SHORT AND LONG TERM VARIATIONS IN THE CONCENTRATIONS OF GASEOUS AND PARTICULATE POLLUTANTS IN ANKARA AND ASSESSMENT OF TRAFFIC CONTRIBUTION

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ABSTRACT

SHORT AND LONG TERM VARIATIONS IN THE CONCENTRATIONS OF GASEOUS AND PARTICULATE POLLUTANTS IN ANKARA AND ASSESSMENT OF TRAFFIC CONTRIBUTION

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Spatial and temporal variations and factors affecting these variations in concentrations of measured parameters at two different groups of stations in Ankara are investigated in this study. The first group consists of three curbside stations that are under the direct influence of traffic emissions, on the other hand, the other group is composed of eight residential stations in which domestic heating is the main emission source.

State of air quality in Ankara is determined through comparison with air quality data generated in other countries and available air quality standards. Based on this comparison, although air quality has improved in recent years, it is still not one of the clean cities around the world. Although measured concentrations of pollutants comply with standards in the Turkish Air Quality Regulation, further reduction in concentrations will be necessary, if EU directives become effective in the country.

Relation between measured concentrations and meteorological parameters are also investigated. Wind speed and mixing height are the two parameters that are most closely related to measured concentrations at residential stations. However, at curbside stations concentrations are determined by emissions.

Qualitative comparison of two groups of stations emphasizes the contribution of motor vehicle emissions on residential areas. Seasonal and diurnal variations of measured parameters and lower winter-to-summer ratio of SO₂ indicate contribution of diesel vehicle emissions to SO₂ levels at curbside stations. Contribution of traffic emissions are also observed in terms of well defined bimodal traffic pattern of SO₂ and PM-10 at non-curbside stations.

Seasonal and diurnal pollutant ratios are investigated to apportion different source types that are effective in each group of station. PM-to-SO₂, NO-to-NO₂, PM-10-to-NO_x and SO₂-to-NO_x ratios are found to be good tracers for qualitative assessment of source groups, namely traffic and domestic heating.

Different statistical methodologies are demonstrated to determine the source regions of pollutants with respect to wind direction. Air quality level of Ankara, instead of air quality level in each station, is determined in terms of daily API. One by one correlation between API and meteorological factors are investigated, maximum wind speed and daily thermic excursion is found to be the highest correlated variables. The relation between API and these variables is analyzed by multiple linear regression method and then air pollution forecast model highly correlated with API and meteorological variables is developed. The assimilative capacity of Ankara is calculated in terms of ventilation coefficient and found to be highest in summer and lowest in winter. In winter poor dispersion conditions favor the poor air quality in the city.

Key Words: Urban Air Pollution, Motor Vehicles, Meteorological Factors, Pollutant Ratios, API, Ventilation Coefficient, Ankara

ANKARA'DAKİ GAZ VE PARTİKÜL KİRLETİCİLERİN KISA VE UZUN DÖNEM DEĞIŞİMLERİNİN BELİRLENMESİ VE TRAFİĞİN HAVA KALİTESİNE KATKISI

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Bu çalışmada, Ankara'da iki farklı grup istasyonda ölçülen kirletici konsantrasyonlarının zamansal ve mekansal değişimi ve bu değişimleri etkileyen faktörler incelenmiştir. İlk grup trafiğin doğrudan etkisi altında olan üç farklı kavşaktaki istasyondan oluşurken, diğer grup evsel ısıtmanın birincil emisyon kaynağı olduğu yerleşim bölgelerinde yer alan sekiz farklı istasyondan oluşmuştur.

Ankara'daki hava kirliliğinin durumu literatürdeki diğer ülke şehirlerinin durumu ve hava kalitesi standartlarıyla karşılaştırıldığında, hava kalitesinin eskiye göre iyi olduğu fakat halen Ankara'nın hava kalitesi bakımından temiz bir şehir sayılamayacağını göstermiştir. Ölçülen tüm kirleticiler uzun dönem Türk Hava Kalitesi Standartlarını sağlasa da, yakın gelecekte kirletici konsantrasyonlarında azalma Avrupa Birliği'ne aday olma yolundaki Türkiye için zorunlu hale gelecektir.

ÖΖ

Meteorolojik değişkenlerin ölçülen kirletici konsantrasyonlarına etkisi incelenmiş ve kirletici kaynaklarındaki değişimin meteorolojik değişkenlere oranla kavşaklardaki istasyonlarda daha etkin olguğu saptanmıştır. Öte yandan, meteorolojik değişkenlerin (rüzgar hızı ve karışım yüksekliği) yerleşim bölgelerindeki istasyonlar üzerinde daha etkin olduğu bulunmuştur.

İki grup istasyon arasında yapılan nitel kıyaslama, yerleşim bölgelerindeki istasyonlarda ölçülen kirletici konsantrasyonlarında trafik emisyonlarının katkısının varlığını bir kez daha vurgulamıştır. Kavşaklardaki istasyonlarda, mevsimsel ve günlük değişimin yanında SO₂ seviyelerindeki düşük kış/yaz oranı kavşaklardaki istasyonlarda ölçülen SO₂ konsantrasyonlarına dizel araç emisyonlarının katkısı olduğunu göstermektedir. Yerleşim bölgelerinde ölçülen kirleticilere trafiğin katkısının varlığı, kirleticilerin bu istasyonlarda da tipik trafik değişimi göstermesiyle desteklenmiştir.

Kirletici oranlarındaki günlük ve mevsimsel değişimler her grup istasyonda etkin olan kaynakların belirlenmesi için kullanılmıştır. PM/SO₂, NO/NO₂, PM-10/NO_X ve SO₂/NO_X oranlarının trafik ve evsel ısıtma kaynaklarının belirlenmesinde kullanılabileceği bulunmuştur.

Yerleşim bölgelerinde kaynak bölgelerinin belirlenmesi için rüzgar yönüne bağlı olarak çalışan üç farklı istatistiksel metodun kullanımı gösterilmiştir. Ankara'daki hava kalitesi düzeyi, tek tek isyasyonlar bazında değilde tüm şehir için hava kalitesi indeksi (HKİ) hesaplanarak bulunmuştur. HKİ'nin meteorolojik değişkenlerle bire bir ilişkisi incelenmiştir. Maksimum rüzgar hızı ve günlük sıcaklık farkının HKİ ile en yüksek korelasyonu gösterdiği bulunmuştur. HKİ ile bu değişkenler arasındaki ilişki çok değişkenli varyasyon tekniği kullanılarak incelenmiş ve bunlara bağlı olarak HKİ tahmin modeli geliştirilmiştir. Ankara atmosferinin kendini yenileme kapasitesi havalandırma katsayısı kullanılarak hesaplanmıştır. Kendini yenileme kapasitesinin yazın en yüksek, kışın ise en düşük olduğu bulunmuştur. Düşük seyrelme oranları kışın şehirde düşük hava kalitesinin görülmesine sebep olmaktadır.

Anahtar Kelimeler: Kentsel Hava Kirliliği, Motorlu Kara Taşıtları, Meteoroloji, Kirletici Oranları, HKİ, Havalandırma Katsayısı, Ankara.

To my family...

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CHAPTER 1

FRAMEWORK AND OBJECTIVE

1.1. Framework

Urban air pollution problem appeared as a consequence of coal combustion for space heating in 1960s due to high concentrations of both SO_2 and PM-10 mass. Therefore, urban air pollution studies focused on health effect of both pollutants between 1960 and 1970. The fossil fuel based pollution was controlled by improving the engine technology and fuel at the end of 1970s. Today the levels of SO_2 in the cities of developed countries are comparable with the levels at rural areas.

As the fossil fuel combustion based pollution lessens, the traffic emissions which are not considered before are becoming the important contributor of air pollution in urban areas. It is well known that the main sources of nitrogen oxides and hydrocarbons in ambient air are the motor vehicular emissions. These pollutants have direct health effect. In the atmosphere they are oxidized and form ozone and other oxidants that have detrimental health effect on human and vegetation, besides causing visibility degradation.

Urban air pollution problem in Turkey first appeared as the air pollution at Ankara in 1970s and then similar problems were observed in most of the other cities in Turkey. The problem was due to combustion of coal with high sulfur content and refractory fractions for space heating. The problem was the most serious in the cities located at central and southern parts of the country due to long and cold winter in these regions and less pronounced in coastal cities with mild winters. However, coal based pollution in cities has been decreasing since 1990s since natural gas is now being used for domestic heating. The decrease is very sharp between 1990 and 1995, and continues at a lower pace.

As in other countries, motor vehicular emissions became an important issue after the decline of the coal based air pollution. Emissions from motor vehicles were part of the atmospheric constituents for a long time, but they were masked by heavy sulfur based pollution.

Air quality in urban areas without a substantial industrial activity, like Ankara, is determined by local meteorology and two different types of emissions, namely emissions from motor vehicles and emissions from combustion for residential heating. Development of effective strategies to improve air quality in Ankara (and in other cities like Ankara) require quantitative information on the types and contributions of sources on air quality levels as well as understanding of the role of meteorology on the measured concentrations. Such information can be generated either using numerical model simulations or by measurements of very specific natural tracers for each source category. For the time being, quantitative source apportionment is not possible in Ankara, because neither tracer measurements for receptor modeling, nor emission inventory for numerical modeling are available. However, there is a need, for at least a qualitative assessment of the role of traffic on air quality, because combustion related emissions decreased significantly in last 10 years and relative contribution of traffic emissions on concentrations of pollutants are expected to increase, but there is no information whatsoever on contribution of motor vehicle emissions on residential areas. This study emerged from such a need.

1.2. Aim of the Study

The main objective of this study is to understand and establish differences and similarities and the factors causing these differences and similarities in concentrations of air quality parameters measured at two group of stations, namely in three curbside stations which are strongly impacted from traffic emissions and eight residential stations, which are impacted by combustion emissions from space heating. Conventional air quality data used in this study is measured by the Ministry of Health in the years 1999 and 2000. It should be noted that conventional pollutants measured by the Ministry of Health, Refik Saydam Hygeine Center, namely SO₂, PM-10, NO, NO₂ and CO are not the most suitable compounds for source apportionment, because they are emitted, to different degrees from both motor vehicles and combustion. Because of this, qualitative assessment, rather than quantitative apportionment is set as the objective. The general purpose of this study can be divided into following, more specific aims:

- To assess pollution level in each station by
 - Comparing pollutant concentrations between the group of stations (curbside and non-curbside) and
 - Comparing the measured levels of pollutants in Ankara with comparable data from other world cities and reported in the literature and with available air quality standards and/or guideline values,
- To understand temporal variations of pollutant concentrations and factors affecting their variations in each station,
- To understand the role of meteorological variables on air quality levels,
- To compare the performances of different statistical tools in determining local source areas within the city, which affect SO₂ and PM-10 concentrations measured at different stations,
- To develop API (air pollution index) for Ankara and to assess its usefulness,
- To develop a statistical tool for forecasting air pollution 24 hrs ahead and,
- To investigate the assimilative capacity of Ankara atmosphere.

CHAPTER 2

BACKGROUND

2.1. Air Pollution Problem

Air pollution problem consists of several distinct problems which can be distinguished by their scale. There are four dimensions that establish scale (Table 2.1). The first is the horizontal dimension-how much of the earth's surface is involved. The second is the vertical dimension-how great a depth of the atmosphere is involved. The third is time-over what time scale the problem develops and over what time scale its control may be resolved. The fourth is the scale of organization required for its resolution (Stern, 1984).

Table 2.1. Categories of the Air Pollution Problem (Stern, 1984)

Category	Vertical scale	Temporal scale	Scale of organization
Local	Height of stacks	Hours	Municipality
Urban	Lowest mile (mixing height)	Days	County or multicounty
Regional	Troposphere	Months	State, provincial, or national
Continental	Stratosphere	Years	National or international
Global	Atmosphere	Decades	International

2.2. Urban Air Pollution

Urban air pollution is caused by a mixture of pollutants including sulfur oxides (SO_x) , nitrogen oxides (NO_x) , carbon monoxide (CO), organic compounds such as benzene, toluene, xylene and benzo(a)pyrene and particulate matter (PM), several of which are very toxic and/or carcinogenic (NIS-WHO, 2002).

Most urban areas consist of a center city surrounded by its suburbs, which in turn are surrounded by a nonurban hinterland. On a long enough averaging time, such as seasonal average, the pollution concentration over the region looks like Figure 2.1.



Figure 2.1. Annual average pollution concentration over an urban area (Stern, 1984)

According to figure, on an annual average basis, the pollution concentration is highest at the center city, lower in both suburbs and the lowest in the surrounding rural area. The concentration in the surrounding rural area is called the "background concentration" with respect to that in the city (Stern, 1984).

Urban air pollution was originally considered as a local problem mainly associated with space heating and industry. Emissions from industry and space heating are by and large controllable with significant improvement in fuel and engine technology, i.e., control of sulphur emissions becomes straightforward with the use of clean fuels and proper control technology. Traffic emissions are more difficult to control, since they arise from large number of small and mobile units. Thereby present day urban environments are mostly dominated by traffic emissions with documented impacts on human health (Fenger, 1999; Colvile et al., 2001; Vardoulakis et al., 2003).

Urban air pollution and its impact on urban air quality is a world-wide problem. It manifests itself differently in different regions depending upon the economical, political and technological development, upon the climate and topography, and last but not least, upon the nature and quality of the available energy sources (Fenger, 1999).

Rapid demographic changes and high urbanization decrease the urban air quality throughout the world. The world population was about 2.5 billion after the Second-World War, and today (mid-2004) it is 6.4 billion (Population Reference Bureau, 2004). In the last 50 years, the global urbanization, defined as the fraction of people living in settlements above 2000 inhabitants, has risen from below 30 to 44%. In the developed countries more than 75% of all people live in cities. Although developing nations are still more rural, with just 35% of citizens living in cities, urbanizations is very fast in these countries. Number of people living in urban areas in developing world is twice as high from what it was 50 years ago (UNEP, 1997; Population Reference Bureau, 1998; Fenger, 1999; Baldasano et al., 2003).

Developed countries have made great efforts to improve air quality through the adoption of clean air plans which included measures such as: demanding emission and air quality regulations, continuous air quality monitoring in urban and industrial centres, and use of cleaner fuels such as natural gas. At the same time, migration from the countryside to the city in developing countries, because of a mechanization of farming and opportunities in new industries and public services, has brought as a consequence greater emissions into the atmosphere, mainly produced by the increase of traffic (Scholorling, 2000), and rapid growth

of energy use. All of these factors have far-reaching changes in air quality in urban contexts (Baldasano et al., 2003).

From a review of trends in air quality in different cities made by Mage et al. (1996), it is quite evident that *"history repeats itself"*. The experience of the current megacities in the developed countries is being repeated in the developing countries. As shown in Figure 2.2, before rapid industrial development takes place, air pollution is mainly from domestic sources and light industry; concentrations of air pollutants are generally low and increase slowly as population increases. As industrial development and per capita energy use increase, air pollution levels begin to rise rapidly (WHO, 1988). Then urban air pollution becomes a serious public health concern, and emission controls are introduced. Owing to the complexity of the situation, an immediate improvement in air quality cannot generally be achieved; at best the situation is stabilized, and serious air pollution persists for some time (Mage et al., 1996).



Figure 2.2. Schematic presentation of a typical development of urban air pollution levels

(Fenger, 1999; based on WHO/UNEP, 1992 and Mage et al., 1996)

2.3. Sources of Urban Air Pollution

Urban air pollution comes from many sources, stationary and mobile, as well as natural ones, such as soil erosion. In many cities, urban air pollution is magnified by heavily polluting industrial complexes, which, although initially located and built outside the city, following urban developments are now located within the city or close to its periphery. Power plants, heating systems, industry and transport often use poor quality fuels or continue to operate obsolete technologies. At the same time, both the absolute and relative amounts of pollution emitted by mobile sources are becoming more important, as traffic increases and emissions from industry decreases as a result of restructuring of transition economies (NIS-WHO, 2002).

Since combustion is the dominant cause of urban air pollution, the various sources emit to a large extent the same pollutants but in varying proportions. Table 2.2 indicates the typical relative importance of source categories (x: 5-25%; xx: 25-50%; xxx: more than 50%) for emission of the main pollutants (Fenger, 1999).

2.3.1. Motor Vehicles

Although there is considerable variation in the pattern of vehicle emissions at different locations and in different regions of the world, pollution from motor vehicle emissions is increasing as the numbers of vehicles increases throughout the world. When anthropogenic emissions are considered on a global basis, it has been estimated that motor vehicles can account for about 25-30% of emissions of NO_x, 50% of HC, 60% of lead and as much as 60% of CO (Faiz and de Larderer 1993). In city centres, vehicles may be responsible for 90-95% of CO and lead and 60-70% of NO_x and HC. As vehicle emissions usually occur near to the breathing zone of people, exposures can be high and they can represent substantial health risks (WHO, 2000). Because of the health effect, most developed countries have declined the ambient concentrations of vehicle-

Source Catego	ory	Pollutant						
		SO ₂	NO ₂	CO	TSP	Organic	Pb	Heavy
								metals ^a
Power		XX	х	Х				x/xx
generation								
(Fossil fuel)								
Space heating	Coal	xx	х	хх	xx	xx/x		x/xx
	Oil	xx	х					
	Wood				xx	xx/x		
Traffic	Gasoline		xx	ххх		хх	xxx	
	Diesel	х	xx		xx	хх		
Solvents						х		
Industry		х		х	х	х	х	xx/xxx

Table 2.2. Main emission sources and pollutants in air pollution in commercial non industrial cities (Fenger, 1999; based on Stanners and Bourdeau, 1995)

^a With the exception of lead (Pb).

related air pollutants over the last two decades by improving engine design and operating conditions, and tailpipe control technologies despite increasing number of vehicles and kilometers traveled. However, both vehicle emissions and ambient concentrations of vehicle-related air pollutants have increased in most of the developing countries (WHO, 1997) due to poor fuel quality, inadequate emissions controls, poor maintenance and high average age of the vehicle fleet (Faiz and de Larderer 1993; WHO, 2000).

2.4. Urban Air Pollutants

To date nearly 3000 different anthropogenic air pollutants have been identified most of them organic (including organometals). Combustion sources, especially motor vehicles, emit about 500 different compounds. However, only for about 200 of the pollutants have the impacts been investigated, and the ambient concentrations are determined for an even smaller number. This complex nature of air pollution, especially with respect to health impacts in cities, has prompted attempts to define the so-called indicators (Wiederkehr and Yoon, 1998), which condense and simplify the available monitoring data to make them suitable for public reporting and decision makers (Fenger, 1999).

