Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. pp. 858-867, 26-30 September 2005, Istanbul – Turkey

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

Irem Onoğlu and Aysel T. Atimtay

Middle East Technical University, Department of Environmental Engineering, 06531 Ankara, Turkey, irem7@yahoo.com, aatimtay@metu.edu.tr

ABSTRACT

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 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.

Key Words: Emission Factors, BTEX Emissions, CO/HC Emissions, Turkish Fleet of Passenger Cars.

1. 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).

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).

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).

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. 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 (SEPA, 2004).

1.2. Objective of the Study

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. 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.

Also, there are no emission factors available for cars. Corinair or U.S. EPA drived emission factors are used for estimating traffic-caused emissions. However, these factors do not fit correctly to Turkish car fleet. Therefore, 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.

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.

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. Calculate the emission factors for the BTEX compounds.

3.1. Experimental

In order to determine the composition of exhaust gasses, samples were collected from the tail pipe and benzene, toluene, xylene, ethylbenzene, m-xylene, o-xylene and 1,2,4 trimethylbenzene (pseudocumene) compounds 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 included 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 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 1 and the flow diagram of the exhaust gas collection system is shown in Figure 2. The gas samples from the tail pipe were collected while the car was going at certain speed limits.

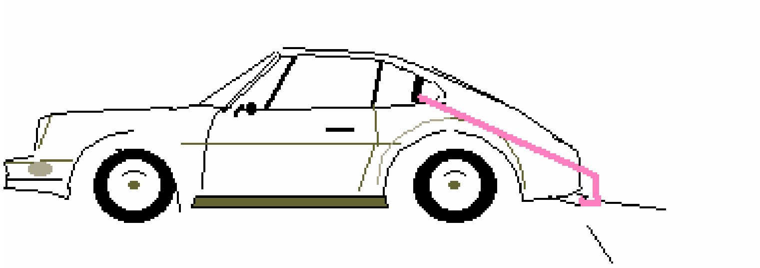

Figure 1. The experimental set up for exhaust gas collection

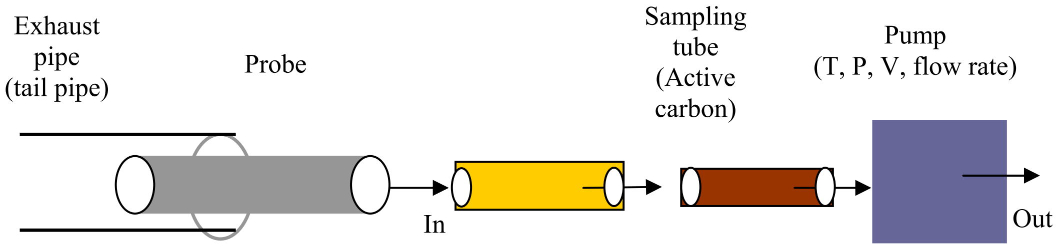

Figure 2. The flow diagram of the exhaust gas collection system

The sampling probe was 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 ends of the drier tube are plugged with quartz wool. An Orbo-32 tube containing active carbon particles is placed after the drier tube in the sampling system. 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 driving and sampling. All other parts of the experimental set up are outside the car attached to the back bumper. The pump works with 12 V and the power supply of the pump is connected to the battery of the car. Active sampling method was used for gas sampling. VOCs adsorbed on the active carbon particles in the Orbo-32 tube were extracted by liquid CS_2 in the laboratory after the sampling is over. The extraction procedure was followed according to EN/ISO DIS 13528-3 and the components of the extract were analyzed by using a GC having a FID.

The statistical distribution of vehicle categories in Turkey according to the results of the first part of this study show that the cars named under ‘‘Murat (Tofas) and Fiat’’ constitute 34.7% and Renault cars constitute 29.7% of total cars. Therefore, Tofas/ Fiat cars were taken for our further studies, because these are widely used cars in Turkey.

In this study passenger cars were divided into mainly two basic categories: 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. Cars with a catalytic converter are about 4-5-year old cars. The cars chosen for this study without catalytic converter are: Murat-Kartal SLX (1993), Fiat-Tipo (1993), Murat-Dogan SLX (1996); and with catalytic converter are: Murat Kartal (2001), Fiat Marea (2005), Fiat Palio (2000).

Each group of vehicles was examined for three different conditions: cold start (at idle condition), driving condition, and 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.

