INVESTIGATION OF TRAFFIC RELATED INHALABLE PARTICULATE MATTER IN ISTANBUL

by

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APPROVAL PAGE

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

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Assist. Prof. Dr. Sami GÖREN
Head of Department

This is to certify that I have read this thesis and that in my opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

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M. S. Thesis – Environmental Engineering
August 2007

Supervisor: Assist. Prof. Dr. Omar ALAGHA

ABSTRACT

In this work, eighty four daily fine ($PM_{2.5}$) and coarse ($PM_{2.5-10}$) particle samples were collected in the period between 19.10.2006 and 02.07.2007 onto 37-mm diameter Teflon PTFE filters on alternate days continuously at Yıldız Technical University Campus (41.0307° N, 29.0033° E) by using Dichotomous Model 245 Sequential Air Sampler. Hourly concentrations of criteria air pollutants such as CO, SO_2, NO, NO_2, NO_x, and TSP were colleted from the continuous air quality monitoring station at Yıldız Technical University. Hourly meteorological data and traffic data of Yıldız area were also obtained from related institutions. General statistical tests were performed for all variables by using SPSS 15.0 software package. As a result of distribution tests, distribution of all parameters except total daily rain fits to normal distribution. Multiple correlation statistics were performed for all parameters. The correlation order of variables with coarse particles is wind direction (0.347) > TSP (0.268) > SO_2 (0.256) > Wind Speed [- 0.230] > NO_2 (0.215) > NO_x (0.190). Fine particle concentration is inversely proportional to the traffic count (- 0.255) but directly proportional to the traffic flow (0.241). Three models were formed for fine particles, coarse particles, and PM_{10} and R values of these models are 0.49, 0.52 and 0.55, respectively.

Keywords: Traffic, air pollution, PM_{10}, $PM_{2.5}$, statistical treatment, modeling.

İSTANBUL'DAKİ TRAFİK KAYNAKLI SOLUNABİLEN ASKIDA PARÇACIK MADDELERİN ARAŞTIRMASI

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ÖZ

Bu çalışmada, 24 saatlik örnekleme süresi boyunca ince ($PM_{2.5}$) ve kaba (PM_{10}) olmak üzere 19.10.2006 – 02.07.2007 tarihleri arasında 84 tane numune toplanmıştır. Örnekler 37 mm çaplı ve 2 mikron gözenekli PTFE Teflon filtreler üzerine değişik günlerde otomatik ardışık Dichotomus (Model 245) örnekleyici sayesinde Yıldız Teknik Üniversitesi Kampüsünde (41,0307° N, 29,0033° E) toplanmıştır. Kriter hava kirleticileri olan CO, SO_2, NO, NO_2, NO_x ve TSP'lerin saatlik konsantrasyonları Yıldız Teknik Üniversitesi'ndeki sürekli hava kalitesi izleme istasyonundan alınmıştır. Yıldız bölgesine ait olan meteoroloji verileri ve trafik verileri de ilgili kurumlardan elde edilmiştir. Genel bir istatistik değerlendirmesi tüm değişkenler için SPSS 15.0 programı kullanılarak yapılmıştır. Dağılım testleri sonuçlarına göre günlük yağmur parametresi dışındaki tüm verilerin dağılımları normal dağılıma uymaktadır. Çoklu korelasyon istatistiğine göre; kaba partiküler maddeler ile korelasyon sırası; rüzgar yönü (0.347) > TSP (0.268) > SO_2 (0.256) > rüzgar hızı [-0.230] > NO_2 (0.215) > NO_x (0.190) şeklindedir. İnce partiküler maddeler de trafik sayımıyla ters orantı (- 0.255), trafik hızıyla ise doğru orantı (0.241) göstermiştir. Kaba partiküller, ince partiküller ve PM_{10} için üç model geliştirilmiştir. Bu modellerin R değerleri sırasıyla 0.49, 0.52 and 0.55 tir.

Anahtar Kelimeler: Trafik, hava kirliliği, PM_{10}, $PM_{2,5}$, istatistiksel işleyiş, modelleme.

DEDICATION

To my dear, precious, and esteemed family

ACKNOWLEDGMENT

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LIST OF SYMBOLS AND ABBREVATIONS

SYMBOLS/ABBREVATIONS

AAS	Atomic Absorption Spectrophotometry
ACGIH	American Conference of Governmental Industrial Hygienists
ACS	American Cancer Society
AQCD	Air Quality Criteria Document
AQG	Air Quality Guidelines
AQI	Air Quality Index
ATDL	Atmospheric Turbulence and Diffusion Laboratory
CEN	European Standardization Committee
CFR	Code of Federal Regulations
CO	Carbon Monoxide
D_a	Aerodynamic Diameter
D_p	Stokes Particle Diameter
EPA	Environmental Protection Agency
FRM	Federal Reference Method
H	Henry's Law Constant
IPM	Inhalable Particulate Matter
ISO	International Standards Organization
IT	Interim Target
NAAQS	National Ambient Air Quality Standards
NO_x	Nitrogen Oxides
PCA	Principal Component Analysis
PM	Particulate Matter
$PM_{2.5}$	Fine Particulate Matter
PM_{10}	Combination of Coarse and Fine Particulate Matter
PM_{10-25}	Coarse Particulate Matter
PTFE	Polytetrafluoroethylene (Teflon)

RPM	Respirable Particulate Matter
SFU	Stack Filter Unit
SO_x	Sulfur Oxides
SO_2	Sulfur Dioxide
SPSS	Statistical Package for the Social Sciences
TEOM	Tapered Element Oscillating Microbalance
TPM	Thoracic Particulate Matter
TSP	Total Suspended Particulate
THEES	Total Human Environmental Exposure Study
UF	Ultra Fine
WHO	World Health Organization
WRAC	Wide Range Aerosol Classifier
XRF	X-Ray Fluorescence

CHAPTER 1

INTRODUCTION

1.1 AIR POLLUTION IN ISTANBUL

Istanbul is the most populated city of Turkey and the fourth in Europe with nearly 10,018,735 million inhabitants and annual growth rate of population is about 33.09 % (Turkey's Statistical Yearbook, 2006). Air pollution is one of the challenging environmental problems in Istanbul. Some regions of Istanbul have been continuously exposed to high pollution levels in heating seasons (November to March period) especially by SO_2 that exceeds the short-term air quality standards (Karaca et al., 1995; Tayanç et al., 1997a). Topographical and meteorological factors also play an important role in the formation of high pollutant levels. The high emission is due to the low quality lignite and fuel-oil which have been widely used in the winter months. The Istanbul Metropolitan Municipality has taken precautions to lower the high air pollution levels since 1995. Although the desired air quality standards have not been reached yet, an improvement in the air quality in Istanbul has been observed since 1996 (Tayanç et al., 1996, 1997b). Nowadays, its thought that domestic-based air quality in Istanbul has reached the desired values because natural gas usage have become widespread and low quality lignite usage was restricted. On the other hand, traditional air pollution is changing its dimension and air pollution does not diminish. It's widely accepted that one of the most important causes of air pollution in Istanbul is exhaust gases produced from motor vehicles. Ozone and particulate matter pollution is accepted as basic pollutant of the 21th century not only in Turkey but also in the World (NTV, 2006). Other environmental issues affecting the area are uncontrolled migration to the city and urbanization, possible El Nino effects, and global warming problems that are explained in Tayanç and Toros (1997), Tayanç et al. (1997a, 1998a).

1.2 PREVIOUS AIR POLLUTION STUDIES IN ISTANBUL

Criteria air pollutants such as SO_2, PM_{10}, NO, NO_2, NO_x, and CO have been monitored at 10 stations by Istanbul Metropolitan Municipality since 1995 (see http://www.ibb.gov.tr/tr-TR/HavaKalitesi/).

The Ministry of Health of Turkey has monitored SO_2 and particulate matter pollutants in Istanbul. Monthly reports are examined by Refik Saydam Hıfzıssıhha Center and technical evaluations are sent to Turkish Statistical Institute in order to be published as monthly bulletins.

1.2.1   Previous Studies on Air Pollution Prediction & Modeling

The first study about deterministic modeling of air pollution in Istanbul was done by Ertürk (1986). In this study, a modified version of the Atmospheric Turbulence and Diffusion Laboratory (ATDL) urban dispersion model was applied to estimate annual SO_2 and suspended particulate concentrations in the Golden Horn region of Istanbul. The emissions were categorized as area sources (residential and commercial districts or small industries) and point sources (power plants and large industries). Öztürk (1983) achieved the following study which was about CO concentration produced from motor vehicles at Beyoğlu Street. High correlations were found between observed and mathematical model calculations in both studies.

In İşli's (1990) study, statistical relations of meteorological parameters together with pollution parameters and pollution data were analyzed as time series to predict future data. Ak (1995) examined SO_2 and PM data by mathematical models and air pollution of Istanbul was evaluated. Şen (1998) established an estimation method for air pollutant concentrations at discrete points by making use of the amounts recorded at air pollution measurement sites within urban and in suburban areas of the city.

In Tayanç's (2000) research, sulfur dioxide concentration levels are investigated in Istanbul to assess air pollution during the heating seasons in which the concentration of air pollutants reach high levels due to the consumption of low-quality fossil fuels. Koçak et al. (2000) used a local prediction method predict O_3 concentration over

Istanbul City at different stations. The relative error between model outputs and observations is within the practically acceptable limits pointing out that O_3 concentration is governed by a deterministic chaotic system. In Saral's (2000) research, air pollution prediction of the day after tomorrow was done by modeling air pollution dependent upon meteorological parameter with the help of artificial neural network models which generally gives very successful results on atmospheric applications. A similar study belongs to Karaca et al. (2002) who developed a method for predicting daily SO_2 level by using artificial intelligence and induction techniques.

In a different study, Karaca et al. (2005) collected 86 daily aerosol samples between July 2002 and July 2003. The annual mean concentration of $PM_{2.5}$ 20.8 $\mu g/m^3$ was found higher than The United States EPA standard of 15 $\mu g/m^3$. The statistics and relationships of fine, coarse, and inhalable particles were studied. Kindap et al. (2006) identified and analyzed the contribution of long-range aerosol transport to air pollution in the city of Istanbul. It had been found through model simulations that the responses of Istanbul background PM_{10} levels to the emissions of individual European countries can range from 0.5 to 13%. The result suggested that trans-boundary sources may be responsible for as much as half of the background PM_{10} in Istanbul.

1.2.2   SPM & Street Dust Studies

In Sezgin et al.'s (2003) study, street dusts have been collected from E-5 Highway from Topkapi to Avcilar regions that spans about 18 km in Istanbul, Turkey, and Pb, Cu, Mn, Zn, Cd and Ni concentrations have been detected in street dust. According to the results of this study, Pb, Cu and Zn concentrations in E-5 Highway between Topkapi and Avcilar region in Istanbul were higher than maximum concentration levels of these heavy metals in normal soil. This situation indicates that there is heavy metal pollution in the inspected area in E-5 Highway in Istanbul.

Toröz et al. (2002) measured suspended particulate matter in Kadıköy and Tuzla area of Istanbul between January and April 2002 and analyzed Pb, Ni, Cd, Zn, Fe, Mn, and Br elements by XRF and AAS methods. Results indicated that measured values are suitable for international standards during sampling period.

1.3 SIMILAR STUDIES IN TURKEY

Tuncel et al. (2000) collected fine and coarse aerosol samples between February and June 1993, in Ankara, Turkey using a stack filter unit (SFU). Collected samples were analyzed for approximately 40 trace elements and major ions using a combination of instrumental neutron activation analysis, atomic absorption spectrometry and ion chromatography. Change in the concentrations of anthropogenic elements in Ankara atmosphere is consistent with the history of regulatory actions taken to reduce air pollution. Turalıoğlu et al. (2005) analyzed the relationship between daily average total suspended particulate (TSP) and sulfur dioxide (SO_2) concentrations with meteorological factors, such as wind speed, temperature, relative humidity, pressure and precipitation, in 1995–2002 winter seasons by using the stepwise multiple linear regression analysis. The statistical models of SO_2 and TSP including meteorological parameters gave R^2 of 0.74 and 0.88, respectively. The new model for SO_2 enhanced considerably ($R^2 = 0.92$), but for TSP new model was not enhanced ($R^2 = 0.89$).

Taşdemir et al. (2006) collected thirty-three ambient air samples during spring and summer (2003) in the metropolitan area of Bursa, Turkey. Their result suggested that industrial activities along with traffic emissions and suspension of street dusts have important effects on ambient air concentrations of trace metals at the end of prevailing winds, EF, and PCA studies. Yıldırım and Bayramoğlu (2006) proposed an adaptive neuro-fuzzy logic method to estimate the impact of meteorological factors on SO_2 and total suspended particular matter (TSP) pollution levels over an urban area. The model forecasted satisfactorily the trends in SO_2 and TSP concentration levels, with performance between 75–90% and 69–80 %, respectively.

Yatkın and Bayram (2007) determined the concentrations of particulate matter (PM) fractions ($PM_{2.5}$ and PM_{10}) concurrently at suburban and urban sites in Izmir, Turkey. It was found that the PM concentrations in winter were higher than in summer at urban site, whereas the summer concentrations of suburban site were higher than the winter values. The results indicated that the major sources that contributed to the PM concentrations were the traffic emissions, the fossil fuel burning emissions, and soil/soil related industries.

1.4 THE PURPOSE OF THIS STUDY

This study focuses on the determination of inhalable PM mass concentration over Istanbul city. Yıldız Technical University (YTU) as a sampling site enabled us to estimate the quantity of traffic-related particulate matter that is being emitted by motor vehicles and could have serious human health effects and ecological disturbances. The method depends on separation and collection of 2 sizes (Coarse and fine) of aerosol on Teflon filters using Andersen Automatic Dichotomous Sampler. The sample collection was on daily bases to catch the possible monthly and seasonal variation of PM. Mass concentrations of the collected PM samples were calculated and compared to national and international limit values of PM_{10} and $PM_{2.5}$.

Concentrations of criteria air pollutants such as CO, SO_2, NO, NO_2 NO_x, and TSP was colleted from the continuous air quality monitoring station at the same sampling station. Concentrations of these air pollutants were also compared to national and international limit values. Hourly meteorological parameters such as temperature, pressure, humidity, wind direction, wind speed, and rain, between October 2006 and June 2007, were taken from Republic of Turkey Ministry of Environment and Forest's Turkish State Meteorological Service. Seasonal and monthly variations of meteorological parameters investigated. Hourly traffic data such as traffic count and traffic flow between October 2006 and June 2007 were taken from Traffic Control Center of the Istanbul Metropolitan Municipality by official petition.

Finally, all collected data was statistically treated with SPSS 15 software package to put the data set in informative manner. Descriptive statistics, distribution tests, correlation statistics, and multi linear regression steps were carried out for the data set. Possible sources of all collected air pollutants, relation of these air pollutants to each other, effects of meteorological data and traffic data on formation of these air pollutants were investigated. In other words, the picture of the ambient air quality at Yıldız area was tried to be taken. Conclusions and suggestions were finally defined at the end of this study.

CHAPTER 2

PHYSICS AND MEASUREMENT OF PARTICULATE MATTER

2.1 BASIC CONCEPTS

Atmospheric particles originate from a variety of sources and possess a range of morphological, chemical, physical, and thermodynamic properties. Examples of atmospheric particles include combustion-generated particles, such as diesel soot or fly ash; photochemically produced particles, such as those found in urban haze; salt particles formed from sea spray; and soil-like particles from resuspended dust. Some particles are liquid; some are solid. Others may contain a solid core surrounded by liquid. Atmospheric particles contain inorganic ions, metallic compounds, elemental carbon, organic compounds, and crustal compounds. Some atmospheric particles are hygroscopic and contain particle-bound water. The organic fraction is especially complex, containing hundreds (probably thousands) of organic compounds. Primary particles are emitted directly from sources; whereas secondary particles are formed from gases through chemical reactions in the atmosphere involving atmospheric oxygen (O_2) and water vapor (H_2O); reactive species such as ozone (O_3); radicals such as the hydroxyl ($\cdot OH$) and nitrate ($\cdot NO_3$) radicals; and pollutants such as sulfur dioxide (SO_2), nitrogen oxides (NO_x), and organic gases from natural and anthropogenic sources. The particle formation process includes nucleation of particles from low-vapor pressure gases emitted from sources or formed in the atmosphere by chemical reactions, condensation of low-vapor pressure gases on existing particles, and coagulation of particles. Thus, any given particle may contain PM from many sources. Because a particle from a given source is likely to be composed of a mixture of chemical components and because particles from different sources may coagulate to form a new

particle, atmospheric particles may be considered a mixture of mixtures. The composition and behavior of particles are fundamentally linked with those of the surrounding gas. An aerosol may be defined as a suspension of solid or liquid particles in air. The term aerosol includes both the particles and all vapor or gas phase components of air. However, the term aerosol is sometimes used to refer to the suspended particles only.

A complete description of the atmospheric aerosol would include an accounting of the chemical composition, morphology, and size of each particle, as well as the relative abundance of each particle type as a function of particle size (Friedlander, 1970). However, the physical and chemical characteristics of particles are usually measured separately. Size distributions by particle number used to calculate surface area and volume distributions often are determined by physical means, such as electrical mobility, aerodynamic behavior, or light scattering. Chemical composition usually is determined by analysis of collected samples, although some species can be measured in situ. The mass and average chemical composition of particles segregated according to aerodynamic diameter by cyclones or impactors can also be determined. However, recent developments in single particle analysis techniques by electron microscopy with X-ray analysis of single particles (but not agglomerates) collected on a substrate or by mass spectroscopy of individual suspended particles provide elemental composition of individual particles by particle size and, thus, are bringing the description envisioned by Friedlander closer to reality (Air Quality Criteria for PM, 2004).

2.2 PHYSICAL PROPERTIES AND PROCESSES

2.2.1 Definitions of Particulate Matter

The diameter of a spherical particle may be determined by optical or electron microscopy, by light scattering and Mie theory, by its electrical mobility, or by its aerodynamic behavior. However, atmospheric particles often are not spherical. Therefore, their diameters are described by an "equivalent" diameter (i.e., the diameter of a sphere that would have the same physical behavior). An optical diameter is the diameter of a spherical particle, with the same refractive index as the particle used to

calibrate the optical particle sizer that scatters the same amount of light into the solid angle measured. Diffusion and gravitational settling are important physical behaviors for particle transport, collection, and removal processes, including deposition in the respiratory tract. Different equivalent diameters are used depending on which process is more important. For smaller particles, diffusion is more important and the Stokes diameter is often used. For larger particles, gravitational setting is more important and the aerodynamic diameter is often used (Air Quality Criteria for PM, 2004).

The Stokes diameter, D_p, describes particle size based on the aerodynamic drag force imparted on a particle when its velocity differs from that of the surrounding fluid. For a smooth, spherically shaped particle, D_p exactly equals the physical diameter of the particle. For irregularly shaped particles, D_p is the diameter of an equivalent sphere that would have the same aerodynamic resistance. Electrical mobility analyzers classify particles according to their electrical mobility. Particles of equal Stokes diameters that carry the same electric charge will have the same electrical mobility. Hence, for spherical particles, the electrical mobility diameter would equal the Stokes diameter. The mobility diameter can be considered the diameter of a spherical particle that would have the same electrical mobility. The particle mobility can be related to the particle diffusion coefficient and Brownian diffusion velocity through the Stokes-Einstein equation. Thus, the Stokes diameter is the appropriate parameter for particle behavior governed by diffusion. The Stokes diameter, D_p, is used in size distributions based on light scattering and mobility analysis. The Stokes diameter is independent of density.

The aerodynamic diameter, D_a, however, depends on particle density. It is defined as the diameter of a spherical particle with an equal gravitational settling velocity but a material density of 1 g/cm^3. Cascade impactors separate particles based on their aerodynamic diameter, and aerodynamic particle sizers measure the aerodynamic diameter. Respirable, thoracic, and inhalable sampling and $PM_{2.5}$ and PM_{10} sampling are based on particle aerodynamic diameter. For particles greater than about 0.5 μm, the aerodynamic diameter is generally the quantity of interest. For smaller particles, the Stokes diameter may be more useful. Particles with the same physical size and shape but different densities will have the same Stokes diameter but different aerodynamic diameters. The aerodynamic diameter, D_a, is related to the Stokes diameter, D_p, by:

$$Da = Dp \times \sqrt{\frac{\rho \times Cp}{Ca}} \qquad\qquad \text{(2.1)}$$

where D is the particle density, and C_p and C_a are the Cunningham slip factors evaluated for the particle diameters D_p and D_a respectively. The slip factor is a function of the ratio between particle diameter and mean free path of the suspending gas (0.066 μm for air at one atmosphere pressure and 20 °C). C is an empirical factor that accounts for the reduction in the drag force on particles due to the "slip" of the gas molecules at the particle surface. C is an important factor for particles less than 1 μm in diameter, for which the surrounding air cannot be modeled by a continuous fluid. For large particles (D_p > 5 μm) C = 1; while for smaller particles C > 1. For particles with diameters greater than the mean free path, λ, the aerodynamic diameter given by equation (2.1) is approximated by:

$$Da = Dp \times \sqrt{\rho} \qquad \text{(for Dp} \gg \lambda) \qquad \text{(2.2)}$$

This expression, which shows that aerodynamic diameter is directly proportional to the square root of the particle density, is often used for particles as small as 0.5 μm. For particles with diameters much smaller than the mean free path, the slip factor must be taken into account. In this case, the aerodynamic diameter is directly proportional to the particle density,

$$Da = Dp \times (\rho) \qquad \text{(for Dp} \ll \lambda) \qquad \text{(2.3)}$$

Detailed definitions of the various sizes and their relationships are given in standard aerosol textbooks (e.g., Friedlander [2000], Reist [1984, 1993], Seinfeld and Pandis [1998], Hinds [1999], Vincent [1989, 1995], Willeke and Baron [1993], Baron and Willeke [2002], and Fuchs [1964, 1989]).

2.2.2   Aerosol Size Distributions

Particle size, as indexed by one of the "equivalent" diameters, is an important parameter in determining the properties, effects, and fate of atmospheric particles. The atmospheric deposition rates of particles and, therefore, their residence times in the

atmosphere are a strong function of their Stokes and aerodynamic diameters. Particle diameters also influence the deposition patterns of particles within the lung. Because light scattering is strongly dependent on the optical particle size, the amount of light scattering per unit PM mass will be dependent on the size distribution of atmospheric particles. Therefore, the effects of atmospheric particles on visibility, radiative balance, and climate will be influenced by the size distribution of the particles. Studies using cascade impactors or cyclones measure the particle-size distribution directly in aerodynamic diameter. The diameters of atmospheric particles range from 1 nm to 100 μm, spanning 5 orders of magnitude. A variety of different instruments, measuring a variety of equivalent diameters, are required to cover this range.

Older particle counting studies used optical particle counters to cover the range of 0.3 to 30 μm diameter. Diameters of particles below 0.5 μm were measured as mobility diameters. The particle diameters used in size distribution graphs from these studies usually are given as physical or Stokes diameters rather than aerodynamic diameters. In recent years, aerodynamic particle sizers have been developed that give a direct measurement of the aerodynamic diameter in the range of approximately 0.7 to 10 μm diameter. These instruments have been used with electrical mobility analyzers that measure the mobility diameter of particles from 3 nm to approximately 0.5 μm (McMurry, 2000). Unfortunately, there is no agreed-upon technique for combining the various equivalent diameters. Some workers use various assumptions to combine the various measurements into one presentation; others report each instrument separately. Therefore, the user of size distribution data should be careful to determine exactly which equivalent diameter is reported.

2.2.2.1 Particle Size Distribution Functions

The distribution of particles with respect to size is an important physical parameter governing particle behavior. Because atmospheric particles cover several orders of magnitude in particle size, size distributions often are expressed in terms of the logarithm of the particle diameter on the X-axis and the measured differential concentration on the Y-axis: $\Delta N/\Delta(\log D_p)$ = the number of particles per cm^3 of air having diameters in the size range from $\log D_p$ to $\log(D_p + \Delta D_p)$. Because logarithms do not have dimensions, it is necessary to think of the distribution as a function of

log(D_p/D_{p0}), where the reference diameter $D_{p0} = 1$ μm is not explicitly stated. If $\Delta N/\Delta(\log D_p)$ is plotted on a linear scale, the number of particles between D_p and $D_p + \Delta D_p$ is proportional to the area under the curve of $\Delta N/\Delta(\log D_p)$ versus $\log D_p$. Similar considerations apply to distributions of surface, volume, and mass. When approximated by a function, the distributions are usually given as $dN/d(\log D_p)$ rather than $\Delta N/\Delta(\log D_p)$ (Air Quality Criteria for PM, 2004).