According to Wiederkehr and Yoon (1998), the air pollutants can be divided into two groups : The traditional *Major Air Pollutants* (MAP, comprising sulphur dioxide, nitrogen dioxide, carbon monoxide, particles, lead and the secondary pollutant ozone) and the *Hazardous Air Pollutants* (HAP, comprising chemical, physical and biological agents of different types). The HAP are generally present in the atmosphere in much smaller concentrations than the MAP, and they appear often more localized, but they are - due to their high specific activity- nevertheless toxic or hazardous. Both in scientific investigations and in abatement strategies HAP's are difficult to manage, not only because of their low concentrations, but also because they are in many cases not identified (Fenger, 1999).

2.4.1. Sulphur Dioxide

Sulphur dioxide (SO₂) is the classical air pollutant associated with sulphur in fossil fuels (Fenger, 1999). It is a colorless gas that is readily soluble in water. Ambient SO₂ results largely from stationary sources such as coal and oil combustion, steel mills, refineries, pulp and paper mills and from nonferrous smelters (EPA, 2004).Oxidation of sulfur dioxide, especially at the surface of particles in the presence of metallic catalysts, leads to the formation of sulfurous and sulfuric acids (WHO,2000).Hence, SO₂ is a primary contributor to acid

deposition, or acid rain, which causes acidification of lakes and streams and can damage trees, crops, historic buildings and statues. In addition, sulfur compounds in the air contribute to visibility impairment in large parts of the country (EPA, 2004). Neutralization, by ammonia, leads to the production of bisulfates and sulfates (WHO, 2000).

The emission can be successfully reduced using fuels with low sulphur content e.g. natural gas or oil instead of coal. On large plants in industrialized countries desulphurization of the flue gas is an established technique (WHO, 2000).

2.4.2. Nitrogen Oxides

The major source of anthropogenic emissions of nitrogen oxides into the atmosphere is the combustion of fossil fuels from stationary sources (heating, power generation) and in motor vehicles (WHO, 2000). The main part of the nitrogen oxides, especially from cars, is emitted in the form of the nontoxic nitric oxide (NO). In ambient conditions, nitric oxide is rapidly transformed into the secondary "real" pollutant NO₂, which is soluble in water, reddish-brown in colour, and a strong oxidant, by atmospheric oxidants such as ozone. Most of the nitrogen dioxide is formed from the oxidation of nitric oxide in this way, although some is released directly from source (WHO, 2003). Simplified relationship of nitrogen oxides emissions with formation of NO₂ and other harmful reaction products including O_3 and PM is given in Figure 2.3.

Natural sources of nitrogen oxides include volcanoes (Mather et. al., 2004), oceans (Anderson et. al., 2003), biological decay and lightning strikes (Olivier et. al., 1998). In most urban locations, the nitrogen oxides that yield NO₂ are emitted primarily by motor vehicles, making it a strong indicator of vehicle emissions (including other unmeasured pollutants emitted by these sources). NO₂ (and other nitrogen oxides) is also a precursor for a number of harmful secondary air pollutants, including nitric acid, the nitrate part of secondary inorganic aerosols and photo oxidants (including ozone) (WHO, 2003).



Figure 2.3. Simplified relationship of NO_x emissions with formation of NO_2 and other harmful reaction products including O_3 and PM (WHO, 2003)

Nitrogen dioxide is an important atmospheric trace gas, not only because of its health effects but also because (*a*) it absorbs visible solar radiation and contributes to impaired atmospheric visibility; (*b*) as an absorber of visible radiation it could have a potential direct role in global climate change if its concentrations were to become high enough; (*c*) it is, along with nitric oxide (NO), a chief regulator of the oxidizing capacity of the free troposphere by controlling the build-up and fate of radical species, including hydroxyl radicals; and (*d*) it plays a critical role in determining ozone (O₃) concentrations in the troposphere because the photolysis of nitrogen dioxide is the only key initiator of the photochemical formation of ozone, whether in polluted or unpolluted atmospheres (EPA, 1993; EPA, 1995; WHO, 2000).

The emissions of nitrogen oxides can be reduced by optimization of the combustion process (low NO_x burners in power plants and lean burn motors in motor vehicles) or by means of catalytic converters in the exhaust (Fenger, 1999; Brunekreef et al., 2002).

2.4.3. Particulate Matter

Particulate air pollution is a mixture of solid, liquid, or solid and liquid particles suspended in the air (Dockery et al., 1997). Atmospheric particles vary in size, composition and origin. It is convenient to classify particles by their aerodynamic properties because: (1) they govern the transport and removal of particles from the air; (2) they also govern their deposition within the respiratory system; and (3) they are associated with the chemical composition and sources of particles. These properties are conveniently summarized by the aerodynamic diameter, which is the size of a unit-density sphere with the same aerodynamic characteristics (WHO, 2000). Figure 2.4 shows the size distributions of atmospheric particles and their formation and deposition mechanisms in the atmosphere. In the atmosphere the actual size distribution show quantitative differences with e.g. more pronounced mass peaks for fine particles in urban and suburban sites (Fenger, 1999).

Particulate matter originates from a variety of sources, including diesel trucks, power plants, wood stoves and industrial processes. As mentioned above, the size of suspended particles varies, from a few nm to tens of μ m. Mass and composition in urban environments tend to be divided into two groups: coarse particles and fine particles. Coarse particles have a diameter of more than 2.5 μ m and fine particles less than 2.5 μ m. In practical terms, a distinction is made between PM-10 (" thoracic" particles smaller than 10 μ m in diameter that can penetrate into the lower respiratory system), PM2.5 ("respirable" particles smaller than 2.5 μ m that can penetrate into the gas-exchange region of the lung), and ultrafine particles smaller than 100 nm which contribute little to particle mass but which are most abundant in terms of numbers and offer a very large surface area, with increasing degrees of lung penetration (EPA, 1997; Brunekreef et al., 2002).

The largest particles (coarse fraction) are generally emitted from sources such as vehicles traveling on unpaved roads, materials handling, and crushing and grinding operations, and windblown dust. As being large in size and mass, they



Figure 2.4. Ideal scheme of aerosol size distribution based on mechanisms of aerosol formation and extraction from the atmosphere (Seinfeld and Pandis, 1998)

removed from the atmosphere by gravitational settling. Fine particles (< 2.5μ m) result from fuel combustion (from motor vehicles, power generation, industrial facilities), residential fireplaces and wood stoves (EPA, Health and Environmental Effects of Particulate Matter, 1997). Fine particles divide into two ranges: "nucleation" and "accumulation". Particles smaller than 0.08 μ m are fall into nucleation range and are produced by gas to particle conversion at ambient temperature or combustion processes. The lifetime of these particles is very short as they rapidly coagulate and form bigger particles. Particles which have particle sizes from 0.08 to 2.5 μ m are fall into accumulation range. They are produced generally from condensation of low vapor pressure vapors from combustion process and coagulation of small particles. The residence time of these particles are longer than the particles in nucleation range.

A major contribution to particulate pollution in urban areas is believed to be attributed to traffic, and especially to emissions from diesel fuelled vehicles. Ultrafine particles emitted from petrol as well as diesel engines are formed at high temperature in the engines, in the exhaust pipe, or immediately after emission to the atmosphere (Palmgren et al., 2003).

2.4.4. Carbon Monoxide

Carbon monoxide (CO) is a colorless, odorless, tasteless and poisonous gas that is poorly soluble in water. The annual global emissions of carbon monoxide into the atmosphere have been estimated to be as high as 2600 million tonnes, of which about 60% are from human activities and about 40% from natural processes (EPA, 1991). Anthropogenic emissions of carbon monoxide originate mainly from incomplete combustion of carbonaceous materials. The largest proportion of these emissions are produced as exhausts of internal combustion engines, especially by motor vehicles with petrol engines. Other common sources of CO include various industrial processes, power plants using coal, and waste incinerators. Petroleum-derived emissions have greatly increased during the past few decades (Cullis et al., 1989). Some widespread natural nonbiological and biological sources, such as plants, oceans and oxidation of hydrocarbons, give rise to the background concentrations outside urban areas (WHO, 2000).

The ambient concentrations measured in urban areas depend greatly on the density of combustion powered vehicles, and are influenced by topography and weather conditions. In the streets, the carbon monoxide concentration varies greatly according to the distance from the traffic (Rudolf, 1994). In cities, automobile exhaust can cause as much as 95 percent of all CO emissions. These emissions can result in high concentrations of CO, particularly in local areas with heavy traffic congestion. Since the principal source of carbon monoxide in urban areas is motor vehicle exhaust, CO concentrations correlate closely with traffic volume (Seinfeld, 1986).Furthermore, carbon monoxide levels have a close quantitative and temporal association with the levels of other primary exhaust pollutants such as nitrogen monoxide and volatile organic compounds (Derwent et al., 1995; Dor et al., 1995).

2.5. Factors Affecting Air Pollution

Air quality in cities is the result of a complex interaction between natural and anthropogenic environmental conditions. The air pollution path of the urban atmosphere consists of emission and transmission of air pollutants resulting in the ambient air pollution. Each part of the path is influenced by different factors as shown in Figure 2.5. During transmission, air pollutants are dispersed, diluted and subjected to photochemical reactions (Mayer, 1999); hence the relations between emissions and resulting concentrations are by no means simple (Fenger, 1999).

As indicated above emitted air pollutants are dispersed and diluted in the atmosphere (Lyons and Scott, 1990). Chemical reactions producing, for example, photochemical ozone occur frequently during this transmission process (Alloway and Ayres, 1993; Bloomfield et al., 1996). Dispersion and dilution of air pollutants are strongly influenced by meteorological conditions, especially by wind direction, wind speed, turbulence, and atmospheric stability



Figure 2.5. Schematic illustration of the air pollution path in the atmosphere (Mayer, 1999)

(Mayer, 1999). Vignati et al. (1996) shows that for comparable emissions Milan has higher pollutants levels than Copenhagen, due to the high frequency of low wind speeds in Milan.

Topographical siting and urban structures like street canyons, for example, have a great effect on these meteorological parameters (Mayer, 1999). Topography (e.g. hills) may stop lateral transmission of air, while atmospheric stability (low mixing height) hinders vertical air movement.

Chemical reactions also depend on ambient weather conditions because they are influenced by shortwave radiation (e.g. formation of O_3), air temperature, and air humidity (Mayer, 1999).

2.6. Health Effect of Urban Air Pollutants

Studying the human health effects of air pollution has often been challenging, because it is difficult to isolate from other factors that also influence health, such as smoking, diet, and exposure to poor indoor air quality (Baldasano et al., 2003).

Exposure to elevated concentrations of ambient air pollutants causes adverse human health effects. A critical question in many urban environment is not whether the air in cities is unhealthy, but given that air quality is poor, how severely is health affected (Hall, 1996; Mayer, 1999).

In the literature, there are two methods which rely on to quantify the relationships between pollutants and specific effects. These are: human clinical experiments and epidemiological (or community exposure) studies. Animal toxicological studies can be used to indicate the existence of an effect, but not the rate of the effect in humans. Each method has limitations as a basis for quantifying the level of adverse effects anticipated in a given human population as a result of exposure. Some limitations are inherent in the method (Hall, 1996). In general, individuals responses to a given concentration of air pollution

dependant upon a number of factors: age and general health of the individual, type of pollutant, activity being undertaken when exposed to air pollution, and concentration and length of exposure to the pollutant (ACE, 2002).

There are number of studies in the literature to determine the health effects of ambient air pollutants. According to these studies, the concentrations of ambient air pollutants, which prevail in many urban areas, are sufficiently high to cause increased mortality, morbidity, deficits in pulmonary function and cardiovascular and neurobehavioral effects (Schwartz and Dockery, 1992; Dockery et al., 1993).

Adverse human health effects may be caused by a single pollutant or the synergistic effect, the acting together, of a number of pollutants. Individual pollutants have differing effects on human health. Table 2.3 summarizes the main effects of individual air pollutants on health. There are also concerns about the "cocktail" or mix of pollutants in urban air although little is known to date about the health effects of a combination of pollutants (ACE, 2002).

Children and elderly people are the most susceptible group to the air pollution. Studies estimates that tens of thousands of elderly people die prematurely each year from exposure to ambient levels of fine particles. The average adult breathes 13.000 liters of air per day; children breathe 50 percent more air per pound of body weight than adults. Because children's respiratory systems are still developing, they are more susceptible to environmental threats than healthy adults (EPA, 1997).

2.7. Other Impacts of Urban Air Pollution

In addition to health effect, urban air pollution has a series of impacts on materials, vegetation (including urban agriculture) and visibility. These impacts depend on the relevant levels, but also on other factors, for material damage (Tidblad and Kucera, 1998) thus on temperature and humidity and the possibility of interaction between different components (Fenger, 1999). Furthermore, being

a major source of regional and global atmospheric pollution and certain greenhouse gases by urban agglomerations or "supercities" constitutes another impact of urban air pollution (Mage et al., 1996).

Pollutant	Effects on human health
Sulphur dioxide (SO ₂)	Can cause respiratory problems, leading to chronic
	bronchitis, can cause narrowing of the airways and
	can affect asthmatics.
Carbon monoxide (CO)	Interferes with blood's capacity to absorb and
	circulate oxygen. Worsens emphysema, chronic
	bronchitis and other lung disease. Can affect those
	suffering from heart disease and can have impacts
	on the central nervous system.
Nitrogen dioxide (NO ₂)	Can cause respiratory disorders such as altered
	lung function, lung tissue damage, and increased
	prevalence of acute respiratory illness. Young
	children and asthmatics are most at risk.
Particulates (PM-10)	Can cause acute respiratory disorders and
	decrements in lung function and can lead to
	premature death.

Table 2.3. The effects of air pollution on human health (ACE, 2002)

2.8. Air Quality Monitoring

Nowadays, automated monitoring networks operate in many European cities providing detailed air quality information on a regular basis. There are several techniques available for monitoring gaseous pollutants (e.g. continuous monitoring using standard gas analysers, diffusive and pumped sampling using tubes filled with an appropriate adsorbent, grab sampling using canisters) and particulate matter (e.g. filtration and impaction). Each one of them can be

associated with a number of advantages and disadvantages that make it suitable or not for a specific application (Vardoulakis et al., 2003).

The response time, which is the time over which the sample is taken, is one of the major factors that determine the suitability of a method. Standard gas analysers are sufficiently sensitive and fast to give real time (i.e. typical response time: 1-2 min) measurements of CO, NO_x and O₃ concentrations. The results can then be averaged over short time periods and compared to the regulatory standards (Vardoulakis et al., 2003).

Diffusive samplers have a relatively long response time (e.g. typically from one/two days to four weeks), which makes them less suitable for observing atmospheric pollutants responsible for short-term health effects. On the other hand, long response times might be preferable when sampling substances like benzene, whose impact on human health is due to cumulative exposure. In these cases, peak concentrations are of minor concern and therefore diffusive samplers appear to be the ideal choice (Brown et al., 1999; Cocheo et al., 2000; Skov et al., 2001; Vardoulakis et al., 2001). Furthermore, diffusive samplers are portable devices and do not need electrical power supply, which makes them very suitable for spatial distribution measurements, air quality mapping, personal exposure studies, and detection of long-term pollution trends (Vardoulakis et al., 2003).

The total number of air quality monitoring stations or sampling locations within a city is limited by practical constraints. Since pollutant concentrations might vary with a factor of 5 from a street canyon to an urban background area (Palmgren and Kemp, 1999), the selection of monitoring/sampling locations becomes fundamental. In general, monitoring stations and/or samplers should be located near places of expected air pollution hotspots, but also must be reasonable with respect to population exposure over the averaging times associated with the regulatory values. Permanent air quality stations within a city maybe classified into two broad categories: (a) the roadside and (b) the urban background stations (Vardoulakis et al., 2003).

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Roadside stations are usually located on the pavement of busy streets, avenues or intersections, within few meters distance from the roadway and with their sampling head at 1.5–3 m height above ground. On the other hand, background stations are placed in parks or other urban locations (urban residential areas) away from road traffic (Vardoulakis et al., 2003).

The following general criteria were adopted for the selection of the stations:

1. The stations should be located within the city borders and very close to the population centroid.

2. The stations cannot be placed too close to local source emissions, particularly industrial, and they should be generally located in residential areas. 3. The daily correlation among the selected stations should be reasonably high ($\sim > 0.7$), to exclude outliers or monitors measuring "hot spots" instead of regional background concentrations.

4. The stations should provide a sufficient number of data ($\sim > 50\%$ of possible data must be valid for a given period of time).

5. To ensure an adequate representation of the population exposure, at least two stations are to be selected for each city (WHO, 2002: Health Impact Assessment of Air Pollution in the Eight Major Italian Cities).

2.9. The Previous Studies Concerning the Air Pollution of Ankara

Air pollution problem in Ankara has been known since 1926; people underlined the possible future air quality problems and suggested that Ankara was not a suitable urbanization region (Tinçer et.al., 1975; Yatin M, 1994).

Trace elements levels in Ankara were studied by Ölmez and Aras in 1977. Kut and Sarıkaya in 1981 studied the selenium levels in Ankara atmosphere. Other study in 1986 was performed by Sabuncu and colleagues in Middle East Technical University Campus in Ankara to determine trace element content. In another study, Savaş (1992) analyzed the chemical components in rain water of Ankara. A Nato Project, 'Investigation of the Causes of Air Pollution in Ankara for its Reduction', was studied by Durmaz et al., (1993). Kaya and Tuncel (1997) performed a detailed investigation of elemental and ionic composition of precipitation over a two year period. METU (1993) prepared an emission inventory for Ankara using the 1990 data. Health effect of CO exposure on traffic policemen who worked at the most crowded street junctions in Ankara was studied by Atimtay et al., (2000). Chemical composition of fine aerosols in Ankara atmosphere was investigated by Yatin et al., (2000). Recently, preliminary assessment of Ankara ambient air quality has been studied by Refik Saydam Center of Hygiene through MATRA Project (2004).

2.10. Recent Trends in Urban Air Quality Studies

In most of the industrialised world urban air pollution is now monitored routinely. Since 1974 WHO and UNEP have, within the `Global Environment Monitoring System' (GEMS), collaborated on a project to monitor urban air quality, the socalled GEMS/AIR (Fenger, 1999).

GEMS/AIR was implemented to strengthen urban air pollution monitoring and assessment capabilities, to improve validity and comparability of data among cities, and to provide global assessments on levels and trends of urban air pollutants, and their effects on human health. Approximately 170 monitoring stations in 80 cities in 47 countries participate in the programme. Most cities have established three monitoring sites: one in the industrial zone, one in a commercial area and one in a residential area. The majority of participants measure SO₂ and suspended particulate matter (55 cities in 33 countries) with other stations measuring NO_2 , CO, O_3 and Pb. Efforts are underway to improve data completeness and timeliness to make GEMS/AIR's data representative of world-wide urban air quality. Results have been published by UNEP and the WHO. In addition, long-term trends have been calculated, for all cities providing regular data (UNEP/GEMSAIR, 2005).

