INVESTIGATION OF EMISSION FACTORS OF NON-METHANE HYDROCARBONS FOR SOME WIDELY USED PASSENGER CARS IN TURKEY

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Approval of the Graduate School of Natural and Applied Sciences

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ABSTRACT

INVESTIGATION OF EMISSION FACTORS OF NON-METHANE HYDROCARBONS FOR SOME WIDELY USED PASSENGER CARS IN TURKEY

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The objectives of this study are to measure the non-methane volatile organic carbon (NMVOC's) emissions from passenger cars in Turkey having gasoline engines, to determine emission factors of these vehicles for BTEX compounds and comparison of emission factors obtained in this study with the emission factors of the other countries.

This study was conducted in two parts: The first part was to determine the categories of passenger cars widely used in Turkey, and also to determine the average carbon monoxide (CO) and hydrocarbon (HC) emissions at idle condition for these car types based on the exhaust emission measurements of Ankara Çevre Koruma Vakfı (ANÇEVA). The second part of the study was to analyze the gas composition of exhaust gasses at different road conditions for BTEX components by using gas chromatography.

The results of the study have shown that the cars named under ‘‘Tofas’’ constitute 31.5% and ‘‘Fiat’’ 13.1% of the total cars in Turkey and they are manufactured by the same company. Therefore, studies have been performed with ‘‘Tofas/Fiat’’ cars.

The highest emission factors among hydrocarbons investigated in this study were found for toluene and m-xylene. Generally, as driving speed increases the emissions of HC’s are found to decrease in concentration. It was interesting to note that the highest emissions occur at 30 km/hr speed which is the mostly used speed in crowded streets and busy intersections. Therefore, it was concluded that it is very important to take measures for emissions in the city traffic. Cold start emissions were also found to be higher than the hot start emissions.

Keywords: Emission factors, BTEX emissions, CO/HC emissions, Turkish fleet of passenger cars.

ÖZ

TÜRKİYE'DE YAYGIN OLARAK KULLANILAN BAZI BİNEK ARABALARI İÇİN METAN DIŞINDAKİ HİDROKARBONLARIN EMİSYON FAKTÖRLERİNİN ARAŞTIRILMASI

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Bu çalışmanın amacı, ülkemizde en çok kullanılan benzin motorlu binek arabalarında ekzos gazı içerisindeki NMVOC konsantrasyonlarını ölçmek, metan içermeyen uçucu organik karbonlar (NMVOC) için "emisyon faktörlerini" çıkarmak, NMVOC içinde bulunan bileşenleri saptamak ve bunlar için emisyon faktörlerini ayrıca tayin etmek ve bulunan emisyon faktörlerini diğer ülkelerin faktörleriyle karşılaştırmaktır.

Bu çalışma iki kısımda yürütülmüştür. Çalışmanın ilk kısmında Türkiye'de kullanılan binek araçlarının hangi marka ve kategoride olduğu bulunmuştur. Ayrıca Ankara Valiliği Çevre Koruma Vakfı (ANÇEVA) tarafından rölanti koşullarında yapılan karbon monoksit (CO) ve toplam hidrocarbon (HC) ölçümlerine dayalı olarak bu binek araçları için ortalama CO ve HC emisyonları belirlenmiştir. Çalışmanın ikinci kısmında değişik araç hızlarında, ekzos borularından alınan egzos gazı örneklerinde BTEX bileşenleri Gaz Kromatografi yöntemi ile tayin edilmiştir.

ANÇEVA çalışmasından elde edilen sonuçlar toplam benzinli araçların % 31.5'ini ‘‘Murat’’ ve % 13.1’ini ‘‘Fiat’’ arabaların oluşturduğunu göstermiştir. Bu iki arabanın yapımcısı aynı firmadır. "Murat/Fiat’’ marka arabalar en çok kullanılan arabalar oldukları için çalışmalar bu araçlarda gerçekleştirilmiştir.

İncelenen hidrokarbonlar içerisinde en fazla emisyon faktörü değerleri toluen ve m-xylene için bulunmuştur. Aracın sürüş hızı arttıkça genel olarak HC emisyonlarının azaldığı tespit edilmiştir. Burada dikkati çeken nokta en yüksek emisyonların 30 km/saat hız için bulunması, bu hızın da kalabalık kavşaklarda ve caddelerde en çok kullanılan hız olmasıdır. Bu nedenle, trafiğin yoğun olduğu yerlerde trafikten kaynaklanan emisyonlar için önlem alınmasının çok önemli olduğu kanısına varılmıştır. Araç motorunun soğuk başlama koşullarındaki emisyonları, sıcak başlama koşullarındaki emisyonlardan daha fazla bulunmuştur.

Anahtar Kelimeler: Emisyon faktörleri, BTEX emisyonları, CO/HC emisyonları, Türkiye araba envanteri.

To ***my family***

and

to ***Baran***

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LIST OF ABBREVIATIONS

AAM	Association of Automobile Manufacturers
AC	Active carbon
ANÇEVA	Ankara Çevre Koruma Vakfı
atm	Atmosphere
benz	Benzene
^{o}C	Degrees Celcius
CC	Cylinder volume in the cars
cm	Centimeter
CM	Calibration mixture
Corinair	Coordination of Environmental Air
cs	cold start
Drv con	Driving condition
EC	European Community
ECE	Economic Commision for Europe
EF	Emission factor
EPA	USA Environmental Protection Agency
EPER	European Pollutant Emission Register
EU	European Union
g	Gram
GC	Gas Chromatograph
HC	Hydrocarbon
hPa	HektoPascal
hr	Hour
hs	hot start
^{o}K	Degrees Kelvin
km	Kilometer
L	Liter

m^3	Meter cube
METU	Middle East Technical University
mg	Miligram
min	Minutes
µL	Microliter
mL	Milliliter
mm	Millimeter
mVsec	Mili volt sec
NAEI	UK National Atmospheric Emission Inventory
NMVOC	Non-methane volatile organic carbon
ppmv	Parts per million by volume
pseud	Pseudocumene
PTFE	Poly Tetrafluoro Ethylene
rpm	Revolutions per minute
R	Correlation coefficient
RH	Relative Humidity
SIS	State Institute of Statistics
SEPA	Scottish Environment Protection Agency
TS	Turkish Institute of Standardization
UBA	Umweltbundesamt Berlin and INFRAS AG Bern
UK	United Kingdom
USA	United States of America
V	Average speed
VOC	Volatile organic carbon
WHO	World Health Organization
wt	Weight
w/o	without

CHAPTER I

INTRODUCTION

1.1. General

The rapid improvement in automotive industry, increase in the life standard, and fast increase in the number of the motor vehicles with increase in population caused air pollution by motor vehicles to become an important problem in the world. Today most of the big cities suffer from air pollution due to traffic.

Air pollution from the road traffic depends on both vehicle emissions and the number of vehicles in the traffic. Personal and collective driving conditions are also effective in producing pollution. In the USA, hydrocarbon (HC), carbon monoxide (CO) and nitrogen oxide (NO) pollution from transportation is 34.3%, 62.6%, and 34.3% of the total pollution, respectively (De Nevers, 1995).

The distribution of HC emissions among various sources in the USA in 1999 is shown Figure 1.1. Although the largest portion (53%) of HC emissions comes from non-mobile sources including engines and equipment used for construction, agriculture, transportation, recreation and many other purposes, it is seen from the figure that HC emissions from on-road mobile sources including vehicles used on roads for transportation of passengers or freight make 29% of the total HC emissions. Nonroad mobile sources which are for example railroads, marine, aircraft constitute the 18 % of the total HC emissions (Anon (i), 1999a).

The distribution of HC emissions among various vehicles in the USA in 1999 is given in Figure 1.2. It is seen from the figure that cars and motorcycles have the largest share in HC emissions with 55%. This is followed by the emissions of the "light gasoline trucks" with 33% (Anon (i), 1999a).

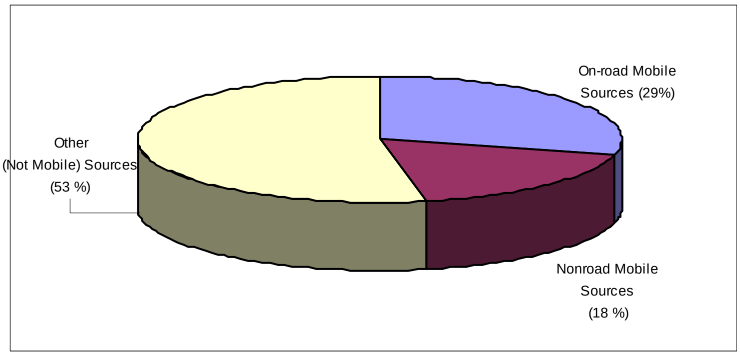

Figure 1.1 Distribution of hydrocarbon emissions among various sources in the USA (Anon (i), 1999a).

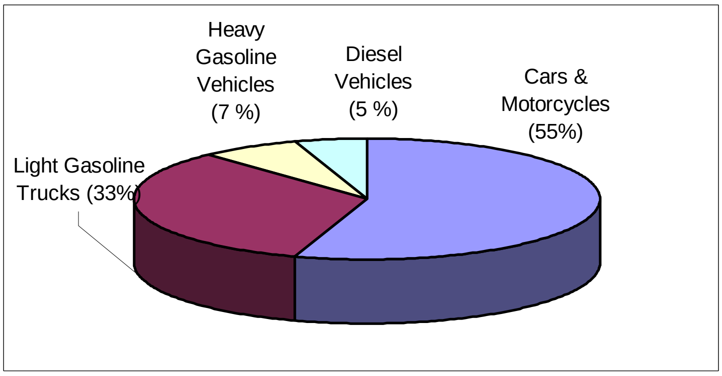

Figure 1.2 Distribution of hydrocarbon emissions among various vehicles in the USA (Anon (i), 1999a).

Motor vehicles are generally divided into two classes as *gasoline* and *diesel engine* vehicles. Theoretical emissions obtained from complete combustion of hydrocarbon fuels (fossil fuels) are CO_2 and H_2O. However, in practice it is impossible to have 100% complete combustion in gasoline and diesel engines. Therefore, some compounds are produced due to incomplete combustion. Exhaust gasses from motor vehicles contain "incomplete combustion products (ICP)" like aldehydes, ketones, carboxylic acids and CO, NO_x, SO_2, lead compounds, particulate matters (Perkins, 1974; Wark and Warner, 1990; Müezzinoğlu, 2004 İçingür, 1991).

Emissions from vehicles are divided into four categories:

1- Evaporation from the fuel tank
2- Fuel evaporation from carburetor
3- Crankcase emission
4- Exhaust gasses

The amount of exhaust gasses emitted and compounds present in the gasses depend on several factors such as:

- Air to fuel ratio
- Residence time of fuel in the combustion chamber
- Geometry of the combustion chamber
- Engine rpm
- Type of the fuel
- Geographic factors
- Load of the vehicle
- Condition of the road

(Anon (h), 2002; Anon (j), 1999b)

As we compare the gasoline and diesel engine vehicles, it is seen that diesel engines have less emissions of CO, HC, $NO_{x,}$ and more SO_2 and particulate emissions than gasoline engines. The reason for this is that the air-to-fuel ratio in diesel vehicles is more than in the gasoline vehicles. Gasoline vehicles have less particulate emissions except for the condition of the rich air-to-fuel ratio (AFR). On the other hand, the concentration of particulates is about 10 to 20- fold higher in the exhaust gases from diesel fuelled vehicles than the gasoline vehicles (Anon (l), 1996; Barlas, 1997).

BTEX is the term used to describe a group of chemicals (hydrocarbons) related to benzene. This includes a variety of compounds: toluene (methylbenzene), ethyl benzene, xylenes and benzene itself. These compounds are usually colorless, sweet-smelling liquids which evaporate easily. They mix well with organic solvents, but do not dissolve well in water (and may float on the surface before evaporating into the air). BTEX compounds are part of the group of compounds known as volatile organic compounds (VOCs).

Benzene, toluene, ethylbenzene and xylene (BTEX) can enter the body either by inhalation of air contaminated with BTEX vapors, ingestion of contaminated water or food containing BTEX, or by dermal contact with BTEX in liquid form. The health effects associated with BTEX are dependent on the composition of the mixture (Anon (c), 2004).

Inhalation of air containing elevated levels of BTEX over a long period of time can lead to a range of adverse health effects including tiredness, dizziness, confusion, irritation of the nose, throat and respiratory system, nausea, memory loss, and depression of the central nervous system. Unintentional short-term exposure to very high levels of BTEX can lead to tiredness, loss of consciousness and, in extreme cases, death. Ingestion of high levels of BTEX and the associated health effects is not widely reported in humans. Dermal contact with large amounts of BTEX can cause irritation of the skin and eyes. Some BTEX can be involved in the formation of ground level ozone, which is known to exacerbate existing respiratory conditions such as asthma (Anon (c), 2004).

The International Agency for Research on Cancer has designated the components of BTEX as carcinogen (e.g. benzene), possible carcinogen (e.g. ethylbenzene) and not classifiable as to their carcinogenicity to humans (toluene, xylene). However, exposure to BTEX at normal background levels is unlikely to have any adverse effect on human health (Anon (c), 2004).

Hydrocarbons have various effects on human beings. Some are harmless to the human health, some are odorous, and others cause severe diseases like cancer (e.g. benzene). They mainly cause problems in respiratory system and eyes. Polycyclic aromatic compounds usually produce hydrocarbons which may cause cancer (Emri, 1995).

The need for the clean air is about 15 m^3/day per person and a vehicle which has no emission control system can make this air very polluted, harmful and inconvenient for breathing in a very short time (Kara et al., 1991; Uğurbilek, 1995). The pollutants have a direct and toxic effect on human health. Therefore, emissions from motor vehicles are more important than the other sources. Besides some of these emissions are carcinogenic.

Nonmethane hydrocarbons emitted to the atmosphere have an important role on the "Photochemical Smog" formation (Stern et al., 1994). Methane is always present in exhaust gases and it is quite unreactive in producing photochemical smog. Therefore, it is generally not counted for air pollution purposes as an exhaust hydrocarbon (De Nevers, 1995). Today, most of the cities in Europe and United States have ozone problem (ground level ozone), which is one of the photochemical smog product and causes health problems in humans such as difficulty in breathing, lung damage, and reduced cardiovascular functioning. Studies to determine the ozone concentration in the atmosphere have started in Europe and the most important studies among those are the BERLIOZ project performed in Berlin, Germany and the EVA project performed in Ausburg, Austuria. In both of these projects, it is determined that HC's and nitrogen oxides due to traffic play an important role on the formation of ozone (Volz-Thomas et al., 2003).

1.2. Current Situation in Turkey

There has been a rapid increase in the number of passenger cars, buses, and shared taxis (dolmush) during recent years in Turkey. Because of this rapid increase in number of cars during the last 15 years, air quality in big cities has been affected adversely from this situation. There were 3 800 900 vehicles in 1994 in Turkey. This number has increased to 7 477 000 in 2002 according to the reports of the State Institute of Statistics (SIS) (SIS, 2003). Passenger cars, shared taxis (dolmush) and buses are the vehicles mostly used in transportation since subway and rail systems are not developed extensively for public transportation.

The distribution of vehicles in Turkey among different groups in year 2002 is given in Figure 1.3. As can be seen from the figure passenger cars form 61% of the total number of vehicles. Motorcycles and small trucks follow this group with 14% and 12%, respectively.

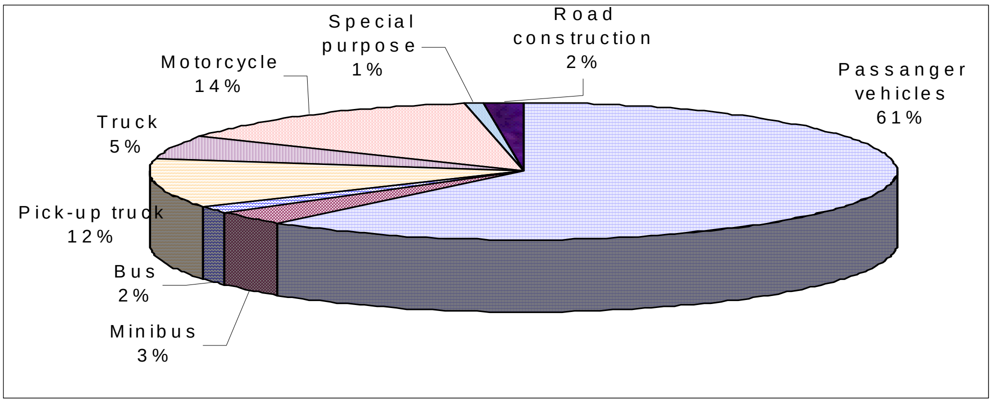

Figure 1.3 Distribution of vehicles in Turkey among different groups (Anon (d), 2002)

In most of the European countries and in the USA, emission limits for the motor vehicles were determined, standards and regulations have been issued and started to be enforced in 1960's. On the other hand, in our country emission control standards are not complete and enforcement of these standards is poor. In addition to this, the unconscious usage of motor vehicles and lack of maintenance on these vehicles make motor vehicles very important source of emission.

European Union (EU) countries have started to improve their engine technologies and increased the supply of unleaded gasoline since 1985. After the very wide distribution of the unleaded gasoline was completed in 1993, it was obligatory to use catalytic converter for all types of vehicles. In our country, automobile industry has started to manufacture their engines with catalytic converter in 1993 and catalytic converter usage in the cars has rapidly increased after year 1994. The increase between years 1994 and 2001 is given in Figure 1.4 (Anon (a), 1995; Anon (b), 2001).

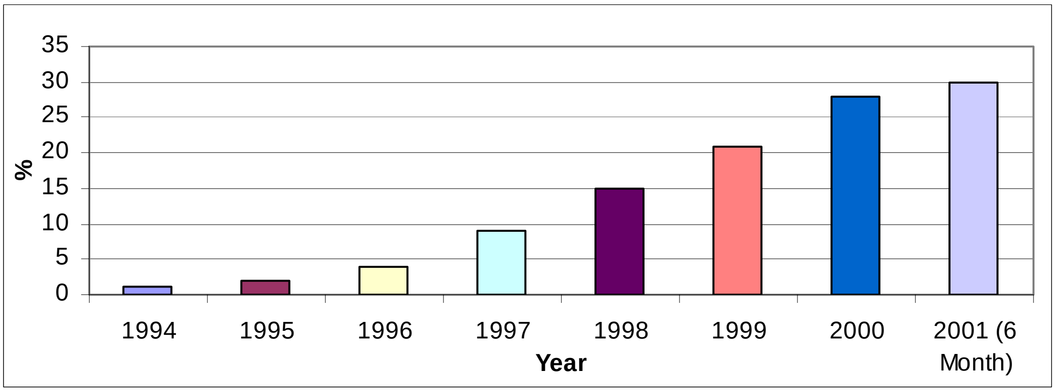

Figure 1.4 Increase in the number of cars with catalytic converter in Turkey (Anon (b), 2001)

The composition of fuel used in the vehicles is also very important for emissions. Ministry of Environment and Forestry in Turkey has made some recent studies on reducing vehicle emissions. A regulation on " Quality of Gasoline and Diesel Fuel" has been issued on 11.06.2004. This regulation brings strict standards for the fuels used in gasoline and diesel cars. Present benzene content of normal and super gasoline is maximum 5% by volume, and that of unleaded gasoline is maximum 2.5-5.0% by volume in Turkey (http://www.tupras.com.tr/faaliyet_3_1.htm, 2004). This benzene content is high and planned to be reduced to maximum 1% by volume until 01.01.2006 according to the recent regulation. Also this regulation brings some standard for the aromatic content of fuels which is 42% v/v for the present and planned to be reduced to 35% by volume after 01.01.2009. Lead content of gasoline which is 0.4 g/L for super gasoline for the present will be reduced to maximum 0.15 g/L after 01.01.2005 and 0.005 g/L after year 2007. Distribution of the leaded gasoline will be allowed to a maximum of 0.5% of total sales for old technology vehicles after 01.01.2006 (Anon (f), 11.06.2004).

1.3. Objectives of the Study

The major difficulty in the emission inventories performed for the ‘‘Clean Air Plans" according to the Turkish Air Quality Control Regulation (1986) is the determination of the emissions from vehicles. The most practical way to determine the emission inventories for vehicles is to use ‘‘emission factors’’. However, there are not ‘‘emission factors’’ available for Turkish cars.

Emission factors used in Europe and the USA can not be used confidently in Turkey. Use of emission factors developed for Europe or the USA does not give correct results in our emission calculations because the vehicle park and composition of fuel used in Turkey is different from Europe and the USA (Üner et al., 2000b). For example, benzene concentration of the fuels used in Turkey is 3-5% by vol. However, it is 1.5-3.0% by volume in Japan, maximum 2.4% by volume in Europe, and maximum 1.0% by volume in the USA. Another example is the aromatic compounds. The maximum amount of aromatic compounds of fuels used in Turkey is 42% by volume. However it is 30, 33 and 25% by volume in Japan, European Union and the United States, respectively. This data shows that fuel composition used in Turkey is different from that in the developed countries (Üner et al., 2000b). Therefore, the emissions will be different, too.

The objectives of this study are:

(i) to determine the non-methane volatile organic carbon (NMVOC's) emissions from passenger cars (Tofas/Fiat cars were chosen for this study because they are the most widely used brand names in Turkey) having gasoline engines,

(ii) to determine the emission factors of these vehicles for NMVOC's and the concentrations of benzene, toluene, xylene, ethylbenzene m-xylene, o-xylene and 1,2,4 trimethylbenzene (pseudocumene) compounds in the NMVOC's,

(iii) to compare the obtained emission factors with the emission factors of the other countries.

CHAPTER 2

THEORETICAL BACKGROUND AND LITERATURE SURVEY

2.1. Role of Hydrocarbons in Photochemical Smog

When hydrocarbons of anthropogenic or natural origin react with hydroxyl (OH) radicals, peroxy radicals can be formed which, by re-forming OH radicals, tend to cause oxidation of the NO to NO_2.

In the clean troposphere OH radicals react with CO and CH_4, according to the following reactions (Baumbach, 1996):

$$\mathrm{O\dot{H} + CH_4 \rightarrow H_2O + C\dot{H}_3}$$

The H atoms and hydrocarbon radicals ($\mathrm{C\dot{H}_3}$, or generally $\mathrm{R\,C\dot{H}_3}$) attach themselves to oxygen molecules to form peroxy radicals, $\mathrm{\dot{H}O_2}$ or $\mathrm{\dot{R}O_2}$ (R= alkyl or aryl groups).

$$\mathrm{\dot{H} + O_2 \rightarrow \dot{H}O_2}$$

$$\mathrm{RC\dot{H}_3 + O_2 \rightarrow RC\dot{H}_3O_2}$$

The peroxy radicals react with NO, whereby NO_2 is formed and OH radicals are reformed (Baumbach, 1996):

$$\mathrm{NO + \dot{H}O_2 \rightarrow NO_2 + \dot{O}H}$$

$$\mathrm{NO + C\dot{H}_3O_2 \rightarrow NO_2 + C\dot{H}_3O}$$

or generally:

$$NO + R\dot{O}_2 \rightarrow NO_2 + R\dot{O}$$

$\dot{O}H$ radicals are very reactive and enter into many different reactions in the atmosphere. Particularly under the influence of solar radiation, $\dot{O}H$ radicals are present in significant concentrations.