2.2.2.2 Atmospheric Aerosol Size Distributions

Whitby (1978) published an analysis of over 1,000 particle size distributions measured at various locations in the United States. Figure 2.1 shows the number, surface area, and volume distributions for the grand average continental size distribution. Volume, surface area, and number distributions are plotted on an arithmetic scale such that the volume, surface area, or number of particles in any specified size range is proportional to the corresponding area under the curve. These distributions show that most of the particles are quite small, below 0.1 μm; whereas most of the particle volume (and therefore most of the mass) is found in particles > 0.1 μm. Other averaged atmospheric size distributions are shown in Figures 2.2 and 2.3 (Whitby, 1978; Whitby and Sverdrup, 1980). Figures 2.2a and 2.2b describe the number of particles as a function of particle diameter for rural, urban-influenced rural, urban, and freeway-influenced urban aerosols. For some of the same data, the particle volume distributions are shown in Figures 2.3a and 2.3b. Whitby (1978) observed that the size distributions typically had three peaks which he called "modes." The entire size distribution could be characterized well by a trimodal model consisting of three additive log-normal distributions. The mode with a peak between 5 and 30 μm diameter formed by mechanical processes was called the coarse particle mode; the mode with a peak between 0.15 and 0.5 μm formed by condensation and coagulation was called the accumulation mode; and the mode with a peak between 0.015 and 0.04 μm whose size was influenced by nucleation as well as by condensation and coagulation was called the transient nuclei or Aitken nuclei range, subsequently shortened to the nuclei mode. The nuclei mode could be seen in the number and surface distribution but only in special situations was it noticeable in the mass or volume distributions. The accumulation and nuclei modes taken together were called fine particles. An experimental size distribution showing modes and formation mechanisms is given in Figure 2.4. This size distribution

was measured in traffic. Therefore, the nuclei mode is clearly separated from the accumulation mode and larger than it would be in size-distributions measured farther from sources of nuclei-mode particles.
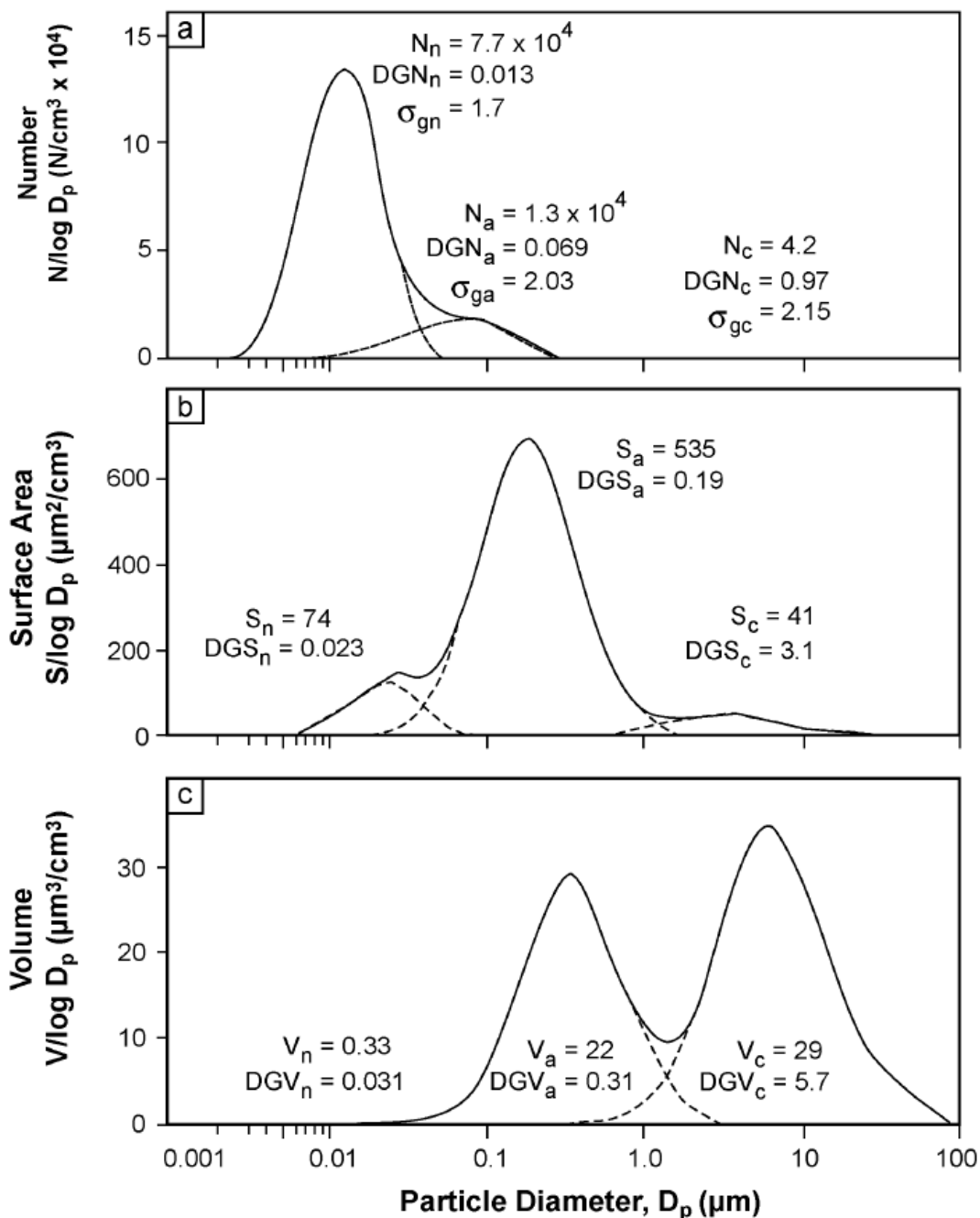
Figure 2.1 Distribution of coarse (c), accumulation (a), and nuclei (n) mode particles by three characteristics: (a) number, N; (b) surface area, S; and (c) volume, V for the grand average continental size distribution. DGV = geometric mean diameter by volume; DGS = geometric mean diameter by surface area; DGN = geometric mean diameter by number; D_p = particle diameter (Whitby, 1978).
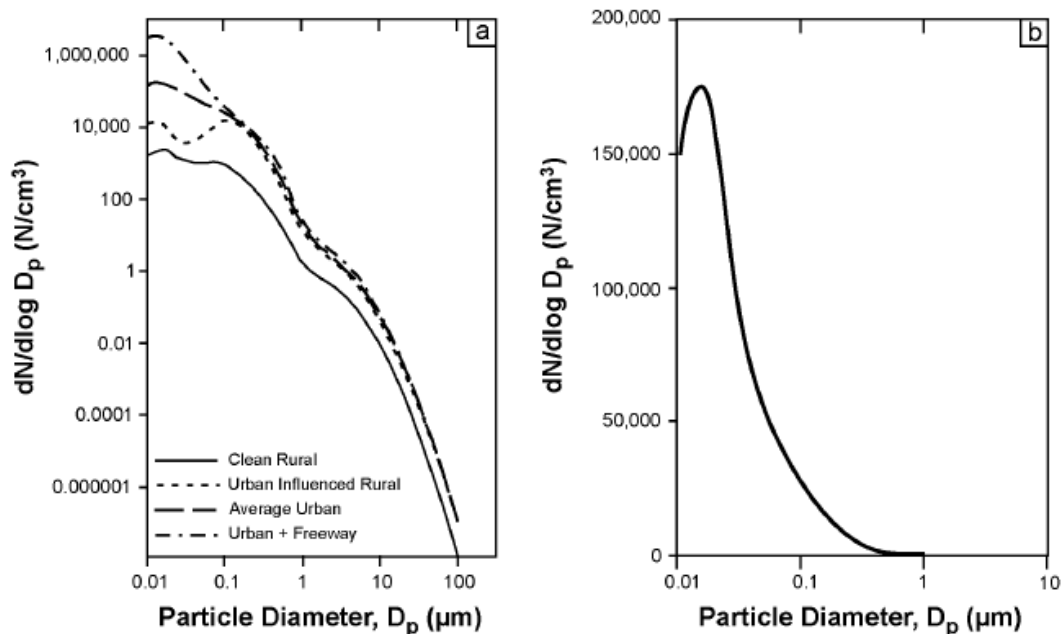
Figure 2.2 Particle size distributions by number: (a) number concentrations are shown in a logarithmic scale to display the wide range by site and size; (b) number concentrations for the average urban distribution are shown on a linear scale. For the linear scale, the area under any part of the curve is proportional to particle numbering that size range (Whitby, 1978; Whitby and Sverdrup, 1980).
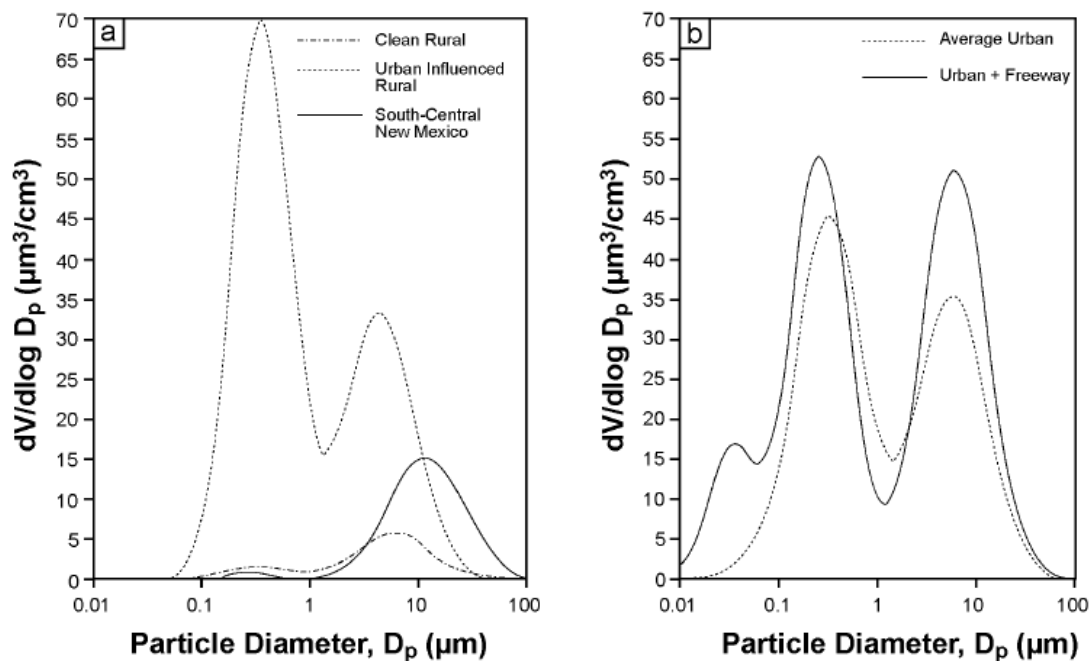
Figure 2.3 Size distributions by volume for averaged (a) rural and urban-influenced rural number distribution shown in Figure 2.2a and a distribution from south-central New Mexico, and (b) urban and freeway-influenced urban number distributions shown in Figure 2.2a (Whitby and Sverdrup, 1980; Kim et al., 1993).

Whitby's (1978) conclusions were based on extensive studies of size distributions in a number of western and Midwestern locations during the 1970s (Whitby et al., 1974; Willeke and Whitby, 1975; Whitby, 1978; Wilson et al., 1977; Whitby and Sverdrup, 1980). No size distribution studies of similar scope have been published since then. Newer results from particle counting and impactor techniques, including data from Europe (U.S. Environmental Protection Agency, 1996) and Australia (Keywood et al., 1999, 2000), show similar results for the accumulation and coarse modes. Extensive measurements of particle size distributions, as part of the EPA's supersites program, are providing considerable new data for analysis.
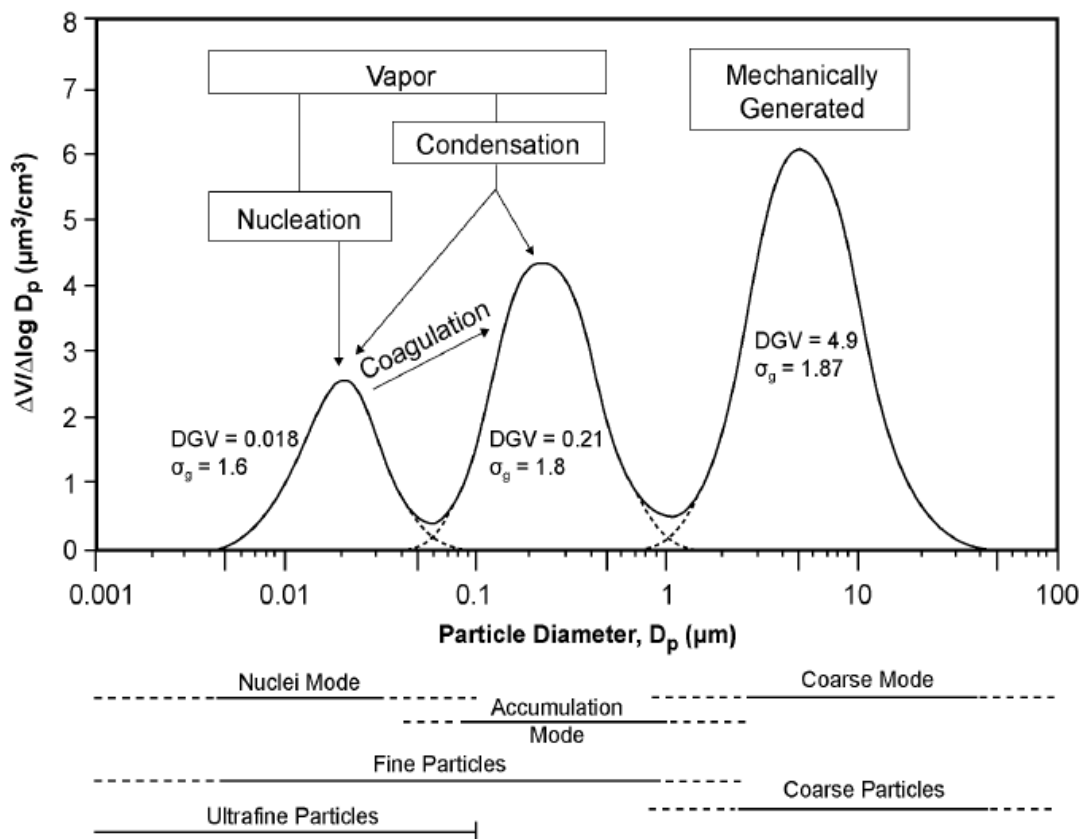
Figure 2.4 Volume size distribution, measured in traffic, showing fine and coarse particles and the nuclei and accumulation modes of fine particles. DGV (geometric mean diameter by volume, equivalent to volume median diameter) and σ_g (geometric standard deviation) are shown for each mode. Also shown transformation and growth mechanisms (e.g., nucleation, condensation, and coagulation) (Wilson et al., 1977; Wilson and Suh, 1997).

Whitby's (1978) conclusions have held up remarkably well. However, ideas about the sub-0.1 μm diameter range have changed somewhat as newer instruments provided measurements extending to smaller sizes and with greater resolution in size and time (McMurry et al., 2000). Depending on the source, temperature, saturated vapor pressure of the components, and the age of the aerosol, size distributions have been observed with peaks (including multiple peaks) throughout the sub-0.1 μm diameter size range. Sub-0.1 μm diameter peaks have been observed in rural areas (O'Dowd, 2002) as well as for brief periods (nucleation bursts) in urban areas (Woo et al., 2001). Aerosol scientists now classify particles in the sub-0.1 μm size range as *ultrafine particles* and divide this size range into a *nucleation region* (< 10 nm) and an *Aitken (nuclei) region* (10 to 100 nm), as shown in Figure 2.5. Other studies, have shown that in fog or clouds or at very high relative humidities the accumulation mode may split into a larger size (more hygroscopic or droplet) submode and a smaller size (less hygroscopic or condensation) submode.
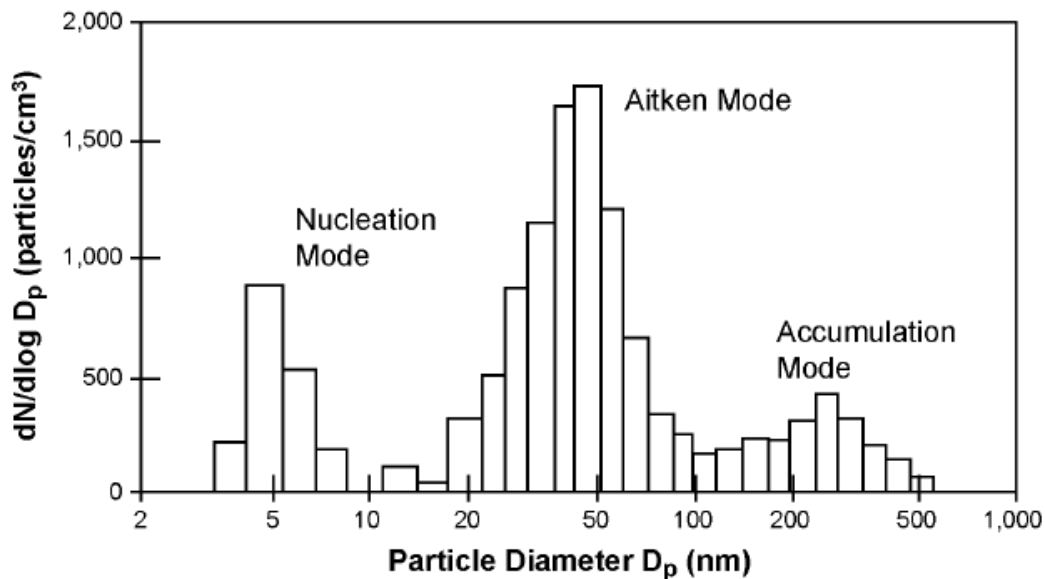
Figure 2.5 Sub-micrometer number size distribution observed in a boreal forest in Finland showing the trimodal structure of fine particles. The total particle number concentration was 1.011 particles/cm³ (10-min average) (Mäkelä et al., 1997).

2.2.2.3 Definitions of Particle Size Fractions

Aerosol scientists use several different approaches or conventions in the classification of particles by size. These include:

(a) Modes, based on the observed size distributions and formation mechanisms,

(b) Dosimetry or occupational health sizes, based on the entrance into various compartments of the respiratory system,

(c) Cut point, usually based on the 50% cut point of the specific sampling device, including legally specified, regulatory cut points for air quality standards.

Modal. The modal classification as first proposed by Whitby (1978) is shown in Figures 2.1 and 2.4. The newer modes introduced since 1978 are shown in Figure 2.5. An idealized distribution showing all four modes is shown in Figure 2.6.
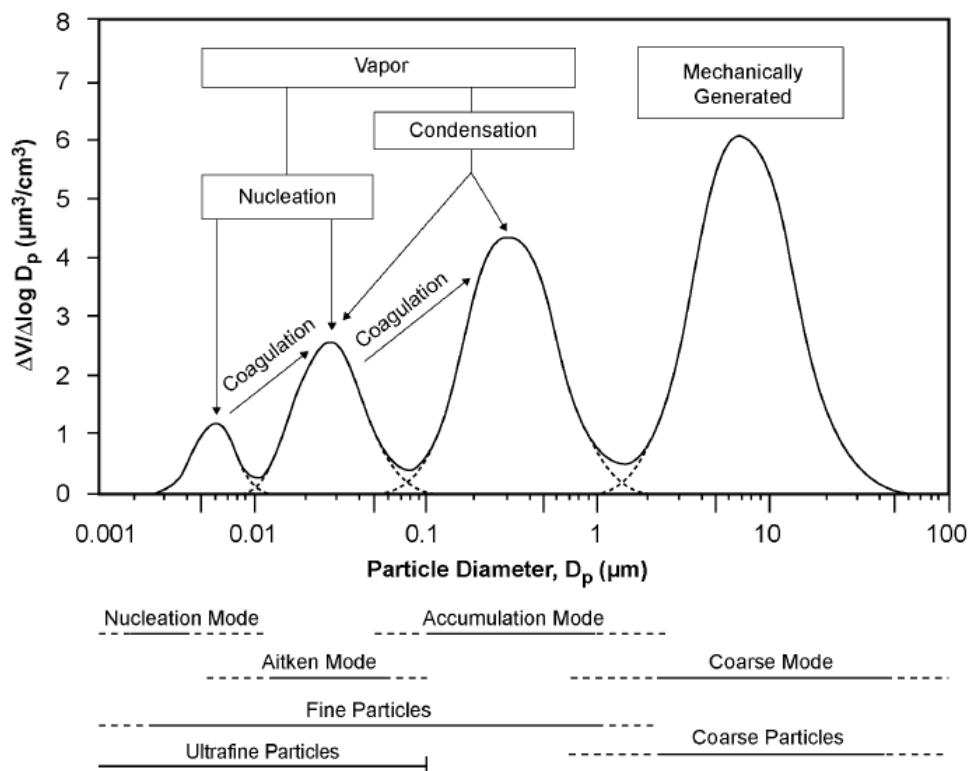
Figure 2.6 An idealized size distribution, that might be observed in traffic, showing fine and coarse particles and the nucleation, Aitken, and accumulation modes that comprise fine particles. Also shown are major formation and the growth mechanisms of the four modes of atmospheric particles (Air Quality Criteria for PM, 2004).

The nucleation and Aitken modes are best observed in the number distribution. However, the Aitken mode can be seen in the volume distribution in traffic or near traffic or other sources of ultrafine particles (Figures 2.3b and 2.4). The observed modal structure is frequently approximated by several lognormal distributions. Definitions of terms used to describe size distributions in modal terms are given below.

Nucleation Mode: Freshly formed particles with diameters below about 10 nm, observed during active nucleation events. The lower limit, where particles and molecular clusters or large molecules overlap, is uncertain. Current techniques limit measurements to particles 3 nm or greater.

Aitken Mode: Larger particles with diameters between about 10 and 100 nm. The Aitken mode may result from growth of smaller particles or nucleation from higher concentrations of precursors.

Accumulation Mode: Particles with diameters from about 0.1 μm to just above the minimum in the mass or volume distributions which usually occurs between 1 and 3 μm.

Fine Particles: Fine particles include the nucleation, Aitken, and accumulation modes, i.e., particles from the lowest measurable size, currently about 3 nm, to just above the minimum in the mass or volume distribution which generally occurs between 1 and 3 μm.

Coarse Mode or Coarse Particles: Particles with diameters mostly greater than the minimum in the particle mass or volume distributions, which generally occurs between 1 and 3 μm.

Ultrafine Particles: Ultrafine particles are not a mode. In the air pollution literature, they are generally defined by size alone, i.e., particles with diameters of 0.1 μm (100 nm) or less. They include the nucleation mode and much of the Aitken mode. They may also be defined as particles whose properties differ from those of the bulk material because of their small size.

Modes are defined primarily in terms of their formation mechanisms but also differ in sources, composition, transport and fate, as well as in size. Nucleation mode applies to newly formed particles which have had little chance to grow by condensation or coagulation. Aitken mode particles are also recently formed particles that are still actively undergoing coagulation. However, because of higher concentrations of precursors or more time for condensation and coagulation, Aitken particles have grown to larger sizes. Fine particles grow by coagulation (two particles combining to form one) or by condensation (low-equilibrium vapor pressure gas molecules condensing on a particle). As the particle size increases, the rate of growth by coagulation and condensation decreases and particles "accumulate" in the accumulation mode size range. Thus, accumulation-mode particles normally do not grow into the coarse particle size range. However, during conditions of high relative humidity, hygroscopic accumulation mode particles grow in size, increasing the overlap of fine and coarse particles. The accumulation mode may split into a (hygroscopic) droplet mode and a (non-hygroscopic) condensation mode. In addition, gas-phase pollutants may dissolve and react in the particle-bound water of hygroscopic particles, leading to an increase in the dry size. The combination of nucleation, Aitken, and accumulation modes are called fine particles (or sometimes fine-mode particles). Fine particles are formed primarily by combustion or chemical reactions of gases yielding products with low saturated vapor pressures. Fine particles are composed of metals (and metal oxides), black or elemental carbon, primary and secondary organic compounds, and sulfate, nitrate, ammonium and hydrogen ions.

The coarse mode refers to particles formed by the mechanical breakdown of minerals, crustal material, and organic debris. In addition to primary minerals and organic material, the coarse mode may include sea salt, nitrate formed from the reaction of nitric acid with sodium chloride, and sulfate formed from the reaction of sulfur dioxide with basic particles. The accumulation mode and the coarse mode overlap in the region between 1 and 3 μm (and occasionally over an even larger range). In this region, the chemical composition of individual particles can usually, but not always, allow identification of a source or formation mechanism, permitting identification of a particle as belonging to the accumulation or coarse mode.

Occupational Health or Dosimetric Size Cuts. The occupational health community has defined size fractions in terms of their entrance into various compartments of the respiratory system. This convention classifies particles into inhalable, thoracic, and respirable particles according to their upper size cuts. Inhalable particles enter the respiratory tract, beginning with the head airways. Thoracic particles travel past the larynx and reach the lung airways and the gas-exchange regions of the lung. Respirable particles are a subset of thoracic particles that are more likely to reach the gas-exchange region of the lung. In the past, exact definitions of these terms have varied among organizations. As of 1993, a unified set of definitions was adopted by the American Conference of Governmental Industrial Hygienists (ACGIH, 1994), the International Standards Organization (ISO), and the European Standardization Committee (CEN). The curves which define inhalable (IPM), thoracic (TPM), and respirable (RPM) particulate matter are shown in Figure 2.7. These curves should not be taken to indicate that particles > 4 μm D_a do not reach the gas exchange regions or that particles < 4 μm D_a do not deposit in the bronchi.
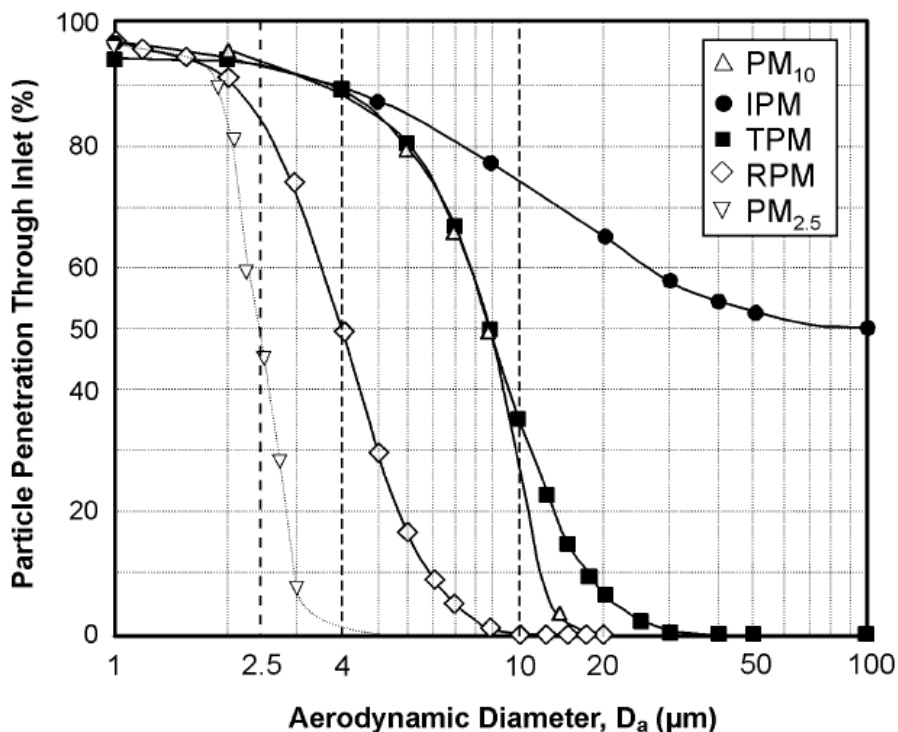
Figure 2.7 Specified particle penetration (size-cut curves) through an ideal (no-particle-loss) inlet for five different size-selective sampling criteria (Air Quality Criteria for PM, 2004).

In Figure 2.7, regulatory size cuts are defined in the Code of Federal Regulations ($PM_{2.5}$ [2001c], PM_{10} [2001a]). $PM_{2.5}$ is also defined in the Federal Register (1997).Size-cut curves for inhalable particulate matter (IPM), thoracic particulate matter (TPM), and respirable particulate matter (RPM) size cuts are computed from definitions given by American Conference of Governmental and Industrial Hygienists (1994).

Size-Selective Sampling. Another set of definitions of particle size fractions arises from considerations of size-selective sampling. Size-selective sampling refers to the collection of particles below or within a specified aerodynamic size range. Size fractions are usually specified by the 50% cut point size; e.g., $PM_{2.5}$ refers to particles collected by a sampling device that collects 50% of 2.5 μm particles and rejects 50% of 2.5 μm particles. However, size fractions are defined not merely by the 50% cut point, but by the entire penetration curve. Examples of penetration curves are given in Figure 2.7. Thus, as shown by Figure 2.7, a $PM_{2.5}$ sampler, as defined by the Federal Reference Method, rejects 94% of 3 μm particles, 50% of 2.5 μm particles, and 16% of 2 μm particles. Samplers with the same 50% cut point, but differently shaped penetration curves, would collect different fractions of PM. Size-selective sampling has arisen in an effort to measure particle size fractions with some special significance (e.g., health, visibility, source apportionment, etc.), to measure mass size distributions, or to collect size-segregated particles for chemical analysis. Dichotomous samplers split the particles into smaller and larger fractions that may be collected on separate filters. However, some fine particles (≈10%) are collected with the coarse particle fraction. Cascade impactors use multiple size cuts to obtain a distribution of size cuts for mass or chemical composition measurements. One-filter samplers with a variety of upper size cuts are also used, e.g., $PM_{2.5}$, PM_{10}.

An idealized particle size distribution with the normally observed division of ambient aerosols into fine and coarse particles and the size fractions collected by the WRAC, TSP, PM_{10}, $PM_{2.5}$ and $PM_{10-2.5}$ samplers is shown in Figure 2.8. PM_{10} samplers collect all of the fine-mode particles and part of the coarse-mode particles. The upper cut point is defined as having 50 % collection efficiency at 10 ± 0.5 μm aerodynamic diameter. The slope of the collection efficiency curve is defined in amendments to 40 CFR, Part 53 (Code of Federal Regulations, 2001b).

