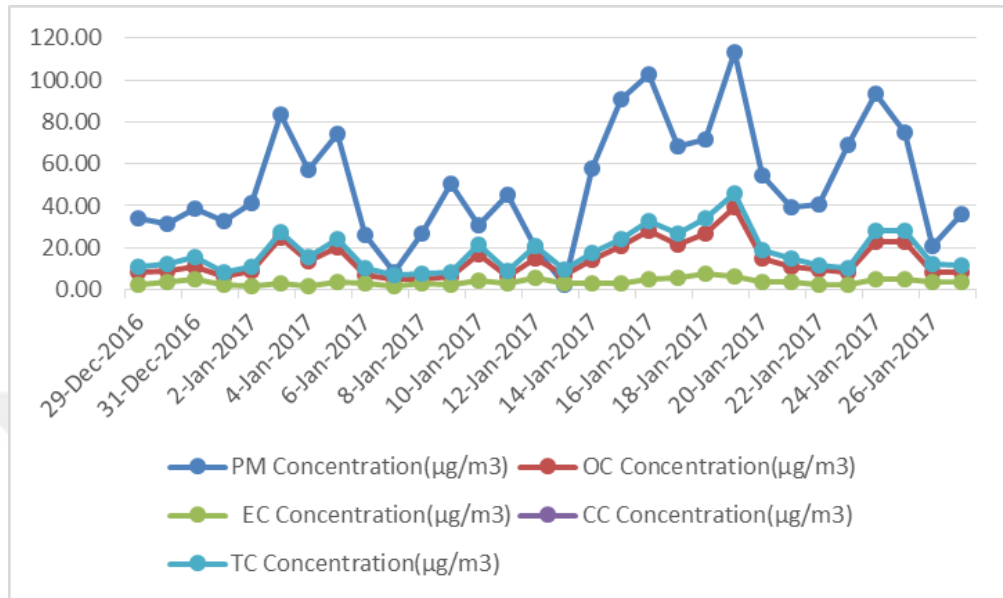


**Figure 4.36.** Winter site 5-day back trajectories representing: (1) Russia - Ukraine - Black Sea, (2) Central - Eastern Europe, (3) Canada, (4) North Africa, (5) Barents Sea - Russia - Ukraine - Black Sea, and (6) Atlantic Ocean - Northern Europe

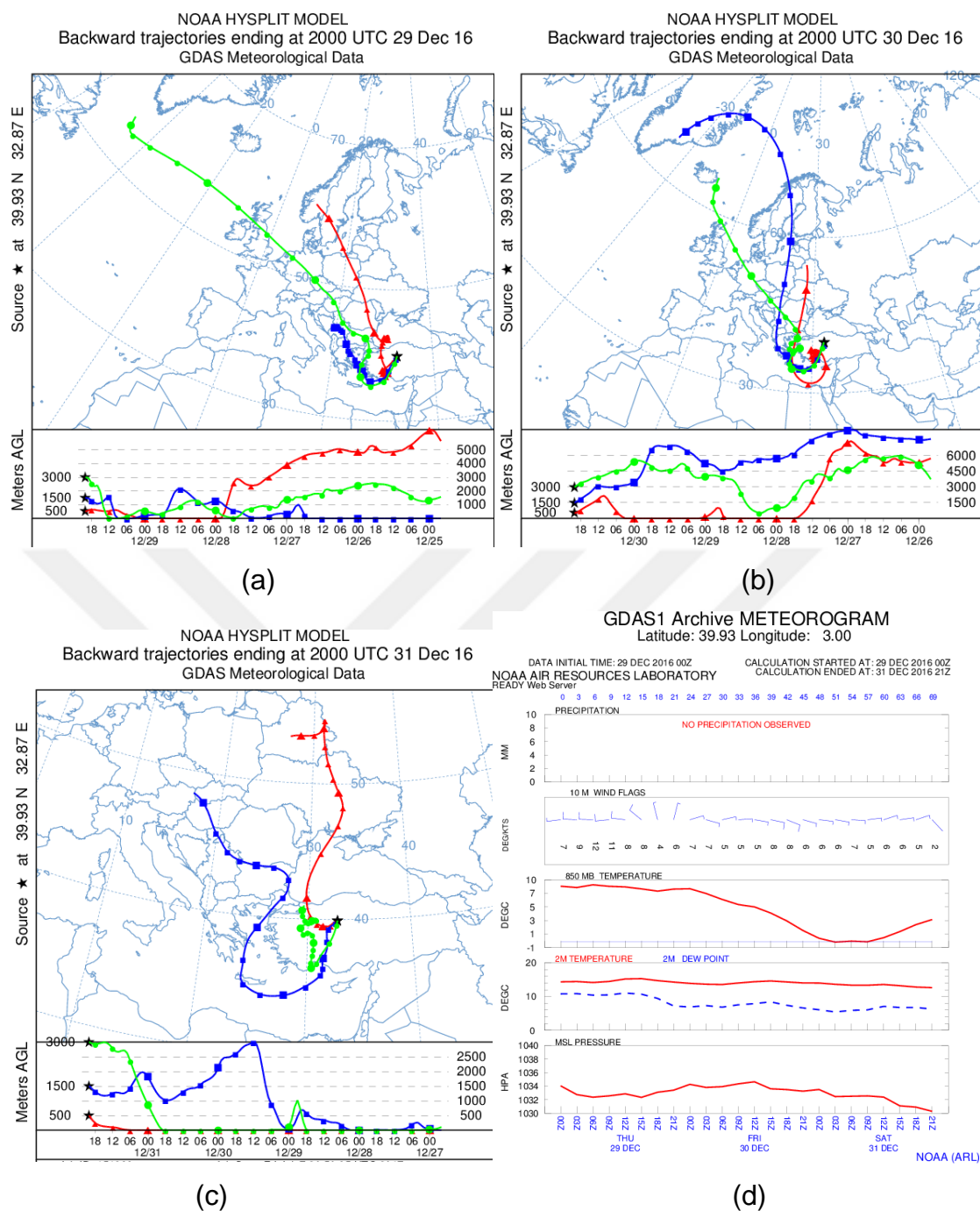
Figure 4.36 is showing cluster 5-day back trajectory of winter campaign. Cluster back trajectory flow pattern for winter campaign demonstrates that 25% of air mass is originated from Canada, 23% from Russia - Ukraine - Black Sea, 20% from Central - Eastern Europe, 12 % from Atlantic Ocean - Northern Europe, 11 % from North Africa and 6% from Barents Sea - Russia - Ukraine - Black Sea.

#### 4.15.1 120-hour back trajectory During Winter Sampling Period

Figure 4.37 is showing variation of PM<sub>2.5</sub>, OC, EC, CC and TC concentration at urban site during winter period.

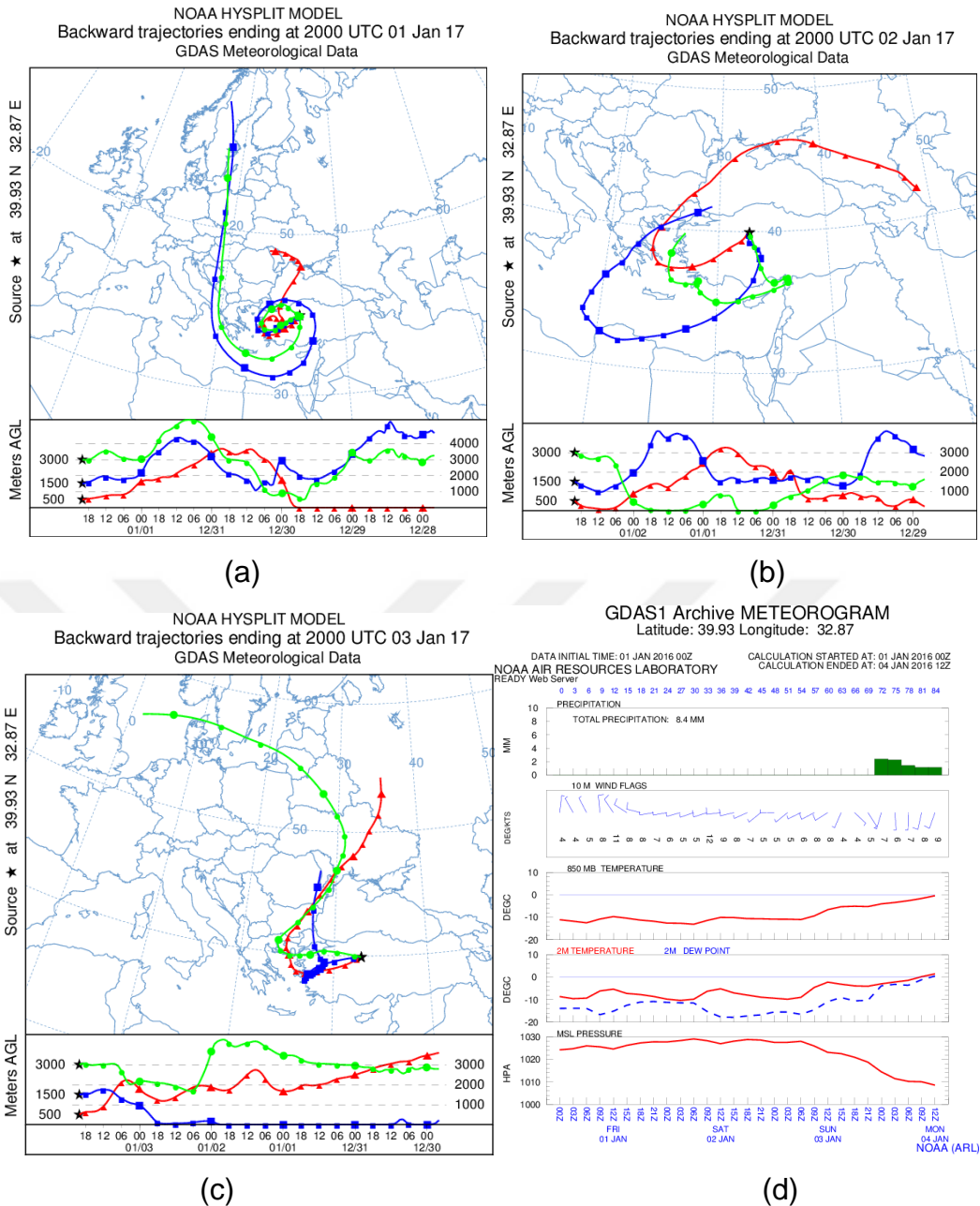


**Figure 4.37.** Daily mean concentrations of PM<sub>2.5</sub>, OC, EC, CC and TC at urban site during winter period



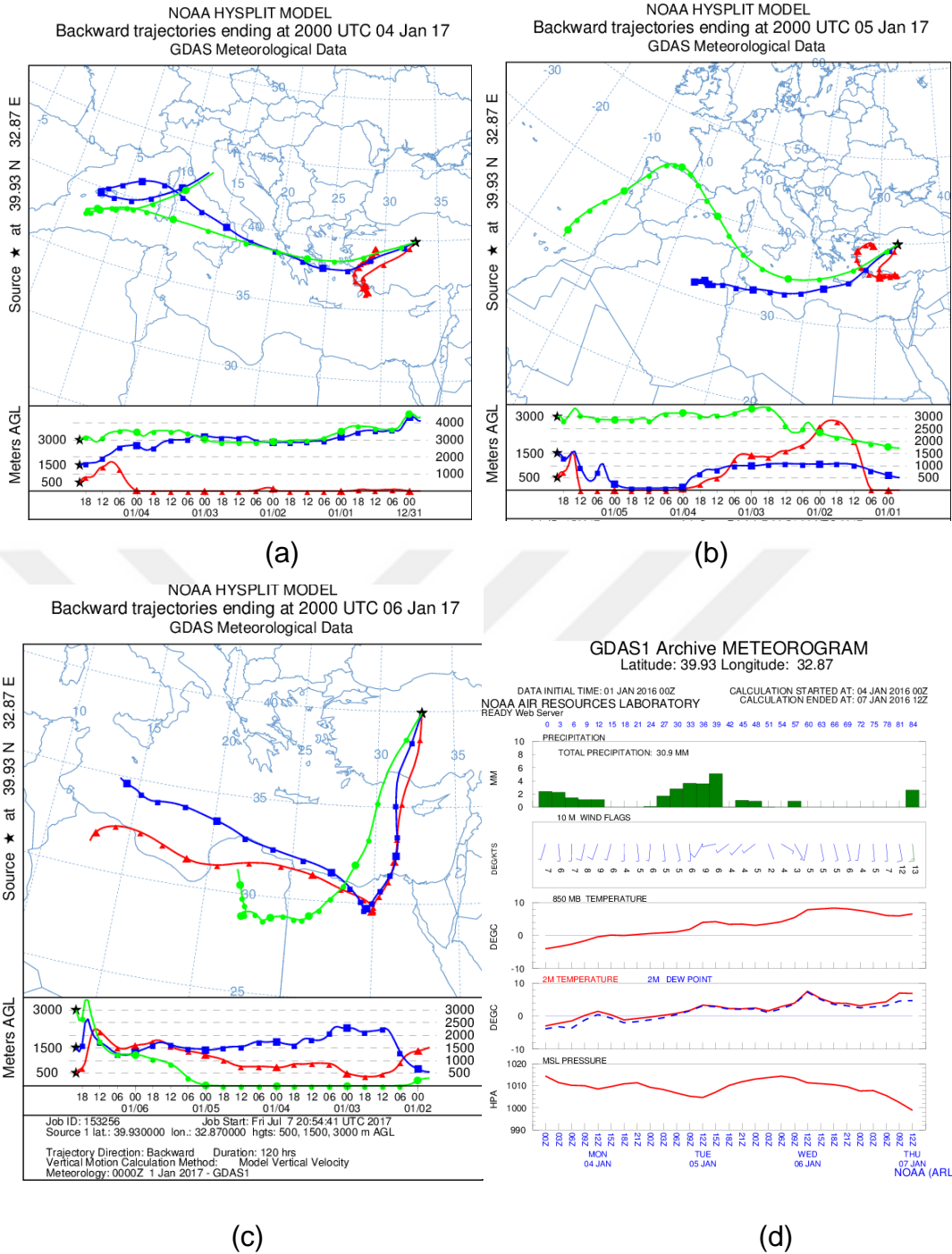
**Figure 4.38.** 120-hour back trajectory for Ankara on a) December 29<sup>th</sup> b) 30<sup>th</sup> and c) 31<sup>st</sup> d) Meteorological condition in Ankara on December 29<sup>th</sup>, 30<sup>th</sup> and 31<sup>st</sup>

Figure 4.38 is showing 120-hour back trajectory for Ankara on December 29<sup>th</sup>, 30<sup>th</sup> and 31<sup>st</sup>. 5-day back trajectory for 30<sup>th</sup> and 31<sup>st</sup> of December 2016 is showing that air mass is Northern, temperature decreases for about 10 degrees, mixing height is low on 31<sup>st</sup> especially in the afternoon indicating an inversion. OC and EC concentrations are considerably high 10.69 and 4.66  $\mu\text{g m}^{-3}$  respectively.