Thus with the $\dot{O}H$ radicals, oxidizing agents (peroxide radicals) are formed from hydrocarbons, without the OH radicals being consumed in the process. Different hydrocarbons participate in varying degrees to the formation of oxidizing agents or to the reformation of $\dot{O}H$ radicals, thus to the formation of ozone (Baumbach, 1996).

Ozone formation in the atmosphere takes place according to the following reactions:

$$NO_2 + h\nu \rightarrow NO + \dot{O}$$

$$\dot{O} + O_2 \rightarrow O_3$$

The depletion of ozone can take place by reaction of O_3 with NO in the atmosphere:

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

The reactions are also diagrammatically shown in Figure 2.1.

For the accumulation of O_3 in the troposphere, NO in the atmosphere needs to be oxidized by an oxidizer other than O_3. These oxidizers (the free radicals, like peroxy radicals) are provided by the hydrocarbons as a result of their interaction with the sunlight, as seen in the lower cycle in Figure 2.1. Therefore, NO in the atmosphere is mostly taken up by the radicals produced by hydrocarbons and O_3 in the troposphere accumulates. This causes the increase in the O_3 concentration in the troposphere during day time.

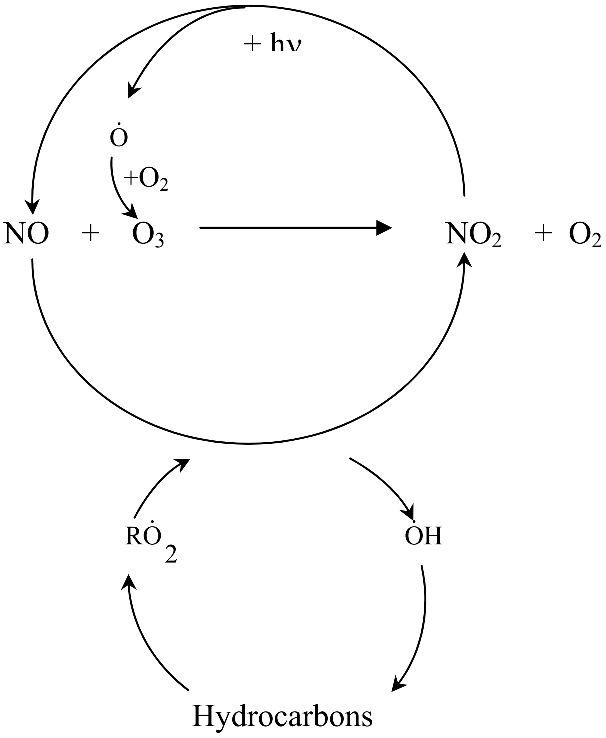

Figure 2.1 Diagram illustrating NO-NO_2-O_3 Cycle with contribution of hydrocarbons (Baumbach, 1996)

2.2. Emission Factors

2.2.1. General

Emission factors and emission inventories have long been fundamental tools for air quality management in Europe and in the United States. Emission estimates are important for developing emission control strategies, determining applicability of permitting and control programs, ascertaining the effects of sources and appropriate mitigation strategies, and a number of other related applications by an array of users, including national and local agencies, consultants, and industry. Data from source-specific emission tests or continuous emission monitors are usually preferred for estimating the emissions from a source because those data provide the best representation of the tested source's emissions. However, test data from individual sources are not always available and, even then they may not reflect the variability of actual emissions over time. Thus, emission factors are frequently the best or only method available for estimating emissions, in spite of their limitations (Stern et al., 1994).

An emission factor is a representative value that attempts to relate the quantity of a pollutant released to the atmosphere with an activity associated with the release of that pollutant. These factors are usually expressed as the weight of pollutant divided by a unit weight, volume, distance, or duration of the activity emitting the pollutant (e. g., kilograms of particulate matter emitted per ton (megagram) of coal burned). Such factors facilitate estimation of emissions from various sources of air pollution. In most cases, these factors are simply averages of all available data of acceptable quality, and are generally assumed to be representative of long-term averages for all facilities in the source category (i.e., a population average).

The general equation for estimating the emissions from a pollution source by using an emission factor is given in Equation 2.1.

$$\text{Emissions [g]} = \text{Emission factor [g/km]} \times \text{Vehicle kilometers traveled [km]} \qquad (2.1)$$

The passage of the Clean Air Act Amendments of 1990 (CAAA) and the Emergency Planning And Community Right-To-Know Act (EPCRA) of 1986 in the U.S.A. has increased the need for emission limits, emission factors as well as the inventories for Hazardous Air Pollutants (HAP). The "Emission Factor and Inventory Group" (EFIG), in the U. S. Environmental Protection Agency's (EPA) "Office of Air Quality Planning and Standards" (OAQPS), developed and maintained emission estimating tools. The AP-42 which is the publication containing a series of emission factors determined by the EPA, is the principal means by which EFIG can document the emission factors. These factors are cited in numerous other EPA publications and electronic data bases, but without the process details and supporting reference materials (Anon (k), 1991).

Emission factor ratings in AP-42, which will be discussed in the next section, provide indications of the robustness or appropriateness of emission factors for estimating average emissions for an activity source. Usually, data are insufficient to indicate the influence of various process parameters such as temperature and reactant concentrations on emissions.

2.2.2. Use of Emission Factors

Emission factors may be appropriate to use in a number of situations such as making source-specific emission estimates for area wide inventories. These inventories have many purposes including ambient dispersion modeling and analysis, development of control strategy, and screening sources for compliance investigations. Use of emission factors may also be appropriate in some permitting applications, such as determinations and in establishing the operating permit fees.

Two steps are involved in *AP- 42 emission factor* ratings. The first step is an appraisal of data quality that is the reliability of the basic emission data that will be used to develop the emission factor. The second step is an appraisal of the ability of the factor to stand as a "national annual average emission factor" for that source activity.

The quality of the test data is rated as A through D, according to the following criteria (Anon (j), 1999).

A= Statistically significant emission factors based on sufficiently large set of measured and evaluated data

B= Emission factors non statistically significant based on a small set of measured re-evaluated data.

C= Emission factors estimated on the basis of available literature

D= Emission factors estimated applying similarity considerations and/or extrapolation. Tests are based on a generally unacceptable method, but the method may provide an order-of-magnitude value for the source

Emission factors for European Union can be obtained from the web page of National Atmospheric Emissions Inventory, http://www.naei.org.uk/emissions. Emission factors calculated in year 2000 for light duty gasoline vehicles in the U.K. are given in Table 2.1.

Table 2.1 Emission factors for light duty gasoline vehicles in the U.K. (http://www.naei.org.uk/emissions, 2004)

Driving condition	Emission factors for Non Methane VOC	Emission factors for Benzene
Cold Start	2.35 g/cycle	0.08 g/cycle
Urban driving	1.05 g/km	0.01 g/km
Rural driving	0.48 g/km	0.00696 g/km
Motorway driving	0.67 g/km	0.00727 g/km

As can be seen from Table 2.1 emission factors for the cold start and urban driving in the U.K. are higher than emission factors for rural and motorway driving. Also, the highest emission factor of benzene belongs to urban driving among various types of driving conditions.

Emission factors based on the Corinair study (1999) are given in Table 2.2.

Table 2.2 Estimated Emission Factors (Anon (j), 1999)

	NO_x	CH_4	VOC	CO	N_2O	CO_2
Estimated Emission Factors for Gasoline Passenger Cars						
	Uncontrolled: Fuel Economy 11.2 L/100 km					
Total g/km	2.24	0.07	5.40	46.5	0.005	269
Exhaust g/km	2.24	0.07	4.03	46.5	0.005	269
Evaporative g/km			1.37			
g/kg fuel	26.6	0.83	64.0	551	0.059	3183
	Early non-catalyst controls: Fuel Economy 9.4 l/100 km					
Total g/km	2.05	0.08	5.31	28.6	0.005	225
Exhaust g/km	2.05	0.08	3.94	28.6	0.005	225
Evaporative g/km			1.37			
g/kg fuel	29.0	1.13	75.2	405	0.071	3183
	Non-catalyst controls: Fuel Economy 8.3 L/100 km					
Total g/km	2.30	0.07	4.58	18.7	0.005	199
Exhaust g/km	2.30	0.07	3.32	18.7	0.005	199
Evaporative g/km			1.26			
g/kg fuel	36.7	1.12	73.2	298	0.080	3183
	Three-way catalyst: Fuel Economy 8.5 L/100 km					
Total g/km	0.520	0.02	0.47	2.86	0.050	203
Exhaust g/km	0.520	0.02	0.41	2.86	0.050	203
Evaporative g/km			0.06			
g/kg fuel	8.16	0.314	7.37	44.9	0.784	3183
Estimated Emission Factors for Diesel Passenger Cars						
Total g/km	0.66	0.005	0.19	0.71	0.010	190
g/kg fuel	10.9	0.083	3.14	11.7	0.165	3138
Estimated Emission Factors for LPG Passenger Cars						
Total g/km	2.16	0.06	1.55	7.10	-	178
g/kg fuel	36.8	1.02	26.4	121	-	3030

As VOC emission factors from Table 2.2 are compared for cars with and without catalytic converter, it is seen that emission factors for cars having catalytic converter are lower than the ones having no catalytic converter.

The change of VOC emission factors with speed for passenger cars having gasoline engine is given in Table 2.3.

Table 2.3 Speed dependency of VOC emission factors for gasoline passenger cars (Anon (j), 1999)

Vehicle Class	**Engine Capacity, L**	**Speed range (km/h)**	**VOC Emission Factor (g/km)**	**R^2**
PRE ECE	All capacities All capacities	10-100 100-130	$30.34V^{-0.693}$ 1.247	0.980 -
ECE 15-00/01	All capacities All capacities	10-50 50-130	$24.99V^{-0.704}$ $4.85V^{-0.318}$	0.901 0.095
ECE 15-02/03	All capacities All capacities	10-60 60-130	$25.75V^{-0.714}$ $1.95 - 0.019V + 0.00009V^2$	0.895 0.198
ECE 15-04	All capacities	10-60	$19.079V^{-0.693}$	0.838
	All capacities	60-130	$2.608 - 0.037V + 0.000179V^2$	0.341
	Improved CC < 1.4 L	10-130	$2.189 - 0.034V + 0.000201V^2$	0.766
	Conventional 1.4 L < CC < 2.0 L	10-130	$1.999 - 0.034V + 0.000214V^2$	0.447
	Open Loop CC < 1.4 L	10-130	$2.185 - 0.0423V + 0.000256V^2$	0.636
	1.4 L < CC < 2.0 L	10-130	$0.808 - 0.016V + 0.000099V^2$	0.490
	CC < 1.4 L	10-130	$0.5278 - 0.0129V + 0.000087V^2$	0.219
	91/441/EEC 1.4 L < CC < 2.0 L	10-130	$0.4590 - 0.0106V + 0.0000672V^2$	0.258
	CC > 2.0 L	10-130	$0.2721 - 0.00566V + 0.0000376V^2$	0.101

V: Average speed expressed in km/h
R^2 : Correlation coefficient
CC: Cylinder volume in the cars
ECE: Economic Commission for Europe
PRE ECE: Before ECE

The formulas given in the table for various cars having different cylinder volumes can be used to calculate emission factors for various speeds. However, R^2 values for some formulas are very low which indicates the non-reliability of the formula given in the table.

Chassis dynamometer tests, tunnel and model studies are mainly used in studies related with emission and emission factor calculations in European countries and in the USA.

Averaged emission factors for large vehicle fleets are calculated efficiently by analysis of the concentration of individual pollutants in the air of road tunnels in the USA and European Union countries. The outcomes of these tunnel studies are widely used to estimate the emissions of pollutants related to road traffic. Thus, several tunnel studies have been performed and the data obtained represents car populations in various velocity and acceleration conditions. Besides the predominant engine condition during the tunnel driving, the car fleet with respect to engine and exhaust gas treatment technology strongly influences the average emission factors. Therefore, the emission data obtained also resembles the actual traffic policy in a country with respect to speed limits as well as age and technical status of the car fleet. Velocity-dependent emission factors determined by correlation of the average speed of the car fleet and the corresponding mean concentration of a pollutant in the tunnel air are only representative for the rather narrow velocity range driven in the tunnel. Thus, the emission data presented by Hampton et al. (1983), Pierson et al. (1996), Sagebiel et al. (1996), Staehelin et al. (1997) and Staehelin et al. (1998), either represent highway driving in the range of 60-100 km h^{-1} or urban driving from 0 to 60 km h^{-1} (Dufy and Nelson,1996; Haszpra and Szilagyi, 1994). Furthermore, the emission factors obtained are influenced by the topography of the tunnel (up hill or down hill driving) and in addition are affected by the rather smooth driving style if the speed is limited or overtaking is forbidden. Thus, all of the cited tunnel studies only cover a limited set of the possible velocity and acceleration situations of a car fleet. Therefore, alternative concepts have been developed to obtain velocity-dependent emission factors from chassis dynamometer measurements (Anon (e), 1995). Although only a limited number of cars can be tested with tunnel studies a complete set of velocity and acceleration situations can be simulated on a modern chassis dynamometer.

2.3. Driving Cycles (Test Cycles) for Vehicle Emissions

Chassis dynamometer is used to obtain driving conditions complying different cycles which was devised to stimulate the speed and power demands of any area. Chassis dynamometer test cycles are used for emission and fuel economy measurement and these tests cycles are conducted over real-world driving cycles to obtain emission factors by using emission data from in-use vehicles. These cycles are representative for specific part of the world traffic. Some types of test cycles used in the USA are given in Table 2.4. These cycles are called Federal Test Procedure (FTP). There are two types of FTP; one is FTP 72 and the other is FTP 75. (Anon (i), 1999)

Table 2.4 Test cycles used in the U.S.A. (Anon (i), 1999)

Test Cycle	Description
FTP 75	A transient test cycle for cars and light duty trucks derived from the FTP-72. Used for emission certification testing of cars and light duty trucks in the U.S.A.
FTP 72	A transient test cycle for cars and light duty trucks performed on a chassis dynamometer. Simulates a urban route with frequent stops.

FTP 75 is more advanced cycle than FTP 72 and today FTP 75 is used for emission certification. Therefore, more detailed information is given about FTP 75 in the following pages.

The entire FTP-75 cycle consists of the following segments:

- cold start phase (0-505 s)
- transient phase (505-1369 s)
- hot start phase (0-505 s)

The following are basic parameters of the cycle:
Distance travelled: 11.04 miles (17.77 km),
Duration: 1874 s,
Average speed: 21.2 miles per hour (34.1 km/h).

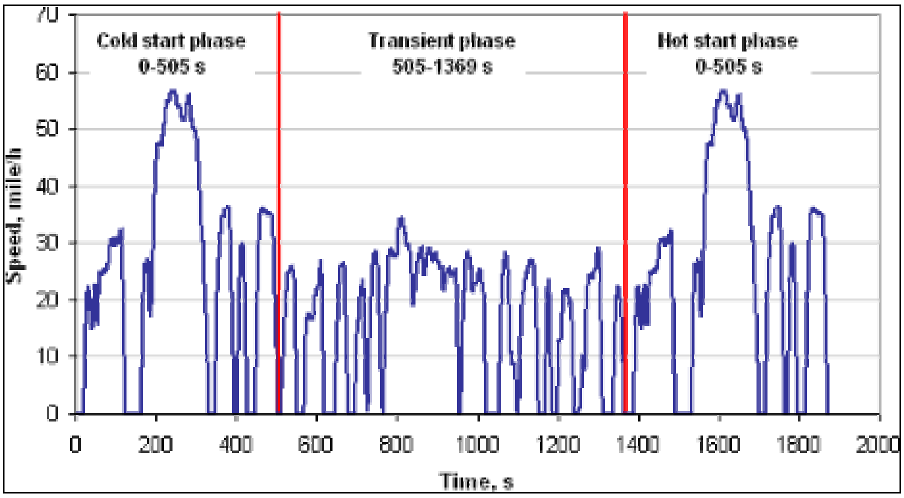

Figure 2.2 FTP-75 Cycle (Anon (i), 1999)

The emissions from each phase are collected in a separate PTFE bag, analyzed and expressed in g/mile (g/km). The weighting factors are 0.43 for the cold start, 1.0 for the transient phase and 0.57 for the hot start phase. The FTP-75 cycle is known in Australia as the ADR-37 (Australian Design Rules) cycle.

Table 2.5 Test cycles in the European Union (http://www.dieselnet.com/standards/cycles, 2004)

Test Cycle	Description
ECE+EUDC	A combined chassis dynamometer test used for emission testing and certification in Europe. It is composed of four ECE Urban Driving Cycles, simulating city driving, and one Extra Urban Driving Cycle (EUDC), simulating highway driving conditions.

ECE: Economic Commission for Europe
EUDC: Extra Urban Driving Cycle

The ECE+EUDC test cycle is performed on a chassis dynamometer. The cycle—also known as the MVEG-A cycle—is used for emission certification of light duty vehicles in Europe [EEC Directive 90/C81/01].

The entire cycle includes four ECE segments as shown in Figure 2.3. These four segments are repeated without interruption, and this is followed by one EUDC segment as shown in Figure 2.4. Before the test, the vehicle is allowed to soak for at least 6 hours at a test temperature of 20-30°C. It is then started and allowed to idle for 40 s.

Effective year 2000, that idling period has been eliminated, i.e., engine starts at 0 s and the emission sampling begins at the same time. This modified cold-start procedure is sometimes referred to as the “new European driving cycle” or NEDC.

Emissions are sampled during the cycle according the “Constant Volume Sampling” technique, analyzed, and expressed in g/km for each of the pollutants.

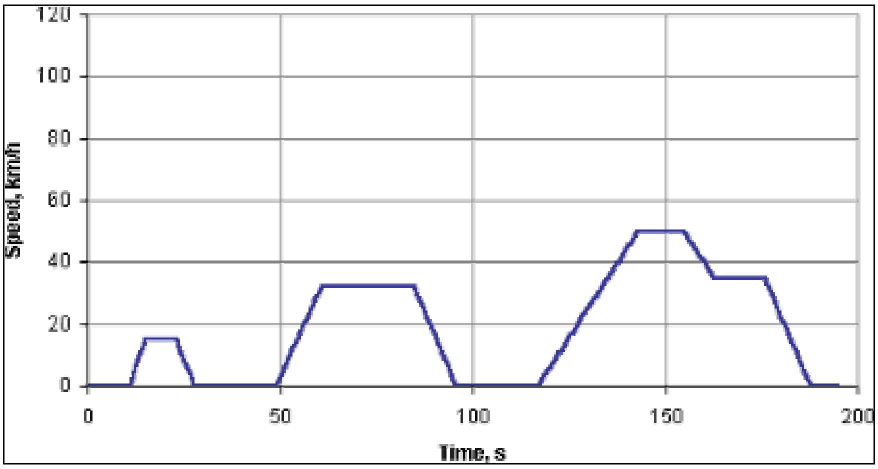

Figure 2.3 ECE 15 Cycle (http://www.dieselnet.com/standards/cycles, 2004)

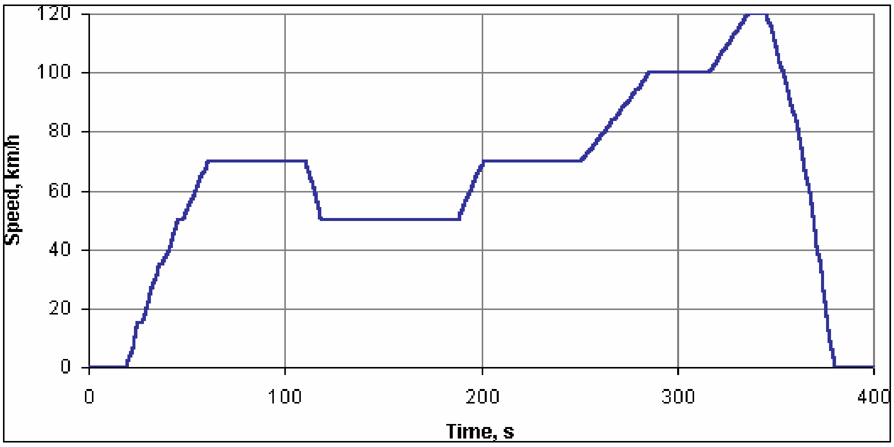

Figure 2.4 EUDC Cycle (http://www.dieselnet.com/standards/cycles, 2004)

The ECE cycle is an urban driving cycle, also known as UDC. It was devised to represent city driving conditions, e.g. in Paris or Rome. It is characterized by low vehicle speed, low engine load, and low exhaust gas temperature.

The EUDC (Extra Urban Driving Cycle) segment has been added after the fourth ECE cycle to account for more aggressive, high speed driving modes. The maximum speed of the EUDC cycle is 120 km/h. An alternative EUDC cycle for low-power vehicles has been also defined with a maximum speed limited to 90 km/h and the cycle is shown in Figure 2.5.

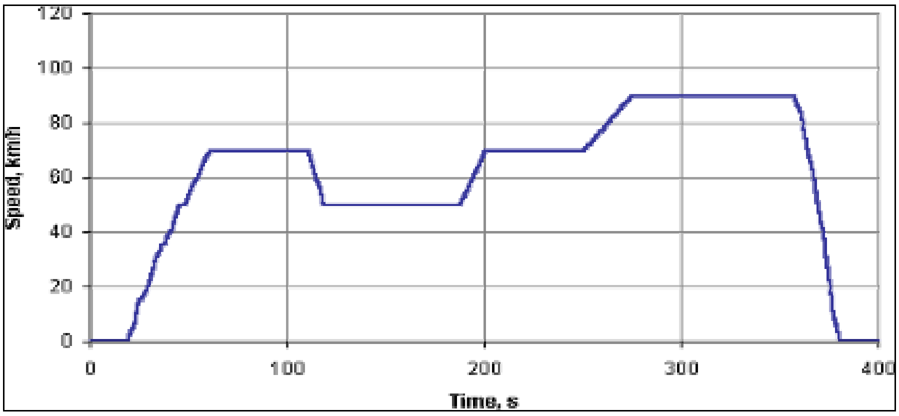

Figure 2.5 EUDC Cycle for low-power vehicles (http://www.dieselnet.com /standards/cycles, 2004)

The following Table 2.6 includes a summary of the parameters for both the ECE and EUDC cycles.

Table 2.6 Summary of the ECE and EUDC cycles (http://www.dieselnet.com/ standards/cycles, 2004)

Characteristics	Unit	ECE 15	EUDC
Distance	km	4×1.013=4.052	6.95
Duration	s	4×195=780	400
Average Speed	km/h	18.7 (with idling)	62.6
Maximum Speed	km/h	50	120

The driving cycle in Japan is also given in Table 2.7. Emission certificates to light-duty vehicles are given according to '10-15 Mode cycle".

Table 2.7 Test cycle in Japan (http://www.dieselnet.com/standards/cycles, 2004)

Test Cycle	Description
10-Mode Cycle	Urban driving cycle used for emission testing from light-duty vehicles, later replaced by the 10-15 mode cycle.
10-15 Mode Cycle	Urban driving cycle that is currently used in Japan for emission certification of light-duty vehicles.