An example of a PM$_{2.5}$ size-cut curve is also shown in Figure 2.7. The PM$_{2.5}$ size-cut curve, however, is defined by the design of the Federal Reference Method (FRM) sampler. The basic design of the FRM sampler is given in the Federal Register (1997, 1998).
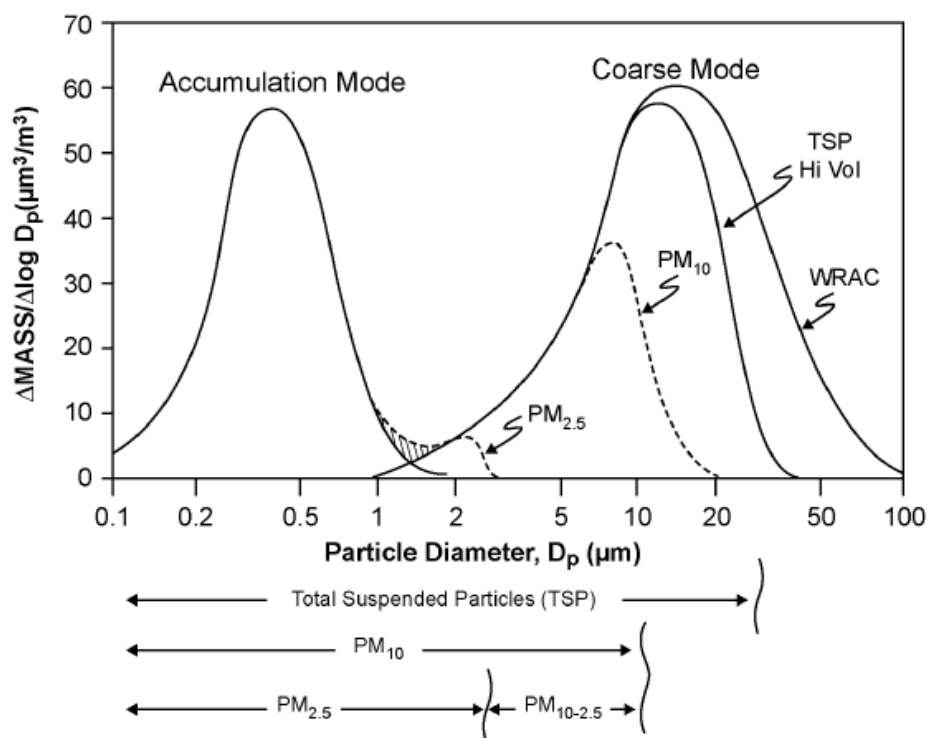
Figure 2.8 An idealized distribution of ambient particulate matter showing fine-mode particles and coarse-mod particles and the fractions collected by size-selective samplers. WRAC is the Wide Range Aerosol Classifier which collects the entire coarse mode (Wilson and Suh, 1997; Whitby, 1978).

Papers discussing PM$_{10}$ or PM$_{2.5}$ frequently insert an explanation such as "PM$_X$ (particles less than x μm diameter)" or "PM$_X$ (nominally, particles with aerodynamic diameter ≤ x μm)." While these explanations may seem easier than "PM$_X$ (particles collected with an upper 50% cut point of x μm aerodynamic diameter and a specified penetration curve)," they are not entirely correct and may be misleading, because they imply an upper 100% cut point of x μm. Some countries use PM$_{10}$ to refer not to samplers with a 50% cut at 10 μm D$_a$, but to samplers with 100% rejection of all

particles greater than 10 μm D_a. Such samplers miss a fraction of coarse thoracic PM. An example is shown in Figure 2.9.
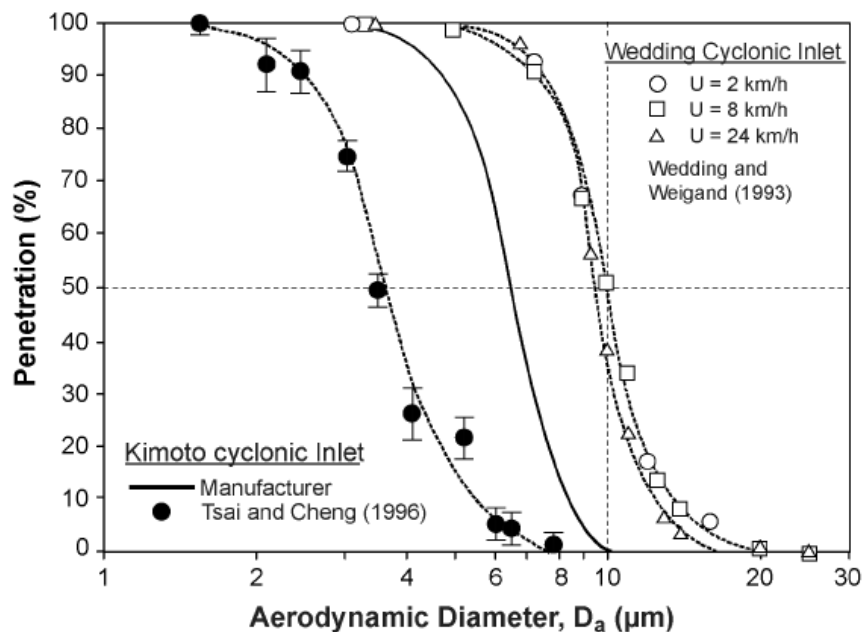
Figure 2.9 Comparison of penetration curves of two PM_{10} gauge samplers using cyclone inlets. The Wedding PM_{10} samplers uses the EPA definition of PM_X as x = 50% cut point. The Kimoto PM_{10} defines PM_X as x = the 100% cut point (or zero penetration) (Tsai and Cheng, 1996).

PM_{10}, as defined by EPA, refers to particles collected by a sampler with an upper 50% cut point of 10 μm D_a and a specific, fairly sharp, penetration curve. $PM_{2.5}$ is analogously defined. Although there is not yet an FRM, $PM_{10-2.5}$ refers either to particles collected by a sampler with an upper 50% cut point of 10 μm D_a and a lower 50% cut point of 2.5 μm D_a or to the difference between the particle concentration measured by a PM_{10} monitor and a $PM_{2.5}$ monitor. In all cases, the fraction of PM collected depends on the entire penetration curve (or curves); i.e., for $PM_{2.5}$ some particles > 2.5 μm D_a are collected and not all particles < 2.5 μm D_a are collected. A $PM_{10-2.5}$ size fraction may be obtained from a dichotomous sampler or by subtracting the mass collected by a $PM_{2.5}$ sampler from the mass collected by a PM_{10} sampler. The resulting $PM_{10-2.5}$ mass, or $PM_{10-2.5}$, is sometimes called "coarse" particles or "thoracic coarse" particles. However, it would be more correct to call $PM_{10-2.5}$ an indicator of the thoracic component of coarse particles (because it excludes some coarse particles below

2.5 μm D_a and above 10 μm D_a). Also, $PM_{2.5}$ should be considered an indicator of fine particles (because it contains some coarse particles). It would also be appropriate to call PM_{10} an indicator of thoracic particles. PM_{10} and thoracic PM, as shown in Figure 2.7, have the same 50% cut point. However, the thoracic cut is not as sharp as the PM_{10} cut; therefore, thoracic PM contains some particles between 10 and 30 μm diameter that are excluded from the PM_{10} fraction.

Over the years, the terms *fine* and *coarse*, as applied to particles, have lost the precise meaning given in Whitby's (1978) definition. In any given article, therefore, the meaning of fine and coarse, unless defined, must be inferred from the author's usage.

2.2.3 Atmospheric Lifetimes and Removal Processes

The lifetimes of particles vary with size. Nuclei-mode particles rapidly grow into the accumulation mode. However, the accumulation mode does not grow into the coarse mode. Accumulation-mode fine particles are kept suspended by normal air motions and have very low deposition rates to surfaces. They can be transported thousands of km and remain in the atmosphere for a number of days. Coarse particles can settle rapidly from the atmosphere (within hours) and normally travel only short distances. However, when mixed high into the atmosphere, as in dust storms, the smaller-sized coarse-mode particles have longer lives and travel greater distances. Dry deposition rates are expressed in terms of a deposition velocity that varies with particle size, reaching a minimum between 0.1 and 1.0 μm aerodynamic diameter (Lin et al., 1994). Accumulation-mode particles are removed from the atmosphere primarily by cloud processes. Fine particles, especially particles with a hygroscopic component, grow as the relative humidity increases, serve as cloud condensation nuclei, and grow into cloud droplets. If the cloud droplets grow large enough to form rain, the particles are removed in the rain. Falling rain drops impact coarse particles and remove them. Ultrafine or nuclei-mode particles are small enough to diffuse to the falling drop, be captured, and be removed in rain. Falling rain drops, however, are not nearly as effective in removing accumulation-mode particles as the cloud processes mentioned above. Acid deposition and PM are intimately related, first, because particles contribute to the acidification of rain and, secondly, because the gas-phase species that lead to dry deposition of acidity

are also precursors of particles. Therefore, reductions in SO_2 and NO_X emissions will decrease both acidic deposition and PM concentrations.

Sulfate, nitrate, and some partially oxidized organic compounds are hygroscopic and act as nuclei for the formation of cloud droplets. These droplets serve as chemical reactors in which (even slightly) soluble gases can dissolve and react. Thus, SO_2 can dissolve in cloud droplets and be oxidized to sulfuric acid by dissolved ozone or hydrogen peroxide. These reactions take place only in aqueous solution, not in the gas phase. Sulfur dioxide may also be oxidized by dissolved oxygen. This process will be faster if metal catalysts such as iron or manganese are present in solution. If the droplets evaporate, larger particles are left behind. If the droplets grow large enough, they will fall as rain; and the particles will be removed from the atmosphere with potential effects on the materials, plants, or soil on which the rain falls. Atmospheric particles that nucleate cloud droplets also may contain other soluble or nonsoluble materials such as metal salts and organic compounds that may add to the toxicity of the rain. Sulfuric acid, ammonium nitrate, ammonium sulfates, and organic particles also are deposited on surfaces by dry deposition. The utilization of ammonium by plants leads to the production of acidity. Therefore, dry deposition of particles can also contribute to the ecological impacts of acid deposition.

2.3 COMPARISON OF FINE AND COARSE PARTICLES

The physical and chemical properties of fine particles (including ultrafine particles and accumulation-mode particles) and coarse particles are summarized for comparison purposes in Table 2.1. These include important differences in sources, formation mechanisms, composition, atmospheric residence time, removal processes, and travel distances. Fine and coarse particles differ in aspects of concentrations, exposure, dosimetry, toxicology, and epidemiology. Collectively, these differences continue to warrant consideration of fine particles as a separate air pollutant class from coarse particles and the setting of separate standards for fine and coarse particles.

Table 2.1 Comparison of ambient particles, fine particles (ultrafine plus accumulation-mode), and coarse particles (Wilson and Suh, 1997).

	FINE		COARSE
	Ultrafine	**Accumulation**	
Formation Processes:	Combustion, high temperature processes, and atmospheric reactions		Break-up of large solid/droplets
Formed by:	Nucleation Condensation Coagulation	Condensation Coagulation Reaction of Gases in or on particles Evaporation of fog and cloud droplets in which gases have dissolved and reacted	Mechanical disruption (crushing, grinding, abrasion of surfaces) Evaporation of sprays Suspension of dust Reaction of Gases in or on particles
Composed of:	Sulfate Elemental carbon Metal Compounds Organic compounds with very low saturation vapor pressure at ambient temperature	Sulfate, nitrate, ammonium, and hydrogen ions Elemental carbon Large variety of organic compounds Metals: compounds of Pb, Cd, V, Ni, Cu, Zn, Mn, Fe, etc. Particle-bound water	Suspended soil or street dust Fly ash from uncontrolled combustion of coal, oil, and wood Nitrates/chlorides/Sulftates from HNO_3/HCl/SO_2 reactions with coarse particles Oxides of crustal elements (Si, Al, Ti, Fe) $CaCO_3$, $CaSO_4$, NaCl, sea salt Pollen, mold, fungal spores Plant and animal fragments Tire, break pad, and road wear debris
Solubility:	Probably less soluble than accumulation mode	Largely soluble, hygroscopic, and deliquescent	Largely soluble and nonhygroscopic
Sources:	Combustion Atmospheric transformation of SO_2 and some organic compounds High temperature processes	Combustion of coal, oil, gasoline, diesel fuel, wood Atmospheric transformation products of NOx, SO_2, and organic compounds, including biogenic organic species (e.g. terpenes) High temperature processes, smelters, steel mills, etc	Resuspension of industrial dust and soil track onto roads and streets Suspension from disturbed soil (e.g. farming, mining, unpaved roads) Construction and demolition Uncontrolled coal and oil Combustion Ocean spray Biological sources
Atmospheric half-life:	Minutes to hours	Days to weeks	Minutes to hours
Removal processes:	Grows into accumulation mode Diffuses to raindrops	Forms cloud droplets and rains out Dry deposition	Dry deposition by fallout Scavenging by falling raindrops
Travel distance:	< 1 to 10s of km	100s to 1000s of km	< 1 to 10s of km (small size tail, 100s to 1000s in dust storms)

2.4 MEASUREMENT OF PARTICULATE MATTER

2.4.1   Particle Measurements of Interest

There are many PM components and parameters that are of interest across the various types of uses to which PM measurement data are applied. These uses include analyses of compliance with air quality standards and trends; source category apportionment studies related to the development of pollution reduction strategies and the validation of air quality models; studies related to health, ecological, and radiative effects; and characterization of current air quality for presentation to the public in the context of EPA's Air Quality Index. Particulate matter measurement components and parameters of specific interest for these various purposes are summarized in Table 2.2.

Particle measurements are needed to determine if a location is in compliance with air quality standards, to determine long-term trends in air quality patterns, and for use in epidemiologic studies. For these purposes, the precision of the measurements made by a variety of measurement instruments in use is a critical consideration. Therefore, the intercomparisons of various samplers under a variety of atmospheric and air quality conditions are important.

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In order to reduce pollution to attain a standard, pollution control agencies and national research organizations need measurements to identify source categories and to develop and validate air quality models. For these purposes, PM parameters other than mass, such as chemical composition and size distribution, must also be measured. Moreover, measurements are needed with shorter time resolutions in order to match changes in pollution with the diurnal changes in the boundary layer.

Table 2.2 Particulate matter components/parameters of interest for health, ecological or radiative effects; for source category apportionment studies; or for air quality modeling evaluation studies (Air Quality Criteria for PM, 2004).

- Particle number

- Particle surface area

- Particle size distribution

- PM mass (fine PM mass [$PM_{2.5}$] and coarse thoracic PM mass [$PM_{10-2.5}$]) including both nonvolatile mass as measured by the current Federal Reference method and total mass (including semivolatile components such as ammonium nitrate and semivolatile organic compounds, but not particle-bound water)

- Ions (sulfate, nitrate, and ammonium)

- Strong acidity (H^+)

- Elemental carbon

- Organic carbon (total, nonvolatile, and semivolatile; functional groups and individual species)

- Transition metals (water soluble, bioavailable, oxidant generation)

- Specific toxic elements and organic compounds

- Crustal elements

- Bioaerosols

- Particle Refractive index (real and imaginary)

- Particle density

- Particle size change with changes in relative humidity

A number of PM measurements are needed for use in epidemiologic and exposure studies and to determine components of PM to guide the planning and interpretation of toxicologic studies. Thus, size and chemical composition measurements are important, as are measurement across different time intervals. For epidemiologic studies of acute

(i.e., short-term) PM exposures, 1-h or continuous measurements can provide important information beyond that provided by 24-h measurements. However, for epidemiologic studies of chronic PM exposures, measurements that permit integration over longer intervals (e.g., a week to a month) are more relevant. For dosimetric studies and modeling, information will be needed on the particle size distribution and on the behavior of particles as the relative humidity and temperature changes found in the atmosphere are increased to those found in the respiratory system.

For studies of ecological effects and materials damage, measurements of particles and of the chemical components of PM in rain, fog, and dew are needed to understand the contributions of PM to the soiling of surfaces and damage to materials and to understand the wet and dry deposition of acidity and toxic substances to surface water, soil, and plants. Some differentiation into particle size is needed to determine dry deposition.

For studies of visibility impairment and radiative effects, information is needed regarding how particles scatter and absorb light, including data on refractive index, ratio of scattering to absorption, size distribution, and change in particle size with change in relative humidity.

2.4.2 Time Resolution

The classic 24-h filter collection technique is being supplemented by a variety of continuous monitors for various PM constituents. This process is being accelerated by the lower operational cost of continuous monitors and the availability of new continuous monitors for mass, number, and certain chemical components, as well as refinements of older methods based on beta attenuation or light scattering. Most epidemiologic studies have used 24-hour concentrations as exposure indicators. However, one epidemiologic study of chronic effects uses a filter sampler with a 2-week collection period (Gauderman et al., 2000). Another recent study used 1 to 2 h concentrations (see Peters et al., 2000).

2.4.3   Monitoring Methods

2.4.3.1 PM$_{2.5}$

In contrast to the performance-based FRM standard for PM$_{10}$, the FRM for PM$_{2.5}$ (Code of Federal Regulations, 2001a) specifies certain details of the sampler design, as well as of sample handling and analysis, whereas other aspects have performance specifications (Noble et al., 2001). The PM$_{2.5}$ FRM sampler consists of a PM$_{10}$ inlet/impactor, a PM$_{2.5}$ impactor with an oilsoaked impaction substrate to remove particles larger than 2.5 μm D$_a$, and a 47-mm PTFE filter with particle collection efficiency greater than 99.7%. The sample duration is 24 h, during which time the sample temperature is not to exceed ambient temperatures by more than 5 °C. A schematic diagram of the PM$_{2.5}$ FRM sample collection system is shown in Figure 2.10. After collection, samples are equilibrated for 24 h at temperatures in the range of 20 to 23 °C (± 2 °C) and at relative humidities in the range of 30 to 40% (± 5%). The equilibration tends to reduce particle-bound water and stabilizes the filter plus sample weight. Filters are weighed before and after sampling under the same temperature and relative humidity conditions. For sampling conducted at ambient relative humidity < 30%, mass measurements at relative humidities down to 20% are permissible (Code of Federal Regulations, 2001a).

The PM$_{10}$ inlet specified for the PM$_{2.5}$ FRM is modified from a previous low flow rate PM$_{10}$ inlet that was acceptable in both EPA-designated reference and equivalent PM$_{10}$ methods. The modification corrects a flaw that was reported for the previous sampler in that under some meteorological conditions the inlet may allow precipitation to penetrate the inlet. The modification includes a larger drain hole, a one-piece top plate, and louvers. Tolocka et al. (2001) evaluated the performance of this modified inlet in a series of wind tunnel experiments. The modified inlet was found to provide a size cut comparable to the original inlet, for both PM$_{2.5}$ and PM$_{10}$ sampling. Because the modification did not change the characteristics of the size cut, the modified inlet may be substituted for the original inlet as part of a reference or equivalent method for PM$_{10}$ and PM$_{2.5}$ (Tolocka et al., 2001).
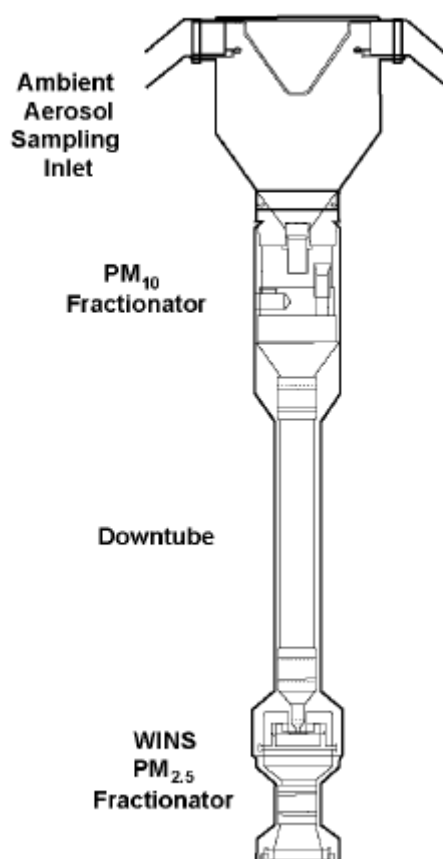
Figure 2.10 Schematic diagram of the sample collection portion of the PM$_{2.5}$ FRM sampler (Noble et al., 2001)

2.4.3.2 PM$_{10-2.5}$

Measurement techniques for PM$_{10-2.5}$ are somewhat more complex than those for PM$_{2.5}$ or PM$_{10}$, because it is necessary to isolate a size fraction between an upper 50% cut point of 10 μm D$_a$ and a lower 50% cut point of 2.5 μm D$_a$ for PM$_{10-2.5}$. EPA is currently developing an FRM for PM$_{10-2.5}$. Several candidate techniques are the difference method, multistage impaction, and virtual impaction.

Virtual Impaction. The problems of bounce and blow off of particles from impactors, especially for the collection of large quantities of particles, was addressed by aerosol scientists in the mid-1960s by the development of what is now known as "virtual" impaction (Hounam and Sherwood, 1965; Conner, 1966).

In a virtual impactor, a hole is placed in the impaction plate just below the accelerating jet. Two controlled flows allow a fraction, e.g., 10% (or another predetermined fraction, typically 5 to 20%), of the air containing the coarse particles to go through the hole and through a filter (minor flow). A 10% minor flow gives a coarse channel enrichment factor of 10. The remaining fraction (e.g., 90% of the airflow) containing the fine particles follows a different path and goes through a second filter (major flow). The upper cut point is usually set by the inlet (e.g., 10 μm D_a). The flow rates, pressures, and distance from the nozzle to the virtual impactor surface can be varied to direct particles with an D_a greater than the lower cut point (i.e., > 2.5 μm) to go through the hole and be collected on the first filter and to direct smaller particles (i.e., < 2.5 μm) to flow around the impactor and be collected on the second filter. Large particles "impact" into the hole with a small amount of the air flow. The smaller particles follow the major air flow around the impactor plate. This technique overcomes the problem of bounce. An example of the separation into fine and coarse particles is shown in Figure 2.11.
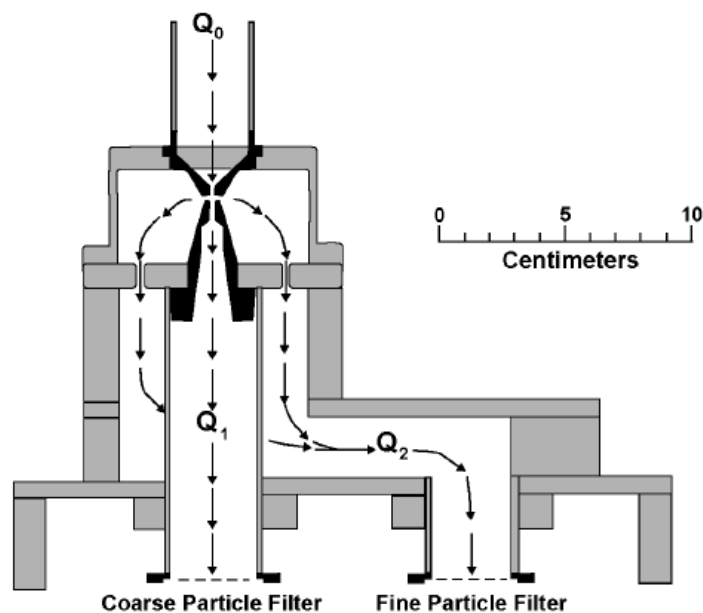
Figure 2.11 Schematic diagram showing the principle of virtual impaction. The initial flow, Q_0, is split into minor flow, Q_1, which carries the larger particles that impact into the hole, to the coarse particle filter and a major flow, Q_2, which carries the smaller particles that can follow the airflow, to the fine particle filter (Loo et al., 1976).

The usefulness of this technique for collecting samples of fine and coarse particles for chemical analysis was recognized by the EPA in the mid-1970s and led to the development of the now well-known "dichotomous sampler" (a virtual impactor that separates particles into two size fractions) and an associated XRF analyzer (Dzubay and Stevens, 1975; Loo et al., 1976; Jaklevic et al., 1977; Dzubay et al., 1977). The dichotomous sampler was originally developed for use in the Regional Air Monitoring Study (RAMS), part of the Regional Air Pollution Study (RAPS), conducted in St. Louis, MO in the mid-1970s. Dichotomous samplers were a novel concept at that time. Concern over particle losses and other problems at cut point sizes < 2.5 μm D_a influenced the decision to choose 2.5 instead of 1.0 as the cut point diameter.

Now virtual impactors, with rectangular slits or round holes, are used to (a) provide cut point sizes as low as 0.15 μm D_a and (b) concentrate coarse, accumulation, and ultrafine mode particles for use in health studies (Solomon et al., 1983; Marple et al., 1990; Sioutas et al., 1994a,b,c).

The slit impactor can also be used to concentrate coarse particles for measurement (Misra et al., 2001) or exposure studies (Chang et al., 2002). In addition, ultrafine particles (> 0.1 μm) can be concentrated by first separating ultrafine particles from larger particles, adding water vapor to saturate the air containing the ultrafine particles, cooling the air to cause supersaturation and growth of the ultrafine particles into the 1.0 to 4.0 μm size range, then concentrating these particles with a slit virtual impactor, and finally, heating the air to return the particles to their original size (Sioutas and Koutrakis, 1996; Sioutas et al., 1999; Sioutas et al., 2000; Kim et al., 2001a,b; Geller et al., 2002).

CHAPTER 3

EFFECTS OF AIRBORNE PARTICULATE MATTER

3.1 ENVIRONMENTAL EFFECTS

3.1.1 Effects on Vegetation and Ecosystem

Exposure to a given mass concentration of airborne PM may lead to widely differing phytotoxic responses, depending on the particular mix of deposited particles. Effects of particulate deposition on individual plants or ecosystems are difficult to characterize because of the complex interactions among biological, physicochemical, and climatic factors. Most direct effects, other than regional effects associated with global changes, occur in the severely polluted areas surrounding industrial point sources, such as limestone quarries, cement kilns, and metal smelting facilities. Fine particles are more widely distributed from their sources than are coarse particles. Experimental applications of PM constituents to foliage typically elicit little response at the more common ambient concentrations. The diverse chemistry and size characteristics of ambient PM and the lack of clear distinction between effects attributed to phytotoxic particles and to other air pollutants further confound understanding of the direct effects on foliar surfaces. The majority of the documented toxic effects of particles on vegetation reflect their chemical content (e.g., acid/base, trace metal, nutrient), surface properties, or salinity. Studies of the direct effects of particles on vegetation have not yet advanced to the stage of reproducible exposure experiments. The difficulties of experimental application of ambient particles to vegetation have been discussed by Olszyk et al. (1989). Studies indicate many phytotoxic gases are deposited more readily, assimilated more rapidly, and lead to greater direct injury of vegetation than do most common particulate materials (Guderian, 1986). The dose-specific

responses (dose-response curves) obtained in early experiments following the exposure of plants to phytotoxic gases generally have not been observed following the application of particles.

Unlike gaseous dry deposition, neither the solubility of the particles nor the physiographical activity of the surface is likely to be of first order importance in determining deposition velocity (V_d). Factors that contribute to surface wetness and stickiness may be critical determinants of deposition efficiency. Available tabulation of deposition velocities are highly variable and suspect. However, high-elevation forests receive larger particle deposition loadings than equivalent lower elevations sites because of higher wind speeds and enhanced rates of aerosol impaction, orographic effects on rainfall intensity and composition, increased duration of occult deposition, and, in many areas, the dominance of coniferous species with needle-shaped leaves (Lovett, 1984). Recent evidence indicates that all three modes of deposition (wet, occult, and dry) must be considered in determining inputs to ecosystems or watersheds, because each may dominate over specific intervals of space.

Atmospheric PM may affect vegetation directly following deposition on foliar surfaces or indirectly by changing the soil chemistry or by changing the amount of radiation reaching the Earth's surface through PM-induced climate change processes. Indirect effects, however, are usually the most significant because they can alter nutrient cycling and inhibit plant nutrient uptake.