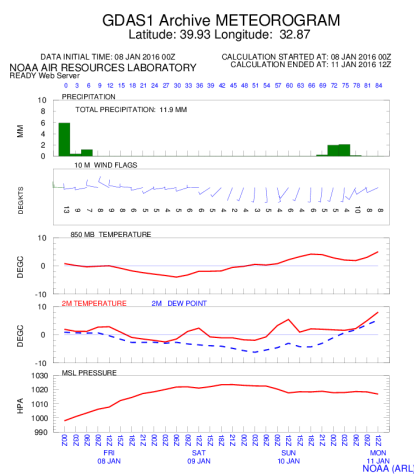
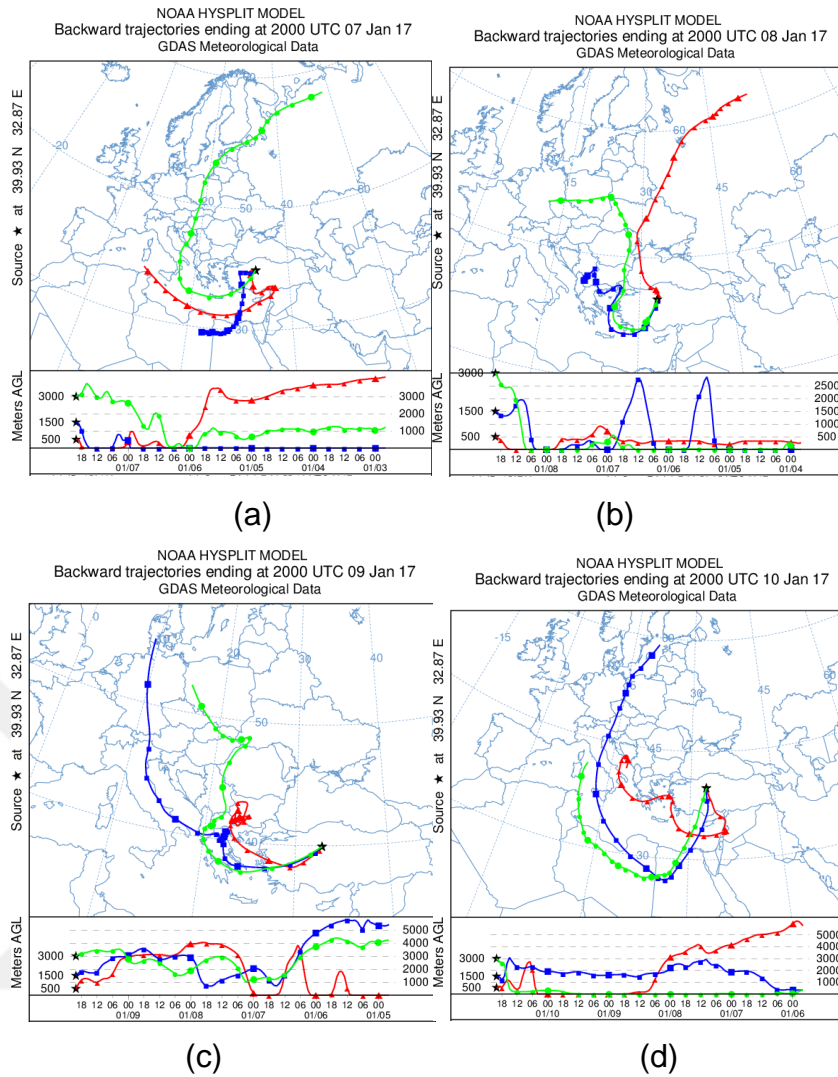
**Figure 4.39.** 120-hour back trajectory for Ankara on a) January 1<sup>st</sup> b) 2<sup>nd</sup> and c) 3<sup>rd</sup> d) Meteorological condition in Ankara on January 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup>

Figure 4.39 is showing 120-hour back trajectory for Ankara on January 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup>. On 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> air mass is Northern, not heavy winds are blown, temperature is low about average -7, and there is an inversion on 2<sup>nd</sup> and 3<sup>rd</sup> and 4<sup>th</sup> according to the mixing height data. On the 3<sup>rd</sup>, PM<sub>2.5</sub>, OC and EC concentrations are considerably high 83.82, 24.71 and 3.02  $\mu\text{g m}^{-3}$  respectively probably due to inversion and regional pollution.



**Figure 4.40.** 120-hour back trajectory for Ankara on a) January 4<sup>th</sup> b) 5<sup>th</sup> and c) 6<sup>th</sup> d) Meteorological condition in Ankara on January 4<sup>th</sup>, 5<sup>th</sup> and 6<sup>th</sup>

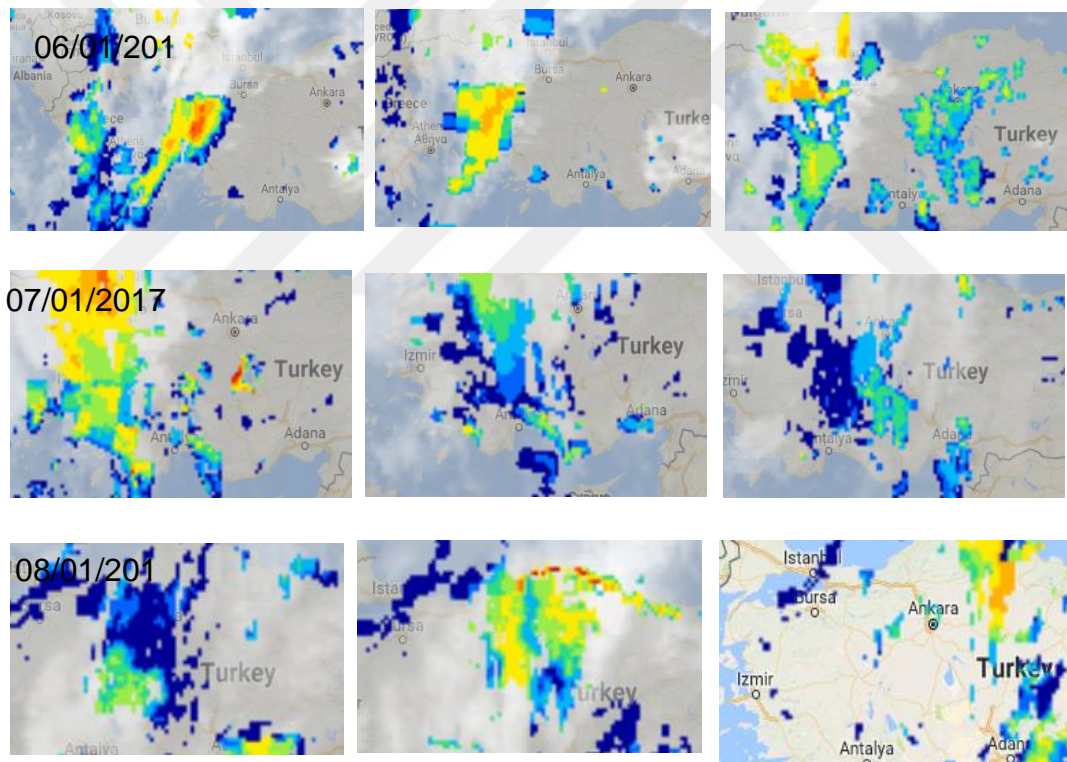
Figure 4.40 is showing 120-hour back trajectory for Ankara on January 4<sup>th</sup>, 5<sup>th</sup> and 6<sup>th</sup>. From the 5<sup>th</sup>, wind direction changes to western and wind speed increases that is the reason of an elevation in PM<sub>2.5</sub>, OC and EC concentrations which definitely is the effect of Sahara dust event in this period.



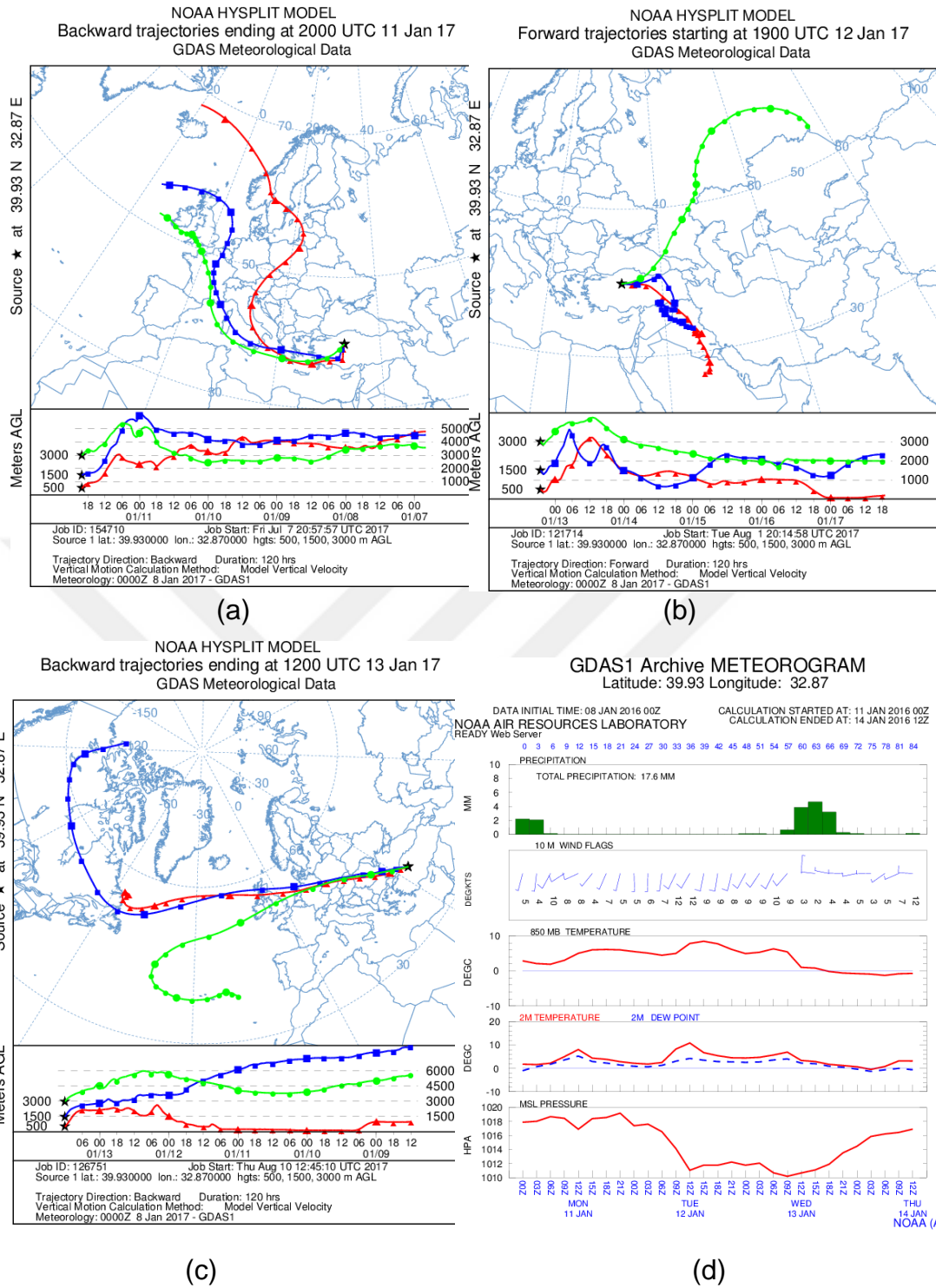
(e)

**Figure 4.41.** 120-hour back trajectory for Ankara on a) January 7<sup>th</sup> b) 8<sup>th</sup> and c) 9<sup>th</sup> d) 10<sup>th</sup> e) Meteorological condition in Ankara on January 7<sup>th</sup>, 8<sup>th</sup>, 9<sup>th</sup> and 10<sup>th</sup>

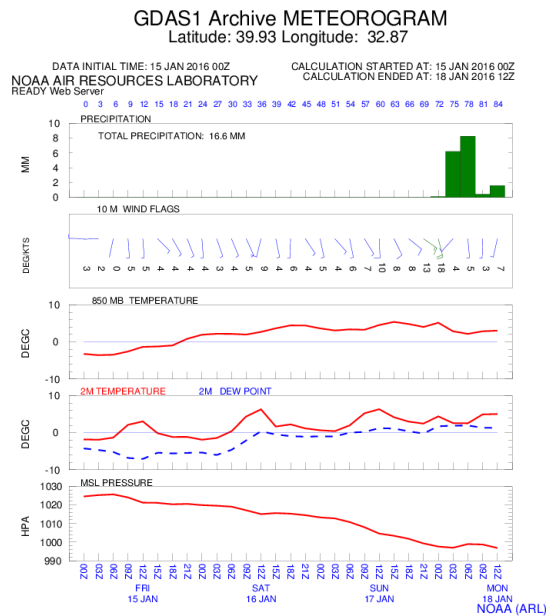
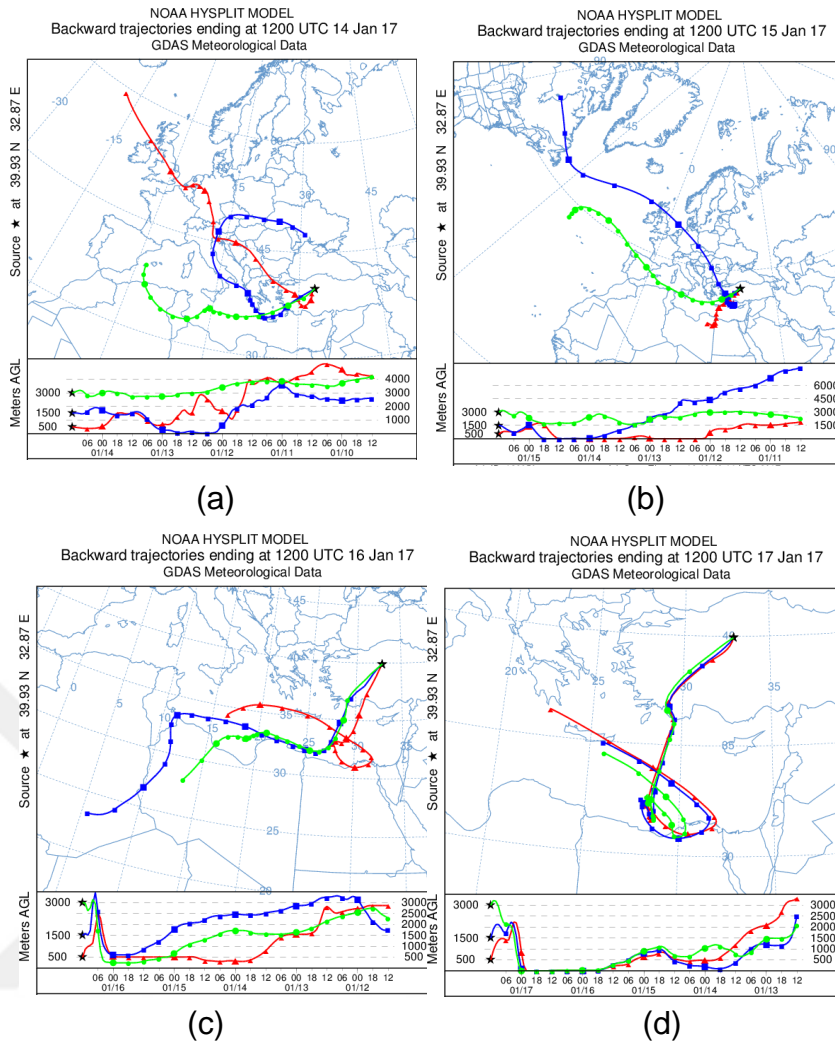
Figure 4.41 is showing 5-day back trajectory for Ankara on January 7<sup>th</sup>, 8<sup>th</sup>, 9<sup>th</sup> and 10<sup>th</sup>. On the 6<sup>th</sup>, 7<sup>th</sup> and 8<sup>th</sup> a dust event is obvious. PM<sub>2.5</sub> concentration is 26.93, 8.32 µg m<sup>-3</sup> and 26.93 µg m<sup>-3</sup> respectively. On 7<sup>th</sup>, PM<sub>2.5</sub>, OC and EC concentrations are low probably due to precipitation. We have checked the rain fall on GSMAP (Global Satellite Mapping of Precipitation) to map the rain fall on 6<sup>th</sup>, 7<sup>th</sup> and 8<sup>th</sup> which are shown in figure 4.42 and it shows that precipitation is heavy on the 7<sup>th</sup> along the down track of the rain fall map and low concentrations are due to wash out. On the 10<sup>th</sup> wind direction changes from west to south, temperature increases due to air flows from Libya. OC and EC concentrations are pretty high, 17.14 and 4.18 µg m<sup>-3</sup> respectively. This demonstrates a different source's contribution. From 7<sup>th</sup> to 12<sup>th</sup> PM<sub>2.5</sub> concentrations are low possibly due to precipitation and cold northern wind as well on these days.



