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GRADUATE SCHOOL OF NATURAL AND APPLIED

SCIENCES

DETERMINATION AND MODELING OF EMISSION FACTORS USING A HIGHWAY TUNNEL

by

Nihan KARA

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İZMİR

DETERMINATION AND MODELING OF EMISSION FACTORS USING A HIGHWAY TUNNEL

A Thesis Submitted to the
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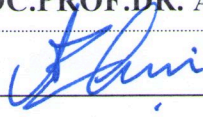**Environmental Engineering**

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M.Sc. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"DETERMINATION AND MODELING OF EMISSION FACTORS USING A HIGHWAY TUNNEL"** completed by **NİHAN KARA** under supervision of **ASSOC.PROF.DR. ALPER ELÇİ** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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DETERMINATION AND MODELING OF EMISSION FACTORS USING A HIGHWAY TUNNEL

ABSTRACT

Carbon monoxide, nitrogen oxides, particulate matter, total suspended solids and sixteen polyaromatic hydrocarbon compounds including naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranhene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3,cd)pyrene, dibenz(a,h)anthracene, benzo(g,h,i)perylene were investigated in the tunnel air of the Karşıyaka tunnels in Izmir, with the aim to calculate emission factors based on tunnel sampling data and estimations by the vehicle emission simulator MOVES. Karşıyaka tunnel air sampling was carried out at two locations in the tunnel and in two seasons (winter and summer) to study seasonal variations of carbon monoxide, nitrogen oxides and sixteen poly aromatic hydrocarbons. As a result of the tunnel measurements, emission factors are calculated as 2263.34 and 1047.1 milligrams per vehicle per kilometer for carbon monoxide and nitrogen oxides, respectively. The highest polyaromatic hydrocarbon emission factor determined for naphthalene was 110.27 micrograms per vehicle per kilometer, if the concentrations of gaseous and particulate phase polyaromatic hydrocarbons are taken as total concentration. Average emission factor of particulate matter smaller than 10 micrometer diameter are calculated as 67.11 milligrams per vehicle per kilometer. Emission factor for total suspended solids was determined as 159.99 milligrams per vehicle per kilometer. Emission factors were also estimated using the vehicle emission model MOVES. The average difference between the results of modeling with the results of the samples was 6 percent.

Keywords: Carbon monoxide, emission factors, motor vehicle emission simulator (MOVES), nitrogen oxides, poly aromatic hydrocarbons.

BİR OTOYOL TÜNELİNİ KULLANARAK EMİSYON FAKTÖRLERİNİN BELİRLENMESİ VE MODELLENMESİ

ÖZ

Karbon monoksit, azot oksitler, partikül maddeler, toplam askıda partikül maddeler ve naftalen, asenaftelen, asenaften, fluoren, fenantren, antrasen, fluoranthene, piren, benz (a) antrasen, chrysene, benzo (b) fluoranhene, benzo (k) fluoranthene, benzo (a) piren, indeno (1,2,3,cd) piren, dibenz (a,h) antrasen, benzo (l,g,h,i) perilen gibi on altı poli aromatik hidrokarbon bileşikleri İzmir Karşıyaka tünelinde incelendi ve emisyon faktörleri örnekleme ölçümleri ve MOVES modeli ile hesaplandı. Karşıyaka tüneli örneklemeleri tünelin girişi ve çıkışı olmak üzere iki örnekleme bölgesinde yapılmıştır ve örneklemeler yaz ve kış aylarında tekrarlanmıştır. Yapılan ölçümler sonucunda karbon monoksit için bir kilometre de araç başına düşen ortalama emisyon faktörü 2263,34 ve azot oksitler için bir kilometre de araç başına düşen ortalama emisyon faktörü 1047,1 miligram olarak hesaplanmıştır. İzmir Büyükşehir Belediyesine ait araçla ölçülen parametreler içerisinde en yüksek emisyon faktörü karbon monoksite aittir. Gaz ve partikül fazdaki poli aromatik hidrokarbon konsantrasyonları toplam olarak göz önüne alındığında, taranan 16 poli aromatik hidrokarbon bileşiği içinde bir kilometre de araç başına düşen en yüksek emisyon faktörü 110,27 mikrogram ile naftalen dir. Aerodinamik çapı 10 mikrometre den küçük partikül maddenin bir kilometre de araç başına düşen ortalama emisyon faktörü ise 67,11 miligramdır. Toplam askıda partikül maddenin bir kilometre de araç başına düşen ortalama emisyon faktörü ise 159,99 miligramdır. Örneklerin sonuçları ile modelleme sonuçları arasındaki fark ortalama yüzde 6'dır.

Anahtar Kelimeler: Azot oksitler, emisyon faktörleri, karbon monoksit, motorlu taşıt emisyon simülatörü (MOVES), poli aromatik hidrokarbonların emisyon faktörleri.

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CHAPTER ONE

INTRODUCTION

Air pollution is a serious environmental problem that needs to be addressed. One of the most important sources of air pollution is traffic. Motor vehicles are a significant source of urban air pollution and are increasingly important contributors of anthropogenic gas emissions. As awareness of the potential health effects of air pollutants has grown, many countries have implemented more stringent emission measures and made continuous progress in reduction of emissions from motor vehicles. However the rapid growth of the motor vehicle fleet due to population growth and economic improvement, the expansion of metropolitan areas and increasing dependence on motor vehicles resulted in the increase of scientific research on traffic emissions and health effects throughout world.

The qualification of motor vehicle emissions is critical in estimating their impact on local air quality and traffic related exposures and requires the collection of travel activity data over space and time and the development of emission inventories. The objective of this study is to determine motor vehicle emissions by monitoring emissions in a tunnel and to derive emission factors. In this thesis study, the Karşıyaka tunnels located in Izmir are used to determine the traffic related pollutant emissions. Tunnels are suitable settings to determine emission factors since they are controlled environments. To achieve the objective of this study, monitoring of polyaromatic hydrocarbons, carbon monoxide and nitrogen oxides and particulate matter are conducted for summer and winter periods. Emission factors of the polyaromatic hydrocarbons, carbon monoxide and nitrogen oxides are calculated from monitoring and sampling data. Emission factors are also derived from the emission model MOVES and the results are compared with sampling derived emission factors.

CHAPTER TWO

LITERATURE REVIEW

This chapter presents background information on general properties of the air pollutants that are investigated in this study. Also background information emission factor is given. These are polyaromatic hydrocarbons (PAHs), carbon monoxide (CO), nitrogen oxides (NO_x), particulate matter (PM_{10}) and total suspended particulate matter (TSP). Furthermore, other relevant tunnel studies published in the scientific literature are briefly reviewed.

2.1 Sources of PAHs, CO, NO_x, PM_{10}, TSP

The main sources of air pollutants are industry, transport, agriculture, heating and the use of raw materials for industries. The percent distribution of these sources is shown in Figure 2.1.

PAHs usually occur as complex mixtures. A number of PAHs are used in medicines and to make plastics, dyes and pesticides. Others are contained in asphalt used in road construction. They may be found in substances crude oil, coal, coal tar pitch, creosote, and roofing tar (ATSDR, 1995). PAHs are created and released to the environment through natural and anthropogenic sources. Primary natural sources are volcanoes and forest fires. Anthropogenic sources include wood burning, automobile exhausts, industrial power generators, incinerators, aluminum smelting, carbon black production, iron smelting, production of coal tar, coke, asphalt and petroleum, incomplete combustion of coal, oil, gas, garbage and tobacco. Atmospheric PAHs are primarily emitted from the combustion of fossil fuels, wood burning, refuse burning and coal tar (Dabestani & Ivanov, 1999).

Carbon monoxide (CO) occurs through the partial oxidation of carbon-containing compounds; it forms when there is not enough oxygen to fully oxidize the carbon compound to carbon dioxide (CO_2), such as when operating a stove or an internal combustion engine in a closed space. Some processes in conventional technology

like iron smelting, still produce CO as a byproduct. The biggest source of CO is natural in origin, due to photochemical reactions in the troposphere that generate about 5×10^{12} kg/year worldwide. Other natural sources of CO are volcanoes, forest fires, and other forms of combustion.

NO_x is a general term for mono-nitrogen oxides NO and NO_2 (nitric oxide and nitrogen dioxide). They are produced from the reaction of nitrogen and oxygen gases in the air during combustion. In areas of high motor vehicle traffic the amount of nitrogen oxides emitted to the atmosphere may be significant. In atmospheric chemistry, NO_x concentration is equal to the total concentration of NO and NO_2. NO_x gases are formed in every environment, where combustion occurs. Also, NO_x are central to the formation of tropospheric ozone and NO_x react to form smog and acid rain.

PM_{10} known as particulate matter (PM) are solid or liquid substances that have an aerodynamic diameter smaller than 10μm. They are usually suspended in the atmosphere as atmospheric aerosol, a term which refers to the particulate/air mixture. But, it is common to use the term aerosol to refer to the particulate component alone. PM_{10} can have significant effects on human health. It also has impacts on climate and precipitation. Subtypes of atmospheric particle matter include suspended particulate matter (SPM), respirable suspended particle; fine particles and soot. Some particulate matter appear naturally, originating from volcanoes, dust storms, forest, grassland fires, living vegetation, and sea spray. Human activities like the burning of fossil fuels in vehicles, power plants, various industrial processes and generate significant amounts of particulates. Coal combustion is the first method for heating homes and supplying energy in developing countries (Harner et al., 2000).

Small airborne particles or aerosols that are less than 100 μm are known as total suspended particulate matter (TSP). These particles incessantly enter the atmosphere from many different sources. Anthropogenic sources include motor vehicle use, combustion products, industrial processes; power generation. Natural sources include soil, bacteria, viruses, fungi, molds, yeast, pollen, salt particles (Chirico et al., 2011).
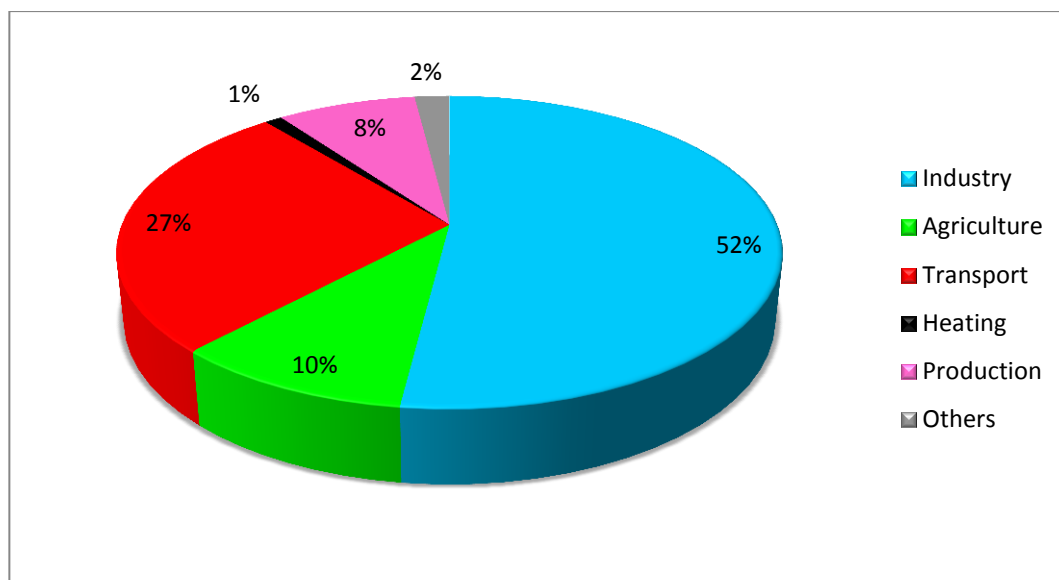
Figure 2.1 Sources of emissions of air pollutants (ATSDR, 1995).

2.2 Chemical Properties of PAHs

PAHs are a complex class of organic compounds containing two or more fused aromatic rings, comprised of only carbon and hydrogen. The PAHs include about 660 substances. Approximately 30 to 50 of them usually occur in the environment (Slaski, Archambault & Li, 2000). 16 PAHs have been classified by the Environmental Protection Agency (EPA) as priority pollutants. These are naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, flouranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)flouranthene, benzo(k)flouranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, dibenzo(b,c)fluoranthene, benzo(g,h,i)perylene (Galarneau et al., 2006). 16 PAHs are shown in Figure 2.2.The common characteristics of this class of compounds are high melting and boiling points, low vapor pressure, and very low water solubility (Odabasi, 1998). PAHs are generally colorless, white, or pale yellow-green solids. They might have a faint, pleasant odor (ATSDR, 1995). PAHs may be divided into two classes based on their physical, chemical, and biological characteristics. This classification can be done as natural and anthropogenic origin. The lower molecular weights PAHs have important acute toxicity to aquatic organisms, but high molecular weight PAHs, 4 to 7 ring do not. However, several members of the high

molecular weight PAHs can be carcinogenic (Environmental Protection Division, 1993). Toxicity of PAHs is associated with their photochemical transformation to more toxic photoproducts (Dabestani & Ivanov, 1999).
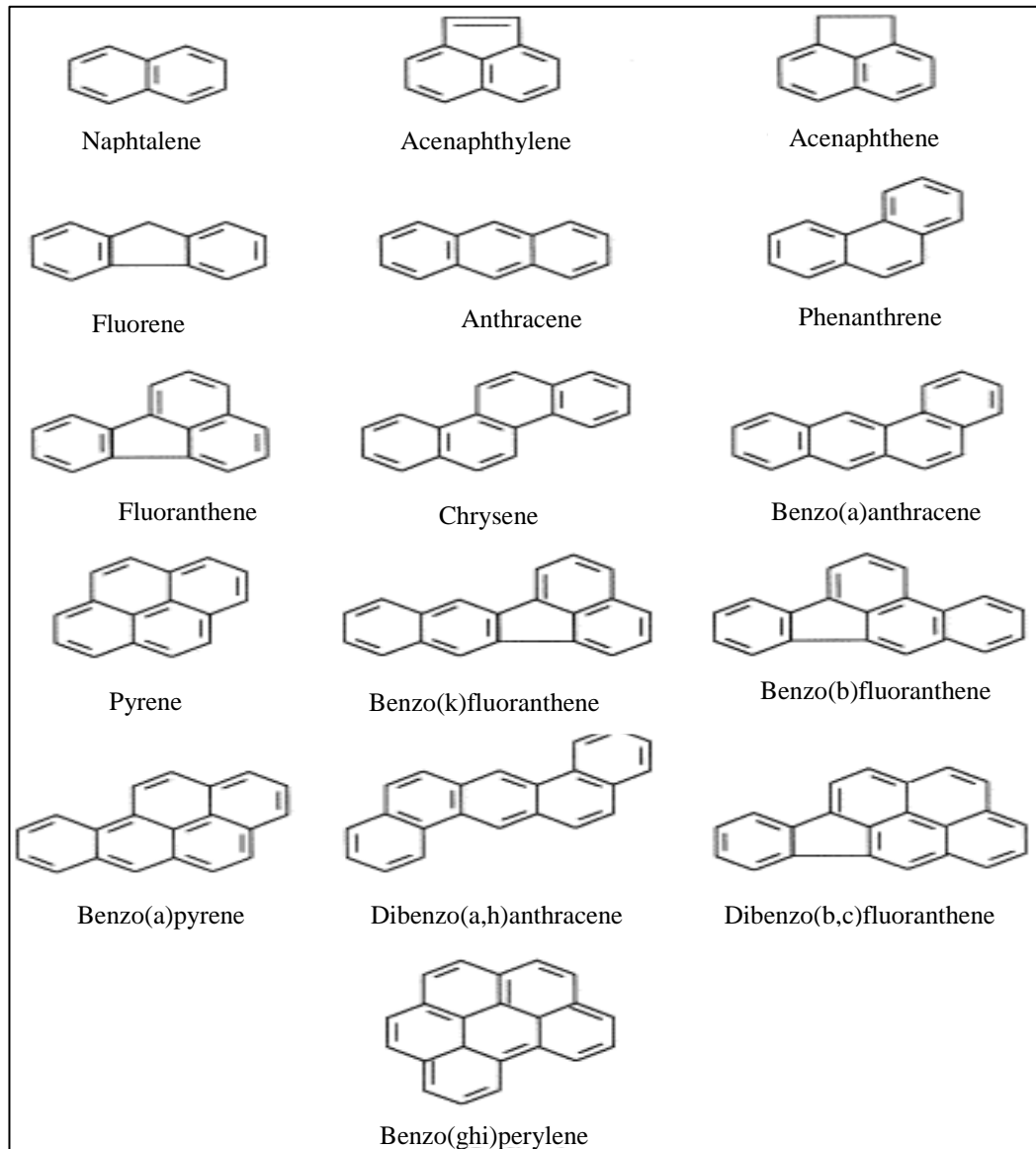
Figure 2.2 Forms of PAHs.

