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Concept Paper

Characteristics of Real-World Non-Exhaust Particulates from Vehicles

Sunhee Mun, Hwansoo Chong, Jongtae Lee and Yunsung Lim *

Transportation Pollution Research Center, National Institute of Environmental Research, Incheon, Republic of Korea
* Correspondence: yun911@korea.kr

Abstract: The need to regulate the non-exhaust particulate emissions from vehicles has been discussed worldwide due to the toxicity to the human body as well as the atmosphere. In-depth studies have been conducted on precise analysis of the non-exhaust particulates, in particular, accurate measurement of tire-brake-road wear particles, and their proportion in the atmosphere. In this study, the influence of tire and road wear particles (TRWP) on particulate matter (PM) in the atmosphere was investigated through tire and PM samples. PM samples were collected from the atmosphere using a high-volume sampler equipped with a quartz filter. Additionally, polycyclic aromatic hydrocarbons (PAHs) and heavy metals in tire rubber were analyzed as markers by pyrolysis-gas chromatography/mass spectrometry (GC/MS), GC/MS, and inductively coupled plasma/mass spectrometry (ICP/MS). More vinylcyclohexene was detected than dipentene in the markers measured in the samples of tires equipped with vehicles driving on the road with the high-volume sampler installed, while more dipentene was detected in total suspended particles (TSP) samples. Among the PAHs measured in tire samples, pyrene exhibited the highest concentration. In TSP samples, benzo(b)fluoranthene showed the highest concentration. Among the heavy metals, zinc exhibited the highest concentration in all tire samples and calcium in TSP samples.

Keywords: non-exhaust particle; rubber; vinylcyclohexene; dipentene; metal

1. Introduction

Tire and road wear particles (TRWP) are mainly generated at the frictional surface between tires and roads, and contain various substances that were used in the tire tread and road pavement. Heavy particles of the generated TRWP accumulate on roads and roadsides by vehicular movement and wind, while lighter particles are suspended in the atmosphere and then descend onto the ground to accumulate on roads and roadsides after the stabilization of the traffic and atmospheric conditions over time. Such particles either settle in soil with moisture during rains or road-washing, or they flow into rivers and seas. Therefore, TRWP impacts the atmosphere, soil, as well as the aquatic environment [1~4]. Studies have been conducted under various conditions to understand the environmental impact throughout the life cycle of TRWP and the mechanism thereof [2,3,5-8]. Various studies have been conducted on tires, mainly focusing on the shape and size of wear particles, emission characteristics, marker analysis, physicochemical composition, contribution to particulate matter (PM) in the atmosphere, influence in the natural world, and toxicity. Owing to the toxicity of TRWP to the human body as well as to the environment, a need to regulate TRWP emissions along with the PM from automobile exhaust gas is being discussed worldwide. Detailed investigations are required to precisely analyze the physical and chemical properties of TRWP, accurate measurement of emissions, and proportion of TRWP in the atmosphere.

Tires are generally manufactured with rubber, fillers, process oils, additives, and vulcanization agents. Natural rubber (NR) and styrene-butadiene rubber (SBR) account for 40 to 60% of a tire. Fillers, which are mainly made of carbon black, represent 20 to 35% [9].

Chemical marker analysis has been used to analyze TRWP in the atmosphere, with vinylcyclohexene, dipentene, styrene, and butadiene serving as markers [1,6]. These markers are analyzed to understand the physical and chemical properties of tires and to evaluate the proportion of TRWP in the PM sampled in the atmosphere. The impact and emission of TRWP in the atmosphere have also been analyzed through the analysis of organic and inorganic matters such as polycyclic aromatic hydrocarbons (PAHs) and heavy metals [5; 10-13].

Previous studies on the physical and chemical properties of TRWP reported changes in the characteristics of tires and PM in the atmosphere by conducting thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), and pyrolysis-gas chromatography/mass spectrometry (GC/MS) on tire samples and wear particles collected in the atmosphere [1,4,14,15]. In [1], the pyrolysis–GC/MS analysis revealed that the contributions of tire particles (TP) and TRWP in PM10 are 0.23–1.24% and 0.45–2.48%, respectively.