In the study by Westerholm et al. (1996), emission factors of both regulated (CO, HC, NO_x and particulates) and unregulated pollutants (aldehydes, monocyclic aromatic compounds) were examined under three different driving conditions, i.e. Phase 1- cold transient, Phase 2- stabilized and Phase 3- hot transient. The US FTP-75 driving cycle obtained by the chassis dynamometer was used to simulate these three driving conditions. Two three-way catalyst equipped light duty passenger cars were investigated in the study. All exhaust sampling regarding both regulated and unregulated pollutants was carried out on diluted exhaust gases in a dilution tunnel and sampling tube was connected to a Constant Volume Sampling System (CVS).

As expected, in the first phase when the catalyst and engine are at relatively very low temperatures (cold start) the emissions of gaseous components (CO, HC, NO_x) are highest.

Emissions of monocyclic aromatic compounds which are given in Fig. 2.6 like benzene, toluene, ethylbenzene, xylene, propylbenzene and ethyltoluene from both vehicles behave in a similar manner to the gaseous regulated components i.e. minimum emission is obtained in phase 2 and the maximum emission in phase 1.

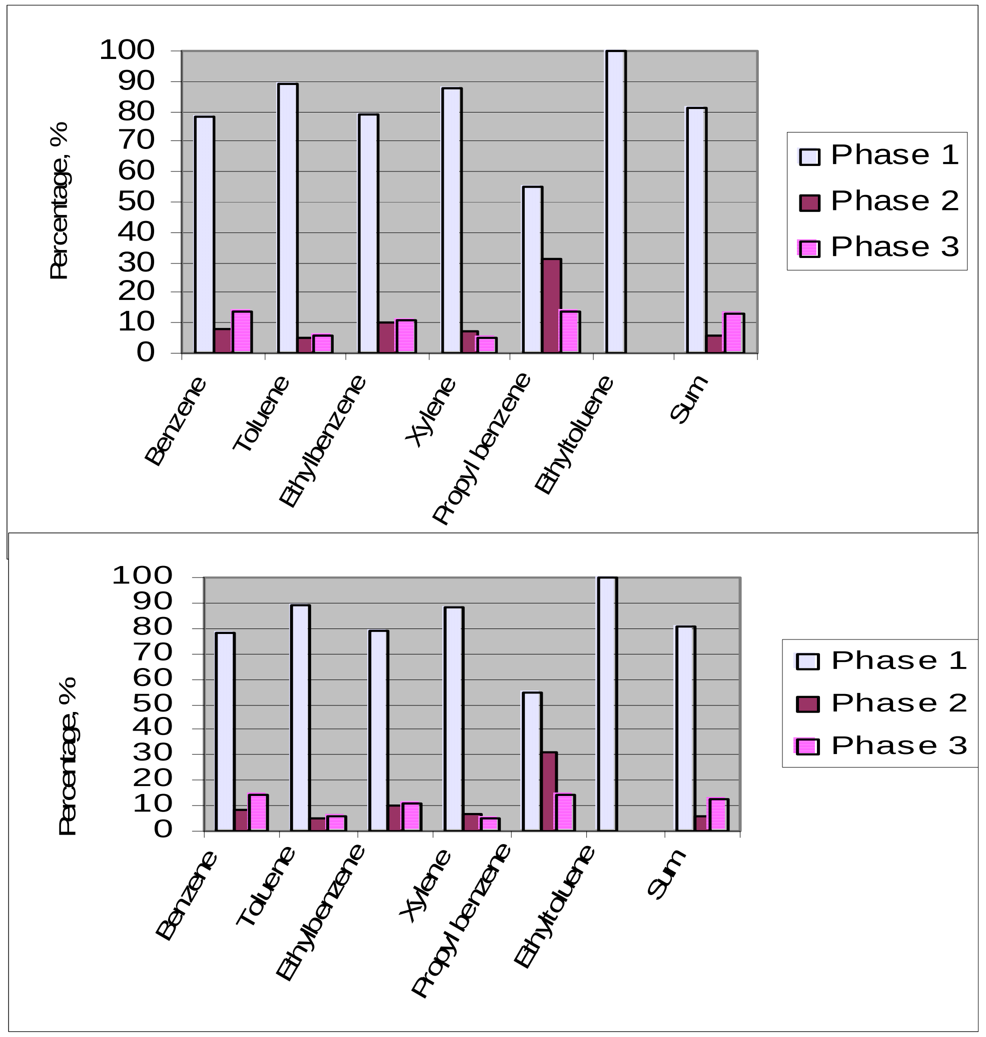

Figure 2.6 The relative amounts of pollutants emitted in each phase. The total amount emitted of each compound (sum of the three phases) is defined as 100%. (Monocyclic aromatic compounds (BTX)) (Westerholm et al., 1996)

Unfortunately, well-accepted driving cycles like the US Urban Driving Cycle (FTP 75) or the European Driving Cycle (EDC) only represent a selected set of real-world driving conditions.

Different types of driving cycles are also used in some studies. For example, a set of seven different driving cycles including the European Driving Cycle (EDC), the US Urban (FTP 75) and highway driving cycles have been used in the study by Heeb et al. (2000). In this study emission factor of benzene, toluene, the C_2 -benzenes (xylenes and ethyl benzene) and nitrogen monoxide of gasoline-driven passenger cars (1.4 L, Model year 1995) with or without catalytic converter were determined with respect to the velocity.

The benzene concentrations (ppmv) of the collected exhaust gas samples were analyzed with gas chromatography having a flame ionization detector (GC-FID), as well as with chemical ionization mass spectrometry (off-line CI-MS). The results were compared with that of the integrated benzene emission profiles obtained by on-line CI-MS. The velocity data and the benzene emission factors for selected parts of the test cycles are given in Table 2.8 together with the mean benzene concentrations found in corresponding exhaust gas samples collected in bags. The average velocity dependent emission factors for benzene, toluene, C_2 benzenes and nitrogen monoxide without catalytic exhaust treatment is given in Table 2.9.

Results of this study have shown that the benzene concentrations in dilute exhaust gases can be determined with good reliability by both methods, independently.

By means of time-resolved exhaust gas analysis a wide variety of engine or catalyst conditions can be studied and averaged emission factors can be derived form such emission data. Thus, individual vehicles can be tested under driving conditions which are, for example, not found in tunnel driving.

Another study on the emission factors with respect to speed was about the hot emission factors of passenger cars equipped with a three-way catalyst and performed by Ntziachristos and Samaras (1999). The effects of using cycles with similar mean speed but different dynamics on the variability of speed dependent emission factors were examined. As a result of the study, it is seen that variability of emission over the same cycle is more important than the variability of emissions over different cycles.

Apart from any cycle effects, emission estimates obtained by the application of such emission factors are associated with significant uncertainty due to the highly scattered experimental data. In order to understand some of the sources of variability, the impacts of engine capacity and mileage on emissions have been studied by statistically analyzing the collected data (analysis of variance test).

The statistical analysis conducted in that study shows no clear correlation (especially for HC) between engine capacity and emissions for any pollutant except CO_2, where a distinct increase with capacity was observed, as expected. It is found that, in contrast to engine capacity, vehicle age, as reflected by vehicle mileage, is responsible for increases in the average level of emissions of all non-CO_2 major pollutants. Statistically significant differences were not established for the very first and last mileage classes (Ntziachristos and Samaras, 1999).

It was concluded by authors that this might be the result of either the small sample or a typical behavior of the fleet population. For the higher mileage classes, engine repair and component replacement in high-emitting vehicles would result in the stabilization of the fleet-averaged emissions.

Table 2.8 The velocity data and the benzene emission factors for selected parts of the test cycles (Heeb et al., 2000)

Sampling time (s)	**Distance (km)**	**Mean velocity (kmh^{-1})**	**Benzene EF* without cat.[a] (mg km^{-1})**	**Benzene EF with cat.[a] (mg km^{-1})**	**Benzene conversion efficiency [b]**	**Benzene conc. CI-MS (on line) without cat. (ppm)**	**Benzene conc. CI-FID (on line) without cat. (ppm)**	**Benzene conc. CI-MS (on line) with cat. (ppm)**	**Benzene conc. CI-FID (on line) with cat. (ppm)**
0-506	5.75	40.9	76.4	24.1	0.68	1.68		0.59	
506-1376	6.14	25.4	73.7	11.9	0.84	i no		0.18	
0-506	5.76	41.0	55.5	7.2	0.87	1.19		0.18	
0-780	3.99	18.4	86.6	60.9	0.30	0.95	1.04	0.66	0.65
780-1180	6.93	62.3	47.6	3.9	0.92	1.76	1.76	0.14	0.15
1200-1965	16.43	77.3	35.5	1.2	0.97	1.63	1.69	0.06	0.09
300-776	12.07	91.3	38.8	1.2	0.97	2.11	1.92	0.06	0.07
820-1336	15.95	111.3	50.4	5.8	0.88	3.34	2.92	0.39	0.34
1356-2436	35.94	119.9	56.0	7.3	0.87	4.00	3.44	0.52	0.45
300-1185	15.71	63.9	49.7	6.6	0.87	0.25	0.24	0.25	0.24
1206-1440	4.27	65.8	42.0	0.5	0.99			0.02	
1460-2536	22.23	74.3	36.0	0.9	0.98	1.59	1.47	0.04	0.07
300-527	3.33	52.7	49.8	2.9	0.94	1.58	1.45	0.09	0.13
527-788	3.47	47.8	69.7	12.8	0.82	2.15	1.77	0.40	0.35
820-1095	3.65	47.7	48.1	3.0	0.94	1.37		0.09	
1184-2184	33.25	116.4	520.6	369.8	0.29	4.09	3.40	2.90	2.35
300-1311	8.32	29.6	87.8	20.5	0.77	1.56		0.36	
1331-2153	5.20	22.8	84.2	16.9	0.80	1.15		0.23	
2173-2513	0.64	6.8	122.5	28.4	0.77	0.50	0.57	0.11	0.18

[a] Emission factors are calculated based on the integrated CI-MS benzene concentration profile.

[b'] Conversion efficiency of the three-way catalyst was calculated according to formula (l-(EF (with cat.)/EF (without cat.))).

*EF= Emission factor **cat= Catalytic converter

Table 2.9 Average velocity-dependent emission factors (mgkm^{-1}) of benzene, toluene, C_2 benzenes and nitrogen monoxide without catalytic exhaust gas treatment (Heeb et al., 2000)

Velocity (km/h)	**Number of data Points**	**Benzene EF (mg/km)**	**Rel. Std-dev (%)**	**Toluene EF (mg/km)**	**Rel. Std-dev (%)**	**C_2-Ben EF (mg km^{-})**	**Rel. Standard deviation (%)**	**N0 EF[c] (mg/km)**	**Rel. Std-dev (%)**
0	990	0.53[a]	127	2.42[a]	142	3.93[a]	158	7.4[a]	75
5	662	192	74	830	87	1318	97	1804	86
15	848	135	78	611	80	1005	81	948	83
25	889	110	82	476	80	788	78	906	72
35	1634	88	68	343	80	569	84	1067	51
45	1597	68	72	255	80	420	83	1220	47
55	1196	56	75	197	94	327	104	1172	54
65	1418	48	69	162	88	267	103	1284	48
75	1845	42	44	129	72	208	106	1492	37
85	1015	41	34	117	43	172	62	1923	32
95	715	39	21	106	22	147	23	2222	27
105	588	49	19	113	23	152	25	2634	29
115	851	57	16	121	19	156	20	3076	20
125	741	64	15	127	24	157	26	2959	18
135	241	76	11	172	15	225	16	2066	15
145	66	85	7	163	10	217	10	226	13

[a] Emission factors during loading of the engine are given in (g h^{-1}).

[b] 'Quantification of C_2-benzenes was carried out using the detector response o-xylene present in the calibration gas.

[c] The NO, emissions can be calculated from the NO emission data assuming complete oxidation to NO

Since tunnel studies were proposed to study real world traffic emissions with special emphasis on the problem of the maintenance of vehicles, results from suitable dynamometric test measurements must be compared with road traffic emissions.

In the study by Heeb et al (2000), the velocity-dependent emission factors obtained from time-resolved emission data of hypothetical car fleets with variable proportions of three-way catalyst vehicles can be calculated assuming that the tested cars represent the actual car fleet. A comparison was made to verify the significance of such weighted emission factors with published data of a recent Swiss highway tunnel study (Buwal, 1995). The reported averaged- emission factors at 60 and 90 km h^{-1} are based on a car fleet from which 70% were found to be equipped with catalysts, mainly regulated three-way catalysts.

Analysis of the same data set of the cited tunnel study with another statistical model which distinguished between gasoline and diesel powered vehicles instead of light duty and heavy duty vehicles resulted in slightly different emission factors for the aromatic hydrocarbons but with significantly reduced NO_2 emission factors (Staehelin et al., 1997). The authors reported, e.g. emission factors for benzene at an average vehicle speeds of 83, 92 and 94 km/hr as 15.77±2.24 mg/km, 15.04±2.22 mg /km and 13.35±2.12 mg/km as well as NO_2 emission factors of 316±148 mg/km, 623±102 mg/km and 654±46 mg/km, respectively.

This comparison showed that the limited knowledge of vehicle emission data from tunnel studies can be extended by additional test stand measurements of representative vehicles so that the emissions of most real-world driving conditions can be estimated. Thus, methodology used in Heeb et al. (2000), may be employed to obtain reliable emission inventories of the road traffic for selected pollutants such as for the class of aromatic hydrocarbons.

In the study of (John et al., 1998) several suitable statistical models were developed to derive emission factors (EF) from the tunnel studies. EF for NO_x, total NMVOC and CO are available from dynamometric tests. These dynamometric tests were done for more than 300 vehicles which were randomly selected from private owners in Germany and Switzerland (Anon (g), 1995). CAREAIR/TRANSPORT, a module of the traffic emission model, was used to adapt the results from dynamometric tests to the tunnel study.

Results of emission calculations using emission factors from UBA (1995) based on results of dynamometric test measurements are compared with the emission factors of NO_x, VOC and CO of a road tunnel study performed in September 1993 in the Gubrist tunnel, close to Zurich, Switzerland. The average speed, the gradient of the road, detailed composition of the vehicle fleet in the tunnel and the special aerodynamics in a tunnel are taken into consideration in the emission calculations.

Between the results of the tunnel study and the emission modeling except for NO_x emission factors for heavy duty vehicles, no evidence for a discrepancy was found. In addition to this, the measured emission factors of individual hydrocarbons of light duty vehicles were in good agreement with the expectations for most components.

Strongly skewed distribution of single vehicle emission was obtained from remote sensing technique. Main result of this is the large differences of vehicles which are caused by different exhaust gas regulations e.g. old passenger cars without exhaust gas reduction in contradiction to new cars with controlled catalytic converters From tunnel study, no information for "stop and go" traffic and "cold start" emissions can be obtained. This means that conclusions are only valid for highway driving conditions (John et al., 1998).

European Union exhaust gases emission norms have been in force since 1996 for gasoline and diesel cars having capacity less than 6 and weight less than 2500 kg. The USA has emission programs which are called as ‘‘Tier’’. Tier programs define exhaust gas limit values for different years. For example, Tier 1 program has been valid up to 2000. Tier 2 program and exhaust gas emission limit values specified in this program is valid after 2000. Japanese also have exhaust gases emission norms which have been in force since 1978 for gasoline cars having capacity less than 10 and have been in force since 2000 for diesel small passenger cars (weight less than 1265 kg) (Müezzinoğlu, 2004). European Union, the USA and Japanese exhaust gases emission limits are given in Table 2.10.

Table 2.10 EU, the USA and Japanese exhaust gases emission limits (Müezzinoğlu, 2004).

Type of cars	**EU (1996)**	**The USA (California) Tier 1**	**Japanese**
Gasoline	CO: 2.2 g/km HC+NO_x: 0.5 g/km	NMHC: 0.155 g/km CO: 2.11 g/km NO_x: 0.25 g/km PM: 0.05 g/km	Hot start/1978 HC: 0.25 g/km CO: 2.1 g/km NO_x: 0.25 g/km
Gasoline			Hot start/1978 HC:1.7 g/km CO: 14.7 g/km NO_x: 1.1 g/km
Diesel	CO: 1.0 g/km HC+NO_x: 0.7 g/km PM: 0.008 g/km		Hot start/1978 HC:0.4 g/km CO: 2.1 g/km NO_x: 0.08 g/km
Diesel with direct injection	CO: 1.0 g/km HC+NO_x: 0.9 g/km PM: 0.008 g/km		

The USA has started a new program called as Tier 2 given in Table 2.11 since 2000. This program is performed between 2000 and 2030.

This can be seen from the Table 2.11 that after year 2030 pollutant emissions of small cars will be decreased to zero. This means that small passenger cars are planned to be operated by electricity after 2030. According to the Tier 2 program, automotive sector in the USA can design their cars which suits vehicle category 1 to 10 up to 2005. After year 2006, vehicle category of 10 and 9 can not be produced and number of the vehicle category will be decreased to 8. And also, after Tier 2 program control parameter of exhaust gases will be non methane VOCs instead of total HCs.

Table 2.11 The USA exhaust gas limit values for small passenger and small commercial cars between yeas 2000 and 2030 according to Tier-2 program (Müezzinoğlu, 2004)

Category of car	**NO_x (g/mile)**	**Non methane VOCs (g/mile)**	**CO (g/mile)**	**Formaldehyde (HCHO) (g/mile)**	**PM (g/mile)**
10	0.6	0.156	4.2	0.018	0.08
9	0.3	0.090	4.2	0.018	0.06
8	0.2	0.125	4.2	0.018	0.02
7	0.15	0.009	4.2	0.018	0.02
6	0.1	0.009	4.2	0.018	0.01
5	0.07	0.009	4.2	0.018	0.01
4	0.04	0.070	2.1	0.011	0.01
3	0.03	0.055	2.1	0.011	0.01
2	0.02	0.010	2.1	0.004	0.01
1	0	0.000	0	0	0.01

2.4. Emission Characterization Studies in Turkey

According to regulations in Turkey, limit values of the exhaust gasses are given in the units of ppmv for HC and % by volume for CO.

In Turkey, the CO and HC limit values of gasoline vehicles must conform with TS 11366 (Anon (m), 1998). According to this regulation, maximum CO emission of cars for models before 01.10.1975, between 01.10.1975 - 01.01.1986 and after the 01.10.1986 is 6% by volume, 4.5% by volume 3.5% by volume, respectively. According to TS 11366, the limit for HC emission for gasoline vehicles is 800 ppmv with catalytic converter and 1200 ppmv without catalytic converter.

There are just a few studies carried out on the exhaust gas emissions in Turkey and these are mainly performed at idle conditions. ANÇEVA (Ankara Çevre Koruma Vakfı) performs regular exhaust gas analyses on all vehicles according to TS 11365 and TS 11366 at idle conditions by using the equipment of Sun Gas Analyzer- MGA which gives results in the unit of ppmv for HC (as propane) and % volume for CO, CO_2, O_2 and corrected CO. This equipment also measures the air to fuel ratio (AFR), engine revolution rate (rpm) and the temperature of the exhaust gas.

In a study performed by Üner et al. (2000a), data obtained from the exhaust gas measurements of cars at METU Campus by ANÇEVA for only one month (June 1999) was used. The exhaust gas measurement results of total 123 light duty vehicles were considered in this study. 25 of the vehicles were made by Tofas and 13 of them by Renault. The rest was from other manufacturers. A statistical analysis of the measurements of CO, HC and AFR for 123 vehicles was performed and average emissions were calculated. The results of the analysis are given in Table 2.12.

Table 2.12 Averages and standard deviations of CO, HC concentrations and AFR values (Üner et al., 2000a)

	ALL VEHICLES	TOFAS	RENAULT
Average CO (% by volume)	2.24±0.87	2.44±1.06	2.07±0.57
Average HC (ppmv volume)	220.37±73.59	235.44±80.51	221.46±61.51
Average AFR (kg/kg)	18.79±3.40	20.12±3.21	17.7±2.70

Another study by Atimtay and Önoğlu (2002) was conducted on emission measurements of ANÇEVA for vehicles working with LPG and diesel fuels at idle condition. However, for this study the measurement results for one year period were included in the analysis. These data also have been analyzed statistically and exhaust gas emissions (CO, HC, CO_2 and O_2) of 329 vehicles using LPG as fuel were examined.

The distribution of vehicles using LPG among different names is given in Figure 2.7 and average emission values of these vehicles with respect to their manufacturers are given in Table 2.13.

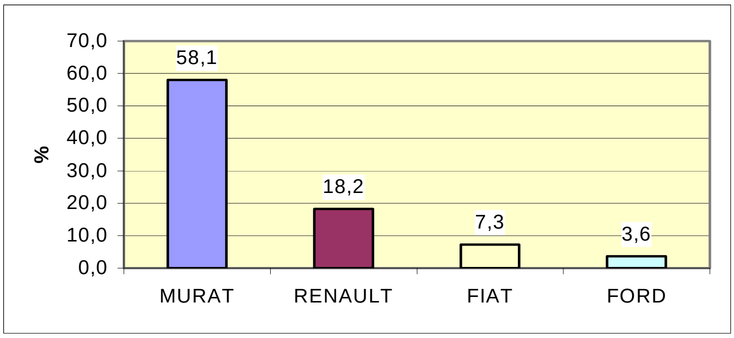

Figure 2.7 The profile of vehicles using LPG as fuel (Önoğlu and Atimtay, 2002)

Table 2.13 Average emission values of LPG vehicles with respect to their models (Önoğlu and Atimtay, 2002)

MODEL	CO (% by volume)	CO_2 (% by volume)	HC (ppmv)	O_2 (%)	Lambda (λ)
FIAT	0.92±0.74	13.24±1.45	194±122	0.45±0.57	0.981±0.981
FORD	1.33±1.17	12.79±1.02	272±136	0.87±0.87	0.993±0.063
MURAT	1.48±1.09	12.33±1.71	273±184	1.00±1.17	1.019±0.111
RENAULT	1.72±1.11	12.45±1.26	266±191	1.39±1.58	1.015±0.151

Lambda (λ): 1/Φ
Φ: AFR stoichometric/AFR actual
AFR: Air to fuel ratio during combustion

As can be seen from Table 2.13 Renault and Murat cars have more CO emissions than other models (1.72 and 1.48%, respectively). As far as the HC emissions are concerned, highest HC emissions belong to Murat and Ford type cars, with concentrations of 273 and 272 ppmv, respectively. The next one following these types are Renault type cars with 266 ppmv HC emissions.

The emission results obtained with cars using LPG are compared with the emission values of the vehicles using gasoline as fuel. The result of the comparison is given in Table 2.14. The results have shown that the CO and total hydrocarbon emissions of Murat cars using LPG as fuel are less than the emissions of the vehicles working with gasoline.

