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Seasonal vehicle emission rate of chemical compounds related to fuel type from on-road tunnel measurement

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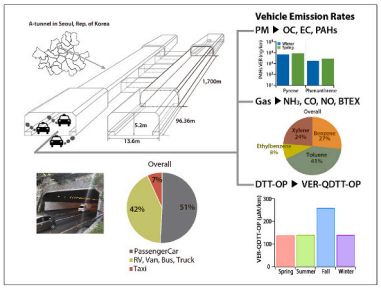
HIGHLIGHTS

- On-road measurement inside and outside of Tunnel at the same time.
- Determination of vehicle emission rates of chemical compounds and oxidative potential.
- Seasonal Characteristics of vehicle emission rate.

GRAPHICAL ABSTRACT



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ABSTRACT

The vehicle emission rates (VER) of particulate matter (PM) and gaseous compounds were determined using analysis of the concentrations inside and outside the tunnel. The types of vehicles flowing during the observation period were classified into gasoline, diesel, and liquefied petroleum gas (LPG) vehicles, and factors affecting the calculated vehicle emissions were identified. This study presented $PM_{2.5}$, OC, EC, NH_3, CO, and NO at 11.21, 3.81, 2.82, 16.74, 563.61, and 257.50 mg/km, respectively. The $PM_{2.5}$ and NO were higher in winter than in summer. The VER of chemical compounds, such as polycyclic aromatic hydrocarbons, benzene, toluene, ethylbenzene, and xylene, were presented. The study results present the characteristics of vehicle emission rate according to the fuel type during the holiday and non-holiday periods. It is expected that the results of this study can be used as data for international responses to reduce vehicle emissions in the future.

1. Background

Air pollutants are known to be a factor that increases the incidence of respiratory and cardiovascular diseases, and the resulting death rate (Kim et al., 2015; Kirrane et al., 2019). In particular, 55% of the world's population resides in urban areas due to the high-level of

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industrialization and urbanization, and in Africa and Asia, the number of residents living in urban areas is projected to increase to 68% by 2050 (Tran et al., 2021). High-density population consequently increases air pollutant exposure to the human body (Tran et al., 2021). Traffic emission using gasoline and diesel vehicles has been indicated as a primary source of air pollutants in urban areas (Matsumoto et al., 2006; Perrino et al., 2002). Known air pollutants from traffic emission consist of PM (e.g., PM_{10}, $PM_{2.5}$, poly-aromatic hydrocarbons (PAHs), nitrogen oxides, metals, and black carbon) and gaseous compounds (e.g., volatile organic compounds (VOCs), nitrogen oxides, CO, and CO_2, etc.) (Hallquist et al., 2009; Ng et al., 2007; Shakya and Griffin, 2010). In particular, the chemical compounds emitted through traffic emission, such as benzene, formaldehyde, benzo(a)pyrene, and black carbon, are sufficiently harmful to the human body to be classified as carcinogens by the International Agency for Research on Cancer (IARC). Therefore, there is a need to understand the contribution of traffic emissions to air quality management in urban areas. To this end, it is necessary to investigate realistic VER to quantify the characteristics of vehicle emissions.

Based on previous research, the vehicle emission rates (VER) can be classified into three main methods: (1) chassis dynamometer test, (2) analysis of roadside pollutant concentrations using satellite imagery, and (3) experiment with measuring vehicle emissions using tunnels. The chassis dynamometer test is a method for measuring individual VER under controlled conditions. It is useful for examining the efficiency of fuel quality from different engine systems, direct measurement of air pollutants, and their control devices (Chiang et al., 2012; Heeb et al., 2003). In addition, the chassis dynamometer test has to date been adapted in many countries as a standard for vehicle emissions test (Chiang et al., 2012; Kim Oanh et al., 2010; Nelson et al., 2008). However, the chassis dynamometer test has drawbacks, in that it is difficult to reflect the effect of actual driving conditions, such as the driver's driving method, and road conditions (Gaga et al., 2018). Analysis of roadside pollutant concentrations using satellite imagery has various advantages, such as remote sensing, generation of extensive time series data, and confirmation of roadside air pollutant concentration according to the amount of traffic (Alvarado et al., 2020; Song et al., 2022). However, the analysis of roadside pollutant concentration using satellite has the technical limitation that it is impossible to quantify the concentration of specific compounds, such as VOCs, and only provides information on the optical aerosol depth and the like (Alvarado et al., 2020; Song et al., 2022; Yang et al., 2020). Meanwhile, an experiment on measuring vehicle emissions using tunnels can deliver many benefits to understand the detailed characteristics of air pollutants according to traffic emissions in a real tunnel condition. The experiment on measuring vehicle emissions in tunnels is characterized by excluding external environmental factors that only belong to a relatively closed system (Chirico et al., 2011). The previous study reported the observation of air pollutants using an Aerosol Mass Spectrometer (AMS) in the Gubrist tunnel in Switzerland, measurement of PM and CO in Yan'an Road tunnel in Shanghai, China, confirmation of air pollutants before/after changes in air emission standards, and cytotoxicity test for vehicle-generated $PM_{2.5}$ (Chirico et al., 2011; Gaga et al., 2018; Osada et al., 2019; Niu et al., 2020). These studies have great significance in conducting a study on air pollutants emitted by vehicles driving in the tunnel. However, since the above studies were performed by estimating the traffic emission in the tunnel, these studies have the limitation that they cannot even suggest the difference in vehicle emissions according to the type of fuel, which is one advantage of the chassis dynamometer test. Moreover, to manage air pollutants in urban areas, it is necessary to understand the difference in emission chemical compounds according to the fuel type of vehicle, and confirm the vehicle types that emit the primary air pollutants to be managed.