**Figure 4.42.** Rain fall map on January 6<sup>th</sup>, 7<sup>th</sup> and 8<sup>th</sup>



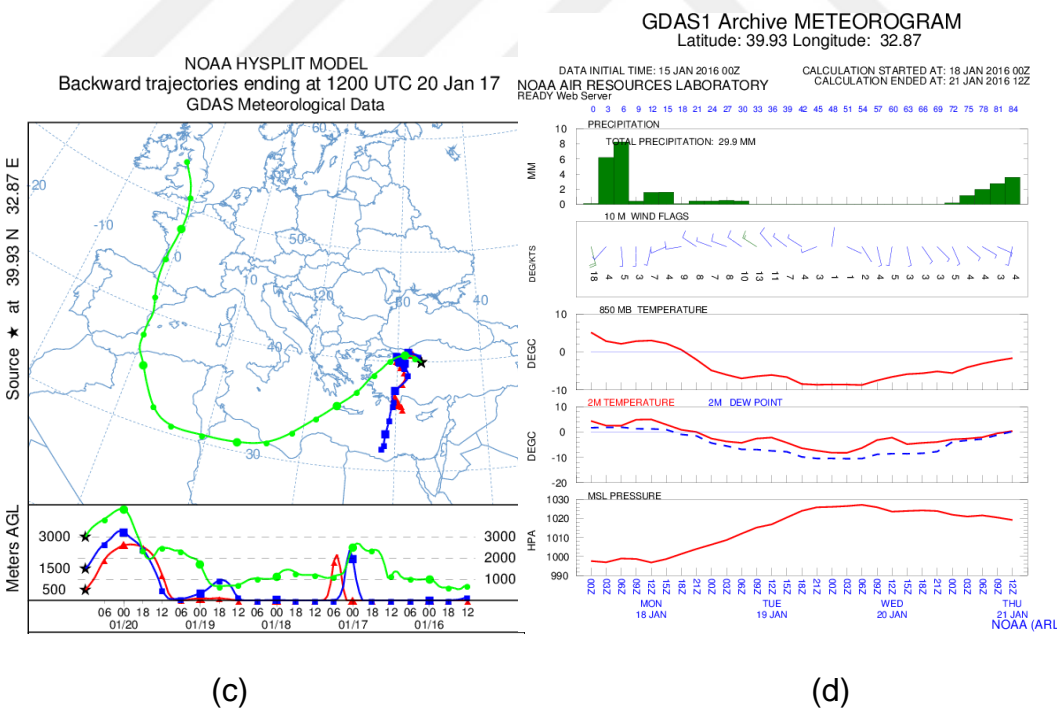
**Figure 4.43.** 120-hour back trajectory for Ankara on a) January 11<sup>th</sup> b) 12<sup>th</sup> and c) 13<sup>th</sup> d) Meteorological condition in Ankara on January 11<sup>th</sup>, 12<sup>th</sup>, 13<sup>th</sup>



(e)

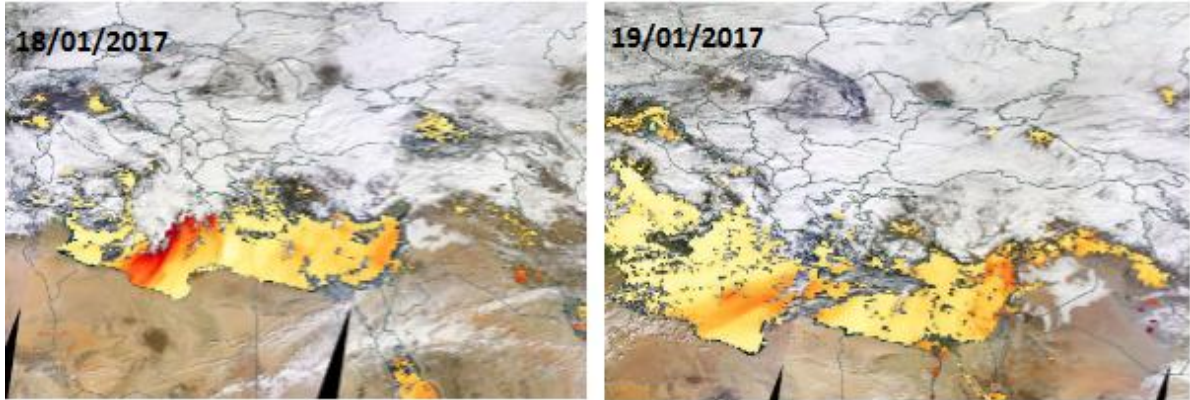
**Figure 4.44.** 120-hour back trajectory for Ankara on a) January 14<sup>th</sup> b) 15<sup>th</sup> and c) 16<sup>th</sup> d) 17<sup>th</sup> e) Meteorological condition in Ankara on January 14<sup>th</sup>, 15<sup>th</sup>, 16<sup>th</sup> and 17<sup>th</sup>

Figure 4.44 is showing 120-hour back trajectory for Ankara on January 14<sup>th</sup>, 15<sup>th</sup>, 16<sup>th</sup> and 17<sup>th</sup>. On 14<sup>th</sup> and 15<sup>th</sup> PM<sub>2.5</sub> concentration is high because of Sahara dust event. On 15<sup>th</sup>, 16<sup>th</sup> and 17<sup>th</sup> also air mass flows from south but amount of dust is not considerable.

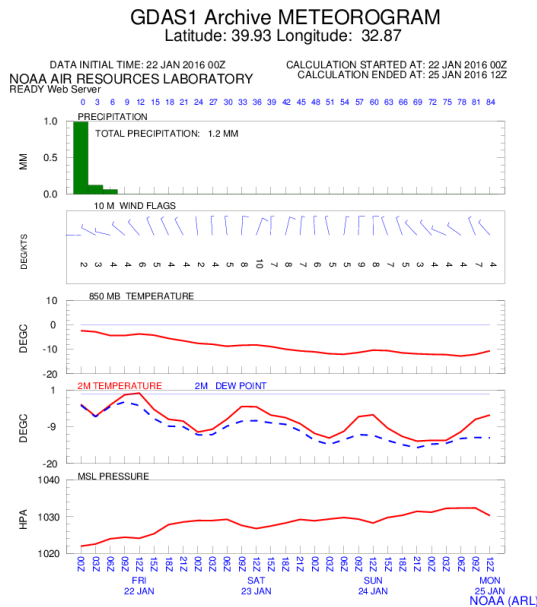
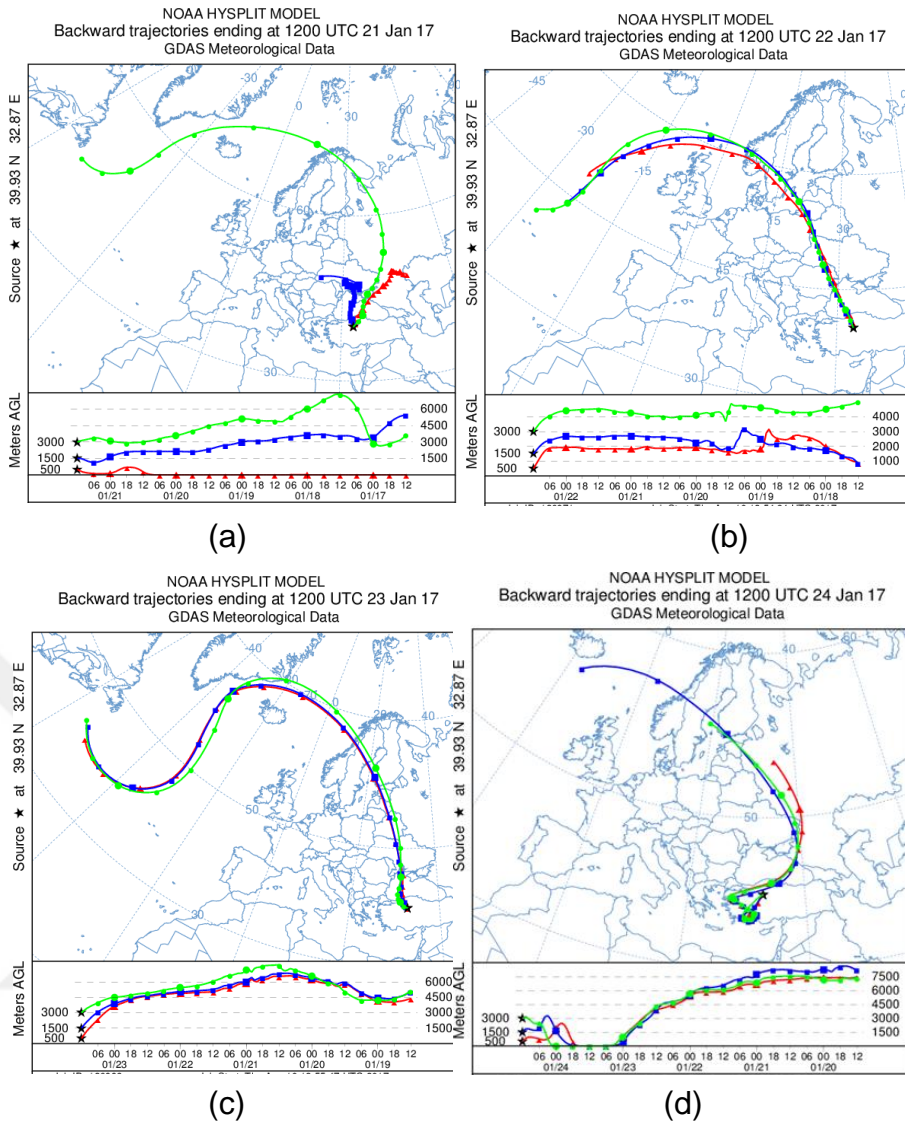


**Figure 4.45.** 120-hour back trajectory for Ankara on a) January 18<sup>th</sup> b) 19<sup>th</sup> and c) 20<sup>th</sup> d) Meteorological condition in Ankara on January 7<sup>th</sup>, 8<sup>th</sup>, 9<sup>th</sup> and 10<sup>th</sup>

Another dust event is seen to be started on January 18<sup>th</sup> from Libya and the 19<sup>th</sup> is a dusty day with the highest amount of PM<sub>2.5</sub> and OC concentrations in sampling period 113.28 and 39.25  $\mu\text{g m}^{-3}$  which is shown in figure 4.46.



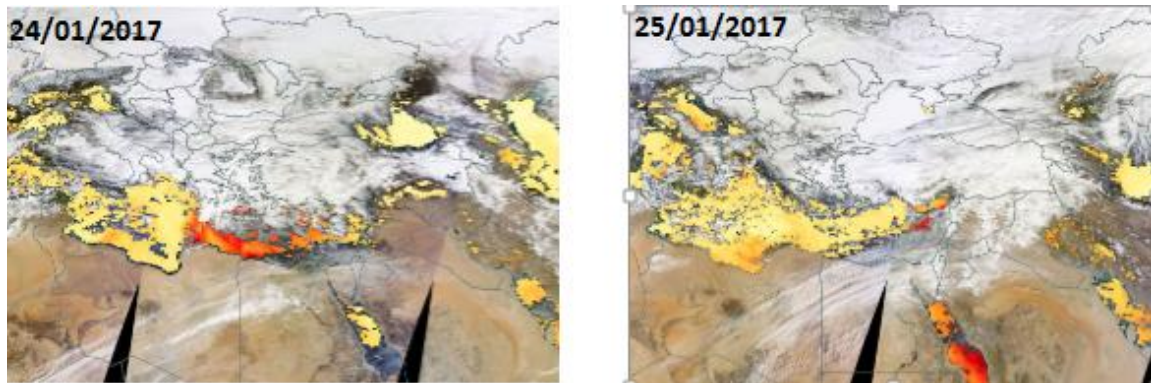
**Figure 4.46.** Dust event on 18<sup>th</sup> and 19<sup>th</sup> of January



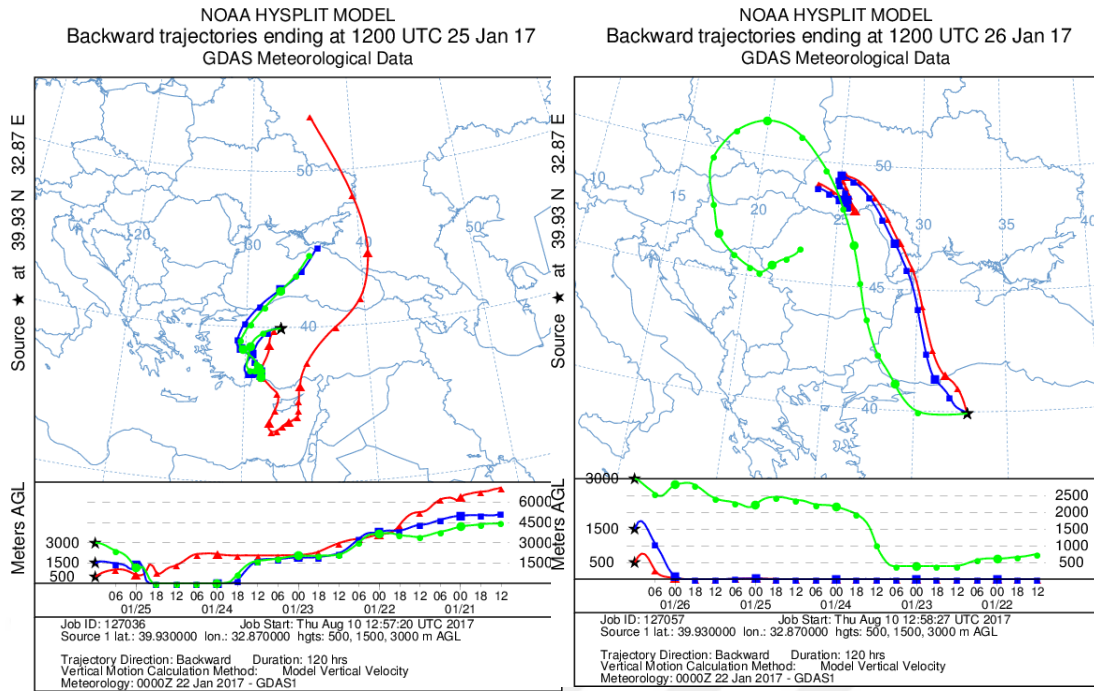
(e)

**Figure 4.47.**120-hour back trajectory for Ankara on a) January 21<sup>st</sup> b) 22<sup>nd</sup> c) 23<sup>rd</sup> d) 24<sup>th</sup> e) Meteorological condition in Ankara on January 21<sup>st</sup>, 22<sup>nd</sup>, 23<sup>rd</sup>, 24<sup>th</sup>

Figure 4.47 is showing 120-hour back trajectory for Ankara on January 21<sup>st</sup>, 22<sup>nd</sup>, 23<sup>rd</sup> and 24<sup>th</sup>. From 22<sup>nd</sup> air mass turns to be Northern. On 23<sup>rd</sup> and 24<sup>th</sup> air mass is also Northern. On 23<sup>rd</sup> air mass comes from a long distance. It could be a representative of long range transport for pollutants. Temperature has a descending trend. Average mixing height also decreases from 22<sup>nd</sup> to 24<sup>th</sup> and is the lowest on 24<sup>th</sup>. On 24<sup>th</sup> OC and EC concentrations are considerably high (22.84 and 4.94  $\mu\text{g m}^{-3}$  respectively) probably due to inversion. On 24<sup>th</sup> and 25<sup>th</sup> another dust event is observed which is shown in Figure 4.48.