PAHs have been analyzed mainly by a high-performance liquid chromatography (HPLC) and a GC/MS to investigate the characteristics of tire samples and PM in the atmosphere [16-22]. PAHs are organic compounds in which two or more benzene rings are connected [11]. They are mainly adsorbed on gaseous or fine particulate matter [23] and are reported to be potentially toxic, carcinogenic, and mutagenic substances [20,24] which are very harmful to the human body [25]. Long-term and short-term extraction methods have been used to extract PAHs-containing compounds from the atmosphere for analysis [11,19,26,27].

For analyzing heavy metals, many experimental methods have been developed using various instruments such as energy-dispersive X-ray spectroscopy (EDX), X-ray fluorescence (XRF), and inductively coupled plasma-optical emission spectroscopy/mass spectrometry (ICP-OES/MS), depending on the research purpose. It was reported that tire treads contain heavy metals, such as Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb [13], and that they partially contribute to the PM concentration in the atmosphere [12,28]. Zinc oxides are added as activators during the vulcanization process and they are known to constitute 0.4 to 4.3% of tire treads [13]. Zinc from tires is known to be a major pollutant of soil, air, road dust, and urban atmosphere [4,29,30]. It was also reported other aforementioned heavy metals constituting tire treads also contaminate the environment [12; 31].

In this study, the influence of TRWP on PM in the atmosphere was investigated by examining tire and PM samples. The markers from the rubber used in tires were derived via pyrolysis-GC/MS, GC/MS, and ICP/MS. Additionally, PM samples from the atmosphere, and PAHs and heavy metals from tire samples were analyzed. A short-term extraction method based on accelerated solvent extraction (ASE) was applied for PAH analysis. The extracted compounds were analyzed by the EPA Method TO-13A, using internal standards. Finally, the measured marker concentrations were analyzed to investigate the influence of tire wear particles on PM in the atmosphere.

2. Materials and Methods

2.1. Collection of particulate matter samples in the atmosphere

The aerial image of the sampling site for investigating the emission characteristics of TRWP according to roadside separation distance is presented in Figure 1. Total suspended particles (TSP) samples were collected with high-volume samplers at two points, 20 m (region B) and 70 m (region A) away from the roadside (see Figure 2). The vehicles usually driving near region A were heavy-duty vehicles and various construction machinery, owing to the industry complex and construction site around region A. On the other hand, region B placed around the road interaction was various vehicles from small size passenger vehicles to heavy-duty vehicles. The average velocity of vehicles in region A is around 22 ± 5km/h, due to the speed limit zone of 30km/h. The average speed of vehicles driving in the region B was in the range of 22 km/h to 45km/h. The TSP samples were collected

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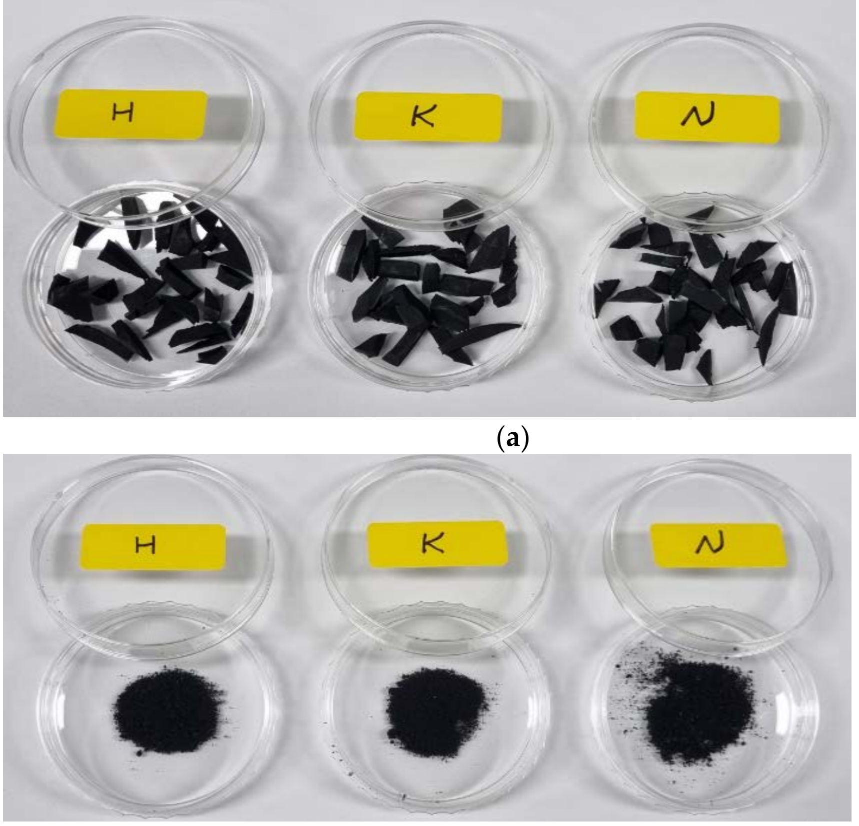
three times at 24-h intervals. During the collection, the average wind speed, temperature, and precipitation were recorded as 1.1 m/s, 24.2℃, and 0.1 mm, respectively. For the pretreatment of the quartz fiber filter, impurities were removed through 5-h heat treatment at 600℃. The filter was then stored in a chamber with constant temperature and humidity, and was weighed using an analytical balance. The filter paper on which samples were collected was stored under the same conditions.