3.1.1.1 Physical Effects

Dust can cause physical and chemical effects. Deposition of inert PM on above-ground plant organs sufficient to coat them with a layer of dust may result in changes in radiation received, a rise in leaf temperature, and the blockage of stomata. Increased leaf temperature and heat stress, reduced net photosynthesis, and leaf chlorosis, necrosis, and abscission were reported by Guderian (1986). Road dust decreased the leaf temperature on *Rhododendron catawbiense* by ~4 °C (Eller, 1977); whereas foundry dust caused an 8.7 °C increase in leaf temperature of black poplar (*Populus nigra*) under the conditions of the experiment (Guderian, 1986). Deciduous (broad) leaves exhibited larger temperature increases because of particle loading than did conifer (needle) leaves,

a function of poorer coupling to the atmosphere. Inert road dust caused a three- to four-fold increase in the absorption coefficient of leaves of English ivy (Eller, 1977; Guderian, 1986) for near infrared radiation (NIR; 750 to 1350 nm). Little change in absorption occurred for photosynthetically active radiation (PAR; 400 to 700 nm). The increase in NIR absorption may be accounted for by a decease in reflectance and transmission in these wavelengths. The amount of energy entering the leaf increased by ~30% in the dust-affected leaves. Deposition of coarse particles increased leaf temperature and contributed to heat stress, reduced net photosynthesis, and caused leaf chlorosis, necrosis, and abscission (Dässler et al., 1972; Parish, 1910; Guderian, 1986; Spinka, 1971).

Starch storage in dust-affected leaves increased with dust loading when under high (possibly excessive) radiation, but decreased following dust loading when radiation was limiting. These modifications of the radiation environment had a large effect on single-leaf utilization of light. The boundary layer properties, determined by leaf morphology and environmental conditions, strongly influenced the direct effects of particle deposition on radiation heating (Eller, 1977; Guderian, 1986) and on gas exchange. Brandt and Rhoades (1973) attributed the reduction in the growth of trees to crust formation from limestone dust on the leaves. Crust formation reduced photosynthesis and the formation of carbohydrates needed for normal growth, induced premature leaf-fall, damaged leaf tissues, inhibited growth of new tissue, and reduced starch storage. Dust may decrease photosynthesis, respiration, and transpiration; and it may allow penetration of phytotoxic gaseous pollutants, thereby causing visible injury symptoms and decreased productivity. Permeability of leaves to ammonia increased with increasing dust concentrations and decreasing particle size (Farmer, 1993).

Dust also has been reported to physically block stomata (Krají Ková, and Mejstĺík, 1984). Stomatal clogging by PM from automobiles, stone quarries, and cement plants was also studied by Abdullah and Iqbal (1991). The percentage of clogging was low in young leaves when compared with old, mature leaves and the amount of clogging varied with species and locality. The maximum clogging of stomata observed was about 25%. The authors cited no evidence that stomatal clogging inhibited plant function. The heaviest deposit of dust usually occurs on the upper surface of

broad-leaved plants; whereas the majority of the stomata are on the lower surface where stomatal clogging would be less likely.

3.1.1.2 Chemical Effects

The chemical composition of PM is usually the key phytotoxic factor leading to plant injury. On hydration, cement-kiln dust liberates calcium hydroxide, which can penetrate the epidermis and enter the mesophyll; in some cases, this has caused the leaf surface alkalinity to reach a pH of 12. Lipid hydrolysis, coagulation of the protein compounds, and ultimately plasmolysis of the leaf tissue reduce the growth and quality of plants (Guderian, 1986). In experimental studies, applications of cement-kiln dust of known composition for 2 to 3 days yielded dose-response curves between net photosynthetic inhibition or foliar injury and dust application rate (Darley, 1966). Lerman and Darley (1975) determined that leaves must be misted regularly to produce large effects. Alkalinity was probably the essential phytotoxic property of the applied dusts.

3.1.2 Effects on Visibility

Visibility, referring to the appearance of scenic elements in an observer's line of sight, depends on more than the optical characteristics of the atmosphere. Numerous scene and lighting characteristics are important to this broad definition of visibility. However, under a variety of viewing conditions, visibility reduction or haziness is directly related to the extinction coefficient.

Light extinction, the sum of the light scattered and absorbed by particles and gases, is frequently used to estimate the effect of air pollution on visibility. Light extinction is usually quantified using the light extinction coefficient, i.e., the sum of the light scattering and absorption coefficients for gases and particles.

The influence of particles on visibility degradation is dependent on the particle size, composition, and solubility (Pryor and Steyn, 1994). Fine particles (particles with mass mean diameters ≤ 2.5 μm) scatter more light than coarse particles. Fine particle species include sulfates (assumed to be ammonium sulfate), nitrates (assumed to be

ammonium nitrate), organics, light-absorbing carbon, and soil (Malm et al., 1994). Of the fine particle species, sulfates and nitrates are the most hygroscopic and require the use of a relative humidity adjustment factor. The effect of particle light extinction can be determined by totaling the scattering and absorption of light by multiplying the mass-specific efficiency values and the mass concentration for each of the particle species.

Figure 3.1 shows the relationship between fine particle mass and calculated light extinction. The figure, as reported in Chow et al (2002), was generated using data reported by Samuels et al. (1973). According to Samuels et al. (1973), there was a direct correlation between particle mass concentration, light scattering, and visibility. However, there were large standard errors in the scattering coefficient.
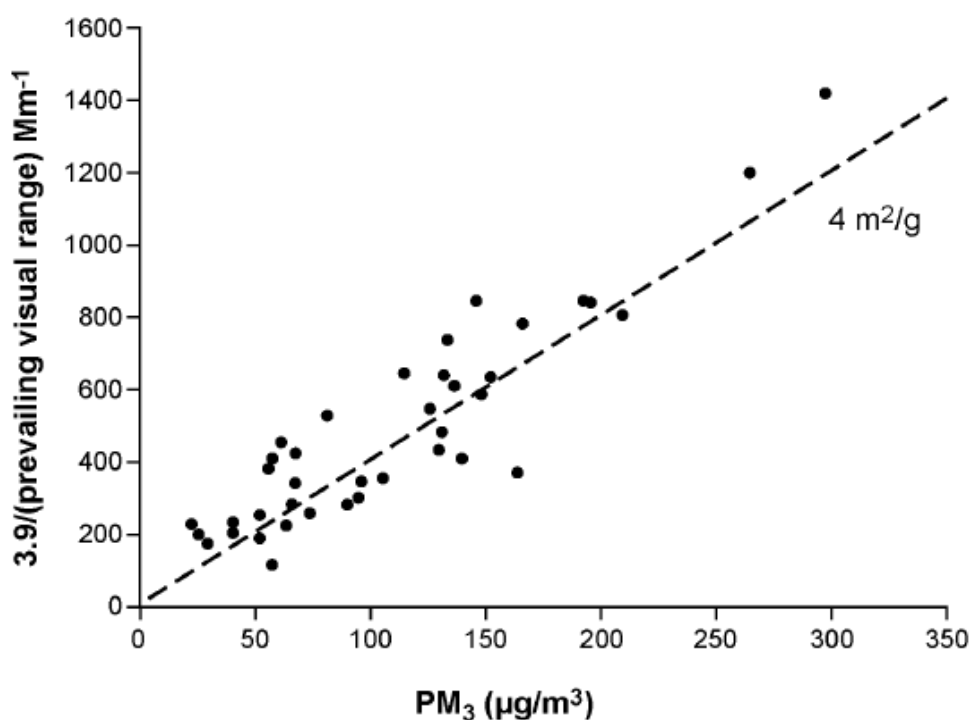
Figure 3.1 Proportionality of observed daytime haziness to fine particle mass concentration in Los Angeles. Visual ranges are 8-h averages of hourly human observations, plotted as extinction according to Koschmieder Formula. Mass concentrations are from 8-h samples collected behind a cyclone with 3-μm cut point. Relative humidities were ≤ 70% (Chow et al., 2002).

3.1.3 Effects on Materials

Effects of air pollution on materials are related to both aesthetic appeal and physical damage. Studies have demonstrated that particles, primarily carbonaceous compounds, cause soiling of commonly used building materials and culturally important items, such as statutes and works of art. Physical damage from the dry deposition of air pollutants, such as PM (especially sulfates and nitrates) and SO_2, and the absorption or adsorption of corrosive agents on deposited particles also can result in the acceleration of naturally occurring weathering processes of man-made building and cultural materials.

In the atmosphere, PM may be "primary," existing in the same form in which it was emitted, or "secondary," formed by the chemical reactions of free, absorbed, or dissolved gases. The major constituents of atmospheric PM are sulfate, nitrate, ammonium, and hydrogen ions; particle-bound water; elemental carbon; a great variety of organic compounds; and crustal material. A substantial fraction of the fine particle mass, particularly during the warmer months, is secondary sulfate and nitrate. Sulfates may be formed by the gas-phase conversion of SO_2 to H_2SO_4 by OH radicals and aqueous-phase reactions of SO_2 with H_2O_2, O_3, or O_2. During the day, NO_2 may be converted to nitric acid (HNO_3) by reacting with OH radicals. Nitrogen dioxide also can be oxidized to HNO_3 by a sequence of reactions initiated by O_3.

3.1.4 Effects on Climate Change

Atmospheric particles alter the amount of solar radiation transmitted through the Earth's atmosphere. The absorption of solar radiation by atmospheric particles, together with the trapping of infrared radiation emitted by the Earth's surface by certain gases, enhances the heating of the Earth's surface and lower atmosphere i.e., the widely-known "greenhouse effect." Increases in the atmospheric concentration of these gases due to human activities may lead to impacts, due to climate change, on human health and the environment. Lesser consequences of airborne particles include alterations in the amount of ultraviolet solar radiation (especially UV-B, 290 to 315 nm) penetrating through the Earth's atmosphere and reaching its surface where UV radiation can exert

various effects on human health, plant and animal biota, and other environmental components.

The effects of atmospheric PM on the transmission of electromagnetic radiation emitted by the sun at ultraviolet and visible wavelengths, and by the Earth at infrared wavelengths, depend on the radiative properties (extinction efficiency, single-scattering albedo, and asymmetry parameter) of the particles, which depend, in turn, on the size and shape of the particles, the composition of the particles, and the distribution of components within individual particles. In general, the radiative properties of particles are size- and wavelength-dependent, with the extinction cross section tending toward its maximum when the particle radius is similar to the wavelength of the incident radiation. This means that fine particles present mainly in the accumulation mode would be expected to exert a greater influence on the transmission of electromagnetic radiation than would coarse particles.

Knowledge of the effects of PM on the transfer of radiation in the visible and infrared spectral regions is needed for assessing relationships between particles and climate change processes, as well as environmental and biological effects. Knowledge of the factors controlling the transfer of solar radiation in the ultraviolet spectral range is needed to assess potential the biological and environmental effects associated with exposure to UV-B radiation.

3.2 EFFECTS ON HUMAN HEALTH

The evidence on airborne PM and public health is consistent in showing adverse health effects at exposures experienced by urban populations in cities throughout the world, in both developed and developing countries. The range of effects is broad, affecting the respiratory and cardiovascular systems and extending to children and adults and to a number of large, susceptible groups within the general population. The risk for various outcomes has been shown to increase with exposure and there is little evidence to suggest a threshold below which no adverse health effects would be anticipated. In fact, the lower range of concentrations at which adverse health effects has been demonstrated is not greatly above the background concentration which has

been estimated at 3-5 $\mu g/m^3$ in the United States and Western Europe for particles smaller than 2.5 micrometer, $PM_{2.5}$. The epidemiological evidence shows adverse effects of particles after both short-term and long-term exposures.

Current scientific evidence indicates that guidelines cannot be proposed that will lead to complete protection against adverse health effects of particulate matter, as thresholds have not been identified. Rather, the standard-setting process needs to achieve the lowest concentrations possible in the context of local constraints, capabilities, and public health priorities. Quantitative risk assessment offers one approach for comparing alternative scenarios of control and estimating the residual risk with achieving any particular guideline value. The United States Environmental Protection Agency and the European Commission have recently used this approach in making recommendations for revisions of the existing standards for particulate matter. Countries are encouraged to consider an increasingly stringent set of standards, tracking progress through emission reductions and declining concentrations of particulate matter. The numerical guideline values given in the tables provide guidance on the concentrations at which increasing, and specified mortality responses due to PM are expected based on current scientific insights. As mentioned, to the extent that health effects associated with ambient PM have been reported at relatively low ambient concentrations, and that there is substantial inter-individual variability in exposure and response in a given exposure, it is unlikely that any PM standard or guideline level will provide universal protection for every individual against all possible PM-related effects.

The choice of indicator for particulate matter also merits consideration. The most recent and extensive epidemiological evidence is largely based on studies using PM_{10} as the exposure indicator. Further, at present the majority of monitoring data is based on measurement of PM_{10} as opposed to other particulate matter metrics. As an indicator, PM_{10} comprises the particle mass that enters the respiratory tract and includes both the coarse (PM_{10}-$PM_{2.5}$) and fine ($PM_{2.5}$) particles considered to contribute to the health effects observed in urban environments. In most urban environments, both coarse and fine mode particles are likely to be prominent, the former primarily produced by mechanical processes such as construction activities, road dust resuspension and wind, and the latter primarily from combustion sources. The composition of particles in these

two size ranges is likely to vary substantially across cities around the world depending upon local geography, meteorology and specific sources. Combustion of wood and other biomass can be a major contributing source to outdoor air pollution as well; the resulting combustion particles are largely in the fine ($PM_{2.5}$) mode. Although few epidemiological studies exist comparing the relative toxicity of combustion from fossil fuel versus biomass, similar effect estimates have been reported over a wide range of cities in both developed and developing countries. Therefore, it is reasonable to assume generally similar effects of $PM_{2.5}$ from these different sources. In the developing world, large populations are exposed to high levels of combustion particles indoors, and the WHO AQG for PM also applies to these situations (WHO Air Quality Guidelines Global Update, 2005).

PM_{10} is suggested as an indicator with relevance to the majority of the epidemiological data and for which there is more extensive measurement data throughout the world. However, as discussed below, the numerical guideline value itself is based on studies using $PM_{2.5}$ as an indicator and a $PM_{2.5}/PM_{10}$ ratio of 0.5 is used to derive an appropriate PM_{10} guideline value. This ratio of 0.5 is close to that observed typically in developing country urban areas and at the bottom of the range (0.5 – 0.8) found in developed country urban areas. If justified by local conditions, this ratio may be changed based on the local data when the local standards are set.

Based on known health effects, both short-term (24-hour) and long-term (annual) guidelines are needed for both of the PM indicators. Tables 3.1 and 3.2 provide a range of values of which the lowest is designated as the WHO Air quality guideline. The WHO AQGs themselves are;

$PM_{2.5}$: 10 $\mu g/m^3$ annual mean, 25 $\mu g/m^3$ 24-hour mean
PM_{10}: 20 $\mu g/m^3$ annual mean, 50 $\mu g/m^3$ 24-hour mean

The annual average guideline value of 10 $\mu g/m^3$ for $PM_{2.5}$ was chosen to represent the lower end of the range over which significant effects on survival have been observed in the American Cancer Society Study (ACS) (Pope et al., 2002). Adoption of a guideline at this level places significant weight on the long-term exposure studies

using the ACS and Harvard Six-Cities data (Dockery et al., 1993; Pope et al., 1995; Krewski et al., 2000, Pope 2002, Jarrett 2005). In these studies, robust associations were reported between long-term exposure to $PM_{2.5}$ and mortality. The historical mean $PM_{2.5}$ concentration was 18 μg/m^3 (range of 11.0 to 29.6 μg/m^3) in the Six-Cities study and 20 μg/m^3 (range of 9.0 to 33.5 μg/m^3) in the ACS study. Thresholds were not apparent in either of these studies, although the precise period(s) and pattern(s) of relevant exposure could not be ascertained. In the ACS study, statistical uncertainty in the risk estimates becomes apparent at concentrations of about 13 μg/m^3, below which the confidence bounds significantly widen since the concentrations are relatively far from the mean. In the Dockery et al. study, the risks are similar in the cities at the lowest long-term $PM_{2.5}$ concentrations of 11 and 12.5 μg/m^3. Increases in risk are apparent in the city with the next-lowest long-term $PM_{2.5}$ mean of 14.9 μg/m^3, indicating likely effects in the range of 11 to 15 μg/m^3. Therefore, an annual concentration of 10 μg/m^{3}would be below the mean of the most likely effects levels indicated in the available literature. Targeting a long-term mean $PM_{2.5}$ concentration of 10 μg/m^3 would also place some weight on the results of daily exposure time-series studies examining relationships between $PM_{2.5}$ and acute adverse health outcomes. These studies have long-term (three to four year) means in the range of 13 to 18 μg/m^3. Although adverse effects on health cannot be entirely ruled out even below that level, the annual average WHO AQG represent levels that have been shown to be achievable in large urban areas in highly developed countries, and attainment is expected to effectively reduce the health risks.

Besides the guideline values, three interim targets (IT) were defined, which have been shown to be achievable with successive and sustained abatement measures. Countries may find these interim targets helpful in gauging progress over time in the difficult process of steadily reducing population exposures to PM.

As the IT-1 level a mean $PM_{2.5}$ concentration of 35 μg/m^3 was selected. This level is associated with the highest observed values in the studies on long-term health effects and may also reflect higher but unknown historical concentrations that may be responsible for observed health effects. This level has been shown to be associated with significant mortality in the developed world.

The IT-2 interim level of protection is µg/m^3 and places greater emphasis on the studies of long-term exposure associated with mortality. This value is above the mean value observed in these studies at which health effects have been observed, and is likely to be associated with significant impacts from both long-term and daily exposures to PM$_{2.5}$. Attainment of this IT-2 value would reduce risks of long-term exposure by about 6% (95%CI: 2 – 11%) relative to the IT-1 value. The IT-3 level is 15 µg/m^3 and places even greater weight on the likelihood of significant effects related to long-term exposure. This value is close to the mean concentrations observed in studies of long-term exposure and provides an additional 6% reduction in mortality risk relative to IT-2.

Table 3.1 Air quality guideline and interim targets for particulate matter: annual mean (WHO, 2005)

Annual mean level	PM$_{10}$ (µg/m^3)	PM$_{2.5}$ (µg/m^3)	Basis for the selected level
WHO interim target-1 (IT-1)	70	35	These levels are estimated to be associated with about 15% higher long-term mortality than at AQG
WHO interim target-2 (IT-2)	50	25	In addition to other health benefits, these levels lower risk of premature mortality by approximately 6% [2-11%] compared to WHO-IT1
WHO interim target-3 (IT-3)	30	15	In addition to other health benefits, these levels reduce mortality risk by another approximately 6% [2-11%] compared to WHO-IT2 levels
WHO Air quality guidelines (AQG)	**20**	**10**	These are the lowest levels at which total, cardiopulmonary and lung cancer mortality have been shown to increase with more than 95% confidence in response to PM$_{2.5}$ in the ACS study (Pope et al., 2002). The use of PM$_{2.5}$ guideline is preferred

In addition to WHO AQGs and interim targets for PM$_{2.5}$, WHO recommends AQGs and interim targets for PM$_{10}$. This is because coarse PM (the fraction between 10 and 2.5 µm) cannot be considered harmless, and having a PM$_{2.5}$ guideline alone would provide no protection against harmful effects of coarse PM. At the same time, the quantitative evidence on coarse PM is considered insufficient to provide separate

guidelines. In contrast, there is a large literature on short-term effects of PM_{10}, which has been used as a basis for the development of the WHO AQGs and interim targets (Table 3.1).

The 24-hour average values refer to the 99th percentile of the distribution of daily values - that is the 4th next highest value of the year. The frequency distribution of daily $PM_{2.5}$ or PM_{10} values is most often roughly log-normal. Depending on the specific characteristics of their sources and location, countries may find that either the 24-hour guidelines or ITs given in this document, or the annual average values are more restrictive. When evaluating the WHO AQG and interim targets, the annual average is suggested to take precedence over the 24-hour average since, at low levels, there is less concern about remaining episodic excursions. Meeting the guideline values for 24 hour mean should protect against peaks of pollution that would lead to substantial excess morbidity or mortality. It is recommended that countries with areas not meeting these guideline values undertake immediate action to achieve these levels in the shortest possible time.

Table 3.2 Air quality guideline and interim targets for particulate matter: 24-hour mean (WHO, 2005).

24-hour mean level[*]	PM_{10} ($\mu g/m^3$)	$PM_{2.5}$ ($\mu g/m^3$)	Basis for the selected level
WHO interim target-1 (IT-1)	150	75	Based on published risk coefficients from multi-centre studies and meta-analyses (about 5% increase of short-term mortality over AQG)
WHO interim target-2 (IT-2)[*]	100	50	Based on published risk coefficients from multi-centre studies and meta-analyses (about 2.5% increase of short-term mortality over AQG)
WHO interim target-3 (IT-3)[**]	75	37.5	(about 1.2% increase of short-term mortality over AQG)
WHO Air quality guidelines (AQG)	**50**	**25**	Based on relation between 24-hour and annual PM levels

[*]   99th percentile (3 days/year)
[**]   For management purposes, based on annual average guideline values; precise number to be determined on basis of local frequency distribution of daily means

Multi-city studies of 29 cities in Europe (Katsouyanni et al., 2001) and 20 cities in the United States (Samet et al., 2000) reported short-term mortality effects for PM_{10} of 0.62% and 0.46% per 10 μg/m^3, respectively. A meta-analysis of 29 cities from outside Western Europe and North America reported an effect of 0.5% (Cohen et al., 2004). A meta-analysis confined to Asian cities reported an effect of 0.49% (HEI International Oversight Committee, 2004). This suggests that the health risks for PM_{10} are likely to be similar in cities in developed and underdeveloped countries at around 0.5%. Therefore, a concentration of 150 μg/m^3 would relate to roughly a 5% increase in daily mortality, an impact that would be of significant concern, and one for which immediate mitigation actions would be recommended. The IT-2 level of 100 μg/m^3 would be associated with approximately a 2.5% increase in daily mortality. The IT-3 level and AQG for the 24-hour average for PM_{10} are 75 and 50 μg/m^3, respectively and reflect the relationship between 24-hour and annual average discussed above.

In addition to $PM_{2.5}$ and PM_{10}, ultra fine particles (UF) have recently attracted significant scientific and medical attention. These are particles smaller than 0.1 micrometer and are measured as number concentration. While there is considerable toxicological evidence of potential detrimental effects of UF particles on human health, the existing body of epidemiological evidence is insufficient to reach a conclusion on the exposure/response relationship to UF particles. Therefore no recommendations can be provided as to guideline concentrations of UF particles at this point.

CHAPTER 4

EXPERIMENTAL

4.1 SAMPLING

4.1.1 Sampling Site & Selection

In most cases, the sampling site selection criteria are based on EPA guidelines but the criteria are not absolutes because the aim of our sampling is specific. So, in order to achieve our aim of the sampling, the following sampling site selection criteria were formed without staying out of EPA guidelines. The site selection criteria fall into seven categories which are listed below:

(A) Representative sampling: The site must represent traffic related activities. For this purpose, the site must be close to a road or a highway which has high daily traffic congestion.

(B) Distance from nearby emitters: The monitor should be outside the zone of influence of stationary sources located within the designated zone of representation for the monitoring site. By this way, dominant source of sample will be the traffic.

(C) Long-term site commitment: Sampling sites are meant to measure trends as well as compliance, and a long-term commitment from the property owner for continued monitoring is required. Public buildings such as schools, fire stations, police stations, recreation halls, and hospitals often have more stability and a motive for public service than do private or commercial buildings.

(D) Sufficient operating space: A large, flat space, elevated at least 1 m but no more than 14 m above ground level, is needed to place a sampler. The space available for samplers should be at least 5 m distant and upwind (most common wind direction) from building exhaust and intakes and at least 2 m from walls, parapets, or penthouses that might influence air flow. Buildings housing large emitters, such as coal-, waste-, or oil-boilers, furnaces or incinerators, should be avoided.

(E) Access and security: Access to the sampling platform should be controlled by fencing or elevation above ground level. Sampler inlets should be sufficiently distant (> 10 m) from public access to preclude purposeful contamination from reaching them in sufficient quantities to bias samples. Access should be controlled by a locked door, gate, or ladder.

(E) Safety: Wiring, access steps, sampler spacing, and platform railings should comply with all relevant codes and workplace regulations, as well as common sense, to minimize potential for injury to personnel or equipment.

(F) Power: Electrical power should be sufficient for samplers to be operated on a long-term basis, as well as for special study and audit samplers to be located at a site. Where possible, a separate circuit breaker should be provided for each instrument to prevent an electrical malfunction in one monitor from shutting off power to the other monitors at the site.

According to these criteria, for the purpose of achieving "investigation of traffic related inhalable particulate matter in Istanbul" research project, the sampling site was chosen as Yıldız Technical University (41.0307° N, 29.0033° E) which is close to main artery with daily traffic congestion. All mentioned sampling site selection criteria were provided by this selection. The sampling site is faraway 1.15 km from the Bosporus and 6.45 km from the Sea of Marmara. The sampling site is shown in Figure 4.1.

Figure 4.1 The sampling site (see maps.google.com).

4.1.2 Filter Membrane Used in Sampling and Its Properties

Polytetra-Fluoroethylene (PTFE) Teflon membrane filters shown in Figure 4.2 with a 37 mm diameter and 2 μm pore size were used in sampling. PTFE filters are recommended by EPA for gravimetric determination of particulate matter due to low pressure resistance and low concentration values for clean filter. Membrane filters are ideal for low-volume samplers. Clear concentrations, pore sizes, and diameters of these filters are known very well. The disadvantage of Teflon filters is their expensiveness (Karaca, 2005).

Before and after usage, filters are stored in a desiccator at least 24 hours for preventing weight loss due to humidity. By this manner, equal conditions are provided for each filter and errors occurring from humidity are significantly reduced. Each filter was stored in air-proof Petri dishes after gravimetric analysis and labeled.

Figure 4.2 Teflon PTFE filter and rings (The image was taken in our lab).

4.1.3 Dichotomous Sampler

The automatic dichotomous sampler shown in Figure 4.3 was used for $PM_{10-2.5}$ and $PM_{2.5}$ monitoring in this study. The Dichotomous sampler operates at a flow rate of 1 m^3/h (16.7 L/min) and it has an electronic digital programmable timer. First EPA designated "Reference Method" Dicot (RFPS-0789-073). Separate sampling and control modules allow for flexibility in deployment. The weather resistant control module houses the diaphragm vacuum pump, precision flow meters, flow selector valves, vacuum gauges, flow controller, and flow recorder.

The PM_{10} Inlet and 2.5 Virtual Impactor ensures accurate particulate collection. The unique design of the PM_{10} inlet allows only particles smaller than 10 microns to enter the virtual impactor, where they are separated into two size fractions (fine and coarse) and collected on Teflon® membrane filters. The coarse (PM_{10} to 2.5) particle receiver tube has a flow rate of 0.1 m^3/h (1.67 L/min) for collection of the coarse particles while the fine particles, less than 2.5 microns follow a flow of 0.9 m^3/h (15 L/min) to the fine particle filter.

Figure 4.3 The image of Andersen Automatic Dichotomous sampler (Image 1, 2007).

4.1.4 Sampling Method and Period

Before sampling, the Teflon membrane filters were placed into a desiccator at room temperature in open plastic Petri dishes for at least 24 h to reach a constant humidity. Afterwards, they were weighed with a four digit sensitive balance. After weighting, the empty filters were placed into standard polypropylene filter holders and were put together into a dichotomous sampler carousel. The carousel is able to contain 20 fine filter rings and 20 coarse filter rings, totally 40 filter rings. The carousel was then carried to the sampling site in a closed plastic tray to prevent any contamination during transportation.

The carousel containing pre-weighted filters were placed into sampling unit of the sampler which was used to collect two ranges (fine and coarse) of aerosol samples. The sampling flow rate used was 1 m^3 per hour and the sample collection period was 24 h for all collected samples.

After sampling, the filters were transferred to the laboratory. They were placed in the desiccator again for 24 h, and then weighted under exactly the same conditions as the empty filters. For each sample, three repeated weight determinations were performed and the average was reported.