4. RESULTS AND DISCUSSIONS

The samples collected on active charcoal particles in Orbo-32 tubes were analyzed for BTEX compounds. Overall, average exhaust gas VOC concentrations of cars investigated without catalytic converter for three speeds are shown in Figure 3 and with catalytic converter in Figure 4, respectively. As can be seen from these figures, the average exhaust gas VOC concentrations for cars without cat/converter were about 4-6 times more than the average exhaust gas VOC concentrations of cars with cat/converter. The highest concentrations belonged to toluene and m-xylene. When toluene and m-xylene concentrations were 230 and 300 mg/m^3 on the average, respectively, for cars without cat/converter, the corresponding concentrations for the same compounds were 50 and 55 mg/m^3, respectively, for cars with cat/converter.

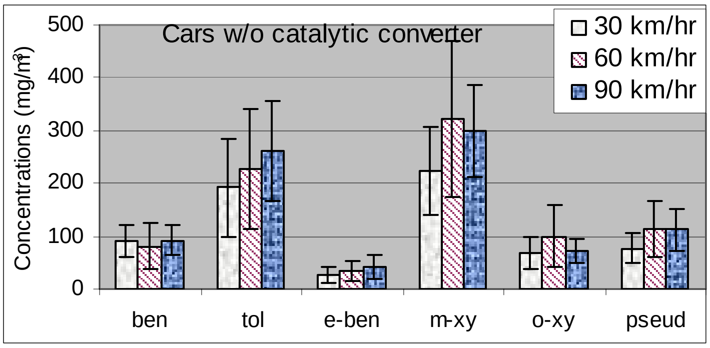

Figure 3. Average exhaust gas VOC concentrations of cars without cat/converter

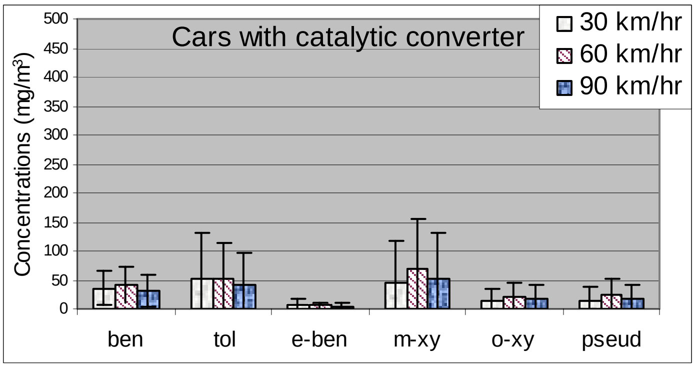

Figure 4. Average exhaust gas VOC concentrations of cars with cat/converter

Average exhaust gas VOC concentrations at idle condition for cars without catalytic converter and with catalytic converter are shown in Figure 5 and 6, respectively. Again the highest concentrations belong to toluene and m-xylene for the idle-cold start and idle-hot start conditions. However, there is not a big difference between the cars with cat/converter and without cat/converter.

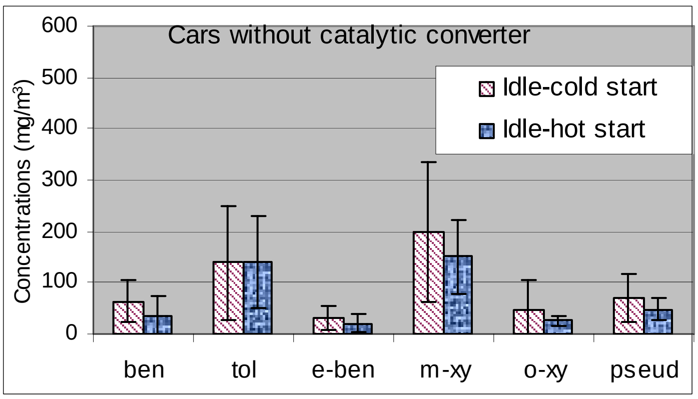

Figure 5. Average exhaust gas VOC concentrations of cars without cat/converter

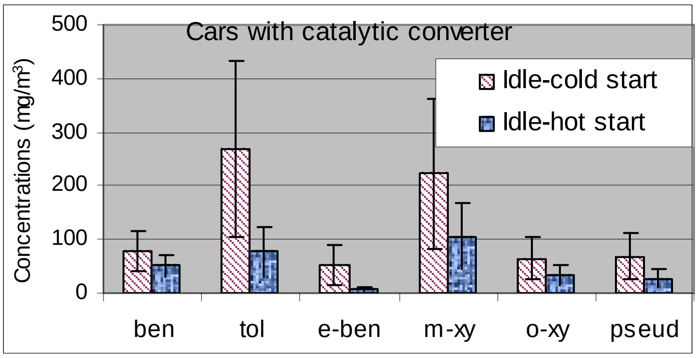

Figure 6. Average exhaust gas VOC concentrations of cars with cat/converter

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.