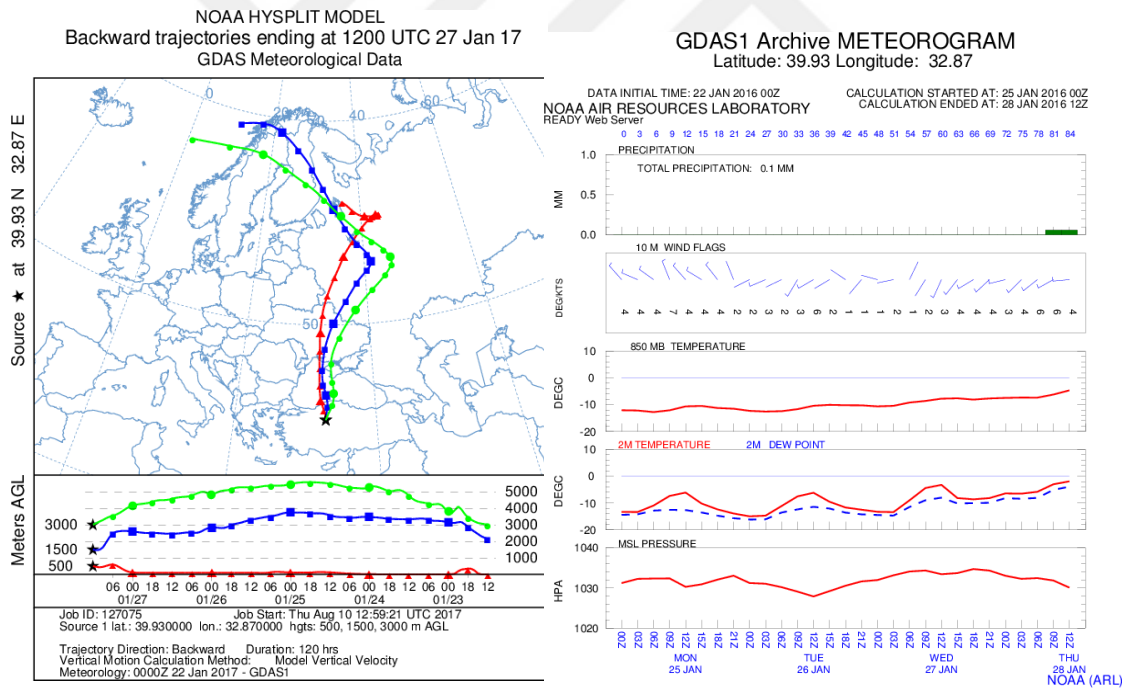


**Figure 4.48.**Dust event on 24<sup>th</sup> and 25<sup>th</sup> of January



(a)

(b)



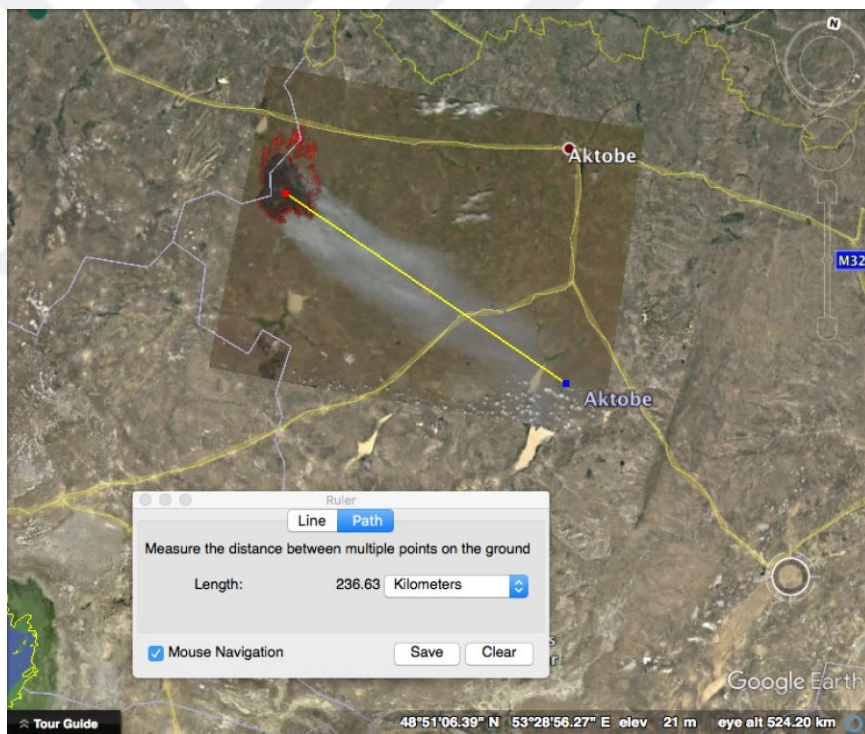
(c)

(d)

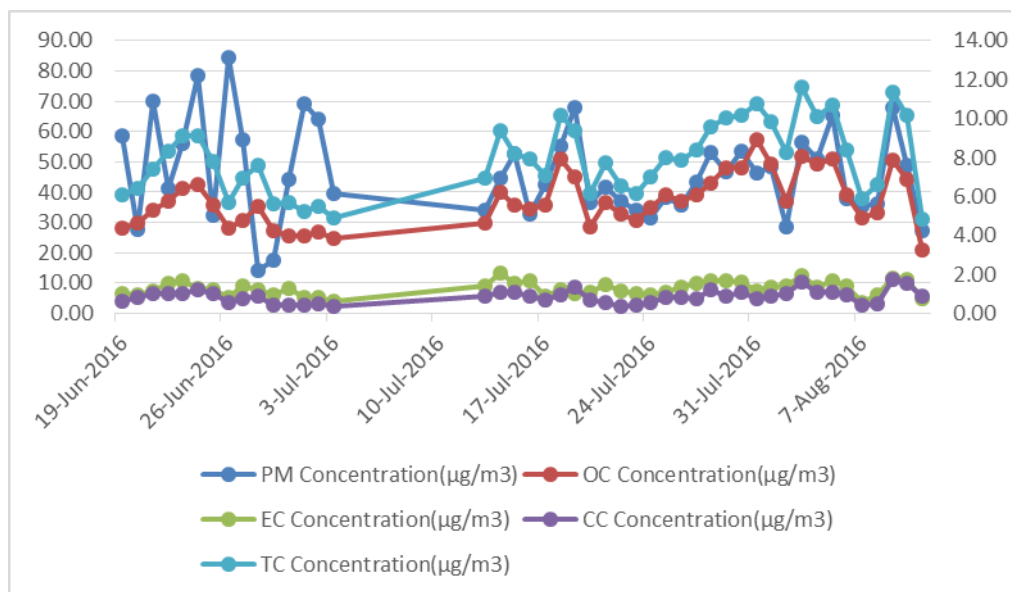
**Figure 4.49.** 120-hour back trajectory for Ankara on a) January 25<sup>th</sup> b) 26<sup>th</sup> c) 27<sup>th</sup> meteorological condition in Ankara on January 25<sup>th</sup>, 26<sup>th</sup>, 27<sup>th</sup>

#### 4.15.2 Back Trajectory for Campus during Summer Sampling Period

In Turkey and in northern countries agricultural post-harvest burning during the summer months is a big event that can be easily observed by the satellites. The lack of cloudiness during the summer shows us the white fumes of active fog, which is in result of the burning of the stubble showing combustion gases. Via satellite data it is possible to observe the extent of clouds up to 250 km quite easily. Although it would be hard to trace the smoke due to dilution and dispersion, it is possible to trace fire burning via their signature on EC or OC. For example the stubble burning observed at northern Caspian region on 2<sup>nd</sup> July 2017 is shown in Figure 4.50 together with the 236 km path length of the white clouds that can be traceable via naked eye.



**Figure 4.50.** Extension of fog and smoke resulting from agriculture waste burning on 2<sup>nd</sup> July 2017

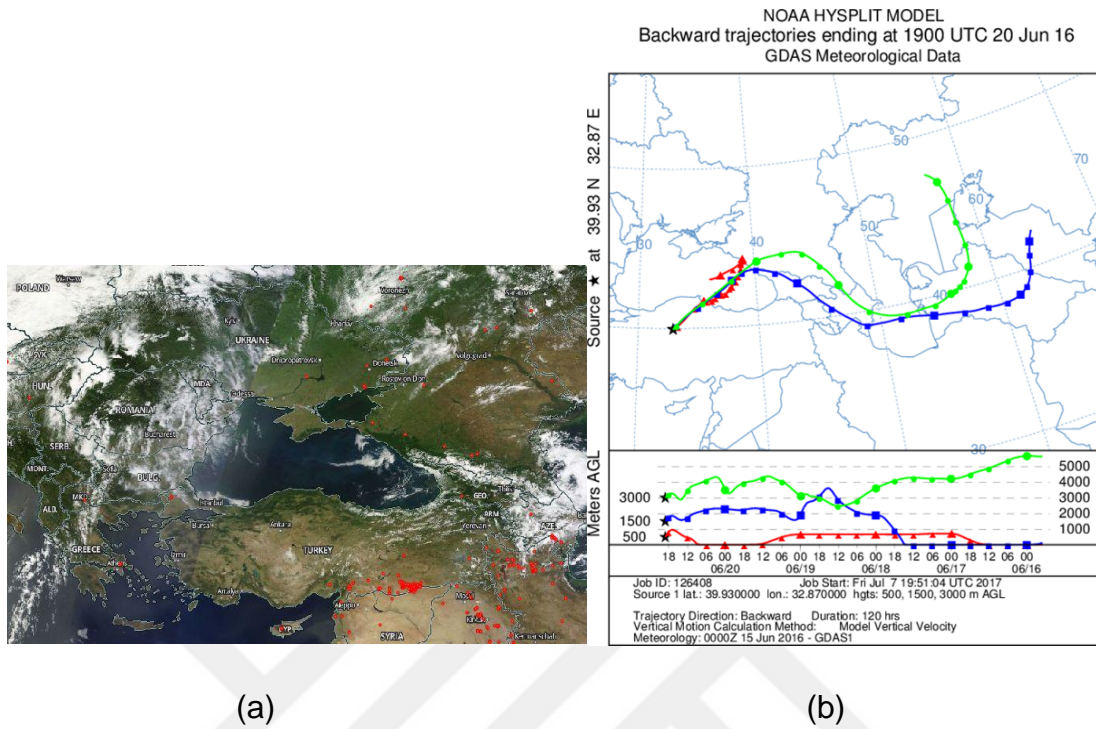


**Figure 4.51.** Variation of PM<sub>2.5</sub>, OC, EC, CC and TC concentration in semi-urban site during winter sampling period

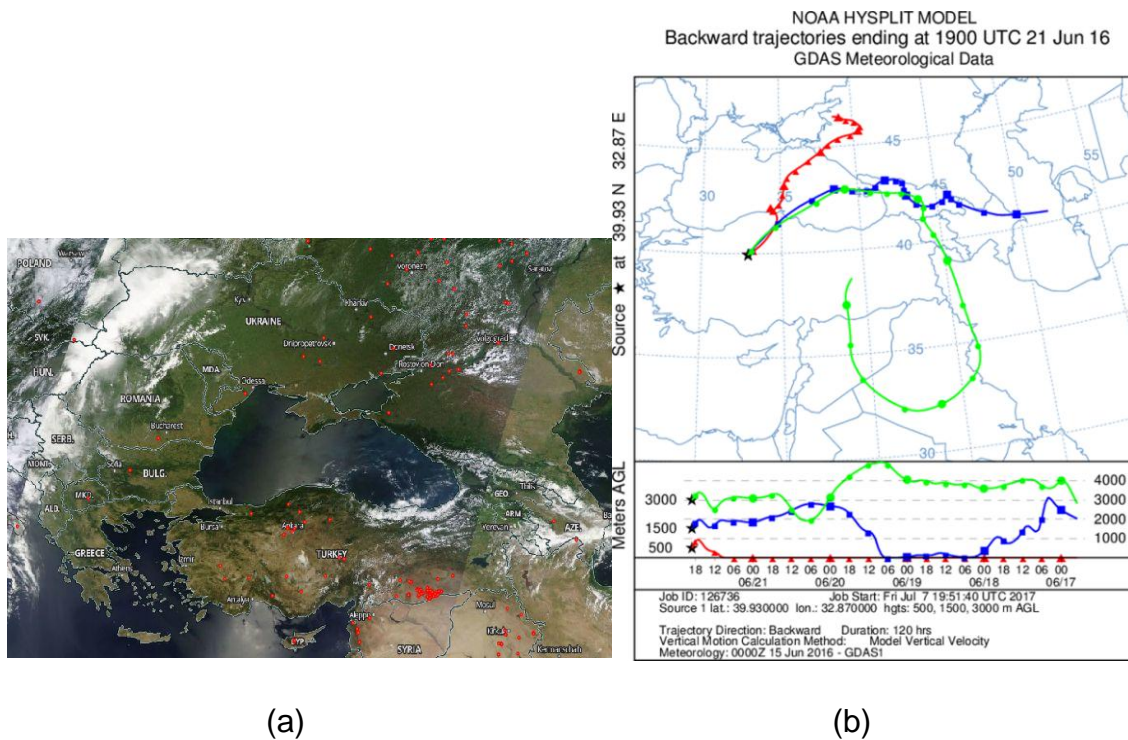
Figure 4.51 is showing variation of PM<sub>2.5</sub>, OC, EC, CC and TC concentration in sub-urban site during winter sampling period. PM<sub>2.5</sub> mean mass concentration is calculated 46.43  $\mu\text{g m}^{-3}$  with maximum 84.26 and minimum 13.99  $\mu\text{g m}^{-3}$  respectively. OC mean concentration in this period is calculated 5.80  $\mu\text{g m}^{-3}$  with maximum 8.89 and minimum 3.27  $\mu\text{g m}^{-3}$  respectively. EC mean concentration was calculated to be 1.27 with maximum 2.09 and minimum 0.53 respectively. Wind is blown dominantly from North and northeast. Average wind speed is 3.48 m/s. Maximum wind speed is 9.7 m/s. Average temperature is 21(°C). Average humidity is 45.61%.

As it is seen in figure 4.48, there is an increase in concentration of PM<sub>2.5</sub>, OC and EC on June 21<sup>st</sup> from 27.72, 4.64 and 0.96 to 70.26, 5.27 and 1.12  $\mu\text{g m}^{-3}$  respectively. 120-hour back trajectory at 1500 m level for 20<sup>th</sup> and 21<sup>st</sup> of June shows that air mass originated from Kazakhstan and Uzbekistan and moved through Azerbaijan and Georgia to Turkey. Checking the fires and thermal anomalies shows nearly the same number of red spots of biomass burning activities on both days. The reason of increase seems to be considerably elevated numbers of red spots inside Turkey on 21<sup>st</sup> comparing to 20<sup>th</sup> especially at North, Northwest and Southeast.