2.3 Health Effects of PAHs, CO, NO$_x$, PM$_{10}$, TSP

The effects of PAHs on human health depend mainly on the length and route of exposure. The toxicity of the PAHs is proportional with the concentration of PAHs. A variety of other factors may affect health impacts including subjective factors like existing health status and age. However, the ability of PAHs to induce short term health effects in humans is not clear. Vocational exposures to high levels of pollutant mixtures containing PAHs have resulted in symptoms like eye irritation, nausea, vomiting, diarrhoea and confusion. But, it is not known which components of the mixture are responsible for these effects. Mixtures of PAHs can cause skin irritation and inflammation. Anthracene, benzo(a)pyrene and naphthalene are direct skin irritants while anthracene and benzo(a)pyrene cause an allergic skin response in animals and humans. PAHs might cause decreased immune function, cataracts, kidney and liver damage, breathing problems, asthma-like symptoms, and lung function abnormalities. Naphthalene may cause the breakdown of red blood cells if inhaled or ingested in large amounts. Though PAHs can have toxic effects, a major concern is the ability of the reactive metabolites, such as epoxides and dihydrodiols. Biochemical deductions and cell mutations can cause developmental formations, tumors, and cancer. Mixtures of PAHs are carcinogenic effect on humans. But, it isn't clear from some studies if exposure to PAHs was the main cause as workers were simultaneously exposed to other cancer-causing agents (e.g. aromatic amines). The most common PAH is benzo(a)pyrene, which causes cancer in animals. The Environmental Protection Agency (EPA) classifies seven PAH compounds as carcinogens; these are benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenz(ah)anthracene, and indeno(1,2,3-cd)pyrene. The Center for Children's Environmental Health studies show that exposure to PAH pollution during pregnancy is premature delivery, and heart malformations. High prenatal exposure to PAH may be childhood asthma and DNA of babies can be damaged. Both in rodents and in vitro tests using mammalian cell lines have been shown genotoxic effects for some PAHs. Genotoxicity plays important role in the carcinogenicity process and can in some forms of developmental toxicity. Immune reaction effects of PAHs have been found in rodents. The precise mechanisms of

PAHs induced immunotoxicity aren't clear; but, PAHs may induce cancer (European Commission DG Environment, 2001).

Carbon monoxide enters the bloodstream through the lungs and binds to hemoglobin, the substance in blood that carries oxygen to cells. Thus, decreases the amount of oxygen that reaches our body's tissues and central nervous system such as particularly the heart and brain. Exposure to carbon monoxide can impair their judgment and ability to respond rapidly in traffic is shown by tests of automobile drivers. Exposure to carbon monoxide is serious for people who suffer from cardiovascular diseases. While doing exercise, they can experience chest pain and other cardiovascular symptoms because they can be exposed to the gas. People who have cardiovascular and respiratory problems chronic obstructive lung disease, congestive heart failure are at greater risk from carbon monoxide exposure, insomuch that healthy individuals exposure to higher levels of carbon monoxide can lead to mental alertness, work capacity and vision, headaches and affect manual dexterity (Dachs & Eisenreich, 2000).

NO_x can react with ammonia, moisture, and other compounds to form nitric acid vapor and related particles. These particles can penetrate into sensitive lung tissue and damage it, causing premature death in extreme cases. Inhalation of these particles may cause respiratory diseases, such as emphysema or bronchitis, or may also aggravate existing heart disease. NO_x can react with volatile organic compounds in the presence of sunlight to form ozone.

The health effects of inhaling particulate matter are asthma, lung cancer, cardiovascular issues, respiratory diseases, birth defects, and premature death. The size of the particle is an important factor that determines the effect. Thus, particles on the order of 10 μm or less (PM_{10}) may penetrate the deepest part of the lungs such as the bronchioles or alveoli. Larger particles may be filtered in the nose and throat via cilia and mucus, but particulate matter smaller than about 10 μm can cause health problems in the bronchi and lungs. But has been agreed upon for monitoring of

airborne particulate matter by the air quality regulation agencies, the 10 μm size does not represent a strict boundary between respirable and non respirable particles.

Particles smaller can than 2.5μm penetrate into the gas exchange regions of the lung. Small particles can penetrate right into bronchioles whereas PM which can penetrate to alveoli and hence the circulatory system are termed respirable particles. An article published by the American Medical Association shows that $PM_{2.5}$ can cause vascular inflammation and atherosclerosis a hardening of the arteries that reduces elasticity, which can lead to heart attacks and other cardiovascular problems. This article describes how nanoparticles may damage the cardiovascular system of such a small particles Nanoparticles can pass through cell membranes and migrate into other organs, including the brain. They can also harm Alzheimer patients (European Commission DG Environment, 2001).

2.4 Traffic Related Air Pollution Emissions

Vehicles of transport are a part of our daily lives. These vehicles pollute our environment with their polluting gases and particles. 27 % of the air pollution is caused by motor vehicles (California). Therefore, urban road tunnels can accumulate significant amounts of air pollutants. These pollutants vary according to the type of engine. Mainly two types of engines are used in motor vehicles which are gasoline and diesel engines. The main emission sources for gasoline vehicles are exhaust pipe, fuel tank, air conditioning cartel, carburetor, brake pads and tires. The main emission sources in diesel fueled vehicles are exhaust pipe, brake pads and tires. Three types of smoke occur in the exhaust gas. Black smoke is formed by uncombusted fuel particles. Gray-white smoke is produced by complete combustion of fuel and constitutes of waste gases. Blue smoke occurs when uncombusted fuels is mixed with engine oil (Bamford, Poster & Baker, 1999).

Carbon dioxide (CO_2), water vapor (H_2O), hydrogen (H_2) and nitrogen (N_2)are not considered as polluting gases in the exhaust gases, although CO_2 is considers as a greenhouse gas and contributes to climate change. CO, particulate matters (soot,

dust, granule, etc.), heavy metals, NO_x, and PAHs are generally considered as polluting gases in exhaust gases. Emission factors for these pollutant scan be calculated manually or using modeling methods. In this study, emission factors are calculated manually and compared with estimations from the Motor Vehicle Emissions Simulator (MOVES).

2.5 Several Case Studies on Tunnels

In this section, an overview of related other studies published in the literature is presented. Although there are many studies that involve some sort of measurements in a road tunnel setting, studies that are similar to this study in terms of measured air quality parameters and the overall methodology could not be found in the current literature.

In a study by Marr, Kirchstetter & Harley (1999), measurements of gas and aerosol phase composition examined for a mixed vehicle fleet in the Gubrist tunnel (Switzerland) was presented. PM_{10} composition measurements were made with a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (AMS) and a Multi Angle Absorption Photometer (MAAP). Gas phase measurements of CO, CO_2, NO_x and total hydrocarbons (THC) were performed with standard instrumentation. During weekdays a characteristic diurnal pattern was observed; 2 concentration peaks for all traffic related species corresponding to high vehicle density (~300±30 vehicles per 5 min) in the morning rush hour between 06:00 and 09:00 and in the afternoon rush hour from approximately 15:30 to 18:30. The emission factors (EF) of organic aerosol (OA) were heavily influenced by the OA mass loading. To exclude this partitioning effect, only OA mass concentrations from 60 mg m^{-3} to 90 mg m^{-3} were considered and for these conditions the EF (OA) value for HDV was 33.7± 2.3 mg km^{-1} for a temperature inside the tunnel of 20 - 25 ˚C. An even higher EF (OA) value for HDV of 47.4 ±1.6 mg km^{-1} was obtained when the linear fit was applied to all data points including OA concentrations up to 120 mg m^{-3}. Similar to the increasing EF, the OA/BC ratio in the tunnel was also affected by the organic loading and it increased by a factor of ~3 over the OA range 10-120 mg m^{-3} (BC: Black Carbon).

For OA concentrations lower than 40mg m^{-3} the OA/BC mass ratio has been below 1, while at an OA concentration of 100-120 mg m^{-3} the OA/BC ratio has been ~1.5. The AMS mass spectra (MS) acquired in the tunnel were highly correlated with the primary organic aerosol (POA) MS from a EURO-3 diesel vehicle with a speed similar to the average tunnel speed.

In another study, atmospheric aerosols of four aerodynamic size ranges were collected using high volume cascade impactors in an extremely busy roadway tunnel in Lisbon (Portugal) by Fre, Bruynseraede & Kretzschmar (1991). Dust deposited on the tunnel walls and guardrails was also collected. Average particle mass concentrations in the tunnel atmosphere were observed more than 30 times higher than in the outside urban background air, revealing its origins almost exclusively from fresh vehicle emissions. Most of the aerosol mass (65%) was concentrated in submicrometer fractions, and polycyclic aromatic hydrocarbons (PAHs) were even more concentrated in the finer particles with an average of 84% of total PAHs present in sizes smaller than 0.49 μm. The most abundant PAHs were methylated phenanthrenes, fluoranthene and pyrene. About 46% of the total PAHs mass were attributed to lower molecular weight compounds (two and three rings), suggesting a strong influence of diesel vehicle emissions on the production of local particulate PAHs. The application of diagnostic ratios confirmed the relevance of this source of PAHs in the tunnel ambient air.

Handler et al. (2008) investigated size segregated emissions of particle-phase species from on-road motor vehicles in the Kaisermühlen Tunnel (Vienna, Austria). Emission factors were calculated from concentration differences between samples from inside and outside the tunnel, the distance between the tunnel entrance and sampling location, the ventilation rate and the number of vehicles passing the tunnel. For a mixed car fleet with an average contribution of 9.6% heavy duty vehicles (HDVs), mean particle mass emissions of 26±10 mg veh^{-1}km^{-1}of PM$_{2.5}$, 62±18 mg veh^{-1}km^{-1}of PM$_{10}$ and 129±45 mgveh^{-1}km^{-1}of total suspended particulates (TSPs) were observed. The released particles mainly consisted of elemental carbon (EC), organic carbon (OC) and the mineral components (MC) Si, Fe, Ca, Al and Mg. They

accounted for 34.4% (EC), 30.3% (OC) and 18.2% (MC) of total PM_{10} emissions and 68.5%, 8.7% and 14.9% of $PM_{2.5}$ emissions, respectively. Emissions of coarse particles were found to be dominated by resuspended matter as well as by brake wear, whereas fine particles were mainly derived from combustion processes. On weekends for some components distinctly reduced emissions were observed which could be explained with changes in driving conditions and/or fleet composition.

Kristensson et al. (2004) conducted measurements to determine real-world traffic emission factors for a number of gaseous and particle pollutants in a road tunnel in Stockholm. 49 different PAHs, CO, NO_X, benzene, toluene, xylenes, aldehydes, elements and inorganic/organic carbon contained in particles, the sub-micrometer aerosol number size distribution, $PM_{2.5}$ and PM_{10} were in investigated this study. The exhaust pipe emission factors were determined separately for heavy-duty vehicles (HDV) and light-duty vehicles (LDV) by virtue of automated traffic counts. The LDV fleet contained 95% cars powered by petrol and the total fleet contained about 5% HDV. When data permitted, the emission factors were further calculated for different vehicle speeds. As a result, average CO, NO_x and benzene emission factors amounted to 5.3, 1.4 and 0.017 g $veh^{-1}km^{-1}$, respectively. PAH emission factors were 2–15 times higher than found with dynamometer tests. Most particles were distributed around 20 nm diameter.

With regard to automotive traffic, a tunnel-type semi enclosed atmosphere is shown to be characterized by a higher concentration of gaseous pollutants than on urban traffic roads and highlights the gaseous effluent species having an impact on material degradation in a study by Bouddabbous, Kasperek, Barbier, Harel & Hannoyer (2012). The real world traffic concentrations of experimental exposure conditions were given by gaseous pollutant measurements carried out in a road tunnel in Rouen (France). SO_2, NO_2, BTEX and aldehyde sampling were carried out in the summer and winter. Effluent profiles in the upward and downward tunnel tubes were established. The study showed that SO_2, NO_2, formaldehyde, acetaldehyde, propanal and butanal must be considered in the degradation process of materials in a stuffy environment. With regard to NO_2, its concentration depended on

the composition of the automotive fleet. Total aldehyde concentrations indicated no particular trend between the two tubes. Formaldehyde, acetaldehyde, propanal, butanal and acrolein species were the most abundant species emitted by vehicles and represent 90−95% of the total aldehyde emissions.

In another study, concentrations of semi-volatile PAHs, hydrocarbons (HCs), particulate matter (PM 1, 2.5 and 10 μm) and TSPs were measured in a traffic tunnel in Gothenburg, Sweden (Wingfors, Sjödin, Haglund & Brorström-Lunden, 2001) in order to calculate emission factors . Some variables were assumed to provide good estimates of average vehicle emissions, since all types of vehicle, using all types of fuel, pass through this tunnel. It was shown that the majority of particle-associated PAHs were found on particles with an aerodynamic diameter of 1 mm. The concentrations of PAHs were shown to be one order of magnitude higher in air samples from the tunnel than in air samples at two urban locations. However, the PAH profiles of air samples from the tunnel and the urban sites were shown to be similar. This was demonstrated using principal component analysis. Finally, and notably, no significant change in total emissions occurred when the proportion of HDVs increased from 8% to 24%. Previously, diesel vehicles were found to release larger quantities of PAHs and related substances. Advances in fuel quality, and HDV engines and exhaust system design during the last decade might have contributed to this promising result. But, it was shown, using partial least squares regression to latent structures that some of the measured parameters displayed correlations with the proportions of HDVs and light-duty vehicles LDVs. Concentrations of total HCs, TSPs, dibenzothiopene, phenantrene, anthracene and monomethyl-derivatives of phenantrene and anthracene were all correlated to the proportion of HDVs. The concentrations of naphthalene, some mono- and dimethylnaphthalenes and most large PAHs (with 5–7 fused rings) were correlated to the proportion of LDVs.

Ho et al. (2009) quantified real-world vehicle emission factors for seventeen gas and particulate PAHs in the Shing Mun Tunnel, Hong Kong during summer and winter 2009. Fluoranthene and pyrene were the most abundant in the particle phase while naphthalene, acenaphthylene, and acenaphthene were the most abundant gas

PAHs. Whereas most of the particle-phase PAHs were in four- (~60%) and five-ring (~17%) for fresh exhaust emissions, most (98%) of the gas PAHs consisted of two- and three-aromatic rings. Average emission factors for the gas- and particle PAHs were 950–2564 μg veh^{-1} km^{-1} and 22–354 μg veh^{-1} km^{-1}, respectively. Good correlations were found between diesel markers (fluoranthene and pyrene; 0.85) and gasoline markers (benzo [ghi] perylene and indeno [1, 2, 3 cd] pyrene; 0.96). Higher PAH emission factors were associated with a higher fraction of diesel-fueled vehicles (DV) passing through the tunnel. Separate emission factors were determined from diesel and non-diesel exhaust by the regression intercept method. The average PAH emission factor (i.e., sum of gas and particle phases) from DV (3085±1058 μg veh^{-1} km^{-1}) was 5 times higher than that from non-diesel-fueled vehicles (NDV, 566±428 μg veh^{-1} km^{-1}). Ratios of DV to NDV emission factors were high for diesel markers (>24); and low for gasoline markers (<0.4).

A comprehensive characterization of PM$_{2.5}$ emissions was reported in the study for the Zhujiang Tunnel in the Pearl River Delta region of China (Hely et al., 2008). The chemical speciation included EC, OC, inorganic ions, trace elements, and organic compounds. The emission factors of individual species and their relative distributions were obtained for a mixed fleet of HDVs (19.8%) and LDVs (80.2%). In addition, separate emission factors of PM$_{2.5}$ mass, EC, and organic matter for HDVs and LDVs were also derived. As compared to the results of other previously conducted tunnel studies, this study found that the abundances and distributions of the trace elements in PM$_{2.5}$ emissions varied more. In contrast, the characteristics of the trace organic compounds in thePM$_{2.5}$ emissions in this study were consistent with characteristics found in other tunnel studies and dynamometer tests.

Li, Chen, Lai & Wang (2011) measured concentrations of CO and NO$_x$ in a cross-mountain Hsuehshan traffic tunnel stretching 12.9 km and containing eastward and westward tubes. Traffic and pollutant concentrations during the weekends exceeded those during the weekdays. Measured concentrations of CO at the two tunnel outlets (14.45–22.77 ppm) were approximately three times higher than those at the two tunnel inlets (3.17–7.33 ppm), while concentrations of NO$_x$ at the two tunnel outlets

(1.92–2.88 ppm) were approximately four to five times higher than those at the two tunnel inlets (0.32–0.78 ppm). The emission factors for the upslope, west-ward lanes (CO = 1.90 ± 0.43 g km^{-1} vehicle^{-1}; NO$_x$ = 0.38 ± 0.07 g km^{-1} vehicle^{-1}) were higher than those for the down-slope, eastward lanes (CO = 1.45 ± 0.13 g km^{-1} vehicle^{-1}; NO$_x$ = 0.26 ± 0.03 g km^{-1} vehicle^{-1}). High traffic volume and low traffic speed resulted in high concentrations and emission factors of the pollutants in the tunnel.

