

The Composition of Non-methane Hydrocarbons Determined from a Tunnel of Seoul During Winter 2000

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Abstract

Measurements of non-methane hydrocarbons (NMHC) were carried out in the Sangdo tunnel and on a nearby roadway in Seoul during the periods of heavy (low speed with $\sim 20 \text{ km h}^{-1}$) and light (high speed with $\sim 60 \text{ km h}^{-1}$) traffic in February 2000. In the tunnel, the total NMHC levels during the heavy traffic period were higher than those during the light traffic period by a factor of 2. This was due to the increase of emissions at the low vehicle speed period and the higher dilution effect derived from faster flow of tunnel air at the high vehicle speed period. The average total NMHC concentration in the tunnel was 1.7 times as high as that on the roadway. The species with the highest concentration in the tunnel was ethylene (50.1 ppb), followed by n-butane (34.1 ppb) and propane (21.9 ppb). The concentration ranking in the tunnel was generally in good agreement with that on the roadway, suggesting that the NMHC compositions in the tunnel and on the nearby roadway were primarily determined by vehicle exhausts. However, the NMHC compositions in the Sangdo tunnel do not agree well with other foreign study results, reflecting that the characteristics of vehicle exhausts of Seoul is different from those of other cities. The most prominent difference between this study and other studies is the high mass fractions of butanes and propane. It may be attributed to the wide use of butane-fueled vehicles.

Key words : Tunnel study, Non-methane hydrocarbon, Vehicular emissions, Vehicle speed dependency of emissions

1. INTRODUCTION

In most urban areas, emissions of non-methane hydrocarbons (NMHC) from motor vehicles have been recognized as one of the major contributors to the formation of photochemical smog and the detrimental effects on human health. Consequently, several studies

on motor vehicle emissions have been carried out in various urban areas (see, for example, Staehelin *et al.*, 1998; Duffy and Nelson, 1996; Sagebiel *et al.*, 1996). In Korea, most of the measurements of vehicular emissions have been limited to total hydrocarbons (THC), CO, CO₂, SO₂, and NO_x. There is only one reported tunnel study for individual NMHC in Seoul (Kim *et al.*, 1999). Speciation of NMHC is very important to understand the effects of motor vehicle emissions on atmospheric environment and on human health since each hydrocarbon species has different toxicity and/or

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ozone-forming potential.

There are two widely used methods to determine the vehicular emission profiles: dynamometer test on individual vehicle and the measurements in a tunnel. In the former approach, operating conditions and fuel composition can be controlled. However, it is disadvantageous for cost and the amount of time consumed and does not represent a composite of many on-road vehicles. The latter method, the one which we chose in this study, has been widely used to determine the NMHC speciation of vehicle emissions in the past decade (Mugica *et al.*, 1998; Gertler *et al.*, 1996; Haszpra and Szilágyi, 1994; Pierson *et al.*, 1990). The compositions of the NMHC species in the tunnel air are believed to be representative of a large number of vehicles and fuel types used broadly in urban areas (Lonneman *et al.*, 1986).

At present, all gasoline-fueled vehicles in Korea are equipped with catalytic converters and have used only unleaded fuels since 1989. The total number of vehicles in Seoul as of February 2000 is over 2.3 million. Butane-fueled (generally known LPG) vehicle is about 10% of the total number of vehicles in Seoul corresponding to a total number of about 220,000 (Seoul Information, 2000). It implies that the compositions of vehicle exhaust in Seoul can be different from those of other foreign urban areas. Therefore, this tunnel study is thought to give a unique result.

Most of the tunnel studies have focused on high-speed driving conditions in the highway tunnels (Touaty and Bonsang, 2000; Fraser *et al.*, 1998; Gertler *et al.*, 1996). This driving pattern may not be realistic enough to represent traffic-related pollution in urban areas because vehicles travel in a various velocity such as accelerating, cruising, and decelerating stage.

In this study, to obtain actual vehicular emission profiles for the NMHC in Seoul, measurements were carried out from a tunnel under high and low speed driving conditions with both moving and standstill of vehicles. A tunnel measurement also was carried out on a roadway near the tunnel to compare the NMHC composition between inside the tunnel and on the road-

way. Furthermore, to examine the distinguishing characteristics of vehicle emissions in this study, we compared the results of the speciation of vehicle exhausts with the results from other recent tunnel studies.