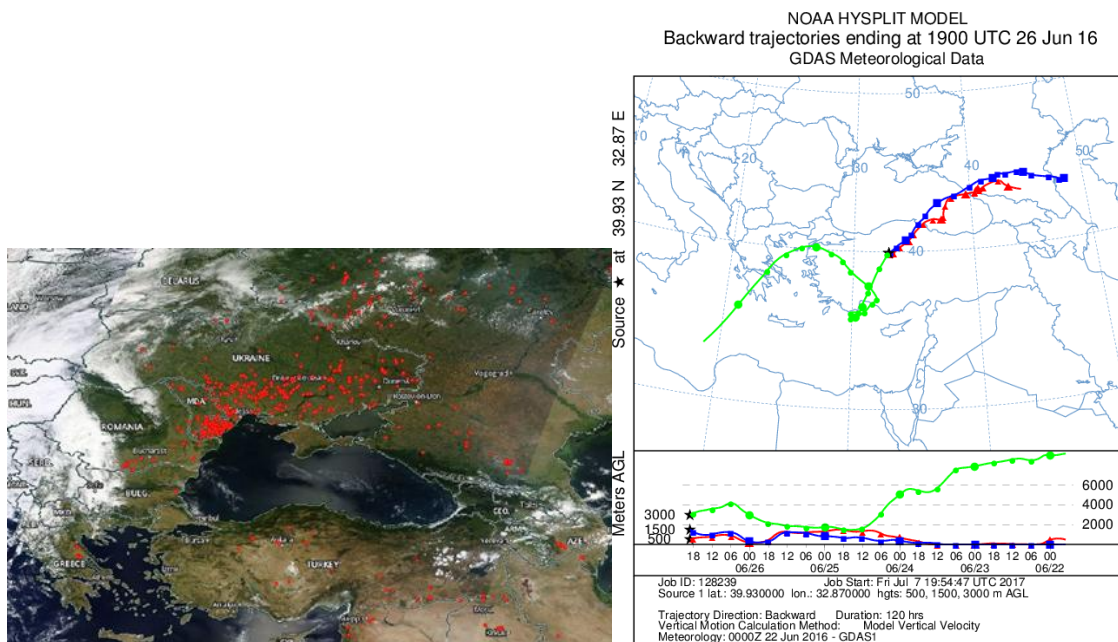
Figures 4.52 to 4.67 are showing fires and thermal anomalies and 120-hour back trajectory for Ankara in summer sampling period.



**Figure 4.52.** a) Fires and thermal anomalies on 20<sup>th</sup> of June 2016 b) 120-hour back trajectory for Ankara on 20<sup>th</sup> of June 2016



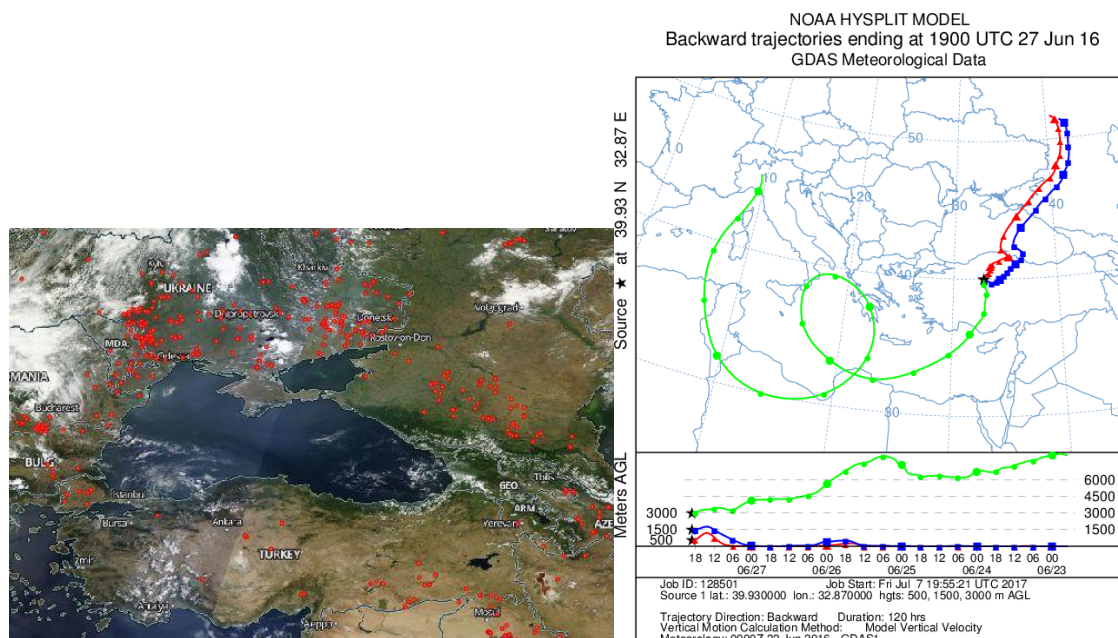
**Figure 4.53.** a) Fires and thermal anomalies on 21<sup>st</sup> of June 2016 b) 120-hour back trajectory for Ankara on 21<sup>st</sup> of June 2016



(a)

(b)

**Figure 4.54.** Fires and thermal anomalies on 26<sup>st</sup> of June 2016 b) 120-hour back trajectory for Ankara on 27<sup>st</sup> of June 2016



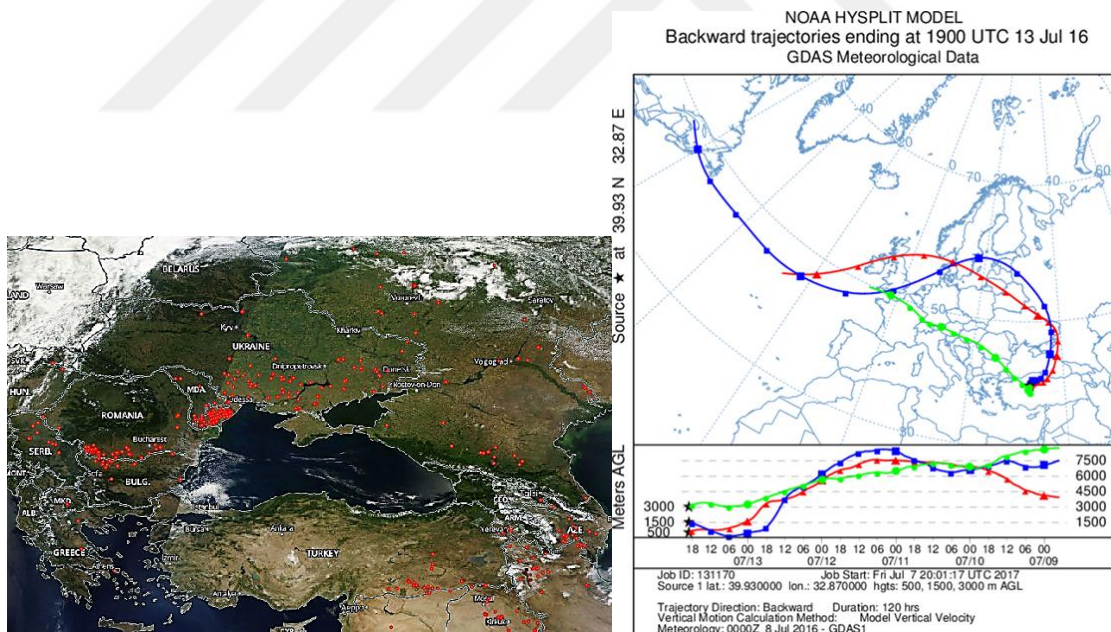
(a)

(b)

**Figure 4.55.** Fires and thermal anomalies on 27<sup>st</sup> of June 2016 b) 120-hour back trajectory for Ankara on 27<sup>st</sup> of June 2016

Figures 4.54 and 4.55 are showing fires and thermal anomalies on 26<sup>th</sup> and 27<sup>th</sup> of June. There is an increase of PM<sub>2.5</sub>, OC and EC concentration on 26<sup>th</sup> and 27<sup>th</sup> of June at Beytepe. It is possibly due do dust event on these days. After 26<sup>th</sup> with high PM<sub>2.5</sub> concentration of 84.26 µg m<sup>-3</sup>, on 27<sup>th</sup>, there is a considerable decrease in PM<sub>2.5</sub> concentration and decreasing trend is continuous until 29<sup>th</sup>. ( 84.26, 57.22, 13.99 and 17.46 µg m<sup>-3</sup> on 26<sup>th</sup>, 27<sup>th</sup>, 28<sup>th</sup> and 29<sup>th</sup> respectively). The increase in OC seems to be resulting from increasing agricultural biomass burning activities in Turkey. Referring meteorological data reveals that temperature shows a decreasing trend from 26<sup>th</sup> to 29<sup>th</sup> (24.12, 21.98, 19.3 and 17.1 respectively) while humidity increases 39.14, 49.85, 65.72 and 70.46 %.Wind speed shows gradual increase too. The decrease in PM<sub>2.5</sub> concentration seems to be resulting from increasing humidity and cloudy hours which finally on 29<sup>th</sup> ended in precipitation and a decrease on OC and EC concentrations.

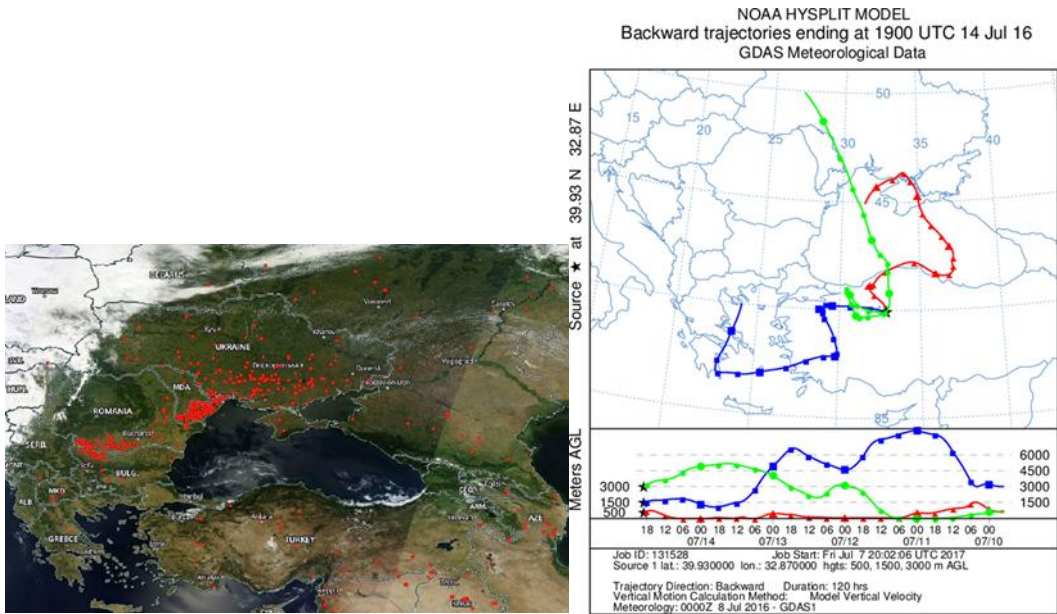
PM<sub>2.5</sub> concentration lowers considerably on 29<sup>th</sup> and it is probably due to precipitation on that day.



(a)

(b)

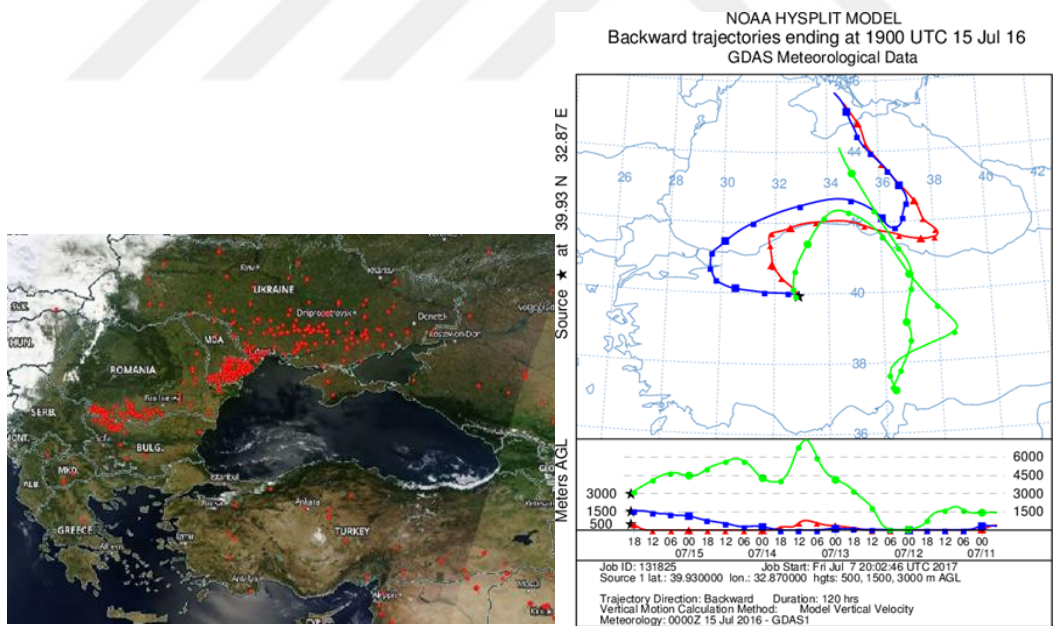
**Figure 4.56** a) Fires and thermal anomalies on 13<sup>th</sup> of July 2016 b) 120-hour back trajectory for Ankara on 13<sup>th</sup> of June 2016



(a)

(b)

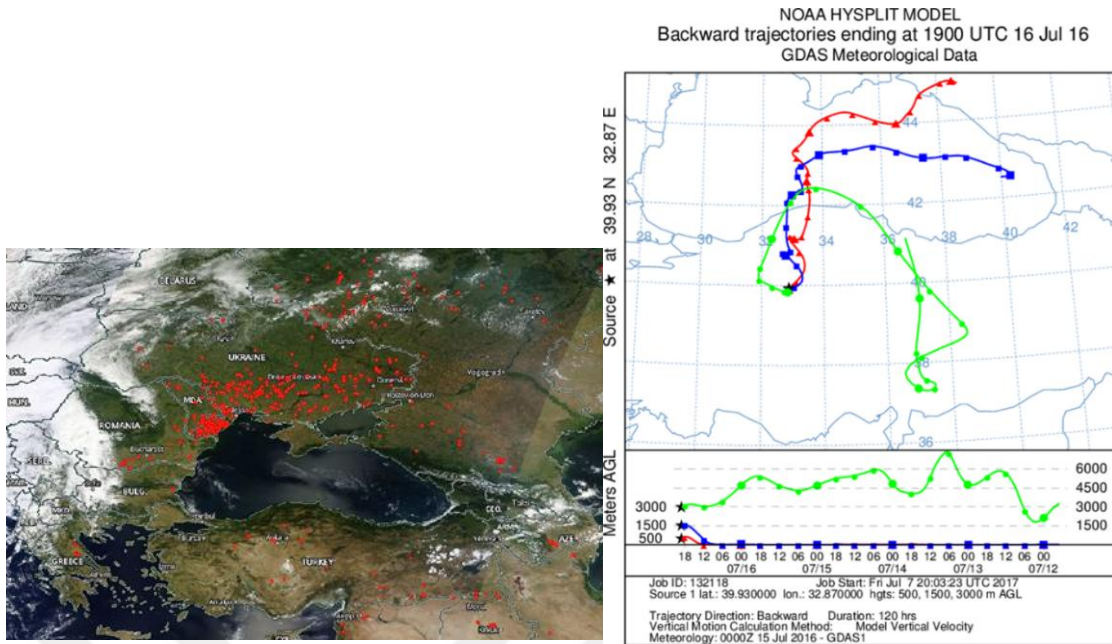
**Figure 4.57.** a) Fires and thermal anomalies on 14<sup>th</sup> of July 2016 b) 120-hour back trajectory for Ankara on 14<sup>th</sup> of June 2016