This study was conducted to analyze the vehicle emission rate from the tunnel, and to present the characteristics of air pollutant emission according to the fuel type of vehicle. For this study, gaseous chemical compounds, such as $PM_{2.5}$, organic carbon (OC), elemental carbon (EC), VOCs, PAHs, elemental chemical compounds, NO, NO_2, and NH_3, were measured inside and outside the tunnel for four seasons. The number of vehicles that passed the tunnel and the fuel type during the research period were confirmed using video identification and statistical methods. In addition, the study results present the characteristics of VER according to the fuel type during the holiday and non-holiday periods.

2. Method

2.1. Measurement location and period

The tunnel for this study is the second longest tunnel in Seoul, Korea, and located on the Inner Circulation Road. The tunnel is formed as two unidirectional tunnels, in which the length of the tunnel is 1700 m, and the width and height of the tunnel entrance are 13.6 m and 5.2 m, respectively, as shown in Fig. S1 of the Supplementary Information (SI). The air pollutants were measured for a total of 45 days from 28 July to 6 August, 29 September to 7 October in 2018, 28 January to 8 February in 2019, and 14 April to 27 April in 2019 for summer, fall, winter, and spring, respectively. The detailed information for the sampling location can be found elsewhere (Park et al., 2021).

2.2. Traffic volume and wind velocity in tunnel

The diffusion of air pollutants in the tunnel can be affected by wind velocity. In addition, the number and type of vehicles in the tunnel have a close relationship with the air pollutant emissions. In this study, the number and type of vehicles and the wind velocity in the tunnel were measured during the observation period. The number and velocity of vehicles were measured by HD Digital Wave Radar (Smart Sensor HD Model 126, Wavetronix, Provo, UT, USA). Previous study indicated that the uncertainty rate showed less than 2% from the comparison of wind speed of approximately 3.0 m/s, 4.8 m/s, and 5.8 m/s under the two temperature conditions (Park et al., 2021). In addition, wind speed presented less than 10% differences between the cross-section and measurement points.

The fuel types of vehicles were classified into gasoline, diesel, and LPG. The criteria for the vehicle type were automobiles, taxis, and RV/trucks, which represent gasoline, LPG, and diesel, respectively, as fuel types of vehicles based on the official statistical database in Korea. In this study, a total of about three million vehicles (about 70,000 vehicle per day) were monitored by HD Digital Wave radar. To analyze the fuel type of vehicles, a sampling method using video identification was utilized. The automobiles, taxis, and RV/trucks were manually counted for every 10 min per hour during the entire periods. In statistical hypothesis for the sampling method, a result has statistical significance with a 95% confidence level and 3.3% error. The detailed approach can be found in the SI.

The wind velocity inside the tunnel was measured in real-time by a Digital Thermo Air Velocity Transmitter (FTS85, Eyc-tech Inc., China). To confirm the accuracy of the Digital Thermo Air Velocity Transmitter, a separate anemometer was used. As a result of the verification, the deviation between the Digital Thermo Air Velocity Transmitter and the anemometer was less than 2%.

2.3. Experimental method

2.3.1. Analysis of particulate matter

To analyze the concentrations of vehicle emissions inside and outside the tunnel, a set of instruments and samplers were operated as the same time. The concentrations of $PM_{2.5}$ were hourly measured using a set of beta-ray monitor (Model 5014i Beta, ThermoFisher Inc., USA) under a flow rate of 16.67 L/min. Teflon and Quartz filters using 6-h integrated samplers were collected both inside and outside of tunnels at the same time. The analysis of the compounds in $PM_{2.5}$ includes carbon materials (OC, EC) and PAHs (acenaphthylene, fluorene, and phenanthrene) were

analyzed from Quartz filters. The water-soluble ionic compounds (e.g., NO_3^-, SO_4^{2-}, and NH_4^+) and trace elements (e.g., Si, Cl, K, Ca, Ti, Fe, Cu, and Zn) were analyzed from Teflon filters. The analysis of OC and EC adopted the National Institute of Occupational Safety & Health (NIOSH5040) protocol using a Lab-based OCEC Carbon Aerosol Analyzer (Sunset Laboratory Inc., USA). For the analysis of water-soluble ionic components, the Teflon filter was ultrasonically extracted with ultrapure water, and analyzed using ion chromatography (Metrohm 883, Switzerland). The analysis of elements was conducted using an Energy Dispersive X-Ray Fluorescence (ED−XRF) (ARL QUANT'X, Thermo Inc., USA). PAHs were analyzed using daily composite Quartz samples (four samples per day) after OCEC analyses. PAHs were analyzed by GC/MS (GC; 7890A, MS; 5975C, Agilent Technologies, USA) after extracting the filter in which $PM_{2.5}$ was collected in dichloromethane and nitrogen blow-down. The detailed analytical method can be found elsewhere (Song et al., 2020, 2021).