In the literature there are studies concerning the continuous measurements of gaseous and particulate pollutants at urban, suburban and rural areas (Mayer, 1999; Baldasano; 2003; Kukkonen et al., 1999; Kukkonen et al., 2000).

Since motor traffic is known as a major source of air pollution in most of the world cities (Mayer, 1999), most of the works in the literature rely on measurements on busy streets to determine the effects of motor traffic on ambient air quality (Hamilton et al., 1990; Joumard, 1993; Hamilton and Harrison, 1996; Harrison and Hamilton, 1999; Namdeo et al., 1999).

Source apportionment is also studied to help in air pollution management (Kumar et al., 2001; Hopke, 1980; Palmgren et al., 2003; Wahlin and Palmgren, 2000; Wahlin et al., 2001a; Swietlicki et al., 1996). Urban air pollution modeling studies also constitute a big part of the urban studies in the literature (Mensink et al., 2005; Xia and Shao, 2004; Borrego et al., 2003; Carras et al., 2002; Bogo et al., 2001; Karppinen et al., 2000; Valkonen et al., 1996).

CHAPTER 3

MATERIALS AND METHODS

Ankara, which is the capital of Turkey, has been urbanized faster due to migration from countryside to the city. 25% increase in population of Ankara from 1990 to 2000 is reported by State Institute of Statistics (SIS, 2004). As a result of high urbanization Ankara is growing towards the western parts. However, commercial and public services are located in central parts of the city. Therefore citizens travel more kilometers every day to reach these services which result in busy traffic axis in the city centre. Vehicles generally move slowly in busy traffic juctions and heavy traffic congestion can be observed during peak traffic hours. In Figure 3.1 the traffic congestion at Kızılay junction is illustrated.

3.1. Ambient Air Measurement Sites

This study is based on hourly CO, NO, NO₂, SO₂ and PM-10 data measured at three curbside stations which are placed at the most crowded street corners of Ankara, namely Iskitler, Kavaklidere and Kızılay, and eight non-curbside stations which are not under direct influence of traffic activities. The data are measured by the Ministry of Health, Refik Saydam Hygiene Center, between October 1999 and August 2000. Locations of measurement stations used in this study are given in Table 3.1.

All the measurement stations are chosen to represent the urban area of Ankara. The location of the measurement sites on the population map of Ankara is given in Figure 3.2. As can be seen from the figure all the stations are located on heavily populated parts of the city.

Table 3.1. /	Ambient air	measurement	stations

Station Type	Station Name			
Curbside Stations	İskitler, Kavaklidere,Kizilay			
Non-curbside Stations	Sihhiye, Küçükesat, Çankaya,			
	Beşevler, Demetevler, Keçiören,			
	Yenidoğan, Cebeci			



Figure 3.1. Traffic congestion at Kızılay junction (at 07:30 pm, August 2005)

A fully automatic mobile laboratory is used for measurements at curbside stations, but since there were only one such station measurements at curbsides are not continuous and are not simultaneous, but performed for approximately one week in each month. Because of this measurement strategy, comparison of hourly data generated at different curbside stations is not possible and assessments in this study are based on comparison of annual average data.



Figure 3.2. Locations of the ambient air measurement sites

However, measurements at non-curbsides are continuous as these stations are regular monitoring stations of Ankara Air Quality Monitoring Network. Although the data at curbside stations included both winter and summer months, no data are available for the summer season in non-curbside stations, because summer time measurements in Ankara Air Quality Network was initiated in 2003.

3.2. Ambient Air Measurement Procedures

Automated instruments are used for the ambient measurements of CO, NO, NO_2 , SO_2 and PM-10 of Ankara atmosphere.

The Environment S.A Model 48C Gas Filter Correlation (GFC) CO Analyzer is used to measure CO concentration with 15 minute intervals. The Model 48C is based on the principle that carbon monoxide (CO) absorbs infrared radiation at a wavelength of 4.6 microns. Because infrared absorption is a non-linear measurement technique, it is necessary for the instrument electronics to transform the basic analyzer signal into a linear output. The Model 48C uses an exact calibration curve to accurately linearize the instrument output over any range up to a concentration of 10,000 ppm.

NO and NO₂ are measured separately with 15 minute intervals by gas-phase chemiluminescence detection by the Environment S.A. Model AC 31M Chemiluminescence Nitrogen Oxide Analyzer. Chemiluminescence corresponds to an oxidation of NO molecules by ozone molecules ($NO + O_3 \rightarrow NO_2^* + O_2$). The return to a fundamental electronic state of the excited NO₂^{*} molecules is made by luminous radiation on a spectrum of 600 to 1200 nanometers ($NO_2^* \rightarrow NO_2 + hv$). The reaction chamber is separated from the detector by an optical filter which only lets pass the radiation of wavelengths greater than 610 nanometers, thus eliminating interferences due to hydrocarbons. In this instrument, NO and NO_x (NO + NO₂) are measured in two separate channels. In one of the channels NO is measured as described above and in the second channel first all NO₂ is reduced to NO at high temperature in a Mo oven, NO + NO₂ in the sampled air is measured with the same principle.

The DKK, Model GRH-72M Atmospheric SO₂ Analyzer is used to measure SO₂ concentration with one hour intervals. The Model GRH-72M is based on the solution-conductometry principle of JIS B7952 (1977) Continuous Analyzers for Sulfur Dioxide in Ambient Air. In this measurement system, the analyzer introduces the sample air into hydrogen peroxide solution acidified by sulfuric acid, and measures the quantity of sulfuric acid produced in the solution as the result of chemical reaction between the reagent and the ambient SO₂.

PM-10 is measured with one hour intervals by beta ray absorption principle (sealed radiation source ¹⁴⁷Pm) by the Model DUB-12 Atmospheric Dust Analyzer. The beta-ray absorption method is the most popular method of SPM measurements. An indicated value as a mass concentration is obtained from the increase of the absorption amount of beta-rays due to particles collection on filter-paper. The beta-ray analyzer is an instrument based on the principle that absorption rate of beta-ray increases in proportion to the mass of the substance when its quality remains constant and the ray at a low energy level irradiates the

substance. Thus the beta-ray irradiation on the particulate matter collection on the filtration paper gives information about its quantity.

3.3. Meteorological Station

There are two meteorological stations in Ankara operated by the Turkish State Meteorological Service, one located at İncirli, which is within the downtown area, and the other one at Etimesgut, which is at the outskirts of the city. As the measurements in this study performed at urban area, the meteorological data from the İncirli station is used. The İncirli meteorological station is located on 39° 57` in latitude and 32° 53` in longitude. Surface and aloft meteorological data obtained from the İncirli station consist of hourly measurement of wind speed, wind direction, temperature, precipitation and relative humidity and morning and afternoon mixing height values that are calculated from the radiosonde data.

3.4. Data Analysis Techniques

The concentrations of measured parameters are categorised hourly for each station. After categorizing the data means, standard deviations, medians and simple box plots of the data are constructed in order to show simple differences and similarities between pollutants and stations, while t-tests and ANOVAs are calculated to show the statistical significance of the differences and similarities.

Box-and Whisker plots are drawn to get a better summary of the distribution by utilizing relative position of data rather than exact values. Box-and Whisker plots consist of five-number summary of the data which are the minimum data point, the first quartile (Q_1) which is the 25th percentile of the data point, the median (Q_2) which is the 50th percentile of the data point, the third quartile (Q_3) which is the 75th percentile of the data point, and the maximum data point. Simplified explanation of box-and-whisker plot is given in Figure 3.3. Thus these five numbers display the full range of variation (from minimum to maximum), the common range of variation (from first to third quartile), and a typical value (the median).



Figure 3.3. Explanation of Box-and-Whisker plot

Temporal variations of each measured parameter in each station is depicted to identify the periods and sources of the pollutants that affect the each station. Scatter diagrams (Lotus and Excel) and simple correlations are also performed to assess linkages.

The relationship between air pollution and different meteorological factors is also investigated by simple regression analysis. Air pollution due to SO₂ and PM-10 over the whole urban Ankara is calculated by a proposed air pollution index (API). This API works as a quantitative scale to describe the magnitude of air pollution and its potential hazards and focuses on health. After calculation of API of Ankara during the measurement period, the relationship between API and meteorological factors are then analyzed one by one by simple regression analysis. Finally, multiple regressions are performed to construct a simple mathematical model to explain the effect of most correlated meteorological variables on API. The dispersion of the pollutants in the Ankara atmosphere is also determined in terms of ventilation coefficient which is the product of mixing height and average wind speed through the mixing layer.

Three different statistical methodologies namely pollution rose approach, Vossler et al., (1989) approach and surface trajectory approach are used to qualitative determination of apportion the source regions of SO₂ and PM-10 at two non-curbside stations. Furthermore, performance of the each methodology according to data used in this study is investigated.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. General Meteorological Features in Ankara

The city of Ankara is located on the Anatolian Plateau, therefore experiencing typical inland climate with dry and hot summers and cold and relatively wet winters. The summary of the meteorological parameters recorded at Incirli station during the 10- year period (1994-2003) are given in Table 4.1. The daily mean temperature in winter 2.4°C, and 22.8°C during the summer. The coldest month is January and the warmest is July. However, extreme temperatures can go down to -20°C in winter and close to 40°C in summer. The annual mean rainfall is about 420 mm, which is among the lowest in the country, and the annual mean relative humidity is 61%. The highest insolation is observed in May (1228 Wm⁻²), while the lowest is observed in January (614 Wm⁻²). Ankara is characterized by very slow winds, both in summer and winter. Average wind speed is approximately 2 m s⁻¹ in both seasons. This low annual wind speed was the main reason for extremely strong pollution episodes observed in the past.

The annual wind rose for Ankara during last 10-year period is given in Figure 4.1. Although the ordering of the prevailing wind directions changes in some months, generally the prevailing wind direction is NE (northeast). The other prevailing wind directions are ENE (east-northeast) and WSW (west-south west), respectively.

	Temperature ^a (°C)	Precipitation ^b (mm)	Wind Speed (m sec ⁻¹)
Winter	2.43 (-0.97-6.40)	118	2
Summer	22.83 (15.87-28.97)	70	2.3
Annual	12.4 (7.10-17.90)	420	2.0

 Table 4.1. Average long-term meteorological parameters recorded at İncirli

 Meteorological Station

^avalues in parentheses are ranges.

^baverage total precipitation amounts.



Figure 4.1. The annual wind rose of Ankara city (during 1994-2003 periods)

4.2. Traffic Counts

Motor vehicles are known as the major sources of CO, NO and NO₂ in many urban areas (Mage et al., 1996). Therefore, one expects good correlation between these pollutants and traffic volume. Unfortunately, traffic counts were not performed at the time of measurement that is used in this study.

There are two sets of data that are used in this study. One of these was generated at the Kızılay junction by EGO in 1992 and the second one was performed by Kuntasal at the Akay Tunnel in the year 2003. The counts at Kızılay were recorded hourly between 8 am and 6 pm, for one week in 1992 summer.

The counts at Akay Tunnel was performed with two hour intervals and three times a day (morning, noon and afternoon), 5 days in summer and 5 days in winter of the year 2003. Since, neither of these counts exactly match with the stations used in this study and time in which the measurements are performed, one-to-one correspondence is not expected with the concentrations of measured parameters. However, available traffic count data can be used to understand general features of traffic pattern, such fractions of traffic accounted for different vehicle groups, seasonal and diurnal variation in traffic density etc.

Contribution of vehicle categories to total number of vehicles at Kızılay junction and Akay tunnel are drawn in Figure 4.2. Personal cars (PC) have the highest contribution 51% and 70% and the second highest contributor is taxi with 35% and 18% at both Kızılay and Akay tunnel, respectively. These are followed by bus (6%), minibus (5%) and other vehicles (trucks and motorcycles) (4%) at Kızılay. However, the order changes at Akay tunnel that minibus (9%), other vehicles (2%) and bus (1%) contributes in the given percentages.

Determination of diurnal patterns of vehicle categories is important as they emit different pollutants in different amounts. Therefore diurnal variations of contribution of different vehicle categories in Kızılay and Akay tunnel are investigated. Contribution of PC is high in the morning (51%), relatively low in noon (46%) and reaches its maximum (58%) in the afternoon hours in Kızılay. Taxis are fairly similar (30%) in the morning and afternoon and higher (40%) in noon. Minibuses have uniform contribution (5%) during the day. Contribution of buses is highest (7%) in the noon, while morning contribution is slightly higher (5%) than afternoon. Other motor vehicles (trucks and motorcycles) are lowest (2%) in the noon, highest (8%) in the morning and relatively lower (4%) in afternoon hours.



Figure 4.2. Percent contribution of vehicle category at Kızılay junction (1992) and Akay tunnel (2004)

At Akay tunnel PC are uniformly increased throughout the day (63%, 72% and 74% during the morning, noon and afternoon hours). Taxis are highest in the morning (22%), relatively lower (18%) in the noon and lowest in the afternoon (15%). Minibus is fairly similar (10%) in the morning and afternoon and lower (8%) in the noon. Contribution of buses is lowest (0.5%) in the morning and relatively higher (1%) in the noon and afternoon. Other motor vehicles are highest (4%) in the morning, lower (1%) in the noon and lowest (0.5%) in the afternoon hours.

A report prepared by State Institute of Statistics (SSI,1998), based on the fuel consumption types of PCs, showed that 94%, 6% and 1% of PCs are gasoline, diesel and liquefied petroleum gas (LPG) powered, respectively. Most of the taxis in Ankara are powered with LPG. By taking into account these statements, average daily vehicle fleet at Kızılay is composed of 69% gasoline, 19% LPG and 12% diesel powered vehicles, while 54% gasoline, 35% LPG and 11% diesel powered vehicles forms the daily average vehicle fleet in Akay tunnel.

As can be seen from Figure 4.3, gasoline powered vehicles and LPG constitutes nearly 90% of total contribution. Contribution of diesel powered vehicles is around 10% at the two records and relatively higher in the morning hours.

No traffic counts are available in Kızılay junction for winter period. However, Akay Tunnel counts have showed that the average number of vehicles recorded in tunnel is 922 vehicle/hour and 561 vehicle/hour during winter and summer, respectively. Recording lower number of vehicles in summer is due to lower number of people staying in the city during the summer. People usually take their vacation in summer time in Ankara. Therefore both increased number of vehicles and poor meteorological conditions (will be discussed later) in winter periods favor pollution episodes in Ankara.

Although the traffic count in Kızılay junction (1992) does not represent the real traffic pattern of Kızılay at the time of measurements conducted, diurnal trends of vehicle counts do not change much (rush-hour peaks). Therefore to see the

effect of traffic volume on measured concentrations of traffic related pollutants, namely CO,NO and NO₂, at Kızılay station, Kızılay (1992) traffic counts are used. Diurnal variations of these traffic related pollutants and total traffic counts are drawn in Figure 4.4.



Figure 4.3. Percent contribution of vehicle category based on fuel consumption at Kızılay junction (1992) and Akay tunnel (2004)

Concentrations of CO and NO vary with the vehicle counts nearly at the same time intervals. However, dependence of NO_2 on traffic volume is not as clear as CO and NO. This is due to secondary nature of NO_2 , because most of the NO_2 is not directly emitted by vehicles, instead NO is emitted and then it is oxidized to NO_2 in the atmosphere. Furthermore meteorological variables, especially solar flux and presence of ozone determine the oxidation rate of NO₂.

SO₂ and PM-10 also show good correlation with traffic volume. However, sulfur content of gasoline in Ankara is 0.005%, while this is insignificant compared to S content of diesel fuel which is 0.7% (TÜPRAŞ). Therefore, SO₂ and PM-10 concentrations and total vehicle count and diesel vehicle counts are drawn in Figure 4.5.The better correlation is observed for concentrations and diesel vehicle counts.

Although sulfur content of gasoline is very low, nearly 54% of the total vehicles are gasoline powered and therefore their contribution to observed SO₂ levels at heavy traffic junctions is also expected.

4.3. General Characteristics of the Data

This study involves statistical evaluation and interpretation of concentrations of inorganic gaseous pollutants, namely CO, NO and NO₂, measured at three busy street corners with 15 minute intervals and concentrations of SO₂ and PM-10 measured not only at three busy street corners but also at eight regular stationary monitoring stations with hourly intervals, between October 1999 and August 2000.

The stations located at İskitler, Kızılay and Kavaklıdere corners will be referred to as "**curbside stations**" and regular monitoring stations will be referred to as "**residential stations or non-curbside stations**" throughout the manuscript, to differentiate between the two station groups.



Figure 4.4. Traffic and concentrations of CO, NO and NO₂ at Kızılay junction



Figure 4.5. Variation of SO₂ and PM-10 concentrations with respect to vehicle category at Kızılay junction

4.3.1. Curbside Stations

Curbside stations were located at İskitler, Kavaklıdere and Kızılay junctions. Unlike in residential stations, pollutant concentrations measured in these stations are under strong influence of traffic emissions at the immediate vicinity of the measurement point. Summary of the descriptive statistics of the gaseous and particulate pollutants at each curbside station is given in Table 4.2. The columns in the table include the number of data points, arithmetic mean, associated standard deviation, geometric mean and the median values.

Although there are large differences between arithmetic and geometric mean concentrations, geometric mean and median concentrations of measured parameters are fairly similar. This is a typical behavior of the most of the atmospheric data in the literature, which are generally log-normally distributed (Ott, 1990).

Arithmetic mean values of measured parameters in each curbside are higher than corresponding median and geometric mean values. This is typical for the right skewed distributions and suggests that all of the measured parameters at curbside stations depict a right skewed distribution. The frequency histograms of CO concentrations at each curbside station are given in Figure 4.6. The upper tail of the distribution in all histograms extends toward large values, which indicates that the distribution is positively (right) skewed. Skewness is a value to measure the degree of asymmetry in a distribution around its arithmetic mean. In ideal Gaussian distribution, the value of skewness is zero which indicates that the values of arithmetic mean, median and mode are identical. Non-zero values of skewness indicate deviation from Gaussian distribution. The skewness values of all measured parameters are calculated by using Stat Graphics program and found positive which support the previous finding of measured parameters are positively (right) skewed.