4.1 Calculation of emission factors

Average emission factors for cars without catalytic converter

The results obtained from the first group of three cars were used to calculate the average emission factors (EF) for cars **without catalytic converter.** These cars had approximately the same cylinder volume and the models 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 1.

Table1. 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

It can be easily seen from Table 1 that emission factors generally decrease as the speed increases from 30 km/hr to 90 km/hr. This is attributed to the better combustion efficiency at higher speeds. 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.

Average emission factors for cars with catalytic converter

The experimental results obtained from the second group of three cars were used to calculate the average emission factors (EF) for cars **with catalytic converter.** These cars had approximately the same cylinder volume and the models 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 2.

Table 2. 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 2, 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 1 and Table 2 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, these emission factors in exhaust gas emission calculations should be used carefully.

It can be seen from Tables 1 and 2 that emission factors of cars without catalytic converter were up to 10 times higher than the emission factors of cars with catalytic converter. It can also be seen 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.

4.2. Total Hydrocarbon (HC) Analysis

Total HCs were analyzed in the exhaust gases of Marea and Palio at idle-hot and idle-cold start conditions. Results of the measurements are given in Table 3.

Table 3. Total HC concentrations of idle-hot start and cold start emissions

Car Type	**Total 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 3 that total 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 Marea was used less than the other one.

4.3. Comparison of the Results with Literature

Total HC concentrations of Marea and Palio cars in this study were higher than the results obtained in Üner's study (2000). Results of HC concentrations of this study and that of (Üner et al., 2000) which are given in Table 4 were close to each other, although (Üner et al., 2000) 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. Average HC concentrations (Üner et al. (2000) and this study)

Type of cars	**Average HC (ppmv) (this study)**	**Average HC (ppmv) (ÜNER et al., 2000)**
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 that of this study for light gasoline vehicles are compared in Table 5.

Table 5. 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 (this study)	Cars with catalytic converter (this study)
	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.

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.

5. CONCLUSIONS AND RECOMMENDATIONS

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.

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. 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.

It is better to analyze HC's in g/km to be comparable with the EU emission factors. Results of this study showed that exhaust emissions of cars are very high at 30 km/hr velocity which is mainly used in crowded streets and busy intersections. Therefore, exhaust emissions are more during stop-and-go traffic. In order to decrease these emissions synchronization of traffic lights, underpass and overpasses are recommended in crowded streets and busy intersections to decrease the stop-and-go traffic, and the exhaust emissions.

REFERENCES

De Nevers, N., 1995. Air Pollution Control Engineering, McGraw-Hill, Inc.

İçingür, İ., 1991. Hava Kirliliği ve Motorlarda Emisyon Kontrolu, Yanma ve Hava Kirliliği Kontrolu I. Ulusal Sempozyum Bildiriler Kitabı, Gazi Üniversitesi, Ankara.

Müezzinoğlu, A., 2004. Hava Kirliliğinin ve Kontrolunun Esasları, Dokuz Eylül Üniversitesi Yayınları, İzmir.

Perkins, H.C., 1974. Air Pollution, McGraw Hill, New York

Stern, A.C., Boubel, R.W., Turner, D.B., Fox, D.L., 1994. Fundamentals of Air Pollution, Third Ed., Academic Press.

Scottish Environment Protection Agency (SEPA), 2004. European Pollutant Emission Register (EPER) Reporting, Substance Information.

United Kingdom (UK) National Atmospheric Emission Inventory, 2004.

http://www.naei.org.uk/emissions/.

Üner, D.Ö., Akay, G., Erişmiş, B, 2000. Egzoz Gazlarından Kaynaklanan Hidrokarbon (HC) Emisyonlarinin Analizi ve Değerlendirilmesi, Hava Kirliliği ve Yanma, VI, Ulusal Sempozyumu, Fırat Üniversitesi.

Wark, K, Warner, C.F., Davis T. W., 1990. Air Pollution Its Origin and Control, Harper Row Publication.