An experiment aimed at comparing PM and PAH concentrations produced in a road tunnel by buses were described in an article by Kiss, Varga-Puchony, Rohrbacher & Hlavay (1998). The experiment took place in Bologna where a couple of buses belonging to the public transport fleet were driven backward and forward in a road tunnel that was closed to all other vehicles. Average daily concentrations of PM of different sizes and of 12 PAHs were measured and outcomes for different fuels were compared to assess ''real-world'' exhaust emissions of different fuels. According to the results was higher than the actual amount of PM and PAHs pollutants.

In a study by Marr, Kirchstetter & Harley (1999) PAH concentrations were quantified in gasoline and diesel fuel samples that were collected in northern California, U.S.A. Naphthalene was the predominant PAH in both fuels, with concentrations of up to 2600 mg L^{-1} in gasoline and 1600 mg L^{-1} in diesel fuel. Particle phase PAH size distributions and exhaust emission factors were measured in two tubes of a roadway tunnel. Emission factors were determined separately for LDVs and for heavy duty diesel trucks, based on measurements of PAHs, CO, and CO$_2$. Particle-phase emission factors, expressed per unit mass of fuel burned ranged up to 21 µg kg^{-1} for benzo-[ghi] perylene for LDVs and up to 1000 µg kg^{-1} for pyrene for heavy-duty diesel vehicles. LDVs were found to be a significant source of heavier (four- and five-ring) PAHs, whereas heavy-duty diesel engines were the dominant source of three-ring PAHs, such as fluoranthene and pyrene. While no correlation between heavy-duty diesel truck PAH emission factors and PAH concentrations in diesel fuel was found, LDV PAH emission factors were found to be

correlated with PAH concentrations in gasoline, suggesting that gasoline reformulation may be effective in reducing PAH emissions from motor vehicles.

Beyea, Hatch & Gammon (2008) identified 13 historical measurements of PAHs in U.S. vehicular traffic tunnels in this study. Emission factors for benzo[a]pyrene for a tunnel fleet operating under cruise conditions were highest prior to the 1980s and fell from more than 30 μg per vehicle-km to approximately 2-μg/km in the 1990s, an approximately 15-fold decline. Total annual U.S. (cruise) emissions of benzo[a]pyrene decreased by a lesser factor, because total annual km driven increased by a factor of 2.7 during the period. Other PAH compounds measured in tunnels over the 40-year period (e.g., benzo [ghi] perylene, coronene) showed comparable reduction factors in emissions.

Air pollution measurements during April are reported from the Craeybeck highway tunnel in Antwerp, Belgium (Fre et al., 1991). The tunnel was used daily by an average of 45,000 vehicles, of which 60% were gasoline fueled passenger cars, 20% diesel cars, and 20% trucks. Tunnel air concentrations of NO_x, sulphur dioxide, CO_2, CO, nonmethane hydrocarbons, volatile organic compounds, PAHs and lead were presented. The traffic emissions in the tunnel were calculated using the carbon balance method, where the increase of the total carbon concentration in the tunnel air is implemented as the reference quantity. The fraction of diesel fuel used by the tunnel traffic was determined from sulphur to carbon ratios in tunnel air. A calculation procedure with breakdown of emission factors according to vehicle categories was used to estimate countrywide emissions. The estimated emissions were compared to results from the Flanders Emissions Inventory [Emissie Inventaris Vlaamse Regio (EIVR)] and calculated emissions according to the emission factors proposed by the European Commission's CORINAIR Working Group. For NO_x there was excellent agreement. For CO and hydrocarbons, the tunnel data produced higher emissions than the CORINAIR model would predict but lower than the official EIVR statistics. The estimated lead emissions from traffic are found to be 22 to 29% of the lead in gasoline.

2.6 Some Case Studies Involving the Motor Vehicle Emissions Simulator (MOVES)

In a study by Ho et al. (2009) fuel consumption for passenger cars related to driving characteristics was investigated. This study explores the influence of driving patterns on fuel consumption using a portable emissions measurement system on ten passenger cars. It shows that vehicle fuel consumption per unit distance is optimum at speeds between 50 and 70 km/h, fuel consumption increasing significantly with acceleration. MOVES was developed to calculate vehicle fuel consumption in this study, and produced good results compared to the measured data.

The Motor Vehicle Emission Simulator MOVES (version 2010a) was used for deriving on-road vehicle emissions by Park, Kim & Kang (2010) in Japan in the other study. All simulations were conducted for a winter month (February) and summer month (July). Inputs other than motor vehicle emissions such as meteorology and emissions from other source sectors were obtained from the prior study. $PM_{2.5}$ concentration is found 29.0μg/m^3 the highest monthly averaged in 2008.

In the other study, fuel emission factors are calculated with MOVES for the municipality of Querétaro for the year 2005 by Aidee (2005). In Table 2.1 emission factors are shown for NO_x, VOC, CO, and PM, for each type of fuel used. The results were higher than expected.

Table 2.1 Vehicle emission for the municipality of Querétaro (2005)

Fuel usage	Annual Emissions (mg year^{-1})			
	NO_x	VOC	CO	PM
Gasoline vehicles	3295.4	13565.6	84081.7	3379
Diesel vehicles	9831.8	1479.9	5341.6	1379.5
LPG vehicles	1101.6	1540.9	4629.5	1453.5
Total municipality	14228.9	16586.6	94052.9	1717.4
Total state	24789.9	31950.8	182234.5	2937.1

CHAPTER THREE

MATERIALS AND METHODS

The air sampling conducted in the Karşıyaka tunnels and the experimental methods used for the measurement of particulate matter (PM_{10}), carbon monoxide (CO), nitrogen oxides (NO_x) and polycyclic aromatic hydrocarbons (PAHs) during this study are reported in this third chapter.

3.1 Tunnel Description

The Izmir Ring Road (54 km) was built to relieve traffic in the city of Izmir. The bay of Izmir is surrounded by two branches. The north branch extends from Işıkkent to Çiğli; the south branch extends from İkiztepe to Işıkkent and merges with the north branch. The Karşıyaka tunnels are located on the north branch. Izmir Ring Road and Karşıyaka tunnels were opened to service in 2007. Tunnels, viaducts and other structures on the ring road were designed and constructed compliant to world standards. The Karşıyaka tunnels feature automatic fire suppression, ventilation, lighting and electronic monitoring systems. The tunnels are constructed as two tubes, both with three lanes conveying traffic from Karşıyaka towards Bornova in the south tube and the reverse direction in the north tube (Figure 3.1). Cross-sectional area, slope and length of the tunnel are 94 m^2, ± 2.3 % and 1866 m, respectively. The slope is uphill in the south tube (Bornova direction).

A plan view of the tunnels is shown in Figure 3.2. There are four emergency exit gates in both tubes, i.e. in both directions. The emergency exit gates are numbered from 1 to 4; the size of gates 1 and 3 are suitable for passage of vehicles and of gates 2 and 4 are only suitable for pedestrians. The first exit gate is 360 m away from the tunnel entrance towards the Karşıyaka direction (north tube) and exit gate 3 is 741 m away from the tunnel exit towards the same direction.
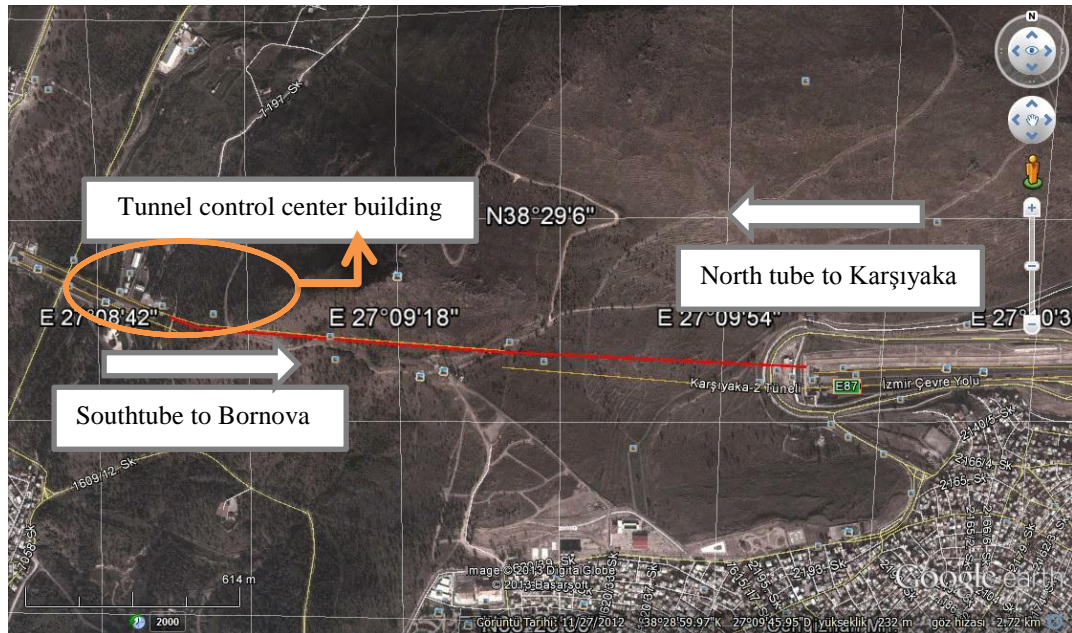
Figure 3.1 Satellite image of the Karşıyaka tunnels.
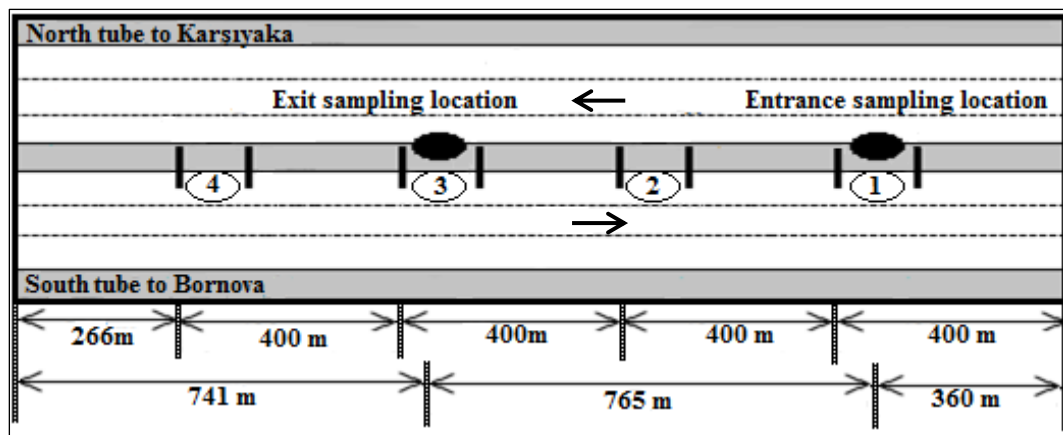
Figure 3.2 Plan view of the Karşıyaka tunnels.

3.2 Equipment and Materials Used

Arrangements were made to use the mobile air quality monitoring station owned by the Izmir Metropolitan Municipality which is a trailer that can be transported to any location (Figure 3.3). The following air quality parameters were measured at the mobile ambient air quality measurement station: particulate matter (PM_{10}), hydrocarbons (methane and non-methane total hydrocarbon), carbon monoxide (CO), nitrogen oxides (NO_x), ozone (O_3), humidity, temperature and pressure. Air

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pollutants measuring devices by the mobile air quality monitoring station Izmir Metropolitan Municipality are devices of the Thermo Inc. branded and devices that are approved by the EPA (Figure 3.4). The methods used in the measurements are given in Table 3.1.

Figure 3.3 The mobile air quality monitoring station belonging to the Izmir Metropolitan Municipality.

Figure 3.4 The interior of the mobile ambient air quality monitoring station owned by the Izmir Metropolitan Municipality.

Table 3.1 Air quality parameters measured with the mobile station and methods used

Parameter	Method
PM_{10}	Beta ray adsorption method
VOCs	Flame ionization
O_3	Double-cell UV photometer method
CO	Infrared method
NO_x	Chemiluminescence method

The devices used for the PM_{10} samplings measuring are sampled using the Thermo Scientific branded (Partisol 2000-FRM Model) PM_{10} sampling device. PM_{10} was also sampled in the mobile measurement station with the beta radiation method. The Thermo-Scientific branded PUF sampler (Figure 3.5) is used to sample for organic matter and PAH content in the gas phases.

Figure 3.5 The PUF sampling device.

3.3 Sampling Events

Inside the tunnel, wind speed and CO measuring devices are located at meters 150, 1700 in the north tube. These are operated by the 2nd Regional Directorate of Highways, which has a tunnel management office near the outlet of the tunnel towards Karşıyaka.

The north tunnel (towards Karşıyaka direction) is selected for all sampling activities since traffic count data is more accurate according to the administration of highways. Emergency exit gates 1 and 3 of the tunnels are used as sampling locations for the mobile station since they are suitable to set up the mobile monitoring station. The first gate is selected for the measurement of tunnel entrance concentrations and the third gate is selected for the measurement of tunnel exit concentrations. The mobile station was placed at these two emergency exit gates for a period of one week between 20.02.12-27.02.12 and 14.07.12-21.07.12. In the first four days of the sampling events the mobile station is placed at the first gate and the last four days at

the third gate. During these periods, the other sampling equipment Partisol 2000 for PM monitoring and PUF sampling device are operated simultaneously with the mobile air quality monitoring station at the entrance and exit sampling locations to obtain data that can be used to verify sampling results.

3.4 Sampling Method

3.4.1 Preparation for Sampling

Sampling of air inside the tunnel requires meticulous preparation of all equipment, glassware and filters that are utilized during the sampling process. Firstly, all glassware used for the sampling and also during the analysis in the laboratory is first washed with dish washing detergent, and then rinsed in sequence with cold and hot water, and with distilled water. The glassware is finally rinsed with acetone (polar) and hexane (non-polar) solutions. The washed glassware is kept dry and capped with aluminum foil.

Quartz filters used in the PUF sampler and glass fiber filters used for metal and organic matter analysis in TSP are wrapped loosely with aluminum foil and heated in a muffle furnace at 450°C overnight to remove any organic residues. Then they were allowed to cool to room temperature in a desiccator. PUF cartridges used in PUF samples are cleaned by Soxhlet extraction using a (1:1) acetone-hexane mixture by exposing the cartridges to the solution for 12 hours. The Soxhlet extraction system is halted for 30 minutes to cool down. After extraction the cartridges are wrapped loosely with aluminum foil and dried in an oven at 70°C. Cleaned cartridges are stored in glass jars capped with Teflon lids (Odabasi, Çetin & Sofuoglu, 2006).

3.4.2 Collection of Samples and Transport of Samples to the Laboratory

Teflon filters are placed in Petri dishes before transporting them to the PM_{10} sampling venue. The Petri dishes are wrapped with stretch film to prevent exposure with ambient air during transportation. Blank samples are taken every two days for quality assurance and control purposes. Quartz filters, glass fiber filters, and PUF cartridges are all kept in aluminum foil and in bags individually locked so that they are not subject to any cross-contamination at the sampling site and during transportation to the laboratory. After sampling is complete, again the samples were wrapped aluminum foil and put into the Teflon-capped glass jar. Ice boxes are used during the transportation of the samples. The samples are brought to the laboratory, weighed and stored at −20 °C before analysis.

3.4.3 PM_{10} sampling

Top compartment lid of Thermo Scientific device is opened, Glass fiber filters is placed between the two circles into top compartment of the Thermo Scientific Device. Particle samples are collected on glass fiber filters to determine the contents total suspended solid particulate matter TSP and organic matter OM. Filter is placed in the Thermo Scientific Device and is operated for 24hours with a constant flow rate of 16.67 l/min. The device is set to automatically stop sucking ambient air after 24 hours. Pollutants are collected on the filter, which is removed from the device and brought to the laboratory by taking necessary measures. These measures include the following. The samples were carried in stiff bags, samples were taken from the device with care, and the samples were weighed immediately.

3.4.4 PUF sampling

Quartz filters and PUF cartridges are used for PUF sampling. Sequential 2 pieces polyurethane foam cartridge are placed into each PUF glass jar (Figure2.4). After the PUF cartridge is installed in the device, the filter is placed into the top compartment of the device. The quartz filter and PUF cartridge are taken from the device after

approximately 23.5 hours of air sampling with 200 L min^{-1} sampling flow rate. The quartz filter and PUF cartridge are then wrapped in aluminum foil and put in a glass jar with Teflon lid. During transportation glass jars are placed into the cold storage bag and are then taken to the laboratory.