Twenty-four-hour fine ($PM_{2.5}$) and coarse ($PM_{2.5-10}$) particle samples were collected onto 37-mm diameter Teflon PTFE filters on alternate days continuously at Yıldız Technical University Campus by using Dichotomous sampler. Accordingly, 84 daily aerosol samples were collected between 19.10.2006 and 02.07.2007.

4.1.5 Quality Control

Quality control of gravimetric procedures is assured by the inclusion of blank filters during the weighing procedure. Blank samples are treated in an identical manner to samples, but are not exposed in the field. A typical weighing sequence consists of an initial control filter, a sequence of three sample filters, a further control filter, etc. This procedure effectively eliminates the effect of drift resulting from either instrumental

anomalies or other environmental variables and, together with the use of anti-static measures, ensures accurate measurements of particle mass (Jennings et al., 2006).

4.1.6 Calculation of PM Mass Concentrations

The most common measurement provided by the Model 245 is the average over the sampling time, t, of the atmospheric particle mass concentrations C_c and C_f of the coarse and fine particle fractions, respectively or of the total inhalable particle mass concentration C_i. Normally a correction is made for the relatively small mass of fine particles collected on the coarse filter:

$$C_f = \frac{M_f}{Q_f \times t} \tag{5.1}$$

$$C_c = \frac{[M_c - (C_f \times Q_c \times t)]}{Q_t \times t} \tag{5.2}$$

$$C_i = C_f + C_c = \frac{M_f + M_c}{Q_t \times t} \tag{5.3}$$

Where;

M_f = the particulate mass on the fine-particle filter (µg)

M_c = the particulate mass on the coarse-particle filter (µg)

t = the sampling time (hours)

Q_f = fine particle flowrate (m^3/hr)

Q_c = coarse particle flowrate (m^3/hr)

Q_t = total flowrate (m^3/hr)

Inserting the operating values of flowrates of 0.1, 0.9, and 1.0 m³/hr for Q*c*, Q*f*, and Q*t*, respectively, in the equations 5.1, 5.2, and 5.3, we calculate the concentrations as:

$$Cf = \frac{1.11 \times Mf}{t}$$ (5.4)

$$Cc = \frac{[Mc - (0.111 \times Mf)]}{t}$$ (5.5)

$$Cl = \frac{Mf + Mc}{t}$$ (5.6)

4.1.7 Method Detection Limit (MDL)

Method detection limit (MDL) is described as the minimum concentration of a substance that can be measured and reported with 99-percent confidence that the analyte concentration is greater than zero. Additional steps in an analysis may add additional error to method. Since detection limits are defined in terms of error, this will naturally increase the measured detection limit. This detection limit (with all steps of the analysis included) is called the MDL. The practical method for determining the MDL is to analyze 7 samples of concentration near the expected limit of detection. The standard deviation is then determined. The one-sided t distribution is determined and multiplied versus the determined standard deviation (Berthouex and Brown, 2002). MDL value of this study was calculated as 2.31 µg/m³.

4.2 DATA COLLECTION

4.2.1 Criteria Air Pollutants

Hourly concentrations of criteria air pollutants such as CO, SO_2, NO, NO_2, NO_x, and TSP were colleted by the continuous air quality monitoring station at Yıldız

Technical University. This station belongs to Environmental Protection & Control Directorship of Istanbul Metropolitan Municipality. The data obtained from this station belongs to time period from October 2006 to June 2007. Analysis method used by Environmental Protection & Control Directorship in order to measure each mentioned criteria air pollutant are given in Table 4.1.

Table 4.1 Criteria air pollutants and their analysis methods (IMM, 2007).

Parameter	Analysis Method
CO	Chemiluminescence Method (Model AC 31M, Automatic Analyser)
SO_2	UV Fluorescence Method (Model AF 21M, Automatic Analyser)
NO_x	IR Absorption Method (Model CO 11M, Automatic Analyser)
TSP	Beta Gauge Method (Model MP 101M, Automatic Analyser)

4.2.2 Traffic Data

Hourly traffic data such as traffic count and traffic flow between October 2006 and June 2007 were taken from Traffic Control Center of the Istanbul Metropolitan Municipality by official petition. The traffic data in Istanbul are measured by special sensors and detectors located on designated points of traffic network. Traffic counts and traffic flow data are measured automatically by non-invasive detectors and this measured data are transmitted to the Traffic Control Center with the help of wireless communication between detectors and the Traffic Control Center. The closest sensor to our sampling area was on the Yıldız connection (sensor number is 25) to the 1st Bridge; moreover, it is the only sensor which can give the accurate traffic data within the sampling area. So, traffic data of the sensor on the Yıldız connection was taken from the Traffic Control Center for this study. The image representing the related sensor is shown in Figure 4.4
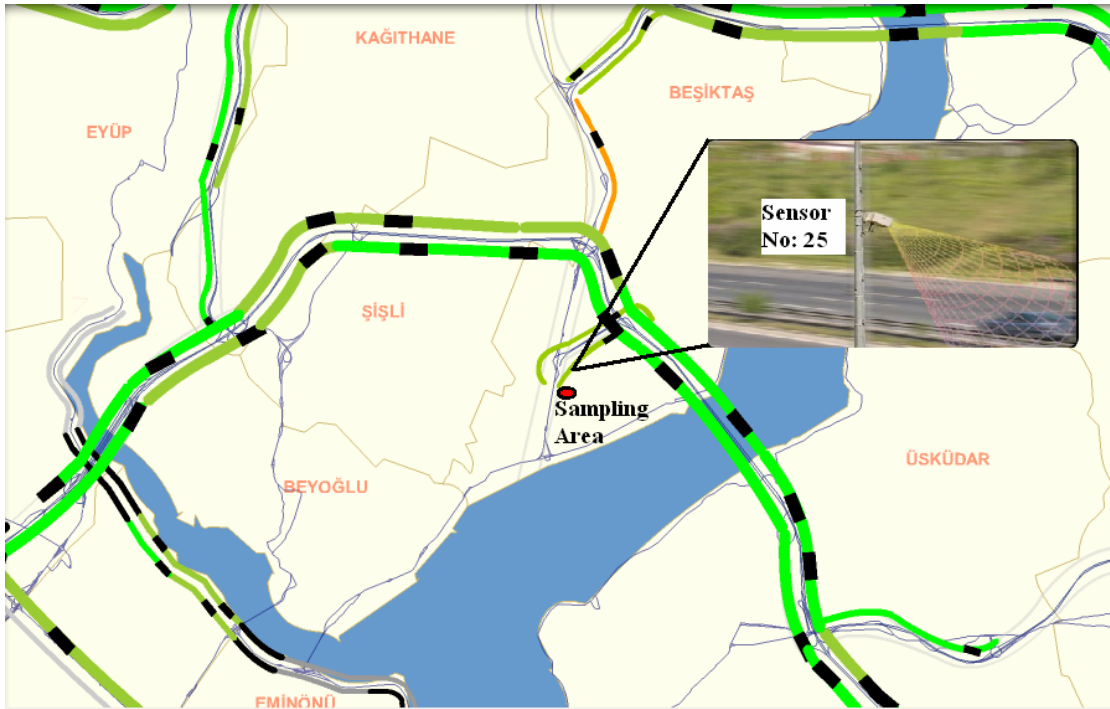
Figure 4.4 Location of the selected sensor for traffic data (see http://tkm.ibb.gov.tr/)

4.2.3 Meteorological Data

Hourly meteorological parameters such as temperature, pressure, humidity, wind direction, wind speed, and rain, between October 2006 and June 2007, were taken from Republic of Turkey Ministry of Environment and Forest's Turkish State Meteorological Service. Meteorological data was also obtained by official petition. The closest weather station to our sampling area is located on the Sarıyer-Kireçburnu area and the station number is 17061. The type of the station is a synoptic station, which provides working remotely and much more parameters than regular weather stations. The purpose behind the selection of this station was that it would represent the meteorological characteristics of the sampling area.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 MEASURED AND COLLECTED PARAMETERS

5.1.1 Mass Concentrations of $PM_{2.5}$, $PM_{10-2.5}$, and PM_{10}

During this study, 84 daily fine and coarse samples were collected between 19.10.2006 and 02.07.2007. As a result of $PM_{2.5}$, $PM_{10-2.5}$, and PM_{10} mass concentrations, average concentrations of all collected $PM_{2.5}$, $PM_{10-2.5}$, and PM_{10} samples are 8.45 $\mu g/m^3$, 23.88 $\mu g/m^3$, and 32.34 $\mu g/m^3$, respectively. The highest monthly averages of $PM_{2.5}$, $PM_{10-2.5}$, and PM_{10} are 10.08 $\mu g/m^3$, 30.29 $\mu g/m^3$, and 39.88 $\mu g/m^3$ which were seen on January 2006, October 2007, and October 2006, respectively. Annual and daily mean of PM limit values according to Environmental Protection Agency (EPA), World Health Organization (WHO), European Union (EU), and Regulation of Air Pollution Control (HKKY-in Turkey) are given in Table 5.1

Table 5.1 International and national PM limit values.

PM type	Average Time	PM Limit Values ($\mu g/m^3$)			
		EPA	WHO	EU	HKKY
PM_{10}	24-hour	150	50	50	300
	Annual	50	20	40	150
$PM_{2.5}$	24-hour	35	25	---	---
	Annual	15	10	---	---

Daily PM_{10} and $PM_{2.5}$ concentrations have exceeded WHO and EU limit values for 9 days and WHO limit value for 1 day, respectively. Both PM_{10} and $PM_{2.5}$ concentrations were higher than daily WHO limits on only one day, namely 27.02.2007. Time series of PM concentration results are given in Figure 5.1 where the episodic events can be seen for both PM_{10} and $PM_{2.5}$ daily concentrations.
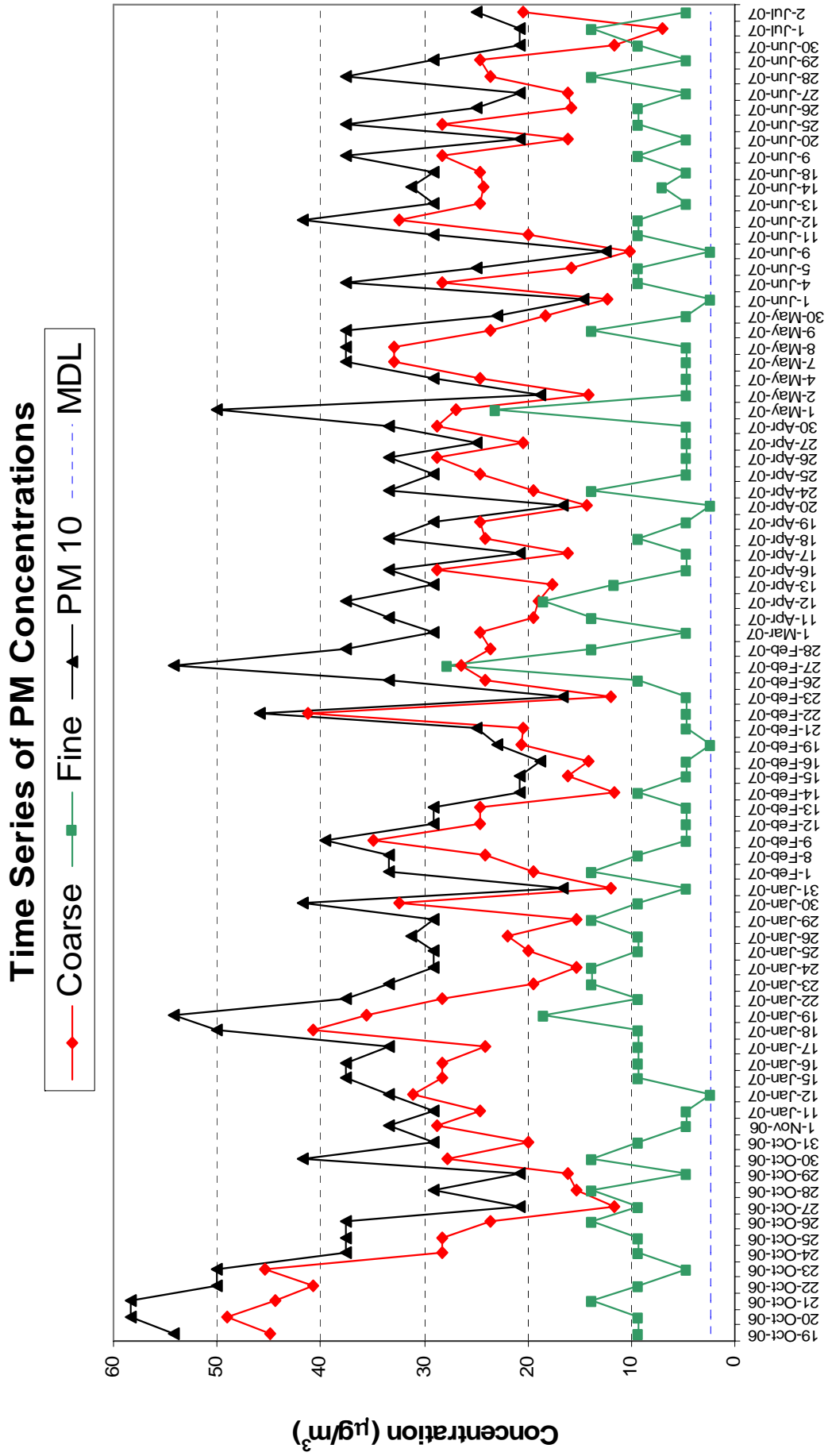
Figure 5.1 Particulate matter concentrations of all collected samples.

5.1.2 Concentrations of Criteria Air Pollutants

Hourly concentrations of criteria air pollutants such as CO, SO$_2$, NO, NO$_2$, NO$_x$, and TSP were colleted by the Istanbul Metropolitan Municipality at Yıldız Technical University. Period of taken concentrations is from October 2006 to June 2007.

5.1.2.1 Total Suspended Particulates (TSP)

There is no international or national limit value for TSPs due to less detrimental health effects on humans than PM$_{2.5}$ and PM$_{10}$. TSP monitoring is used to determine the total amount of SPM present in the atmosphere. TSP samples are currently used for lead determinations.

Eight TSP episodes (75th percentile) between October 2006 and June 2007 were seen on 16.12.06 3:00, 8.12.06 22:00, 5.10.06 6:00, 5.10.06 7:00, 19.12.06 22:00, 8.12.06 23:00, 5.10.06 8:00, and 5.10.06 9:00. Threshold value for 75th percentile is 300 µg/m^3 and episode concentrations are 307, 314, 321, 327, 349, 371, 375, and 457 µg/m^3, respectively. Daily variations of TSP concentrations are shown in Figure 5.2.

5.1.2.2 Carbon Monoxide (CO)

Daily, 8-hour, and 1-hour means of PM limit values according to EPA, WHO, EU, and HKKY are shown in Table 5.2. Figure 5.3 shows all collected daily CO concentrations. WHO 1-hour limit value was exceeded 75 times and also EPA 1-hour limit value was exceeded 16 times by measured CO concentrations during sampling period. This situation exactly means that CO concentrations of 16 hourly measurements exceeding international limit values were not suitable for public health at Yıldız area.

Table 5.2 International and national CO limit values.

Average Time	CO limit values (mg/m^3)			
	EPA	WHO	EU	HKKY
24-hour	---	---	---	30 (10, Annual)
8-hour	10	10	10	---
1-hour	40	30	---	---

Time Series of TSP (Oct 06-June 07)
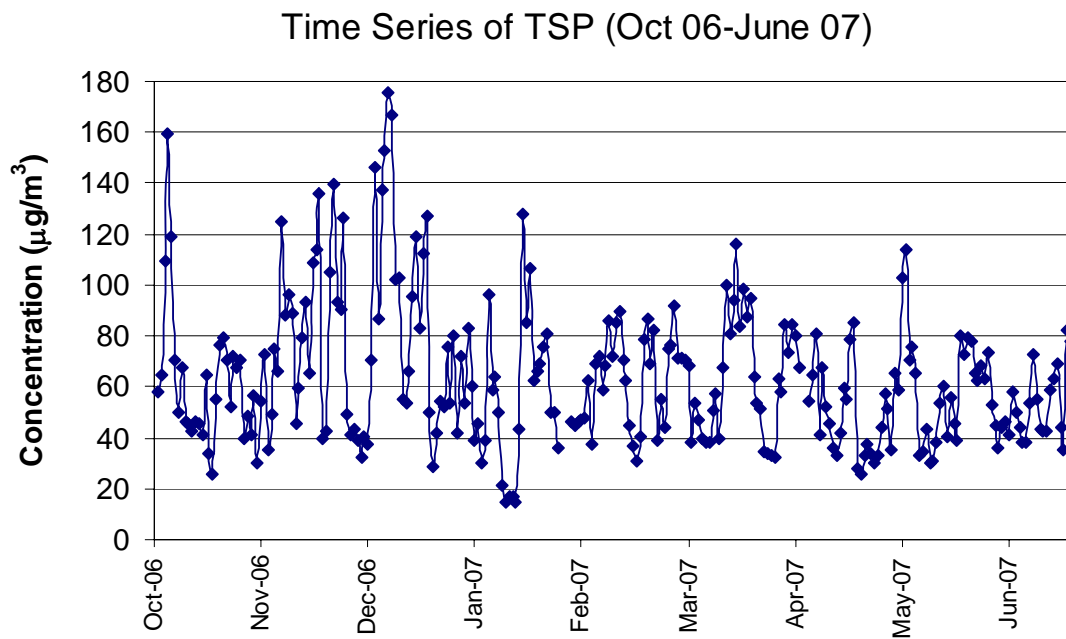
Figure 5.2 Daily variations of TSP concentrations.

Time Series of CO (Oct 06-June 07)
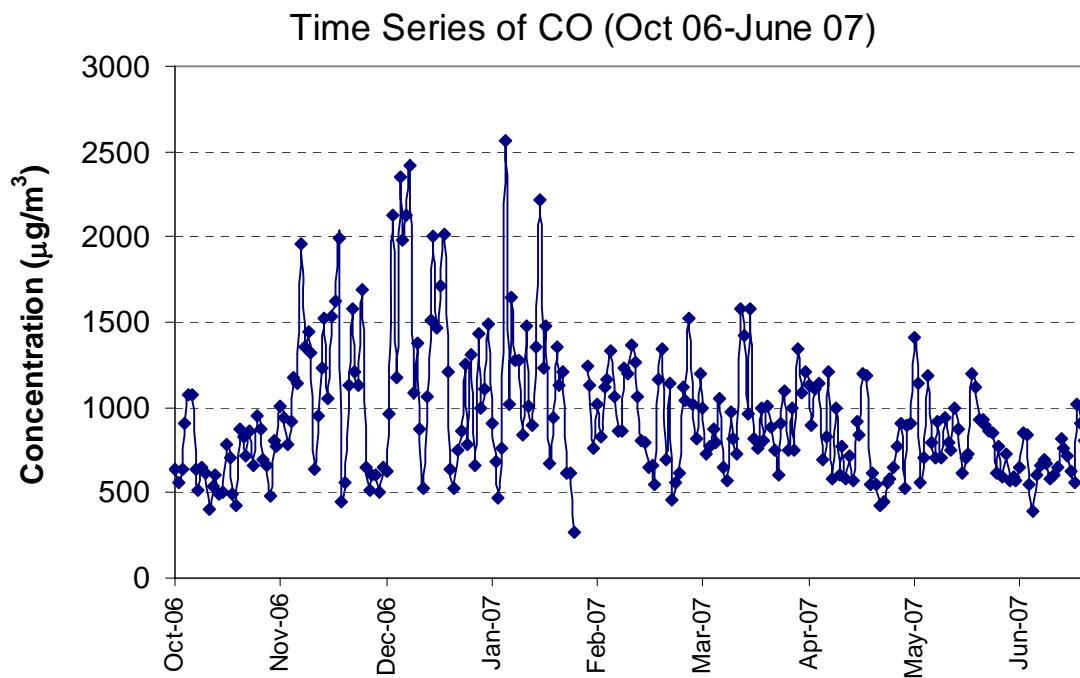
Figure 5.3 Daily variations of CO concentrations.

5.1.2.3 Sulfur Dioxide (SO₂)

Annual and daily means of SO_2 limit values according to EPA, WHO, EU, and HKKY are shown in Table 5.3. Time series of SO_2 concentrations are given in Figure 5.4.

Table 5.3 International and national SO_2 limit values.

Average Time	SO_2 limit values ($\mu g/m^3$)			
	EPA	**WHO**	**EU**	**HKKY**
Annual	80	50	---	150
24-hour	365	125	125	400
3-hour	1300	---	---	---

All SO_2 concentrations are lower than 24-hour limit values of WHO, EPA, EU, and HKKY. Hourly threshold value for 75th percentile is 150 $\mu g/m^3$. Three SO_2 episodes (75th percentile) were seen on 24.11.06 13:00, 10.5.07 15:00, and 23.6.07 19:00. Episode concentrations are 429, 172, and 185 $\mu g/m^3$, respectively.

5.1.2.4 Nitrogen Dioxide (NO₂)

NO_2 limit values according to EPA, WHO, EU, and HKKY are shown in Table 5.4. Figure 5.5 shows all measured daily NO_2 concentrations.

Table 5.4 International and national NO_2 limit values.

Average Time	NO_2 limit values ($\mu g/m^3$)			
	EPA	**WHO**	**EU**	**HKKY**
Annual	100	40	40	100
24-hour	---	---		300
1-hour	---	200	200	---

Threshold value for 75th percentile is 200 $\mu g/m^3$. Seven NO_2 episodes (75th percentile) between October 2006 and June 2007 were seen on 10.3.07 11:00, 10.5.07 17:00, 22.1.07 19:00, 22.1.07 18:00, 28.12.06 8:00, 18.1.07 19:00, and 8.1.07 18:00. Episode concentrations are 320, 256, 242, 235, 213, 207, and 200 $\mu g/m^3$, respectively. These values are higher than 1-hour limit values of WHO and EU.
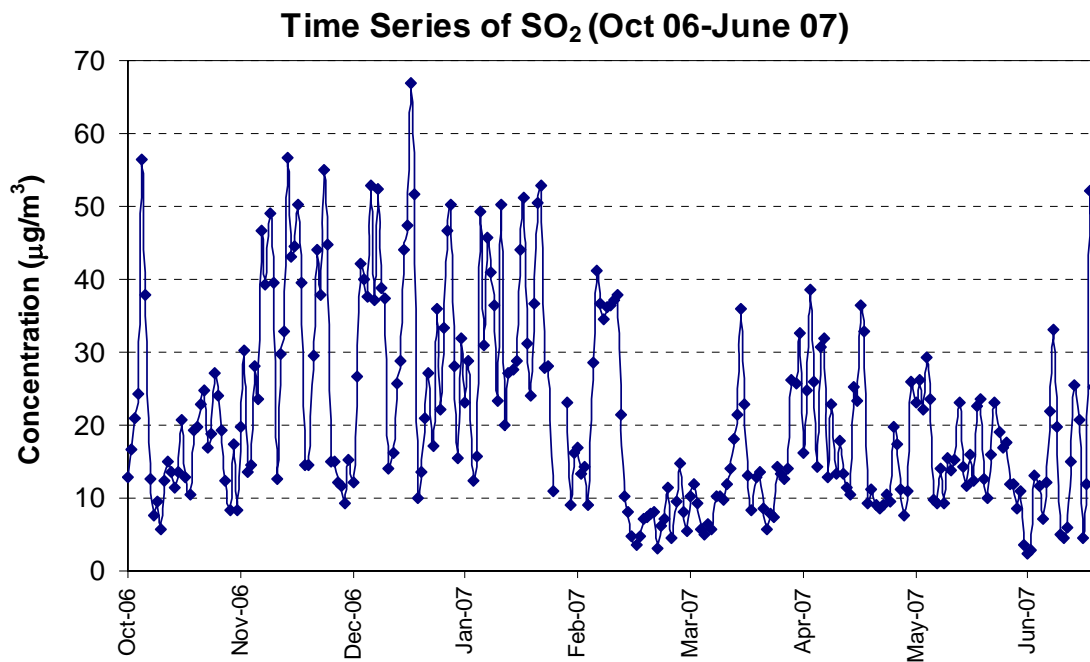
Figure 5.4 Time series of SO$_2$ concentrations.
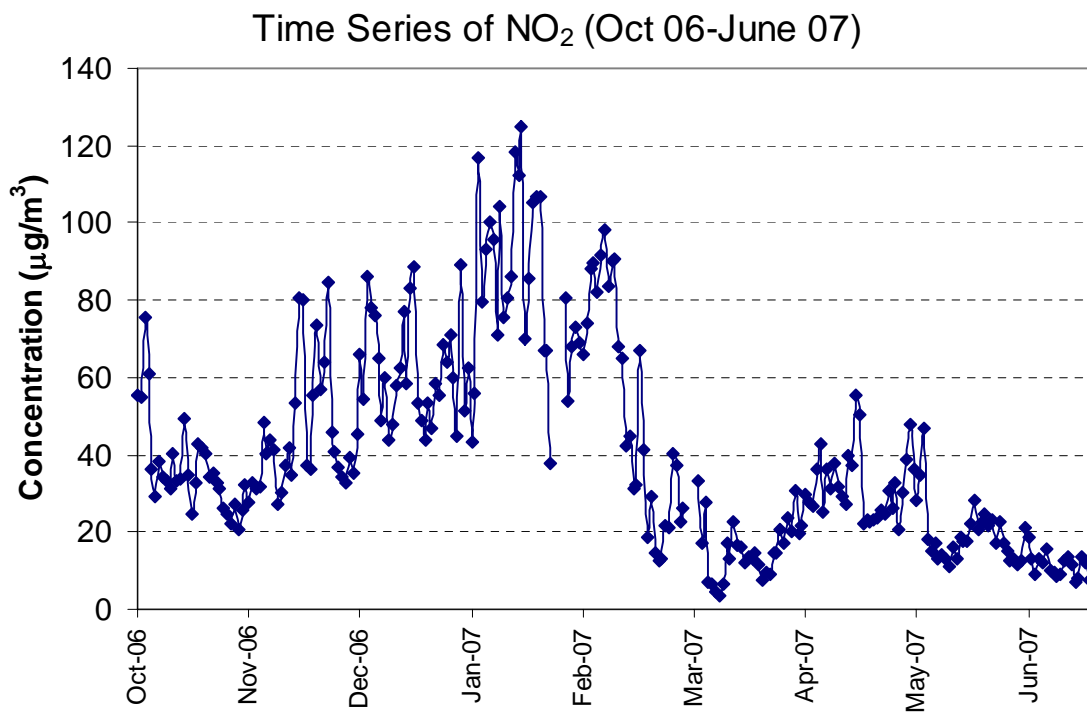
Figure 5.5 Measured daily NO$_2$ concentrations.

5.1.2.5 Nitrogen Oxide (NO) and Nitrous Oxide (NO$_x$)

Seven NO episodes (75th percentile) between October 2006 and June 2007 were observed on the following days: 28.12.06 8:00, 18.3.07 1:00, 18.3.07 2:00, 18.3.07 0:00, 18.3.07 3:00, 6.5.07 10:00, and 17.3.07 23:00. Their corresponding NO concentrations (300 µg/m^3 is threshold value) are 550, 353, 345, 338, 314, 308, and 303 µg/m^3, respectively. Daily variations of NO concentrations are shown in Figure 5.6.

On the other hand, six NO$_x$ episodes (75th percentile) between October 2006 and June 2007 were seen on 10.3.07 11:00, 6.12.06 10:00, 22.1.07 19:00, 22.1.07 18:00, 8.1.07 18:00, and 7.3.07 19:00. Episode concentrations (400 µg/m^3 is threshold value) are 573, 456, 426, 424, 416, and 416 µg/m^3, respectively. Figure 5.7 shows all measured daily NO$_x$ concentrations.