2. EXPERIMENTAL

2.1 Tunnel descriptions

The sketch of the Sangdo tunnel is illustrated in Fig. 1. The tunnel is a two-bore tunnel with two-lanes per bore with the dimension of 566 (long), 9 (wide), and 7 m (high). The cross sectional area of the tunnel is 57 m², and the internal volume of the tunnel is 32,400 m³. The tunnel connecting the Han River Bridge is located in Sangdo village, a part of Seoul city. This tunnel is not equipped with any forced ventilation system. Also, since people were not allowed to pass through the tunnel, all the emissions of NMHC in the tunnel mainly come from motor vehicles. Heavy traffic usually begins at about 07:30 am and comes to an end at about 09:30 am. During this time period, all vehicles traveling through the tunnel experience repetitive steps of start, moving, and stop with an average speed of ~20 km h⁻¹. Whereas, traffic was relatively light from 07:00 am to 07:30 am except for sporadic light braking or slowdown at the exit. During this time period, the average speed of traveling vehicles was approximately ~60 km h⁻¹. The compositions and number of vehicles passing through the tunnel were determined by direct counting. A total of 9,548 vehicles during the whole sampling period was counted, 67% of them were gasoline-fueled vehicles, 20% of diesel-fueled vehicles, 12% of butane-fueled vehicles, and 1% of gasoline-fueled motor cycles.

2.2 Sampling and analysis

The NMHC measurements were carried out during the four-day periods, between 21 and 28 February 2000. Grab sampling was performed by putting air into a 6-L SUMMA polished stainless steel canister treated under the vacuum of 10⁻⁴ torr. In the tunnel, two samples were collected with the sampling time of 30 min

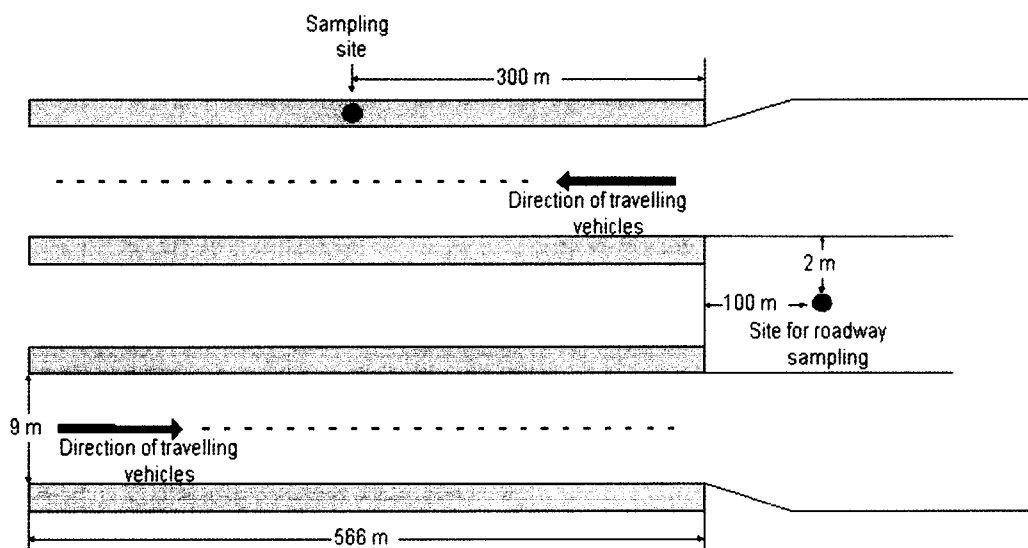


Fig. 1. The sketch of the Sangdo tunnel used in this study.

Table 1. Individual runs in the Sangdo tunnel study.

Run	Date	Sampling time		Vehicles	Temperature (°C)	Relative Humidity (%)
		Inside of tunnel	Roadway			
1	2/21/2000	07:00 ~ 07:30	07:00 ~ 08:00	1,254	-5.0	44
		07:30 ~ 08:00		1,035	-4.9	44
2	2/24/2000	07:00 ~ 07:30	07:00 ~ 08:00	1,087	-5.8	48
		07:30 ~ 08:00		1,224	-5.9	49
3	2/25/2000	07:00 ~ 07:30	07:00 ~ 08:00	1,420	-5.8	52
		07:30 ~ 08:00		1,195	-5.5	53
4	2/28/2000	07:00 ~ 07:30	07:00 ~ 08:00	1,304	-5.8	38
		07:30 ~ 08:00		1,029	-5.7	41