3.5 Preparation for Analysis

3.5.1 Extraction of PUF and Quartz Filters

Samples are brought to laboratory and quartz filters, and PUF cartridges are stored in the dark at –20°C until they are analyzed. After unthawing the samples, the quartz filters and PUF cartridges are placed in a 250 ml and 500 ml Soxhlet extractors. Samples are added to the 500 µl standard mixture. A mixture of dichloromethane (DCM) to petroleum ether (PE) with a volumetric ratio of 20:80 is prepared and added to the Soxhlet system. All samples are extracted for 12 hours with this system. A rotary evaporator is used to concentrate all extracts. The temperature of the water bath is maintained at 30°C during sample concentration and solvent exchange. After the sample extracts are reduced to approximately 5 ml by evaporation, the solvent is exchanged into hexane by addition of 15 ml of 95% hexane solution and evaporating the mixture to about 5 ml, again by addition of 10 ml of 95% hexane solution and evaporating the mixture to about 5 ml. The evaporation of 5 ml hexane is transferred to a vial. To account for remaining analyses, the flask used for evaporation is also rinsed with 5 ml hexane and added to the same vial. Then, the contents of the vial are treated with a high purity stream of nitrogen (150-200 ml/min) to reduce the volume from 10 ml to about 2 ml. This sample is then injected to the column system to separate PAHs and PCB. And of these samples were evaporated until 5 ml with the rotary evaporator. The samples were exchanged into hexane by addition of 15 ml hexane (%99) and evaporating the mixture to ~5 ml, again by addition of 10 ml hexane (%99) and evaporating the mixture to ~5 ml. The sample in 5 ml hexane was transferred into a vial. The flask used for evaporation was rinsed with 5 ml hexane and this was also added into the same vial. Then, the sample (~10 ml) was blown down to ~1 ml with a high purity stream of nitrogen (150-200 ml min$^{-1)}$. The division

of fractionation and purification of samples operation were performed containing 3 g of silicic acid, and 2 g alumina in the column with chromatography method.

3.5.2 Preparation of the PAHs and PCB Separation Column

Silicic acid and alumina are PAHs and PCB column materials. These materials must be prepared before the column. Silicic acid (H_4O_4Si) in a flask covered loosely with aluminum foil is dried in the oven at 100°C for several hours in order to remove moisture. After letting it cool to room temperature, 3 g of silicic acid is activated by adding 100 μL of deionized water and subsequently shaking the mixture. The mixture is rested at room temperature for about 1 hour before use. Alumina is prepared by oven drying at 450°C for several hours. It was cooled in a desiccator. 2 g of alumina is activated by addition of 120 μL of deionized water. Na_2SO_4 placed in beakers and baked in a muffle furnace at 450 °C for several hours, then cooled to room temperature in a desiccatorandthenNa_2SO_4 is placed to the column that is placed into a glass wool. Subsequently silicic acid and alumina are placed into the colon. The column was prewashed with 20 ml DCM fallowed by 20 ml PE. The sample in 2 ml hexane was added into the column with a 2 ml rinse of PE and eluent was collected in a vial at a rate of two drops per second. After letting the sample was pass through column, 20 ml PE was added and eluent was collected in the same vial. This part (part 1) contained the PCBs and PCNs. Then the vial used for eluent collection was changed, 20 ml DCM was added into the same rate. Part 2 contained the PAHs and most of the pesticides. For both parts the solvent was exchanged into hexane and the final sample volume was adjusted to 1 ml by nitrogen blown-down.

3.6 Determination of TSP and its Organic Matter (OM) Content

Firstly, glass fiber filters are wrapped with aluminum foil and heated in a muffle furnace at 450°C for 2 hours. They were then allowed to cool to room temperature in a desiccator and weighed using a micro balance capable of weighting 0.1 mg. After sample collection, glass fiber filters are kept in a desiccator overnight and they are reweighed. TSP is determined by subtracting the final weight from the initial weight. After the weighing process, filters are stored in the oven at 450°C for 2 hours, followed by cooling in a desiccator and weighing. OM content is determined by subtracting the final weight (after heating) from the initial weight (before heating).

3.7 Determination of PM$_{10}$ Concentrations

PM$_{10}$ filters are placed in plastic Petri dishes overnight in a desiccator by opening their lids. They were weighed before and after storing in the desiccator. After sampling filters are kept in a desiccator for one night in Petri dishes. The difference between the first and the last weighing gives the amount of particulate matter that is sampled.

3.8 Determination of PAHs Concentrations

PAHs samples are analyzed with the GC-MS device (THERMO FINNIGAN TRACE GC ULTRA –TRACE DSQ Mass Spectrometer). DB-5 column (DB5-MS, 30 m, 0.25 mm, 0.25 μm) is used. The initial oven temperature is held at 50°C for 1 min and raised to 200°C at 25°C min^{-1}, 200 to 300°C at 8°C min^{-1}. The injector, ion source, and quadropole temperatures are 295, 300, and 180°C, respectively. High purity helium is used as the carrier gas at constant flow mode (1.5 ml min^{-1}).Retention times of analytes defined according to the destination and verification ions. GCMS operating conditions are shown Table 3.2. The internal standard method is used.

Table 3.2 GC- MS operating conditions

Parameters	Explanation
GC-MS	THERMO FINNIGAN TRACE GC ULTRA –Mass Spectrometer
GC column	DB5-ms, 30m, 0.25 mm, 0.25 μm
Temperature of the oven	The initial temperature is 50 ° C. After 1 minute, temperature is increased to 200 ° C with an increase 25 ° C per minute. And then, temperature is increased to 300 ° C with an increase 8 ° C per minute.
Block Injection temperature	295°C
Carrier gas and flow rate	High-purity helium gas flow rate is1.5 ml min^{-1}
Injection volume	1 μl
Ion source temperature	300°C
Quadropole temperature	180°C
Injection type	splitless

All of the glass fiber filters and PUF cartridges attended a mixture of (4 mg ml^{-1}) PAH Standard with a mixture of Internal Standard at recycling study before the extraction. Recovery values of PUF cartridges and glass fiber filters are shown in the concluding section.

Blank samples were taken at the sampling locations by placing PUF cartridges and glass fiber filters into the measurement equipment at the same time of the sampling. Cartridges and glass fiber filters were then removed immediately from the devices. Blank samples were prepared to ensure accuracy of samples.

Signal values are obtained from 0.04 ppm calibration standard (S).And then noise signals obtained from blanks (N). Then, while S / N ratio is 3, the concentration value is determined and LOD values are determined. Identification of detection limits and analytes are shown Table 3.3.

Table 3.3 Identification of detection limits and analytes

ANALYTE	LOD ng m^{-3}		LOQ ng m^{-3}		S/N (0,04 ppm)	
	PUF	Filter	PUF	Filter	PUF	Filter
Naphthalene	1.54	0.63	5.11	2.10	4.71	11.49
Acenaphthylene	0.05	0.04	0.16	0.12	150.64	198.43
Acenaphthene	0.07	0.03	0.23	0.08	103.92	291.22
Fluorene	0.14	0.08	0.45	0.26	53.32	93.95
Phenanthrene	0.18	0.16	0.60	0.54	40.11	44.64
Anthracene	0.03	0.03	0.10	0.10	252.04	241.69
Fluoranthene	0.05	0.08	0.17	0.26	143.00	92.71
Pyrene	0.04	0.06	0.15	0.21	164.89	117.15
Benz(a)anthracene	0.25	0.25	0.82	0.82	29.33	29.34
Chrysene	0.03	0.04	0.09	0.13	255.61	188.17
Benzo(b)fluoranhene	0.01	0.12	0.05	0.40	498.18	60.95
Benzo(k)fluoranthene	0.01	0.02	0.03	0.05	705.56	483.65
Benzo(a)pyrene	0.01	0.03	0.03	0.09	846.90	266.92
İndeno(1,2,3cd)pyrene	0.01	0.03	0.03	0.10	848.79	277.40
Dibenz(a,h)anthracene	0.01	0.03	0.04	0.10	574.20	241.76
Benzo(g,h;i)perylene	0.01	0.03	0.02	0.10	1128.90	254.59

Calibration standards are prepared for 0.04, 0.4, 1.0, 4.0, 6.0, 10.0 µg ml^{-1} concentrations. Concentrations of mixed standards were set as 4µg ml^{-1} for each concentration of calibration. Mixed standards were used in the recoveries of analytical determination. The regression coefficients is determined as r^2=0.993 and r^2=0.999 for calibrations standards and less volatile species, respectively.

Before the samples are analyzed with GC-MS, the instrument is calibrated with Standard Auto Tune operation as a method belonging to the GC-MS device. The GC-MS device is calibrated with this method. After the samples are injected to the device, calibration of the device is checked daily with a 4 µg ml^{-1} standard solution of PAH. The device Auto was recalibrating Tune process when the difference between the area values exceeds 20 % daily injections. PAHs pollutants are injected into the GC-MS device. The GC-MS device separates according to the limit values

for the types of PAHs. If the difference between the two limits is 20%, the GC-MS device must be calibrated.

3.9 Motor Vehicle Emissions Simulator

MOVES is a computer program designed by the US Environmental Protection Agency (EPA) to estimate air pollution emissions from mobile sources. MOVES2010b can be used to estimate national, state and county level inventories of criteria air pollutants, greenhouse gas emissions, and some mobile source air toxics from highway vehicles. Essentially MOVES2010b is known as a model of the moving source emissions. Model is used to estimate emission factors at different scales for many air pollutants and greenhouse gas emissions occurring from highway vehicles such as cars, trucks, buses and motorcycles. Besides, this model can be used in the evaluation of various scenarios for the management of air quality. MOVES2010b model can work with the default database or a custom database entered by the user. It is operated using a graphical user interface unlike previous versions of the model. Also the database queries are made through the MySQL database management program. The MOVES2010b database contains results of studies, surveys, and many scientific research projects, emission measurement studies about motor vehicle emissions in U.S.

Vehicle types, vehicle operating characteristics and road types are basic input data that must be defined by the user. Information such as chemical composition of fuels, weather data and age distribution of vehicles is available in the default database model; however these can be defined specifically for the problem being studied. After completion of data entry, model performs calculations and provides estimates for total emission or emission factor. MOVES2010b can a large number of traffic related air pollutants. The user can select the desired parameters from a list of 43 contaminants. The most important ones are CO, NO, NO_2, N_2O, SO_2, VOC, total hydrocarbons, PM_{10}, $PM_{2.5}$, CO_2, benzene, ethanol, PAHs, metals and dioxin compounds. Emissions of selected contaminants are calculated by considering the various emission points in vehicles. These emission points are provided as engine

running exhaust, brake and tire wear (only for PM_{10} and $PM_{2.5}$), fuel evaporation from a vehicle and fuel leaks, oil sump and exhaust at idle. In this thesis study, CO and NO_x were modeling as contaminant parameter.

3.9.1 Preparation of MOVES for Modeling

The necessary data to create runspec were given in material and method part. Firstly, a runspec file must be prepared for the operation of the MOVES model. This file contains information about data of the project.

First, tabs on the navigation panel were selected corresponding to the study. Purpose of the study is provided in the "Description" tab. Then, the workspace of the model was determined and "Project" tab is selected in the Scale tab. Subsequently, year, month, day, and hour of the study were selected in the "Time Spans" tab.

Custom Domain is selected in the Geographic Bounds tab since the modeling was performed for a study area outside the U.S.A.. Then, passenger car, intercity bus, single unit long haul truck and combination long haul truck were selected in the "Vehicles / Equipment" tab. Rural and Urban Unresrected Access were selected as the "Road Type" tab since the tunnels are located on a highway that connects urban areas to rural areas. CO, NO_x and PAHs were activated as pollutants. Running Exhaust, and Extended Idle Exhaust processes were selected as sources for the pollutants (Figure 3.6).
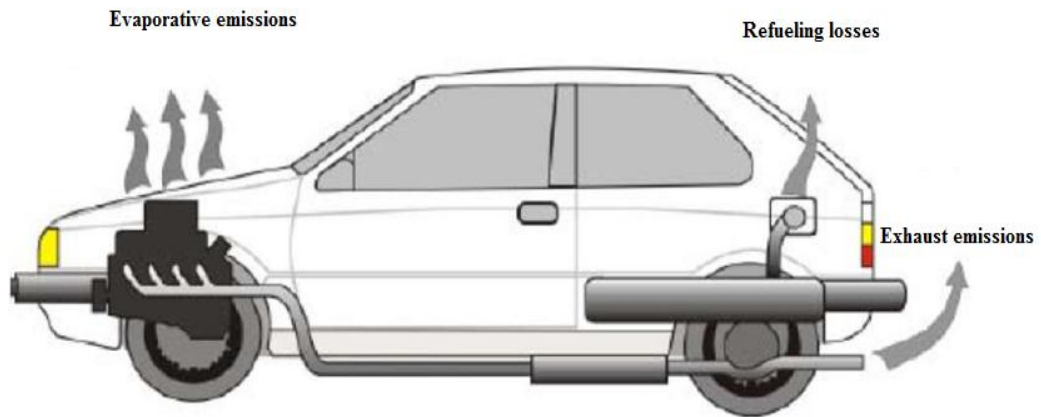
Figure 3.6 Emissions released by vehicles.

Finally, the output file was created to record the output parameters in the "Output" tab. Contents and settings of the input file were selected as follows:

First, the operating mode distributions were defined in the input file. In this study, road LinkID is 1 because of the only type road. Afterwards, the zone table was populated. Country and city were defined here. A different code from America's CountryID and zoneID codes was selected for the study is performed in Turkey. CountryID and ZoneID were taken as 99001 and 990010, respectively.

Fuel types and technologies table were defined in two tables. These were the Fuelsupply and Fuelformulation tables. Two different FuelformulationID were assigned for gasoline and diesel in the Fuelformulation table. FuelformulationID were assigned as 20000 for gasoline and 10 for diesel fuel. Fuel composition data were obtained from Tüpraş, the major refinery in Turkey. Later, the selected FuelformulationID is added to the Fuelsupply table. In addition, fuel contents and usage quantities were defined from data received from received Tüpraş.

The Off-Network table was not used because there parking areas were not present in the study area. SourceTypeHourFraction and SourcetypeID data were added in the Link Source Types table. SourcetypeIDs used in this were 21, 41, 62, and 53 for the passenger car, intercity bus, combination long haul truck and single unit long haul truck, respectively. Source type codes are shown Table 3.4.

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Table 3.4 Source type codes used in MOVES

Source type = 21	gasoline passenger car
Source type = 41	diesel intercity bus
Source type = 53	diesel passenger car
Source type = 62	single unit long haul truck

The SourceTypeHourFraction is the fraction of daily number of vehicles passing during the duration of sampling. This fraction is defined for every source type, i.e. vehicle type. The number of vehicles data was obtained from the Izmir Highways General Directorate. LinkID, CountryID, zoneID, roadTypeID, the path length, the total number of vehicles per day, the average speed of vehicles and highway slope were entered in the Links table. Road slope and the path length data were obtained from the Izmir Highways General Directorate. Temperature (° F) and humidity (%) data were obtained from meterology records and were added to the relevant data table in MOVES. Meteorological data was recorded at the mobile air quality monitoring station. Meterology data were important to affect particle or gas phase from the pollutants.

Finally, the age distribution of the vehicle fleet was required. Age Distribution data were taken from the default database of MOVES. After the completion of the input file, MOVES was executed to obtain daily contaminant loads (g) per km of highway were obtained.

CHAPTER FOUR

RESULTS

This chapter presents results of winter and summer air sampling in the tunnel for all parameters, and emission factor calculations for CO and NO_x. Furthermore, CO and NO_x emissions obtained from the MOVES model are presented and compared with CO, NO_x emission measurements in the tunnel. PAHs were not calculated in MOVES, because according to the developers of the software, some default datasets, including the ones related to PAH, are not suitable for use outside the U.S.A.. Meteorology data monitored at the mobile air sampling station are given in Tables 4.1 4.2.