2.3.2. Measurement of gaseous compounds

The gaseous compounds (i.e., NH_3, CO, O_3, SO_2, NO, NO_2, benzene, toluene, ethylbenzene, and xylene (BTEX)), were observed. The NH_3, CO, O_3, SO_2, NO, and NO_2 quantities were measured using a real-time measuring instrument. The VOCs, such as benzene, toluene, ethylbenzene, and xylene, were collected using self-customized samplers for every 24 h. The NH_3 measurement equipment used in this study was real-time measuring equipment (Los Gatos Research (LGR), ABB Inc., Quebec, Canada). The NH_3 measurement instrument was calibrated by a dilution device using a specifically prepared standard. The CO was measured using a Fourier Transform Infrared Spectroscopy (FTIR) gas analyzer (48iQ Carbon Monoxide Analyzer, Thermo Fisher Scientific, USA), and NOx was measured using a chemiluminescence measuring instrument (42iQ NO–NO_2−NOx Analyzer, Thermo Fisher Scientific, USA). All real-time measurement equipment was used before and after performing calibration of the background value. Samples for BTEX were collected using a thermal desorption tube under a flow rate of 50 mL/min for 2 h. The samples were double-sealed immediately with a sealing pack, and refrigerated at 4 °C, before analysis. GC/MS–Thermal Desorption (TD) which can completely separate VOCs without an organic solvent, was used for BTEX analyses. The detailed analytical method can be found elsewhere (Song et al., 2020, 2021). In addition, the previous study clearly indicated that the concentration from the external point 20 m distant from the tunnel can be verified as an indicator of the tunnel entrance (Park et al., 2021).

2.3.3. Analysis of dithiothreitol oxidation potential normalized to quinone (QDTT−OP)

To evaluate the toxicity to $PM_{2.5}$, the oxidative potential (OP) using dithiothreitol (DTT) was evaluated. In detail, the DTT-OP was determined by measuring the absorbance of the residual DTT and the reaction product 2-nitro-5-thiobenzoic (TNB), according to the reaction time between the active oxygen component and DTT in $PM_{2.5}$, with the color development reaction of the residual DTT. In this study, normalization analysis was performed using quinone to improve the reliability of the analysis results. Normalization analysis was divided into two stages, and in the first step, the calibration curve using seven different concentrations of quinone to DTT-OP (QDTT−OP) was set. Then, a tunnel sample was extracted by methanol and deionized water (1:1). The analyzed DTT−OP of tunnel samples was applied to the QDTT−OP calibration curve to determine the tunnel QDTT−OP.

2.4. Vehicle emission rate

The vehicle emissions of PM and gaseous compounds in the tunnel by vehicle numbers and distance were calculated using the analyzed concentrations inside and outside the tunnel. The inlets, started from the two reference points of common distance of each 20 m from the inside and outside of the tunnel entrance, respectively, penetrated into the measurement station with the flow rate of 18 m/s. A previous study showed that the concentration from the external point 20 m distant from the tunnel can be verified as an indicator of the tunnel entrance (Park et al., 2021). To calculate vehicle emissions, the number of vehicles in the tunnel based on the actual measurement, the concentrations inside and outside the tunnel, and the area and wind speed of the tunnel entrance were used. The VER can be determined as shown in Eq. (1):

$$\text{VER (mg/km)} = \sum(C_{in} - C_{out}) \times A \times U \times t \,/\, [N \times L] \quad (1)$$

where, C_{in} and C_{out} are the concentrations of each pollutant measured at the tunnel inside and outside, A is the cross-sectional tunnel area (m^2), U is the wind speed in the tunnel (m/s), t is the analysis reference time (s), N is the number of vehicles that passed through the tunnel at the collection time (#), and L is the length of tunnel (m). The above equation calculates the difference between the concentration of PM and gaseous compounds in the tunnel. Equation (1) can be simplified as Eq. (2):

$$\text{VER (mg/km)} = \triangle C \times \delta \quad (2)$$

where, ΔC is the difference in concentration of PM and gaseous compounds inside and outside the tunnel, and δ is the measured tunnel flow coefficient (m^3/km, Tunnel Flow Coefficient, TFC). The TFC can evaluate the major emission sources of △C by using the vehicle type that passed through the tunnel at the same time as △C measured by component.