(a)

(b)

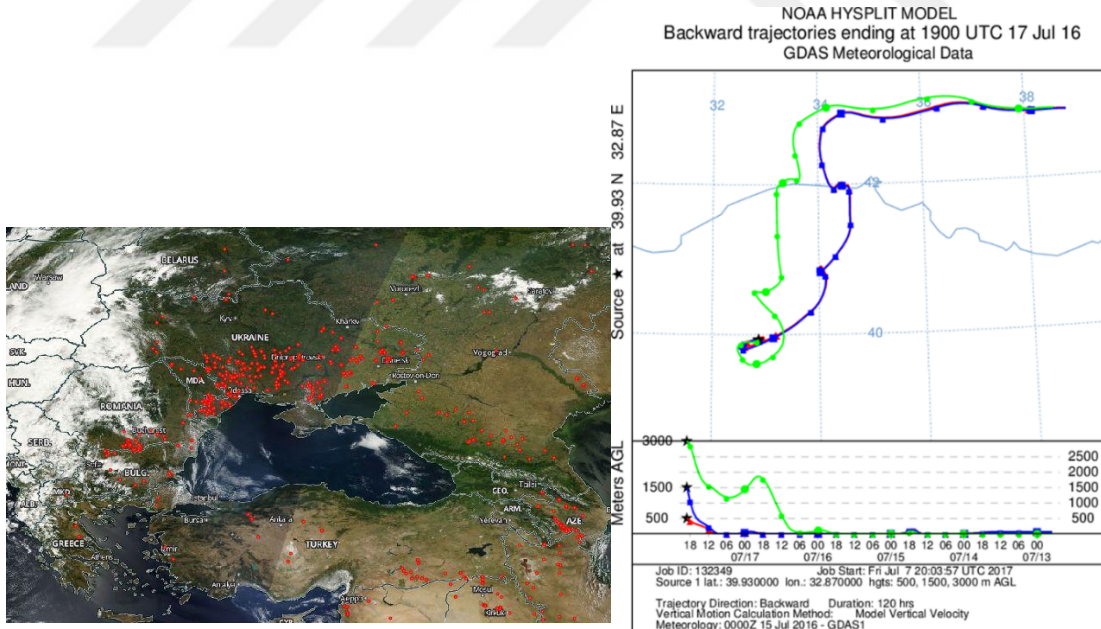
**Figure 4.58** a) Fires and thermal anomalies on 15<sup>th</sup> of July 2016 b) 120-hour back trajectory for Ankara on 15<sup>th</sup> of June 2016



(a)

(b)

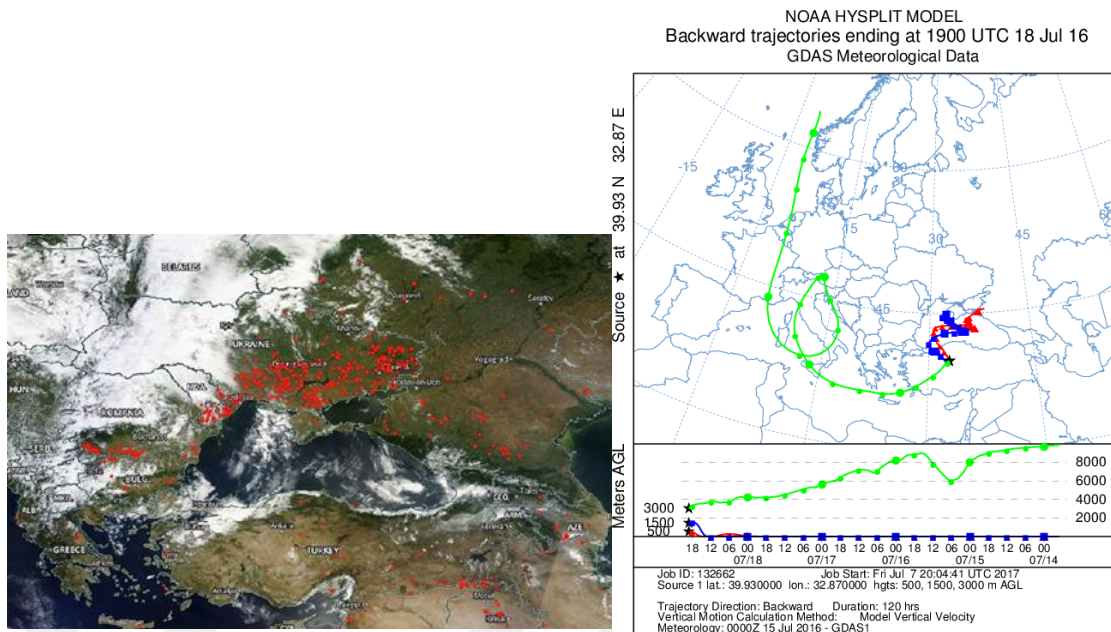
**Figure 4.59.** a) Fires and thermal anomalies on 16<sup>th</sup> of July 2016 b) 120-hour back trajectory for Ankara on 16<sup>th</sup> of June 2016



(a)

(b)

**Figure 4.60.** a) Fires and thermal anomalies on 17<sup>th</sup> of July 2016 b) 120-hour back trajectory for Ankara on 17<sup>th</sup> of June 2016



(a)

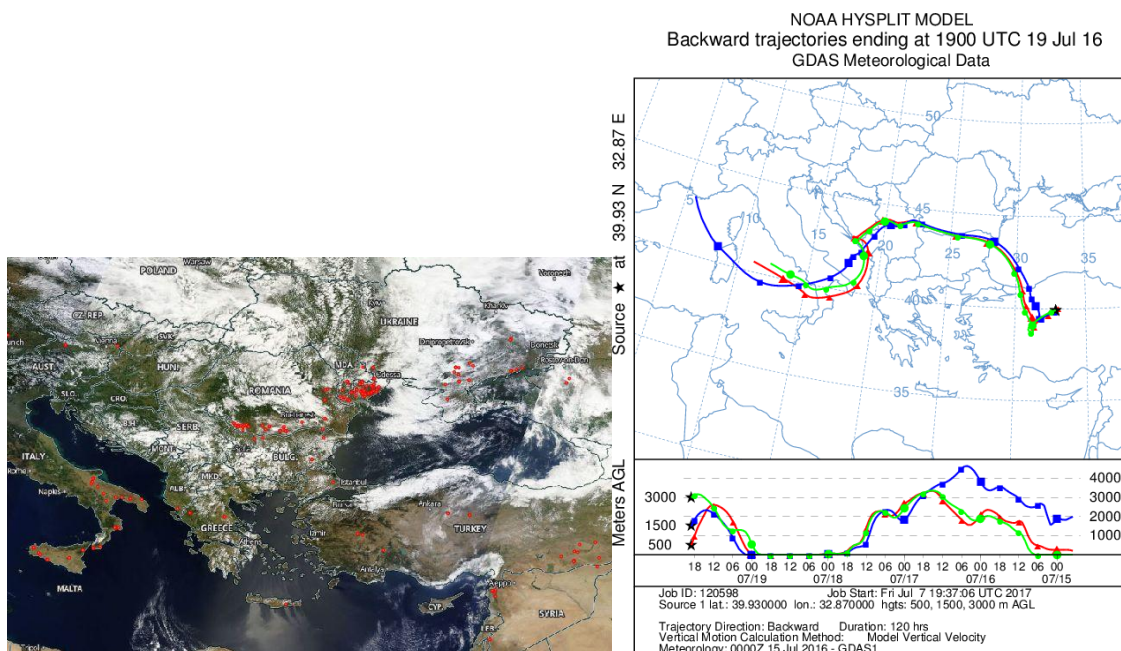
(b)

**Figure 4.61.** a) Fires and thermal anomalies on 18<sup>th</sup> of July 2016 b) 120-hour back trajectory for Ankara on 18<sup>th</sup> of June 2016

Figure 4.61 is showing fires and thermal anomalies on 18<sup>th</sup> of July 2016. On 18<sup>th</sup> of July there is an increase of PM<sub>2.5</sub>, OC, EC and CC concentration which is not very considerable for PM<sub>2.5</sub> but OC and EC concentrations increased from 5.53 to 7.96  $\mu\text{g m}^{-3}$  and 0.86 to 1.22  $\mu\text{g m}^{-3}$  respectively in comparison with 17<sup>th</sup>. Meteorological data review show a change of wind speed from 1.36 to 0.81 m/s and temperature from 27.59 to 24.6 ( $^{\circ}\text{C}$ ). Humidity does not show a great difference.

On 20<sup>th</sup> of July there is a decline in PM<sub>2.5</sub> and OC concentrations respectively from 68.06 to 36.51 and 7.96 to 7.03  $\mu\text{g m}^{-3}$ . Meteorological data review show precipitation on 20<sup>th</sup> of July, so PM<sub>2.5</sub> and OC are washed up by rain.

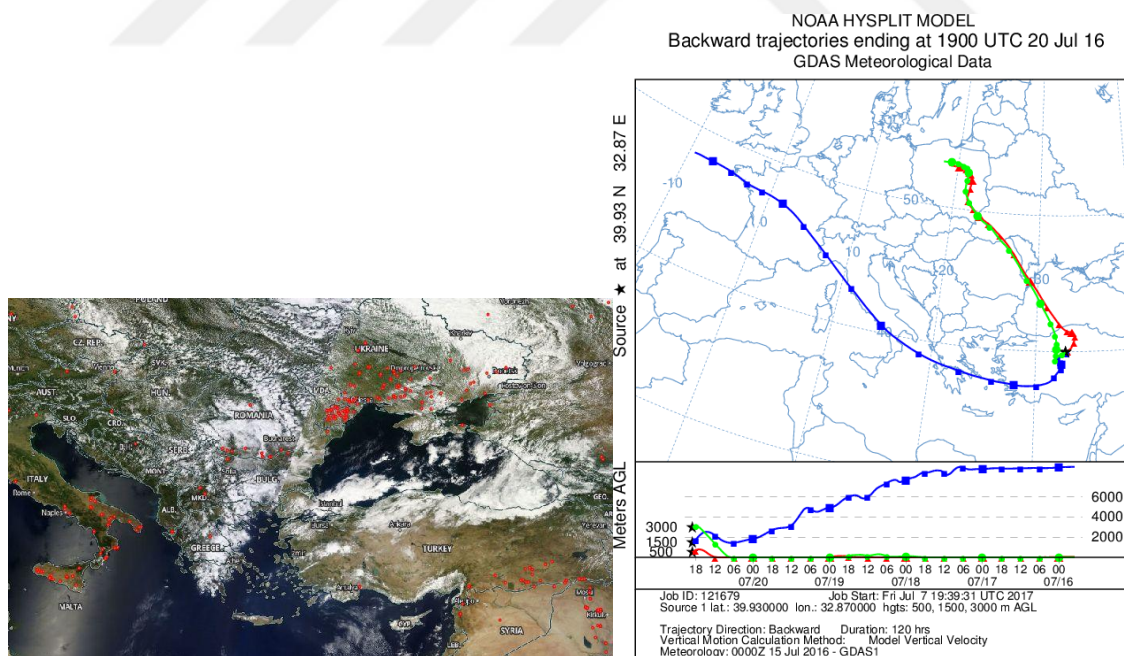
OC concentration started to increase on 27<sup>th</sup> comparing to 26<sup>th</sup>. This gradual increase is as following 5.76, 6.10, 6.71, 7.47  $\mu\text{g m}^{-3}$  and 8.89  $\mu\text{g m}^{-3}$ .



(a)

(b)

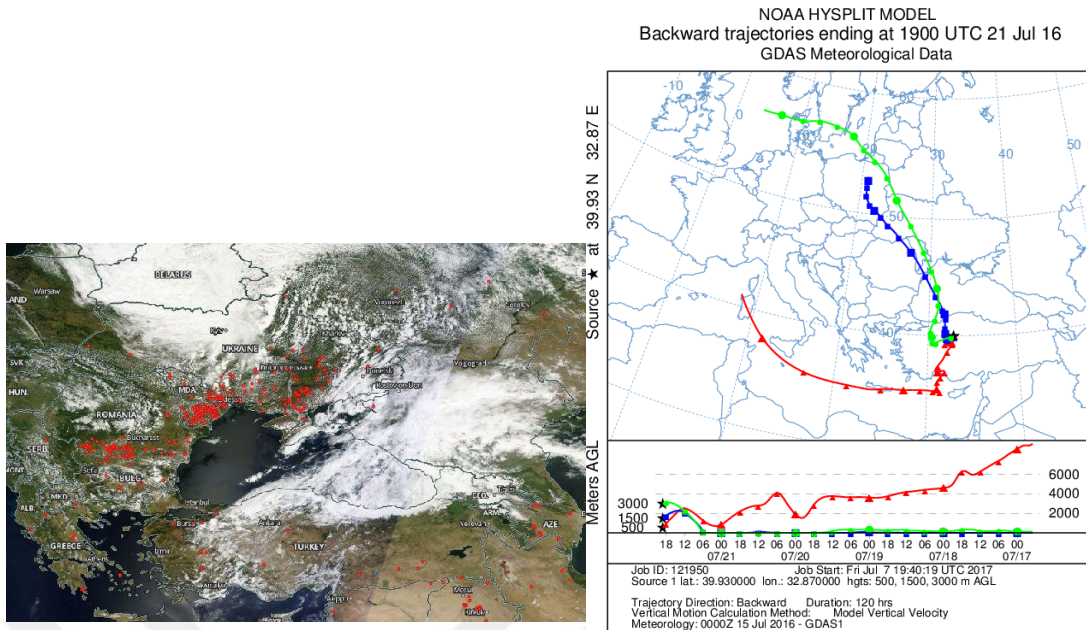
**Figure 4.62.** a) Fires and thermal anomalies on 19<sup>th</sup> of July 2016 b) 120-hour back trajectory for Ankara on 19<sup>th</sup> of June 2016



(a)

(b)