Table 4.1 Summary of the meteorology data for the winter sampling campaign

Date	Daily Average Temperature (˚C)	Daily Average Humidity (%)	Daily Average Pressure (mbar)
20.02.2012	11.09	42.76	1009.09
21.02.2012	11.36	48.82	1009.12
22.02.2012	12.05	43.51	1004.68
23.02.2012	12.74	45.35	1000.32
24.02.2012	11.27	56.74	996.95
25.02.2012	12.28	75.04	982.89
26.02.2012	7.06	53.03	987.28
27.02.2012	5.03	39.77	988.13
28.02.2012	12.71	52.90	995.62
29.02.2012	13.53	56.79	990.37

Table 4.2 Summary of the meteorology data for the summer sampling campaign

Date	Daily Average Temperature (˚C)	Daily Average Humidity (%)	Daily Average Pressure (mbar)
16.07.2012	34.53	35.38	985.00
17.07.2012	34.45	37.82	986.24
18.07.2012	33.24	30.48	986.25
19.07.2012	33.67	31.69	986.39
20.07.2012	33.21	45.09	989.05
21.07.2012	33.65	35.83	987.98
22.07.2012	32.83	40.92	986.51
23.07.2012	34.35	37.84	989.33
24.07.2012	33.92	44.14	990.24
25.07.2012	33.90	46.14	987.86
26.07.2012	31.68	54.64	990.23

4.1 PM_{10}, CO, NO_x and PAHs Emissions Measured in the Karşıyaka Tunnels

4.1.1 PM_{10}, TSP and Organic Matter Measurement Results

After sampling is completed, PM_{10}, organic matter content of TSP are calculated based on laboratory analysis results. The measurement results are shown in Tables 4.3 through 4.8.

Table 4.3 PM$_{10}$ concentrations measured in the tunnel (winter sampling campaign)

Date and time of sampling				PM$_{10}$ (µg m^{-3})		
Start		Stop		Tunnel entrance	Tunnel exit	Number of vehicles
Date	Time	Date	Time			
22.02.2012	09:05	23.02.2012	09:05	149.70	223.30	31801
23.02.2012	09:07	24.02.2012	09:07	162.49	226.67	32808
24.02.2012	09:09	25.02.2012	09:09	144.92	218.54	33266
26.02.2012	09:05	27.02.2012	09:05	103.24	143.71	25255
27.02.2012	09:07	28.02.2012	09:07	82.04	117.92	31018
28.02.2012	09:09	29.02.2012	09:09	98.02	143.45	30288
29.02.2012	09:11	01.03.2013	09:11	89.81	159.78	30276

Table 4.4 PM$_{10}$ concentrations measured in the tunnel (summer sampling campaign)

Date and time of sampling				PM$_{10}$ (µg m^{-3})		
Start		Stop		Tunnel entrance	Tunnel exit	Number of vehicles
Date	Time	Date	Time			
05.07.2012	09:09	06.07.2012	09:09	120.70	160.73	32836
06.07.2012	09:11	07.07.2012	09:11	123.36	166.07	36093
07.07.2012	09:13	08.07.2012	09:13	92.82	124.45	33014
08.07.2012	09:15	09.07.2012	09:15	83.18	99.58	29586
09.07.2012	09:17	10.07.2012	09:17	105.38	155.88	34474
10.07.2012	09:19	11.07.2012	09:19	105.69	140.00	34861
11.07.2012	09:21	12.07.2012	09:21	118.73	152.55	35016

Table 4.5 TSP concentrations measured in the tunnel (winter sampling campaign)

Date and time of sampling				TSP (µg m^{-3})		
Start		Stop				
				Tunnel entrance	Tunnel exit	Number of vehicles
Date	Time	Date	Time			
25.02.2012	09:03	26.02.2012	09:03	136.07	223.45	29408
26.02.2012	09:05	27.02.2012	09:05	168.73	278.34	25255
27.02.2012	09:07	28.02.2012	09:07	112.80	176.93	31018
28.02.2012	09:09	29.02.2012	09:09	130.40	241.42	30288

Table 4.6 TSP concentrations measured in the tunnel (summer sampling campaign)

Date and time of sampling				TSP (µg m^{-3})		
Start		Stop				
				Tunnel entrance	Tunnel exit	Number of vehicles
Date	Time	Date	Time			
08.07.2012	09:15	09.07.2012	09:15	97.35	159.35	29586
09.07.2012	09:17	10.07.2012	09:17	106.06	198.81	34474
10.07.2012	09:19	11.07.2012	09:19	103.06	176.23	34861

Table 4.7 OM fractions measured in the tunnel (winter sampling campaign)

Date and time of sampling				OM (%)		
Start		Stop				
				Tunnel entrance	Tunnel exit	Number of vehicles
Date	Time	Date	Time			
22.02.2012	09:05	23.02.2012	09:05	26.43	27.63	31801
23.02.2012	09:07	24.02.2012	09:07	27.39	28.11	32808
24.02.2012	09:09	25.02.2012	09:09	32.58	32.79	33266

Table 4.8 OM fractions measured in the tunnel (summer sampling campaign)

Date and time of sampling				OM (%)		
Start		Stop		Tunnel entrance	Tunnel exit	Number of vehicles
Date	Time	Date	Time			
04.07.2012	09:07	05.07.2012	09:07	30.83	31.99	32836
05.07.2012	09:09	06.07.2012	09:09	32.79	36.35	36093
07.07.2012	09:13	08.07.2012	09:13	25.36	21.61	33014

4.1.2 CO and NO_x Measurement Results

CO and NO_x parameters were measured at the mobile air quality measurement station. 24-hour measurements were performed. The results were downloaded to the computer directly from the devices in the mobile station. To calculate the contaminant load, measured concentrations are multiplied by the relevant sampling volumes. Sampling results are shown in Tables 4.9 and 4.10. Comparisons of results are presented in Figures 4.1 and 4.2.

Table 4.9 CO and NO_x concentrations measured in the tunnel (winter sampling campaign, values in parentheses show exit sampling concentrations)

Date	Number of vehicles	Measurement CO $\mu g\ m^{-3}$	Measurement NO_x $\mu g\ m^{-3}$
20.02.2012	27458	1420.1 (2720.1)	155 (580.1)
21.02.2012	28090	1542.4 (2601.3)	163 (641.2)
22.02.2012	34386	1133.5 (2823.5)	161 (872.1)
23.02.2012	38391	1570.3 (3222.1)	153 (981.1)
24.02.2012	30132	1354.5 (2501.1)	166 (633.1)

Table 4.10 CO and NO_x concentrations measured in the tunnel (summer sampling campaign, values in parentheses show exit sampling concentrations)

Date	Number of vehicles	Measurement CO ($\mu g\ m^{-3}$)	Measurement NO_x ($\mu g\ m^{-3}$)
14.07.2012	29040	1321.1 (2411.5)	231.4 (855.1)
15.07.2012	27000	1272.1 (2522.3)	204.4 (783.4)
16.07.2012	37000	1423.2 (2484.5)	208.4 (841.5)
17.07.2012	35818	1377.6 (2453.4)	281.4 (901.3)
18.07.2012	34747	1193.4 (2555.4)	295.3 (890.4)
19.07.2012	32014	1174.5 (2402.3)	244.5 (848.3)
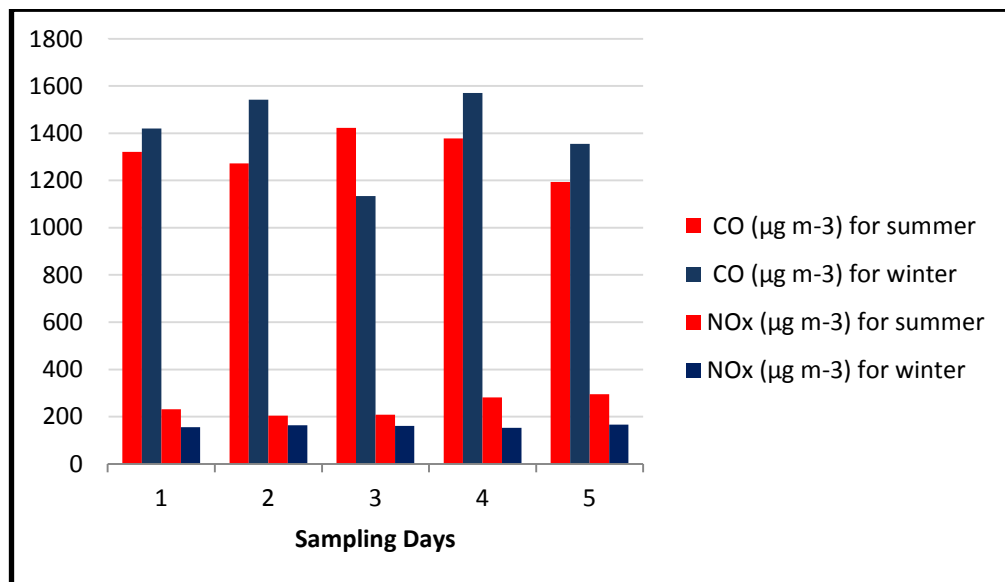
Figure 4.1 Comparison of CO and NO_x entrance concentrations diagram (1.day: 20.02.12 for winter and 14.07.12 for summer sampling, 2.day: 21.03.12 for winter and 15.07.12 for summer sampling, 3.day: 22.03.12 for winter and 16.07.12 for summer sampling, 4.day: 23.03.12 for winter and 17.07.12 for summer sampling, 5.day: 24.03.12 for winter and 18.07.12 for summer sampling).
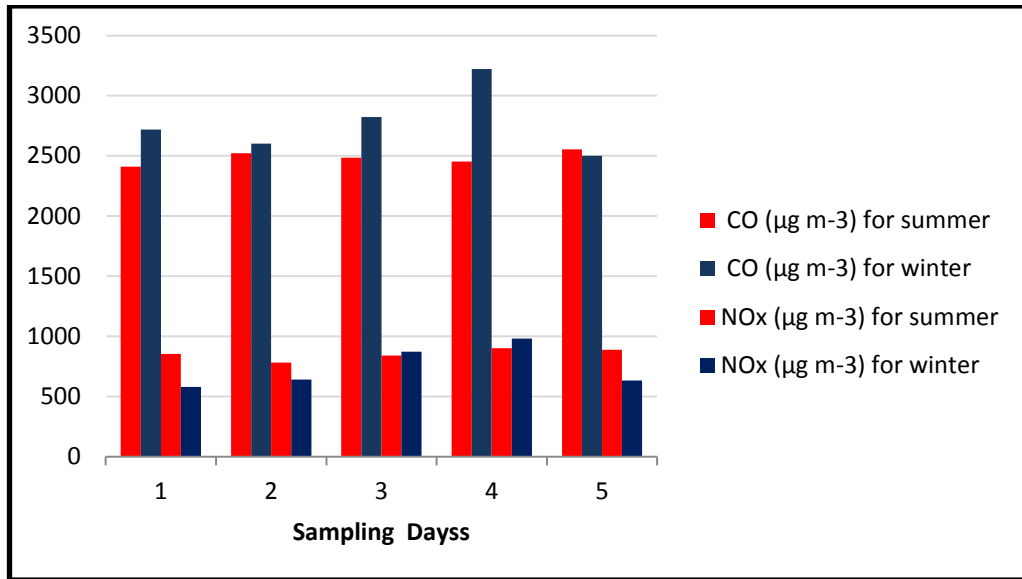
Figure 4.2 Comparison of CO and NO$_x$ exit concentrations diagram (1.day: 20.02.12 for winter and 14.07.12 for summer sampling, 2.day: 21.03.12 for winter and 15.07.12 for summer sampling, 3.day: 22.03.12 for winter and 16.07.12 for summer sampling, 4.day: 23.03.12 for winter and 17.07.12 for summer sampling, 5.day: 24.03.12 for winter and 18.07.12 for summer sampling).

Also, the relationship between the number of vehicles with CO and NO$_x$ concentrations were determined. Figures 4.3 through 4.6 show concentration values against vehicle numbers. A correlation between number of vehicles and concentration was found only for NO$_x$ measurements at the tunnel exit. Correlation for other data pairs was found to be insignificant. For the case of NO$_x$ it can be concluded that the contaminant load is proportional with the traffic volume as it was found in the study conducted by Ho et al. (2009).
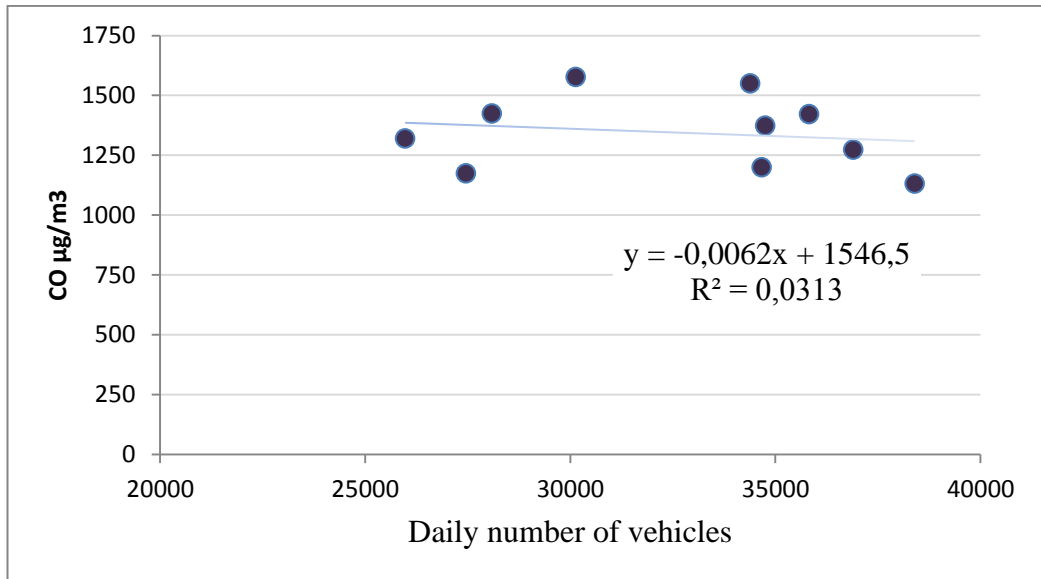
Figure 4.3 Relationship between number of vehicles and CO concentrations at the tunnel entrance
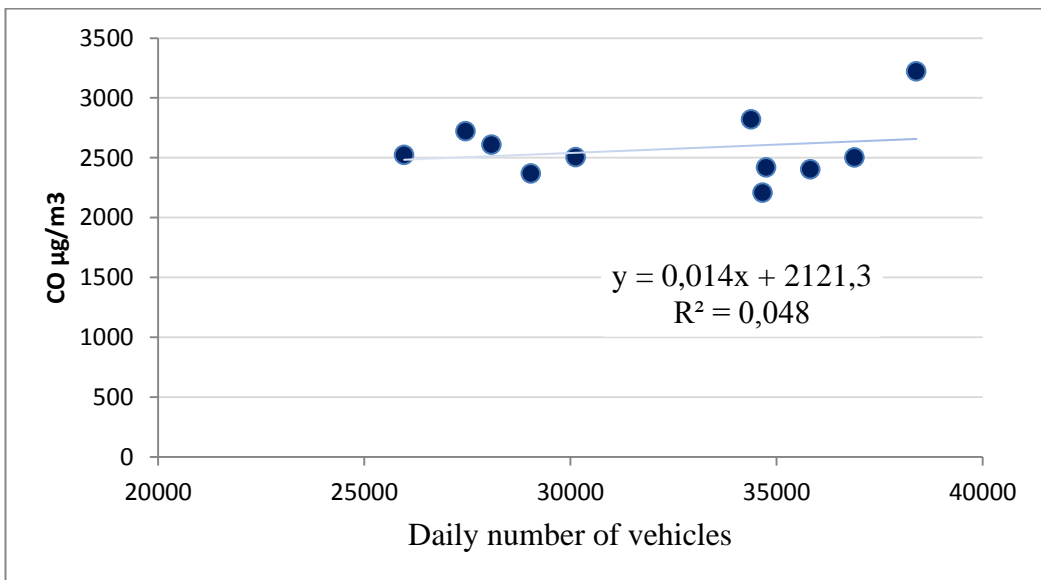
Figure 4.4 Relationship between number of vehicles and CO concentrations at the tunnel exit
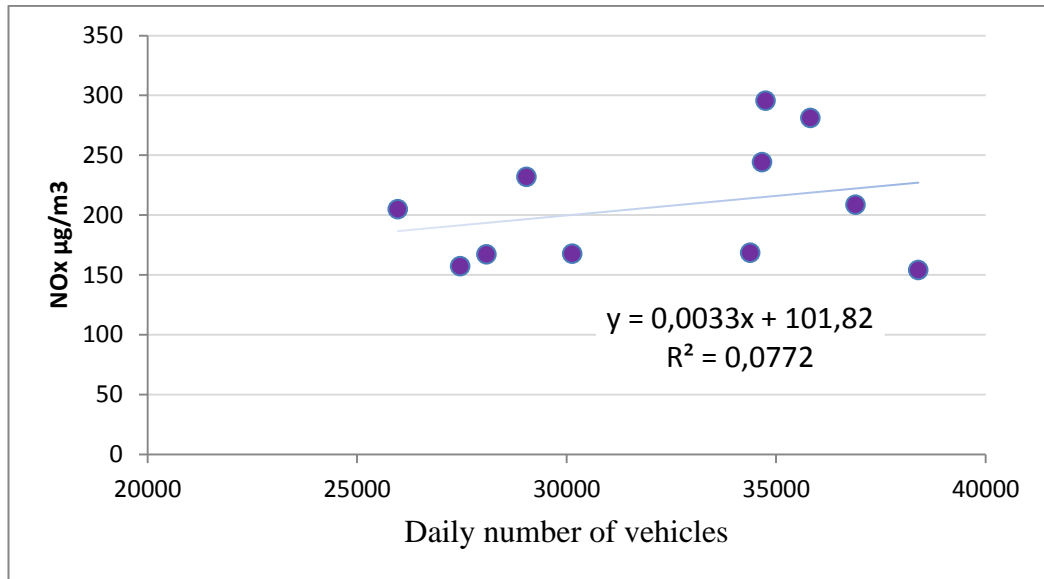
Figure 4.5 Relationship between number of vehicles and NO_x concentrations at the tunnel entrance
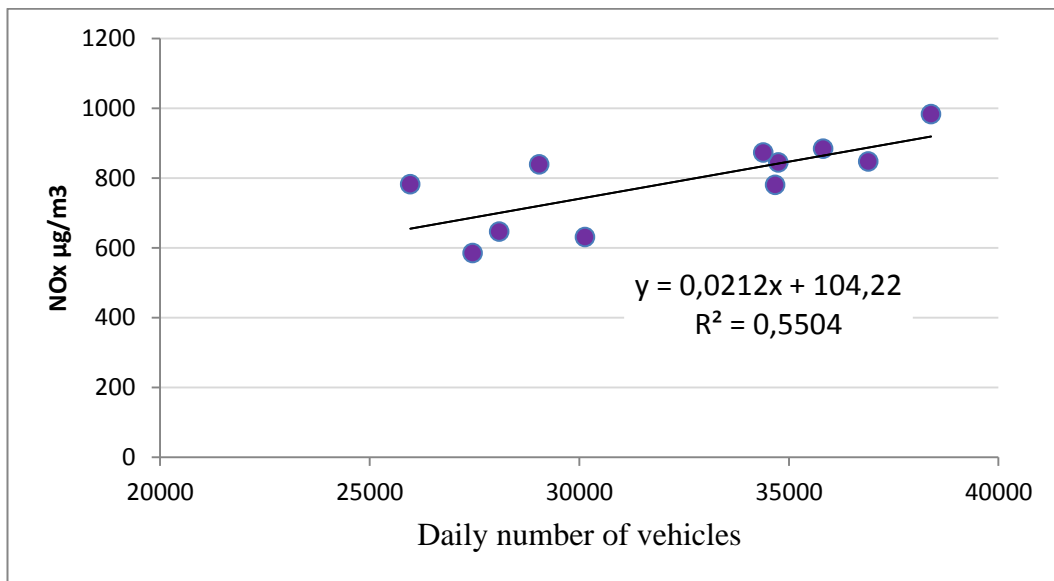
Figure 4.6 Relationship between number of vehicles and NO_x concentrations at the tunnel exit