3. Results

3.1. Tunnel flow coefficient

The purpose of this study is to present the VER using observation concentrations inside and outside the tunnel. However, as in Eq. (1), vehicle emissions are affected both by the difference in the concentration of compounds inside and outside the tunnel, and by the area of the tunnel, wind velocity, and the number of vehicles. Factors affecting vehicle emissions are expressed as TFC (δ). That is, the TFC can evaluate the effect of vehicle speed other than the concentration difference of compounds inside and outside the tunnel, wind velocity in the tunnel, and traffic rate on unit vehicle emissions.

Fig. S2 of the SI presents the vehicle speed, number of vehicles, and TFC observed in the tunnel for each hour during the study period. The TFC showed a proportional relationship to the vehicle speed flowing in the tunnel. Specifically, looking at the correlation between the vehicle speed and the TFC, the coefficient of determination (r^2) was 0.90. Table S1 of the SI presents the temperature and wind velocity measured during the sampling period. The average of the TFC in fall, winter, spring, and summer is 339.93, 281.27, 218.06, and 198.06 m^3/km, respectively, in the order of highest to lowest. Since there is no significant difference in the vehicle speed and traffic rate at different times in different seasons, the TFC is determined by the influence of the temperature and wind velocity in the tunnel. Also, it is determined that the emissions of air pollutants due to traffic increase in proportion to fuel consumption due to vehicle speed. The detailed results can be found in the SI.

3.2. Concentration of chemical compounds inside and outside the tunnel

Table S2 in SI shows the average concentrations of major compounds observed at inside and outside of the tunnel during the sampling period. The $PM_{2.5}$ concentration observed inside and outside the tunnel was 2.4 times higher than outside. The difference between the inside and outside of the tunnel for water-soluble ions among the $PM_{2.5}$ components were 89.01–127.96%, which was not large, compared to the difference in $PM_{2.5}$ concentration inside and outside the tunnel. On the other hand, in the case of OC and EC constituting $PM_{2.5}$, the inside of the tunnel was higher than the outside of the tunnel on average. The characteristics of

gaseous chemical compounds emitted by traffic were confirmed. Table S2 of the SI shows that the inside of the tunnel was found to show NH_3, CO, SO_2, and NO at 193, 212, 260, and 290%, compared to the outside of the tunnel. That is, among the 6 observed gaseous $PM_{2.5}$ generating precursors, all chemical compounds except O_3 were higher inside the tunnel than outside, due to photochemical reactions. It is estimated that the change in the amount of outside air flowing into the tunnel due to the temperature difference between the inside and outside of the tunnel also affected the results. The detailed results can be found in the SI.

The concentration of the seven element materials, such as Si, Ti, and Fe, was found to be 185% higher on average inside the tunnel, than outside. According to previous studies, the elemental chemical compounds in $PM_{2.5}$ along the road were divided into three categories: (1) road resuspended dust, (2) combustion emissions, and (3) tire wear (Farahani et al., 2021). In this study, winter and spring show higher concentrations than summer and fall. This is determined to be the effect of NaCl sprayed on the road when the road freezes. The concentrations of Na and Cl both inside and outside the tunnel were found to be up to 3700 times higher in winter and spring than in summer and fall. That is, the concentration of elemental chemical compounds in winter and spring is determined by the influence of NaCl sprayed on the roadside, and when determined, based on the fact that the measurement point is a highway, and the speed of the vehicle is high. The elemental material has a greater effect of road resuspended dust than vehicle emissions. The detailed results can be found in the SI.

3.3. Characteristics of vehicle emission rates

The VERs (mg/km) were calculated using the difference in concentration at inside and outside the tunnel, and the TFC (Table 1). The VERs of $PM_{2.5}$, OC, EC, NH_3, CO, and NO at 11.21, 3.81, 2.82, 16.74, 563.61, and 257.50 mg/km, respectively. The $PM_{2.5}$ and NO were higher in winter than in summer, and EC & NH_3 were higher in summer than in winter, which was similar to the results of previous studies (Saha et al., 2018; Wang et al., 2018; Healy et al., 2017). As a result of examining the causes of the increase in $PM_{2.5}$ in winter based on previous studies, it is confirmed that cold air increases the condensation of emission gases. This can increase the number and size of particles. Here, chemical compounds involved in the condensation of vehicle emission gas include semi-volatile organic compounds (SVOC), moisture, SOx, and organic compounds (Du and Yu, 2006; Kittelson et al., 2006; Wang et al., 2017; Grieshop et al., 2006; Robinson et al., 2010). The VER of $PM_{2.5}$ in winter has higher than in summer. There is a possibility of moisture condensation due to cold air.