each while on the roadway one sample with the sampling time of 60 min was collected. Sampling period was between 07:00 am and 08:00 am. Sampling runs of 30-min and 60-min duration were conducted simultaneously at the center of the tunnel and on the roadway, respectively. The total number of samples collected in the tunnel and on the roadway were eight and four, respectively. Table 1 gives the conditions for each tunnel run in the study. The sampling time was chosen to represent each characteristic of high and low speed driving. As shown in Fig. 1, tunnel sampling site is 300 m away from the entrance of the tunnel and its

position was 1.8 and 2.0 m from the ground level and passing vehicles, respectively. The roadway sampling was carried out on a site 100 m from the entrance of the tunnel. The roadway site is highly dominated by motor vehicle traffic. The sampling method used on the roadway was identical to the tunnel one. Airflow speed in the tunnel was monitored by a portable anemometer at the center of the tunnel.

The canisters were analyzed by a GC/FID (STAR 3600CX, Varian, USA) and GC/MS (3400CX GC & Saturn 2000 MS, Varian, USA) at Korea Institute Science and Technology (KIST). A GC/FID was used to

quantify C₂-C₃ hydrocarbons. GC/MS was used to identify C₂-C₉ hydrocarbons and quantify C₄-C₉ hydrocarbons. Precision, as determined from five replicate analyses of the standards and samples, is within $\pm 15\%$ for the compounds at the concentrations above 5 ppbC and the lower quantifiable limits were between 0.1 and 0.5 ppbC depending on component for the 200 ml of sample concentrated. The accuracy was demonstrated through the comparison analysis with Atm AA, an environmental consulting laboratory, USA on four of the same samples. The results show that the relative errors calculated on the basis of Atm AA range from 3 to 49%. The analytical methodology has been outlined previously (Na and Kim, 2000).

3. RESULTS AND DISCUSSION

3.1 General characteristics

The average concentrations and standard deviations of non-methane hydrocarbons (NMHC), and their classes measured in the Sangdo tunnel and on the roadway are given in Table 2. The total NMHC levels in the tunnel at the low vehicle speed period (1,398.9 ppbC) were a factor of approximately 2 higher than those at the high vehicle speed period (765.3 ppbC). When the vehicle speeds were low and high, the ranges of air flow speeds in the tunnel were 0.6 ~ 1.5 m s⁻¹ and 3.8 ~ 5.5 m s⁻¹, respectively. It shows that airflow rate in the tunnel depends on the speed of vehicle passing through the tunnel. A recent study by Touaty and Bonsang (2000) reported that the total NMHC emission factor decreases with increasing vehicle speed in the velocity ranges of 10 to 100 km h⁻¹. Similarly, it was reported that in the velocity ranges of 10 km h⁻¹ to 100 km h⁻¹, benzene, toluene, and ethylbenzene emissions were reduced as vehicle speed increases (Heeb *et al.*, 2000). Thus, lower NMHC levels at the high-speed period may be caused by stronger dilution effect derived from the higher air flow speed and the decrease of emissions with high vehicle speed.

In the tunnel, alkanes is the most abundant, followed by aromatics, alkenes, alkynes, and naphthenes. This

pattern of concentration ranking is consistent with that on the roadway. The average total NMHC concentration in the tunnel (1,082 ppbC) was 1.7 times as high as that on the roadway (622.9 ppbC). It may be attributed to the degree of dispersion and the effects of mixing with fresh air. The most abundant compounds observed in the tunnel were ethylene (50.1 ppb), followed by n-butane (34.1 ppb) and propane (21.9 ppb). Higher concentrations of butane and propane are a distinguishing feature of the Sangdo tunnel compared to other reported tunnel study results. The reason for this will be explained in section 3.2. The concentration ranking of NMHC in the tunnel is generally in good agreement with that on the roadway, suggesting that the NMHC compositions of the tunnel and roadway are primarily determined by the vehicle exhausts.