			Geometric					
Station	Parameter	Ν	Average	STD	Mean	Median		
Station	Falameter	IN	(µg m⁻³)	(µg m⁻³)	(µg m⁻³)	(µg m⁻³)		
	CO	1771	8369.4	6642	5856.4	6908		
Ë	NO	1589	285.92	253.81	169.51	222		
İSKITLER	NO ₂	1590	79.08	99.64	50.66	45.5		
İSK	SO ₂	1729	128.67	91.01	97.77	108		
	PM-10 1691		95.49	76.3	73.84	74		
	CO	1095	7056.1	5065	4889.2	5782		
KAVAKLIDERE	NO	1028	157.43	130.93	101.32	128.25		
	NO ₂	1028	40.83	32.12	34.59	34.75		
AVAI	SO ₂	1056	77.25	59.68	61.28	63		
X X	PM-10	999	61.96	42.32	50.53	50		
	CO	1044	6477.3	3934.7	5245	5752.3		
≻	NO	957	248.18	243.48	153.15	167.75		
KIZILAY	NO ₂	957	107.1	111.42	67.35	51.5		
KI	SO ₂	805	130.26	94	100.98	112		
	PM-10	720	79.65	66.66	59.6	60		

 Table 4.2. Arithmetic mean, standard deviation, geometric mean and median

 values of measured parameters

As pointed out before, log-normal distribution of atmospheric data are frequently reported in the literature (Georgopoulos and Seinfeld, 1982; Mage and Ott, 1984; Kao and Friedlander, 1995; Burkhardt et al., 1998). Consequently, positive skewness observed in concentrations of all parameters at curbside stations could be owing to their log-normal distributions. However, positive skewness in the data does not necessarily indicate a log-normal frequency distribution. To understand if the parameters measured at curbside stations are log-normally distributed, Kolmogorov-Smirnov (K-S DN) statistic, which is a

goodness of the fit test, is applied, with priory assumption that the distributions are log-normal. Testing distributions is important because, if the pollutant concentrations are log-normally distributed, log transformation of the data could improve statistical data treatment, but if the distributions are not log-normal, log transformation can not be rationalized. Results of the goodness of the fit test showed that, distributions of the concentrations of all measured parameters at all curbside stations are not log-normal with statistical confidence > 0.95, except for NO₂ concentration at Kavaklidere station. With this conclusion, log transformations of data were not considered as an option to improve statistical data treatment.

4.3.2. Non-curbside Stations

There are 8 routine air quality monitoring stations in Ankara, which are operated by the Ministry of Health, Refik Saydam Hygiene Center, which are located within residential areas at Sihhiye, Küçükesat, Çankaya, Beşevler, Demetevler, Keçiören, Yenidoğan and Cebeci. The only parameters measured in these stations are SO₂ and PM-10 mass. Particulate matter and SO₂ are measured on an hourly basis in seven of these stations. At Cebeci station however, measurements are daily average concentrations. The descriptive statistical summary of the measured parameters (SO₂ and PM-10) is given in Table 4.3.

As can be seen in Table 4.3 arithmetic mean of all measured parameters are higher than the median values. For that reason, we can say that the distributions of all measured parameters at the eight regular monitoring stations are positively skewed, as three curbside stations. This finding is supported by the calculated skewness values of non-curbside stations which are greater than zero.



(b)



Figure 4.6. Frequency histograms for CO at (a) İskitler, (b) Kavaklıdere and (c) Kızılay

SO₂ and PM-10 frequency histograms for non-curbside stations are studied and the frequency histograms of these parameters at Sihhiye station are given in Figure 4.7. As indicated before, SO₂ and PM-10 concentrations show right skewed distribution at Sihhiye like other non-curbside stations.

K-S DN statistic results of SO_2 and PM-10 concentrations at non-curbside stations show that log-normal distribution does not fit the data set with 99 % confidence level.

Station	Parameter	N	Average (µgm ⁻³)	STD (µgm ³)	Geometric mean (µgm ⁻³)	Median (µgm ⁻³)
SIH	SO ₂	2369	70.27	47.79	55.99	60
	PM-10	2397	87.97	71.4	66.9	70
KES	SO ₂	2388	60.83	46.02	47.65	47
INEO	PM-10	2261	103.82	78.95	82.02	85
ÇAN	SO ₂	2412	45.74	38.9	34.51	32
Ϋ́́Ϋ́	PM-10	2401	51.98	42.22	39.33	40
BEŞ	SO ₂	2249	100.57	83.24	74.38	79
DLÇ	PM-10	2184	108.02	103.27	74.86	80
DEM	SO ₂	1146	58.72	49.62	40.18	44
DEIW	PM-10	1642	116.33	110.44	79.79	85
KEÇ	SO ₂	2260	76.90	77.84	52.18	55
ΝĽϘ	PM-10	2350	93.68	95.91	60.6	60
YEN	SO ₂	2338	64.73	65.45	42.08	41
	PM-10	2271	105.52	110.71	67.32	69
CEB	SO ₂	74	24.90	14.01	21.58	21
	PM-10	74	43.19	24.27	37.54	36

Table 4.3. Arithmetic mean, standard deviation, geometric mean and medianvalues of measured parameters at regular monitoring stations



Figure 4.7. Frequency histograms of (a) SO₂ and (b) PM-10 concentrations at Sihhiye station

4.4. Comparison of Concentrations of Parameters between Stations

Comparison of concentrations of parameters measured at different stations can provide preliminary information on relative importance of source strengths and meteorology on the measured concentrations.

Since strengths of sources affecting different stations are unlikely to be similar throughout the city, concentrations of parameters that are primarily affected from variations in source strengths can be similar in some of the stations but not in all. However, if the concentrations of a parameter are primarily determined by meteorological factors, their concentrations are expected to be fairly similar in most of the stations. Since generally concentrations of air quality parameters are determined by both emission strength and meteorology, complete uniformity in all stations due to influence of meteorology or very drastic differences due to variations in source strengths should not be expected, and because of this, comparison only can not be used as a conclusive evidence for meteorology or source dependence of measured concentrations of parameters. Furthermore it is important to note that the standard deviations of measured parameters at both curbside and non-curbside stations (Table 4.2 and Table 4.3, respectively) are relatively high (ranging from 50-95% of the average), indicating that the pollutant concentrations at these stations are most likely a complex function of sources and meteorological conditions.

Comparison also provides information on the air quality level in different parts of the city. In this study mean and median concentrations of measured parameters are compared for the two reasons discussed in previous paragraphs. Since almost all the measured pollutants at each station show skewed distribution, the median represents the data than does the mean. The median is insensitive to extreme scores therefore it is a better measure of central tendency than is the mean. However, in distributions that are not badly skewed the mean and the median are nearly the same (Brase, 1991).

Statistical significance of similarities or lacks of similarity between parameters are tested using student-t test for means and using Mann-Whitney test for medians. In the following discussion the term "**different**" refers to statistically significant difference and the term "**similar**" refers to lack of statistically significant difference between concentrations of parameters compared within 95% confidence level.

Box and Whisker plots of CO, NO, NO₂, SO₂ and PM-10 concentrations measured at three curbside stations are depicted in Figure 4.8 (see definition of box-and-whisker plot in section 3.4). Other stations are not included in the







figure, because many of these parameters are not measured in those noncurbside stations. Comparison of SO₂ and PM-10 concentrations between all curbside and non-curbside stations will be discussed in subsequent sections.

Concentrations of all pollutants in all three curbside stations are statistically different from each other. Pollutants measured in this study are strongly influenced from motor vehicle emissions at curbside stations. The difference between concentrations indicates different traffic density in each of them. The curbs at which these three stations are located are among the most crowded ones in Ankara, however traffic density do change at İskitler, Kızılay and Kavaklıdere junctions, resulting in different emissions and hence different concentrations. However, concentrations measured at Kavaklıdere station is smaller than concentrations measured in the İskitler and Kızılay stations. Concentrations measured in the later two stations are more comparable (but they are not statistically similar). This pattern exists for all measured parameters and signifies the importance of traffic intensity in determining measured concentrations in these curbside stations.

Box and whisker plots for SO₂ and PM-10 concentrations measured in all stations are given in Figure 4.9. The median PM-10 values in all stations vary between 36 and 85 µg m⁻³. The highest PM-10 concentrations are measured at Küçükesat, Beşevler and Demetevler stations, whereas the lowest values are measured at Çankaya, Kavaklıdere (curbside) and Keçiören stations. Statistical differences of median PM-10 concentrations between different stations are evaluated using Mann-Whitney test and results are depicted in Figure 4.10.The non-curbside stations can be separated into two groups depending on the similarity of PM-10 concentrations. The first group consists of Sihhiye, Esat and Beşevler stations. The second group includes Demetevler, Keçiören, Yenidoğan and Çankaya stations. The PM-10 concentrations measured in the stations making up each group are statistically similar, but concentrations measured in these stations are statistically different from the stations in the other group.





Figure 4.9. Box and Whisker plots for (a) SO₂ and (b) PM-10 concentrations measured at all stations (curbside and residential stations)

The median SO₂ values in all stations vary between 21 μ g m⁻³ at Cebeci station and 112 μ g m⁻³ at Kızılay station (curbside). Statistically significant similarities and differences in SO₂ concentrations measured in all stations are depicted in Figure 4.11. As in the case of PM-10, monitoring stations in Ankara can be separated into two groups based on the statistical similarities of SO₂ data. Sıhhıye (60 μ g m⁻³), Küçükesat (47 μ g m⁻³) and Beşevler (79 μ g m⁻³) stations have similar median SO₂ concentrations and make up the first group. The second group consists of Demetevler, Keçiören, Yenidoğan and Çankaya stations, where SO₂ concentrations are 44, 55, 41 and 32 μ g m⁻³, respectively.

It should be noted that stations included in two groups are the same for both PM-10 and SO₂. The first group which includes Sihhiye, Beşevler and Küçükesat represent areas in the city with high SO₂ and PM-10 concentrations and the second group includes stations located at Demetevler, Keçiören, Yenidoğan and Çankaya. This group represents areas in the city with relatively low SO₂ and PM-10 concentrations.

There are two interesting points that should be noted in Box and whisker plots (Figures 4.9.a and 4.9.b). First, the PM-10 concentrations are rather similar in curbside and non-curbside stations. This is unexpected, because in urban atmosphere, traffic emissions is a significant component in PM-10 levels. Since curbside stations are under strong influence of traffic emissions, as well as other emission types, such as emissions from combustion sources, resuspended soil and resuspended road dust, one would expect higher concentrations of PM-10 at curbside stations. However this is not observed and indicates that traffic PM-10 emissions are not dominating even at the curbside stations on an annual base. Although this statement is correct for a long term, the situation may be different at different seasons, because all PM-10 sources in an urban airshed are expected to have different strengths in summer and winter seasons. Summer and winter median PM-10 concentrations at all stations are depicted in Figure 4.12. The PM-10 concentrations are higher at non-curbside stations during winter season. Since PM-10 emissions from combustion sources are high in winter, it can be concluded that, during winter season, combustion is more important than traffic as a PM-10 source. Please note that 67% of the

PM-10	SIH	ESA	ÇAN	BES	DEM	KEÇ	YEN	CEB
SIH		S	D	S	D	D	D	D
ESA	S		D	S	D	S	D	D
ÇAN	D	D		D	S	S	S	D
BES	S	S	D		D	D	D	D
DEM	D	D	S	D		S	S	D
KEÇ	D	S	S	D	S		S	D
YEN	D	D	S	D	S	D		D
CEB	D	D	D	D	D	D	D	

Figure 4.10. Statistical significance of the differences between observed PM-10 concentrations in non-curbside stations (**S**: statistically similar median concentrations; **D**: statistically different median concentrations)

SO2	SIH	ESA	ÇAN	BES	DEM	KEÇ	YEN	CEB
SIH		S	D	S	S	D	S	D
ESA	S		D	S	S	D	D	D
ÇAN	D	D		D	D	D	D	D
BES	S	S	D		D	D	D	D
DEM	S	S	D	D		S	S	S
KEÇ	D	D	D	D	S		S	S
YEN	S	D	D	D	S	S		S
CEB	D	D	D	D	S	S	S	

Figure 4.11. Statistical significance of the differences between observed SO₂ concentrations in non-curbside stations(**S**: statistically similar median concentrations; **D**: statistically different median concentrations)

residences in Ankara are still being heated by burning coal (Ankara Municipality, unpublished data), which means although a substantial effort was spent to convert heating units to natural gas, coal combustion is still an important source of combustion related pollutants in the city. Median PM-10 concentrations in summer are significantly higher at curbside stations compared to non-curbside ones. Obviously, during summer, when PM-10 emissions from combustion decrease, traffic becomes an important source of PM-10.

On an annual base, SO₂ concentrations are higher at the curbside stations than concentrations observed at non-curbside stations. This is also not expected, because SO₂ is primarily a combustion related pollutant. The SO₂ emissions from traffic is not expected to be high. However, higher SO₂ concentrations at curbside stations suggests that traffic is an important source of SO₂, at least in regions, which are close to major roads with fairly high traffic density. An assumption of low SO₂ emissions from traffic was based on emission data from gasoline powered vehicles. Diesel fuel do contain S in it and consequently SO₂ emissions from diesel powered vehicles is not as low as SO₂ emissions from gasoline powered vehicles. The diesel fuel used in Ankara contains 3000-7000 ppmw (TÜPRAŞ) S while this ratio is lower than 500 ppmw in most of the European countries. Higher SO₂ observed at curbside stations compared to non-curbside ones indicate that emissions from diesel powered vehicles is an important source of SO₂ at areas close to roads with high traffic density.

Median SO₂ concentrations measured in all stations during summer and winter seasons are given in Figure 4.13. The patterns observed are fairly similar to the patterns observed in PM-10 concentration. During winter, SO₂ measured at curbside and non-curbside stations are not significantly different, indicating that SO₂ concentrations over most parts of the city are determined by emissions from residential heating. However, SO₂ concentrations measured in summer are significantly higher at curbside stations. As in the case of PM-10, this is attributed to decrease in residential heating emissions in summer, and indicates that SO₂ concentrations at districts close to major roads is probably determined by diesel emissions.



PM-10 Winter



Figure 4.12. Comparison of (a) summer and (b) winter median concentrations of PM-10 at all stations



SO2 Winter



Figure 4.13. Comparison of (a) summer and (b) winter median concentrations of SO_2 at all stations

4.4.1. Comparison with Literature

There are two ways to assess the air quality level in an urban air shed; (1) by comparing measured concentrations with regulatory standards that are effective in the country, the region or the whole globe and (2) by comparing measured concentrations with data reported from comparable sites. Although comparison with regulatory standards is the simplest way to determine air quality level in a city, it should be noted that standards are not static and changing (decreasing) almost continuously in time. For example, air quality in Ankara can be described as fairly good, based on Turkish Air Quality Regulation (TAQR) today, but the same levels of pollutants can be defined as poor air quality some years later when standards decrease, or when they are compared with EU standards or WHO guideline values. Comparison of measured concentrations with data reported from comparable sites in other parts of the world can provide an alternative way to assess the level of air quality in the city.

In order to assess the state of pollution in Ankara, comparison of the curbside stations with regulatory standards (Turkish Air Quality Regulatory Standards (TAQRS), EU Air Quality Directives (AQD) and WHO Air Quality Guidelines (AQG) and some world cities is depicted in Figure 4.14.

The cities selected for comparison included Cape Town (South Africa) (CEROI, 2001), Johannesburg (South Africa) (WRI-WB, 2001), Brussels (Belgium) (AIRBASE, 2002), Helsinki (Finland) (AIRBASE, 2002), Paris (France) (AIRPARIF, 2002), Berlin (Germany) (AIRBASE, 2002), Stuttgart (Germany) (AIRBASE, 2002), Athens (Greece) (AIRBASE, 2002), Milan (Italy) (AIRBASE, 2002), Amsterdam (Netherlands) (AIRBASE, 2002), St Petersburg (Russia) (OECD, 2001), Sevilla (Spain) (AIRBASE, 2002), Toronto (Canada) (NAPS/Min.Env, 2002), Chicago (US) (EPA, 2001), Los Angeles (US) (EPA, 2001), New York (US) (EPA, 2001), Santiago (Chile) (Cepis-CONOMA, 2001), Taiyuan (Chinia) (WRI, 2001), Guiyang (Chinia) (WRI, 2001),Hong Kong (Chinia) (EPD, 2001), Tbilisi (Georgia) (CEROI, 2001),Bombay (India) (WRI, 2001), Singapore (Min.Env-Sing., 2001), Melbourne (Australia) (NSW-EPA,

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Figure 4.14. Comparison of measured concentrations with the literature

2001). These cities are randomly selected from Baldasano et al., (2003) to have a reasonable variability in PM-10, SO_2 and NO_2 concentrations.

The PM-10 concentrations measured in most curbside and non-curbside stations in Ankara are significantly higher than corresponding values reported for other cities around the world. Generally high PM concentrations in Turkey are attributed to arid nature of the region and high resuspended dust component in the atmospheric particle mass. However, this explanation does not work this time, because some of the cities used for comparison, such as cities in Asia, are under strong influence of dust events. PM-10 concentrations reported for those cities are lower than values measured in Ankara. Consequently, high PM-10 levels measured in this study are due to high anthropogenic emissions rather than high natural emissions.

The long term regulatory standard in TAQR is 150 μ g m⁻³ (should be compared with annual average) for PM-10. Based on this, PM-10 levels in the city are all below the standard and air quality in terms of particles is fairly good. However, the long term EU standard for PM-10 particles is 40 μ g m⁻³. This value will be the one that will be enforced if Turkey joins EU. Based on comparison with EU standard, none of the stations used in this study comply with the directive, indicating poor air quality in terms of atmospheric particles.

The SO₂ levels measured in curbside and non-curbside stations are higher than those measured in other cities around the world. There are three exceptions to this general trend. Concentrations of SO₂ measured in two Chinese cities, namely Taiyuan (211 μ g m⁻³), Guiyang (424 μ g m⁻³) and in Tbilisi (Georgia) (190 μ g m⁻³) are higher than those measured in Ankara. It is well documented that Chinese cities suffer from poor air quality (Zhang, 1991; Zhang et al., 1999; Quin et al., 2001; Xi et al., 2000), which means lower SO₂ concentrations in Ankara compared to Chinese cities is not a relief. The SO₂ concentrations measured in all stations are lower than the long-term standard given in TAQR, but as in the case of PM-10, they are higher than standard given EU directive and WHO guideline value.

Only NO₂ concentrations measured at the curbside stations are compared with corresponding values from other cities, because this parameter is not measured in non-curbside stations. The NO₂ levels measured at Kızılay and İskitler junctions are higher than values reported for other cities, but NO₂ at Kavaklıdere station are comparable with those measured in world cities. The NO₂ levels at Kızılay are even higher than the long term standard given in TAQR, whereas NO₂ concentrations in İskitler are not. Annual NO₂ levels at Kızılay and İskitler are both higher than long term NO₂ standard in EU directive and WHO guideline value. However, the NO₂ level at Kavaklıdere station is comparable with those standards.