When examining the VER of gaseous chemical compounds, it was confirmed that the average of the four seasons for NH_3, CO, and NO was 16.74, 564, and 258 mg/km, respectively. The CO was higher in fall, and NO was observed to be higher in winter. The NH_3 showed relatively constant VER in spring, summer, and fall, while winter was lower than the other seasons. The winter NH_3 vehicle emissions can be influenced by temperature. According to previous studies, temperature is an important factor affecting NH_3, wherein NH_3 is reported to exhibit emissions 2 to 20 times higher during daytime when temperatures are high, doubling at night when the temperatures are low (Ye et al., 2022; Zhao et al., 2008). Therefore, the vehicle emission of NH_3 in winter is determined to be relatively low compared to spring, summer, and fall, due to the influence of the surrounding environment.

Table 1
Seasonal VER for $PM_{2.5}$ and gaseous compounds.

Compound	spring	summer	fall	winter	Average
$PM_{2.5}$ mass (mg/km)	7.04	9.65	13.41	14.75	**11.21**
OC (mg/km)	4.39	3.21	3.82	3.80	**3.81**
EC (mg/km)	0.74	2.58	6.78	1.16	**2.82**
NH_3 (mg/km)	20.00	18.21	23.86	4.89	**16.74**
CO (mg/km)	462	558	794	441	**564**
NO (mg/km)	226	197	273	334	**258**
Benzene (mg/km)	0.38	0.72	1.42	2.88	**1.35**
Toluene (mg/km)	0.74	1.38	3.85	2.41	**2.10**
Ethylbenzene (mg/km)	0.00	0.51	0.77	0.45	**0.43**
m&p-Xylene (mg/km)	0.21	0.75	1.51	0.76	**0.81**
o-Xylene (mg/km)	0.09	0.61	0.57	0.31	**0.40**
VER-QDTT-OP (μM/km)	138	140	259	140	**169**

Fig. 1 shows the concentrations of BTEX measured inside and outside the tunnel and the concentration of vehicle emission. The average concentration of BTEX outside the tunnel showed 3.16, 14.83, 4.39, and 6.39 μg/m^3, respectively, meeting the global average exposure range of BTEX at 1.5 to 6.95, 7.17 to 26.9, 0.59 to 2.06, and 4.01–17.43 μg/m^3, respectively (Bolden et al., 2015; Dehghani et al., 2018; Hazrati et al., 2015; Hinwood et al., 2007; Hsieh et al., 2020). However, the average concentration of BTEX inside the tunnel presented 10.34, 25.61, 6.44, and 12.81 μg/m^3, respectively. In addition, the benzene concentration inside the tunnel was higher than the concentration range of the roadside benzene, 4.8 to 6.1, and the ratios of BTEX were also found to be 1.0 : 2.48: 0.62 : 1.24, which are different from the 1.0 : 4.3: 0.7 : 1.4 suggested in previous studies (Chan et al., 2003; Lau and Chan, 2003). These results are interpreted as differences between observations in tunnels belonging to a relatively closed system, than in the other studies. The VER of BTEX in spring, summer, fall, and winter were 1.43, 3.97, 8.13, and 6.83 mg/km, respectively, indicating that BTEX is high in the season when the temperature is low. Looking at previous studies on the chassis dynamometer, there is a study result that when the temperature drops from 2 to 0 °C, the emission of VOCs increases by an average of 5.19 times (Zhang et al., 2022). In addition, VOCs result in increased emissions at low temperatures, reduced atmospheric mixture, and low humidity (Liu et al., 2000; Marčiulaitienė et al., 2017; Parra et al., 2008; Sturaro et al., 2010). Therefore, it is determined that vehicle emissions in fall and winter, which are higher than in spring and summer, are due to environmental effects, such as temperature and humidity.

Fig. 2 shows the concentrations of nine PAHs measured at inside and outside of the tunnel. The PAHs measurements were observed only during the study period corresponding to spring and winter, due to sampling availability. The concentration of PAHs inside of the tunnel was 68.38 and 68.64 ng/m^3 in spring and winter, respectively, and the concentration change according to the season was not significant. The inside of the tunnel was 2.75 times higher in spring, and 1.57 times higher in winter. Table S3 of the SI presents the PAHs vehicle emissions suggested in previous studies. The vehicle emissions of PAHs ranged 8–73 μg/km, and the results of this study were relatively low, compared to the previous studies. This could be because of the higher efficiency control system development for vehicle emissions. Pyrene and phenanthrene showed the highest vehicle emission. Pyrene and phenanthrene can be utilized as vehicle emission markers, which are consistent with previous studies (Ho et al., 2009).