There is no international or national limit value for NO and NO$_x$ because they are secondary air quality standards. NO$_2$ shows an increasing trend during wintertime reaching its maximum in January then decreases to reach its minimum during summer. On the contrary, NO concentration has its lowest values during wintertime and reaches its maximum in summer. The reason for decreasing of NO$_2$ could be attributed to the photochemical oxidation of NO$_2$ to form PAN during summer.

Monthly variations in concentrations of all measured air pollutants are given in Figure 5.8. According to this figure, CO, NO$_x$, NO$_2$, TSP, and SO$_2$ have their higher values on fall and winter seasons. This increasing trend is normal because in heating seasons such as fall and winter, extra emissions coming from heating activities increases the concentrations of air pollutants at ambient atmosphere. In other words, the addition of combustion products of fossil fuels to car emission increases the levels of CO, NO$_x$, NO$_2$, TSP, and SO$_2$ on fall and winter seasons. On the other hand, NO has its higher values on spring and summer seasons.
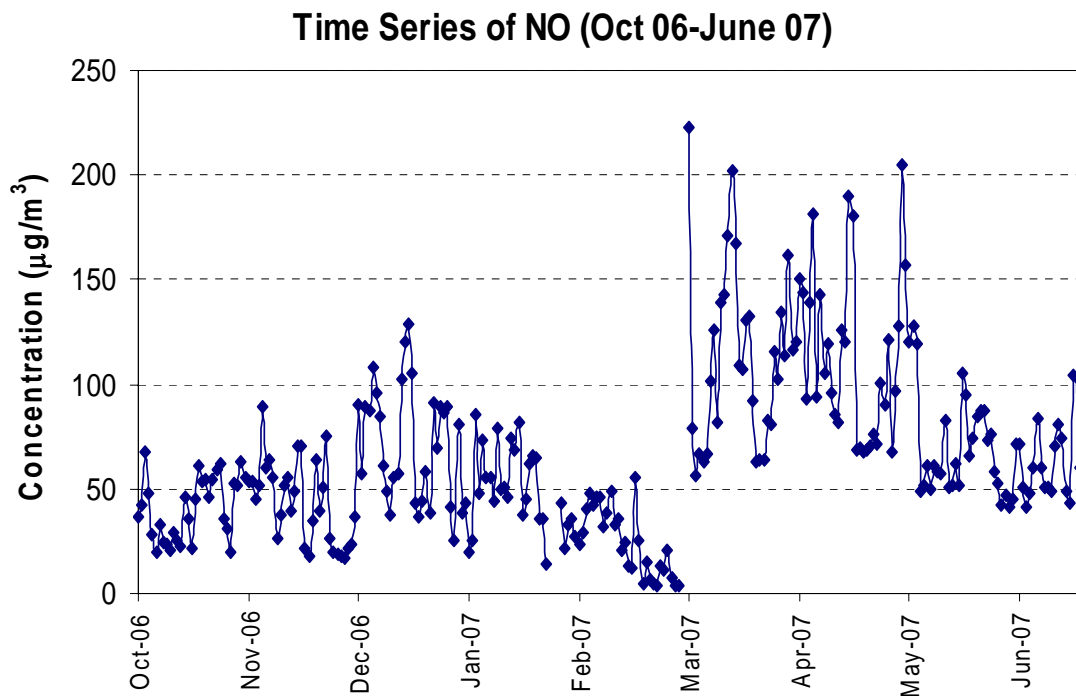
Figure 5.6 Daily variations of NO concentrations.
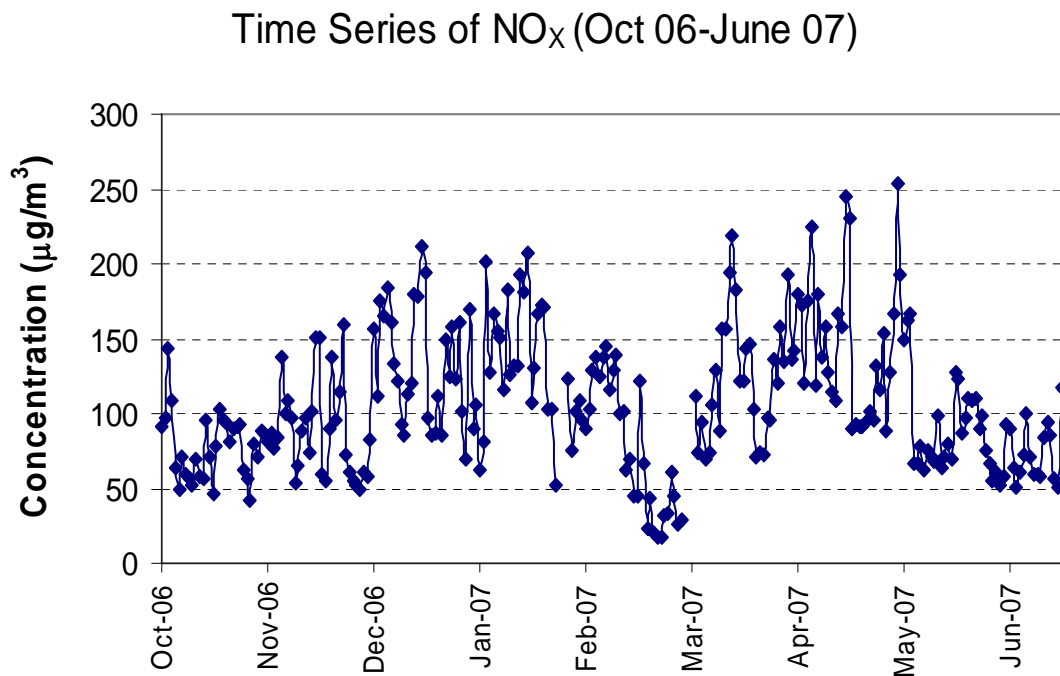
Figure 5.7 Measured daily NO_x concentrations.
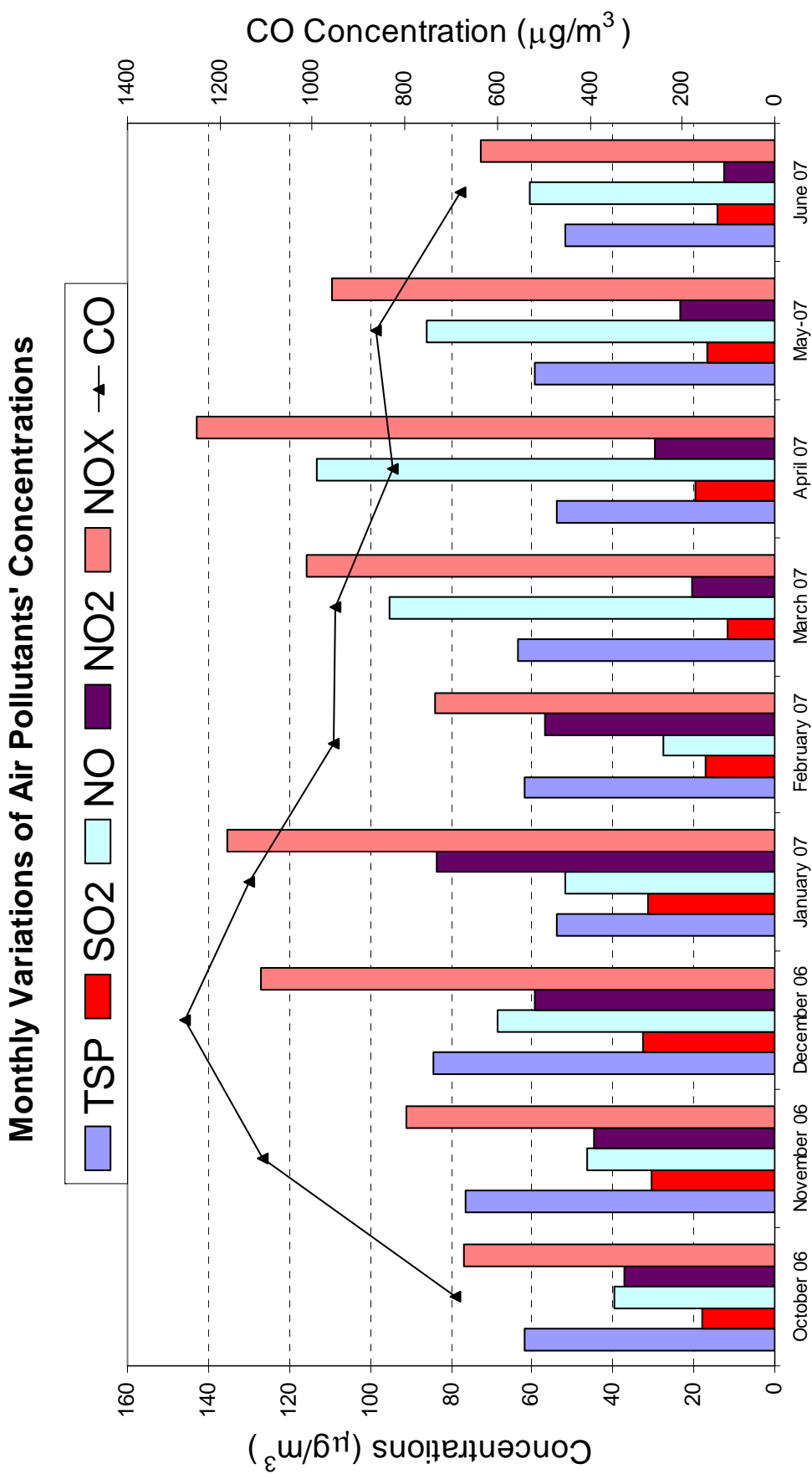
Figure 5.8 Monthly changes in air pollutants' concentrations.

5.1.3 Meteorological Parameters

Hourly meteorological parameters such as temperature, pressure, humidity, wind direction, wind speed, and rain, between October 2006 and June 2007, were taken from Republic of Turkey Ministry of Environment and Forest's Turkish State Meteorological Service. Monthly variations of temperature, pressure, and humidity are shown in Figure 5.9. According to this figure, humidity has its lowest values on November and December 2006. Pressure has its maximum on December 2006 and minimum on January 2007. Changes in temperature for seasons are not far from normality.
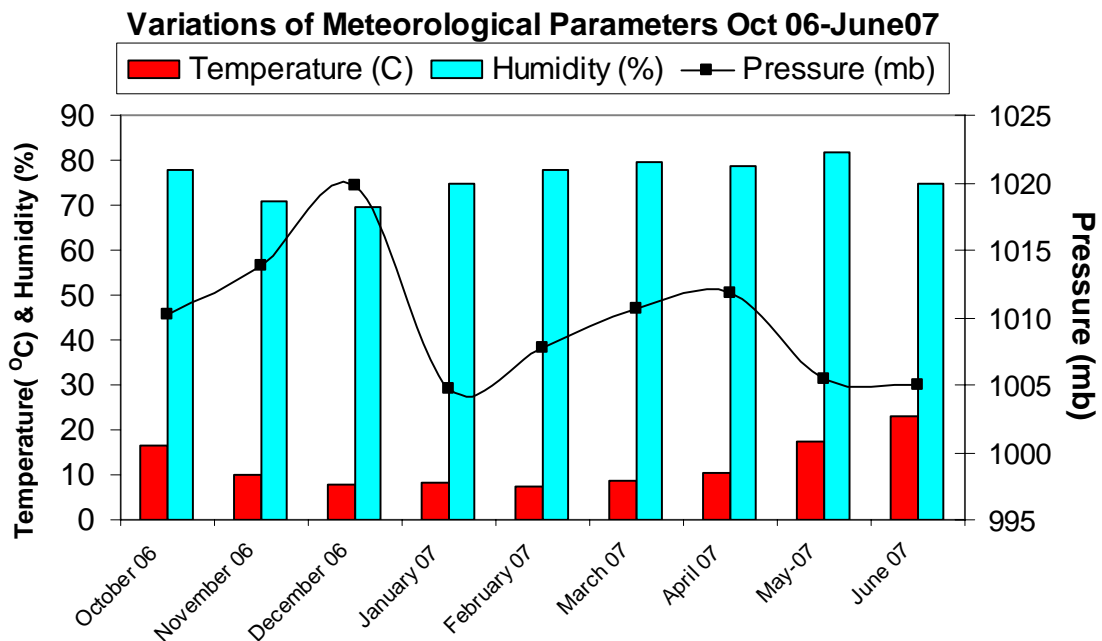
Figure 5.9 Monthly variations of temperature, pressure, and humidity.

Time series of wind speed during sampling period is shown in Figure 5.10. As it's seen on the figure, higher wind speeds were seen between October 2006 and February 2007.

The dominant wind direction can be inferred from percentage distribution of wind direction shown in Figure 5.11. According to this figure, the dominant wind directions during sampling period were SSW and SW.
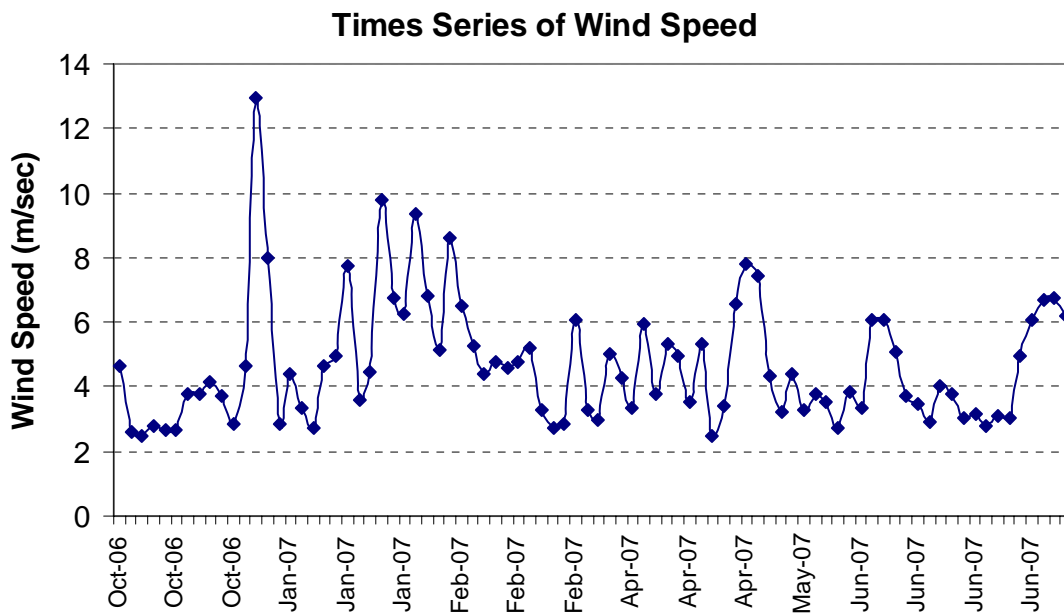
Figure 5.10 Time series of wind speed during sampling period.
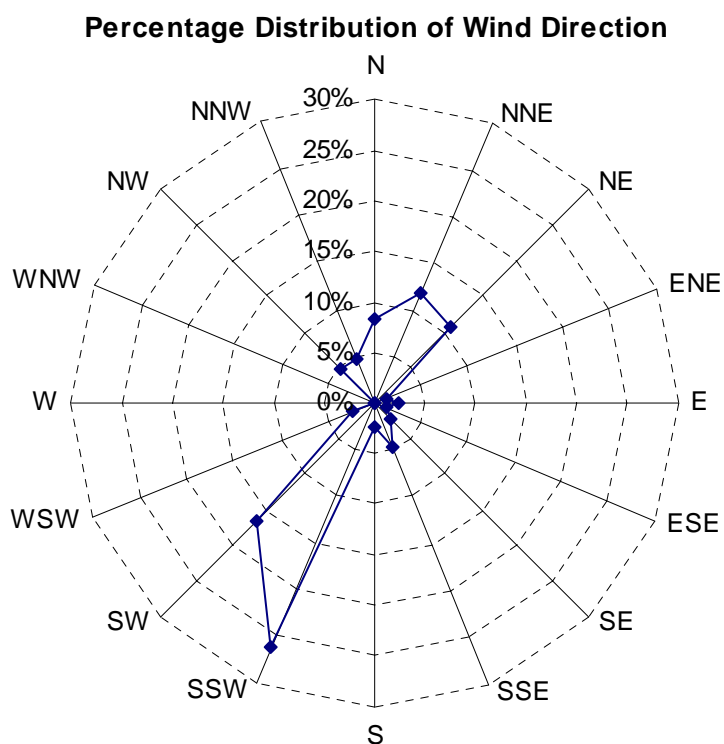
Figure 5.11 Percentage distribution of wind direction during sampling period.

Average and episode $PM_{2.5}$, $PM_{10-2.5}$, and PM_{10} mass concentrations with respect to wind direction are given in Figure 5.12, 5.13, 5.14, and 5.15. As it's comprehended from these figures, high $PM_{2.5}$, $PM_{10-2.5}$, and PM_{10} concentrations come from WSW, SW, SSW, and NNW directions. Cause of this conclusion can strongly be traffic congestion because traffic flows at these directions with respect to Dichotomous sampler, which means wind transfers air pollutants and particulate matters emitted by cars from road to the sampler.
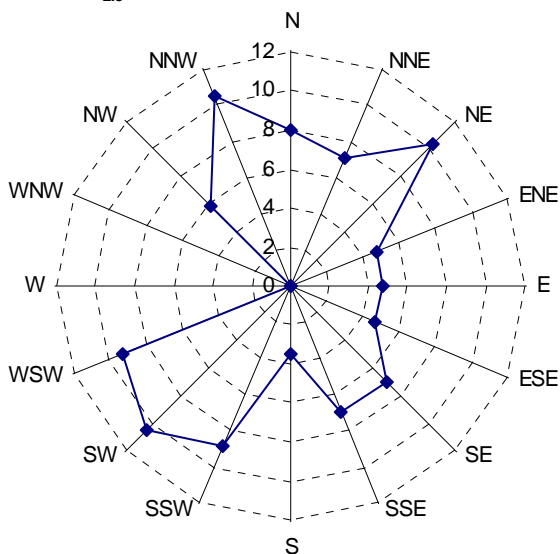
Figure 5.12 $PM_{2.5}$ concentrations related to wind direction during sampling period.

Figure 5.13 $PM_{10-2.5}$ concentrations related to wind direction during sampling period.

Overall PM$_{10}$ concentrations related to Wind Direction
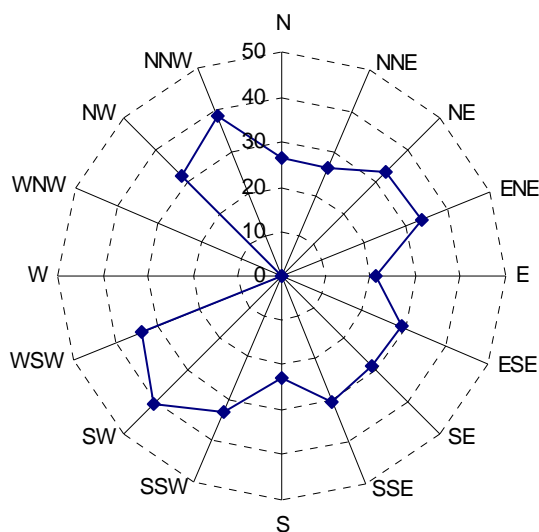
Figure 5.14 PM$_{10}$ concentrations related to wind direction during sampling period.

PM episodes related to Wind Direction
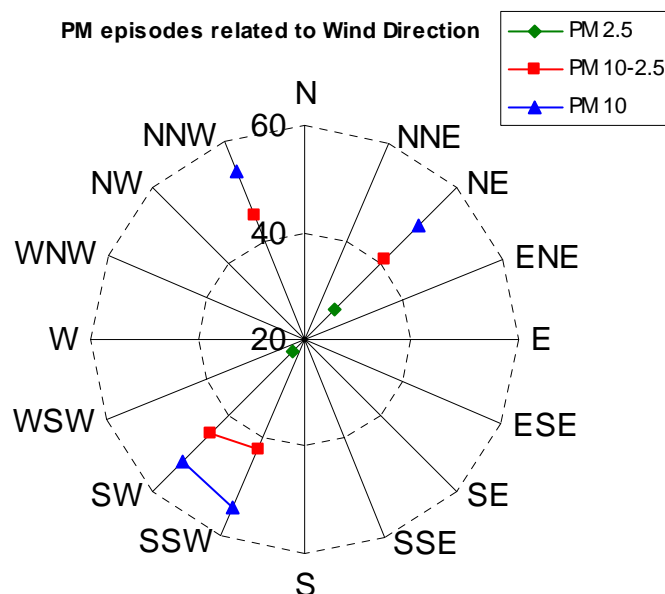
Figure 5.15 Episodes of PM$_{2.5}$, PM$_{10-2.5}$, and PM$_{10}$ concentrations related to wind direction during sampling period.

Time series of total daily rain during sampling period are given in Figure 5.16. The highest amount of rain was seen on October 2006. May 2007 has maximum amount of daily rain as 12.4 mm/day. The poorest month about total rain is June 2007. This may be result of high temperature trend in summer 2007.

Time Series of Total Daily Rain (Oct 06-June 07)
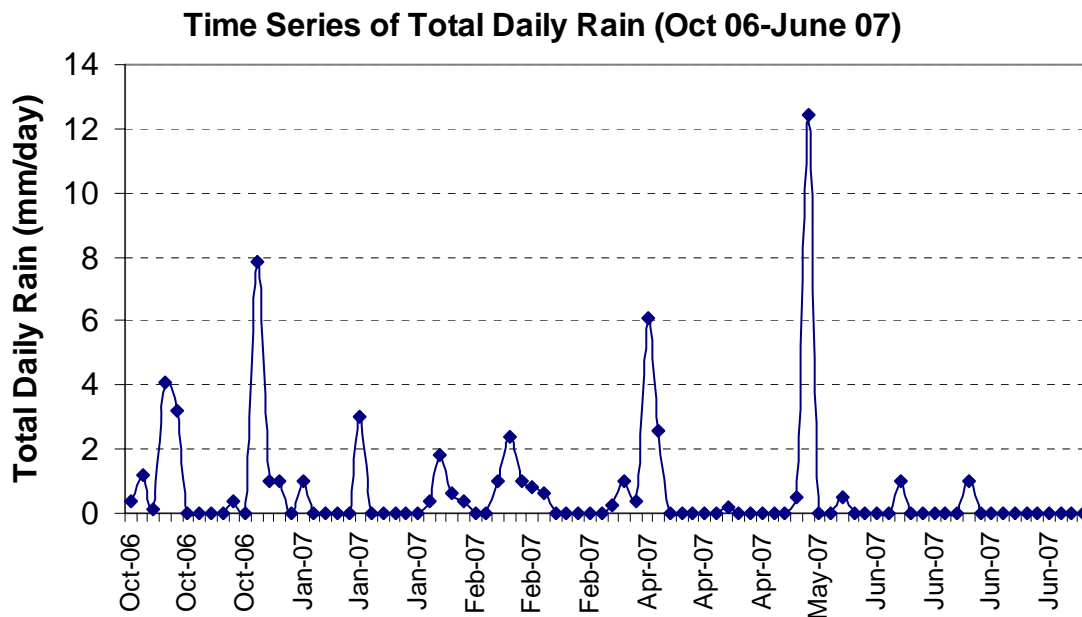
Figure 5.16 Time series of total daily rain during sampling period.

Time Series of Traffic Count & Traffic Flow During Sampling
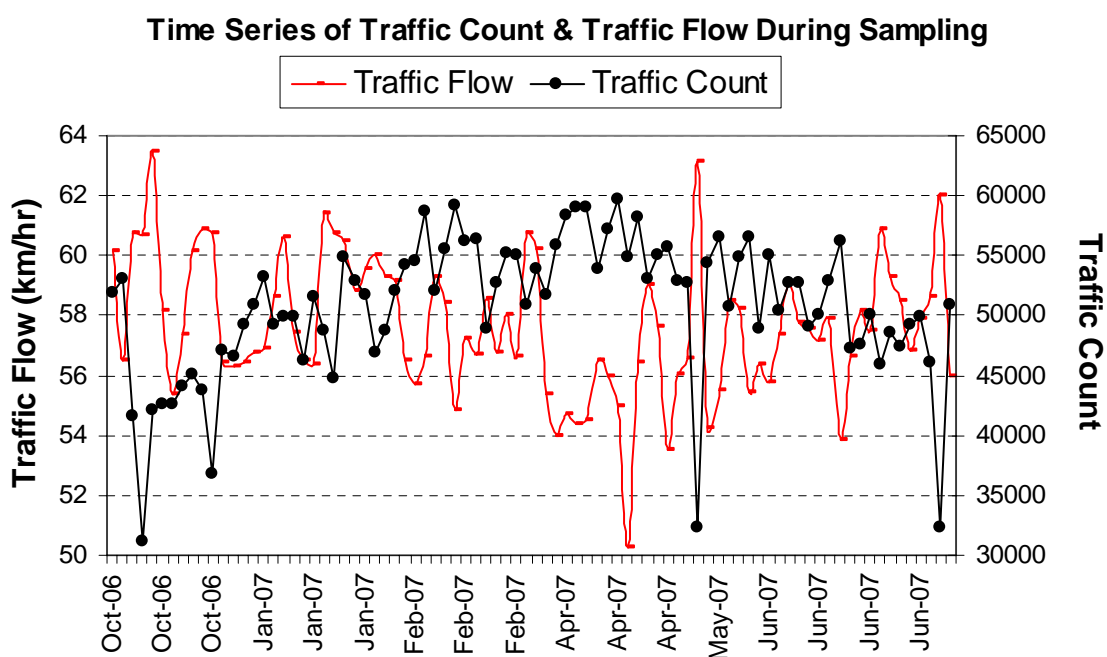
Figure 5.17 Traffic count and traffic flow during sampling period in time series.

5.1.4 Traffic Data

Time series of traffic count and traffic flow during sampling period at Yıldız are given in Figure 5.17. As it's seen from the figure, there is an inverse relationship

between traffic count and traffic flow. This situation is the result of traffic congestion because the number of vehicles per lane is generally high when the average velocity of vehicles on the same lane is low during congested traffic. This information gives an opportunity to estimate the traffic congestion level on designated days.

5.2 STATISTICAL ANALYSIS

5.2.1 Descriptive Statistics

Giving brief explanations of used statistical parameters may be useful for this section. These explanations were taken from help section of the SPSS 15 software package.

Mean: A measure of central tendency. The arithmetic average, the sum divided by the number of cases.

Geometric Mean: The nth root of the product of the data values, where n represents the number of cases. Geometric mean is more representative if the distribution of a data set is not normal (Karaca et al., 2005).

Standard Deviation: A measure of dispersion around the mean. In a normal distribution, 68% of cases fall within one standard deviation of the mean and 95% of cases fall within two standard deviations. For example, if the mean age is 45, with a standard deviation of 10, 95% of the cases would be between 25 and 65 in a normal distribution.

Skewness: A measure of the asymmetry of a distribution. The normal distribution is symmetric and has a skewness value of 0. A distribution with a significant positive skewness has a long right tail. A distribution with a significant negative skewness has a long left tail. As a guideline, a skewness value more than twice its standard error is taken to indicate a departure from symmetry.

Standard Error of Skewness: The ratio of skewness to its standard error can be used as a test of normality (that is, you can reject normality if the ratio is less than -2 or greater than +2). A large positive value for skewness indicates a long right tail; an extreme negative value indicates a long left tail.

Kurtosis: A measure of the extent to which observations cluster around a central point. For a normal distribution, the value of the kurtosis statistic is zero. Positive kurtosis

indicates that the observations cluster more and have longer tails than those in the normal distribution, and negative kurtosis indicates that the observations cluster less and have shorter tails.

Standard Error of Kurtosis: The ratio of kurtosis to its standard error can be used as a test of normality (that is, you can reject normality if the ratio is less than -2 or greater than +2). A large positive value for kurtosis indicates that the tails of the distribution are longer than those of a normal distribution; a negative value for kurtosis indicates shorter tails (becoming like those of a box-shaped uniform distribution).