3.2 Comparison with other tunnel studies

Table 3 compares the compositions of NMHC reported in this study with those from other tunnel studies, and also presents the compositions of winter grade unleaded gasoline used during this study. The gasoline sample was blended on the basis of a market share of the five largest gasoline vendors in Seoul area. Analysis of the sample was conducted by Korea Petroleum Quality Inspection Institute (KPQII) for the purpose of determining its chemical composition. The specifications of the mixed fuels were Reid vapor pressure of 74.5 kPa, 44.0% alkanes, 18.1% alkenes, 30.7%, aromatics, and 7.2% naphthenes on the weight base. It has been reported that motor fuel composition is changed seasonally to promote optimum vehicle start-up and good drive with winter fuels having a higher volatility than summer fuels (Stump *et al.*, 1990). Therefore, it is important to obtain each profile of vehicle fuels for each season.

All compositions are expressed as weight percent of total NMHC. In the case of other studies, the original results are presented without any normalization. As shown in Table 2, the differences between tunnel and roadway in absolute concentrations are large. However, the differences in the weight fractions are not so

Table 2. Concentrations of the non-methane hydrocarbon species in the Sangdo tunnel air in Seoul. (unit: ppb)

	Tunnel				L/H**	Roadway	
	High speed (~ 60 km h ⁻¹ *)		Low speed (~ 20 km h ⁻¹)			Mean	S. D.
	Mean	S.D.	Mean	S. D.			
Ethane	15.4	8.0	16.3	7.1	1.1	11.4	3.2
Propane	17.1	8.0	26.7	9.2	1.6	13.1	4.2
Butane	22.7	10.2	45.4	25.2	2.0	20.1	9.3
i-Butane	13.5	6.2	24.3	11.5	1.8	11.9	5.6
Pentane	4.0	1.5	7.9	3.4	2.0	3.6	2.4
i-Pentane	4.5	1.6	8.4	3.5	1.9	3.8	2.3
2-Methylpentane	3.0	1.1	6.1	2.3	2.0	2.5	1.3
3-Methylpentane	0.6	0.3	1.4	0.5	2.2	0.5	0.2
2,2-Dimethylbutane	0.0	0.0	0.3	0.5	na	0.1	0.2
2,3-Dimethylbutane	2.1	1.0	4.6	1.9	2.2	1.8	1.1
Hexane	1.9	0.7	4.2	1.2	2.3	2.0	1.1
2-Methylhexane	0.7	0.9	1.7	1.3	2.5	0.2	0.2
3-Methylhexane	nd	na	0.5	0.1	na	0.3	0.4
2,3-Dimethylpentane	1.1	0.7	2.8	1.2	2.5	0.9	0.6
2,4-Dimethylpentane	0.2	0.2	0.5	0.2	2.4	0.2	0.2
Heptane	1.1	0.4	2.2	0.9	2.0	0.7	0.5
2,2,4-Trimethylpentane	0.2	0.1	0.3	0.2	1.9	0.0	0.0
2,3,4-Trimethylpentane	0.1	0.1	0.1	0.2	1.1	0.5	0.7
2-Methylheptane	0.2	0.3	0.7	0.3	3.5	0.2	0.3
3-Methylheptane	0.3	0.4	0.9	0.3	3.1	0.3	0.3
Octane	0.4	0.3	0.9	0.3	2.2	0.3	0.3
Nonane	0.2	0.3	0.6	0.2	2.5	0.1	0.1
Ethylene	35.7	16.6	64.6	20.1	1.8	24.7	7.1
Propylene	10.9	5.1	19.5	7.2	1.8	7.4	2.3
1-Butene	4.3	2.1	11.6	7.8	2.7	3.2	2.2
t-2-Butene	1.5	0.7	2.4	0.9	1.6	1.0	0.8
c-2-Butene	1.1	0.5	1.9	1.3	1.7	0.8	1.0
1-Pentene	0.2	0.1	0.8	0.5	3.4	0.2	0.4
Isoprene	0.1	0.2	0.2	0.3	1.2	0.2	0.3
t-2-Pentene	0.7	0.4	1.5	0.7	2.1	0.5	0.6
c-2-Pentene	0.3	0.4	0.9	0.5	2.8	0.2	0.3
2-Methyl-2-butene	1.2	0.6	1.8	0.8	1.5	0.9	0.8
Acetylene	20.5	6.9	21.8	7.5	1.1	15.9	4.0
Cyclopentane	0.4	0.4	1.0	0.6	2.7	0.3	0.5
Methylcyclopentane	1.4	0.5	2.8	1.0	2.0	1.4	0.8
Cyclohexane	0.7	0.4	1.1	0.5	1.6	0.9	0.8
Methylcyclohexane	0.4	0.2	0.9	0.3	2.3	0.3	0.3
Benzene	4.6	1.7	8.5	3.1	1.8	4.2	2.2
Toluene	10.0	3.3	20.4	3.9	2.0	10.3	4.8
Ethylbenzene	1.2	0.5	1.9	0.6	1.6	1.2	0.7
m-+p-Xylene	4.1	4.1	9.3	2.9	2.3	4.8	3.0
o-Xylene	1.8	0.7	2.5	0.8	1.4	1.2	1.0
Styrene	0.1	0.1	nd	na	na	nd	na
1,2,4-Trimethylbenzene	5.5	3.6	7.8	4.4	1.4	1.8	1.5
1,3,5-Trimethylbenzene	1.0	0.6	1.6	0.8	1.7	0.6	0.5
Alkanes (ppbC)	348.6		655.6		1.9	295.6	
Alkenes (ppbC)	144.7		276.7		1.9	101.4	
Alkynes (ppbC)	41.0		43.6		1.1	31.7	
Naphtenes (ppbC)	17.4		34.8		2.0	17.5	
Aromatics (ppbC)	213.6		388.2		1.8	176.7	
Total HCs (ppbC)	765.3		1,398.9		1.8	622.9	