3.4. Vehicle emission rate of quinone normalized dithiothreitol oxidation potential (VER−QDTT−OP)

In this study, the emission of toxicity indicators based on oxidation potential, VER of quinone normalized dithiothreitol oxidation potential (VER−QDTT−OP) were determined by multiplying the QDTT−OP (μM/m^3) and TFC (m^3/km). In spring, summer, fall, and winter, this was found to be 138, 140, 259, and 140 μM/km, respectively. The VER−QDTT−OP in fall was about 1.5 times higher than the overall average. The gaseous chemical compounds, such as EC and CO, NH_3, and VOCs, which showed high concentrations in fall, had a direct or indirect effect on the VER−QDTT−OP concentration. Since VER−QDTT−OP is analyzed on particulate matter, it is not possible to prove the effect on gaseous chemical compounds based only on the research results so far. However, when seasonal high-concentration components are identified based on the analysis compounds, the high

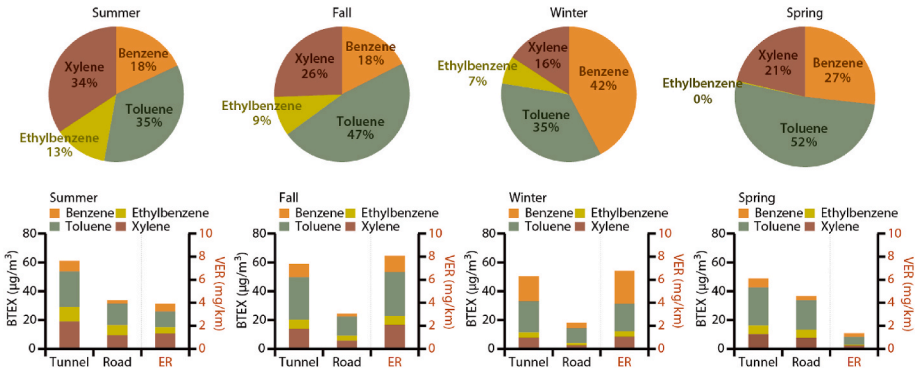

Fig. 1. Seasonal VER and relative ratios for BTEX.

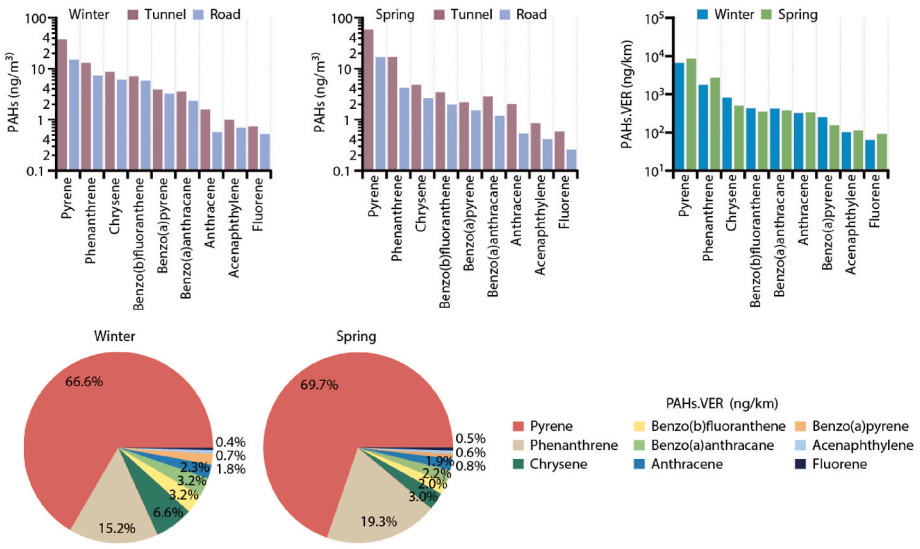

Fig. 2. VER and relative ratios for PAHs in winter and spring.

fall gaseous chemical compounds influence $PM_{2.5}$ production, compared to the previous season, so it can be inferred that the VER−QDTT−OP of $PM_{2.5}$ in fall is high as shown in Table 1.

3.5. *Effect of emission rate on vehicle type*

The vehicle types were analyzed using a statistical sampling method using video identification. The sampling results were divided into three categories: automobiles, taxis, and buses/RVs/trucks. It was considered that automobiles represent gasoline, taxis represent LPG, and buses/RV/trucks represent diesel fuel. The classification was determined by officially 'Total Registered Moter Vehicles' by the Korean government.

Fig. 3, and Fig. S3 of the SI, show the results of sampling based on the vehicle type observed during the study period. The average number of vehicles that pass through the tunnel by hour during the study period was confirmed to be 3113 vehicles per hour. The movement amount of gasoline and diesel vehicles decreased on weekends, and the traffic volume of LPG vehicles increased slightly. From February 3 to 6, 2019, the flow of gasoline vehicles increased significantly, while the flow of diesel vehicles decreased, due to the New Year's holiday in Korea. The winter measurement period for February 3 to 6, 2019 was classified as a 'holiday period', and other periods as a 'weekday period'. The number of gasoline vehicles increased by about 30%, and the number of diesel vehicles decreased by 28%, compared to weekdays, during the holiday period. Therefore, by comparing the two periods, it is possible to confirm the differences between the emission compounds from the gasoline and the diesel vehicle.