Table 2.14 Average CO and HC emission values for Murat type cars for various fuels (Önoğlu and Atimtay, 2002)

Fuel type	CO (% by volume)	HC (ppmv)
Gasoline	1.99	299
LPG	1.48	273

A second study by Üner et al. (2000b) was performed to determine the chemical composition of exhaust emissions. This study was composed of two parts. In the first part of the study the Federal Test Procedure (FTP) of the U.S.A. was used on a Citation and a Nissan car in the USA and exhaust gasses sampled were analyzed by GC. The second part of the study was performed in Turkey and gasoline produced in Turkey was used as fuel. Individual hydrocarbon analyses of the exhaust gasses of gasoline vehicles at idle conditions were performed. GC with FID was used to analyze the collected exhaust gases. A schematic diagram of the sampling unit is given in Figure 2.8. The results of the analysis for benzene, toluene and ethyl benzene are shown in Table 2.15 to 2.17 since they are directly related with this study.

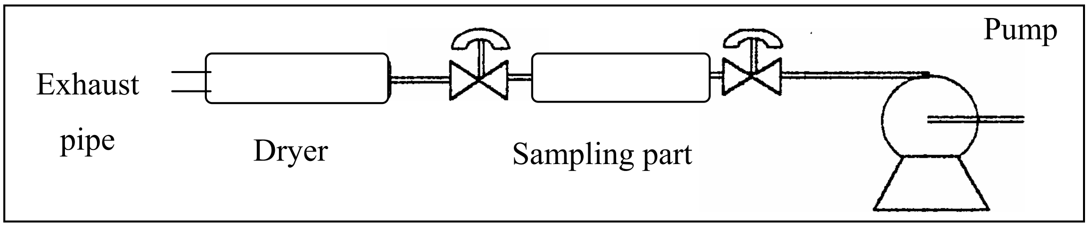

Figure 2.8 Scheme of the sampling unit (Üner et al., 2000b)

Table 2.15 Results of exhaust gas analysis for Citation model car (analysis is before catalytic converter and % removal is after the catalytic converter) (Üner et al., 2000b)

EPA - 75 TEST	**Transient phase**		**Cold start**		**Hot start**	
HC species	**mol %**	**conversion %**	**mol %**	**conversion %**	**mol %**	**conversion %**
Benzene	1.05±1.02	71.41	0.93±0.06	72.79	0.81±0.10	68.21
Toluene	6.17±6.17	72.16	7.75±0.76	81.04	5.14±1.63	69.04
Ethylbenzene	0.41±0.90	100.00	0.72±0.13	100.00	0.20±0.33	100.00

Table 2.16 Results of exhaust gas analysis for Nissan model car (analysis is before catalytic converter and % removal is after the catalytic converter)

EPA - 75 TEST	**Transient phase**		**Cold start**		**Hot start**	
HC species	**mol %**	**conversion %**	**mol %**	**conversion %**	**mol %**	**conversion %**
Benzene	0.67±0.11	47.59	0.55±0.33	100.00	0.51±0.40	72.05
Toluene	5.91±0-90	45.54	6.06±3.63	78.52	4.16±2.65	67.82
Ethylbenzene	0.48±0.07	46.28	0.55±0.57	100.00	0.10±0.43	100.00

According to Table 2.15 and Table 2.16 Citation model cars emits more pollutants than Nissan model cars but catalytic conversion efficiency of Citation car was better than that of Nissan car. 100% catalytic converter removal efficiency was obtained especially for ethyl benzene. Cold start emissions were more than hot start emissions for both types of the cars.

Table 2.17 shows the exhaust gas emissions with dryer was more than exhaust gas emissions without dryer. This shows that moisture of exhaust gasses effect results of analyses. Benzene, toluene and ethyl benzene content of the exhaust gas was found nearly the same for both super and normal gasoline. On the other hand contents of toluene and ethyl benzene in unleaded gasoline were more than that of super and normal gasoline.

Table 2.17 Exhaust gas analyses of a car with carburetor and without catalytic converter (Üner et al., 2000b)

Component	**Exhaust gas without dryer (volume %)**	**Exhaust gas (with dryer (volume %)**
Benzene	2.7575	5.4271
Toluene	3.1091	11.8781
Ethylbenzene	-	3.7612

Hydrocarbon analysis of Turkish gasoline which is given in Table 2.18 shows that for all types of gasoline, toluene content is more than that of benzene and ethyl benzene.

Table 2.18 Hydrocarbon analysis of Turkish gasoline (super, normal and unleaded) (Üner et al., 2000b)

Component	**Super Gasoline (volume %)**	**Normal Gasoline (volume %)**	**Unleaded Gasoline**
Benzene	1.9110	1.9275	0.5223
Toluene	9.1908	9.2222	14.0049
Ethylbenzene	1.6616	1.8537	3.2387

CHAPTER 3

MATERIALS AND METHOD

This study was conducted in two parts. These parts were:

1- a) to determine the distribution of vehicle categories in Ankara and Turkey, and choose the category widely used in Turkey.

b) From the emission measurements of ANÇEVA conducted for different car types, to determine the average CO and HC concentrations for the widely used car types in Turkey.

2- To take gas samples from the exhaust pipes of the widely used car types at different road conditions and analyze the gas composition for BTEX components.

3.1. Distribution of Vehicle Categories

ANÇEVA (Ankara Çevre Koruma Vakfı) performs regular measurements of exhaust gas emissions according to TS 11365 and TS 11366 at idle conditions. Every car in Ankara has to go through these measurements performed every year. Therefore, exhaust emissions of almost all cars are measured once in a year.

Based on the agreement between ANÇEVA and us, all the measurement results between June 2001 and June 2002 were obtained and they were entered into a databank in the computer and results were analyzed with Excel program. Databank was based on the measurements performed on 5729 gasoline, 330 LPG and 392 diesel vehicles. A total of 6451 vehicle exhaust emissions were evaluated for a period of one year.

The exhaust emission measurements are done by using SUN -Gas Analyser / MGA. In all the stations of ANÇEVA, this same equipment was used for emission measurements. The parameters measured with this analyser are:

- CO (% by volume)
- Hydrocarbons (ppmv) (as propane)
- CO_2 (% by volume)
- O_2 (% by volume)
- AFR (Air/ Fuel ratio, dimensionless)
- Engine rpm (revolutions/ min)
- Exhaust gas temperature (^oC)

A statistical analysis of all the emission data was performed and average emission values for each car category together with standard deviations were calculated. Based on these results, the category of cars for the detailed analysis of hydrocarbon emissions was selected.

Also, the distribution of vehicle categories in Turkey was obtained from the data published by the SIS. The distributions in Ankara and in Turkey were compared to see if there is a good correlation between two sets of data.

3.2. Experimental

In Turkey, no data exists showing the composition of exhaust gasses for different categories of cars. These emissions mainly depend on the:

- type of fuel used
- velocity of the car
- driving habits, etc.

In order to determine the composition of exhaust gasses, samples were collected from the tail pipe and analyzed by using GC. The type of fuel used was not variable in the experiments. Only the super-unleaded gasoline sold at the gas stations was used. This gasoline is supplied from Middle Anatolia Refinery located close to Ankara. The driving habits were not also include as a variable, because driving at certain constant velocities were considered. Therefore, the only variable was taken as the velocity of the car. The velocities tested were 30 km/hr, 60 km/hr and 90 km/hr corresponding to the urban, rural and highway driving conditions.

The statistical distribution of vehicle categories in Ankara and Turkey according to this study with respect to their make and model shows that the largest number of vehicles are Tofas/Fiat cars. Therefore, exhaust emissions of ‘‘Tofas/Fiat’’ passenger cars were decided to be studied in this work.

In this study passenger cars were divided into mainly two basic categories:

1) Cars without catalytic converter,
2) Cars with catalytic converter.

Each group of vehicles was examined for three different conditions:

- cold start (at idle condition),
- driving condition,
- hot start (at idle condition)

The method used during calculation of the "emission factors" at driving conditions is to select one single average speed, representative of each of the road types "urban", "rural" and "highway" and calculate the emission factors at these speeds.

3.2.1. Experimental Set Up

The experimental set up consisted of a car, a gas sampling probe to take samples from the tail pipe, a drier, an active carbon tube (Orbo-32) and a suction pump with an adjustable suction rate. A schematic diagram of the car with the experimental set up is shown in Figure 3.1 and the flow diagram of the exhaust gas collection system is shown in Figure 3.2.

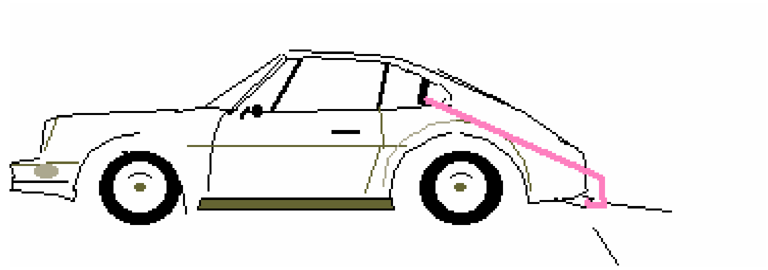

Figure 3.1 The experimental set up for exhaust gas collection

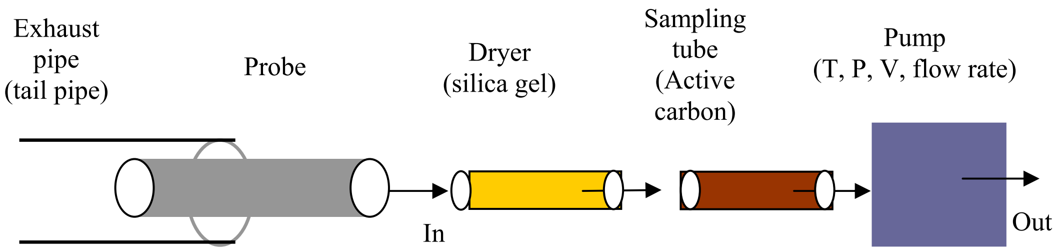

Figure 3.2 The flow diagram of the exhaust gas collection system

As it is seen from Figure 3.2, the sampling probe is placed in the tail pipe of the car. About 100 mm of the probe should be in the tail pipe. The probe is made of stainless steel having an inside diameter of 10 mm and a length of 500 mm. The end of the stainless steel probe is flexible to make a bend about 90^o. The outlet of the probe is connected with a PTFE tube to a drier. Drier is made of a glass tube with a diameter of 10 mm. The inside of drier is filled with silica gel beads to adsorb moisture. Both end of the drier is plugged with quartz wool. After drier tube in the sampling system comes an Orbo-32 tube containing active carbon particles. The specifications of the Orbo-32 tube will be given later in this chapter. The outlet of the Orbo-32 tube is connected to a suction pump (Desega-GS 312) with a PTFE tube. The pump is kept in the car during sampling and driving, and all the other parts of the experimental set up are outside the car attached to the back bumper. The pump works with 12 V and power supply of the pump is connected to the battery of the car. Active sampling method was used for gas sampling.

The following equipments were used for sampling and analysis of exhaust gas from the tail pipe:
- Desega pump (GS 312)
- Orbo-32-tube (Niosh type)
- Gas chromatograph
- Total VOC analyzer (Bernarth Atomic- Model 3006)
- Ultrasonic water bath (Bioblock Scientific)
- Oven

Desaga Pump (Model GS 312)

Exhaust gas of the vehicle tested passes thorough the sampling system with the suction of the pump at a constant flow rate. Desega GS 312 works with 12 V and connected to the battery of the car. This is a pump with a variable flow rate.

The flow rate range of the pump: 0-12 L/min
Accuracy of the pump : + 0.1 L/min

The flow rate of the pump is adjusted to a predetermined value and pump always sucks to sample at this flow rate. A flow rate of 1 L/min was used according to the suggestion of the Orbo- 32 manufacturer. Desega pump also measures the ambient pressure, the ambient temperature at the sampling conditions and the total volume of gas sucked during the sampling period.

ORBO –32 Standard Charcoal Tubes

ORBO adsorption tubes comply with all NIOSH and OSHA specifications for tube dimensions, adsorbent quality and particle size, divider composition and pore size. These tubes are used in conjunction with a portable personal air pump or vacuum pump. Figure 3.3 shows a typical tube divided into two adsorbent parts. Section (a) contains 110 mg active carbon and section (b) contains 55 mg active carbon. Section (b) is a backup section to control if breakthrough of airbone contaminants occurred on the front portion. The adsorbent parts (a) and (b) is separated from each other by retaining plugs and there is a white quartz wool before part (a). Both ends of the tube are sealed. The tips of the tube are broken just before sampling.

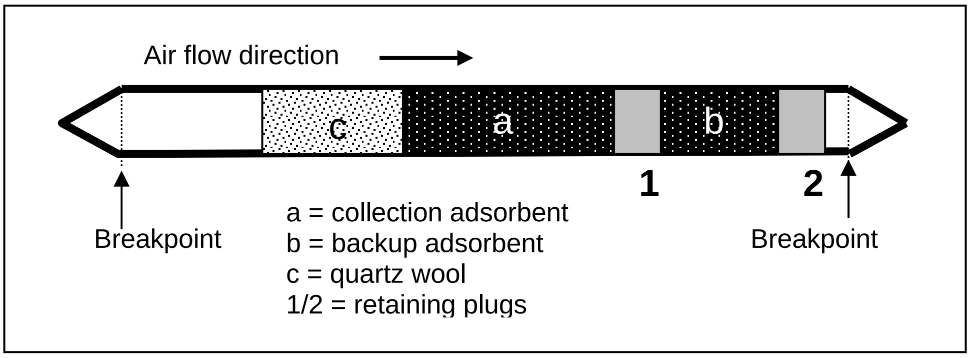

Figure 3.3 ORBO –32 standard charcoal tube

Gas Cramotograph (ATI-Unicam (FID)):

The concentrations of the constituents in the gas samples were measured by using a GC having a FID. GC is a very well established separation technique for the identification and quantification of volatile materials without decomposing. Analyte volatility is one of the major limiting factors in application of this technique.

- Characteristics of Injector Oven:
  Range: 50 °C to 450 °C in 1 °C steps
  Capacity: Two injection systems
  Accuracy: ±1% over range 100 °C to 300 °C
- Characteristics of Column Oven:
  Range: 10 °C above ambient to 450 °C in 1 °C steps
  Accuracy: ±1% over range 100 °C to 300 °C
  Control: ± 0.05 °C
- Characteristics of Detector Oven:
  Range: 50 °C to 450 °C in 1 °C steps
  Accuracy: ±1% over range 100 °C to 300 °C
  Control: ± 0.02 °C
- Characteristics of Flame Ionization Detector:
  Operating Temperature: 100 °C to 450 °C
  Response: typically 1.9x10^{-2} Cg^{-1}
  Detectability: typically 1x10^{-12} gs^{-1} for toluene

The column specifications and operating conditions are given below:

Length : 25 m
Type : Bonded phase
Material : Fused silica

Phase : BP-1 (non-polar)
Film Thickness : 5 micron
ID : 0.32 mm
OD : 0.43 mm

<u>Bernath Atomic- Model 3006-Total VOC Analyzer:</u>

The instrument used for measuring the total NMVOC concentration in the gas samples is Total VOC Analyzer. The probe of the instrument is directly inserted into the tail pipe of the car. The probe is made of stainless steel. This instrument has a FID and measures the total VOC concentration. The gas sample from the probe is transferred to the detector with a heated line at 180 °C. The instrument is calibrated with C_3H_8 (propane) and reports the results in terms of propane. A picture of the instrument is shown in Figure 3.4

Figure 3.4 A general photograph of Total VOC Analyzer

Ultrasonic Water Bath (BIOBLOCK SCIENTIFIC 89202 Model)

An ultrasonic water bath was used to increase the extraction rate of the adsorbed hydrocarbons from activated carbon into liquid Carbon Disulfide (CS_2). Ice water is used to eliminate the evaporation of the VOC's.

Oven:

Oven is used to dry silica gel in the drier tube. The temperature of the oven can be measured with an accuracy of $\pm$2°C. A temperature regulator is used to control the temperature. The silica gel in the drier tube was dried at 105°C before each experiment.

3.2.2. Experimental Procedure

The experiments were performed for cold start, hot start and driving conditions. The cold start and hot start experiments were conducted at idle condition of the car, however for the experiments at driving condition exhaust gas samples were taken while the car was driven at speeds of 30, 60 and 90 km/hr. Therefore, the exhaust gas samples were the samples taken at the ‘‘real condition’’. The following steps were followed in conducting experiments.

- The car to be tested was prepared for the experiment and the probe for exhaust gas sampling was inserted into the tail pipe.
- The drier tube filled with silica gel beads was first dried in the oven at 105 ^{o}C and then preweighed in the laboratory. All the connections between different parts of the sampling train were made. The tips of the Orbo-32 tube were broken just before sampling and connected between the drier and the pump.

- The pump was operated at a certain flowrate.
- For cold start experiments, the car was in stationary position. As soon as the car engine was started, the sampling pump was turned on and sampling continued for 10 min according to TS 11366 (1998). The sampling rate was 1 L/min.
- After the sampling was finished, the pump was turned off. The drier tube and the Orbo tube were taken off the sampling train. Both ends of the drier tube and the Orbo tube were closed with caps. They were taken to the laboratory. The drier tube was reweighed. The difference in weight gave the amount of moisture adsorbed during the experiment. The Orbo tube was placed in the refrigerator until the extraction and analysis were made.
- For hot start experiments, the car engine was turned on and ran for 10 min. After 10 min, the car engine was turned off. One minute after, it was turned on again. This was considered as ‘‘hot start’’. As soon as the ‘‘hot start’’ was made for the car engine, the sampling pump in the car was also turned on and sampling started. The same sampling train and the same experimental procedure was applied for the ‘‘hot start’’ sampling as it was used in the ‘‘cold start’’ sampling.
- For experiments at driving conditions, the same preparations and set up of the sampling system were done as it was explained before. However, this time the car with the sampling train and the pump was driven at the pre-determined speed (e.g. 30 km/hr). After the predetermined speed was reached, the sampling was started by turning the pump on. The car was driven at this constant speed and the sampling continued for 5-10 min period. After the sampling was finished, the pump was turned off, the car was slowed down and stopped. The drier tube and Orbo tube was taken off the sampling system and capped at both ends. Both tubes were kept in an ice box until they were brought to the laboratory. Again the drier tube was weighed and the Orbo tube was kept in the refrigerator until further analysis.
- The extraction of the Orbo tubes and the analysis of the extract were conducted within 24 hours after sampling.

3.2.3. Extraction of the Collected Samples

VOCs adsorbed by the active carbon in the Orbo-32 tubes were extracted by liquid CS_2. The extraction procedure according to EN/ISO DIS 13528-3 was followed and this procedure is given below:

- First the Orbo-32 tube was taken out of the refrigerator and end plugs of the tube were taken out. The tube was cut in the middle by a glass cutter very carefully.
- The charcoal in the front part of the tube was transferred into a 2 ml vial with discarding the mesh. Then the vial was closed with the lid and it was weighed.
- The foam plug in the middle of the tube was taken out very carefully and discarded (no active carbon particles should stay on the foam).
- The back part of the charcoal was transferred into another 2 ml vial. Then the vial was closed with the lid and it was weighed.
- 0.750 ml of CS_2 was injected into each vial containing charcoal samples and the vials with CS_2 were weighed again.
- Ultrasonic bath was prepared with ice water and the vials placed on a holder were kept in the ultrasonic bath for at least 10 minutes.
- Then the vials were taken out of the ultrasonic bath and put into the centrifuge for 10 minutes at 4000 rpm.
- After the vials were taken out of the centrifuge, the clear layer (about 0.2 ml) was taken with a syringe and transferred into a specially prepared glass pipette. The pipettes were sealed in the flame and labeled.
- In the mean time the syringe is cleaned with 2-propanol each time before the sample is transferred from the vial to the pipette.

3.2.4. Gas Chromatography Analysis

Extracted samples were analyzed by using a Gas Chromatograph (GC) with Flame Ionization Detector (FID). Benzene, toluene, xylene, ethylbenzene, m-xylene, o-xylene and 1,2,4 trimethylbenzene (pseudocumene) compounds were examined. Calibration of the Gas Chromatograph under the stated condition was made with standard mixtures and calibration curves were prepared. Calculations and the GC calibration curves are given in Appendix A. The operating conditions of GC is given below:

The Operating Conditions:

Minimum Temperature: 60 ^{o}C
Maximum Continuous Temperature: 280 ^{o}C
Conditioning Temperature: 280 ^{o}C
Carrier Gas: H_2

Column Temperature Programming: 32 ^{o}C for 5 minute
12 ^{o}C /minute to 180 ^{o}C
180 ^{o}C for 10 minute
Detector Temperature: 250 ^{o}C
Injector Temperature: 240 ^{o}C

1 μL of samples from the extract kept in the glass pipettes were injected into GC. Two or three injections were made for each sample.

Sensitivity of the analysis is 1 $\mu g/m^3$ per 100 L of the sample volume. In Gas Chromatographic analysis, hydrogen was used as carrier gas and air was used for combustion of hydrogen. A sample chromatogram is given in Appendix F.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Distribution of Vehicle Categories and Their Emissions

Results of the statistical study performed on the emission measurements for exhaust gases of various categories of cars by ANÇEVA are given in this section.

Out of 5729 cars included in this statistical study,
- 89% was gasoline cars
- 6% was diesel cars
- 5% was LPG cars

This distribution is shown in Figure 4.1.

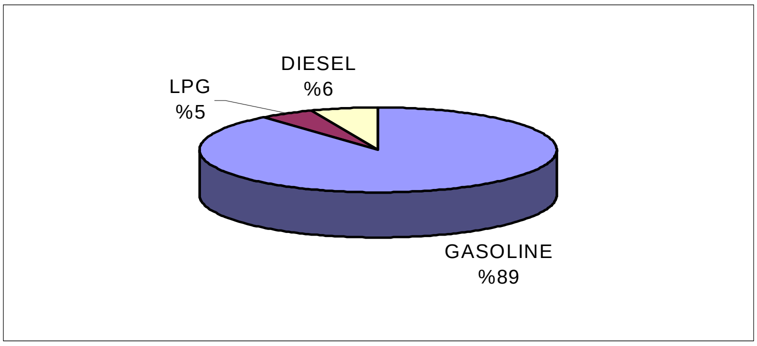

Figure 4.1 The percent distribution of the vehicles examined according to the type of fuel used

The percent distribution of the light duty vehicles (that means passenger cars) in Ankara is given in Figure 4.2.

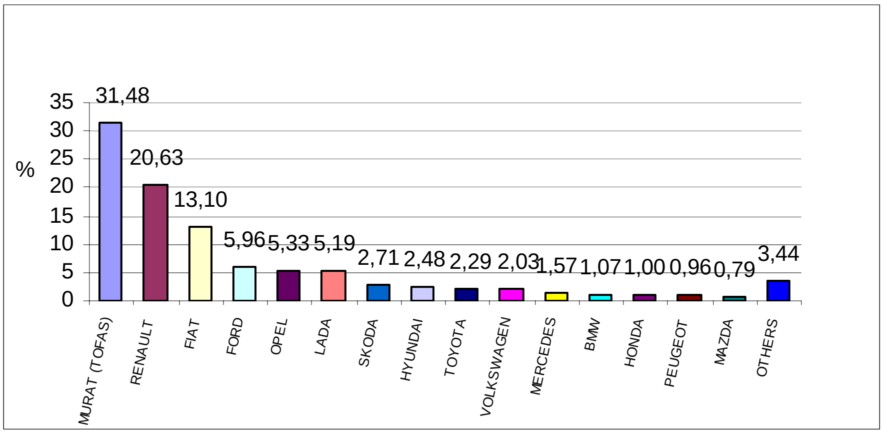

Figure 4.2 Distribution of the light duty vehicles in Ankara

As can be seen from this figure, the cars named under ‘‘Murat (Tofas)’’ constitute 31.5% of the total cars using gasoline and considered for this study in Ankara. ‘‘Renault’’ cars follow this with 20.6% and the ‘‘Fiat’’ cars are in the third row with 13.1%.