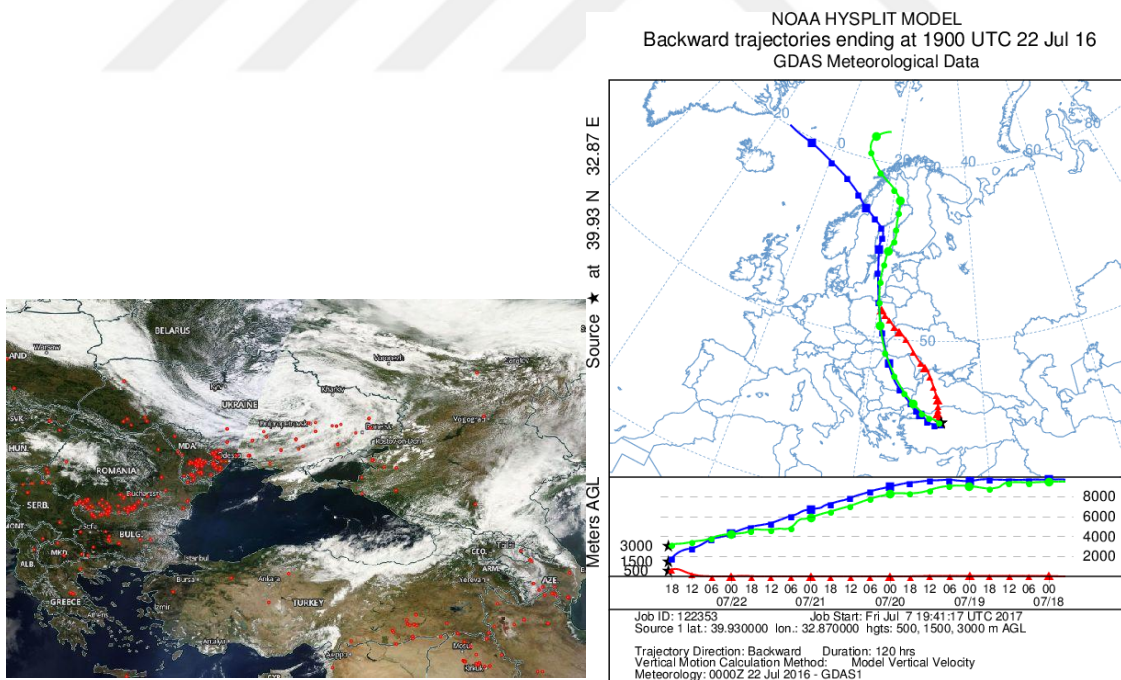
**Figure 4.63** a) Fires and thermal anomalies on 20<sup>th</sup> of July 2016 b) 120-hour back trajectory for Ankara on 20<sup>th</sup> of June 2016



(a)

(b)

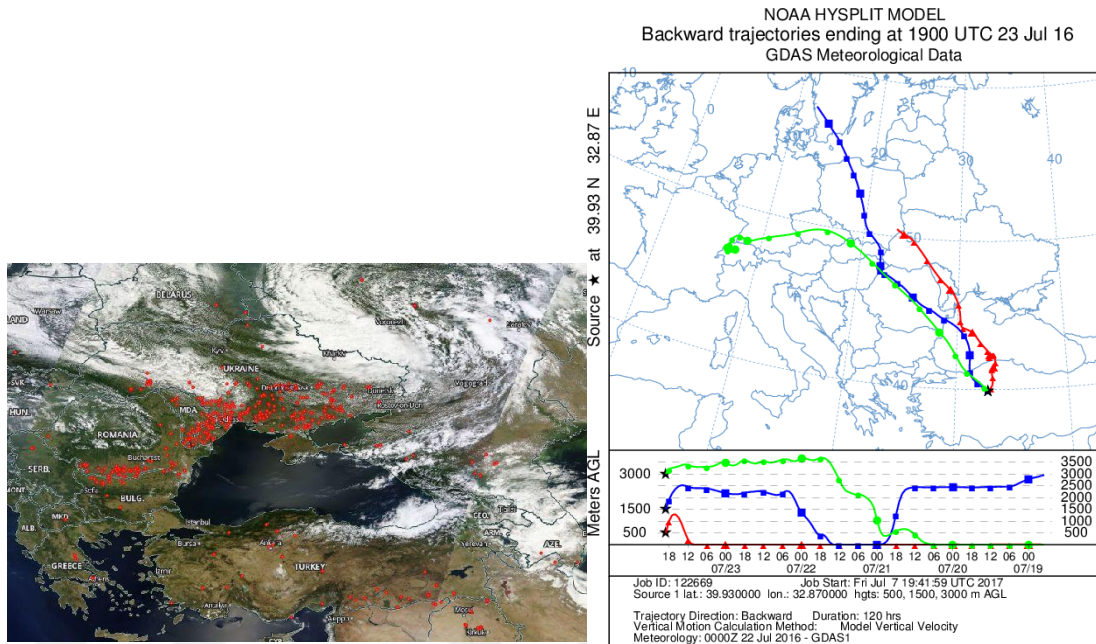
**Figure 4.64** a) Fires and thermal anomalies on 21<sup>st</sup> of July 2016 b) 120-hour back trajectory for Ankara on 21<sup>st</sup> of June 2016



(a)

(b)

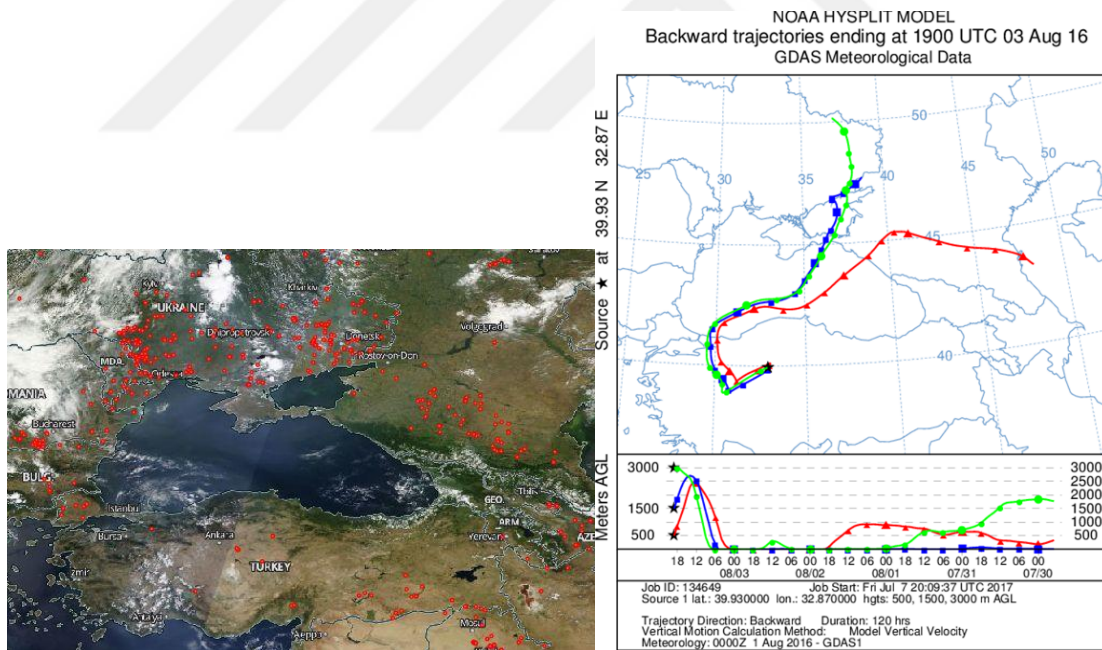
**Figure 4.65** a) Fires and thermal anomalies on 22<sup>nd</sup> of July 2016 b) 120-hour back trajectory for Ankara on 22<sup>nd</sup> of June 2016



(a)

(b)

**Figure 4.66.** a) Fires and thermal anomalies on 23<sup>rd</sup> of July 2016 b) 120-hour back trajectory for Ankara on 23<sup>rd</sup> of June 20



(a)

(b)

**Figure 4.67.** Fires and thermal anomalies on 3<sup>rd</sup> of August 2016 b) 120-hour back trajectory for Ankara on 3<sup>rd</sup> of August 2016

#### 4.16 Dust Events in Sampling Period

It is known that eastern Mediterranean receives considerable amount of dust from North Africa and that dust alters the chemical composition of particulate matter and rain. Saharan dust event are seen mostly in March, April, May and October, but it is also observed in February recently.[13]

Relying on the back trajectories, NASA earth data and Barcelona Dust Forecast Center, 3 dust events were observed in winter sampling period on the 6<sup>th</sup>, 18<sup>th</sup> and 24<sup>th</sup> of January so dusty days are 6<sup>th</sup>, 7<sup>th</sup>, 8<sup>th</sup>, 17<sup>th</sup>, 18<sup>th</sup>, 19<sup>th</sup>, 24<sup>th</sup> and 25<sup>th</sup>.

In summer sampling period it seems to be 2 dust events which are on the 19<sup>th</sup> and 26<sup>th</sup> of June. So dusty days are 19<sup>th</sup>, 20<sup>th</sup>, 21<sup>st</sup>, 22<sup>nd</sup>, 23<sup>rd</sup>, 26<sup>th</sup> and 27<sup>th</sup> of June.

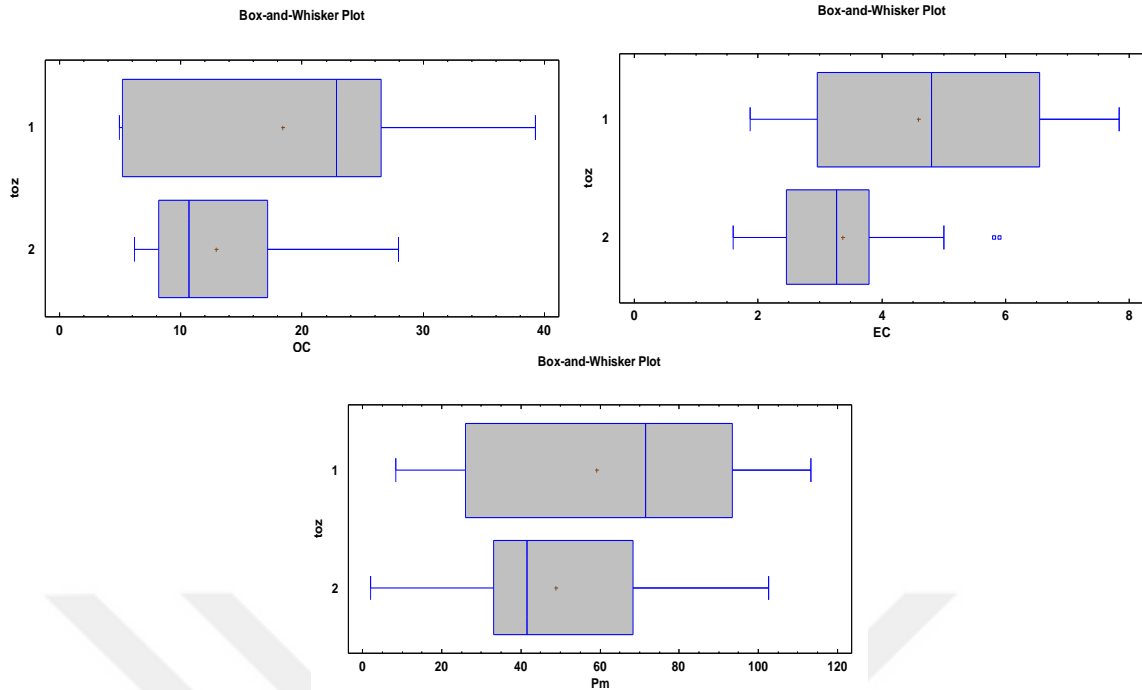
In order to see if there is a statistically difference between mean concentrations of PM<sub>2.5</sub>, OC and EC an ANOVA test was performed between dusty and non-dusty days. The results are given as following.

**Table 4.17.** Mean concentrations and standard deviation during non-dust period (n= 23) and during (n=7) the dust event at urban site in winter ( $\mu\text{g m}^{-3}$ )

Parameter	Dusty days	Non-dusty days
<b>PM<sub>2.5</sub></b>	59.18 ± 39.19	48.87 ± 2 4.20
<b>OC</b>	18.42 ± 13.05	12.93 ± 6.38
<b>EC</b>	4.59 ± 2.11	3.37 ± 1.15

**Table 4.18.** One way ANOVA analysis result and P-values for dust and non-dust period at urban site during winter ( $\mu\text{g m}^{-3}$ )

Parameter	winter	mean	P-value
<b>PM<sub>2.5</sub></b>	Dust 1	59.18	<b>0.4</b>
	Non-dust 2	48.86	
<b>OC</b>	Dust 1	18.42	<b>0.1</b>
	Non-dust 2	12.93	
<b>EC</b>	Dust 1	4.59	<b>0.05</b>
	Non-dust 2	3.36	



**Figure 4.68.** Distribution of PM<sub>2.5</sub>, OC and EC during dust and non-dust period urban site during winter

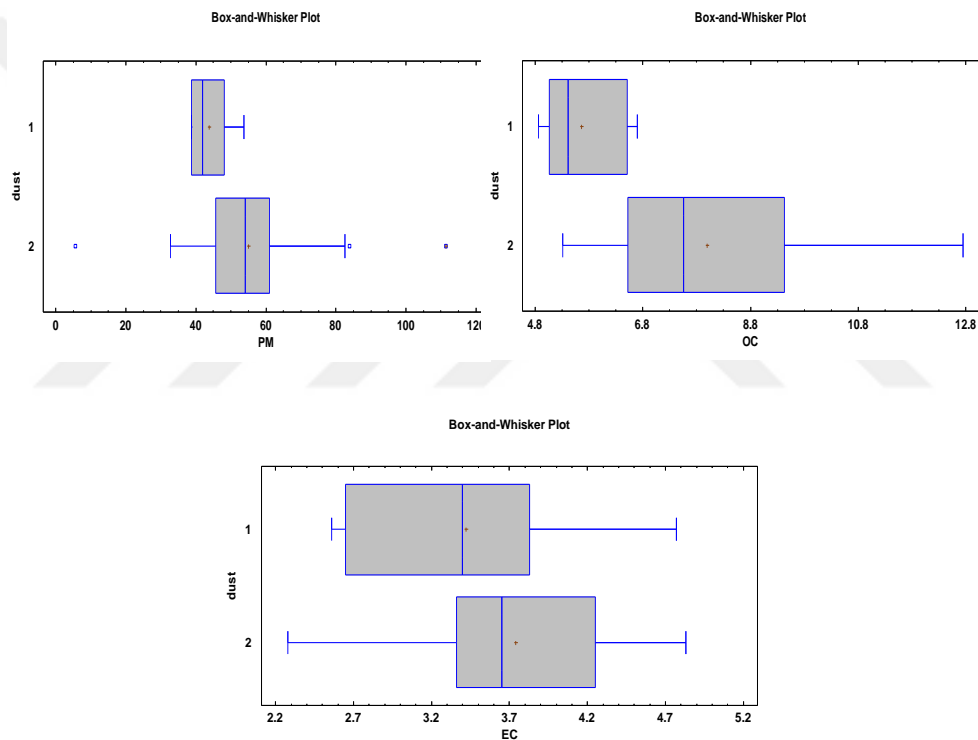
Since the P-value of the F-test is greater than or equal to 0.05, there is not a statistically significant difference between the mean concentrations of PM<sub>2.5</sub> and EC and OC between dusty and non-dusty days at the 95.0% confidence level.