Table 2 shows the vehicle emissions by classifying the holiday and weekday periods. The vehicle emissions of OC and EC were lower during the holiday period, than during the weekday period. It was confirmed

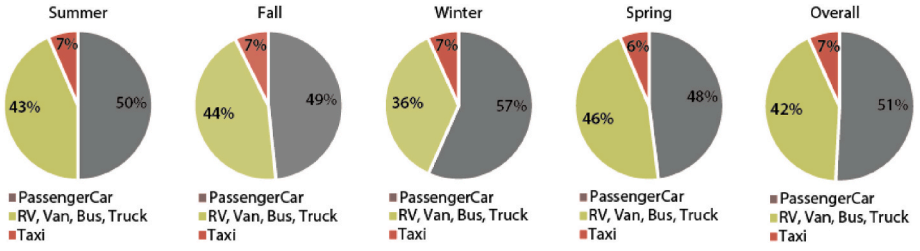

Fig. 3. Seasonal Relative ratios based on type of vehicle.

Table 2
VER for $PM_{2.5}$ and gaseous compounds during Holiday and non-holiday periods in winter.

Compound	Average	Non-Holiday (a)	Holiday (b)	(b)/(a) ratio
$PM_{2.5}$ mass (mg/km)	14.75	14.80	14.73	1.00
OC (mg/km)	3.80	4.19	2.65	0.63
EC (mg/km)	1.16	1.28	0.93	0.73
Acenaphthylene (μg/km)	0.057	0.064	0.044	0.69
Fluorene (μg/km)	0.029	0.033	0.021	0.65
Phenanthrene (μg/km)	1.189	1.026	1.474	1.44
Anthracene (μg/km)	0.206	0.184	0.245	1.34
Pyrene (μg/km)	5.155	4.410	6.458	1.46
Benzo(a)anthracene (μg/km)	0.202	0.134	0.323	2.42
Chrysene (μg/km)	0.329	0.189	0.573	3.03
NH_3 (mg/km)	4.89	2.86	6.71	2.35
CO (mg/km)	441	430	465	1.08
NO (mg/km)	334	381	254	0.67
SO_2 (mg/km)	4.42	4.97	2.88	0.58
NO_2 (mg/km)	89.83	97.17	77.71	0.80
Benzene (mg/km)	1.53	1.61	1.33	0.83
Toluene (mg/km)	1.31	1.52	0.82	0.54
Ethylbenzene (mg/km)	0.26	0.31	0.13	0.42
m&p-Xylene (mg/km)	0.49	0.57	0.31	0.54
o-Xylene (mg/km)	0.21	0.24	0.12	0.50
VER−QDTT−OP (μM/km)	139.68	127.17	162.61	1.28

that diesel vehicles emitted relatively high carbon compounds, compared to gasoline vehicles, which is consistent with the results of previous studies, such as chassis dynamometer experiments (Chiang et al., 2012; Grieshop et al., 2006; Wang et al., 2021). When examining the vehicle emissions of gaseous chemical compounds, there was no significant difference between the holiday period and the weekday period for CO; and for chemical compounds, such as SO_2, NO, and NO_2, the holiday period was lower than the weekday period. Therefore, chemical compounds, such as SO_2, NO, and NO_2, were found to have less emissions from gasoline vehicles, compared to diesel vehicles. However, in the case of NH_3, the holiday period was 2.35 times higher than that of the weekday period. In addition, the average vehicle emission of NH_3 during the winter study period was 4.89 mg/km, the NH_3 vehicle emission during the Holiday was about 1.3 times at 6.71 mg/km, and the net increase of gasoline vehicles was 1.29 times, compared to the holiday period and weekday period. That is, the main emission source of NH_3 generated by the traffic may be estimated as a gasoline vehicle. The NH_3 emissions from gasoline vehicles are interpreted as a result of using three-way catalytic converters (TWC). The TWC is a device to reduce CO and NOx emissions of gasoline vehicles; but when the TWC is used, NH_3 is emitted as a by-product in the NOx reduction process (Fraser and Cass, 1998; Kean et al., 2009). Selective catalytic reduction systems that use elements to reduce NOx in diesel vehicles are also cited as sources of NH_3 emissions from traffic (Carslaw and Rhys-Tyler, 2013; Suarez-Bertoa et al., 2016). In this study, the major source of NH_3 along the road is the flow of gasoline vehicles.