The comparison clearly demonstrated that , although various actions related fuel use are taken to improve air quality in Ankara, the city is far from having good air quality. Concentrations of all pollutants measured in this study are
significantly higher than concentrations reported for cities where air pollution regulations are strongly enforced. Measured concentrations are also higher than long term standards effective in EU limit values and WHO guideline values. Today it is believed that the air quality in Ankara (and also in other Turkish cities) have improved significantly after natural gas started to be used as fuel in space heating. The comparison of measured concentrations with concentrations measured in other cities, and with EU and WHO standards demonstrates that this statement may be true, but the levels of pollutants did not decreased enough to state that Ankara have a good air quality. In other words the air quality in Ankara is better than it was before, but not good enough. This conclusion should be expected, because 67% of the residences in Ankara still use coal as fuel for residential heating. Conversion of these to natural gas would improve the air quality some more, but such conversion would be difficult and costly, because most of these residents are in squatter settlements and semi-squatter settlements districts with limited infrastructure.

4.4.2. Comparison with Rural Stations

Air pollution levels in urban areas should be compared with the pollution levels in rural areas to asses the contribution of air pollutants transported over long distances from adjacent regions or countries or air pollutants produced locally. It is well-known that concentrations of most of the air pollutants in rural areas are lower than that of urban areas; however comparison of the two sites provides one with an understanding of the reasons that cause the concentration differences between rural and urban sites.

In this study, two rural stations located in different parts of Turkey, namely Uludağ and Çubuk stations are used. Uludağ station is located at Sarıalan region of Uludağ Mountain at approximately 20 km south of the city of Bursa. Çubuk station is 50 km away from the city of Ankara and 12 km away from the nearest town.

As can be seen from Figure 4.15 SO₂, PM-10, NO and NO₂ concentrations measured at rural stations are lower than concentrations of these parameters

measured at urban stations (curbside and non-curbside stations), which is an expected result, because these measured parameters are generally due to local sources in urban areas. As there are not any local sources, lower concentrations are observed in rural stations. Rural stations are mostly affected by long range transport of pollutants. While transporting, pollutants are removed by chemical reactions and other removal mechanisms like wet and dry deposition resulting in lower concentrations in rural areas.

However, the differences between the urban and rural concentrations are not same for all parameters. Urban concentrations of SO₂ and NO₂ are in the order of ten higher than the corresponding rural concentrations. The highest difference between the urban and rural concentrations is observed for NO, which is in the order of 100, due to very rapid oxidation of NO to NO₂. While transporting of air masses to the rural areas, most of the NO in air masses is rapidly transformed into NO₂ (Manahan, 2001). However, oxidation of SO₂ to SO₄²⁻ and NO₂ to NO₃⁻ is relatively low (Sasaki et al., 1988).

Concentrations of gaseous pollutants (SO₂, NO and NO₂) measured in rural areas are very low compared to the corresponding concentrations in urban areas. Significant differences of urban and rural concentrations of gaseous pollutants indicate anthropogenic origin. Concentrations of PM-10, on the other hand, are relatively similar in both urban and rural areas. The urban concentration of PM-10 is only a factor of 2-3 higher than the corresponding rural concentrations. This finding indicates that natural origin of particulate matter (resuspended dust) is effective not only on rural areas but also on urban areas. Resuspended dust in rural areas is due to erosion of soil and rocks by wind while in urban areas the main sources are construction facilities and motor vehicles traveling on unpaved roads in the city.



Figure 4.15. Comparison of measured parameters with rural stations

4.5. Temporal Variations

4.5.1. Seasonal Variations

Three source groups namely domestic heating, vehicular traffic and crustal can be thought as the main sources of pollutants in Ankara atmosphere. These potential sources do not affect the stations at the same level throughout the year or even in a day. Investigation of temporal variations in concentrations of measured parameters can be useful to identify the periods in which measured concentrations are affected from different emission types.

Seasonal variations of parameters measured at curbside stations are given in Table 4.4 and visually shown in Figure 4.16. As can be seen from both the table and the figure, parameters show significant differences between summer and winter seasons.

Data for the three curbsite stations are available for eight months. Measurements were not performed in March, May, July and September. However, eight months is sufficient to establish seasonal patterns. It should also be noted that, measurements were not performed simultaneously in all three stations, but this was not a serious drawback as seasonal patterns were based on annual average values.

Carbon monoxide, NO and NO₂ show a similar monthly pattern in all three curbside stations. For these three parameters, concentrations are high in winter and low in summer (June and August). But these differences between summer and winter months are not sharply defined. There are some months in the winter in which concentrations are as low as those observed in summer. These three parameters are well documented tracers for motor vehicle emissions. Consequently, monthly variations in CO, NO and NO₂ concentrations should be related with (1) monthly variation in traffic emissions and (2) meteorology.

Both of these factors, namely variations in emissions and meteorology favor high concentrations of traffic related pollutants in winter months. Observed low

Table 4.4. Winter and Summer Average Concentrations and Median Values of Measured

Parameters at Curbside stations

SUMMER**	Median	1 3582.00	9 253.50	2 108.75	8 124.00	t 60.00	3 2354.13	65.50	3 28.75	0 55.00	7 37.50	9 4791.25	0 212.00	0 150.25	88.00	2 40.00
	STD	3475.21	300.49	157.22	100.28	28.14	2203.43		41.73	22.70	16.47	3006.19	307.90	123.80	62.65	21.82
	Average	4436.24	368.58	173.19	142.86	64.13	2803.92	81.23	37.74	53.59	38.77	5241.98	307.45	156.67	101.71	44.40
	Count	458	411	411	455	461	208	151	151	250	250	416	367	367	418	333
WINTER*	Median	8156.00	180.13	43.25	100.00	89.00	7905.25	134.50	38.00	71.00	60.00	6455.38	158.13	46.38	132.00	90.00
	STD	7004.70	214.77	25.46	88.69	80.64	5117.71	113.31	31.66	67.35	47.65	4253.07	183.74	90.23	111.02	76.64
	Average	10047.30	238.52	47.69	122.88	105.93	8494.16	154.12	43.04	86.81	71.58	7295.56	211.32	76.27	161.11	109.98
	Count	1197	1058	1059	1154	1110	765	762	762	743	641	628	590	590	387	387
		00	Ŋ	N02	S02	PM10	00	Q	N02	S02	PM10	8	Ŋ	N02	S02	PM10
		וצאודרבא				KAVAKLIDERE			, YAJIZIA							

* Winter season includes months between October and April ** Summer season includes months between May and August



Figure 4.16. Monthly Average Concentrations of Measured Parameters at Curbside Stations

summer concentrations of CO, NO and NO_2 are consistent with summer – winter difference in traffic emissions, because as discussed previously in the manuscript, there are fewer vehicles on Ankara roads during summer season. The difference is approximately 35%. This naturally leads to higher traffic emissions and higher concentrations in winter season.

Similarly, micrometeorological factors also favor higher concentrations of pollutants in winter. Mixing height is known to be lower in winter (will be discussed in more detail later in the manuscript), which leads to confinement of emissions into a smaller volume, which in turn results in higher concentrations of all pollutants, including the ones emitted from traffic, in winter period. Observed high concentrations of CO, NO and NO₂ in winter period is probably due to a combination of these two factors operating in Ankara.

Among all non-curbside stations these three parameters are measured only in Sihhiye station on hourly basis between November 2000 and October 2001 period. The monthly variation of these measured parameters at Sihhiye station is depicted in Figure 4.17. Carbon monoxide, NO and NO₂ show a slightly different pattern at the Sihhiye station. Although concentrations of CO, NO and NO₂ are higher in winter as in the case of curbside stations, difference between summer and winter season concentrations are much more pronounced at Sihhiye station compared to differences observed at curbside stations.

This observed distinct difference between summer and winter concentrations at the Sihhiye station is partly due to lower mixing height in winter and partly due to contribution of traffic emissions on concentrations measured in this station which is fairly close to major roads with high traffic intensity. However, if these two factors are the only ones affecting NO, NO₂ and CO concentrations at the Subhiye station, measured monthly pattern should be exactly similar to those observed at curbside stations, which is not the case. More distinct high winter concentrations of these three parameters indicate an additional emission source, which operates only in winter period. The most likely additional winter source is the fossil fuel combustion for space heating. Although traffic emissions is the most important source for measured CO, NO and NO₂ concentrations, CO and NO are also emitted, to a lesser extent, from coal combustion, particularly when the combustion is incomplete in stoves (please remember the newspaper articles which describes deaths due to CO intoxication in stove-heated houses, which are common in winter). Space heating emissions of CO and NO is a winter source and its effect can be more clearly seen at non-curbside stations, which are not affected from traffic emissions as much as curbside stations.











Figure 4.17. Monthly Average Concentrations of CO, NO and NO₂ at Sihhiye Station

Measured concentrations of SO_2 and PM-10 at curbside stations show significant seasonal variations. Higher concentrations are observed in December and January, while concentrations decrease gradually throughout the summer. In contrary to CO, NO and NO₂ the difference between summer and winter concentrations of SO₂ and PM-10 are apparent and consistent. However the seasonal pattern of SO₂ at İskitler station is different than the other curbsides. The reason behind this can not be explained for the time being.

However, İskitler junction is located on the main artery at which motor vehicles coming from İstanbul road enter the city. From this point of view, İskitler junction carries much more high volume of heavy-duty diesel traffic (i.e. trucks, buses, and minibuses) than the Kavaklıdere and Kızılay junctions. Higher diesel emissions at İskitler with respect to Kavaklıdere and Kızılay may determine the SO₂ levels not only in summer but also in winter seasons. Unfortunately this statement can only be accepted as a speculation as there is no traffic count at İskitler junction.

Monthly variations of SO_2 and PM-10 at non-curbside stations are depicted in Figure 4.18. The monthly patterns of these parameters are very similar at both curbside and non-curbside stations, in contrast to monthly patterns of CO, NO and NO₂. However there is an important difference between two groups of stations. Concentrations of SO_2 and PM-10 at non-curbsides approaches to zero level in summer, while the decrease in summer is not so much at curbside stations.

While winter/summer ratio of SO_2 concentrations at non-curbside stations ranges from 1.95 to 3.60, the same ratio ranges from 0.9 to 1.8 at curbsides. The reason for observing lower ratios at curbsides is the contribution of diesel emissions to SO_2 concentrations in summer. Remember in previous sections diesel emissions could be an important source of SO_2 at curbside stations is aforementioned. This will be discussed in more detail in section 4.5.2 (while diurnal patterns of measured parameters are investigated).





At non-curbside stations, where effect of traffic emissions is not as strong as curbside stations, higher SO₂ concentrations in winter is observed but when the residential heating ceases in summer concentrations of SO₂ decrease rapidly. This is an expected situation since there are no other sources of SO₂ rather than combustion at non-curbsides which are away from traffic emissions.

The winter concentrations of SO_2 at curbsides are determined by both diesel emissions and combustion based SO_2 which is transported from other districts of the city (mainly residential areas). Although combustion based SO_2 approaches to zero in summer, traffic emissions (especially diesel vehicle emissions) do not decrease that much. Therefore lower winter/summer ratio is observed for SO_2 at curbsides.

The difference observed for SO_2 between two groups of stations is not observed for PM-10 concentrations although similar monthly variations are observed for SO_2 and PM-10 at the first glance.

The range of winter/summer ratio for PM-10 varies from 1.5 to 2.4 for both groups of stations. The reason behind this discrepancy between SO₂ and PM-10 ratios is being other important sources of PM-10, in contrast to SO₂, rather than combustion at non-curbside stations. A previous study conducted by Yatin et al., (2001) showed that there are five important sources of particulate matter in Ankara. These are coal, fuel oil, traffic emissions, road dust and resuspended soil, respectively. Combustion (coal and fuel oil) and resuspended soil are expected to be more effective sources of particulates at non-curbside stations, while traffic emissions and road dust are for curbsides. Even particulate matter originated from combustion is ceased in summer, resuspended soil increases. Therefore PM-10 concentrations do not approach zero at non-curbside stations.

4.5.2. Diurnal Variations

Diurnal profiles of measured parameters at curbside and non-curbside stations are computed and illustrated in Figure 4.19, Figure 4.20, Figure 4.21 and Figure 4.22 to determine whether patterns exist among stations. Concentrations of motor vehicle related pollutants at curbside stations (Figure 4.19) show well defined diurnal patterns. At three curbside stations NO and CO concentrations increase starting at 6:00 am and reach to a maximum at 9:00 am then decrease and remain relatively low until 2:00 pm, after that show a second maximum at 8:00 pm. This pattern with two rush-hour maxima is typical for most of the traffic related pollutants. The second maximum observed at İskitler is only slightly higher than the morning maximum whereas at Kızılay and Kavaklıdere afternoon maximum is significantly higher than morning one. Furthermore, there is a well defined decrease in CO and NO concentrations after morning rush-hour peak until afternoon maximum. This decrease is not observed in the Kavaklıdere station, where both CO and NO concentrations steadily increase until afternoon rushour peak. These variations between the stations may be attributed to different traffic distributions at stations. However, it can not be confirmed here as there are no traffic counts.

The two rush-hour peaks observed in NO₂ concentrations are less pronounced than the ones observed in NO and CO concentrations, owing to secondary nature of NO₂. The NO₂ concentrations start to increase approximately at the same time with NO and CO, reach to a maximum at 9:00 am - 10:00 am, but then slightly decrease until 2 pm due to decrease in NO, after that show second maxima at 8-9 pm.

For comparison, the diurnal patterns in CO, NO and NO₂ concentrations at the Sihhiye station, which is the only non-curbside station where CO, NO and NO₂ are measured, are also presented in Figure 4.20.Both CO and NO show a similar bimodal traffic pattern, indicating that concentrations of these parameters measured at the Sihhiye station are being transported there from nearby roads, which is expected, because the Sihhiye station is fairly close to major roads.

An interesting observation was made at the Sihhiye station, which can help to understand how concentrations of CO, NO and NO₂ changes as traffic emissions are transported from roads to the inner parts of the residential areas in the city. The CO and NO concentrations measured at the Sihhiye station are



Figure 4.19. Concentrations of CO, NO and NO2, represented as hourly averages, measured at curbside stations



Figure 4.20. Concentrations of CO, NO and NO₂, represented as hourly averages, measured at Sihhiye stations

lower than the concentrations measured at the curbside stations, particularly during rush hour periods. This is expected because, although Sihhiye station are fairly close to a road with high traffic density, it is not located at the curbside and concentrations transported from roads decrease during short transport time due to dilution and chemistry. This small difference in concentrations between real curbside stations and Sihhiye station indicates that CO and NO concentrations should further decrease as they are transported to other noncurbside stations, which are further away from roads. However, NO₂ concentration measured at the Sihhiye stations are both higher than NO₂ concentrations measured at the curbside stations and also shows a well defined traffic pattern with two rush-hour maxima, which is not observed at the curbside stations. This clearly demonstrates that fresh emissions are measured at the curbside stations. Nitrogen dioxide is a secondary compound, which is not directly emitted from vehicles and formed from photochemical oxidation of NO. Its concentration is low at curbside stations, because the Δt between the time at which NO is emitted from exhaust and the time it reaches to inlet of the measurement system is very short and does not allow extensive formation of NO_2 .

At the curbside stations inlets are only few meters away from the road and with an average wind speed of 3 ms⁻¹, Δt is less than a second. However, the Sihhiye station is located some 50 m from the road (also approximately 10 m above the surface where NO is emitted from exhaust) and it takes some time for the emissions to reach the sampling inlet. Longer Δt allows for more extensive formation of NO₂. Consequently, one can expect higher NO₂ concentrations in some of the non-curbside stations which are further away from roads.

The sulphur dioxide concentration and PM-10 mass at curbside stations (given in Figure 4.21) show a similar diurnal pattern with a slight time-shift in the afternoon peak. Their concentrations start to increase approximately at the same time with motor vehicle related pollutants and reach to a maximum at 9:00 am – 10:00 am, then decrease until 5:00 pm and show a second maximum at 8:00 - 9:00 pm.

This diurnal pattern, which is typical for traffic impacted sites, is expected for PM-10 mass concentrations, since a significant fraction of PM-10 mass originates from motor vehicle emissions. However, this pattern was not expected for SO₂, because main source of SO₂ in urban airshed is fossil fuel combustion for residential heating. One can expect domination of combustion based SO₂ at curbside stations as well. However, typical traffic pattern observed at all three curbside stations clearly demonstrate that SO₂ observed at curbside satiations are from traffic. The gasoline used in gasoline powered vehicles is free from S (gasoline used in Turkey contains 0.005-0.1% S (TÜPRAŞ)) and hence gasoline powered vehicles do not emit a significant quantity of SO₂ to atmosphere. However, diesel fuel do contain S as impurity.



Figure 4.21. Concentrations of SO₂ and PM-10, represented as hourly averages, measured at curbside stations

Diesel fuel used in Turkey contains 0.3-0.7% S (TÜPRAŞ) in it. Consequently SO_2 emissions from diesel powered vehicles can contribute observed SO_2 levels in the atmosphere, particularly in areas close to the major roads. The traffic pattern observed in SO_2 concentrations at curbside stations is then due to diesel emissions rather than transported combustion emissions.

For PM-10 mass, afternoon maximum is higher than the morning rush-hour maximum, which is similar to those observed for CO, NO and NO₂. However, afternoon SO₂ maximum is smaller than the morning maximum. Furthermore, at all curbside stations, decrease in SO₂ concentrations during noon time is not as pronounced as those observed in PM-10, CO and NO. This may be either due to variations in relative proportions of gasoline and diesel powered vehicles passing through the junctions or due contribution of combustion on SO₂ concentrations during noon time when traffic contribution is at minimum. Probably contribution of combustion SO₂ can be ruled out, because the similar pattern was observed both in winter and in summer, when there is no heating. Traffic counts in Akay Tunnel have revealed slightly higher diesel traffic density in morning hours and comparable diesel intensity at noon and afternoon, which is in agreement with variation of SO₂ concentrations at curbside stations. However, it should be noted that differences are not dramatic and traffic counts are not made at the measurement sites.

The diurnal profiles of SO₂ and PM-10 concentrations at non-curbside stations are given in Figure 4.22. Interestingly, they show similar pattern with curbside stations with a slight time shift at the peak hours at some non-curbside stations. Hourly averaged SO₂ concentrations at non-curbside stations are nearly a factor of two smaller than curbside SO₂ concentrations. However, hourly averaged PM-10 concentrations at Sinhiye are comparable with curbside concentrations and except Çankaya station other stations show higher PM-10 concentration, especially in the evening hours, than curbside stations. The difference between the two maximum in SO₂ and PM-10 concentrations are also observed for non-curbside stations, which is high morning peak for SO₂ and high evening peak for PM-10.