**Table 4.19.** Mean concentrations and standard deviation during non-dust period (n= 38) and during (n=7) the dust event at urban site in summer ( $\mu\text{g m}^{-3}$ )

Parameter	Dusty days	Non-dusty days
PM <sub>2.5</sub>	43.82 ± 5.45	55.07 ± 17.40
OC	5.66 ± 0.73	7.99 ± 1.80
EC	3.42 ± 0.75	3.74 ± 0.56

**Table 4.20.** One way ANOVA analysis result and P-values for dust and non-dust period at urban site during summer ( $\mu\text{g m}^{-3}$ )

Parameter	Summer	mean	P-value
<b>PM<sub>2.5</sub></b>	Dust 1	43.82	<b>0.09</b>
	Non-dust 2	55.07	
<b>OC</b>	Dust 1	5.66	<b>0.01</b>
	Non-dust 2	7.99	
<b>EC</b>	Dust 1	3.42	<b>0.25</b>
	Non-dust 2	3.73	



**Figure 4.69.** Distribution of PM, OC and EC during dust and non-dust period urban site during summer

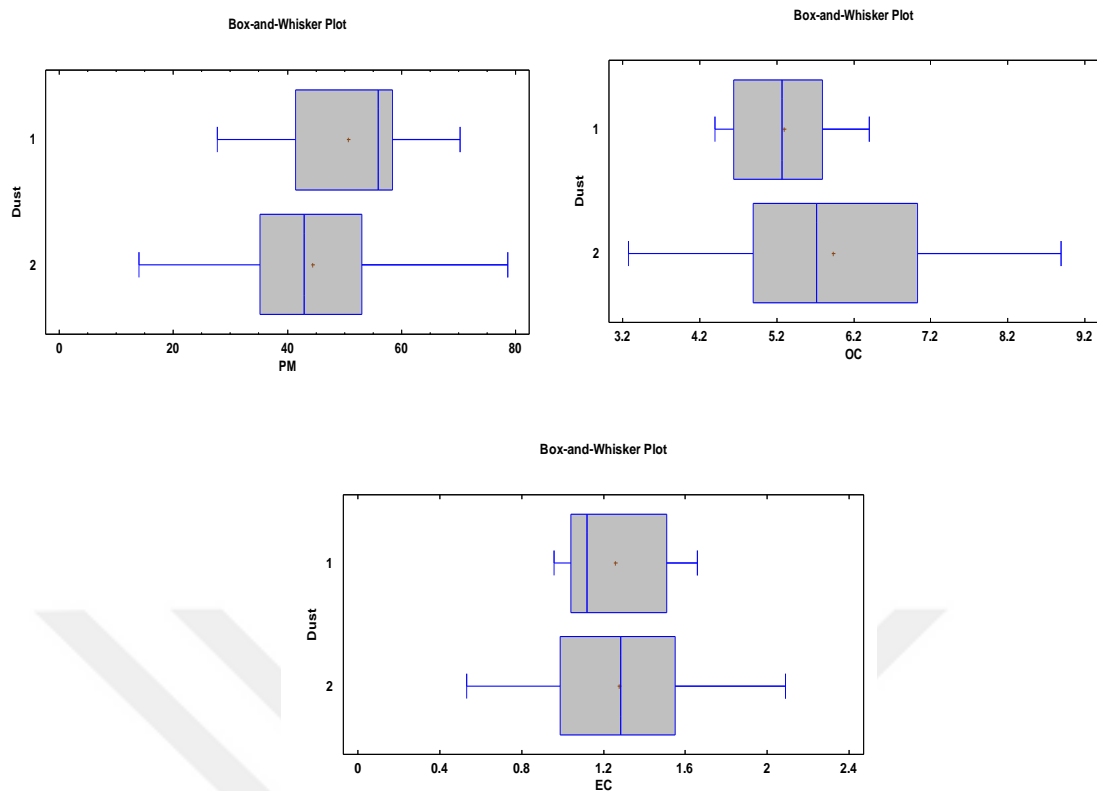
Since the P-value of the F-test is greater than or equal to 0.05, there is not a statistically significant difference between the mean concentrations OC and EC from one level of season to another at the 95.0% confidence level.

**Table 4.21.** Mean concentrations and standard deviation during non-dust period (n= 38) and during (n=7) dust event at sub-urban site in summer ( $\mu\text{g m}^{-3}$ )

<b>Parameter</b>	<b>Dusty days</b>	<b>Non-dusty days</b>
<b>PM<sub>2.5</sub></b>	50.74 ± 16.46	44.49 ± 14.35
<b>OC</b>	5.30 ± 0.82	5.93± 1.40
<b>EC</b>	1.26 ± 0.31	1.28 ± 0.37

**Table 4.22.** One way ANOVA analysis result and P-values for dust and non-dust period at sub-urban site during summer ( $\mu\text{g m}^{-3}$ )

<b>Parameter</b>	<b>Summer</b>	<b>mean</b>	<b>P-value</b>
<b>PM<sub>2.5</sub></b>	Dust 1	50.73	<b>0.37</b>
	Non-dust 2	44.48	
<b>OC</b>	Dust 1	5.93	<b>0.33</b>
	Non-dust 2	5.85	
<b>EC</b>	Dust 1	1.25	<b>0.91</b>
	Non-dust 2	1.27	



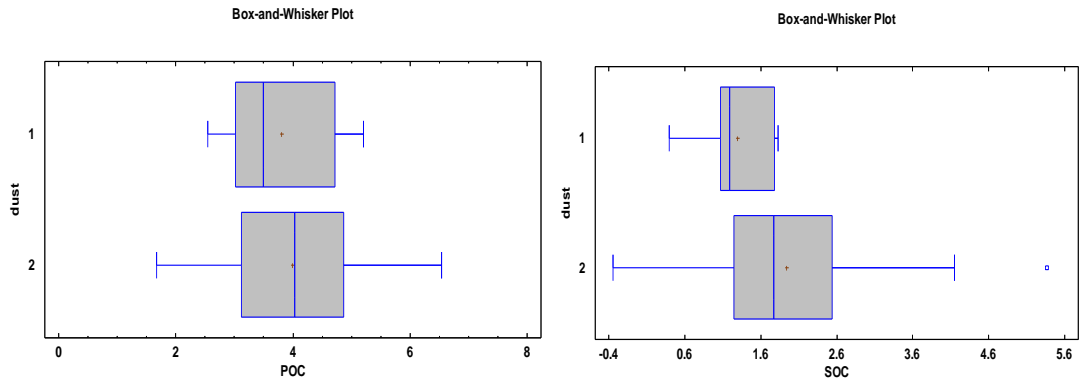
**Figure 4.70.** Distribution of PM, OC and EC during dust and non-dust period at sub-urban site during summer

Since the P-value of the F-test is greater than or equal to 0.05, there is not a statistically meaningful difference between the mean concentrations of PM<sub>2.5</sub> and EC and OC from one level of dusty days to non-dust period at the 95.0% confidence level.

In order to see if there is a statistically difference between POC and SOC of the data between dust and non-dust period, an ANOVA test was performed between daily concentration of POC and SOC of dusty and non-dusty days. The results are given as following.

**Table 4.23.** One way ANOVA analysis result and P-values of POC and SOC for dust and non-dust period at sub-urban site during summer ( $\mu\text{g m}^{-3}$ )

Parameter	summer	mean	P-value
POC	Dust 1	3.80	0.67
	Non-dust 2	3.99	
SOC	Dust	1.28	0.16
	Non-dust	1.93	

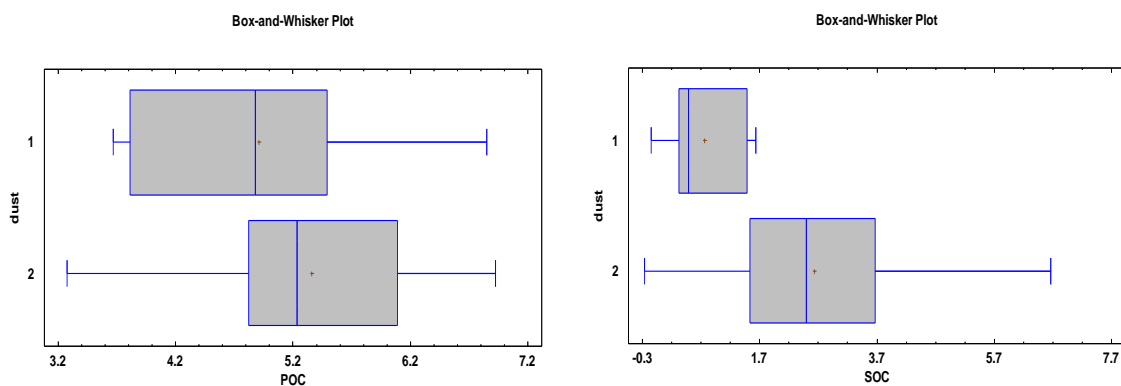


**Figure 4.71.** Distribution of PM.OC and EC during dust and non-dust period at sub-urban site during summer

Since the P-value of the F-test is greater than or equal to 0.05, there is not a statistically significant difference between the mean concentrations POC and SOC among dust and non-dust days by 95.0% confidence level.

**Table 4.24.** One way ANOVA analysis result and P-values of POC and SOC for dust and non-dust period at urban site during summer ( $\mu\text{g m}^{-3}$ )

Parameter	summer	mean	P-value
POC	Dust 1	4.9	0.25
	Non-dust 2	5.3	
SOC	Dust	0.75	0.004
	Non-dust	2.6	

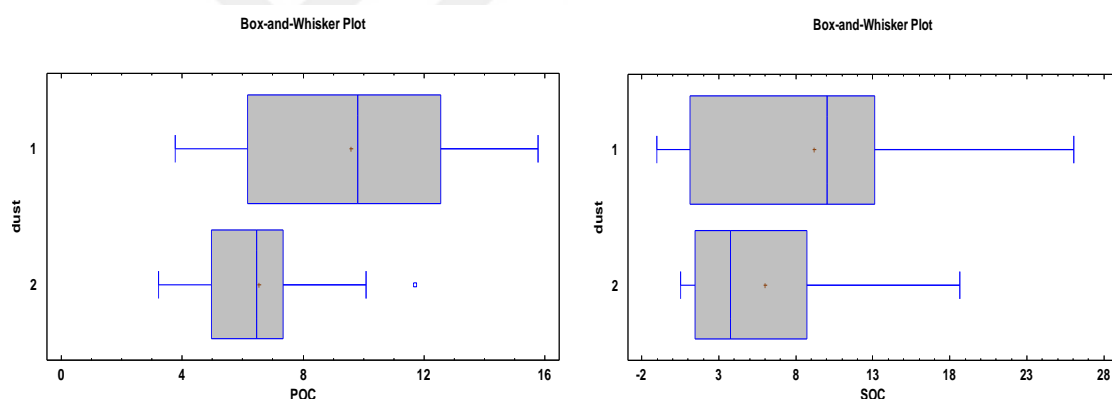


**Figure 4.72.** Distribution of POC and SOC during dust and non-dust period at urban site during summer

Since the P-value of the F-test is greater than or equal to 0.05, there is not a statistically significant difference between the mean concentrations POC among dust and non-dust days by 95.0% confidence level, but for the P-value of the F-test is smaller than 0.05, there is a statistically significant difference between the mean concentrations SOC among dust and non-dust days by 95.0% confidence level.

**Table4.25.** One way ANOVA analysis result and P-values of POC and SOC for dust and non-dust period at urban site during winter ( $\mu\text{g m}^{-3}$ )

Parameter	summer	mean	P-value
POC	Dust 1	9.57	0.21
	Non-dust 2	6.55	
SOC	Dust	9.19	0.25
	Non-dust	6	



**Figure 4.73.** Distribution of POC and SOC during dust and non-dust period at sub-urban site during winter

Since the P-value of the F-test is greater than or equal to 0.05, there is not a statistically significant difference between the mean concentrations POC among dust and non-dust days by 95.0% confidence level.

## 5. Conclusions

In this study, PM<sub>2.5</sub> samples were collected and analyzed in terms of organic carbon and elemental carbon at two different stations, city center (Sihhiye) and suburban site (Hacettepe University, Beytepe campus) in summer and winter. It has to be mentioned that winter samples could not be collected at suburban site in winter so we have lack of data at that site. The findings obtained in this study are presented and discussed.

Concentration of PM<sub>2.5</sub> in summer period has shown to be higher at city center than suburban site resulting from locating downtown, seriously heavier traffic, and comparatively less precipitation at urban site. It is essential to mention that during summer total precipitation at suburban and urban sites was 7.3 mm and 2.4 mm respectively.

Inter-seasonal comparison of PM<sub>2.5</sub> has shown that PM<sub>2.5</sub> concentration is slightly higher in summer than winter at city center. The reason can be explained by being diluted and scavenging effects (rain, snow or fog). There is not a big statistic difference in PM<sub>2.5</sub> concentration at urban site between summer and winter but the change in PM<sub>2.5</sub> in winter is observed in a larger range. This shows that traffic is the dominant pollutant source and is not a season dependent factor.

The results of this study showed that PM<sub>2.5</sub> and carbonaceous species pollution were severe during summer and winter especially at city center. PM<sub>2.5</sub> mean concentration at both locations in winter and summer are above the WHO, EU and EPA standard limits which are 10, 25 and 35  $\mu\text{g m}^{-3}$  respectively. However, referring to (NAAQS 2008) for Turkish Ambient Air Quality Standards for PM and PM components the limit value is 50  $\mu\text{g m}^{-3}$ , so PM<sub>2.5</sub> concentrations at urban site in both winter and summer are above the limit value and for about 50% of sampling days exceeded 50  $\mu\text{g m}^{-3}$ . Since PM<sub>2.5</sub> concentrations are in range of 40.5-65.4  $\mu\text{g m}^{-3}$  they are considered to be known as unhealthy for sensitive groups according to USEPA standards.

During the sampling period, OC was the parameter with the highest contribution to PM<sub>2.5</sub> mass at all the samples. This leads us to the result that OC is the most determining parameter of PM<sub>2.5</sub> composition in the atmosphere.

For urban site, the OC concentration is approximately two times higher in winter. EC concentration in summer and winter are almost the same but a bit higher in summer. The increase for OC which is considerably higher rate reflects that more aerosols emitted from fuel combustions or heating.

The carbonaceous aerosols at urban site accounted for 34.85 % and 23 % of PM<sub>2.5</sub> mass in winter and summer respectively. The carbonaceous aerosols at urban site accounted for 17.08 % of PM<sub>2.5</sub> mass.

Both OC and EC concentrations are higher in urban site comparing to suburban in summer sampling period and EC shows a higher rate of increase than OC. The highest concentration of OC (OC=27.99  $\mu\text{g m}^{-3}$ ) was found at urban site in winter. The highest amount of EC (EC=7.84  $\mu\text{g m}^{-3}$ ) was also found at urban site in winter. Cluster back trajectory analysis for summer campaign shows that the major flow is coming from North (Northeast and Northwest). Elevated amounts of OC and EC in summer were related to combustion transmittance of agricultural post-harvest activities from north and even inside Turkey.

EC and OC concentrations are both higher at urban site indicating that this area is under the effect of more intensive traffic and emissions.

Contribution of POC and SOC to total OC mass at Sihhiye in summer is 72 % and 28 % respectively. Contribution of POC and SOC to total OC mass at suburban site in summer is 68% and 32% respectively. These results reveals that organic carbon is emitted in mostly from primary sources to the atmosphere of the city.

Contribution of POC and SOC to Total OC at Sihhiye station in winter and summer was evaluated. The contribution of POC and SOC to total OC in summer was 72 % and 28 % respectively, while in winter these change to 61% and 39% respectively. The decrease of POC contribution from 72% to 61% in winter and increasing of SOC instead indicates that gaseous emissions condensed on the PM in winter due to low temperature values.

The meteorological estates were found to affect the concentrations of  $PM_{2.5}$ , OC, EC and OC/EC ratio. For instance, in winter some elevated amounts of OC and EC were due to inversion.

OC/EC ratio was less than 2.0 at Sihhiye during summer while the ratio exceeded 2 at Sihhiye in winter. Exceeded OC/EC ratio was observed during heating season with elevated primary emissions. This demonstrates that secondary OC might come from different anthropogenic organic sources.

In this study the correlation between OC and EC concentrations at both sampling sites during winter and summer was examined. The correlation coefficient (R) between EC and OC at Sihhiye in summer was calculated ( $R=0.46$ ) showing not a strong relationship between the variables. The correlation coefficient (R) between EC and OC at Sihhiye in winter was calculated ( $R=0.72$ ) indicating a moderately strong relationship between the variables suggesting that they were originated from common sources and similar atmospheric process during winter at urban site. The correlation coefficient (R) between EC and OC at Beytepe in summer ( $R=0.59$ ) indicates a weak relationship between the variables.

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