BTEX vehicle emissions during the holiday period and the weekday period were 2.71 and 4.25 mg/km, respectively, indicating that the BTEX concentration during the holiday period was low. However, the ratios of BTEX were 1.00 : 0.62: 0.10 : 0.32 during the holiday period, and 1.00 : 0.94: 0.19 : 0.5 during the weekday period, so the ratio of BTEX varies, depending on the ratio of gasoline and diesel vehicles. In addition, about 80% of BTEX generated by traffic was identified as benzene and toluene; and especially for gasoline vehicles, benzene accounted for more than 49% of the total BTEX. This is believed to be because the emission standards for harmful gases in Korea comply with Euro 5. In general, the emissions and ratios of BTEX differ greatly depending on environmental conditions, such as vehicle type, temperature, fuel quality, road characteristics, and national hazardous gas emission standards (Louis et al., 2016; Som et al., 2007). The national hazardous gas emission standards are adopted to emission reduction devices, such as the Diesel Particulate Filter (DPF), Exhaust Gas Recirculation (EGR), Selective Catalytic Reduction (SCR), and Diesel Oxidation Catalyst (DOC), to regulate emissions. These devices were commonly used to meet the emission standards after Euro 4. Using the devices resulted in a change in the emission ratios of vehicle BTEX; the ratio of benzene increased, instead of the ratio of xylene after Euro 4 (Louis et al., 2016; Mamakos et al., 2013; Som et al., 2007). Therefore, the vehicle emissions of BTEX presented in this study represent the results of the highway, low-temperature, low-humidity winter, and Euro 5 emission standards.

The PAHs with differences between holiday period and weekday periods were identified as seven compounds (i.e., acenaphthylene, fluorene, phenanthrene, anthracene, pyrene, benzo(a)anthracane, and chrysene). The concentrations of PAHs in winter, on holiday, and on weekdays, on average, were 7.17, 9.14, and 6.04 μg/km, respectively, indicating that the holiday period was about 50% higher than the weekday period. Based on the number of PAHs benzene rings, the Low Molecular Weight (LMW) in winter, on holiday period, and on weekdays was on average (1.48, 1.78, and 1.31) μg/km, respectively, indicating that the holiday period was higher than that of weekday period. Considering that the PAHs vehicle unit emissions of the four compounds constituting LMW are very low at 1.48 μg/km, and that the daily deviation of the four compounds varies from (0.1–0.85) μg/km, the difference between the holiday period and the weekday period is unlikely. On the other hand, the three compounds of Heavy Molecular Weight (HMW) with 4 benzene rings in winter, during holiday period, and during weekday period showed a clear difference, with an average of (5.69, 7.35, and 4.73) μg/km, respectively. In particular, among HMW, chrysene accounted more than three times higher than that of the weekday period compared to the holiday period, and benzo(a)anthracane also accounted 2.4 times higher than that of the weekday period, compared to the holiday period. Also, HMW showed an increase similar to that of gasoline vehicles, the same as NH_3. As described above in detail, the net increase in gasoline vehicles was 1.29 times, compared to the holiday period and the weekday period, and the increase in vehicle emissions of HMW increased by 1.29 times during the holiday period, compared to the winter average. That is, among the PAHs generated by traffic, HMW is mainly generated by the flow of gasoline vehicles.

4. Conclusion

The seasonal VER of PM and gaseous compounds were determined using analyzed concentrations using the TFC. The types of vehicles flowing during the observation period were classified into gasoline, diesel, and LPG vehicles, and factors affecting the VERs were identified. The results of the study comprehensively suggest VERs for $PM_{2.5}$, OC, EC, NH_3, CO, NO, and QDTT−OP of 11.2, 3.8, 2.8, 16.7, 564, 258, and 169 μM/km, respectively. The main emission source of NH_3 can be the emission of gasoline vehicles from three-way catalytic converters. The high fall gaseous chemical compounds influence $PM_{2.5}$ production, compared to the previous season, so it can be inferred that the VER−QDTT−OP of $PM_{2.5}$ in fall is high. The VER of BTEX in spring, summer, fall, and winter were 1.4, 4.0, 8.1, and 6.8 mg/km, respectively, indicating that BTEX is high in fall and winter when the temperature is low. Pyrene and phenanthrene in PAHs can be utilized as vehicle emission markers. It is expected that the results of this study will be used as data for the international response to reduce vehicle emissions in the future.

CRediT authorship contribution statement

Myoungki Song: Formal analysis, Conceptualization, Methodology, Writing – original draft, Writing – review & editing, experimental

measurements, data analysis, manuscript preparation. **Eunyoung Kim:** Formal analysis, Data curation, Investigation, experimental measurements, data analysis, manuscript preparation. **Yongmin Lee:** Formal analysis, Data curation, Investigation, experimental measurements, data analysis, manuscript preparation. **Sea-Ho Oh:** Formal analysis, Conceptualization, Data curation, Software, chemical analyses, manuscript preparation, model analysis. **Geun-Hye Yu:** Formal analysis, Visualization, chemical analyses, manuscript preparation, model analysis. **Seoyeong Choe:** Formal analysis, Visualization, chemical analyses, manuscript preparation, model analysis. **Gyutae Park:** Formal analysis, Data curation, Investigation, experimental measurements, data analysis, manuscript preparation. **Taehyoung Lee:** Formal analysis, Data curation, Investigation, Validation, experimental measurements, data analysis, manuscript preparation. **Min-Suk Bae:** Formal analysis, Conceptualization, Data curation, Investigation, Software, Supervision, Validation, Writing – review & editing, entire data analyses and manuscript preparation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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