This distribution was checked also by using the SIS (2001) data given for Turkey. The cars named under ‘‘Murat (Tofas)’’ constitute 28.7%, Renault cars constitute 29.7% and Fiat cars constitute 6% of total cars. For Renault and Murat type cars, the percentages are very close. However, for Murat cars there is a difference of about 1%. Nevertheless, the largest percentage belongs to Murat (Tofas) and Fiat types of cars which are both manufactured by Tofas. Therefore, for our further studies, Tofas/ Fiat cars were taken because these are widely used cars in Ankara and Turkey.

According to the SIS 2002 data given in Figure 4.3 the distribution of cars with respect to their models are very similar. Average emission values, as a result of statistical analysis for CO and HC’s and for other parameters are given in Table 4.1.

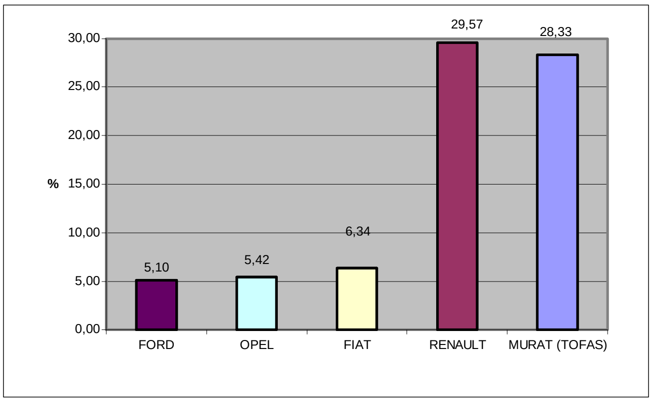

Figure 4.3 Distribution of the light duty vehicles in Turkey according to SIS data (SIS, 2003)

Table 4.1 Average concentrations and standard deviations of CO, CO_2 and HC's for various models of passenger cars

Model		**CO (%)**	**CO_2 %**	**HC (ppmv)**	**O_2 (%)**	**AFR***
MURAT (TOFAS)	Average	1.98	12.60	298.75	0.96	13.94
	Std. Dev.	0.91	1.81	192.64	1.75	0.09
RENAULT	Average	1.53	13.28	237.66	1.19	14.22
	Std. Dev.	1.08	2.12	142.52	1.88	0.63
FIAT	Average	0.83	13.91	168.30	0.86	14.68
	Std. Dev.	0.85	1.66	128.88	1.47	1.99
FORD	Average	0.95	14.30	207.67	0.81	14.25
	Std. Dev.	1.03	1.74	165.09	1.43	1.32

AFR = Air Fuel Ratio
ppmv= ppm volume

From the results given in Table 4.1, it was seen that the CO emissions from ‘‘Murat (Tofas)’’ cars are 1.98% by vol and from Renault cars 1.53% by vol. According to TS 11136, the CO concentration should not exceed 4.5% by vol. Moreover, it was seen from the results that HC emissions from " Murat (Tofas)" and Renault cars are 299±193 ppmv and 230±204 ppmv, respectively.

Although these are the highest emission values among the investigated vehicles, these values are below the limits given in the TS 11136.

In order to see if the emissions have decreased with developing technology, the vehicles were grouped in 5 year intervals according to their models (i.e. the year that they were manufactured) and their CO and HC emissions were plotted with respect to the 5-yr intervals. The results are given in Figures 4.4 and 4.5.

As can be seen from Figure 4.4, the average CO concentration for the passenger cars for the period 1980-1984 was 2.11%. However, it has decreased to 0.75% for the period of 1995-1999, and even less for the following 3 years between 2000-2002.

A similar result can be seen for HC concentrations. The HC concentration for the period of 1980- 1984 was 324 ppmv. For the last 3-yr period it was decreased to 87 ppmv. The decrease in CO emissions is 88% and the corresponding decrease in HC emissions is 73%. This is a very good result which is due to development in car manufacturing.

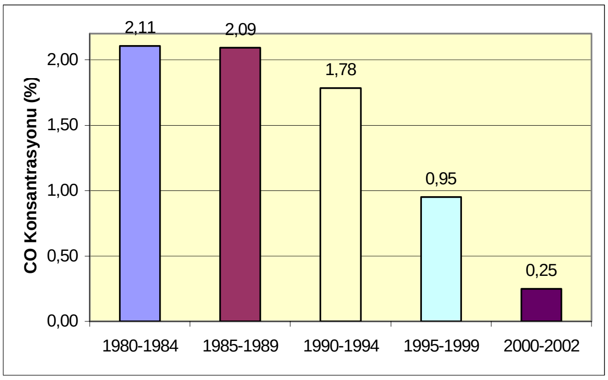

Figure 4.4 Average CO values for 5 year intervals

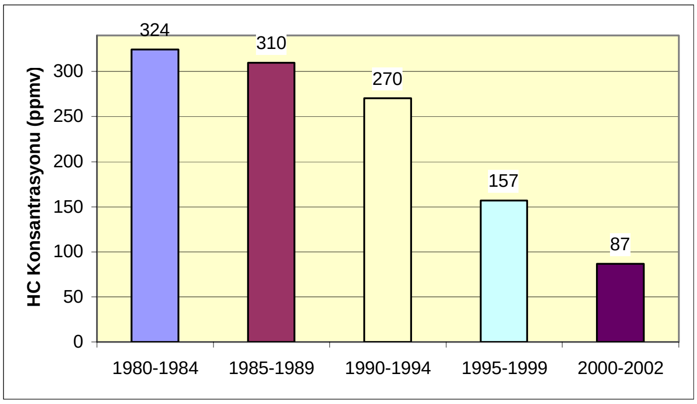

Figure 4.5 Average HC values for 5 year intervals

4.2 Results of GC Analysis for HC Emissions

The samples collected on active charcoal particles in NIOSH tubes were analyzed for BTEX compounds.

According to the statistical analysis performed, Tofas/Fiat types of cars were found to be the largest groups of passenger cars in Ankara and Turkey. Therefore, this type is chosen for the further investigation of HC analysis. First of all Tofas/Fiat type of cars were divided into two groups:

1) Cars without catalytic converter
2) Cars with catalytic converter

Cars without a catalytic converter are about 10-year old cars since the manufacturing of cars with catalytic converter has started in year 1995.

The cars chosen for this study without catalytic converter and their experiment numbers are:

• Murat - Kartal SLX (1993)	Car 1
• Fiat-Tipo (1993)	Car 2
• Murat- Dogan SLX (1996)	Car 3

The cars chosen for this study with catalytic converter and their experiment numbers are:

• Murat Kartal (2001)	Car 4
• Fiat Marea (2005)	Car 5
• Fiat Palio (2000)	Car 6

Detailed information about vehicles can be seen in Appendix C.
The first experiments were made to determine the sampling condition.

4.2.1. Effect of Sampling Time

As it was explained before the HC samples were taken by adsorbing them on active carbon particles in Orbo-32 Tubes. During sampling, the first part of the tube adsorbs the HCs, the second part of the tube was used as control section. There should not be any HC adsorbed in the second section. Therefore, it was important to determine the gas sampling time in order not to have HC's in the second part of the Orbo-32 tube. The experiments were conducted in order to determine the optimum sampling time. The driving conditions of the first set of experiments are given in Table 4.2.

Table 4.2 Driving conditions to determine the effect of sampling time (Car 1)

Sample number	Velocity (km/s)	Time (min)	Sample volume (L)
1	30	5	5.5
2	30	7	8.7
3	30	8	9.7
4	30	10	12.1
5	60	5	5.8
6	60	7	8.6
7	60	8	9.7
8	60	10	11.8
9	90	4	4.8
10	90	5	6.0
11	90	6	7.2
12	90	7	8.2
13	Idle (hot start)	5	5.7
14	Idle (cold start)	10	12.4

From the analysis of the collected samples, it was seen that there was no NMVOC at backup part of the active carbon part (b). This result shows that for all analysis periods, adsorption capacity of part (a) is suitable for exhaust gasses. However, to have constant velocity during sampling, it was decided that the most appropriate time period for sampling is 5 min. For this reason, mainly 5 minutes sampling duration was chosen. Results of analysis for car 1 are given in section 4.2.6.

4.2.2. Effect of Moisture

Moisture content of the exhaust gasses were measured with a humidity probe and it was determined that relative humidity of the exhaust gas is about 90-99 %. Therefore, the gas has to be dried before it passed through the activated carbon tube.

The moisture content of the sample exhaust gases for Car 1 which has no catalytic converter and Car 5 which has catalytic converter (g/Nm^3) are given in Figures 4.6 and 4.7, respectively. As can be seen from Figures 4.6 and 4.7, at 30 km/hr the moisture content is very high. However, when the speed increases to 60 - 90 km/hr, the exhaust gases are at higher temperatures and relative humidity (RH) becomes lower. At idle-hot start condition, it is expected to have a better combustion of gasoline than at cold start condition, and also more moisture content in exhaust gasses are seen.

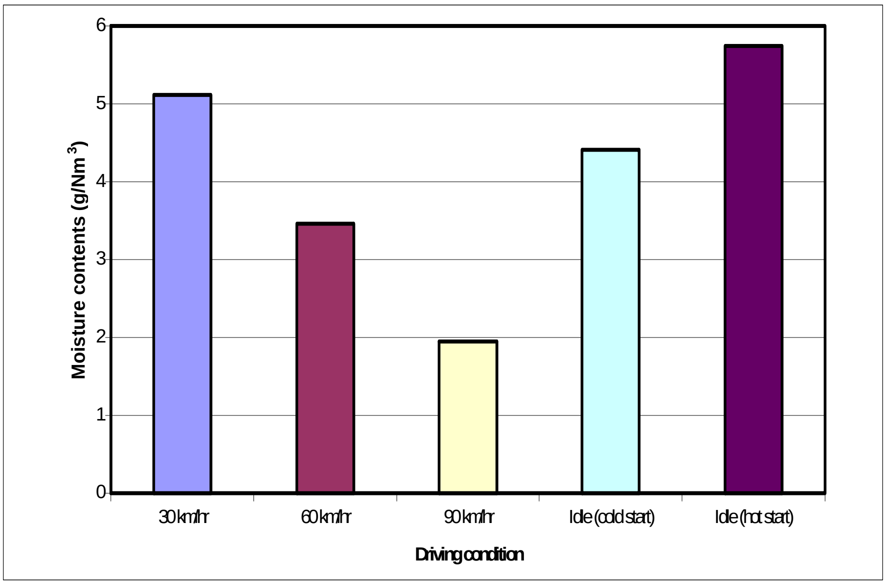

Figure 4.6 Moisture contents of exhaust gasses for Car 1

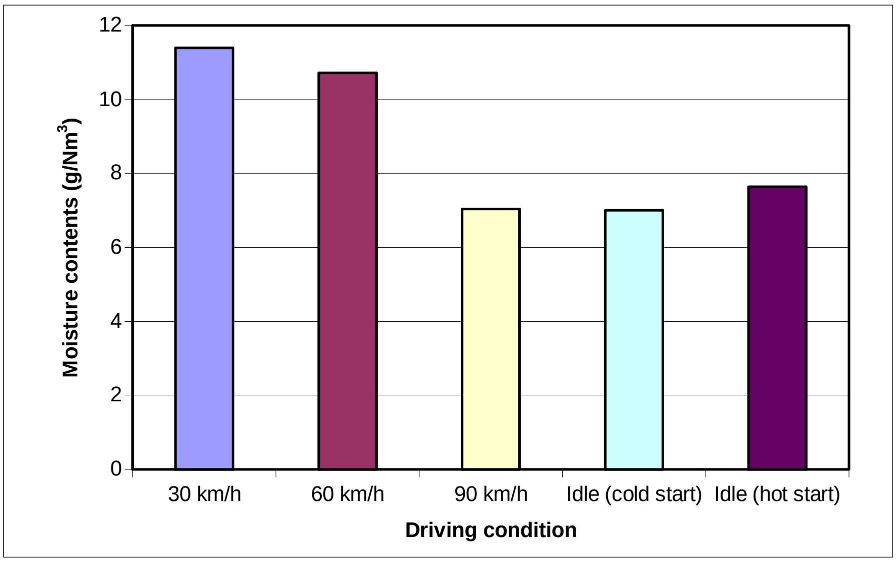

Figure 4.7 Moisture contents of exhaust gasses for Car 5

As a separate study, the effect of moisture on adsorption of hydrocarbons was analyzed by performing measurements at 60 km/hr and 90 km/hr both by not using silica gel and using drying silica gel as a drying agent in Car 2. Results of the analyses showed that, if silica gel were not used, moisture from the exhaust gasses would be adsorbed by the active carbon and the capacity of the part (a) would not be sufficient to adsorb all VOC's from the exhaust gas collected. Since VOC's were also adsorbed by part (b), these results were not taken into the consideration in emission factor calculations. Therefore, a drier tube adsorption of moisture was used in the sampling train.

4.2.3. Effect of Silica Gel

In our experiments, silica gel was used as the drying agent to prevent the effect of moisture on the adsorption of exhaust gases on active carbon in Orbo tubes.

Silica gel, with its wide range of pore sizes, has the capability of adsorbing compounds in addition to water. The relative order of adsorbability is: water, ammonia, alcohols, aromatics, diolefins, olefins and paraffins. When the potential for multicomponent adsorption is present, we expect the more strongly adsorbed compounds, such as water, to displace the more weakly held ones. (http://www.shroomery.org/index/par/23936, 2004).

Because of this, the effect of silica gel on experiments was examined by extraction of HC's from silica gel which was used in the analyses as drying agent. Gas chromatography analysis was also performed for the extract and no NMVOC's were observed. And from this result, it was concluded that in our experiments silica gel tends to adsorb water rather than HC's. Therefore, silica gel was used as a drier before the active carbon tube (Orbo-32).

4.2.4. Type of fuel used

In this study, mainly two types of cars and also two types of fuel were used: cars without catalytic converter using super gasoline and cars with catalytic converter using unleaded gasoline. It can be seen from the Table 4.3 and 4.4 that the BTEX components of both types of gasoline are approximately the same. Although composition of the gasoline used is not different, concentration and emission factors for the cars without catalytic converter which are given in Section 4.2.6.1 is higher than the concentration and emission factors for the cars with catalytic converter which are given in section 4.2.6.2. Therefore it can be said that, the technology of the car is very important for reducing the emissions. Cars with catalytic converter emit less pollutant because of their better technology and catalytic converter. Catalytic converter preferentially lowers the activation energy of the reactions and converts incomplete combustion products to CO_2 and H_2O. Also, NO is reduced to N_2 which is an inert gas.

Table 4.3 METU-Petroleum Research Laboratory analysis results of ''super gasoline'' (PAL, 2004)

Component	**% volume**
Toluene	12.16
Benzene	1.50
m-xylene (1,3-dimethylbenzene)	6.48
o-xylene (1,2-dimethylbenzene)	3.05
Pseudocumene (1,2,4- trimethylbenzene)	2.88
Ethylbenzene	2.21
Toluene/Benzene	8.11

Table 4.4 METU-Petroleum Research Laboratory analysis results of ''unleaded gasoline'' (PAL, 2004)

Component	**% volume**
Toluene	10.47
Benzene	2.12
m-xylene (1,3-dimethylbenzene)	5.67
o-xylene (1,2-dimethylbenzene)	2.91
Pseudocumene (1,2,4- trimethylbenzene)	2.83
Ethylbenzene	2.21
Toluene/Benzene	4.94

4.2.5. Repeatability

During our study, repeatability of the analysis is also performed and statistical analysis results are given with the exhaust gas concentrations and emission factors of cars in Section 4.2.6.

4.2.6. Results of VOC Analysis

4.2.6.1 VOC concentrations of exhaust gasses of cars without catalytic converter

Car 1 (Murat - Kartal SLX (1993))

The results of the emission analysis of Car 1 are graphically shown in Figure 4.8.

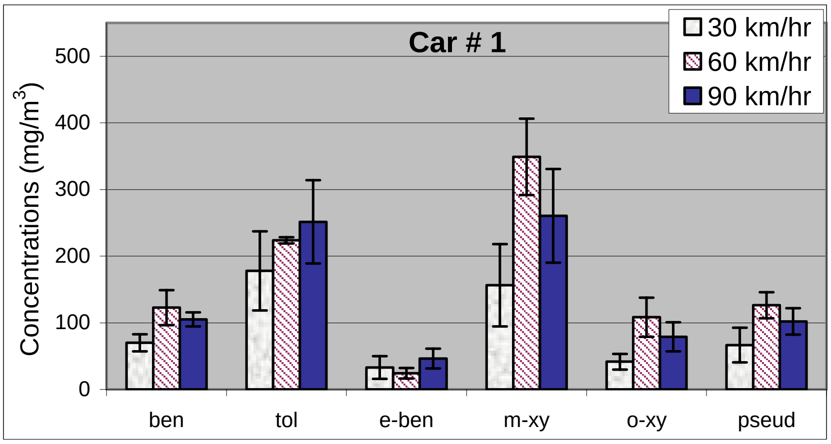

Figure 4.8 Concentration of VOCs for Car 1

The highest concentrations among hydrocarbons investigated in this study were seen for toluene and m-xylene at all driving speeds, and all constituents' concentrations were higher mainly at 60 km/hr and 90 km/hr. These speeds are mainly used at urban and highway driving, respectively.

The results of the analysis conducted at the METU-Petroleum Research Laboratory (2004) for super gasoline used in Turkey were given in Table 4.3. According to Table 4.3, toluene and m-xylene concentrations for super gasoline are higher than other compounds. Also results of our exhaust gas analysis given in Figure 4.8 show that toluene and m-xylene concentrations are more than other compounds which is an expected result. It is interesting to have a toluene/benzene ratio in exhaust gas analysis around 3, as toluene to benzene ratio in super gasoline is 8.11. Also benzene concentration in our analysis is nearly same as o-xylene and pseudocumene concentrations. From these results, it can be said that although the benzene concentration in super gasoline is less than the concentrations of other compounds, its concentration is not less than the other compounds in exhaust gasses, except for toluene and m-xylene. This also shows the importance of the aromatic content in gasoline.

Concentration values at cold start-idle condition which were given in Table 4.5 were found generally higher than at hot start condition which was an expected result since exhaust emissions had reached a stable value until engine reaches its operating temperature.

Table 4.5 Concentration of VOCs at idle condition for Car 1

Drv. con.	**Benzene**	**Toluene**	**e-benzene**	**m-xylene**	**o-xylene**	**pseud**
	Concentration (mg/ Nm^3)					
Idle (cs)	87.51±27.96	250.60±21.90	50.26±12.00	235.36±83.80	11.24±1.55	97.03±23.62
Idle (hs)	80.77±15.90	224.51±70.28	39.99±19.61	205.74±45.71	21.10±3.37	52.30±23.31

Drv. con.: Driving condition, cs: cold start, hs: hot start, pseud: pseudocumene

<u>Car 2 Fiat-Tipo (1993)</u>

The results of the exhaust gas analysis of Car 2 are graphically shown in Figure 4.9.

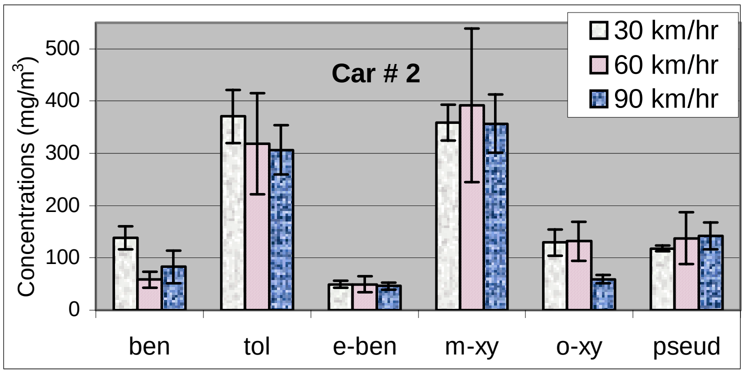

Figure 4.9 Concentration of VOCs for Car 2

Results of the analysis given in Figure 4.9 showed that toluene and m-xylene concentrations are higher than the other compounds, as expected. It is interesting to have toluene/benzene ratio between 2 to 6 except for idle (hot start) condition which is 17.5. Also pseudocumene concentrations in our analysis were found to be nearly the same as o-xylene concentrations. Ethyl benzene concentration was the lowest among the others.

Concentration values at cold start-idle condition which were given in Table 4.6 were found generally higher than at hot start condition which was again an expected result.

Table 4.6 Concentration of VOCs at idle condition for Car 2

Drv. con.	Benzene	Toluene	e-benzene	m-xylene	o-xylene	pseud
	Concentration (mg/ Nm^3)					
Idle (cs)	84.65±7.32	139.31±33.02	38.63±12.28	311.10±88.32	112.93±26.21	94.89±21.29
Idle (hs)	10.09±2.06	151.79±31.26	15.03±7.76	176.48±65.42	34.92±7.83	66.31±16.04

Drv. con.: Driving condition, cs: cold start , hs: hot start, pseud: pseudocumene

Car 3 Murat- Dogan SLX (1996)

The results of the exhaust gas analysis of Car 3 are given graphically in Figure 4.10.

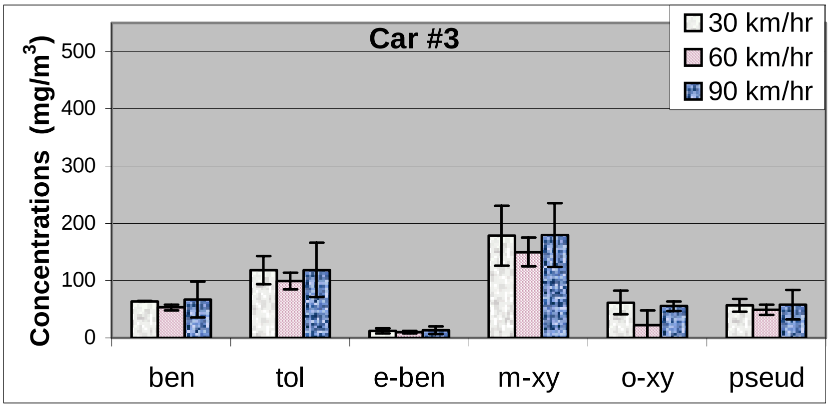

Figure 4.10 Concentration of VOCs for Car 3

The highest concentrations among hydrocarbons investigated in this study are seen for toluene and m- xylene at driving speeds of 30 km/hr and 90 km/hr. It can be seen from the Figure 4.10 that concentrations were about the same for all speeds. Toluene/benzene ratio was found to be around 2 and benzene concentration in our analysis results was nearly same as o-xylene and pseudocumene results.