Figure 4.22. Concentrations of SO₂ and PM-10, represented as hourly averages, measured at non-curbside stations (except Cebeci station)

The rush-hour patterns observed in the concentrations of SO_2 and PM-10 indicates that most of the non-curbside stations are influenced to a certain extent from traffic emissions, or in other words, traffic emissions do contribute SO_2 and PM-10 concentrations measured at the non-curbside stations. This confirms the earlier finding by Yatın et al. (2000), where authors found that even at the top of the METU, Dean's Office of Faculty of Engineering building, which is fairly far from most major roads, approximately 40% of the PM-2.5 particles originate from traffic.

Most of the non-curbside stations used in this study are located in districts where heating is by combustion of natural gas. Since very little SO₂ is emitted from natural gas combustion, traffic contribution becomes more visible. The SO₂ and PM-10 patterns can be different in squatter settlements districts, such as Mamak, where coal combustion is still the most important mode of space heating.

High contribution of traffic emissions on SO₂ and PM-10 concentrations measured at non-curbside stations has also other implications. Currently SO₂ and PM-10 concentrations in Ankara comply with short and long term standards in TAQR. If further reductions in SO₂ and PM-10 concentrations becomes necessary (it will become necessary if EU directives becomes effective in the future), better maintenance of diesel vehicles and use of diesel fuel with smaller S content should be considered as parts of the action plan.

4.6. Sources of Pollutants

4.6.1. Correlations between Parameters

Binary correlation between parameters is one of the simplest statistical methods used to determine the sources of pollutants, or the chemical processes that affect the chemical composition of atmosphere at the receptor site. Although simple, this method gives fair amount of information on how the species co-vary in the data set. Since the receptors at which concentrations of pollutants are measured are generally close to pollution sources, correlation analysis in urban areas determines whether the measured pollutants have similar sources or not, rather than provide information on the chemical and physical processes.

Strong correlation between the concentrations of measured parameters are expected in urban areas, therefore probability of chance constraint is taken as 1 % in this study. In this section the term "correlated" means that there is statistically significant correlation between parameters; i.e. [P(r, n) <0.01] and terms "not correlated" or "there is no correlation" means that [P(r, n)>0.01]. The

correlations of measured parameters are calculated using Stat Graphics program.

The correlations of measured parameters at curbside stations are given in Table 4.5, 4.6 and 4.7. Carbon monoxide correlates well with NO and PM-10 in all stations indicates that contribution of gasoline powered vehicles to PM-10 mass is significant. Furthermore, similar correlations of SO₂ and PM-10 are also observed in all stations which shows that at least a certain fraction of PM-10 originate from diesel vehicular emissions. Relatively weak correlation between NO₂ and other measured parameters is explained by the secondary nature of the NO₂. NO₂ is not directly emitted to the atmosphere, meteorological conditions, particularly the solar flux, which enhances or suppresses conversion of NO to NO₂ play an important role in ambient NO₂ concentrations. However, strong correlation of NO₂ to NO should be observed as NO₂ is formed by oxidation of NO. Weak correlation of NO to NO₂ at Kavaklidere can not be explained for the time being.

Correlation of CO and SO₂ is weak at İskitler and Kavaklidere stations although strong correlation is observed at Kızılay. In fact, correlation of CO and SO₂ is confusing because although they have different sources (CO-gasoline vehicular emission and SO₂- diesel vehicular emissions), their concentrations increase and decrease together according to traffic density, so one may expect strong correlation between these parameters. However the different characteristics of traffic pattern at stations through the day may be the reason for the weak correlation observed.

Correlations of SO₂ and PM-10 at non-curbside stations are also investigated and strong correlations between these parameters are observed at all noncurbside stations except Cebeci station. These two parameters are expected to be correlated, because they are emitted simultaneously from both traffic and combustion sources. The reason of weak correlation in Cebeci station is not clear, but may be due to smaller number of data points in this particular station.

	CO	NO	NO2	SO2	PM-10
CO	СО	0.507		0.368	0.557
NO		NO	0.633	0.613	0.589
NO2			NO2	0.173	
SO2				SO2	0.577
PM-10					PM-10

Table 4.5. Correlations between measured parameters at İskitler

Table 4.6. Correlations between measured parameters at Kavaklidere

	со	NO	NO2	SO2	PM-10
CO	СО	0.563	0.270	0.340	0.606
NO		NO	0.378	0.358	0.569
NO2			NO2	0.446	0.519
SO2				SO2	0.598
PM-10					PM-10

Table 4.7. Correlations between measured parameters at Kızılay

	СО	NO	NO2	SO2	PM-10
CO	СО	0.498	0.163	0.621	0.751
NO		NO	0.815	0.320	0.173
NO2			NO2		-0.184
SO2				SO2	0.531
PM-10					PM-10

4.6.2. Pollutant Ratios

Statistical treatment of data in this study demonstrated that pollutants measured in this study, namely SO₂, NO₂, NO, CO and PM-10 mass, are not very powerful tracers to differentiate between traffic and combustion related emissions, because they are emitted from both motor vehicles and furnaces to different extent, and the non-curbside station are not completely free from influence of traffic emissions. Sometimes, ratios of pollutant concentrations can be more informative than the pollutants themselves to differentiate between different source types. To test these, various ratios were calculated and their temporal and spatial distributions are investigated.

4.6.2.1. PM-10 – to –SO₂ ratio

This is the only ratio that can be calculated in both curbside and non-curbside stations. Summer and winter medians of PM-10 – to $-SO_2$ ratio at each station are given in Table 4.8, together with NO-to-NO₂ and PM-10-to-NO₂ ratios. There are distinct differences between curbside and non-curbside stations in terms of their PM-10 – to $-SO_2$ ratios. At the curbside stations the PM-10 – to $-SO_2$ ratio varies between 0.6 and 0.9 in winter season. The same ratio varies between 1.1 and 2.0 at non-curbside stations, showing a statistically significant difference between the two groups of stations at 95% confidence level. Since resuspended soil component in PM-10 mass is at minimum during winter, the difference between ratios calculated for curbside and non-curbside stations probably indicates the difference between PM-10- to-SO₂ ratios in diesel emissions and combustion related emissions. Note that both fine particles and SO₂ are dominated by diesel emissions, rather than emissions from gasoline powered vehicles. Although fine particles are emitted from vehicles powered by gasoline engine, these emissions are expected to be small compared to emissions from diesel engines, particularly in Turkey, where diesel powered vehicles are not properly maintained.

If the ratios are representing motor vehicle emission at the curbside stations and combustion emissions at the non-curbside stations then they should be the same in summer and winter seasons at the curbside stations but change between seasons at non-curbside stations. The PM-to-SO₂ ratios at curbside stations are not significantly different, but slightly higher in winter season. This indicates a small contribution from combustion sources on SO₂ and PM-10 levels observed at curbside stations. Since PM-to-SO₂ ratio in combustion emissions are higher than the corresponding ratio in diesel emissions, small contribution from combustion for observed higher ratios in winter. Unfortunately summer data are not available at non-curbside stations to assess the seasonal differences.

	PM-10/SO2		NO/N	102	PM-10/NOx		
	Summer	Winter	Summer	Winter	Summer	Winter	
Kizilay	0.50	0.60	1.80	3.30	0.12	0.57	
İskitler	0.50	0.90	2.10	4.00	0.23	0.44	
Kavaklidere	0.50	0.80	2.50	3.10	0.36	0.38	
Sihhiye		1.10	0.30	1.30		0.40	
K. Esat		1.70					
Beşevler		1.00					
Demetevler		2.00					
Keçiören		1.20					
Yenidoğan		1.70					

Table 4.8. Summer and winter median values of selected pollutant ratios

Diurnal pattern in PM-to-SO₂ ratio in curbside and non-curbside stations are depicted in Figure 4.23. The PM-to-SO₂ ratio shows a well defined diurnal pattern at non-curbside stations with lower concentration during day time. The same diurnal pattern can be seen in the temperature. This pattern suggests that contribution of traffic emissions, which has lower PM-to-SO₂ ratio to non-

curbside stations is higher during day time, but combustion emissions dominate at night due to both increased space heating emissions and reduced traffic intensity.



Figure 4.23. Diurnal variation of PM-10/SO₂ ratio in curbside and non curbside stations

Day-time and night-time difference is much less pronounced at curbside stations. Since diurnal variations are calculated using winter data, increase at night time ratios confirms the contribution of combustion emissions at night when traffic intensity decreased to minimum. Note that during day time, when ratio represents overwhelmingly traffic emissions, the ratio decrease to 0.5, which is the average ratio in summer (when there is no heating).

4.6.2.2. NO-to-NO₂ ratio

Nitrogen monoxide-to-NO₂ ratio is an indicator for photochemical activity in the atmosphere. Nitrogen monoxide is the primary pollutant emitted from motor vehicles, but vehicles do not emit NO₂. It is formed in the atmosphere by oxidation of NO. This oxidation reaction is part of the hydrocarbon oxidation cycle. Conversion of NO to NO₂ indicates that organic intermediates such as aldehydes, ketones and PAN (which are known as irritants) forms in the atmosphere. The reaction forming NO₂ from NO is also important, because each molecule of NO₂ formed results in the formation of one molecule of O₃ in the atmosphere (photochemical steady state).

Summer and winter season concentration ratios of NO/NO₂ are given in Table 4.8. The only non-curbside station, where NO and NO₂ are measured, is the Sihhiye station. It is located some 50 m from a major road and in that sense it is more like a curbside station. The only difference between the Sihhiye station and other curbside stations is that emissions from traffic have to travel a little bit more to reach the measurement devices. Sihhiye station is somewhere between a residential station and a curbside station.

Winter season median values of NO-to-NO₂ ratio at three curbside stations vary between 3.1 and 4.0, which is a very small range. Corresponding range in summer season is between 1.8 and 2.5, which is again a small range. In all curbside stations summer values are smaller than winter median values. This is due to enhanced photochemical activity in summer, which enhances conversion

of NO to NO_2 . Since NO concentration decrease and NO_2 concentration increase, as a result of conversion, the ratio gets smaller.

The diurnal variation in the NO-to-NO₂ ratio in these four stations is depicted in Figure 4.24. A very clear and expected diurnal pattern is observed at Sihhiye and İskitler stations. At these two stations, NO/NO₂ ratio increases and reaches to a maximum during morning rush-hour, due to increased fresh emissions, which contains NO but not NO₂. Later in the day fresh emissions decrease (after the rush-hour), but NO that is emitted during rush hour continues to convert to NO₂. Consequently, NO concentration decrease and NO₂ concentration increase, resulting in lower NO/NO₂ ratio observed during the day. Fresh emissions again rapidly increase during afternoon rush-hour and increase the ratio. Late in the night again oxidation of NO to NO₂ decreases the NO/NO₂ until next morning. There are non-photochemical oxidation mechanisms which should be responsible for the night-time decrease observed in the ratio. These mechanisms are slower than photochemical oxidation and hence are not important during day time.

The mechanism for the diurnal pattern observed at İskitler and Sıhhıye stations is well documented and is expected to be observed in all curbside stations. Interestingly, this expected pattern is not observed at Kızılay and Kavaklıdere stations. In these two stations NO/NO₂ ratio increase during morning rush-hour as expected, but do not decrease later in the day. This indicates that the traffic pattern at İskitler is significantly different than the traffic patterns at Kızılay and Kavaklıdere. Since one would not expect a significantly different atmospheric photochemistry at İskitler and Kızılay, the lack of decrease in the NO/NO₂ ratio at Kızılay and Kavaklıdere can only be explained by continuation of fresh emissions throughout the day. It should be noted that diurnal variation in CO concentration, which is not photochemically active (at least not as much as NO), show a similar pattern at Kızılay and Kavaklıdere stations, confirming that observed differences between stations is due to different traffic patterns.



Figure 4.24. Diurnal variation of NO - to - NO2 ratio at İskitler, Kavaklıdere, Kızılay and Sıhhıye stations

4.6.2.3. **PM-10-to-NO**_x ratio

The PM-10/NO_x ratio is investigated with the expectation that it may be helpful to differentiate between diesel and gasoline powered engine contributions. Fine particles are emitted from both gasoline and diesel engines, however fine particle emissions from diesel engines are much higher than corresponding emissions from gasoline engines. This statement is particularly true in Turkey, because heavy duty diesel vehicles are not properly maintained and a majority of them emits a visible black smoke from their exhaust.

Nitrogen monoxide, on the other hand, is a characteristic emission from gasoline engine. However, after it is emitted to atmosphere some unknown fraction of it, which is variable within a day, is converted to NO_2 , modifying NO concentration in the atmosphere. Because of this NO can not be used as a tracer for gasoline engines. In this study NO_x is used as a tracer for gasoline engines. In this study NO_x is used as a tracer for gasoline engine, because no matter how much of the emitted NO is converted to NO_2 , NO_x which is the sum of NO and NO_2 should be directly related to the quantity of emissions.

Summer and winter season median values of PM-10/NO_x ratios are given in Table 4.8. Median values calculated using summer data are smaller than winter medians. The difference is not significant for Kavaklıdere station, but real at Kızılay and İskitler, indicating a stronger diesel contribution during winter season. This is not expected, because during summer Ankara residents leave the city for vacation. This means that some fraction of gasoline powered vehicles do not operate in summer, but heavy duty vehicles, all of which are diesel powered, remains in the city. With this scenario, diesel contribution is expected to be higher during summer, which is exactly opposite to what is observed. Although reason for lower PM-10/NO_x ratios is not clear, one reason may be the different performance and hence different particulate emissions from diesel engines during cold winter season.

The diurnal variation in the PM-10/NO_x ratio is depicted in Figure 4.25. The ratio shows a similar pattern in all four stations, which is characterized by sharp increase between 3 - 5 am, then a decrease until 8 or 9 am and a steady levels throughout the rest of the day. Note that, 5 am is typical time when heavy duty trucks, which travel from other cities arrive to Ankara and it is also the time when heavy duty vehicles are allowed to enter the city.

The sensitivity of the PM-10/NO_x ratio to variations observed in diesel emissions, suggests that it is a promising tracer to assess relative proportions of diesel vs. gasoline emissions. At Kavaklıdere and İskitler stations, PM-10/NO_x ratio does not change significantly after the early morning peak. However, at Sıhhıye and Kızılay stations the ratio remains low until 6 pm, then starts to increase at early night hours and continues to increase throughout the night until it reaches to maximum in the next morning. These different diurnal patterns observed at different stations can confirm different traffic patterns on different roads. The PM-10/NO_x ratio is not the only ratio that depicts the early morning truck peak. The same peak is also observed in CO/NO_x and SO₂/NO_x ratios as well.

4.7. Relation with Meteorological Parameters

Observed variability in concentrations of pollutants measured at curbside and non-curbside stations can either be due to variations in emissions or due to variations in meteorology affecting Ankara region. Variations in meteorology not only affects concentrations of conservative pollutants it also affects chemical processes in the atmosphere and hence can enhance or suppress the formation of secondary products, such as NO₂. Relative importance of meteorology and emissions in determining observed variability in measured concentrations of pollutants can change both in time and space. In this section the relation between concentrations of pollutants and meteorological parameters will be investigated to asses the relative importance of meteorology on observed concentrations.









Figure 4.25. Diurnal variation of PM-10-to-NOx ratio at İskitler, Kavaklıdere,Kızılay and Sıhhıye stations

Two meteorological stations are operated within the Ankara city by the Turkish State Meteorological Service. One of these stations is located in İncirli (Keçiören district), which is well within the downtown area, and the second one at Etimesgut Airport. Since the measurements in this study are performed within urban area, meteorological data from the İncirli station is used throughout the study.

4.7.1. Wind Speed and Direction

Horizontal movement of air is determined by wind which is specified by two factors namely its speed and direction. The direction of wind is expressed as the point of the compass from where the wind is blowing. In this study, 16 sectors are numbered in a clockwise direction, with number 1 spanning due to north to 22.5° NNE. The wind speed is expressed by meters per second.

The overall wind speed frequency distribution during the sampling period is given in Figure 4.26. Almost 60 % of winds during the sampling period blow at a speed between 2 and 4 ms⁻¹ and less than 8 % have a speed higher or equal than 5 ms⁻¹. Thus, the low wind speed dominated throughout the study period.

Extremely low wind speeds and frequent calm conditions is typical for Ankara and suggested to be one of the main reasons for observing high pollution levels in Ankara (Yatin et al., 2000).Diurnal variation in the wind speed during summer and winter seasons in the study period is given in Figure 4.27 (a). As can be seen from the figure, wind speeds are high in the daytime periods and low at night and greater in the summer than in the winter. The maximum in wind speed is reached at approximately 2:00 pm in winter and 4:00 pm in summer.

Mean annual temperature given in Figure 4.27 (b) resembles the mean annual wind speed profile. In order to access the relationship between wind speed and temperature, correlation analysis is performed and statistically significant relationship between the wind speed and temperature is obtained (P<0.01 and R=0.275). This relationship can be explained by the increase in earth surface



Figure 4.26. Frequency histogram of wind speed during measurement period

temperature due to the high solar radiation during the day times (especially in summer period) resulting in higher wind speeds.

The effect of wind speed on the ambient levels of measured parameters at curbside and non-curbside stations are investigated and results from İskitler station are given in Figure 4.28 as an example for curbside stations. Similar patterns were also observed in Kızılay and Kavaklıdere stations.

At curbside stations, a statistically significant effect of wind speed is only observed on PM-10 mass. When the wind speed is high, low concentrations of PM-10 mass are measured at curbsides (Figure 4.28). The reason for observing no direct effect of wind speed on other measured parameters at curbside stations is the short distance between the emissions and the receptor.



Figure 4.27. Mean Annual (a) Wind Speeds and (b) Temperature through the diurnal cycle in Ankara, 1999-2000

As the distance is very short, there is not enough time for dilution of measured parameters by wind. Hence the wind speed is not the parameter that determines the variations of pollutant concentrations at curbside stations, except for PM-10 mass.

Results for non-curbside stations are presented in Figure 4.29, for K. Esat, Çankaya and Keçiören stations. The effect of high wind speeds on measured parameters (SO₂ and PM-10) at non-curbside is more obvious. Statistically significant decreases in SO₂ and PM-10 mass concentrations with wind speed are observed in all non-curbside stations. Since regional concentrations are

measured at regular monitoring stations, wind speed has a dilution effect on measured concentrations.