*: Speed of moving vehicles; **: concentration ratios of low (~ 20 km h⁻¹) to high speed (~ 60 km h⁻¹); na: not applicable; nd: below detection limit (< 0.1 ppbC)

Table 3. Composition of the NMHC in the tunnel. (% of total mass)

	This study		Roadway	Gasoline	Cassiar	Fort McHenry	Harbour	Mexican	Tegel
	Vehicle speeds (km h ⁻¹)								
	~60	~20							
Ethane	4.3	2.5	4.0	0.0	2.2	2.0	2.0	0.6	2.1
Propane	7.0	6.0	6.6	0.0	7.5	0.2	4.4	2.0	1.0
Butane	12.3	13.5	13.4	2.7	4.4	2.4	3.9	2.4	2.9
i-Butane	7.4	7.2	7.9	1.4	0.1	0.3	2.7	0.9	1.6
Pentane	2.7	2.9	3.0	5.6	2.9	3.6	2.5	4.5	2.8
i-Pentane	3.0	3.1	3.2	11.6	7.0	11.8	6.4	5.7	9.1
2-Methylpentane	2.4	2.7	2.5	6.7	2.6	3.8	2.6	2.7	3.7
3-Methylpentane	0.5	0.6	0.5	4.5	1.7	2.1	1.7	1.7	2.0
2,2-Dimethylbutane	0.0	0.1	0.1	0.8	0.3	1.0		0.3	1.7
2,3-Dimethylbutane	1.7	2.0	1.8	1.4	0.8	1.4			
Hexane	1.5	1.9	2.0	4.5	1.5	1.7	1.6	3.0	1.3
2-Methylhexane	0.6	0.9	0.2	5.0	0.8	1.3		1.0	1.2
3-Methylhexane	0.0	0.3	0.3	4.0	0.9	1.8		1.1	1.2
2,3-Dimethylpentane	1.0	1.4	1.0	0.0	1.9			0.4	0.5
2,4-Dimethylpentane	0.2	0.3	0.2	0.8	1.1	0.9	0.4	0.3	0.4
Heptane	1.0	1.1	0.9	2.8	0.6		0.7	1.3	0.9
2,2,4-Trimethylpentane	0.2	0.2	0.0	0.0	2.9	4.3		1.3	1.6
2,3,4-Trimethylpentane	0.1	0.1	0.7	0.1	0.9	1.5		0.6	0.2
2-Methylheptane	0.2	0.4	0.3	1.1	0.3			0.6	0.4
3-Methylheptane	0.3	0.5	0.4	1.3	0.4			0.6	0.4
Octane	0.4	0.5	0.4	1.0	0.3	0.4	0.3	0.9	0.4
Nonane	0.3	0.4	0.1	0.3	0.2	0.3		0.8	0.3
Ethylene	9.4	9.3	8.0	0.0	9.4	8.1	6.3	4.1	9.0
Propylene	4.3	4.2	3.6	0.0	5.1	3.1	5.2	1.7	4.2
1-Butene	2.3	3.3	2.1	0.3	2.7		2.7	0.6	1.6
t-2-Butene	0.8	0.7	0.7	1.1	0.4		0.7	0.3	0.3
c-2-Butene	0.6	0.5	0.5	0.8	0.3		0.6	0.3	0.2
1-Pentene	0.2	0.3	0.1	0.7	0.3			0.5	0.3
Isoprene	0.1	0.1	0.1	0.0	0.1			0.3	0.4
t-2-Pentene	0.5	0.5	0.4	1.9	0.5			0.2	0.5
c-2-Pentene	0.2	0.3	0.2	1.0	0.3			0.5	0.2
2-Methyl-2-butene	0.8	0.6	0.7	2.8	0.8			0.3	0.6
Acetylene	5.0	2.9	4.7	0.0	4.0	2.8	6.7	7.2	4.6
Cyclopentane	0.2	0.4	0.3	0.7	0.4		0.2	0.2	1.2
Methylcyclopentane	1.1	1.2	1.3	2.7	1.0	1.3	1.0	0.9	1.0
Cyclohexane	0.6	0.5	0.9	0.5	0.2		0.4	0.3	
Methylcyclohexane	0.4	0.4	0.3	1.1	0.3		0.5	0.5	0.5
Benzene	3.4	3.4	3.7	2.9	4.5	5.5	5.2	2.6	4.0
Toluene	8.6	9.6	10.9	12.9	8.2	10.7	9.3	5.4	10.6
Ethylbenzene	1.2	1.0	1.5	1.5	1.4	2.6	1.3	1.4	2.0
m-+p-Xylene	4.1	5.1	5.8	5.2	4.5	8.8	4.9	5.0	5.7
o-Xylene	1.8	1.3	1.4	2.2	1.7	3.2	1.8	1.8	2.1
Styrene	0.1	0.0	0.0	0.0	0.3			0.3	0.5
1,2,4-Trimethylbenzene	6.1	4.8	2.5	4.7	1.6	5.6	1.1	1.7	3.1
1,3,5-Trimethylbenzene	1.1	1.0	0.8	1.3	0.5	1.5	0.4	1.0	0.9