Concentration values of idle-cold start condition was similar to concentration at hot start condition which was not an expected result as exhaust emission has been more until engine reaches its operating temperature. The reason for this was that vehicle was not allowed to soak before the cold start measurements.

Concentrations at cold start-idle condition which were given in Table 4.7 were not higher than concentrations at hot start condition which was not an expected result. The result may be due to the engine temperature at cold start condition which was not different from the hot start condition.

Table 4.7 Concentration of VOCs at idle condition for Car 3

Drv. con.	Benzene	Toluene	e-benzene	m-xylene	o-xylene	pseud
	Concentration (mg/ Nm^3)					
Idle (cs)	15.72±2.32	29.20±7.64	3.72±1.61	49.69±12.24	14.74±7.26	17.22±6.21
Idle (hs)	16.10±2.75	36.84±5.77	4.46±1.09	59.45±6.75	16.26±2.65	20.69±3.05

Drv. con.: Driving condition
cs: cold start
hs: hot start
pseud: pseudocumene

4.2.6.2 VOC concentrations of exhaust gasses of cars with catalytic converter

Car 4 (Murat - Kartal (2001))

The results of the exhaust gas analysis of Car 4 are graphically shown in Figure 4.11. As can be seen from the figure, the concentrations of VOC components measured are much lower than those cars without catalytic converter.

The highest concentrations among hydrocarbons investigated in this study were seen for benzene, toluene and m- xylene. As the speed increases from 30 km/hr to 90 km/hr, it is seen from the Figure 4.11 that, except for o-xylene and m-xylene, concentrations were increased.

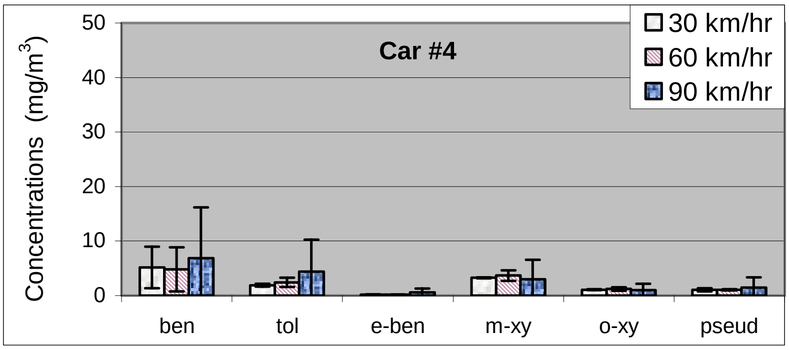

Figure 4.11 Concentration of VOCs for Car 4

The results of the analysis conducted at the METU-Petroleum Research Laboratory (2004) for unleaded gasoline used in Turkey was given in Table 4.4. According to Table 4.4, it is expected to have more toluene and m-xylene concentration in the exhaust gas than the other compounds. In fact results of the GC analysis given in Figure 4.11 showed that toluene and m-xylene concentrations in the exhaust gas are more than the other compounds as expected. It is interesting to have toluene/benzene ratio between 0.1 and 2.5, as toluene to benzene ratio in unleaded gasoline is 4.9. Also benzene concentration in our analysis results was mainly more than the other compounds. From these results it can be said that, although concentration of benzene in unleaded gasoline is less than the concentration of other compounds, its concentration is more than the other compounds in exhaust gases. This also shows the importance of the benzene content in gasoline.

Concentration values at cold start-idle condition which were given in Table 4.8 were found to be higher than at hot start condition which was an expected result.

Table 4.8 Concentration of VOCs at idle condition for Car 4

Drv. con.	**Benzene**	**Toluene**	**e-benzene**	**m-xylene**	**o-xylene**	**pseud**
	Concentration (mg/ Nm^3)					
Idle (cs)	100.82±13.56	363.47±50.58	82.42±47.79	303.66±39.84	92.33±19.57	84.68±10.13
Idle (hs)	58.02±8.47	91.32±20.28	7.17±3.42	114.28±25.25	33.79±11.46	28.88±12.10

Drv. con.: Driving condition
cs: cold start
hs: hot start
pseud: pseudocumene

Car 5 Fiat Marea (2005)

The results of the exhaust gas analysis of Car 5 are graphically shown in Figure 4.12.

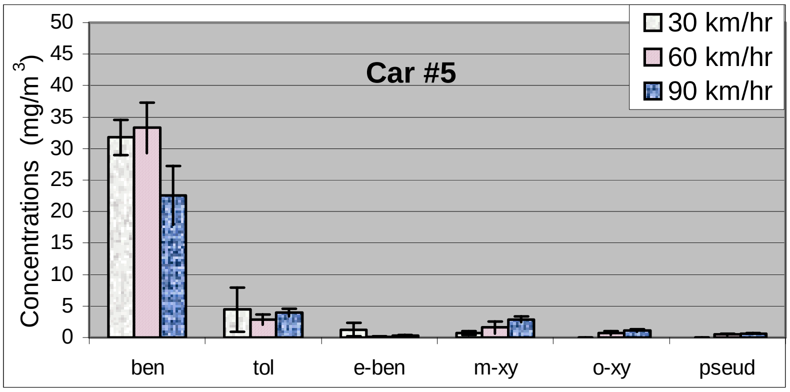

Figure 4.12 Concentration of VOCs for Car 5

The highest concentrations among hydrocarbons investigated in this study were seen for toluene and benzene.

Results of the GC analysis given in Figure 4.12 showed that benzene and toluene concentrations are more than the other compounds, as expected. Toluene/benzene ratio was around 0.15 to 1.5. Also benzene concentrations in our analysis results were higher than the other compounds.

Concentration values at cold start-idle condition which were given in Table 4.9 were found to be higher than at hot start condition which was an expected result.

Table 4.9 Concentration of VOCs at idle condition for Car 5

Drv. con.	**Benzene**	**Toluene**	**e-benzene**	**m-xylene**	**o-xylene**	**pseud**
	Concentration (mg/ Nm^3)					
Idle (cs)	35.98±8.50	77.34±16.03	11.15±5.55	62.43±15.96	21.77±5.11	19.65±4.49
Idle (hs)	26.31±2.61	26.02±6.35	1.94±1.46	39.56±7.39	12.79±1.56	10.63±3.80

Drv. con.: Driving condition
cs: cold start
hs: hot start
pseud: pseudocumene

Car 6 Fiat Palio (2000)

The results of the exhaust gas analysis for Car 6 are graphically shown in Figure 4.13.

Results of the analysis given in Figure 4.13 showed that m-xylene, toluene and benzene concentrations are more than the other compounds, as expected, because the volume % of these components in the unleaded gasoline are higher than other compounds, too. However, concentrations at each speed were close to each other for benzene, o-xylene, and pseudocumene. For toluene and ethylbenzene, a decreasing trend in concentration with increase in speed was seen.

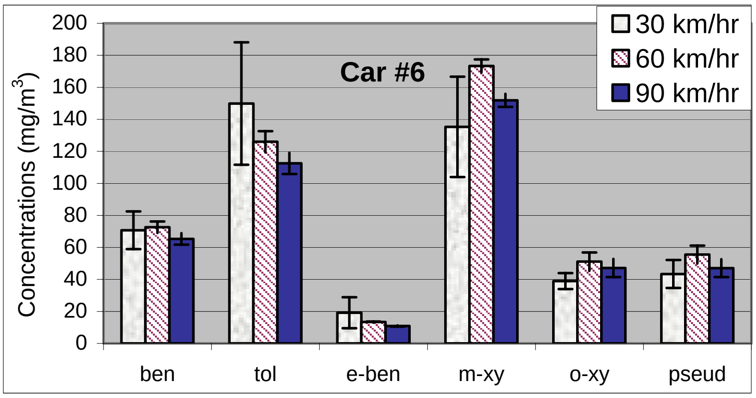

Figure 4.13 Concentration of VOCs for Car 6

Concentration values at cold start-idle condition which were given in Table 4.10 were found to be higher than at hot start condition, and this was an expected result.

Table 4.10 Concentration of VOCs at idle condition for Car 6

Drv. con.	**Benzene**	**Toluene**	**e-benzene**	**m-xylene**	**o-xylene**	**pseud**
	Concentration (mg/ Nm³)					
Idle (cs)	101.98±24.51	362.06±79.24	66.41±2.54	301.93±1.37	80.72±14.65	99.80±6.93
Idle (hs)	67.32±12.25	114.41±32.24	12.76±8.65	162.69±40.52	52.17±16.14	43.94±8.53

Drv. con.: Driving condition
cs: cold start
hs: hot start
pseud: pseudocumene

4.2.6.3 Comparison of VOCs in exhaust gasses of cars

Concentrations of VOCs for cars without catalytic converter which are given in Figures 4.8, 4.9 and 4.10 show that exhaust gas concentrations of VOCs of Car 2 were more than the concentrations of Car 1 and Car 3, and also that of Car 1 were mainly more than that of Car 3. As we look at the model and distance traveled by cars, which are given in Appendix B, it is seen that there was no direct relation between distance traveled by the car and exhaust gases concentration. However, there was a relation between model of the cars and the concentrations of VOCs. Exhaust gas concentrations of Car 2 and Car 1, which are model 1993, were mainly more than that of Car 3. Moreover, emissions of Car 1 were less than that of Car 2 as expected. The reason for this was that carburetor adjustment of Car 1 had been performed just before the exhaust gas measurement. Maintenance of cars also affects the gasoline combustion and hence the exhaust gas concentration.

Concentrations of VOCs for cars with catalytic converter which are given in Figures 4.11, 4.12 and 4.13 show that exhaust gas concentrations of VOCs of Car 6 were more than the concentrations of Car 4 and Car 5. This was an expected result because the distance traveled by the car was too high (about 230,000 km) which was given In Appendix B. Because the model of the Car 5 was very new (2005) and distance traveled by that car was quite small (about 1400 km) exhaust gas concentrations of VOCs for Car 5 was less than that of Car 4 and Car 6.

Overall, average exhaust gas VOC concentrations of cars without catalytic converter as given in Figure 4.14 were about 3 times more than the average exhaust gas VOC concentrations of cars with catalytic converter as shown in Figure 4.15.

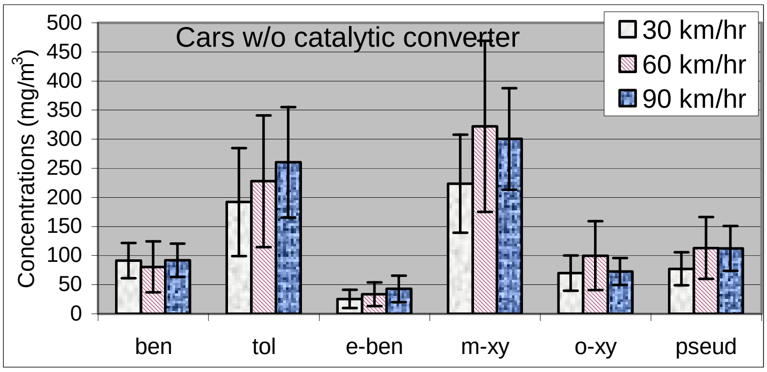

Figure 4.14 Overall average exhaust gas VOC concentrations of cars without catalytic converter

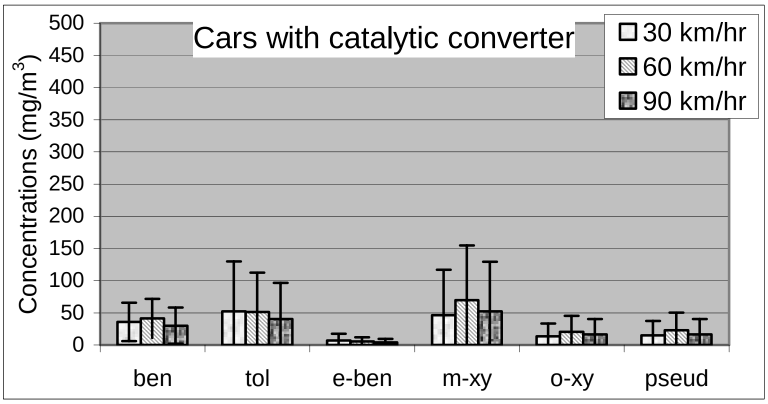

Figure 4.15 Overall average exhaust gas VOC concentrations of cars with catalytic converter

Overall average exhaust gas VOC concentrations at idle condition for cars without catalytic converter and with catalytic converter are shown in Figure 4.16 and 4.17, respectively.

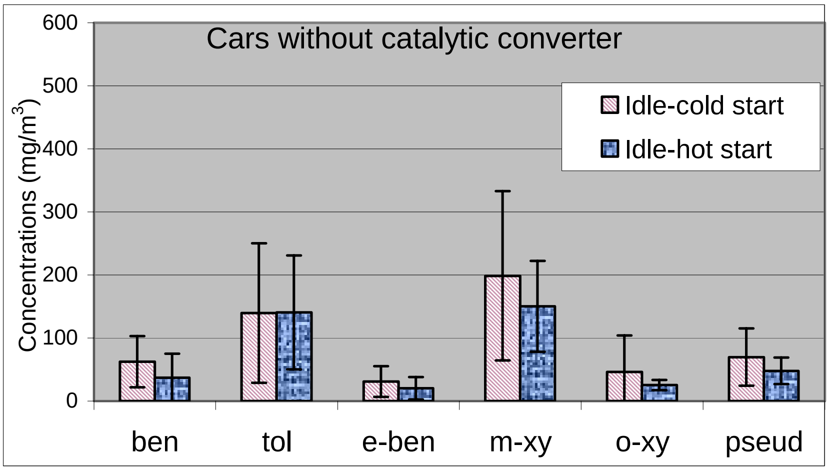

Figure 4.16 Overall average exhaust gas VOC concentrations of cars without catalytic converter

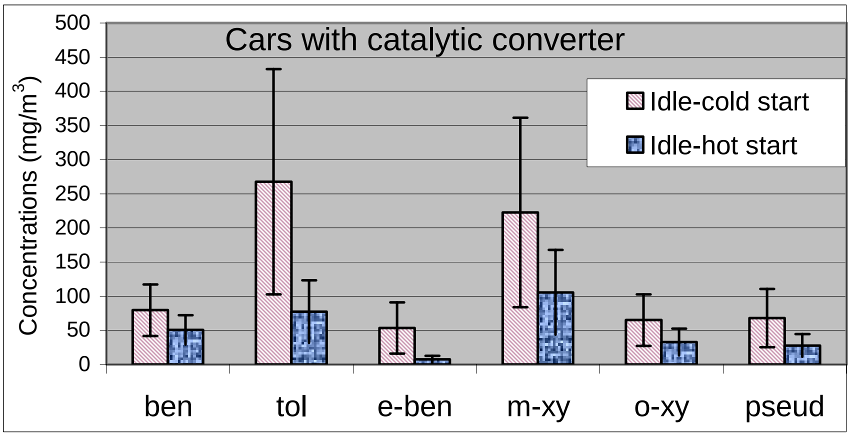

Figure 4.17 Overall average exhaust gas VOC concentrations of cars with catalytic converter

In general, for cars both with catalytic converter and without catalytic converter the VOC emissions at idle-cold start condition are more than the emissions at idle-hot start condition. In cars without catalytic converter the difference is not much. But for cars with catalytic converter the difference becomes sometimes 2-3 times. For both groups of cars, the largest VOC emission occurs for toluene and m-xylene. The emissions of benzene, e-benzene, o-xylene and pseudocumene are almost at the same order of magnitude.

4.2.6.4 Emission factors of cars without catalytic converter

Emission factors calculated for Car 1 are given in Table 4.11. A sample calculation showing how to find an emission factor is given in Appendix B.

Table 4.11 Emission factors with respect to driving condition for Car 1

Parameter	**EF (Emission factor) (g/km)**			**EF (g/hr)**	
	30 km/hr	**60 km/hr**	**90 km/hr**	**Idle (cold start)**	**Idle (hot start)**
Benzene	0.06±0.02	0.05±0.01	0.03±0.00	1.61±0.51	1.49±0.29
Tolune	0.09±0.02	0.09±0.02	0.04±0.00	4.61±0.46	4.13±0.66
e-benzene	0.01±0.00	0.01±0.00	0.01±0.00	0.92±0.18	0.74±0.19
m-xylene	0.13±0.05	0.15±0.06	0.07±0.02	4.33±0.59	3.79±0.30
o-xylene	0.04±0.01	0.05±0.02	0.02±0.00	0.21±0.07	0.39±0.05
Pseudocumene	0.06±0.01	0.05±0.01	0.03±0.01	1.78±0.29	0.96±0.29

Emission factors for Car 1 are higher for m-xylene and toluene than the other compounds, and decrease as the driving speed increases from 30 km/hr to 90 km/hr.

Emission factors calculated for Car 2 are given in Table 4.12. Again emission factors for toluene and m-xylene for Car 2 are higher than the other compounds. Emission factors decrease as the driving speed increases from 30 km/hr to 90 km/hr.

Table 4.12 Emission factors with respect to driving condition for Car 2

Parameter	EF (Emission factor) (g/km)			EF (g/hr)	
	30 km/hr	60 km/hr	90 km/hr	Idle (cold start)	Idle (hot start)
Benzene	0.12±0.02	0.02±0.01	0.02±0.01	2.12±0.18	0.25±0.05
Tolune	0.31±0.04	0.13±0.04	0.09±0.02	3.49±0.37	3.81±0.31
e-benzene	0.04±0.01	0.02±0.01	0.01±0.00	0.97±0.14	0.38±0.12
m-xylene	0.30±0.03	0.16±0.06	0.11±0.03	7.80±1.15	4.43±0.98
o-xylene	0.11±0.02	0.05±0.02	0.02±0.00	2.83±0.44	0.88±0.13
Pseudocumene	0.10±0.00	0.06±0.02	0.04±0.01	2.38±0.36	1.67±0.28

Emission factors calculated for Car 3 are given in Table 4.13. Emission factors of Car 3 for toluene and m-xylene were again higher than the other compounds which can be seen in Table 4.13. Emission factors mainly decrease as the driving speed increases from 30 km/hr to 90 km/hr.

Table 4.13 Emission factors with respect to driving condition for Car 3

Parameter	EF (Emission factor) (g/km)			EF (g/hr)	
	30 km/hr	60 km/hr	90 km/hr	Idle (cold start)	Idle (hot start)
Benzene	0.05±0.00	0.02±0.00	0.02±0.00	0.29±0.04	0.29±0.05
Tolune	0.09±0.02	0.04±0.01	0.03±0.00	0.53±0.07	0.58±0.09
e-benzene	0.01±0.00	0.00±0.00	0.00±0.00	0.07±0.02	0.07±0.02
m-xylene	0.13±0.04	0.06±0.01	0.05±0.00	0.91±0.10	0.94±0.11
o-xylene	0.05±0.02	0.01±0.01	0.01±0.00	0.27±0.11	0.27±0.04
Pseudocumene	0.04±0.01	0.02±0.00	0.01±0.00	0.32±0.09	0.35±0.05

4.2.6.5 Emission factors of cars with catalytic converter

Emission factors calculated based on the results obtained for Car 4 are given in Table 4.14. Toluene, m-xylene and benzene emission factors for Car 4 were found to be higher than the other compounds. Emission factors for Car 4 generally decrease from

30 km/hr to 60 km/hr but then increase at 90 km/hr. The reason for this result may be due to the deviations in the experimental data.

Table 4.14 Emission factors with respect to driving condition for Car 4

Parameter	EF (Emission factor) (g/km)			EF (g/hr)	
	30 km/hr	60 km/hr	90 km/hr	Idle (cold start)	Idle (hot start)
Benzene	0.003±0.002	0.002±0.001	0.007±0.010	1.66±0.22	0.95±0.14
Tolune	0.001±0.000	0.001±0.000	0.005±0.006	5.98±0.13	1.50±0.14
e-benzene	0.000±0.000	0.000±0.000	0.001±0.001	1.36±0.49	0.12±0.03
m-xylene	0.002±0.000	0.001±0.000	0.003±0.004	5.00±0.08	1.88±0.17
o-xylene	0.001±0.000	0.000±0.000	0.001±0.001	1.52±0.21	0.56±0.14
Pseudocumene	0.001±0.000	0.000±0.000	0.002±0.002	1.39±0.07	0.47±0.16

Emission factors calculated for Car 5 are given in Table 4.15. It can be seen from Table 4.15 that emission factors decrease from 30 km/hr to 90 km/hr which was an expected result.

Table 4.15 Emission factors with respect to driving condition for Car 5

Parameter	EF (Emission factor) (g/km)			EF (g/hr)	
	30 km/hr	60 km/hr	90 km/hr	Idle (cold start)	Idle (hot start)
Benzene	0.021±0.002	0.011±0.002	0.004±0.001	0.57±0.14	0.42±0.04
Tolune	0.003±0.002	0.001±0.000	0.001±0.000	1.23±0.10	0.41±0.05
e-benzene	0.001±0.001	0.000±0.000	0.000±0.000	0.18±0.05	0.03±0.02
m-xylene	0.000±0.000	0.001±0.000	0.001±0.000	0.99±0.12	0.63±0.04
o-xylene	0.000±0.000	0.000±0.000	0.000±0.000	0.35±0.06	0.20±0.01
Pseudocumene	0.000±0.000	0.000±0.000	0.000±0.000	0.31±0.05	0.17±0.05

Emission factors calculated for Car 6 are given in Table 4.16. It can be seen from Table 4.16 that, emission factors decrease as the speed increases from 30 km/hr to 90 km/hr which was an expected result.

Table 4.16 Emission factors with respect to driving condition for Car 6

Parameter	EF (Emission factor) (g/km)			EF (g/hr)	
	30 km/hr	60 km/hr	90 km/hr	Idle (cold start)	Idle (hot start)
Benzene	0.047±0.008	0.024±0.001	0.015±0.001	1.60±0.38	1.07±0.20
Tolune	0.100±0.025	0.042±0.000	0.025±0.001	5.67±1.62	1.82±0.26
e-benzene	0.013±0.006	0.004±0.000	0.002±0.00	1.04±0.09	0.20±0.09
m-xylene	0.091±0.021	0.058±0.002	0.034±0.001	4.73±0.48	2.59±0.30
o-xylene	0.026±0.003	0.017±0.000	0.011±0.001	1.26±0.28	0.83±0.19
Pseudocumene	0.029±0.006	0.019±0.000	0.011±0.001	1.56±0.19	0.70±0.09

4.2.6.6 Calculation of overall emission factor

Emission factor calculations which are given in Appendix B were performed for two groups of cars: cars without catalytic converter and cars with catalytic converter.

Overall emission factors for cars without catalytic converter

The results obtained from three cars (Cars 1, 2 and 3) were used to calculate the overall emission factors (EF) for cars without catalytic converter. These cars had approximately the same cylinder volume and they were compatible with each other.

Emission factors for each road condition as urban, rural and highway driving represented by 30 km/hr, 60 km/hr and 90 km/hr, respectively, were calculated by taking the average of the emission factors of 3 cars at the specified speed. The results are given in Table 4.17.