Table 4.11 CO and NO_x emissions measured in the tunnel (winter sampling campaign)

Date	Number of vehicles	CO emission (kg day^{-1})	NO_x emission (kg day^{-1})
20.02.2012	27458	72.79	23.77
21.02.2012	28090	64.69	27.83
22.02.2012	34386	84.92	37.13
23.02.2012	38391	88.66	44.50
24.02.2012	30132	71.04	28.92

Table 4.12 CO and NO_x emissions measured in the tunnel (summer sampling campaign)

Date	Number of vehicles	CO emission (kg day^{-1})	NO_x emission (kg day^{-1})
14.07.2012	29040	62.81	35.73
15.07.2012	27000	71.75	33.04
16.07.2012	37000	60.55	35.98
17.07.2012	35818	62.43	35.92
18.07.2012	34747	80.19	35.29
19.07.2012	32014	68.63	33.75

4.1.3 PAHs Measurement Results

Signals of analytes in blank samples were detected at very low levels and below the lowest calibration standard concentration.

All of the glass fiber filters and PUF cartridges attended a mixture of (4 mg ml^{-1}) PAH Standard with a mixture of Internal Standard at recycling study before the extraction. Recovery values of PUF cartridges and glass fiber filters are shown in Table 4.13. The recovery value for naphthalene is too low to be considered as accurate. Therefore, naphthalene data was excluded from further analysis and emission factor calculations. Also, PAH tunnel entrance and exit concentrations are presented in Tables 4.14 and 4.15.

Table 4.13 Summary of recovery efficiencies (%) of internal standards (average±std)

Surrogate Compound	PAHs	% Recovery Values	
		PUF	Filter
Naphthalene-D8	Naphthalene	31.4 ± 2.3	25.9 ± 22.4
Acenaphthene-D10	Acenaphthylene, Acenaphthene	71.6 ± 18.7	65.7 ± 22.1
Phenanthrene-D10	Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene	98.,4 ± 8.8	98.9 ± 6.1
Chrysene-D12	Benz(a)anthracene, Chrysene, Benzo(b)fluoranhene, Benzo(k)fluoranthene	115.6 ± 13.6	115.6 ± 12.4
Perylene-D12	Benzo(a)pyrene, İndeno(1,2,3-cd)pyrene, Dibenz(a,h)anthracene, Benzo(g,h;i)perylene	119.3 ± 16.3	113.2 ± 18.7

std: standard deviation

Table 4.14 Winter period PAH tunnel entrance and exit concentrations (values in parentheses show exit sampling concentrations).

Date		1st day	2th day	3rd day	4th day	5th day
Number of vehicles		31621 (31349)	6592 (31577)	29251 (24759)	26258 (26765)	30869 (30849)
Naphthalene (ng m^{-3})	PUF	17.46 (101.16)	16.51 (77.82)	8.13 (83.46)	21.84 (91.60)	97.01 (91.60)
	Filter	1.31 (1.73)	2.60 (2.74)	0.67 (1.19)	1.01 (1.36)	1.78 (1.36)
Acenaphthylene (ng m^{-3})	PUF	18.55 (72.04)	11.04 (74.89)	18.38 74.16)	16.70 (92.00)	70.29 (92.00)
	Filter	0.91 (2.93)	2.93 (3.60)	1.99 (3.67)	1.94 (2.83)	3.04 (2.83)
Acenaphthene (ng m^{-3})	PUF	4.00 (7.89)	1.27 (14.72)	5.01 (17.22)	5.89 (20.65)	11.40 (20.65)
	Filter	n.a (0.16)	n.a (0.18)	n.a (0.23)	n.a (0.20)	0.16 (0.20)
Fluorine (ng m^{-3})	PUF	21.67 (60.31)	12.94 (57.35)	12.77 (70.03)	22.57 (44.71)	51.65 (44.71)
	Filter	n.a (0.57)	n.a (0.05)	n.a (0.27)	n.a (0.29)	0.27 (0.29)
Phenanthrene (ng m^{-3})	PUF	14.36 (53.22)	18.95 (37.61)	8.91 (31.55)	10.19 (43.45)	33.16 (43.45)
	Filter	n.a (5.35)	n.a (7.14)	n.a (4.19)	n.a (4.57)	3.65 (4.57)
Anthracene (ng m^{-3})	PUF	4.43 (20.85)	5.38 (19.96)	4.36 (20.76)	3.71 (21.46)	21.12 21.46)
	Filter	n.a (2.32)	n.a (2.85)	n.a (3.12)	n.a (2.74)	2.86 2.74)
Fluoranthene (ng m^{-3})	PUF	7.90 (21.20)	6.15 (21.65)	12.44 (18.96)	11.55 (19.33)	18.95 19.33)
	Filter	6.06 (9.71)	18.37 (3.63)	4.30 (10.17)	10.29 (12.01)	7.87 (12.01)
Pyrene (ng m^{-3})	PUF	4.25 (17.95)	4.46 (18.71)	5.13 (22.93)	5.83 (17.46)	16.50 (17.46)
	Filter	4.06 (9.68)	4.35 (4.60)	5.03 (9.90)	5.44 (10.82)	9.74 (10.82)
Benz(a)anthracene (ng m^{-3})	PUF	0.12 (0.04)	0.03 (0.05)	0.05 (0.05)	0.09 (0.05)	0.05 (0.05)
	Filter	1.03 (2.55)	0.78 (2.68)	0.83 (2.52)	0.92 (3.23)	2.05 (3.23)
Chrysene (ng m^{-3})	PUF	0.22 (0.07)	0.06 (0.11)	0.21 (0.12)	0.37 (0.12)	0.08 (0.12)
	Filter	1.26 (7.33)	0.49 (3.48)	0.68 (6.03)	1.04 (8.05)	3.56 (8.05)
Benzo(b)fluoranhene (ng m^{-3})	PUF	n.a (n.a)	0.00 (0.07)	0.07 (n.a)	0.00 (n.a)	n.a (n.a)
	Filter	1.75 (9.00)	4.07 (5.63)	1.95 (7.85)	3.06 (9.04)	4.96 (9.04)
Benzo(k)fluoranthene (ng m^{-3})	PUF	n.a (n.a)	n.a (n.a)	0.25 (n.a)	n.a (n.a)	n.a (n.a)
	Filter	1.62 (2.88)	2.25 (2.70)	2.14 (3.38)	2.78 (3.69)	1.79 3.69)
Benzo(a)pyrene (ng m^{-3})	PUF	n.a (n.a)	n.a (0.09)	0.08 (n.a)	0.08 (n.a)	n.a (n.a)
	Filter	1.05 (7.08)	6.06 (3.40)	2.71 (7.50)	5.65 (6.83)	3.04 (6.83)
Indeno(123-cd)pyrene (ng m^{-3})	PUF	n.a (n.a)	n.a (n.a)	n.a (n.a)	0.11 (0.12)	n.a (0.12)
	Filter	1.55 (3.11)	2.71 (1.93)	1.33 (2.11)	1.49 (2.25)	1.86 (2.25)
Dibenz(ah)anthracene (ng m^{-3})	PUF	n.a (0.11)	n.a (0.11)	0.09 0.10)	0.10 (n.a)	n.a (n.a)
	Filter	1.17 (1.75)	1.71 (1.33)	1.27 (2.07)	2.03 (2.10)	1.23 (2.10)
Benzo(ghi)perylene (ng m^{-3})	PUF	0.08 (0.07)	0.38 (0.07)	0.07 (0.07)	0.08 (0.08)	0.07 (0.08)
	Filter	2.63 (8.62)	7.21 (3.78)	3.66 (6.49)	5.37 (6.05)	3.55 (6.05)

n.a.: not available 1.day: 29.02.12, 2.day: 02.03.12, 3.day: 03.03.12, 4.day: 05.03.12, 5.day: 06.03.12.

Table 4.15 Summer period PAH tunnel entrance and exit concentrations (values in parentheses show exit sampling concentrations).

Date		1st day	1st night	2th day	2th night	3rd day	3rd night	4th day	4th night	5th day	5th night
Number of vehicles		18048 (17451)	12209 (11718)	12139 (12528)	14428 (14767)	17439 (18355)	15556 (14984)	19480 (21023)	12947 (12386)	21165 (11471)	16382 (16641)
Naphthalene (ng m^{-3})	PUF	37.24 (85.82)	23.50 (55.41)	25.10 (73.23)	24.05 (55.26)	41.15 (107.8)	21.95 (79.17)	81.59 (152.5)	21.20 (56.50)	25.98 (126.5)	27.42 (68.83)
	Filter	n.a (1.14)	n.a (1.02)	n.a (1.35)	n.a (n.a)	n.a (1.77)	n.a (1.04)	n.a (2.41)	n.a (n.a)	n.a (1.89)	n.a (n.a)
Acenaphthylene (ng m^{-3})	PUF	34.82 (43.35)	43.04 (74.40)	26.47 (53.77)	24.19 (42.86)	29.82 (62.64)	33.72 (64.34)	51.42 (110.6)	40.32 (76.99)	58.64 (116.2)	38.85 (66.70)
	Filter	0.24 (0.37)	0.23 (0.30)	0.16 (0.25)	0.22 (0.24)	0.59 (0.44	0.21 (0.33	0.31 (0.57)	0.25 (0.34)	0.29 (0.64)	0.20 (0.34)
Acenaphthene (ng m^{-3})	PUF	2.09 (7.68)	1.79 (6.20)	1.91 (6.60)	1.45 (5.02)	2.08 (7.31)	1.14 (3.98)	1.86 (6.32)	2.02 (6.92)	1.76 (9.49)	1.78 (6.00)
	Filter	0.05 (0.17)	n.a (0.04)	n.a (n.a)	n.a (n.a)	n.a (0.07)	n.a (0.03)	n.a (0.04)	n.a (n.a)	n.a (0.12)	n.a (n.a)
Fluorine (ng m^{-3})	PUF	53.30 (73.92)	41.91 (57.56)	41.37 (67.67)	31.31 (43.58)	39.70 (58.90)	28.30 (37.88)	44.01 (63.05)	38.54 (59.43)	37.56 (111.9)	32.50 (53.96)
	Filter	n.a (n.a)	n.a (n.a)	n.a (n.a)	n.a (n.a)	n.a (n.a)	n.a (n.a)	n.a (n.a)	n.a (n.a)	n.a (n.a)	n.a (n.a)
Phenanthrene (ng m^{-3})	PUF	30.04 (46.69)	22.45 (33.40)	27.08 (40.80)	19.52 (29.47)	21.98 (32.03)	17.90 (29.63)	25.94 (36.41)	20.72 (35.17)	26.78 (44.56)	23.11 (36.69)
	Filter	1.71 (2.83)	1.01 (1.36)	0.94 (1.51)	0.95 (1.41)	1.87 (2.76)	1.26 (1.94)	1.82 (3.01)	1.17 (1.88)	1.63 (3.26)	1.19 (2.05)
Anthracene (ng m^{-3})	PUF	7.33 (10.41)	5.50 (9.28)	6.88 (11.53)	5.20 (9.04)	5.41 (9.03)	4.58 (8.81)	4.85 (9.98)	5.32 (8.63)	6.51 (11.79)	6.33 (9.76)
	Filter	0.47 (7.99)	0.23 (3.54)	0.22 (4.24)	0.24 (3.95)	0.46 (7.99)	0.33 (5.05)	0.44 (8.20)	0.29 (5.30)	0.46 (8.59)	0.25 (8.59)
Fluoranthene (ng m^{-3})	PUF	6.80 (11.26)	6.11 (8.44)	8.33 (12.48)	5.55 (8.56)	5.26 (6.76)	4.32 (7.53)	6.43 (7.60)	5.53 (9.10)	6.62 (9.42)	5.95 (9.47)
	Filter	4.59 (7.39)	2.87 (3.97)	2.77 (4.13)	2.65 (3.68)	4.62 (7.19)	3.21 (4.68)	4.55 (7.01)	3.28 (4.97)	5.01 (9.46)	3.90 (5.06)
Pyrene (ng m^{-3})	PUF	8.67 (14.88)	7.51 (11.44)	10.49 (16.60)	5.55 (11.71)	6.55 (9.57)	5.55 (10.81)	7.78 (11.70)	6.86 (12.77)	8.53 (13.21)	7.38 (12.75)
	Filter	7.66 (13.90)	3.80 (6.18)	4.11 (6.77)	3.57 (5.95)	8.27 (13.71)	4.93 (8.06)	8.05 (14.18)	4.79 (8.33)	8.84 (17.60)	5.53 (8.58)
Benz(a)anthracene (ng m^{-3})	PUF	n.a (n.a	n.a (n.a)	n.a (n.a)	n.a (n.a)	n.a (n.a)	n.a (n.a)	n.a (n.a)	n.a (n.a	n.a (n.a)	n.a (n.a)
	Filter	1.13 (1.97)	0.92 (1.48)	1.24 (2.06)	0.92 (1.45)	1.16 (1.61)	0.71 (1.19)	0.86 (1.47)	0.90 (1.58)	1.15 (1.63)	0.99 (1.58)
Chrysene (ng m^{-3})	PUF	0.10 (0.31)	0.04 (0.09)	0.10 (0.19)	0.06 (0.15)	n.a (0.13)	0.04 (0.16)	0.06 (0.10)	0.03 (0.06)	0.04 (0.10)	n.a (0.08)
	Filter	1.67 (5.20)	1.08 (3.19)	1.58 (4.63)	1.18 (3.21)	1.58 (4.36)	0.94 (2.85)	1.26 (4.16)	1.23 (3.91)	1.40 (4.37)	1.28 (3.80)
Benzo(b)fluoranhene (ng m^{-3})	PUF	0.14 (0.21)	0.09 (0.09)	0.11 (0.14)	0.08 (0.10)	0.11 (0.12)	0.14 (0.13)	0.13 (0.12)	0.09 (0.11)	0.11 (0.19)	0.09 (0.12)
	Filter	1.65 (5.33)	1.55 (3.28)	2.21 (4.59)	1.59 (4.62)	1.64 (4.27)	1.23 (3.64)	1.28 (4.13)	1.75 (3.56)	1.62 (4.89)	1.69 (4.32)
Benzo(k)fluoranthene (ng m^{-3})	PUF	0.02 (0.02)	n.a (0.01)	0.02 (0.02)	n.a (n.a)	n.a (n.a)	0.01 (0.01)	0.02 (n.a)	n.a (0.01)	0.02 (0.03	n.a (n.a)
	Filter	0.65 (0.85)	0.57 (0.67)	0.76 (1.18)	0.59 (0.73)	0.61 (0.65)	0.41 (0.60)	0.49 (0.63)	0.55 (0.76)	0.45 (0.80)	0.53 (0.70)
Benzo(a) Pyrene (ng m^{-3})	PUF	0.02 (0.02)	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)	n.a (n.a)	0.01 (0.01)	n.a (0.01)	0.01 (n.a)	0.01 (n.a)	0.01 (0.01)
	Filter	1.11 (1.81)	1.11 (1.53)	1.67 (2.47)	1.07 (1.61)	1.09 (1.32)	0.84 (1.35)	0.89 (1.26)	1.11 (1.70)	1.17 (1.54)	1.20 (1.97)
Indeno(123-cd)pyrene (ng m^{-3})	PUF	0.02 (0.02)	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)	0.02 (0.01)	0.01 (0.01)	0.01 (0.02)	0.01 (0.01)
	Filter	0.50 (0.65)	0.66 (0.87)	1.08 (1.45)	0.59 (0.93)	0.47 (0.48)	0.48 (0.69)	0.39 (0.53	0.62 (0.87)	0.50 (0.61)	0.62 (0.79)
Dibenz(ah)anthracene (ng m^{-3})	PUF	n.a (n.a)	n .a (n.a)	n.a (n.a)	n.a (n.a)	n.a (n.a)	n.a (n.a)	n.a (n.a)	n.a (n.a)	n.a (n.a)	n.a (n.a)
	Filter	0.17 (0.20)	0.11 (0.12)	0.17 (0.20)	0.13 (0.15)	0.15 (0.17)	0.12 (0.13)	0.14 (0.17)	0.14 (0.16)	0.16 (0.27)	0.12 (0.16)
Benzo(ghi)perylene (ng m^{-3})	PUF	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)	n.a (0.01)	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)	0.01 (0.02)	0.01 (0.01)
	Filter	0.83 (1.35)	1.11 (1.58)	1.86 (2.45)	0.94 (1.61)	0.86 (0.93)	0.81 (1.24)	0.80 (1.09)	0.92 (1.41)	0.93 (1.20)	1.09 (1.38)