General statistical evaluation was performed for all variables. SPSS 15.0 software package was used for statistical analysis. Minimum, maximum, geometric mean, mean, standard deviation, skewness, and kurtosis of all variables are shown in Table 5.5.

In inserting wind data to descriptive statistics, each wind direction was numbered. Wind direction and number matches are; 1: N, 2: NNE, 3: NE, 4: ENE, 5: E, 6: ESE, 7: SE, 8: SSE, 9: S, 10: SSW, 11: SW, 12: WSW, 13: W, 14: WNW, 15: NW, 16: NNW.

Table 5.5 Descriptive statistics of variables.

Statistics Summary						
Variables	Minimum	Maximum	Geometric Mean	Mean ± Std	Skewness ± S.E.	Kurtosis ± S.E.
Coarse Particles ($\mu g/m^3$)	6.90	49.10	22.33	23.87 ± 8.70	0.730 ± 0.263	0.578 ± 0.52
Fine Particles ($\mu g/m^3$)	2.31	27.75	7.28	8.45 ± 4.77	1.332 ± 0.263	2.691 ± 0.52
PM_{10} ($\mu g/m^3$)	12.50	58.33	30.77	32.34 ± 10.16	0.563 ± 0.263	0.229 ± 0.52
TSP ($\mu g/m^3$)	14	128	55	60 ± 22	0.669 ± 0.263	0.581 ± 0.52
SO_2 ($\mu g/m^3$)	4	53	17	21 ± 12	1.018 ± 0.263	0.508 ± 0.52
CO ($\mu g/m^3$)	273	2,216	790	840 ± 311	1.406 ± 0.263	3.554 ± 0.52
NO ($\mu g/m^3$)	4	182	51	62 ± 35	0.944 ± 0.263	1.132 ± 0.52
NO_2 ($\mu g/m^3$)	3	125	30	40 ± 30	1.193 ± 0.263	0.578 ± 0.52
NO_X ($\mu g/m^3$)	17	225	91	101 ± 45	0.591 ± 0.263	0.008 ± 0.52
Traffic Count	31,083	59,616	50,322	50,705 ± 5,882	-1.243 ± 0.263	2.186 ± 0.52
Traffic Flow (km/hr)	50	63	58	58 ± 2	-0.064 ± 0.263	0.383 ± 0.52
Wind Direction (1-16)	1	16	6	8 ± 4	-0.137 ± 0.263	-1.086 ± 0.52
Wind Speed (m/sec)	2.45	12.93	4.35	4.67 ± 1.92	1.564 ± 0.263	3.456 ± 0.52
Temperature (°C)	3.5	30.7	12.7	14.2 ± 6.6	0.621 ± 0.263	-0.422 ± 0.52
Pressure (mb)	995.6	1016.5	1007.3	1007.3 ± 5.3	-0.296 ± 0.263	-0.563 ± 0.52
Humidity (%)	43	100	74	76 ± 13	-0.545 ± 0.263	-0.459 ± 0.52
Total Daily Rain (mm/day)	0.00	12.40	0.01	0.69 ± 1.82	4.454 ± 0.263	23.180 ± 0.52

According to summary statistics, it can be said that all variables except total daily rain almost fit to normal distribution because their skewness and kurtosis values are very close to zero. Fine particles, CO, traffic count, and wind speed slightly leaves from normality because their kurtosises are greater than 2.1. Very simple normality tests were done for all variables. The test consists of 2 steps which are checking the ratio of skewness to its standard error and checking the ratio of kurtosis to its standard error. In both cases, normality may be rejected if the ratio is less than -2 or greater than +2. The ratio of skewness to its standard error and the ratio of kurtosis to its standard error were calculated and represented in Table 5.6.

Table 5.6 Simple test of normality.

Test of Normality		
Variables	**Skewness/S.E.**	**Kurtosis/S.E.**
Coarse Particles ($\mu g/m^3$)	2.78	1.11
Fine Particles ($\mu g/m^3$)	**5.06**	**5.18**
PM_{10} ($\mu g/m^3$)	2.14	0.44
TSP ($\mu g/m^3$)	2.54	1.12
SO_2 ($\mu g/m^3$)	3.87	0.98
CO ($\mu g/m3$)	**5.35**	**6.83**
NO ($\mu g/m^3$)	**3.59**	**2.18**
NO_2 ($\mu g/m^3$)	4.53	1.11
NO_X ($\mu g/m^3$)	2.25	0.02
Traffic Count	**-4.73**	**4.20**
Traffic Flow (km/hr)	-0.24	0.74
Wind Direction (1-16)	-0.52	-2.09
Wind Speed (m/sec)	**5.94**	**6.65**
Temperature (°C)	2.36	-0.81
Pressure (mb)	-1.13	-1.08
Humidity (%)	-2.07	-0.88
Total Daily Rain (mm)	**16.93**	**44.58**

Both the ratio of skewness to its standard error and the ratio of kurtosis to its standard error for fine particles, CO, NO, traffic count, and wind speed are greater than 2 or less than -2, which may mean that they are leaving normality. But it's clearly seen that total daily rain does not fit to normal distribution. In order to be sure that if variables fit to normal distribution or not, some statistical tests were done in the next section.

5.2.2 Distribution of Variables

In order to find out distributions of all variables, a non-parametric test, One-Sample Kolmogorov-Smirnov Test, was applied to variables. The One-Sample Kolmogorov-Smirnov Test procedure compares the observed cumulative distribution function for a variable with a specified theoretical distribution, which may be normal, uniform, or exponential. The Kolmogorov-Smirnov Z is computed from the largest difference (in absolute value) between the observed and theoretical cumulative distribution functions. This goodness-of-fit test tests whether the observations could reasonably have come from the specified distribution (Karaca et al., 2005). One-Sample Kolmogorov-Smirnov test result is shown in Table 5.7.

Table 5.7 One-Sample Kolmogorov-Smirnov Test for all variables.

One-Sample Kolmogorov-Smirnov Test			
Variables	**Kolmogorov-Smirnov Z**		
	Normal	**Uniform**	**Exponential**
Coarse Particles ($\mu g/m^3$)	**1.155**	2.903	3.309
Fine Particles ($\mu g/m^3$)	**2.099**	4.592	3.314
PM_{10} ($\mu g/m^3$)	**1.275**	2.638	3.588
TSP ($\mu g/m^3$)	**0.646**	2.498	3.259
SO_2 ($\mu g/m^3$)	**1.204**	2.852	2.395
CO ($\mu g/m3$)	**1.218**	3.747	3.719
NO ($\mu g/m^3$)	**0.940**	3.249	2.373
NO_2 ($\mu g/m^3$)	1.883	3.869	**1.521**
NO_X ($\mu g/m^3$)	**0.964**	2.264	2.694
Traffic Count	**0.994**	3.435	4.694
Traffic Flow (km/hr)	**1.038**	2.870	5.404
Wind Direction (1-16)	2.121	**1.964**	2.452
Wind Speed (m/sec)	**1.256**	4.462	3.742
Temperature (°C)	**0.975**	2.148	2.708
Pressure (mb)	**0.533**	1.699	5.754
Humidity (%)	**1.020**	1.849	4.137
Total Daily Rain (mm)	**3.226**	7.328	10.976

Kolmogorov-Smirnov Z value must be the lowest and close to zero to define distribution of tested variable. As a result of One-Sample Kolmogorov-Smirnov Test, NO_2 and wind direction moves from normality but their Kolmogorov-Smirnov Z values are very close to normal. For that reason, they can be assumed that they fit to normal. Total daily rain exactly does not fit to normal distribution due to its high Kolmogorov-Smirnov Z value. All parameters except total daily rain fit to normal distribution.

Histogram charts of some variables' frequencies are shown as figures on the following. Histogram charts also shows normal curves of the selected variables.
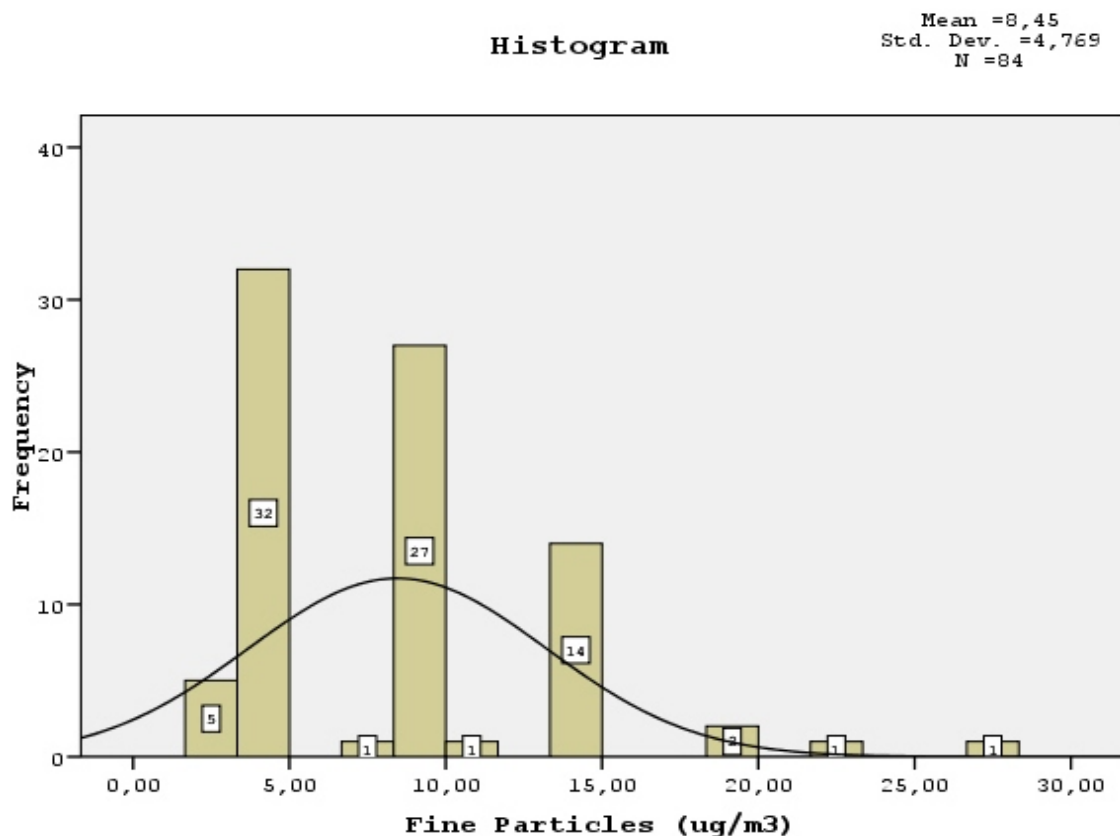
Figure 5.18 Frequency distribution of fine particle concentrations.
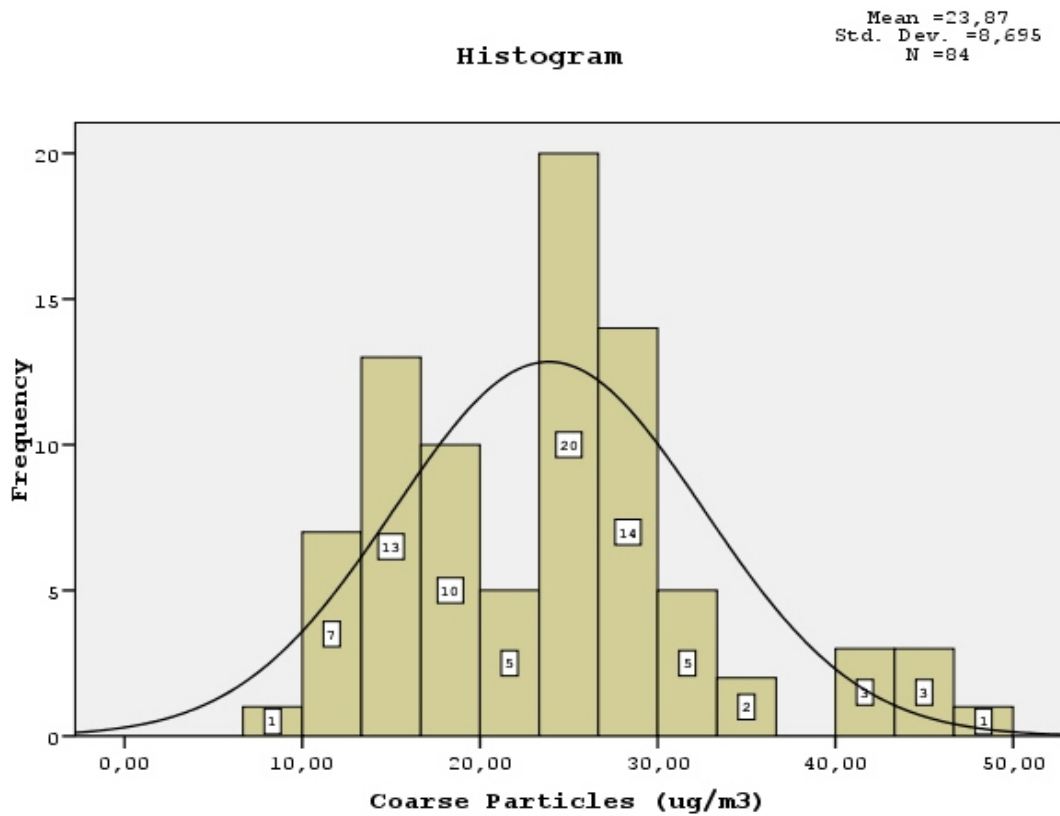
Figure 5.19 Frequency distribution of coarse particle concentrations.
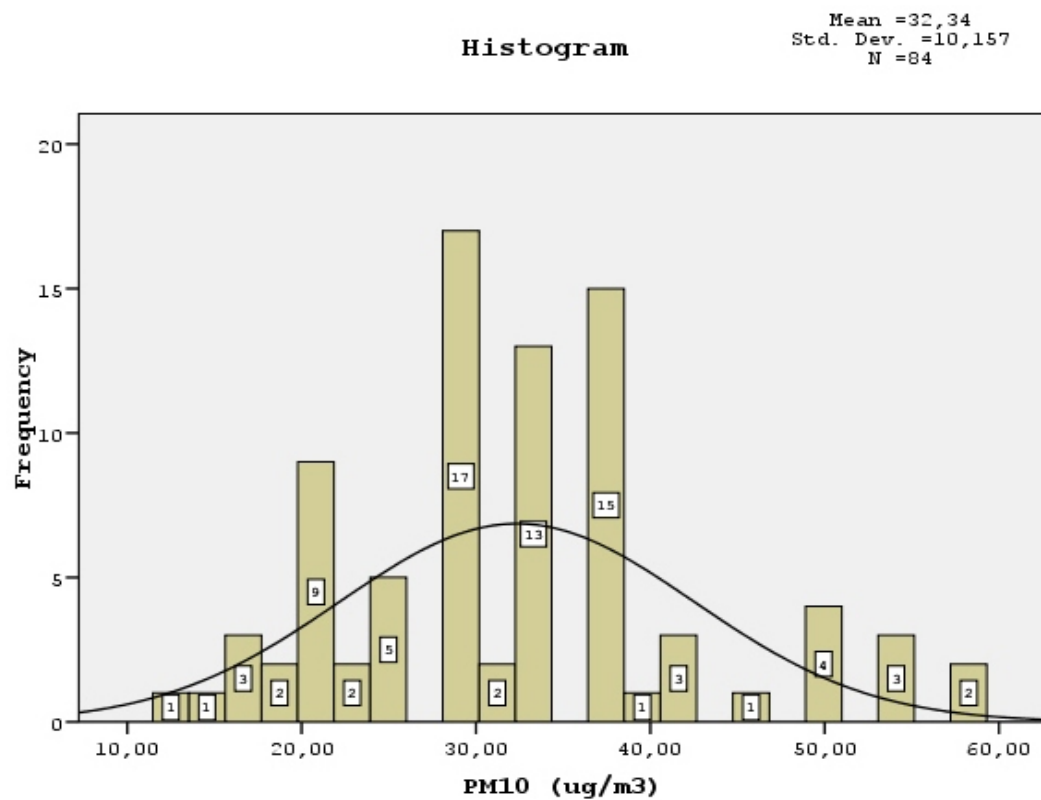
Figure 5.20 Frequency distribution of PM_{10} concentrations.
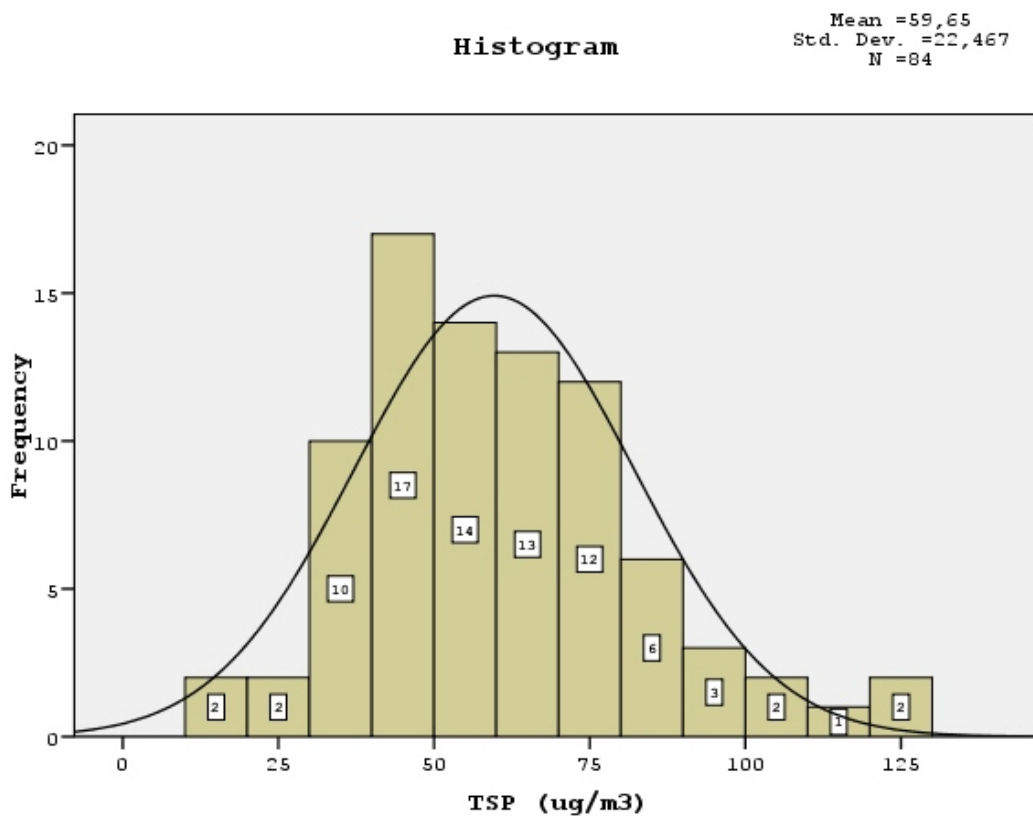
Figure 5.21 Frequency distribution of TSP concentrations.
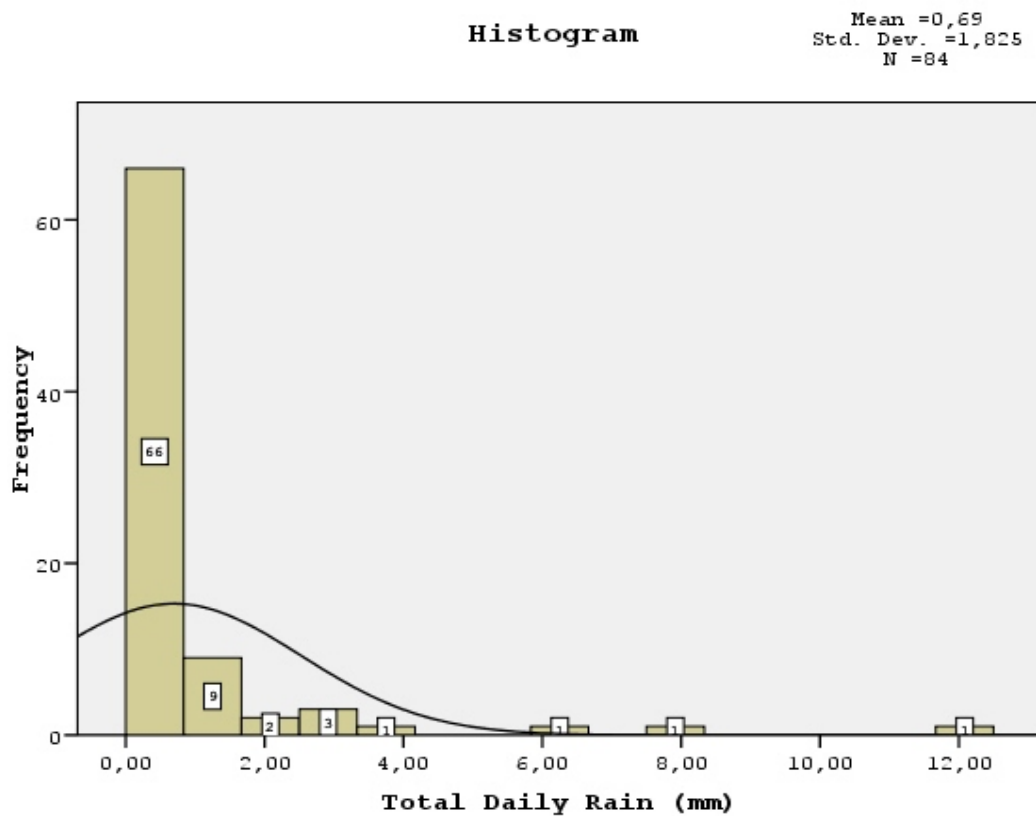
Figure 5.22 Frequency distribution of total daily rain.

As it is concluded from frequency distributions of coarse particles, fine particles, PM_{10}, and TSP, their curves are very close to normal behavior because tails of their curves are symmetrical with respect to their means. This result means that their distributions fit to normal distribution. But total daily rain parameter does not fit to normal distribution because its curve is far from normality and it has very long right-tail on the histogram.

5.2.3 Correlations of Variables

In order to find out any relationship between particulate matters, criteria air pollutants, meteorological data, and traffic data, correlation statistics were performed and shown in Table 5.8. This type of statistical test is a powerful technique to identify the kind of relation that presents between different pollutants that may give information on their common sources, chemistry and transport in the atmosphere.

According to correlation result, airborne coarse particles are directly proportional to TSP, SO_2, NO_2, NO_x, and wind direction but inversely proportional to wind speed. The correlation order of variables with coarse particles is wind direction (0.347) > TSP (0.268) > SO_2 (0.256) > Wind Speed [- 0.230] > NO_2 (0.215) > NO_x (0.190). This correlation indicates that coarse particle concentration is related to TSP, SO_2, NO_2, and NO_x pollutants which are generally emitted by traffic and combustion sources. Prevailing wind from road to sampler increases the coarse particle concentration that may explain the effect and correlation of dominant wind direction on the coarse particle concentration. Inverse relationship between wind speed and coarse particle concentration can be result of dilution effect of wind which reduces coarse particulate matter concentration.

Fine particle concentration is inversely proportional to the traffic count (- 0.255) but directly proportional to the traffic flow (0.241). The traffic count is generally high when the traffic flow on the same lane is low during congested traffic. Traffic congestion causes more fine particulate matter emission due to motor idling. This correlation result indicates the strong effect of traffic on the formation of fine particles; moreover, the main source of fine particle pollution is traffic.

Table 5.8 Correlation statistics of all variables.

Correlations (a)

Variables	Coarse Particles	Fine Particles	PM10	TSP	SO2	CO	NO	NO2	NOX	Traffic Count	Traffic Flow	Wind Direction	Wind Speed	Temp.	Pressure	Humidity	Total Daily Rain
Coarse Particles	1	0,058 / 0,301	,883(**) / 0,000	,268(**) / 0,007	,256(**) / 0,009	0,141 / 0,100	0,058 / 0,299	,215(*) / 0,025	,190(*) / 0,042	-0,141 / 0,101	0,086 / 0,217	,347(**) / 0,001	-,230(*) / 0,018	-0,051 / 0,323	-0,052 / 0,319	0,105 / 0,171	0,050 / 0,325
Fine Particles	0,058 / 0,301	1	,519(**) / 0,000	0,082 / 0,228	0,083 / 0,227	0,015 / 0,444	-0,048 / 0,331	0,033 / 0,383	-0,017 / 0,438	-,255(**) / 0,010	,241(*) / 0,014	0,086 / 0,219	0,088 / 0,213	-0,063 / 0,285	-0,172 / 0,059	-0,055 / 0,308	0,092 / 0,203
PM10	,883(**) / 0,000	,519(**) / 0,000	1	,269(**) / 0,007	,258(**) / 0,009	0,129 / 0,121	0,027 / 0,403	,200(*) / 0,034	0,155 / 0,080	-,241(*) / 0,014	,187(*) / 0,044	,338(**) / 0,001	-0,156 / 0,078	-0,073 / 0,255	-0,125 / 0,128	0,064 / 0,283	0,086 / 0,218
TSP	,268(**) / 0,007	0,082 / 0,228	,269(**) / 0,007	1	,498(**) / 0,000	,610(**) / 0,000	,273(**) / 0,006	,257(*) / 0,009	,386(**) / 0,000	-0,006 / 0,480	-0,001 / 0,495	,301(*) / 0,003	-,324(**) / 0,001	0,134 / 0,112	-,219(*) / 0,022	-0,064 / 0,283	0,001 / 0,496
SO2	,256(**) / 0,009	0,083 / 0,227	,258(**) / 0,009	,498(**) / 0,000	1	,476(**) / 0,000	,370(**) / 0,000	,601(**) / 0,000	,695(**) / 0,000	-0,063 / 0,286	0,064 / 0,281	,450(**) / 0,000	-0,121 / 0,137	,190(*) / 0,042	-,404(**) / 0,000	-,455(**) / 0,000	-0,031 / 0,390
CO	0,141 / 0,100	0,015 / 0,444	0,129 / 0,121	,610(**) / 0,000	,476(**) / 0,000	1	0,103 / 0,175	,638(**) / 0,000	,509(**) / 0,000	0,054 / 0,312	-0,008 / 0,473	,344(**) / 0,001	-,192(*) / 0,040	-,347(**) / 0,001	-0,125 / 0,129	0,137 / 0,107	0,093 / 0,200
NO	0,058 / 0,299	-0,048 / 0,331	0,027 / 0,403	,273(**) / 0,006	,370(**) / 0,000	0,103 / 0,175	1	-0,066 / 0,277	,741(**) / 0,000	,182(*) / 0,048	-,356(**) / 0,000	0,111 / 0,157	-,196(*) / 0,037	,240(*) / 0,014	0,019 / 0,432	-0,023 / 0,416	,200(*) / 0,034
NO2	,215(*) / 0,025	0,033 / 0,383	,200(*) / 0,034	,257(**) / 0,009	,601(**) / 0,000	,638(**) / 0,000	-0,066 / 0,277	1	,621(**) / 0,000	0,110 / 0,160	0,086 / 0,219	,407(**) / 0,000	0,081 / 0,233	-,515(**) / 0,000	-0,173 / 0,058	-0,004 / 0,484	0,031 / 0,390
NOX	,190(*) / 0,042	-0,017 / 0,438	0,155 / 0,080	,386(**) / 0,000	,695(**) / 0,000	,509(**) / 0,000	,741(**) / 0,000	,621(**) / 0,000	1	,217(*) / 0,024	-,223(*) / 0,021	,361(**) / 0,000	-0,096 / 0,191	-0,158 / 0,075	-0,100 / 0,182	-0,022 / 0,421	0,177 / 0,053
Traffic Count	-0,141 / 0,101	-,255(**) / 0,010	-,241(*) / 0,014	-0,006 / 0,480	-0,063 / 0,286	0,054 / 0,312	,182(*) / 0,048	0,110 / 0,160	,217(*) / 0,024	1	-,627(**) / 0,000	-0,144 / 0,096	0,108 / 0,164	-,312(**) / 0,002	0,007 / 0,476	0,143 / 0,097	0,002 / 0,492
Traffic Flow	0,086 / 0,217	,241(*) / 0,014	,187(*) / 0,044	-0,001 / 0,495	0,064 / 0,281	-0,008 / 0,473	-,356(**) / 0,000	0,086 / 0,219	-,223(*) / 0,021	-,627(**) / 0,000	1	0,098 / 0,187	0,065 / 0,187	0,126 / 0,127	-0,074 / 0,252	0,017 / 0,439	-0,160 / 0,073
Wind Direction	,347(**) / 0,001	0,086 / 0,219	,338(**) / 0,001	,301(**) / 0,003	,450(**) / 0,000	,344(**) / 0,001	0,111 / 0,157	,407(**) / 0,000	,361(**) / 0,000	-0,144 / 0,096	0,098 / 0,187	1	-0,149 / 0,088	-0,086 / 0,218	-,323(**) / 0,001	-0,059 / 0,298	,243(*) / 0,013
Wind Speed	-,230(*) / 0,018	0,088 / 0,213	-0,156 / 0,078	-,324(**) / 0,001	-0,121 / 0,137	-,192(*) / 0,040	-,196(*) / 0,037	0,081 / 0,233	-0,096 / 0,191	0,108 / 0,164	0,065 / 0,187	-0,149 / 0,088	1	-0,147 / 0,091	-,188(*) / 0,043	-0,091 / 0,205	0,007 / 0,477
Temperature	-0,051 / 0,323	-0,063 / 0,285	-0,073 / 0,255	0,134 / 0,112	,190(*) / 0,042	-,347(**) / 0,001	,240(*) / 0,014	-,515(**) / 0,000	-0,158 / 0,075	-,312(**) / 0,002	0,126 / 0,127	-0,086 / 0,218	-0,147 / 0,091	1	-,215(*) / 0,025	,323(**) / 0,000	-0,111 / 0,158
Pressure	-0,052 / 0,319	-0,172 / 0,059	-0,125 / 0,128	-,219(*) / 0,022	-,404(**) / 0,000	-0,125 / 0,129	0,019 / 0,432	-0,173 / 0,058	-0,100 / 0,182	0,007 / 0,476	-0,074 / 0,252	-,323(**) / 0,001	-,188(*) / 0,043	-,215(*) / 0,025	1	,323(**) / 0,001	-0,101 / 0,181
Humidity	0,105 / 0,171	-0,055 / 0,308	0,064 / 0,283	-0,064 / 0,283	-,455(**) / 0,000	0,137 / 0,107	-0,023 / 0,416	-0,004 / 0,484	-0,022 / 0,421	0,143 / 0,097	0,017 / 0,439	-0,059 / 0,298	-0,091 / 0,205	,323(**) / 0,000	,323(**) / 0,001	1	,324(**) / 0,001
Total Daily Rain	0,050 / 0,325	0,092 / 0,203	0,086 / 0,218	0,001 / 0,496	-0,031 / 0,390	0,093 / 0,200	,200(*) / 0,034	0,031 / 0,390	0,177 / 0,053	0,002 / 0,492	-0,160 / 0,073	,243(*) / 0,013	0,007 / 0,477	-0,111 / 0,158	-0,101 / 0,181	,324(**) / 0,001	1