Table 4.17 Overall emission factors of cars without catalytic converter

Parameter	30km/hr	60 km/hr	90 km/hr	Idle cold start	Idle hot start
	EF g/km			EF g/hr	
Benzene	0.08±0.04	0.03±0.01	0.02±0.01	1.34±0.95	0.69±0.66
Toluene	0.20±0.09	0.09±0.05	0.07±0.03	2.88±2.10	2.86±0.50
e-benzene	0.03±0.01	0.01±0.01	0.01±0.01	0.65±0.51	0.40±0.29
m-xylene	0.22±0.09	0.13±0.07	0.09±0.04	4.34±3.44	3.09±0.92
o-xylene	0.08±0.03	0.04±0.03	0.02±0.00	1.10±1.50	0.53±0.85
Pseud.	0.07±0.03	0.04±0.02	0.03±0.02	1.49±1.06	1.01±0.52

EF: Emission factor
Pseud: Pseudocumene

From Table 4.17 it can be easily seen that emission factors generally decrease as the speed increases from 30 km/hr to 90 km/hr. For each driving condition emission factors for toluene and m-xylene have been found to be higher than the other VOC compounds investigated, which was an expected result due to the composition of the fuel used.

At idle-hot start condition emission factors were found to be less than idle-cold start condition. This result was also expected because at cold start condition car's engine has not reached yet its normal working temperature.

Overall emission factors for cars with catalytic converter

The experimental results obtained with Cars 4, 5 and 6 were used to calculate the emission factors for cars having catalytic converter. These cars had approximately the same cylinder volume and they were compatible with each other.

The results for the speeds of 30, 60, 90 km/hr and for cold and hot start conditions are given in Table 4.18.

Table 4.18 Overall emission factors of cars with catalytic converter

Parameter	**30km/hr**	**60 km/hr**	**90 km/hr**	**Idle cold start**	**Idle hot start**
	EF g/km			**EF g/km**	
Benzene	0.032±0.018	0.012±0.010	0.009±0.007	1.28±0.61	1.01±0.08
Toluene	0.055±0.051	0.015±0.021	0.010±0.012	4.29±2.66	1.25±0.74
e-benzene	0.008±0.007	0.002±0.002	0.001±0.001	0.86±0.61	0.25±0.15
m-xylene	0.049±0.047	0.020±0.030	0.013±0.017	3.57±2.24	1.50±1.32
o-xylene	0.014±0.014	0.006±0.009	0.004±0.005	1.04±0.62	0.67±0.14
Pseud.	0.016±0.015	0.006±0.009	0.004±0.005	1.09±0.68	0.46±0.25

EF: Emission factor
Pseud: Pseudocumene

From Table 4.18, it can be easily seen that emission factors at lower speeds, e.g. 30 km/hr, was higher than the emission factors at higher speeds, e.g. 90 km/hr. For each driving condition emission factors for toluene and m-xylene have been found to be higher than the other VOCs, as expected. At idle-hot start condition emission factors also were found to be less than the idle-cold start condition. This result was also expected as in the previous case.

Results of the statistical analysis which are given in Table 4.17 and 4.18 show that emission factors found in this study for both cars without catalytic converter and with catalytic converter have large standard deviations from its average values. In order to decrease the standard deviations more data is needed. Therefore, emission factors obtained in this study can only be used to have an idea about the exhaust gas emission factors in Turkey. However, use of these emission factors in exhaust gas emission calculations will not give very accurate results.

Overall emission factors for both groups of cars, i.e. cars with and without catalytic converter, are given in Figure 4.18.

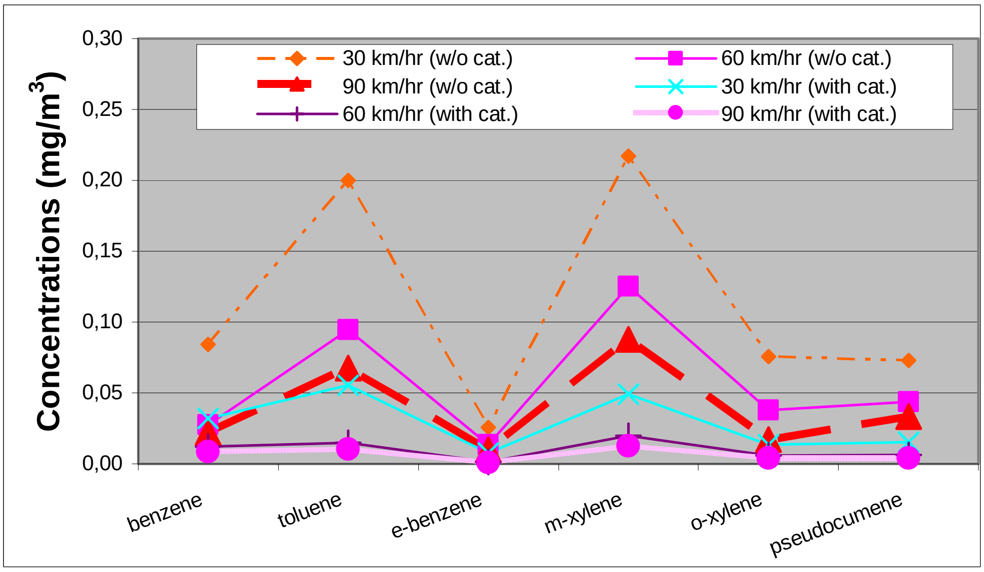

Figure 4.18 Overall emission factors of VOCs

It can be seen from Figure 4.18 that generally emission factors from 30 km/hr to 90 km/hr have decreased, and emission factors for cars having catalytic converter are less than that of cars without catalytic converter. Also emission factors for toluene and m-xylene for all cars are higher than the other VOC components measured.

It can be seen from Tables 4.17 and 4.18 that emission factors of cars without catalytic converter were up to 10 times higher than the emission factors of cars with catalytic converter.

4.2.6.7 Total HC Analysis

Total HCs were analyzed in the exhaust gases of Car 5 and Car 6 at idle-hot and idle-cold start conditions. Results of the measurements are given in Table 4.19.

Table 4.19 Total HC concentrations of idle-hot start and cold start emissions

Car Type	**HC Concentration (ppmv)**	
	Idle (cold start)	**Idle (hot start)**
Car 5 (Marea)	463.99±58.35	426.02±73.18
Car 6 (Palio)	1598.89±72.65	1406.72±205.5

It can be seen from Table 4.19 that HC concentrations at idle-cold start condition was more than that of idle-hot start condition. HC emissions of Car 5 (Marea) were less than that of Car 6 (Palio). This was an expected result because Marea has a better technology than Palio, and it was used less than the other one.

4.3. Comparison of the Results with Literature

As we compare the results of the analysis of ANÇEVA data for total HC concentration with the results of the study given in Table 4.19, it is seen that total HC concentrations of Marea and Palio cars were higher than the results obtained in the ANÇEVA study. Results of HC concentrations of this study and that of Üner et al. (2000a) which are given in Table 4.20 were close to each other, although Üner et al. (2000a) studied one month's data and we have studied one year's data. The results of the study are a little higher than Üner's results.

Table 4.20 Average HC concentrations (Üner et al. (2000a) and this study)

Type of cars	Average HC (ppmv)	Average HC (ppmv) (ÜNER et al., 2000a)
TOFAS	298.75±192.64	235.44±80.51
RENAULT	237.66±142.52	221.46±61.51

Emission factors of UK-NAEI (National Atmospheric Emission Inventory) - 2000 and this study for light gasoline vehicles are given in Table 4.21.

Table 4.21 Emission factors for benzene (UK-NAEI, 2000 and this study) (http://www.naei.org.uk/emissions/, 2004)

Driving condition	UK-NAEI (2000)	Cars w/o catalytic converter	Cars with catalytic converter
	Benzene emission factors (g/km)		
Urban driving	0.01	0.08	0.032
Rural driving	0.00696	0.03	0.012
Highway driving	0.00727	0.02	0.009

As we compare the emission factors of cars in this study with the literature values, emission factors of benzene are 0.01 g/km for urban driving, 0.00696 g/km for rural driving- 0.00727 g/km for highway driving for UK. These values in this study were calculated as 0.08, 0.03, 0.02 for cars without catalytic converter and 0.032, 0.012 and 0.009 g/km for cars with catalytic converter, respectively. Emission factors of this study for cars without catalytic converter are about 3 to 8 times, and emission factors of cars without catalytic converter are about 1 to 3 times higher than the UK-NAEI emission factors. These differences are thought to be mainly due to the high aromatic content of gasoline used and the vehicle technology, available in Turkey.

Emission factors of EPA (Corinair) given in Table 2.3 shows decrease in emission factors as the speed increases. The same trend was also obtained in this study.

As we compare the emission factors at idle condition, it can be easily seen that emission factors found in this study were more than the USA road data of 2000 emission factors. According to this data, VOC emission factor for light-duty gasoline-fueled vehicles (gasoline fueled passenger cars) is 0.352 g/hr in winter and 0.269 g/hr in summer conditions. The values in this study are 1.34 g/hr for idle-cold start and 0.69 g/hr for idle-hot start condition for benzene which are three times higher than emission factors of the USA road data. It can easily be said that this result mainly comes from the high aromatic content of gasoline used in Turkey. These values are 1.27 g/hr and 1.01 g/hr for cars with catalytic converter.

As we compare our emission factors with respect to the Table 2.9 which was given before in Chapter 2, it can be seen that emission factors of both studies were similar for benzene and toluene emissions.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The largest VOC emission occurs for toluene and m-xylene for both car groups (cars with catalytic converter and without catalytic converter). The emissions of benzene, e-benzene, o-xylene, pseudocumene are almost at the same order of magnitude. BTEX components of both types of gasoline are not different from each other. However, concentration and emission factor values of cars without catalytic converter were higher than the concentration and emission factor values for the cars with catalytic converter. Vehicle technology affects the exhaust emissions of the cars. Older passenger cars pollute the environment more than the new technology ones up to 8 times more. This result is mainly due to the vehicle technology used and the catalytic converters of the cars.

Emission factors for all types of cars are higher for m-xylene and toluene than the other compounds, and decrease as the driving speed increases from 30 km/hr to 90 km/hr.

Emission factors calculated in this study were higher than the emission factors found in the literature. These differences are mainly due to the high aromatic content of gasoline used in Turkey and the vehicle technology. Today, Ministry of Environment and Forestry is also trying to reduce emissions coming from these sources by reducing aromatic content in gasoline and encouraging the usage of new technology for car manufacturing.

5.2. Recommendations

In Turkey, exhaust HC emissions are evaluated in ppm by volume. However, it is better to analyze HC's in g/km unit to compare them with the European Union emission factors. To manage these, emission measurements should be performed with chassis dynamometer according to driving cycle which suits our road conditions. This study can be performed together with Ministry of Environment and Forestry, automotive industry and universities.

Results of the study showed that exhaust emissions of car is very high at 30 km/hr velocity which is used mainly in cities. And also, exhaust emissions are more during stop and go traffic. Synchronization of traffic lights and underpass and overpasses can decrease the stop–go traffic and also the exhaust emissions.

In this study, totally 6 passenger cars were evaluated. In order to have more accurate results, more vehicles should be examined for their exhaust gas analysis.

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APPENDIX A

CALIBRATION STANDARDS AND CALIBRATION CURVES OF GC

Properties of calibration standards and calibration results are given below.

Table A.1 Properties of calibration standards

Standard	Company and Catalog No.	Assay (%)	M.W. (g/mole)	B.P (°C)	Density (kg/l)	Retention time (min)
Benzene (C_6H_6)	Fluka 12540	99.9	78.12	80-81	0.879	7:08
Toluene (C_7H_8)	Fluka 89680	99.9	92.14	110-112	0.867	10:11
Ethyl benzene (C_8H_{10})	Fluka 03079	99.5	106.17	135-137	0.87	12:22
m-xylene (C_8H_{10})	Fluka 95670	99.5	106.17	138-139	0.864	12:33
o-xylene (C_8H_{10})	Fluka 95660	99.5	106.17	143-145	0.879	13:03
Pseudocumene (C_9H_{12})	Fluka 82540	99.5	120.2	168-169	0.876	14:58

Two mixtures were prepared for calibration calculations. For each mixture a 2 mL vial was used. In the first mixture 0.1 mL of each of benzene, toluene and ethyl benzene were added into 1 mL of CS_2. In the second mixture the same procedure was repeated by using m-xylene, o-xylene and pseudocumene again in a 2 mL vial. Then, 1 μL of the first calibration mixture was injected into GC and injections were repeated for 2-3 times. The same procedure for GC analysis was repeated for the second calibration mixture. From the chromatogram the concentrations of each component were calculated.

Benzene (C_6H_6)

Table A.2 Gas chromatography peak areas obtained for given concentrations of benzene

Conc. (mg/l)	Area (mVsec)
38.95	64402.74
19.48	30712.88
9.74	13030.93
7.79	11339.32
6.49	8645.42
3.90	5109.77

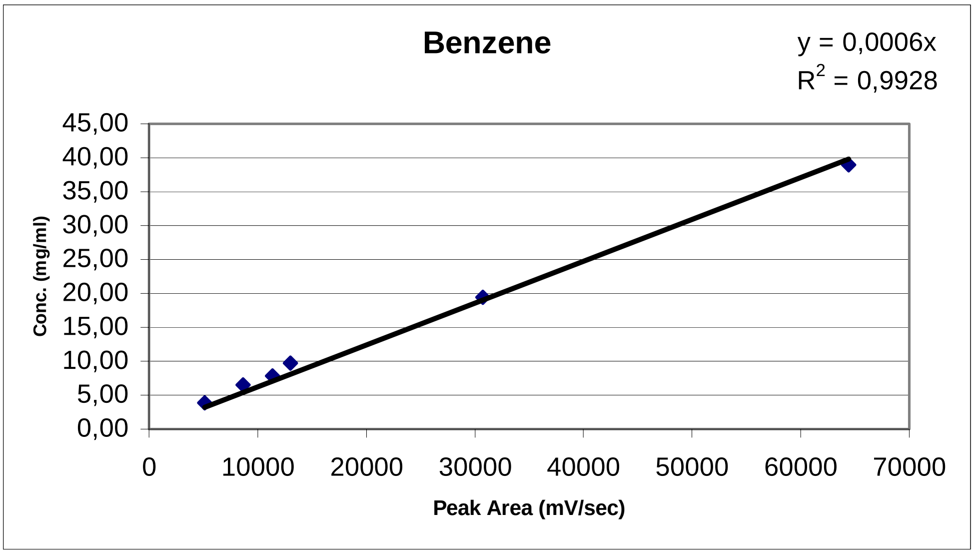

Figure A.1 Calibration Curve for benzene

Toluene (C_7H_8)

Table A.3 Gas chromatography peak areas obtained for given concentrations of toluene

Conc. (mg/l)	Area (mVsec)
7.76	25037.19
6.47	20599.13
3.88	11861.54

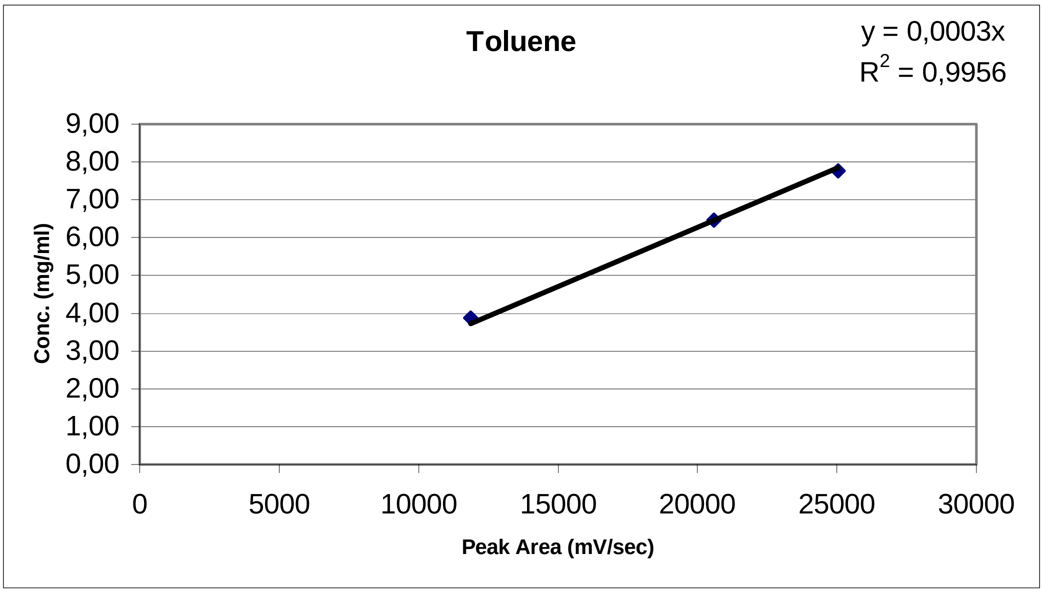

Figure A.2 Calibration Curve for Toluene

Ethyl benzene (C_8H_{10})

Table A.4 Gas chromatography peak areas obtained for given concentrations of ethyl benzene

Conc. (mg/l)	Area (mVsec)
7.70	30548.00
6.48	27311.60
3.89	16104.24

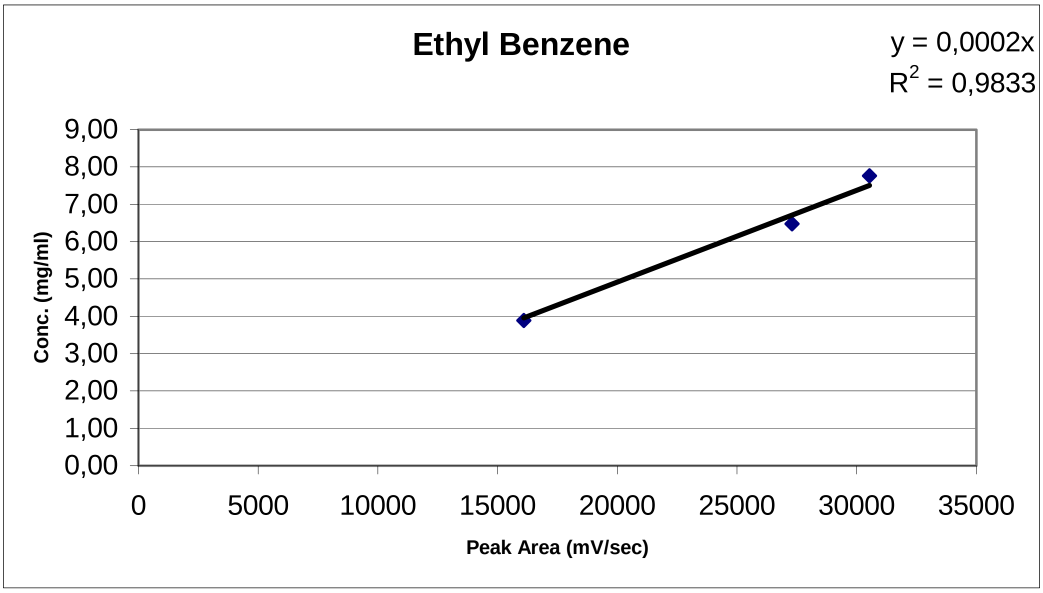

Figure A.3 Calibration Curve for Ethyl benzene *m-xylene (C_8H_{10})*

Table A.5 Gas chromatography peak areas obtained for given concentrations of m-xylene

Conc. (mg/l)	Area (mVsec)
53.30	93492.43
26.44	40736.58
13.33	19982.86
5.33	10618.41
1.78	3690.858

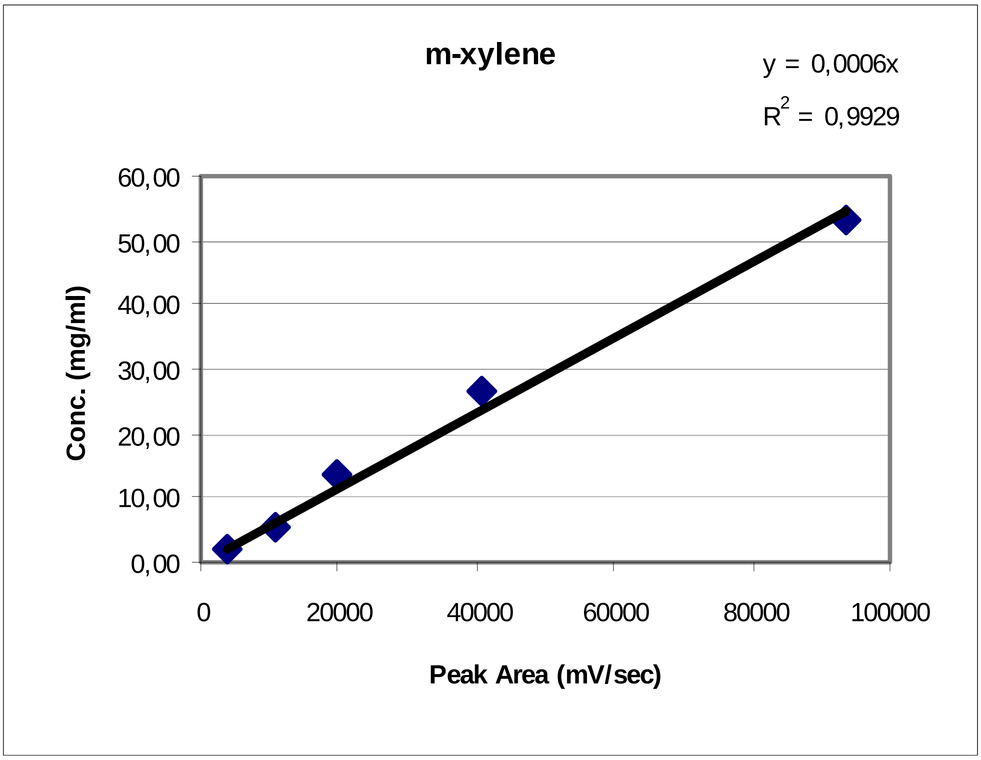

Figure A.4 Calibration Curve for m-xylene

o-xylene (C_8H_{10})

Table A.6 Gas chromatography peak areas obtained for given concentrations of o-xylene

Conc. (mg/l)	Area (mVsec)
49.60	87152.07
24.60	38865.31
12.40	20367.64
4.96	10280.38
1.65	3220.325