Cassiar: Rogak *et al.* (1998); Fort McHenry and Tuscarora: Gertler *et al.* (1996)Harbour: Duffy and Nelson (1996); Mexican: Mugica *et al.* (1998); Tegel: Thijssse *et al.* (1999)

Note: Result of Mexican tunnel study is expressed in terms of ppbC%.

high. Furthermore, a very good correlation between the weight fraction of each compound obtained from the tunnel and roadway was observed (R -square = 0.95, slope = 1.01, intercept = -0.04). It suggests that motor vehicle profile obtained from the roadway measurements can be substituted for that measured from tunnel studies. As shown in Table 3, each of the abundance of NMHC compositions does not agree well with each other, reflecting the characteristics of vehicle exhausts of each urban area.

The most prominent difference between this study and other studies is higher mass fractions of butanes and propane in the Sangdo tunnel. It may be attributed to butane-fueled vehicles. At present, the number of vehicles as of the end of May 2000 is over 2.3 million. Butane-fueled vehicle is about 10% of the total number of vehicles corresponding to about 220,000 (Seoul Information, 2000). The use of butane fuel is limited to only taxicabs and recreational vehicles in Korea. During the cold months (from November to March), propane is added to the butane fuel between 5 and 30 wt%. Propane content in the fuel was 30 wt% during the study period. As shown in Table 3, propane and butane in gasoline are not present. Since the average ambient temperature in the tunnel during the study period was -5°C , the evaporation of butanes might be not so effective. Furthermore, it was reported that evaporative non-methane hydrocarbons contributed $10.3 \pm 0.8\%$ of the total on-road emissions rate on average and unburned gasoline contributed $63.40 \pm 7.0\%$ of exhaust gases for light-duty vehicles operating in steady-state driving conditions (McLaren *et al.*, 1996). Additionally, it was observed that approximately 50% of the emissions from three late model vehicles coming directly from gasoline which has survived the combustion process (Gertler *et al.*, 1996). Therefore, the unburned butane fuel may be a major contributor to large portions of butane and propane in the Sangdo tunnel. To support this suggestion, we illustrated the relationship between the compositions of butane-fueled vehicles passing through the tunnel and the fractions of butane to the total NMHC concentrations during each sampl-