Concentrations of pollutants measured at curbside stations are not expected to be affected significantly by the wind direction, because it was shown in the previous sections that concentrations measured at the curbside stations are primarily affected from nearby traffic emissions. Since these stations are located in the middle of the junctions, traffic emissions come from all directions and consequently predominance of winds from any direction will not affect the measured concentrations.

Concentrations of SO_2 and PM-10 measured at non-curbside stations, on the other hand, can be affected by the wind direction, because SO_2 and PM-10 sources may not be homogeneously distributed around non-curbside measurement sites. When the winds blow from the direction where SO_2 and PM-10 sources are densely populated one can expect high concentrations and if the winds blow from the direction where there are not too many sources, low concentrations of SO_2 and PM-10 should be expected.

Wind direction frequency distribution during the study period is given in Figure 4.30. It is clear from the figure that NE and SW are the dominant wind directions during the study period. Winds from NNE, NE and ENE accounts for approximately 60% of wind direction observations made during this work. Similarly, winds from SSW, SW and WSW accounts for 30% of the observations. These two sectors totally account for 90% of all hourly wind observations during the study. All remaining sectors totally account for only approximately 10% of hourly wind observations. The wind distribution pattern observed during measurement period is similar with the long-term wind rose discussed previously. Calm winds, which have lower than 1m s⁻¹ speeds are not included in calculations.

The effect of wind direction on SO₂ and PM-10 concentrations at non-curbside stations were investigated for Çankaya and Keçiören stations. Calculations were not performed for other non-curbside stations, because one of the methods used was too calculation intensive and the purpose of the investigation





Figure 4.29. Wind speed vs. measured parameters at non-curbside stations
was to demonstrate and compare different methodologies rather than finding wind sectors affecting each station.

The simplest way to understand the contribution of wind direction on measured concentrations is to calculate average concentrations of pollutants corresponding to each wind sector. Results of this simple method, which is called "**pollution rose**" approach, are given in Figure 4.31 for both SO₂ and PM-10. Pollution roses are only drawn for winter since hourly data (wind speed (WS), wind direction (WD) and concentration) are used in pollution rose approach.



Figure 4.30. Frequency histogram of wind direction during measurement period

At Keçiören station, SO_2 concentrations are higher in ENE sector, however relatively similar concentrations are observed at all sectors between NE and S. The similar trend is observed at the two stations for both SO_2 and PM-10. Pollution rose approach showed that there is no prevailing direction and SO_2 and PM-10 at both stations are transported homogenously from the sectors between NE and S.

At low wind speeds pollutants are not transported between areas in the city and simply accumulate. In such cases directional dependence of concentrations can not be expected, because what is measured at any site is the pollutants emitted and accumulated from sources close to the site. As pointed out before, one of the meteorological features, which is characteristic for Ankara, is the very low annual average wind speed. This means that, periods with very low wind speeds is frequent in the city. The source contributions are depicted on the population map of Ankara in Figure 4.31.The lack of directionality in the source contributions shown in Figure 4.31 can be due to such frequent low wind speed periods. To test this hypothesis, calculations were repeated, but this time using only the winds \geq 3 ms⁻¹. Results are depicted in Figure 4.32. As proposed, contributions are more directional when only high wind speeds are included in calculations and lack of directionality observed in the previous figure is due to low wind speeds.

At both stations the sector, which corresponds to the highest SO₂ concentrations is ENE sector. At Keçiören ENE sector corresponds to squatter settlement districts along the road to Airport. At Çankaya the same sector points to another squatter settlement district, namely Mamak. Higher concentrations corresponding to winds blowing from squatter settlement districts is not surprising, because these are the districts where coal combustion is still common. The very sharp concentration peak in SE direction at Keçiören station is probably an artifact resulting from a source, which is very close to station, such as a chimney across the road.

Directional dependence of PM-10 concentrations is very similar to the directional dependence observed in SO_2 , indicating that source areas responsible for observed PM-10 levels in these two stations are the same with source areas responsible for the observed SO_2 levels.

Although pollution rose is a simple and easy to use method to detect source regions affecting measured pollutant levels at a receptor, it provides misleading information about the contribution of these source areas. The sector at which SO₂ or PM-10 has the highest concentrations is not necessarily is the sector which contributes most to observed levels of SO₂ or PM-10 in that particular receptor. It provides misleading information, because it does not take into



Figure 4.31. Pollution roses for SO_2 and PM-10, prepeared using all wind speed data



Figure 4.32. Pollution roses for SO₂ and PM-10, calculated with WS \geq 3 ms-1

account the frequency of winds from each wind sector. A certain wind sector can have very high density of SO_2 sources, if the wind does not blow from that particular sector those sources can not affect SO_2 concentrations measured at the receptor.

A more sophisticated approach, which takes into account both concentration and wind frequency from each sector should be used to determine sector contributions to a receptor. In this study, the method developed by Vossler et al., (1989) was used to calculate sector contributions to SO₂ and PM-10 concentrations measured at Keçiören and Çankaya stations. The method was first developed by Vossler et al., (1989) to determine sector contributions on daily trace element concentrations measured at a rural site in the US, then used by Yatın et al., (2000) for an urban data set. In this study hourly data available at the two stations are first converted to daily averages then used to calculate sector contributions using Vossler et al., (1989) approach. Since daily average concentrations are used, data were available and hence sector contributions were also calculated for summer season as well. The method calculates concentrations at each sector and sector contributions using the following formulations:

$$\left[F_{ij}\right] = \left(\frac{P_{ij}}{N}\right) \tag{4.1}$$

Where,

 P_{ij} is the number of observations in wind sector j for ith day, N is the total number of observations in all sectors for ith day (N is equal to 24 in our case because Met data are hourly bases) and F_{ij} is the wind direction frequency at sector j for ith day,

Finally average concentration from each sector is calculated using the following relation:

$$C_{j} = \frac{1}{F_{j}} \times \sum_{i=1}^{n} \left(C_{i} \times F_{ij} \right)$$
(4.2)

$$F_{j} = \sum_{j=1}^{16} F_{ij}$$
(4.3)

Where,

 F_j is the sum of wind direction frequencies at sector j, n is the number of day, C_i is the average concentration of the pollutant at ith day and C_j is the sector average concentration of the pollutant at jth sector.

And the percent contribution of each sector to the average concentration measured at the station is calculated using the following relation:

$$%C_{j} = \frac{C_{j}}{\sum_{j=1}^{16} C_{j}} \times 100$$
(4.4)

Results are depicted in Figure 4.33. Calculations were performed using wind speeds $\geq 3 \text{ m s}^{-1}$. Sulfur dioxide and PM-10 concentrations during summer season are approximately similar in all wind directions, at both Keçiören and Çankaya stations. Zero concentrations calculated in N, and S sectors in both stations are due to lack of winds from these sectors during summer period. Similarity in concentrations in winds from all directions in summer is not surprising, because heating stops in summer and traffic becomes an important SO₂ source. Since monitoring stations are located relatively far from major roads, the traffic emissions at secondary roads around the station and traffic





al., (1989) approach

emissions transported from distant major roads are the sources of SO₂. Both of these sources have fairly uniform distribution around stations.

However, in winter both SO_2 and PM-10 concentrations show a stronger directional behavior. NE sector has the highest contribution to both SO_2 and PM-10 concentrations at the Keçiören station, which is due to coal combustion for space heating in the squatter settlement regions that are located to the NE of the station. The strong contribution of the SSE sector is probably due to a source in the immediate vicinity of the station.

The SO₂ and PM data at Çankaya station do not show as strong directionality as that observed in Keçiören station. Although the NE sector has also the highest contribution, the difference between contribution of NE sector and other sectors is not as large as that observed in Keçiören station. This is probably due to the fact that Çankaya station is not as close to coal combustion areas as the Keçiören station.

Although Vossler et al., (1989) method nicely calculates sector contributions, taking into account both concentrations of SO_2 and PM-10 at each sector and wind frequency, it has one disadvantage. The method assumes that the air parcel that brings high concentration of a pollutant from a particular sector remains in that sector in all times, which is not the case. An air parcel that corresponds to a certain concentration of SO_2 or PM-10 is assigned to a wind sector depending on the wind direction data at the time it is intercepted at the station. However, that particular parcel can pick up the emissions from another sector several hours ago, then can move to another wind sector depending on the wind direction at that time and, finally can be transported to the station in that new wind sector. In such a case the sector assigned for high concentration will not be the one where emissions actually occur, but it will be the one from where parcel makes its final approach to the station.

To avoid this misleading information, a third approach, which is recently developed in our group and uses surface wind based back trajectories were used to calculate sector contributions. The method used is similar to that used by Bari et al., (2003) to determine source area contributions at a receptor in

more regional scale. The difference of the method from the Bari's method is the usage of local wind based back trajectories instead of higher altitude air mass back trajectories, which are transported longer time in the atmosphere. Since concentrations of pollutants measured at the stations in this study are determined by local sources, methods to calculate source areas affecting a receptor site (station in our case) must use few hour-long, surface trajectories. There is no model which calculates this information. Therefore a method is developed in our group to calculate the paths of the air parcels traveled within the city, before it is intercepted at the station. This method is first developed by Kuntasal (2005) for a limited VOC data. We used the method to a larger, hourly data set at Keçiören and Çankaya stations.

In the method, a puff (a small package of air) is released at the receptor at the time of a measurement. The puff if moved on the surface with the wind direction and speed data generated at the Meteorological station for the same hour. The location of the puff is flagged in a GIS software and coordinates are recorded. Then the puff is moved with the wind speed and direction information generated at the meteorological station one hour before the measurement and a new position and coordinates were determined at the end of one hour period (which corresponds to position at two hours before measurement). The puff is continued to move with wind speed and direction data generated 3-hr, 4-hr, before actual measurement. At each hour the location of the puff is flagged on GIS map and coordinates recorded. The end point of the movement in previous hour was the starting point of the movement in the following hour (with new WS and WD data). This process is repeated until the puff goes beyond \pm 30 km in East – West direction and \pm 25 km in North – South direction (if it goes roughly beyond Beltway around Ankara). One puff is released for every measurement period, which means every hour. Each position of the puff at the end of every hour is called "segment". The sampling performed by Kuntasal (2005) included three 2-hr sampling periods in a day, because of this, the author calculated three surface trajectories and segments associated with them for every sampling day and for two months in summer and two months in winter. However, in this study 24 surface trajectories were calculated every day and continuously for one winter season. Since currently calculations are performed by an automated spreadsheet the method is time consuming and labor intensive if used on an hourly data for a fair period of time. If we feel that it is a useful method, software can be prepared for operation on a main frame computer, which can simplify the process.

The main assumption involved in these calculations is that the wind speed and direction does not change for one hour. Although calculations can be performed with time intervals shorter than one hour, hourly data had to be used as meteorological data from Met stations are hourly.

After the coordinates of the segments are determined, fraction of the time that air parcel, which is intercepted at the measurement station, spends in each of the 16 wind sectors are calculated ,then average concentration from each sector (C_j) and the relative contribution of each sector to the total (%C_j) are calculated using the following relations:

$$C_{j} = \frac{\sum_{k=1}^{N} \sum_{i=1}^{24} C_{ik} \times f_{ij}}{\sum_{i=1}^{24N} f_{ij}}$$
(4.5)

$$%C_{j} = \frac{C_{j}}{\sum_{i=j}^{16} C_{j}} \times 100$$
(4.6)

i =1....24 hour

j =1....16 sectors

Where,

 f_{ij} is the fraction of time on the ith hour that the air mass spent in the jth sector for a particular measurement day; C_{ik} is the concentration of the pollutant for the ith hour of measurement day k; N is the total number of measurement days.

The results for Çankaya and Keçiören stations are depicted in Figure 4.34. For both SO₂ and PM-10 mass concentrations and for both stations NE sector has the highest contribution to observed levels. However, the directionality observed in surface trajectory technique is much less than the directionality observed in the previous two techniques. Fairly similar contributions are observed from most of the sectors. This is because all wind speeds had to be used in trajectory method. If certain hours in a trajectory correspond to WS < 3.0 m s⁻¹ is removed, then there will be uncertainties in the location of end points.

All three methods used to estimate sector contributions showed that the NE sector has the highest contribution on measured winter SO₂ and PM-10 mass concentrations at Keçiören and Çankaya. For Keçiören station NE corresponds to squatter settlement, areas such as, Bağlarbaşı Mahalles, Gazi Mahallesi etc. For the Çankaya station NE sector includes squatter settlement district Mamak. In earlier studies in our group, high concentrations of PAH compounds, which are indicators of coal combustion were found in these squatter settlement districts (Gaga et al., 2003). Consequently these and other squatter settlement districts in Ankara are the main sources of combustion related pollutants. Contributions of sectors and average concentrations at each sector confirm this observation.

Whatever the method used, pollutants do not show a significant directionality when all wind speeds are used in calculations, owing to high frequency of low wind speeds in Ankara. Wind direction dependence becomes stronger and more obvious when low wind speeds are excluded from calculations. However, although main source regions are highlighted when only high wind speeds are included in calculations, results do not represent the real contributions. For real contributions, which can form basis for the regulatory actions to reduce concentrations at a station, all wind speeds has to be included.



Figure 4.34. Sector concentrations calculated using surface trajectory approach

The pollution rose approach is found to be useful, because it is simple and suggested similar source districts for SO_2 and PM-10 mass concentrations at the two station with more sophisticated apportionment methods used. Vossler et al., (1989) approach is found to be useful, because (1) it does provide correct information on source regions, (2) it provides quantitative information on source contributions, and (3) it provides sector based concentrations, which can be directly used in regulatory process. Among the three methods used, the surface trajectory approach is the most realistic one, as aforementioned it takes into account variation of wind sectors during the transport of air masses to the receptor.

4.7.2. Mixing Height

Vertical movement of air is determined by mixing height, which is defined as the depth through which pollutants released to the atmosphere are well mixed by dispersive processes. Dispersion of pollutants in the lower atmosphere is greatly aided by the convective and turbulent mixing that takes place. Mixing height determines the vertical extent of dispersion for releases occurring below that height. Releases occurring above mixing height are assumed to have no ground-level impact (with the exception of fumigation episodes). Therefore, deep mixing height, which indicates a larger volume for dispersion of pollutants, results in dilution of emissions and consequently, reduces concentrations of measured parameters (USEPA, 2004).

Mixing height values were calculated from radiosonde data measured at Incirli Meteorology Station, which were obtained from SMW. Radiosonde measurements are conducted twice daily on 00 UTC and 12 UTC. The hourly values of mixing height were calculated by using a meteorological pre-processor PCRAMMET developed by the US EPA.

Diurnal variation in mixing height calculated for winter and summer seasons are given in Figure 4.35. Mixing height values increase during daytime and decrease during nighttime, with a maximum between 13:00 and 17:00 in winter and 13:00 and 19:00 in summer. Diurnal variation in the mixing height values is

more significant in the summer season due to larger differences between the day and nighttime temperatures during summer. The highest mixing heights observed in winter and summer are 850 m and 2038 m, respectively. However, the minimum mixing heights observed in winter and summer are nearly same. This can also be interpreted as mixing height is not different between summer and winter during night hours.



Figure 4.35. Diurnal seasonal variations of calculated mixing heights

Unstable atmospheric conditions are observed during noontime both in winter and summer that was influenced by the sunrise. During nighttime, however, stable conditions thus poor mixing are observed in both seasons. Unstable conditions are more frequent during the summer season. Duration of the unstable conditions is also longer during summer season. Higher mixing height values and unstable conditions observed during summer season result in better mixing of atmosphere thus better dispersion and lower concentrations of pollutants than that is observed during winter season, if the emission rate in winter and summer are identical.

The effect of mixing height on the ambient concentrations of measured parameters are also investigated. Mixing height versus concentrations of measured parameters are drawn for İskitler and some non-curbside stations in Figure 4.36 and Figure 4.37, respectively. One expects lower concentrations of

pollutants when the mixing height is deep. However, the concentrations of NO,NO_2 and SO_2 at İskitler station and NO and NO_2 concentrations at Kavaklıdere and Kızılay stations does not show this expected decrease, indicating that concentrations of pollutants at curbside stations are not influenced significantly by the variations in mixing height. Please note that concentrations of pollutants at the curbside stations are also not influenced by variations in wind speed and wind direction. These indicate that at curbside stations, where emissions are very close to measurement point, measured concentrations are determined by the emissions. Meteorological factors have no influence on measured concentrations.

At non-curbside stations, concentrations of measured parameters decrease with mixing height. Dependence of concentrations of measured parameters on wind direction and speed at non-curbside stations were aforementioned in the previous section. Therefore one can claim that besides variation in source strength, meteorological factors also play an important role in determining the pollutant concentrations at non-curbside stations.

4.8. Global Urban Air Pollution Index Calculations and Forecast in Ankara

There is generally several air pollution monitoring stations in urban areas that measure variety of air pollutants on an hourly bases. Very large volumes of data are generated every day and relayed onto decision makers and public. It is not easy for decision makers and public to assimilate such large mass of information, consisting of thousands of numbers. In its simplest form air quality data are presented to public on billboards or on internet as hourly and/or daily average concentrations. Since each station represent a certain area around it, for public, it is very difficult to derive information about the general air quality status of the city as a whole from station averages. Air Pollution Index (API) emerged from the need for simplification in this system of data presentation to public. It provides a simple and understandable way to present air quality in the whole city to the public. It also allows the comparison at different cities in a







Figure 4.37. Mixing Height vs. measured parameters at some non-curbside stations

country, and even in another country. In this study, global API is investigated in two phases. In the first phase, API for Ankara is calculated for every day between October 1999 and March 2000. Then, in the second phase, calculated API is used to forecast daily API in the future. There are different approaches to calculate air pollution index for a city. Each one of these has their own weaknesses and strengths. In this study a new approach, which is proposed at CITEAIR Workshop (2005) is used to calculate API.

Sulfur dioxide and PM-10 data generated in all curbside and non-curbside stations are included in API calculations. Other pollutants, namely, NO, NO₂ and CO are not included, because to generate an API value for whole city these parameters should be measured in all stations and CO, NO, NO₂ are not measured at non-curbside stations.

To calculate the daily air pollution index, first hourly highest concentrations of SO₂ and PM-10 mass are selected at each station. Then these highest concentrations of SO₂ and PM-10 are assigned a value of GOOD, ACCEPTABLE or POOR depending on their comparison with values given in Table 4.9. Table 4.9 is obtained form CITEAIR Workshop (2005) and is not generated in this study. Thus, every parameter (SO₂ and PM-10 in our case), in every station has one of the above ratings. Since API, which will eventually be calculated is numerical in nature, the ratings of parameters has to be converted to numerical values. This is accomplished using the criteria developed by Cogliani (2001) and scores are assigned to pollutants depending on their ratings.