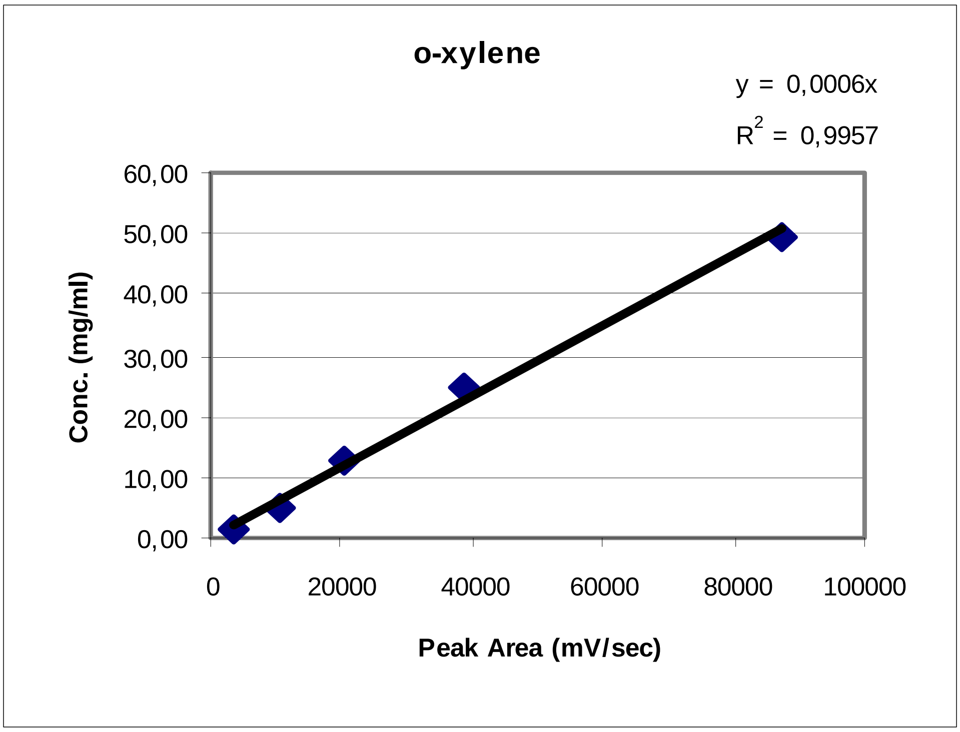

Figure A.5 Calibration Curve for o-xylene

Pseudocumene (C_9H_{12})

Table A.7 Gas chromatography peak areas obtained for given concentrations of pseudocumene

Conc. (mg/l)	Area (mVsec)
54.30	98191.12
26.93	42201.45
13.58	21625.91
5.43	12740.73
1.81	4119.07

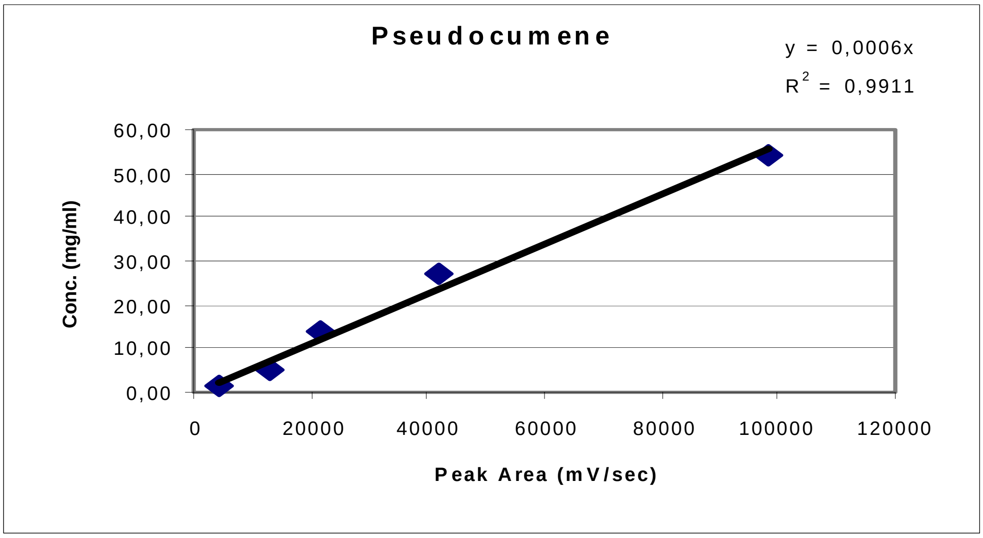

Figure A.6 Calibration Curve for pseudocumene

APPENDIX B

SAMPLE CALCULATIONS

To be more illustrative, the emission factors are calculated as follows. Other emission factors are calculated in the same way as shown above.

Sample emission factor and moisture calculation:

Table B.1. Sampling conditions of car 1

Number of sample	Velocity (km/s)	Time (min.)	Temperature (^oC)	Pressure (^{o}hPa)	Volume of sampling (L)
1	30	5	31	911	5.5
4	Idle (hot start)	5	26.1	904	5.7

Table B.2 Weight results during extraction part of the study

No	Vial (g)	Vial + AC (g)	Vial+AC + CS_2 (g)	CS_2 used in the AC*	No	Vial (g)	Vial + AC (g)	Vial+AC + CS_2 (g)	CS_2 used in the AC*
1a	3.3015	3.4301	4.3830	0.7563	1b	2.5568	2.6144	3.5541	0.7458
4a	2.4881	2.6056	3.5178	0.7240	4b	2.9164	2.9670	3.8907	0.7331

AC= Active carbon

Balance results are given at Table B.2 for both part (1a) and part (1b) of active carbon which is given at Figure 3.3.

Calculation of volume CS_2 used in extraction is given below.

- Volume CS_2 = (Weight of Vial (g) + Weight of active carbon (g) + Weight of CS_2 (g) – (Weight of Vial (g) + Weight of active carbon (g)) / Density of CS_2 (kg/L)

Volume CS_2 = (4.3830- 3.4301) gr/ 1.26 kg/L = 0.7563 mL

Table B.3 Average area values obtained by gas chromatography analysis

Parameter	**30 km/ hour**	**Idle (cold start)**
	Area (mVsec)	
Benzene	789	992

Concentration and emission factor are given below respectively at Table B.4.

Table B.4 Average Concentration of VOCs obtained by gas chromatography analysis

Driving Condition	**Benzene**
	Concentration (mg/ Nm^3)
30 km/hour	80.55
Idle (hot start)	92.84

Results given at Table B.4 are for part (a) of the active carbon. There was no VOC observed from the analysis of the part (b) (backup section). This result shows that capacity of the part (a) is enough for adsorption of exhaust gases.

Calculations of benzene concentration in exhaust gases:

<u>30 km/ hour:</u>

From the calibration curve of the benzene
mg/ml benzene = 0.0006 x Area (mVsec)

Benzene concentration in CS_2 = 0.0006 x Area (mVsec)
= 0.0006 x 789
= 0.473 mg/ ml

Benzene concentration in CS_2 = Concentration of benzene (mg/ml)
x Volume of CS_2 (ml)
= 0.473 mg/ml x 0.7563 ml = 0.358 mg

P_N= 1 atm= 1013 hPa (at Normal Condition)
T_N= Temperature = 273 ^oK (at Normal Condition)

Pressure during sampling = P_s= 911 hPa.
Temperature during sampling = T_s = 31 ^oC = $(273+31)^oK$ = 304 ^oK
Volume of sample = V_s=5.5 L

Volume of sample at normal conditions = V_N

$$PV = nRT \rightarrow \frac{PsVs}{Ts} = \frac{P_N V_N}{T_N}$$

$V_N = (T_N/ P_N) \times (P_s \times V_s / T_s) = (273/ 1013) \times (911 \times 5.5 / (304))$
$V_N = 4.44$ NL $= 4.44 \times 10^{-3}$ N m^3

Concentration of benzene in exhaust gasses without considering recovery:

= Weight of benzene in the sample (mg) / Volume of sample

= 0.358 mg benzene / 4.44 x 10^{-3} N m^3

= 80.5 mg/Nm^3 benzene

Recovery factor for benzene = 0.85

Concentrations of benzene in exhaust gases by considering recovery factor:

= 80.5 mg/Nm^3 benzene x 0.85

= 70.08 mg/Nm^3 benzene

Emission factor calculation:

D_e= Diameter of the exhaust pipe = 4 cm

v_e= Velocity of the exhaust gas (m/s) = 7 m/sec

V_e = Volumetric flow rate of the exhaust gas

C_s= VOC concentration of exhaust gas

C_s= 70.08 mg/Nm^3

V = v x A (L/min)

$V_e = 7\ m/s \times (\prod) \times (4 \times 10^{-2}\ m)^2 / 4)$

$V_e = 8.8 \times 10^{-3}\ m^3/sec$

$V_e = (273/ 1013) \times (911 \times 8.8 \times 10^{-3}\ m^3/s / (304))\ Nm^3/sec$

$V_e = 0.007\ Nm^3/ sec$

Q = V x C

Q_e= 0.007 Nm^3/ sec x 70.08 mg/Nm^3 = 0.49 mg/ sec

EF = Emission factor

EF = Q_e x (measurement period / distance traveled)
EF = Q_e / velocity of the measurement
EF = (0.49 mg/sec x (60 x 60 sec/ 1 h))/ 30 km/h
EF = 58.86 mg/ km = 0.06 g/km

Idle-hot start condition:

Calculations of concentration of benzene were same as calculations of 30 km/hr. Emission factor calculation for hot start emission is given below.

Emission factor calculation:

D_e= Diameter of the exhaust = 4 cm
v_e= Velocity of the exhaust gas (m/s) = 5 m/sec
V_e = Volumetric flow rate of the exhaust gas

C_s= VOC concentration of exhaust gas
C_s= 80.7 mg/Nm^3

V = v x A (L/min)

V_e = 5 m/s x (∏) x (4 x 10^{-2} m)^2 / 4)
V_e = 6.3 x 10^{-3} m^3/sec

Pressure during sampling = P_s= 904 hPa.

Temperature during sampling = T_s = 26.1 ^oC = $(273+26.1)^oK$ = 299.1 ^oK

V_e = (273/ 1013) x (904 x 6.3 x 10^{-3} m^3/s / (299.1)) Nm^3/sec

V_e = 0.005 Nm^3/ sec

Q = V x C

Q_e= 0.005 Nm^3/ sec x 80.7 mg/Nm^3 = 0.40 mg/ sec

EF = 0.40 mg/sec x (1 g/1000mg) x (60x60 sec/ 1 hr)

EF = 1.4 g/km

APPENDIX C

VEHICLE INFORMATION

Samples were collected from the Murat Kartal SLX (1993), Fiat Tipo (1993), Murat Dogan SLX (1996), Murat Kartal (2000), Fiat Marea (2005) and Fiat Palio (2000) model passenger cars. Detailed information of the vehicles are given below.

<u>Passenger cars without catalytic converter:</u>

<u>Murat Kartal SLX (Car 1)</u>

Model : 1993 with carburetor
Gasoline type : Super
Cylinder capacity : 1581 cm^3
Distance traveled : 78000 km
Exhaust pipe diameter : 4 cm

At idle condition:
Velocity of exhaust gasses = 5 m/s
Relative Humidity of exhaust gasses = 90 %
Temperature of exhaust gasses = 30 ^{0}C

At 2500 rpm:
Velocity of exhaust gasses = 7 m/s
Relative Humidity (RH) of exhaust gasses = 99 %
Temperature of exhaust gasses = 54 ^{0}C

Note: RH = Relative Humidity

Fiat Tipo (Car 2)

Model : 1993 with carburetor
Gasoline type : Super
Cylinder capacity : 1372 cm^3
Distance traveled : 71342 km
Exhaust pipe diameter : 4 cm

At idle condition:
Velocity of exhaust gasses = 6 m/s
RH of exhaust gasses = 96 %
Temperature of exhaust gasses = 35 ^{0}C

At 2500 rpm:
Velocity of exhaust gasses = 7 m/s
RHof exhaust gasses = 99.9 %
Temperature of exhaust gasses = 37 ^{0}C

Murat Dogan SLX (Car 3)

Model : 1996 with carburetor
Gasoline type : Super
Cylinder capacity : 1372 cm^3
Distance traveled : 71341 km
Exhaust pipe diameter : 4 cm

At idle condition:
Velocity of exhaust gasses = 5 m/s
RH of exhaust gasses = 90 %
Temperature of exhaust gasses = 26.5 ^{0}C

At 2500 rpm:
Velocity of exhaust gasses = 6.2 m/s
RH of exhaust gasses = 98.3 %
Temperature of exhaust gasses = 54 ^{0}C

Passenger cars with catalytic converter:

Kartal 1.6 IE (Car 4)
Model : 2000 with injection
Gasoline type : Unleaded
Cylinder capacity : 1581 cm^{3}
Distance traveled : 43411 km
Exhaust pipe diameter : 4 cm

At idle condition:
Velocity of exhaust gasses = 4.5 m/s
RH of exhaust gasses = 99 %
Temperature of exhaust gasses = 40 ^{0}C

At 2500 rpm:
Velocity of exhaust gasses = 8.4 m/s
RH of exhaust gasses = 99.5 %
Temperature of exhaust gasses = 49.5 ^{0}C

Fiat Marea 1.6 (Car 5)

Model : 2005 with injection
Gasoline type : Unleaded
Cylinder capacity : 1596 cm^3
Distance traveled : 1434 km
Exhaust pipe diameter : 4 cm

At idle condition:

Velocity of exhaust gasses = 4.3 m/s
RH of exhaust gasses = 70 %
Temperature of exhaust gasses = 31.5 ^{0}C

At 2500 rpm:

Velocity of exhaust gasses = 5.5 m/s
RH of exhaust gasses = 98.2 %
Temperature of exhaust gasses = 37.3 ^{0}C

Fiat Palio EL (Car 6)

Model : 2000 with injection
Gasoline type : Unleaded
Cylinder capacity : 1372 cm^3
Distance traveled : 229269 km
Exhaust pipe diameter : 4 cm

At idle condition:

Velocity of exhaust gasses = 4.3 m/s
RH of exhaust gasses = 70 %
Temperature of exhaust gasses = 31.5 ^{0}C

At 2500 rpm:

Velocity of exhaust gasses = 5.5 m/s

RH of exhaust gasses = 98.2 %

Temperature of exhaust gasses = 37.3 ^{0}C

APPENDIX D

VOC CONCENTRATIONS

VOC concentrations of exhaust gases at 30 km/hr, 60 km/hr and 90 km/hr are given in Tables D.1 to D.6.

Table D.1 Exhaust gases concentration of VOCs for Car 1

Drv. con.	Benzene	Toluene	e-benzene	m-xylene	o-xylene	pseud
	Concentration (mg/ Nm^3)					
30 km/hr	70.08±12.84	178.00±59.39	32.86±17.16	156.38±61.68	41.59±11.89	66.53±26.12
60 km/hr	122.80±26.30	223.81±4.82	24.18±8.00	348.98±57.29	108.44±29.39	126.42±19.50
90 km/hr	105.08±10.55	251.58±62.52	46.28±15.00	260.56±70.31	79.04±21.90	102.12±19.72

Drv. con.: Driving condition
cs: cold start
hs: hot start
pseud: pseudocumene

Table D.2 Exhaust gases concentration of VOCs for Car 2

Drv. con.	Benzene	Toluene	e-benzene	m-xylene	o-xylene	pseud
	Concentration (mg/ Nm^3)					
30 km/hr	138.81±22.22	370.69±50.98	49.48±6.49	358.69±34.54	129.33±25.59	118.09±5.45
60 km/hr	58.26±15.56	318.46±97.34	49.58±15.03	392.00±146.63	131.86±37.54	137.50±49.90
90 km/hr	83.04±31.23	306.71±47.44	45.97±6.25	356.64±55.90	59.17±8.28	142.41±25.55

Drv. con.: Driving condition
cs: cold start
hs: hot start
pseud: pseudocumene

Table D.3 Exhaust gases concentration of VOCs for Car 3

Drv. con.	Benzene	Toluene	e-benzene	m-xylene	o-xylene	pseud
	Concentration (mg/ Nm^3)					
30 km/hr	63.85±0.57	118.57±24.43	12.54±4.18	178.37±52.39	61.86±20.49	56.59±11.34
60 km/hr	53.22±4.79	99.30±14.28	10.33±2.20	149.98±24.72	22.60±24.96	48.99±8.61
90 km/hr	66.40±5.26	118.34±1.42	13.33±1.02	179.58±11.60	55.41±7.64	57.84±4.17

Drv. con.: Driving condition
cs: cold start
hs: hot start
pseud: pseudocumene

Table D.4 Exhaust gases concentration of VOCs for Car 4

Drv. con.	Benzene	Toluene	e-benzene	m-xylene	o-xylene	pseud
	Concentration (mg/ Nm^3)					
30 km/hr	5.15±3.80	1.90±0.26	0.15±0.06	3.26±0.10	1.07±0.08	1.05±0.27
60 km/hr	4.82±4.05	2.43±0.85	0.18±0.02	3.69±0.97	1.20±0.31	1.07±0.13
90 km/hr	6.86±9.32	4.41±5.85	0.56±0.75	3.01±3.54	1.01±1.19	1.48±1.83

Drv. con.: Driving condition
cs: cold start
hs: hot start
pseud: pseudocumene

Table 4.5 Exhaust gases concentration of VOCs for Car 5

Drv. Con.	Benzene	Toluene	e-benzene	m-xylene	o-xylene	pseud
	Concentration (mg/ Nm^3)					
30 km/hr	31.79±2.78	4.42±3.53	1.24±1.05	0.73±0.30	0.00±0.00	0.00±0.00
60 km/hr	33.29±6.21	2.84±1.27	0.14±0.01	1.62±0.09	0.70±0.35	0.48±0.13
90 km/hr	17.87±4.70	3.37±0.61	0.19±0.12	2.48±0.41	0.94±0.16	0.57±0.08

Drv. con.: Driving condition, cs: cold start, hs: hot start, pseud: pseudocumene

Table D.6 Exhaust gases concentration of VOC's for Car 6

Drv. con.	**Benzene**	**Toluene**	**e-benzene**	**m-xylene**	**o-xylene**	**pseud**
	Concentration (mg/ Nm^3)					
30 km/hr	70.68±11.81	149.84±38.24	19.16±9.69	135.27±31.33	38.94±5.02	43.37±8.72
60 km/hr	72.63±2.33	125.97±0.58	13.33±0.75	173.36±4.96	51.08±0.13	55.52±0.32
90 km/hr	65.30±3.60	112.49±6.66	10.90±0.39	151.85±4.08	47.10±5.71	47.03±5.59

Drv. con.: Driving condition
cs: cold start
hs: hot start
pseud: pseudocumene

APPENDIX E

RECOVERY CALCULATIONS

The recovery calculations were done in order to see if any loss happens during the extraction of samples from the active carbon before GC analysis. The recovery experiments were done according to the following procedure.

- Calibration mixtures as explained in Appendix A were prepared.
- The tips of an Orbo – 32 tube were broken.
- 0.1 mL of the first calibration mixture was taken from the vial with a syringe and injected carefully into an Orbo – 32 tube from the top and the tips were capped immediately.
- Again the same procedure was repeated with the second calibration mixture on another Orbo – 32 tube.
- Then, the Orbo tubes were left at room temperature for some time (at least 1 day) in order to make chemicals evaporate in the tube and be adsorbed by activated carbon particles.
- After the adsorption period was completed, the activated carbons in the Orbo tubes were extracted by using the same extraction procedure given in Section 3.2.3.
- GC analyses of the extracted samples were carried out and each sample was injected into GC twice.
- The concentration of each component in the "calibration mixture" was calculated and they are given in Table E.1.
- The concentrations of each component found by "GC analysis" were calculated and these concentrations were the concentration of each component in the extract. These values are given in Table E.1.

- Therefore by comparing the results obtained for each component a recovery factor for the chemicals included in the calibration mixture were calculated. The average of two analysis results was taken as the recovery factor for the constituent. These results are given in table E.2.
- The GC analysis results of each extract obtained during the experiments were corrected by using the average "recovery factor" for each component. (Görmez, 2004)

Table E.1 Concentrations of constituents in the calibration mixture (CM) and extract (Görmez, 2004)

Constituent	**Concentration in CM (mg/mL)**	**Concentration in E1* (mg/mL)**	**Concentration in E2* (mg/mL)**
Benzene	146.3	122.4	132.8
Toluene	147.3	110.3	96.1
Ethyl Benzene	145.7	105.4	98.6
m-xylene	157.5	114.5	121.6
o-xylene	159.3	121.4	133.2
pseudocumene	108.0	84.7	88.1

*E1 = Results of first injection of extract into GC
E2 = Results of second injection of extract into GC

Table E.2 Recovery factors for constituents (Görmez, 2004)

Constituent	**1st Analysis (%)**	**2nd Analysis (%)**	**Recovery Factor (%)**
Benzene	87.15	83.66	85.40
Toluene	74.88	65.24	70.06
Ethyl Benzene	72.34	67.67	70.00
m-xylene	72.70	77.21	74.95
o-xylene	76.21	83.62	79.91
pseudocumene	78.43	81.57	80.00

APPENDIX F

SAMPLE CHROMATOGRAM

Sample chromatogram which was obtained for Car 3 at driving speed of 90 km/hr is given in Figure E.1.

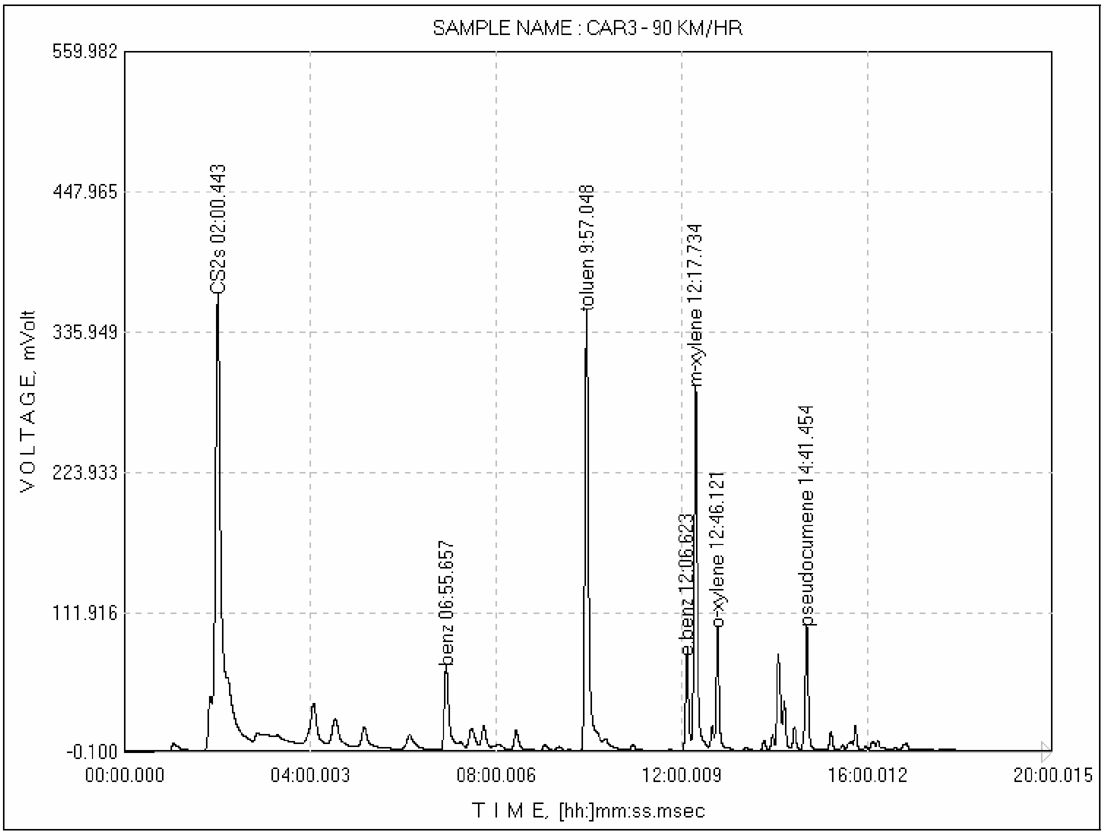

Figure E.1 Sample chromatogram for Car 3