Figure 1. The aerial image of the sampling site for investigating the emission characteristics of TRWP according to the roadside separation distance (http://map.naver.com).

Figure 2. High-volume samplers for sampling the total suspended particles in the environment.

2.2. Collection of tire particle samples

The bulk tire samples were cut from the tread of tires equipped with vehicles running on the road with the high-volume sampler installed, and then very small particle samples made from the bulk samples, as presented in Figure 3. Based on the liquid nitrogen cooling method, the bulk sample cut from the tire tread was immersed in liquid nitrogen and pulverized to create fine samples [17,18,32]. The investigation on tire wear particles was conducted on tires equipped with vehicles driving on the road the high-volume sampler installed. The samples individually obtained from 161 different tires were tested and investigated. The width of tires used in this experiment ranged from 155 to 265 mm and the aspect ratio, which is defined as the cross-sectional height divided by the cross-sectional width and multiplied by 100, ranged from 40 to 80. The load index, which is defined as the weight the tire can support safely, ranged from 75 to 110. The tread depth of tires was the range from 1.02 to 7.75 mm. All the tires used in the experiment were all-season tires.



(**a**)

(**b**)

Figure 3. The bulk sample cut from the tread of equipped with vehicles running on the road with the high-volume sampler installed (**a**) and very tiny particle samples (**b**).

3. Chemical analysis

The markers in the tire rubber were analyzed for TRWP with a quantitative Pyrolysis-GC/MS protocol, based on the ISO/TS 20593 method (ISO/TS 20593, 2017). In this study, SBR and NR were thermally decomposed into the polymers that constitute tire, and vinylcyclohexene(a tracing material of SBR) and dipentene(a tracing material of NR) were measured with GC/MS.

The samples were placed in the sample cup of a pyrolyzer (Pyrolyzer-3030D, Frontier Lab, Japan) and analyzed with GC/MS (Agilent 5975B, USA), and first and second pyrolysis (i.e., double-shot analysis) were conducted. The GC/MS was calibrated using the auto-tune method suggested by the manufacturer. In this method, peaks for the mass ions of 69, 219, and 502 m/z are examined using perfluorotributylamine (PFTBA), and proportions in the three different ranges of 70–69, 220–219, and 503–502 m/z were analyzed by measuring peaks for the isotope mass ions of 70, 220, and 503 m/z. Additionally, the ratios between 69 and 219 m/z and between 69 and 502 m/z were measured to confirm that they were higher than a certain value. The system was calibrated by analyzing the proportions of the precursors of 69, 219, and 502 m/z and through the ratios between 18 and 69 m/z and between 28 and 69 m/z.