**. Correlation is significant at the 0.01 level (1-tailed).

*. Correlation is significant at the 0.05 level (1-tailed).

a. Listwise N=84

PM_{10} is directly proportional to TSP, SO_2, NO_2, traffic flow, and wind direction but inversely proportional to traffic count. The correlation order of the variables with PM_{10} is wind direction (0.338) > TSP (0.269) > SO_2 (0.258) > traffic count [- 0.241] > NO_2 (0.200) > traffic flow (0.187). The obtained results mean that PM_{10} concentration is related to TSP, SO_2, and NO_2 pollutants which are generally emitted by traffic and combustion sources. The dominant wind direction from road to sampler increases the PM_{10} concentration that may explain the effect of wind direction on the PM_{10} concentration in the correlation table. High traffic congestion has increasing effect on PM_{10} like fine particles because PM_{10} is directly proportional to traffic flow and inversely proportional to traffic count. At the same time, high correlation between PM_{10} and wind direction may explain the increasing effect of carried resuspended dust from road to sampler on PM_{10} formation. So, particulate matters from vehicle exhausts and resuspended dust from the road are usual sources of PM_{10} formation in this study.

Total suspended particulate (TSP) concentration is directly proportional to coarse particles , PM_{10}, SO_2, CO, NO, NO_2, NO_x, and wind direction but inversely proportional to wind speed and pressure. The correlation order is CO (0.610) > SO_2 (0.498) > NO_x (0.386) > wind speed [- 0.324] > wind direction (0.301) > NO (0,273) > PM_{10} (0.269) > coarse particles (0.268) > NO_2 (0.257) > pressure [- 0.219]. TSP has high correlations with CO, SO_2, NO_x, NO, NO_2, PM_{10} and coarse particles which are criteria air pollutants and most of them are emitted by mobile sources such as motor vehicles. Effects of wind direction and wind speed on TSP concentration have same explanations with coarse particles.

Correlation order of variables with SO_2 is NO_x (0.695) > NO_2 (0.601) > TSP (0.498) > CO (0.476) > humidity [- 0.455] > wind direction (0.450) > pressure [- 0.404] > NO (0.370) > PM_{10} (0.258) > coarse particles (0.256). SO_2 has high correlations with NO_x, NO_2, TSP, CO, NO, PM_{10} and coarse particles. The high significant correlation of SO_2 with other air pollutants may indicate that they may have been emitted from same source which may be the traffic. Humidity and pressure values are generally low in winter time with respect to summer season (see Figure 5.9) and SO_2 has higher concentration in winter time due to excess SO_2 emissions by heating activities. Effect of wind direction on SO_2 concentration is related with the high amount of carried SO_2 to the sampler when the wind direction is from road to sampler.

Correlation order of variables with CO is NO_2 (0.638) > TSP (0.610) > NO_x (0.509) > SO_2 (0.476) > temperature [- 0.347] > wind direction (0.344) > wind speed (- 0.192). Correlation of CO with NO_2, TSP, NO_x, and SO_2 may mean that they have emitted from traffic or their common source is traffic. The inversely relation of CO with temperature means that the contribution of CO production by heating purposes increases the total CO emission especially in winter time (heating season). Wind direction from road to sampler increases the measured CO concentration and wind speed reduces the measured CO concentration due to dilution effect as in the case of coarse particles.

Correlation order of variables with NO is NO_x (0.741) > SO_2 (0.370) > traffic flow [- 0.356] > TSP (0.273) > temperature (0.240) > wind speed [- 0.196]. The cause of very high correlation between NO and NO_x is that NO_x concentration is summation of concentrations of NO and NO_2. NO concentration is directly proportional to SO_2 and TSP concentrations, which means that their emission sources are similar and the probable emission source of NO, SO_2, and TSP is traffic. NO may go photo-oxidation reaction that leads to the formation of photochemical smog without producing NO_2 during summer time. That's why NO associates with temperature. When the traffic flow decreases, traffic density is generally increases. As a consequence, high traffic density produces more air pollutants like NO, moreover; well-known main source of NO in cities is traffic. High wind speed makes more dilution, which reduces the concentration of NO.

Correlation order of variables with NO_2 is CO (0.638) > NO_x (0.621) > SO_2 (0.601) > temperature [- 0.515] > wind direction (0.407) > TSP (0.257) > coarse particles (0.215) > PM_{10} (0.200). Correlation of NO_2 with CO, SO_2, TSP and coarse particles means that they have emitted from the same source which is probably the traffic. The cause of high correlation between NO_2 and NO_x is that NO_x concentration is summation of concentrations of NO and NO_2. The reason for decreasing of NO_2 in high temperatures could be attributed to the photochemical oxidation of NO_2 to form PAN during summer season.

Traffic flow and traffic count in Beşiktaş Municipality do not show big differences at working days and weekend because Beşiktaş Municipality is one of the biggest business centers of Istanbul. The vehicle number using the main road near the

sampling area is generally constant and the traffic behavior in this area is almost same everyday. That's why the effect of traffic flow and traffic count on air pollutants (especially emitted by traffic) is not observed clearly in the correlation table. But Figure 5.12, 5.13, 5.14, and 5.15 showing particulate matter concentrations with respect to wind directions give some clear results about the effect of traffic on inhalable particulate matter formation on the ambient air of Yıldız area.

In order to find out a correlation between total daily rain, coarse particles, fine particles, PM_{10}, and TSP, all data belonging to rainless days were removed from the data set. The purpose behind this removal is to find out the effect of rain on formation of particulate matters. For this aim, correlation table of 31 data belonging to rainy days were formed by using SPSS 15 software package. Correlation results for total daily rain, coarse particles, fine particles, PM_{10}, and TSP are shown in Table 5.9. According to this correlation table, there is no correlation between total daily rain, coarse particles, fine particles, PM_{10}, and TSP. On the other hand, rain is one of the well-known removal processes of suspended particulate matters in the ambient atmosphere, which means that rain has a decreasing effect on concentration of measured particulate matters. The reason of this conflict may be the usage of insufficient number of data for correlation. If the number of data can be increased, the effect of rain on particulate matter formation may be found.

Table 5.9 Correlation statistics of rainy days' data.

Correlations (a)		Coarse Particles	Fine Particles	PM_{10}	TSP	Total Daily Rain
Coarse Particles	Pearson Correlation	1	0,066	,873(**)	0,240	-0,042
	Sig. (1-tailed)		0,362	0,000	0,097	0,411
Fine Particles	Pearson Correlation	0,066	1	,544(**)	0,073	-0,030
	Sig. (1-tailed)	0,362		0,001	0,347	0,436
PM_{10}	Pearson Correlation	,873(**)	,544(**)	1	0,238	-0,050
	Sig. (1-tailed)	0,000	0,001		0,099	0,395
TSP	Pearson Correlation	0,240	0,073	0,238	1	0,015
	Sig. (1-tailed)	0,097	0,347	0,099		0,467
Total Daily Rain	Pearson Correlation	-0,042	-0,030	-0,050	0,015	1
	Sig. (1-tailed)	0,411	0,436	0,395	0,467	

**. Correlation is significant at the 0.01 level (1-tailed). a. Listwise N=31

5.2.4 Linear Regression

All variables except total daily rain fit to normal distribution. Linear regression can be applied to any variable having normal distribution in order to have strong formulation between dependent and independent variables. To find out any effect of total daily rain on particulate matter formation, total daily rain values also were included in linear regression. In determining weather the model can be simplified, p-values on the independent variable were choose to be less than 0.05. If p-values found to be higher than 0.05, the corresponding independent variable was rejected. This process was repeated using the method of forward selection until all the independent variables are statistically significant.

5.2.4.1 Linear Regression of Fine Particles

In the linear regression of fine particles, all variables were (except coarse particles and PM_{10}) selected and model 1 was formed. R value for model 1 is 0.490. Coefficients of model 1 are shown in Table 5.10.

Table 5.10 Coefficients of model 1 of fine particles.

Variables	Unstandardized Coefficients		Standardized Coefficients
	B	Std. Error	Beta
Dependent Variable: ($PM_{2.5}$)	122.090	132.628	
TSP	0.048	0.034	0.224
SO_2	0.135	0.107	0.344
CO	-0.003	0.003	-0.188
NO	1.165	0.990	8.588
NO_2	1.099	0.992	6.916
NO_X	-1.161	0.989	-10.893
Traffic Count	0.000	0.000	-0.262
Traffic Flow	0.390	0.317	0.194
Wind Direction	-0.070	0.142	-0.066
Wind Speed	0.431	0.333	0.173
Temperature	-0.414	0.148	-0.576
Pressure	-0.120	0.124	-0.132
Humidity	-0.022	0.058	-0.062
Total Daily Rain	0.289	0.320	0.111

Standardized beta coefficients of wind direction and humidity were ignorable and these variables were removed from the model. After removing these variables from the linear regression, model 2 was formed and coefficients are shown in Table 5.11. R value for model 2 is 0.495 and higher than R value of model 1 (0.490). By this manner, the model for fine particles was simplified and ineffectiveness of wind direction and humidity in the model was shown.

Table 5.11 Coefficients of model 2 of fine particles.

Variables	Unstandardized Coefficients		Standardized Coefficients
	B	Std. Error	Beta
Dependent Variable: ($PM_{2.5}$)	102.307	126.244	
TSP	0.045	0.033	0.210
SO_2	0.146	0.096	0.371
CO	-0.003	0.003	-0.187
NO	1.181	0.975	8.705
NO_2	1.112	0.978	7.000
NO_X	-1.179	0.975	-11.057
Traffic Count	0.000	0.000	-0.236
Traffic Flow	0.425	0.305	0.211
Wind Speed	0.488	0.316	0.196
Temperature	-0.390	0.140	-0.543
Pressure	-0.106	0.119	-0.116
Total Daily Rain	0.226	0.299	0.086

Model 2 for fine particles is formulized below;

[Fine particles] = 0.210x[TSP] + 0.371x[SO_2] − 0.187x[CO] + 8.705x[NO] + 7.000x[NO_2] − 11.057[NO_x] − 0.236x[Traffic Count] + 0.211x[Traffic Flow] + 0.196x[Wind Speed] − 0.543x[Temperature] − 0.116x[Pressure] + 0.086x[Total Daily Rain]

5.2.4.2 Linear Regression of Coarse Particles

In the linear regression of coarse particles, all variables were (except fine particles and PM_{10}) selected and model 1 was formed. R value for model 1 is 0.522. Coefficients of model 1 are shown in Table 5.12.

Table 5.12 Coefficients of model 1 of coarse particles.

Variables	Unstandardized Coefficients		Standardized Coefficients
	B	Std. Error	Beta
Dependent Variable: Coarse Particles	-8.237	236.716	
TSP	0.106	0.060	0.275
SO_2	0.241	0.191	0.336
CO	-0.011	0.005	-0.390
NO	-0.428	1.767	-1.728
NO_2	-0.387	1.771	-1.336
NO_X	0.406	1.766	2.086
Traffic Count	0.000	0.000	-0.143
Traffic Flow	-0.124	0.566	-0.034
Wind Direction	0.416	0.254	0.214
Wind Speed	-0.688	0.595	-0.152
Temperature	-0.173	0.263	-0.132
Pressure	0.037	0.222	0.022
Humidity	0.182	0.104	0.280
Total Daily Rain	-0.218	0.571	-0.046

Standardized beta coefficients of traffic flow, pressure and total daily rain were ignorable and these variables were removed from the model. After removing these variables from the linear regression, model 2 was formed and coefficients are shown in Table 5.13. R value for model 2 is 0.528 and higher than R value of model 1 (0.522). By this manner, it is clearly seen that the model 1 was simplified and traffic flow, pressure and total daily rain parameters were ineffective in the model 1.

Table 5.13 Coefficients of model 2 of coarse particles.

Variables	Unstandardized Coefficients		Standardized Coefficients
	B	Std. Error	Beta
Dependent Variable: Coarse Particles	21.386	14.208	
TSP	0.108	0.059	0.278
SO_2	0.241	0.180	0.337
CO	-0.011	0.005	-0.391
NO	-0.532	1.709	-2.150
NO_2	-0.494	1.713	-1.706
NO_X	0.511	1.707	2.626
Traffic Count	0.000	0.000	-0.125
Wind Direction	0.379	0.232	0.195
Wind Speed	-0.715	0.523	-0.158
Temperature	-0.187	0.256	-0.143
Humidity	0.177	0.096	0.272

Model 2 for coarse particles is formulized below;

[Coarse Particles] = 0.278x[TSP] + 0.337x[SO$_2$] – 0.391x[CO] – 2.150x[NO] – 1.706x[NO$_2$] + 2.626x[NO$_x$] – 0.125x[Traffic Count] + 0.195x[Wind Direction] – 0.158x[Wind Speed] – 0.143x[Temperature] + 0.272x[Humidity]

5.2.4.3 Linear Regression of PM$_{10}$

In the linear regression of PM$_{10}$, all variables were (except fine particles and coarse particles) selected and model 1 was formed. R value for model 1 is 0.553. Coefficients of model 1 are shown in Table 5.14.

Table 5.14 Coefficients of model 1 of PM$_{10}$.

Variables	Unstandardized Coefficients		Standardized Coefficients
	B	Std. Error	Beta
Dependent Variable: PM$_{10}$	114,170	270,063	
TSP	0,154	0,069	0,340
SO$_2$	0,376	0,218	0,450
CO	-0,014	0,006	-0,420
NO	0,744	2,016	2,574
NO$_2$	0,718	2,021	2,122
NO$_X$	-0,762	2,014	-3,356
Traffic Count	0,000	0,000	-0,246
Traffic Flow	0,265	0,646	0,062
Wind Direction	0,345	0,290	0,152
Wind Speed	-0,257	0,679	-0,048
Temperature	-0,586	0,300	-0,383
Pressure	-0,083	0,253	-0,043
Humidity	0,160	0,119	0,211
Total Daily Rain	0,071	0,652	0,013

Ignorable standardized beta coefficients belong to traffic flow, pressure, wind speed and total daily rain. After removing these variables from the linear regression, model 2 was formed and coefficients are shown in Table 5.15. R value for model 2 is 0.556 and higher than R value of model 1 (0.553). By this way, model was simplified and ineffectiveness of traffic flow, pressure, wind speed and total daily rain in the model was shown.

Table 5.15 Coefficients of model 2 of PM_{10}.

Variables	Unstandardized Coefficients		Standardized Coefficients
	B	Std. Error	Beta
Dependent Variable: PM_{10}	46.942	15.526	
TSP	0.159	0.066	0.353
SO_2	0.386	0.203	0.462
CO	-0.014	0.006	-0.417
NO	1.078	1.892	3.728
NO_2	1.057	1.900	3.123
NO_X	-1.101	1.890	-4.848
Traffic Count	0.000	0.000	-0.279
Wind Direction	0.386	0.262	0.170
Temperature	-0.566	0.290	-0.370
Humidity	0.158	0.107	0.208

Model 2 for PM_{10} is formulized below;

$[PM_{10}]$ = 0.353x[TSP] + 0.462x[SO_2] − 0.417x[CO] + 3.728x[NO] + 3.123x[NO_2] − 4.848x[NO_x] − 0.279x[Traffic Count] + 0.170x[Wind Direction] − 0.370x[Temperature] + 0.208x[Humidity]

Comparison table of these 3 linear regression models previously discussed are given in Table 5.16. This table shows each model and dependent variables in each model. Beta coefficients are also shown separately, which provides the comparison of which parameter is more effective or less effective in the model.

Comparison of PM_{10} and $PM_{2.5}$ concentrations of previous studies with our study are given in Table 5.17. According to this table, the average PM_{10} concentration of our study is close to average concentrations of other studies which were done in urban area. On the other hand, the average $PM_{2.5}$ concentration of our study is the lowest one of the all other studies shown in the table. The reason behind this situation may be that stagnant air conditions in Yıldız area were not reached very well during sampling period. In addition to that, the average wind speed in the sampling area was 4.67 m/sec, which caused speedily movement of fine particles. So, fine particles could not be sampled efficiently. This situation shows effects of meteorological factors on the measurement of the fine particles in this study.

Table 5.16 Comparison table of 3 linear regression models perviously discused.

(R) $[PM] = \beta_1 [TSP] + \beta_2 [SO_2] + \beta_3 [CO] + \beta_4 [NO] + \beta_5 [NO_2] + \beta_6 [NO_x] + \beta_7 [T.C] + \beta_8 [T.F] + \beta_9 [W.D.] + \beta_{10} [W.S.] + \beta_{11}[Temp] + \beta_{12}[P] + \beta_{13}[Hum] + \beta_{14}[T.D.R]$

$[Fine] = \beta_1 [TSP] + \beta_2 [SO_2] + \beta_3 [CO] + \beta_4 [NO] + \beta_5 [NO_2] + \beta_6 [NO_x] + \beta_7 [T.C] + \beta_8 [T.F] + \beta_{10}[W.S] + \beta_{11} [Temp] + \beta_{12}[P] + \beta_{14}[T.D.R]$

Fine	β_1	β_2	β_3	β_4	β_5	β_6	β_7	β_8	β_{10}	β_{11}	β_{12}	β_{14}
0.495	0.210	0.371	- 0.187	8.705	7.000	- 11.057	- 0.236	0.211	0.196	- 0.543	- 0.116	0.086

$[Coarse] = \beta_1 [TSP] + \beta_2 [SO_2] + \beta_3 [CO] + \beta_4 [NO] + \beta_5 [NO_2] + \beta_6 [NO_x] + \beta_7 [T.C] + \beta_9 [W.D.] + \beta_{10} [W.S.] + \beta_{11} [Temp] + \beta_{13} [Hum]$

Coarse	β_1	β_2	β_3	β_4	β_5	β_6	β_7	β_9	β_{10}	β_{11}	β_{13}
0.528	0.278	0.337	- 0.391	- 2.150	- 1.706	2.626	- 0.125	0.195	- 0.158	- 0.143	0.272

$[PM_{10}] = \beta_1 [TSP] + \beta_2 [SO_2] + \beta_3 [CO] + \beta_4 [NO] + \beta_5 [NO_2] + \beta_6 [NO_x] + \beta_7 [T.C] + \beta_9 [W.D.] + \beta_{11} [Temp] + \beta_{13} [Hum]$

PM₁₀	β_1	β_2	β_3	β_4	β_5	β_6	β_7	β_9	β_{11}	β_{13}
0.556	0.353	0.462	- 0.417	3.728	3.123	- 4.848	- 0.279	0.170	- 0.370	0.208

Where; T.C.: Traffic count, T.F.: Traffic flow, W.D.: Wind direction, W.S.: Wind speed, Temp: Temperature, P: Pressure, Hum: Humidity, T.D.R.: Total Daily Rain.

Table 5.17 Comparison of PM$_{10}$ and PM$_{2.5}$ concentrations of previous studies with our study.

Region	Sampling site	Category	Period	PM$_{10}$	PM$_{2.5}$
Eastern	Finokaliaa	Natural	2004–2005	35.5	18.5
Mediterranean	Erdemlib	Rural	2001–2002	36.4	9.7
	Sde Bokerc	Arid	1995–1997	60.4	15.9
Western	Monagregad	Rural	1999–2000	22	–
Mediterranean	Bemantese	Rural	2001	18.9	13.5
	Tarragonae	Urban	2001	37.4	21.8
	Barcelonaf	Urban	2001	36.8	22.5
	Madride	Kerbside	1999–2000	47.7	34.1
Karaca et al.	İstanbul	Sub-Urban	2002-2003	47.1	20.08
Current study	İstanbul	Urban	2006	32.34 ± 10.16	8.45± 10.16

CHAPTER 6

CONCLUSIONS

This study includes important findings about air quality of the Yıldız area. During the time period from October 2006 to July 2007, coarse, fine, and inhalable particulate matters were sampled daily form Yıldız-Beşktaş area, Furthermore, hourly air quality data, traffic data and meteorological data were obtained as well. All these data were investigated and various findings were appeared. Any research related to the topic of "traffic related inhalable particulate matter in Istanbul" was not studied yet, which makes this study very valuable. Investigation of the change of traffic related air quality in Yıldız area will be made possible by comparison of this study with further studies.

First of all, mass concentrations of sampled particulate matters, air quality data, traffic data and meteorological data were generally evaluated and seasonal variations of all data were examined. Eighty four daily aerosol samples were collected between 19.10.2006 and 02.07.2007. Average mass concentrations of all collected $PM_{2.5}$, $PM_{10-2.5}$, and PM_{10} samples are 8.45 $\mu g/m^3$, 23.88 $\mu g/m^3$, and 32.34 $\mu g/m^3$, respectively. The highest monthly averages of $PM_{2.5}$, $PM_{10-2.5}$, and PM_{10} are 10.08 $\mu g/m^3$, 30.29 $\mu g/m^3$, and 39.88 $\mu g/m^3$ which were observed on January 2006, October 2007, and October 2006, respectively. PM_{10} limit values of WHO and EU were exceeded 9 times and $PM_{2.5}$ limit value of WHO was exceeded one time during sampling period.

Hourly mass concentrations of CO, SO_2, NO, NO_2, NO_x, and TSP were also investigated. It's found that daily concentrations of all these pollutants show monthly and seasonal variations during the time period from October 2006 to June 2007. WHO

1-hour limit value was exceeded 75 times and EPA 1-hour limit value was exceeded 16 times by measured CO concentrations. WHO 1-hour and EPA 1-hour limit values were exceeded 7 times by measured NO_2 concentrations. SO_2 concentrations were lower than all limit values. Episodic events of SO_2, NO, NO_x, and TSP were specified in this study.

Hourly meteorological data and traffic data were studied. Meteorological parameters showed monthly and seasonal variations during the sampling period. Dominant wind directions were determined as SSW and SW for sampling area. Traffic count was inversely proportional to traffic density, which were explained by traffic congestion.

Secondly, statistical analysis were performed for mass concentrations of sampled particulate matters, air quality data, traffic data and meteorological data by using SPSS 15.0 software package. As a result of distribution tests, distribution of all parameters except total daily rain fits to normal distribution. Multiple correlation statistics were performed for all parameters. Some expected, unimagined, and surprising results were found at the end of multiple correlation statistics.

Fine particle formation was only correlated to traffic count and traffic flow. It's very surprising that meteorological parameters and traffic related air pollutants such as CO and NO_x did not show any correlation with fine particle formation. However, it can be said that the main source of fine particle formation is traffic because it was directly proportional to traffic congestion. Airborne coarse particles were directly proportional to TSP, SO_2, NO_2, NO_x, and wind direction but inversely proportional to wind speed. This expected correlation result means that main sources of coarse particle formation are probably traffic and resuspended dust on the ambient air.

Strong correlation of wind direction and wind speed with concentrations of some air pollutants was the effect of meteorological parameters in this study. Wind direction was also an indicator of the effect of traffic congestion on the formation of coarse particles, PM_{10}, TSP, CO, NO_2, and NO_x because blowing wind carries these traffic related air pollutants from road to the sampler. Temperature, pressure, and humidity had also weak correlations with concentrations of some air pollutants. On the other hand, it's unexpected that there was no correlation between total daily rain, coarse particles,

fine particles, PM_{10}, and TSP. Rain is one of the well-known removal processes of suspended particulate matters in the ambient atmosphere and it should have an effect on particulate matter concentration. The reason of this unexpected situation may be the usage of insufficient number of data for the correlation.

Traffic count and traffic flow were correlated to only concentrations of fine particles, PM_{10}, and NO. The vehicle number using the main road near the sampling area is generally constant and the traffic behavior in this area is almost same everyday. That's why the effect of traffic flow and traffic count on traffic related air pollutants was not observed clearly in the correlation table.

Finally, multiple linear regressions were performed for fine particles, coarse particles, and PM_{10}. By this manner, the relation between dependent and independent variables were formulized and made more understandable. At the end of the multiple linear regressions, three models were formed for fine particles, coarse particles, and PM_{10} and R values of these models are 0.49, 0.52 and 0.55, respectively.

In order to find out possible health risks of traffic related inhalable PM pollution at Yıldız area, metal and heavy metal concentrations of collected PM samples should be analyzed as a continuation of this study. Istanbul Metropolitan Municipality and/or the Government should monitor PM_{10} and $PM_{2.5}$ pollution continuously at designated areas where the traffic and industrial activities have potential health risks on human health; moreover, national PM_{10} limit values should be restricted, national $PM_{2.5}$ limit values should be formed by taking international $PM_{2.5}$ limit values into account, and risk assessment of PM pollution should be performed immediately. Realization of these suggestions will not only increase the importance of this study but also make the Turkey a sensitive government about air pollution and public health concepts.

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