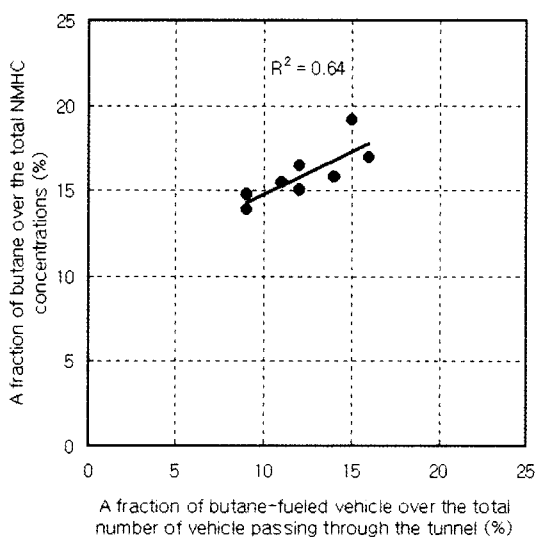


Fig. 2. Relationship between butane-fueled vehicle fractions to the total number of vehicles passing through the tunnel and butane fractions to the total NMHC concentrations.

ing period in Fig. 2. The amounts of butane to the total NMHC show a positive trend with the compositions of the butane-fueled vehicles. It shows that butane vehicles are a major contributor to its concentration in the tunnel. In connection with this phenomenon, as shown in Table 3, the results at the Cassiar tunnel in Canada shows the highest propane mass fractions. This was explained by the presence of propane-powered vehicles in Canada (Rogak *et al.*, 1998). It shows that the ambient concentrations of NMHC are affected by the pattern of fuel usage.

The levels of benzene in vehicle exhausts have attracted a considerable attention because benzene is classified as known or probable carcinogens by the United States Environment Protection Authority (USEPA) (Calabrese and Kenyon, 1991). Vehicle emissions include both combusted hydrocarbons and uncombusted hydrocarbons. Therefore, to reduce target hydrocarbons in vehicle emissions, it is important to cut down their contents in vehicle fuel. Now, Korean governmental regulation on the content (on volume base) of benzene in gasoline fuel is set below 2%. As shown

in Table 3, the Sangdo profiles have somewhat lower benzene compared with those of other studies. It may be attributed to the government regulation on benzene contents in vehicle fuels and the installation of 3-way catalysts to all vehicles. In this study, comparison between gasoline and tunnel compositions in the tunnel air shows that benzene is enriched relative to other aromatics in exhaust compared to its proportion in the gasoline. The reason for this has been explained that benzene is synthesized through the dealkylation of higher molecular weight aromatics (Fraser *et al.*, 1998; McLaren *et al.*, 1996). Additionally, evidence of this process was demonstrated by Kaiser *et al.* (1991) by burning pure toluene in a spark-ignited engine and finding benzene to represent 6% of the combustion product.

4. SUMMARY

The non-methane hydrocarbon (NMHC) concentrations were measured in a tunnel and on the nearby roadway for the two different speeds of vehicles (~ 20 km h⁻¹ and ~ 60 km h⁻¹). In the tunnel, the total NMHC levels at the low vehicle speed period were higher than those at the high vehicle speed period by a factor of 2. This was due to the higher dilution effects derived from faster flow of tunnel air at the high-vehicle speed period and the increase of emissions at the low vehicle speed period. In the tunnel, alkanes is the most abundant, followed by aromatics, alkenes, alkynes, and naphthenes. This concentration ranking is consistent with that on the roadway. The average total NMHC concentration in the tunnel was 1.7 times as high as that on the roadway. It may be originated from the difference of the effects of fresh air on the two sites and the degree of dispersion. The most abundant compounds observed in the tunnel were ethylene, followed by n-butane and propane. This concentration ranking was also in good agreement with that on the roadway, suggesting that the NMHC compositions of the tunnel and the nearby roadway were primarily determined by the vehicle exhausts.

The differences in the absolute concentration between the tunnel and on the roadway were large. However, the differences in the weight fractions were minor. Furthermore, good correlation between the weight fraction of each compound obtained in the tunnel and on the roadway was observed. It suggests that a motor vehicle emission profile obtained from the roadway measurements can substitute for that measured from tunnel studies.

The NMHC compositions in the Sangdo tunnel did not agree well with other foreign studies, reflecting the unique characteristics of vehicle emissions of Seoul. The most prominent difference between this study and other studies is higher mass fractions of butanes and propane in the Sangdo tunnel. It may be attributed to the wide use of butane-fueled vehicles, showing that the ambient concentrations of NMHC are affected by the pattern of fuel usage.

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