The GC/MS was calibrated with two procedures. The check for air and water background, and then mass calibration. For air and water background checks, the air to water background ratio was used to determine a mass spectrometer's "leak tightness" and overall suitability to run samples. The Bench TOF-dx requires that for a leak-tight system, the molar mass of water (i.e., 18 g/mol) is at a higher intensity than both, the molar mass of nitrogen (i.e., 28 g/mol) and the molar mass of oxygen (i.e., 32 g/mol) background. The ratios of 18 to 19, and 28 to 32 indicate instrument performance. The ratios of N_2 to O_2 in ambient air, and H_2O to protonated H_2O were tested to be 4:1 and 9:1, respectively. Automatic mass calibration, as suggested by the manufacturer, was applied using PFTBA. In this method, the peak finding algorithm of the automatic mass calibration assumes that all mass peaks can be found within approximately 1 amu of the initial calibration. First, the mass calibration valve was opened and the liquid calibration vapor, PFTBA, was introduced into the ion source. Thereafter the mass calibration valve was closed and a backup of the old parameter settings was made. A peak finding algorithm identified the predefined mass peaks of the selected calibration substance in the flight time spectra. It then calculated coefficients for the flight time/mass conversion. The new coefficients of the flight time/mass conversion and the new flight times of the mass peaks were displayed and stored as new default values for future measurements. PAHs were analyzed using the following procedure. The mixture of two surrogate standards (D_{10}-fluorene and D_{10}-pyrene) was injected into the tire sample and quartz fiber filter and they were placed in the extraction cell of an accelerated solvent extractor (Accelerated Solvent Extractor 200, Dionex, USA). From the tire sample, PAHs were extracted using 10% acetone/methylene chloride at 100℃ and 1,500 psi. From TSP, which is a sample collected in the atmosphere, PAHs were extracted using the same method but using 10% ethyl ether/hexane. The extracted samples were analyzed using GC/MS (Aglient 7890A, USA/Markes, UK). In [17,18], the tire samples were analyzed with an ASE extractor and GC/MS. EPA 610 PAH Mix (Accustandard, USA) was used as a standard. Phenanthrene, fluoranthene, pyrene, benzo(g,h,i)perylene, and naphthalene were measured using the EPA Method TO-13A for analyzing PAHs samples collected from the atmosphere [33]. The gaseous substance produced through pyrolysis was transported to GC/MS at 1 mL/min using helium gas. The temperatures of the injector and detector were set to 280℃ and 250℃, respectively, and the sample was injected into the GC injector by 1 μL using an automatic sample injector. DB-5MS (Aglient, USA) was used for the separation of PAHs.

For analyzing heavy metals in tire samples, organic matter contained in samples was removed using a microwave decomposition system (IT/START D, Milestone, Italy). This pre-treatment process involves placing a tire sample in a decomposition vessel, adding nitric acid (HNO_3), and decomposing and removing organic matter and interfering substances. The program of the microwave decomposition system had three steps: (1) the temperature was increased to 210℃ over 15 min, (2) 210℃ was maintained for 15 min, and (3) ventilation was performed and the decomposition vessel was cooled to room temperature. Upon the completion of the above process, the vessel was placed in the atmosphere for 2 h until its temperature reduced to 25℃. The sample was filtered using a filter paper and analyzed using ICP/MS (PerkinElmer, USA). ICP/MS was calibrated using the following method: (1) ^{24}Mg, ^{115}In, and ^{238}U, with a concentration of 1 ppb each, were used, (2) the sensitivity for each mass region was measured after confirming that the mass signals of the elements were higher than 5,000, 25,000, and 20,000 cps, (3) to find the plasma with the appropriate power required for the experiment, the generation of monovalent ions was mainly measured using barium. Conditions for generating divalent ions were also measured. Based on these values, conditions for generating no divalent ions were found. The equipment was set so that the values of ^{156}CeO/^{140}Ce and ^{69}Ba/^{138}Ba could be maintained at 0.03 or less, respectively. Assuming that the vehicles traveling in the target area have the same components for their tires and the particle component distribution collected in the quartz filter of the high-volume sampler is homogeneous, the amount of TRWP distributed in the atmosphere can be calculated using the ratio of polymers in tire tread to the components of tire tread, the ratio between TRWP and tire tread, and the polymer content in the tire tread.

4. Data analysis

The weight of TRWP collected in the high-volume sampler filter can be calculated as Equation (1) :

$$m_{TRWP,t} = \left(\frac{A_T}{A_a}\right) \cdot m_{TRWP,i} \qquad (1)$$

where, $m_{TRWP,t}$ is the total mass of TRWP collected in the high-volume sampler filter, A_T the area of the high-volume sampler filter, A_a the quartz filter area of pyrolysis-GC/MS, and $m_{TRWP,i}$ the mass of TRWP collected in the quartz filter of pyrolysis-GC/MS.

The amount of polymers extracted from the high-volume sampler filter and processed by pyrolysis-GC/MS can be expressed by Equation (2):

$$m_{p,i} = \left(\frac{m_p}{m_{Tt}}\right) \cdot m_{Tt,i} \qquad (2)$$

where, $m_{p,i}$ the weight of the polymers measured in pyrolysis-GC/MS, (m_p / m_{Tt}) the ratio of polymers in tire tread to the components of tire tread, and $m_{Tt,i}$ the weight of the tire tread tested in pyrolysis-GC/MS.