n.a.: not available 1.day: 30.06.12, 2.day: 01.07.12, 3.day: 02.07.12, 4.day: 03.07.12, 5.day: 06.07.12.

4.2 Calculation of Emission Factors

Emission factor is a unit value of a certain pollutant (volume, time, space, etc.) average emission amount arising from the any activity or piece of equipment. In this study, contaminants emission factors were calculated using hourly averages of all variables.

The emission factor for any pollutant is determined by:

$$EF = \frac{(C_\circ - C_i) \times U_T \times A_T}{N_T \times L}$$

EF: Emission factor (mg vehicle^{-1} km^{-1})

C_o: Concentration of pollutant at tunnel exit (mg m^{-3})

C_i: Concentration of pollutant at tunnel entrance (mg m^{-3})

U_T: Average wind speed in the tunnel (m s^{-1})

A_T: Cross-sectional area of the tunnel (m^2)

N_T: Number of passing vehicles

L: Distance between tunnel entrance and exit (i.e. between sampling points) (765 m)

Concentration values used in this equation were obtained from sampling results. Numbers of vehicles passing through the tunnel were requested from the Regional Directorate of Highways. Some inconsistencies were detected in the tunnel entrance and exit vehicle numbers. Therefore, arithmetic averages of were used in the calculation of N_T. According to the data provided by the highway authority, considering all days of the week, ratio of light duty vehicles (LDV) passing through the tunnel was 91.6 % and ratio of heavy duty vehicles (HDV) passing through was 8.4 %. Trucks, buses, long haul trucks and shuttle buses to the Aliağa industrial region were considered as HDVs. Automobiles, minibuses, light trucks and motorcycles are counted as LDVs. Traffic volume data in terms of HDV and LDV numbers is presented in Figures 4.7 and 4.8.
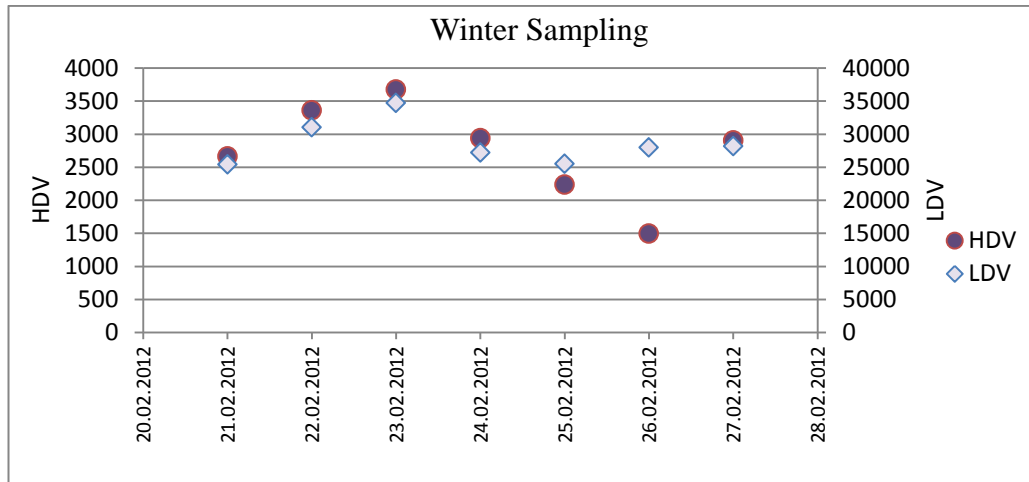
Figure 4.7 Numbers of LDV and HDV for winter sampling dates.
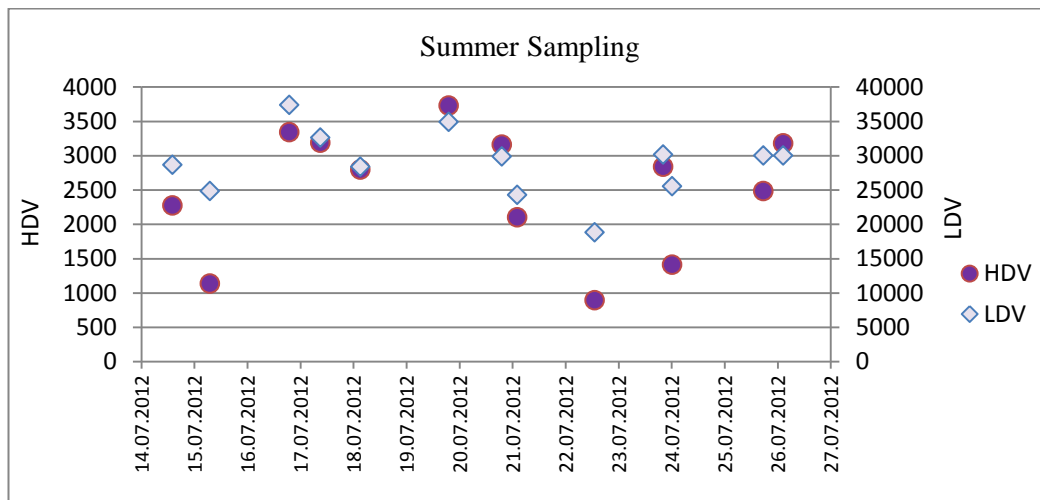
Figure 4.8 Numbers of LDV and HDV for summer sampling dates.

Vehicles are counted on an hourly basis and are provided on the hour. However, as sampling times were variable and not on the hour, it was assumed that traffic counts vary linearly between hours. For example, if we have measurement at 8:18, the traffic counts for 8:00 and 9:00 to obtain the number of vehicles for the sampling time by linear interpolation.

As for the average wind speed in the emission factor equation, wind speed was obtained from measurement data of the mobile air quality measurement station. A constant average wind speed of 5.4 m s^{-1} was used for all sampling periods.

To calculate the emission factors, entrance and exit contaminant concentrations are subtracted from each other. The differences between the concentrations are multiplied by the tunnel area of 94 m^2 and the average wind speed to obtain the contaminant load. Contaminant load is divided by the distance between two sampling points (765 m) and the daily number of vehicles passing through. Calculated emission factors are shown in Tables 4.16, 4.17 and Figure 4.10, 4.11.

Table 4.16 CO and NO_x emission factors determined based on winter and summer tunnel measurements

Date	Period	Emission factor	
		CO (mg km^{-1} vehicle^{-1})	NO_X (mg km^{-1} vehicle^{-1})
14.07.12	S	2162.80	1230.25
15.07.12	S	2657.55	1223.68
16.07.12	S	1636.38	972.40
17.07.12	S	1743.12	1002.94
18.07.12	S	2307.88	1015.55
19.07.12	S	2143.68	1054.33
20.02.12	W	2650.853	865.758
21.02.12	W	2302.896	990.634
22.02.12	W	2469.754	1079.858
23.02.12	W	2309.424	1159.157
24.02.12	W	2357.672	959.633

S: Summer W: Winter

Table 4.17 PAH emission factors based on winter and summer sampling (values in parentheses belong to summer sampling)

Emission factors (μg km^{-1} veh^{-1})	1st day	2th day	3rd day	4th day	5th day
acenaphthylene	97.5	107.8	118.2	124.2	147.4
	(48.445)	(50.212)	(58.071)	(114.762)	(65.587)
acenaphthene	13.7	12.0	20.1	24.3	30.4
	(9.700)	(9.038)	(7.033)	(58.071)	(9.332)

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Table 4.17 Continues

fluorene	54.8	84.7	90.8	100.2	49.3
	(34.503)	(41.372)	(24.566)	(7.033)	(69.141)
phenanthrene	40.7 (26.742)	70.0	72.9	53.6	72.6
		(26.984)	(21.837)	(24.566)	(27.278)
anthracene	35.4	31.4	37.5	42.3	37.6
	(16.416)	(17.860)	(18.099)	(21.837)	(16.889)
fluoranthene	23.3	11.3	17.3	15.3	18.9
	(9.308)	(10.447)	(8.191)	(18.340)	(9.443)
pyrene	32.5	33.3	26.8	45.2	35.9
	(16.535)	(17.616)	(15.518)	(1.251)	(17.241)
benz(a)anthracene	1.7	3.2	3.7	3.3	4.1
	(1.306)	(1.468)	(0.869)	(5.289)	(0.919)
chrysene	3.9	12.1	5.5	10.0	13.5
	(5.320)	(5.732)	(4.374)	(4.127)	(4.617)
benzo(b)fluoranhene	5.8 (4.755)	8.7	7.5	10.0	11.8
		(6.105)	(4.594)	(0.362)	(4.890)
benzo(k)fluoranthene	0.3	1.1	0.6	1.2	0.5
	(0.290)	(0.587)	(0.241)	(0.976)	(0.416)
benzo(a)pyrene	3.6	1.8	1.4 (0.743)	3.7	0.5
	(1.028)	(1.469)		(0.401)	(1.037)
indeno(1.2.3-cd)pyrene	0.6	0.7	1.2	1.1	1.1
	(0.396)	(0.798)	(0.246)	(0.401)	(0.255)
dibenz(a,h)anthracene	0.1	0.3	0.2	0.1	0.4
	(0.036)	(0.055)	(0.027)	(0.046)	(0.113)
benzo(g,h;i)perylene	1.7	1.9	0.3	2.3	1.0
	(0.977)	(1.414)	(0.538)	(0.800)	(0.472)

1st day: 29.02.12 for winter and 30.06.12 for summer, 2th day: 02.03.12for winter and 01.07.12 for summer, 3rd day: 03.03.12 for winter and 02.07.12 for summer, 4th day: 05.03.12 for winter and 03.07.12 for summer, 5th day: 06.03.12 for winter and 06.07.12 for summer.

4.3 CO, NO$_x$ and PAHs Emissions Determined with MOVES

MOVES calculates emissions in units of mass per length of highway. Emission loads for CO and NO$_x$ were obtained using MOVES. MOVES provides results separately for all combination of vehicle and fuel types. Therefore, emission loads from gasoline passenger cars, diesel passenger cars, diesel intercity buses, single unit long haul trucks, and combination long haul trucks were recorded in model output files.

MOVES produces amount of emissions for each fuel type and vehicle type. The sums of these emission calculations found in this study are given in Table 4.18 for each day of sampling. Emissions per kilometer are then divided by the number of vehicles to obtain emission factors that can now be compared to the emission factors obtained directly from sampling results in the tunnel (Table 4.19). Seasonal comparisons of MOVES based emission factor are presented in Figures 4.9 and 4.10. Seasonal comparisons of sampling based emission factors are shown in Figures 4.11 and 4.12. Furthermore, MOVES estimated emission factors are compared to sampling based emission factors and the difference between them was calculated in terms of model error. The sampling result is subtracted from the MOVES value and the difference is expressed as percent model error. The formula used in this calculation is given below:

$$\% \ model \ error = ((\text{MOVES value} - \text{sampling result}) * 100) / \text{MOVES value}$$

The calculation results are shown in Tables 4.20 and 4.21 and Figures 4.13, 4.14 and 4.15

Table 4.18 Total CO and NO$_x$ emissions per kilometer highway estimated by MOVES

Date	Season	Total emission	
		Σ CO (g km^{-1})	Σ NO$_X$ (g km^{-1})
14.07.12	S	78988.500	35755.500
15.07.12	S	64530.000	35910.000
16.07.12	S	60546.060	35978.800
17.07.12	S	62435.072	41513.062
18.07.12	S	79153.666	44093.943
19.07.12	S	70238.716	39153.122
20.02.12	W	71921.000	25539.000
21.02.12	W	69410.000	27046.000
22.02.12	W	83673.000	40242.000
23.02.12	W	79152.000	44100.000
24.02.12	W	69993.000	28986.000

S: Summer, W: Winter

Table 4.19 Emission factors estimated by MOVES (S: Summer W: Winter)

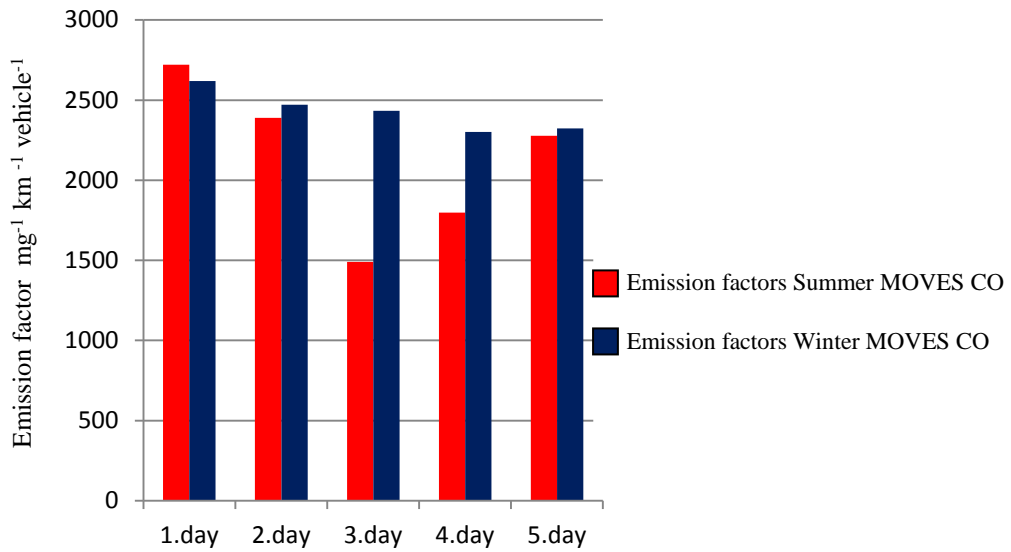| Date	Seasons	Emission per vehicle	
		CO (mg km^{-1}vehicle^{-1})	NO$_X$ (mg km^{-1}vehicle^{-1})
14.0712	S	2720	1127
15.0712	S	2388.222	1330.63
16.0712	S	1491	962
17.0712	S	1797	1159
18.0712	S	2278	1269
19.0712	S	2194	1223
20.02.12	W	2619.309	930.111
21.02.12	W	2470.986	962.834
22.02.12	W	2433.345	1170.302
23.02.12	W	2301.532	1282.312
24.02.12	W	2322.879	961.967

Figure 4.9 Comparison of MOVES emission factors for CO (1.day: 20.02.12 for winter and 14.07.12 for summer sampling, 2.day: 21.03.12 for winter and 15.07.12, 3.day: 22.03.12 for winter and 16.07.12, 4.day: 23.03.12 for winter and 17.07.12, 5.day: 24.03.12 for winter and 18.07.12).