According to these criteria, if any parameter has a GOOD rating then it is assigned the score of 1, if it has a rating of ACCEPTABLE it is assigned the score of 3 and if it is rated POOR then it is assigned the score of 7. The score of 0 is assigned for missing values (if there is no data for that pollutant in a particular station for that day). Then, the scores of pollutants measured at the same station are summed up and compared a new criterion to assign station scores.

Table 4.9. Proposed Air Pollution Index of SO₂ and PM-10

Air Quality Level	Index	Class	ΡΜ-10ª (μgm ⁻³)	SO₂ª (μgm ⁻³)
GOOD	Very Low	0	0	0
		25	25	50
	Low	25	25	50
		50	50	100
ACCEPTABLE	Medium	50	50	100
		75	75	300
	High	75	75	300
	riigii	100	100	500
POOR	Very High	>100	>100	>500

(CITEAIR Workshop, 2005)

^a corresponds to the maximum hourly value on a day

If the sum of the pollutant scores in a station is equal to 2, which corresponds to GOOD rating in both SO₂ and PM-10 the station is assigned the station score of 0 (corresponds to GOOD rating for the station). If the sum is between 4 and 6, which means either SO₂ or PM-10 has a GOOD and the other one has ACCEPTABLE ratings, the station is assigned the station score of 1 (corresponds to ACCEPTABLE rating for the station). If the sum of the pollutant scores is between 8 and 14, which means either SO₂ or PM-10 has POOR rating and the other parameter has GOOD, ACCEPTABLE or POOR ratings, the station is assigned the score of 2 (corresponds to POOR rating for the station). If there is no data for either pollutant in a station for that day, that station is assigned the score of 2 (POOR). The air pollution index (I) for Ankara, for that particular day is simply calculated by summing all station scores calculated for

that day. This procedure is repeated and API (I) is calculated for every day between October 1999 and March 2000.

Unfortunately, there is no defined criteria to rate calculated urban API as good, acceptable and poor. We have developed and used the following criteria to rate the daily calculated value of API:

If $0 < API < 4 \rightarrow Air$ quality in the city is rated as GOOD;

If $4 \le API < 12 \rightarrow Air$ quality in the city is rated as ACCEPTABLE; and

If $API \ge 12 \rightarrow$ then air quality is rated as POOR.

These values are obtained by assuming if the average API per station (which is obtained by dividing city API to eight – for 8 stations) is < 0.49 then the API for that day is assumed to be GOOD, if it ranges between 0.5 and 1.5 it is assumed to ACCEPTABLE and if it is > 1.5 API is rated to be POOR. These threshold values are derived from station scores discussed previously. Since public can have difficulty dealing with decimal numbers, these thresholds are multiplied by eight to get the values that can be directly compared with the city API.

The variation of API between October 1999 and March 2000 is depicted in Figure 4.38. There are only two days in whole winter with API that can be rated as GOOD, there is 16 days with ACCEPTABLE API and 83 days with POOR API.

In the second phase of the study, calculated daily API values are used to predict the API value in the future and accuracy of predictions was tested using air quality data from January – March 2003. To be able to use calculated I values for prediction, firstly meteorological parameters that show close relation with API are found. For this, correlation between the daily air pollution index and the meteorological variables (daily highest temperature, daily lowest temperature,



Figure 4.38. API of Ankara between October 1999 and March 2000

daily average temperature, daily thermic excursion, daily highest wind speed, daily average wind speed, daily average barometric pressure, daily highest mixing height, daily average mixing height and daily average barometric pressure) is investigated.

Daily highest wind speed and daily thermic excursion, which is the difference between the hourly highest temperature and hourly lowest temperature data, showed the highest correlation with daily air pollution index; therefore other meteorological variables that show a weak correlation with the API are discarded.

Daily vehicular traffic is known as the major air pollution source in most urban areas (Mage et al., 1996; Mayer, 1999). Since daily traffic data was missing in this study, previous day's air pollution index value I_{d-1} is used instead. In the literature it is demonstrated that previous days API (I_{d-1}) can be used in the multiple linear regression analysis (MLR) if there is no information on traffic counts (Cogliani, 2001).

The calculated daily city API (I) is regressed against dependent variables

- daily highest wind speed;
- thermic excursion ;and
- previous day's air pollution index.

The MLR resulted in the following regression equation for Ankara and for the period between 1999-March 2000

$$I_c = 14.3101 - 0.503V + 0.178I_{d-1} + 0.145\Delta T$$
(4.7)

Where V, I_{d-1} and Δt are the wind speed, previous days API and thermic excursion, respectively. Once this equation is established, daily forecasted API values (I_c) were calculated using measured V, I_{d-1} and Δt values for another day.

We have calculated I_c values for two different periods; (1) between October 1999 and March 2000, which is the period used to derive the regression coefficients and (2) January – March 2003, which is a totally different period.

The relation between I_c and I for the period October 1999 and March 2000 is depicted in Figure 4.39. Calculated (I) and predicted (I_c) API values agrees nicely in this data set. The correlation between I and I_c is 0.72, which indicates a statistically significant correlation within 99% confidence interval with R^2 =51.23%. The standard error is 2.03. Since the same V, I_{d-1} and Δt values are both used to derive regression coefficients and to calculate I_d values, a reasonable agreement between I and I_c should be expected.

To test the method for a totally different data set, the same regression equation is used with V, I_{d-1} and Δt values measured between January and March 2003. For the same period daily I values are also calculated using the air quality data generated at non-curbside stations at that time.

The temporal variation of I and I_c in this test period is shown in Figure 4.40. The API values predicted, without making any measurements, using the regression equation derived from earlier data agrees reasonably well with the API values



Figure 4.39. I and $I_{\rm c}$ trends versus observation days during the period October 1999-March 2000



Figure 4.40. I and $I_{\rm c}$ trends versus observation days during the period January-March 2003

calculated from SO₂ and PM-10 concentrations measured in the same days. The correlation coefficient (r) is found as 0.45, which is statistically significant within 95% confidence interval with R^2 =20.36%. The standard error is 1.95. Although the correlation decreased from 0.72 to 0.45, this could be accepted as a good forecast, because lower correlations are observed in most of the air pollution index forecast models (Jiang et al., 2004).

In this study, API forecast method is only applied for SO_2 and PM-10 data because unfortunately there is no hourly data of CO, NO_2 and O_3 at noncurbside monitoring stations. If these data were present, the global index of the Ankara would be different. Therefore, measurement of hourly concentrations of CO, NO_2 and O_3 is necessary to calculate the API as these pollutants may determine the sanitary risk.

4.9. Assimilative Capacity and Pollutant Dispersion of Ankara Atmosphere

The dispersion of the pollutants in the atmosphere is governed by the meteorological parameters like wind speed, wind direction, ambient temperature at the surface and also by vertical temperature and wind profiles in the planetary boundary layer (Manju et al., 2002). In the previous sections, effects of meteorology (wind speed, wind direction and mixing height) are investigated. These provide information on either horizontal displacement or vertical displacement of air masses and pollutants associated with those masses. However, urban air quality depends not only on horizontal motions, but also on vertical movements of pollutants in the atmosphere.

In this section assimilative capacity of the Ankara atmosphere is investigated to take into account both horizontal and vertical displacement of pollutants. The assimilative capacity of the atmosphere is defined as the maximum pollutant load that can be discharged into the atmosphere without violating the best-designed use of air resources in the region. This is determined in terms of ventilation coefficient, which is a product of mixing height and average wind speed (Manju et al., 2002).

In this study, surface wind speeds which are obtained from Incirli Meteorology Station operated by the General Directorate of Meteorology and mixing heights, which are calculated from radiosonde data using EPA's PCRAMMET program, are used. The air pollution dispersion categories were defined based on the value of ventilation coefficient. Calculated hourly ventilation coefficients (VCs) were compared with the air pollution dispersion index (ventilation index) which is proposed by the State of Colorado Department of Health in Denver. The indices used for comparison are as follows:

POOR: 0-2000,

FAIR: 2001-4000,

GOOD: 4001-6000 and

EXCELLENT: ≥6001.

The number of days belonging to the each category during the sampling period is given in Figure 4.41. As can be seen from the Figure 4.41 frequencies of days having the poor dispersion conditions are dominant during the sampling period. Even the sum of the frequencies of the fair, good and excellent dispersion conditions are lower than the frequency of the poor dispersion conditions.

Seasonal variations of ventilation coefficients (dispersion conditions) are also investigated and depicted in Figure 4.42. Although the numbers of days are not equal in two seasons, the graph can be used to analyze the general trend of the dispersion conditions during these seasons. Seasonal variations in the ventilation coefficients show that poor dispersion conditions dominate over Ankara during the winter season while the increase in ventilation is obviously observed for summer season.

In the previous section (section 4.8) daily air pollution index over Ankara is calculated during October 1999-March 2000 period which is mainly in winter. Percent occurrence of calculated air pollution levels and air pollution dispersion levels over Ankara which is given in Table 4.10 indicates that poor dispersion



Figure 4.41. Ventilation Coefficients for Ankara during October 1999- August 2000.



Figure 4.42. Seasonal Variations of Ventilation Coefficients for Ankara during October 1999- August 2000.

conditions over Ankara is accompanied by the poor air pollution levels. Furthermore, the number of days with poor air pollution dispersion conditions decreases by about 83% from winter to summer, whereas the concentrations of measured pollutants (SO₂ and PM-10) at non-curbside (regular stations) stations decreased by a factor of 2-4 from winter to summer. Therefore, poor air pollution dispersion conditions besides the usage of coal may explain the higher pollution levels over Ankara in winter season to a considerable extent.

		Dispersion	
Pollution Level	% Occurunce	Level	% Occurunce
GOOD	1	GOOD	2
ACCEPTABLE	14	FAIR	18
POOR	85	POOR	80

Table 4.10. Comparison of Air Pollution and Dispersion Levels over Ankaraduring the winter period

Hourly computed ventilation coefficients during the winter and summer seasons are given in Figure 4.43. Lowest ventilation coefficients during the night and early morning indicate high pollution potential during this period. The highest values of ventilation coefficient are observed during afternoon hours due to increase in solar insolation. Viswanadham and Anil Kumar (1989) stated that when the incoming solar insolation increases as the day progresses the ventilation coefficient also increases during afternoon hours; further during evening hours when the incoming solar radiation ceases the ventilation coefficient also gradually decreases. Therefore, the assimilative capacity of the Ankara is at its best during noon. The lowest ventilation coefficients for both winter and summer are nearly same however the highest ventilation coefficient is about a factor of 4 higher in summer than in winter. Diurnal variations of the mixing height also shows similar pattern in two seasons. The highest value observed is 2038 m in summer and 850 m in winter. The very low values of mixing height that are reflected in the ventilation coefficient during the late nights and early morning hours could be due to the occurrence of ground based inversions that hamper dispersion (Padmanabhamurty and Mandal,1979; Manju et al.,2002). The wind speed in summer is only slightly higher than the winter wind speeds.

However, there is a significant difference between the summer and the winter ventilation coefficients. This could be due to the fact that the contribution by wind speed to ventilation coefficient is less in comparison to mixing height. As stated before calm wind speeds are frequent over Ankara and during such periods, vertical movement of pollutants is the only removal mechanism. Most of these discussions suggest that vertical movement of pollutants appears to be an important mechanism for cleaning atmosphere from emitted pollutants.

To show the effect of ventilation on concentrations of pollutants, calculated ventilation coefficients are plotted against air pollution index discussed in the previous section. Results are given in Figure 4.44. The relation between API and VC is stronger than the relations between measured concentrations of pollutants and wind speed or mixing height alone, which is discussed previously in Section 4.7. All high values of the API, which corresponds to poor air quality in Ankara corresponds to low values of VC and all low values of the API, which corresponds to acceptable or good air quality in the city corresponds to high values of the ventilation index. This clearly demonstrates that vertical and horizontal displacement of pollutants is the most important mechanism for cleaning of the atmosphere. This statement is true for average pollution over the city, which is represented by the API, but necessarily true for individual stations, because some of the stations, such as curbside ones, are very close to emission sources and the role of emissions can be more important in explaining variability of pollutant concentrations than horizontal and vertical movements in the atmosphere. For example comparison of station index obtained for curbside stations do not show as good agreement with the VC as the agreement observed between the city index and VC.



Figure 4.43. Seasonal diurnal variations of (a) ventilation coefficient (V.C) and mixing height

(M.H) (b) wind speed (W.S)



Figure 4.44. Variation of API of Ankara with VCs (ventilation coefficients)

CHAPTER 5

CONCLUSION

In this study, concentrations of traffic related pollutants, namely CO, NO and NO₂, and SO₂ and PM-10 are compared between two groups of stations. Since the relations between emissions and resulting concentrations are by no means simple, variations of resulting concentrations with time, space and meteorology are investigated.

Three curbside stations which are located on the most crowded street corners of Ankara, namely İskitler, Kavaklıdere and Kızılay junctions, are chosen to represent the direct influence of traffic emissions on measured parameters. Eight non-curbside stations, which are the regular stationary monitoring stations of Ministry of Health and located at different residential districts of Ankara, are used to assess the measured pollution levels in where rather than traffic, other sources especially domestic heating are the main emission sources.

Concentrations of CO, NO, NO₂, SO₂ and PM-10 show significant differences between three curbside stations. Although there is no traffic count data for each curbside station, observing different concentrations of measured pollutants are thought to be due to different traffic pattern in each station. On an annual basis, PM-10 concentrations are found similar in both groups of stations while SO₂ concentrations are higher at curbside stations. Seasonal variations of both parameters show that domestic heating is the dominating source of PM-10 and SO₂ in both groups of station in winter, and motor vehicle emissions (diesel vehicles) are found to have high contribution on SO₂ levels at curbside stations.

Non-curbside stations are divided into two groups with respect to similar SO₂ and PM-10 concentrations. Among the non-curbside stations Sihhiye, Beşevler and Küçükesat form the first group that has higher SO₂ and PM-10 concentrations; and Demetevler, Keçiören, Yenimahelle and Çankaya have lower concentrations and form the second group.

Comparison of pollution state of Ankara with other world cities and other regulatory standards show that Ankara is far from having good air quality. Relatively higher urban/rural ratio of NO, SO₂ and NO₂ indicate anthropogenic sources for these pollutants, while lower ratio for PM-10 indicate a strong contribution for natural sources on measured PM-10 concentrations in Ankara.

Winter/summer ratio of SO_2 ranges from 1.95 to 3.60 and 0.9 to 1.8 at noncurbside and curbside stations, respectively. Lower winter/summer ratio at curbside stations indicate the contribution of diesel emissions to observed SO_2 levels. On the other hand, similar winter/summer ratios of PM-10 at both groups of stations show another PM-10 source, rather than combustion, namely resuspended soil at non-curbside stations.

Contribution of traffic emissions are observed in terms of well defined bimodal traffic pattern of SO₂ and PM-10 at non-curbside stations. Binary correlations and ratios of pollutant concentrations are used to differentiate between different source types in two groups of stations. Good correlations of CO with NO and PM-10 indicate that gasoline powered vehicles contribute to observed PM-10 levels at curbside stations. Relatively week correlation between NO₂ and other measured parameters are explained by the secondary nature of NO₂. Strong correlation between SO₂ and PM-10 is attributed to contribution of diesel vehicle emissions to PM-10 at curbside stations. PM-to-SO₂ ratio ≤ 0.5 is found as the tracer of diesel vehicle emission at curbside stations. Higher NO-to-NO₂ ratio at curbside stations is explained by fresh emissions of NO, while this ratio is smaller at Sihhiye station (non-curbside station) due to transported NO₂ from traffic impacted areas. In addition to PM-10-to-NO_x ratio, CO-to-NO_x and SO₂-

to-NO_X ratios are also found as a promising tracer to differentiate between diesel and gasoline powered vehicles.

Measured parameters do not show a strong relation with meteorological parameters at the curbside stations. This is attributed to very short distance between the emissions and measurement devices in these stations. Variations in source strength, rather than meteorological variables (wind speed, wind direction and mixing height), is the main mechanism that determines the pollutant concentrations at curbside stations. At non-curbside stations wind speed, wind direction and mixing height affect the pollutant concentrations. Effect of wind direction on Çankaya and Keçiören stations are assessed by three different approaches. In all approaches SO₂ and PM-10 concentrations show similar directional dependence and indicates similar source areas. NE sector, corresponds to squatter settlements, has the highest contribution at both stations. Among the three approaches, Vossler et al., (1989) approach is found to be convenient for the data set used in this study.

Air quality level of Ankara in 1999 winter is determined by proposed API (air pollution index). 83 days in winter is rated as POOR, 16 days is ACCEPTABLE and only 2 days is GOOD. API is used to develop an air pollution forecast model which is highly correlated with meteorological variables. Model is verified with r=0.45 at 95% confidence level.

The assimilative capacity of Ankara is determined calculating ventilation index, which is the product of wind speed and mixing height. Ventilation index is found to be highest in summer and lowest in winter. The highest values of ventilation coefficient are observed during afternoon hours in both summer and winter. The contribution of mixing height to ventilation coefficient is higher in comparison to wind speed. Lower wind speeds surpass over Ankara, therefore the main dispersion mechanism over Ankara is vertical dispersion.

5.1. Recommendations for Future Studies

Concentrations of combustion related pollutants, namely SO₂ and PM-10 decreased significantly in last 10 years with the improvements in the fuel quality and the use of natural gas for space heating in approximately 43% of the residents. However, any further improvement in combustion related pollutants and traffic related pollutants will be more difficult due to lack of necessary infrastructure for natural gas use in squatter settlement districts and lack of information on the source contributions on observed pollutant levels. Scientifically sound information on sources affecting observed concentrations of pollutants is a must to develop effective air quality attainment plans. Contribution of traffic emissions on air quality at different parts of the city must be particularly identified and quantified as traffic is probably the most important source of air pollution today in Ankara. Following are the high priority issues that must be completed as soon as possible for quantitative source apportionment:

An emission inventory for CO, SO₂, NO, PM-10 and VOCs must be compiled and regularly updated,

A numerical modeling exercise must be performed using generated emission inventory. The model must be calibrated using measurement results.

There were a number of problems in terms of data completeness in this study. Lack of summer data at residential stations, lack of simultaneous measurements at the curbside stations and lack of any NO, NO₂ and CO data at residential measurement points were the most important ones. Obviously a more comprehensive measurement is needed. This need will be fulfilled in the nears future, because Ministry of Health is now setting up 9 new stations where not only SO₂ and PM-10 mass, but also other pollutants such as CO, NO, NO₂ and O₃ will be measured. Measurement of VOCs and metals in at least some of these new stations can be very helpful for source apportionment.

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