Fıgure 4.10 Comparison of MOVES emission factors for NO_x (1.day: 20.02.12 for winter and 14.07.12 for summer sampling, 2.day: 21.03.12 for winter and 15.07.12, 3.day: 22.03.12 for winter and 16.07.12, 4.day: 23.03.12 for winter and 17.07.12, 5.day: 24.03.12 for winter and 18.07.12).
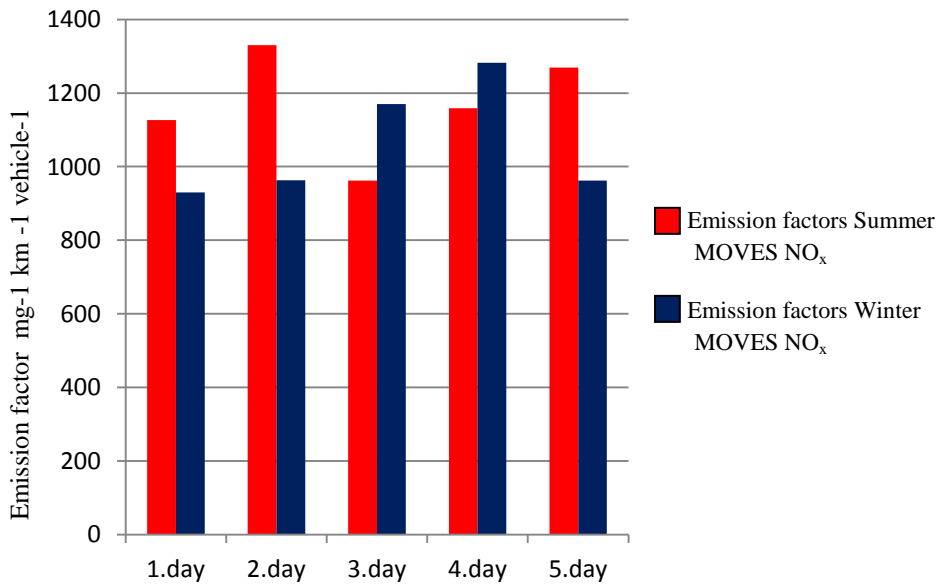
Figure 4.11 Comparison of sampling emission factors for CO (1.day: 20.02.12 for winter and 14.07.12 for summer sampling, 2.day: 21.03.12 for winter and 15.07.12, 3.day: 22.03.12 for winter and 16.07.12, 4.day: 23.03.12 for winter and 17.07.12, 5.day: 24.03.12 for winter and 18.07.12).
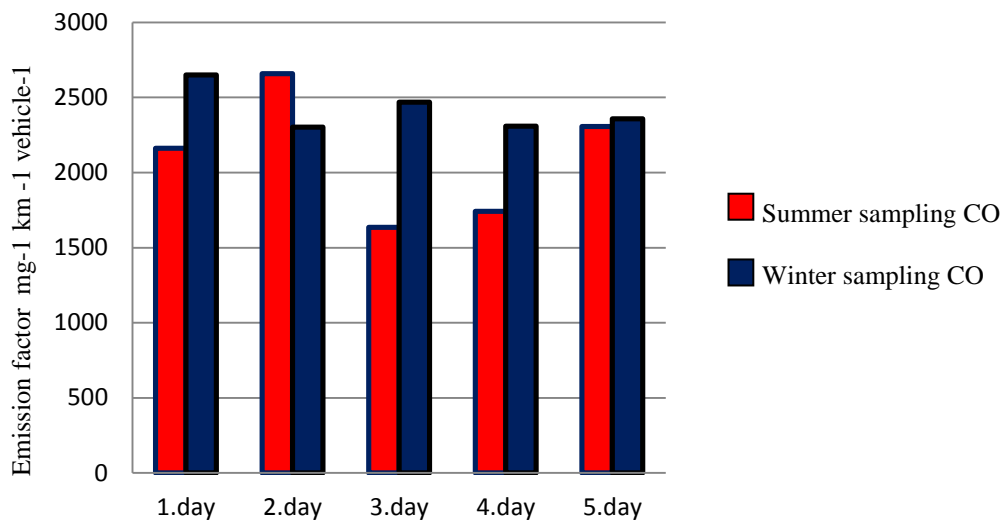

Figure 4.12 Comparison of sampling emission factors for NO_x (1.day: 20.02.12 for winter and 14.07.12 for summer sampling, 2.day: 21.03.12 for winter and 15.07.12, 3.day: 22.03.12 for winter and 16.07.12, 4.day: 23.03.12 for winter and 17.07.12, 5.day: 24.03.12 for winter and 18.07.12).
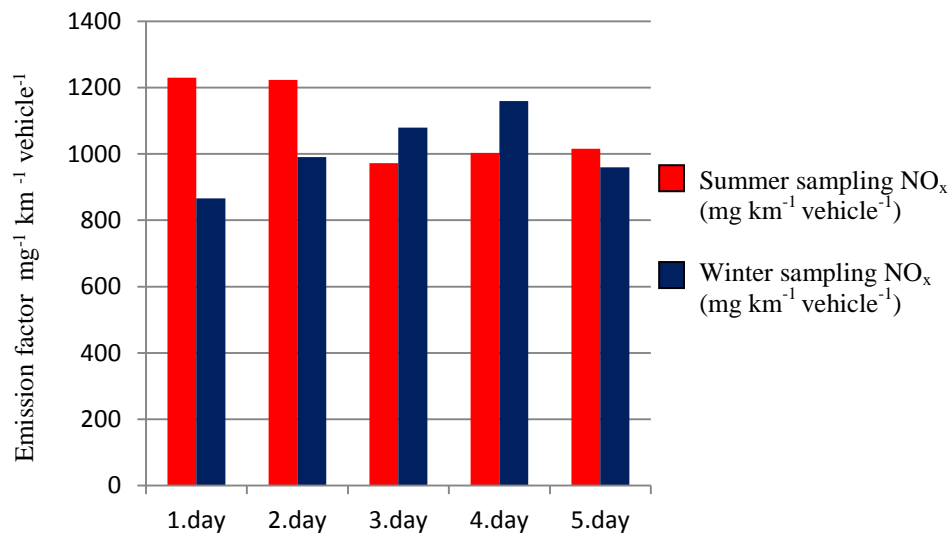
Table 4.20 Comparison of MOVES and sampling emission factors

Date	Seasons	Emission per vehicle			
		CO $(mg\,km^{-1}vehicle^{-1})$		NOx $(mg\,km^{-1}vehicle^{-1})$	
		MOVES	Sampling	MOVES	Sampling
14.07.2012	S	2720	2162.80	1127	1230.25
15.07.2012	S	2388.222	2657.55	1330.63	1223.68
16.07.2012	S	1491	1636.38	962	972.40
17.07.2012	S	1797	1743.12	1159	1002.94
18.07.2012	S	2278	2307.88	1269	1015.55
19.07.2012	S	2194	2143.68	1223	1054.33
20.02.2012	W	2619.309	2650.853	930.111	865.758
21.02.2012	W	2470.986	2302.896	962.834	990.634
22.02.2012	W	2433.345	2469.754	1170.302	1079.858
23.02.2012	W	2301.532	2309.424	1282.312	1159.157
24.02.2012	W	2322.879	2357.672	961.967	959.633

Figure 4.13 Comparison of MOVES and sampling emission factors for CO (1.day: 20.02.12 for winter and 14.07.12 for summer sampling, 2.day: 21.03.12 for winter and 15.07.12, 3.day: 22.03.12 for winter and 16.07.12, 4.day: 23.03.12 for winter and 17.07.12, 5.day: 24.03.12 for winter and 18.07.12).
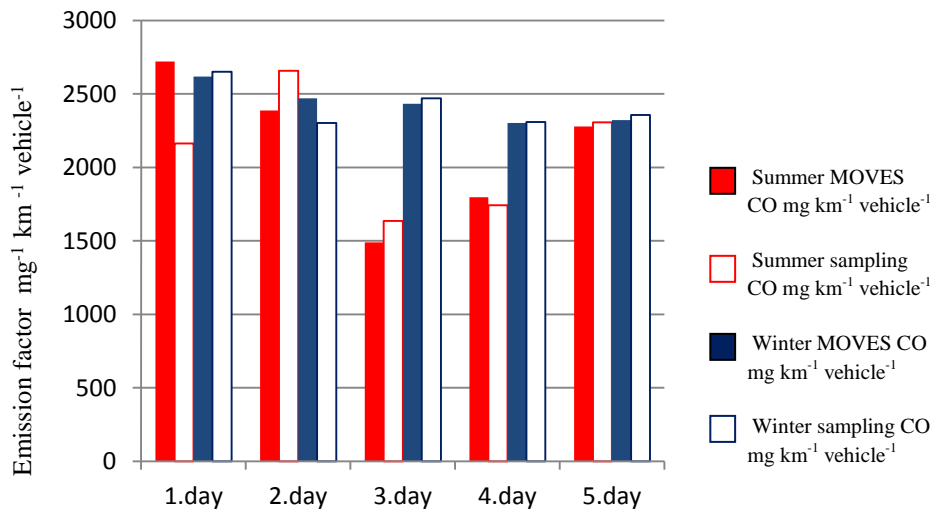
Figure 4.14 Comparison of MOVES and sampling emission factors for NO_x (1.day: 20.02.12 for winter and 14.07.12 for summer sampling, 2.day: 21.03.12 for winter and 15.07.12, 3.day: 22.03.12 for winter and 16.07.12, 4.day: 23.03.12 for winter and 17.07.12, 5.day: 24.03.12 for winter and 18.07.12).
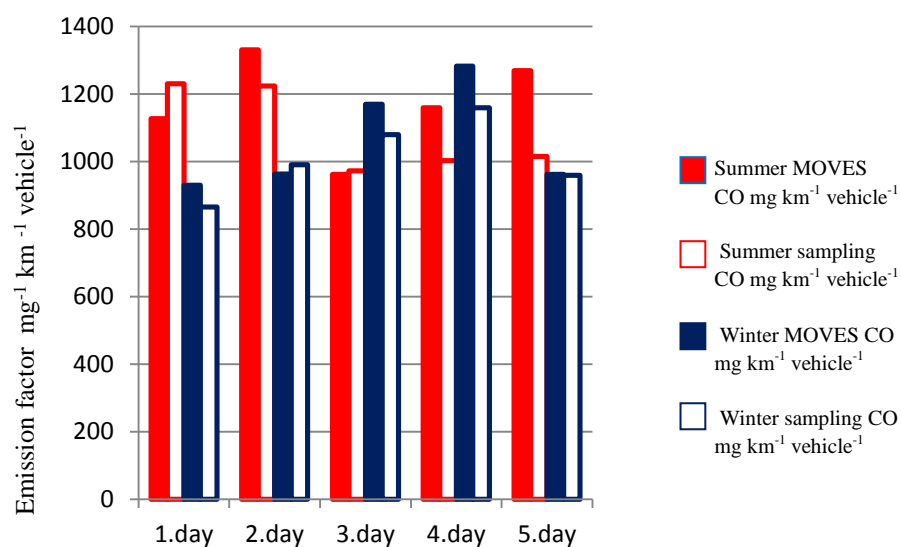
MOVES model errors vary between -9.75 and 20.49 % for CO. The mean and mean absolute model errors were calculated as 0.51 and 5.40, respectively. The maximum model error occurred for the summer sampling campaign. Similarly for NOx modeling results, model errors vary between -9.16 and 19.97 %. The mean and mean absolute model errors were calculated as 6.05 and 8.44, respectively. The maximum model error occurred for the summer sampling campaign as it was the case for CO modeling results. It can be concluded in general for both CO and NOx that MOVES provided more consistent results for the winter sampling period.

Table 4.21 The difference between MOVES and sampling emission factors expressed in terms of model errors (%) (S: Summer W: Winter)

Date	Seasons	CO model error (%)	NO$_x$ model error (%)
14.07.2012	S	20.48	-9.16
15.07.2012	S	-11.27	8.03
16.07.2012	S	-9.75	-1.08
17.07.2012	S	2.99	13.46
18.07.2012	S	-1.31	19.97
19.07.2012	S	2.29	13.79
20.02.2012	W	-1.20	6.91
21.02.2012	W	6.80	-2.88
22.02.2012	W	-1.49	7.72
23.02.2012	W	-0.3429	9.604137
24.02.2012	W	-1.49784	0.242628

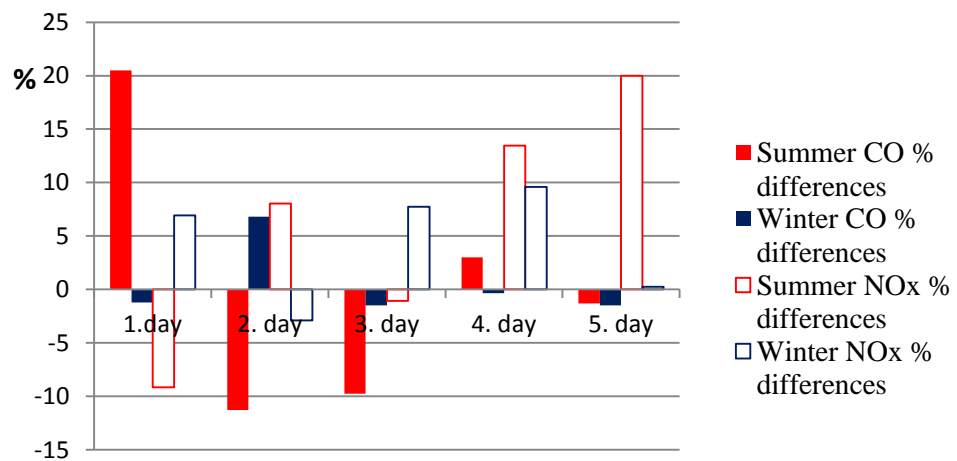Figure 4.15 MOVES modeling errors (%).

CHAPTER FIVE

CONCLUSIONS AND SUGGESTIONS

Emissions of CO, NO_x and sixteen PAH compounds including naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranhene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3,cd)pyrene, dibenz(a,h)anthracene, benzo(g,h,i)perylene were investigated for the Karşıyaka tunnel in Izmir. Sampling campaigns were carried out inside the Karşıyaka tunnel at two sampling locations in the winter and in the summer to determine emission factors from motor vehicles and to investigate seasonal variations of CO, NO_x and PAHs traffic emissions. Emission factors of these pollutants were calculated based on measurements and the emissions model MOVES. Model errors vary within an acceptable range and the mean errors are also acceptable considering that some default databases pertaining to a different country were used. It is possible to improve modeling results by using vehicle age distribution relevant for this study. Furthermore, a more detailed breakdown of vehicles passing through the tunnels during the sampling is required to further improve the accuracy of modeling results.

PAH sampling results indicate that emission factors are higher for the winter than for the summer. The reason for this may be a different vehicle fleet. It should be also noted that the most important source of PAHs is incomplete combustion. Therefore, emissions of PAHs decrease with increasing temperature, because temperature has a negative impact on chemical reactions of PAHs.

Kristensson et al. (2004) conducted measurements to determine real-world traffic emission factors for a number of gaseous and particle pollutants in a road tunnel in Stockholm. As a result, average CO, NO_x emission factors found to 5300, 1400 mg $veh^{-1}km^{-1}$, respectively. These results are comparable with results obtained in this study, although pollutants accumulating in the Karşıyaka tunnels are less with respect to CO and NO_x emissions.

Furthermore, the average emission factor for naphthalene was 159.8µg veh^{-1} km^{-1} in the study by Ho et al. (2003). In our study, the highest PAH emission factor was determined as 110.27 µg veh^{-1} km^{-1}, which was for naphthalene, if the concentrations of gaseous and particulate phase polyaromatic hydrocarbons are taken as the total concentration.

According to the current literature, this study is unique in the sense that it was carried out for a tunnel setting in Turkey for the first time. It is possible using the findings of this study to produce input data for a subsequent study with a dispersion model used to determine air contamination by traffic. With the results of such a modeling study, it is also possible to determine air pollution projections for different vehicle traffic scenarios for this particular section of highway.

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