The amount of tire tread taken out from the high-volume sampler filter and processed by pyrolysis-GC/MS can be expressed by Equation (3):

$$m_{Tt,i} = \left(\frac{m_{Tt}}{m_{TRWP}}\right) \cdot m_{TRWP,i} \qquad (3)$$

where, $m_{Tt,i}$ is the weight of tire tread measured in pyrolysis-GC/MS, (m_{Tt} / m_{TRWP}) the ratio of tire tread to TRWP, and $m_{TRWP,i}$ the weight of TRWP tested in pyrolysis-GC/MS.

Through Equations (2) and (3), the amount of polymers extracted from the high-volume sampler filter and processed by pyrolysis-GC/MS can be calculated as Equation (4):

$$m_{p,i} = \left(\frac{m_p}{m_{Tt}}\right) \cdot \left(\frac{m_{Tt}}{m_{TRWP}}\right) \cdot m_{TRWP,i} \qquad (4)$$

Based on Equations (1) and (4), the weight of TRWP collected in the high-volume sampler filter can be calculated as Equation (5):

$$m_{TRWP,t} = \left(\frac{A_T}{A_a}\right) \cdot \left(\frac{1}{(m_p/m_{Tt}) \cdot (m_{Tt}/m_{TRWP})}\right) m_{p,i} \qquad (5)$$

Assuming the ratio of polymers in tire tread to the components of tire tread and the ratio of tire tread to TRWP as, respectively, Equations (6a) and (6b):

$$F_r = \left(\frac{m_p}{m_{Tt}}\right) \qquad (6a)$$

$$F_{Tt} = \left(\frac{m_{Tt}}{m_{TRWP}}\right) \qquad (6b)$$

Equation (5) can be expressed as Equation (7):

$$m_{TRWP,t} = \left(\frac{A_T}{A_a}\right) \cdot \left(\frac{1}{F_r \cdot F_{Tt}}\right) \cdot m_{p,i} \qquad (7)$$

Since the polymers used in tires are generally composed of SBR and NR, the mass of polymers can be expressed as Equation (8):

$$m_p = m_{SBR} + m_{NR} \qquad (8)$$

Substituting Equation (8) into Equation (7), the weight of TRWP collected in the high-volume sampler filter can be calculated as Equation (9):

$$m_{TRWP,t} = \left(\frac{A_T}{A_a}\right) \cdot \left(\frac{m_{SBR}+m_{NR}}{F_r \cdot F_{Tt}}\right) \qquad (9)$$

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Therefore, the concentration of TRWP in the atmosphere can be calculated as Equation (10):

$$C_{TRWP} = \frac{m_{TRWP,t}}{V} = \left(\frac{A_T}{V \cdot A_a}\right) \cdot \left(\frac{m_{SBR} + m_{NR}}{F_r \cdot F_{Tt}}\right) \qquad (10)$$

Furthermore, the correction formula applied to correct the mass of SBR measured in the pyrolysis-GC/MS analysis using the mass ratio between SBR and BR can be used as Equation (11):

$$m_{SBR} = 0.9 m_S \qquad (11)$$

where, m_s is the mass of SBR obtained from the calibration curve drawn using SBR1500, a standard specimen of SBR.

5. Results

The temperature program and the chromatogram are presented in Figure 4. The temperature was maintained at 40°C for 2 min at the beginning. It was then increased to 320°C at a rate of 20°C/min and maintained for 14 min. In the pyrolysis-GC/MS chromatograms for tire particles and TSP, multiple high-peak sections were observed within 15 min after the start of the analysis and low-level peaks appeared afterward for the tire sample. In the case of TSP, high-level peaks appeared within 5 min after the start of an analysis, and intermittent low-level peaks were observed for 16 min. Afterward, no peak was observed. For the tire sample, the graph gradually increased for approximately 14 min after the start of the analysis and then decreased. For TSP, however, no similar tendency was observed. This difference appears to vary depending on the sample characteristics of the tire and TSP. In the pre-test conducted with the standard specimens of SBR and NR, the retention time (RT) was found to be 4.95 min for vinylcyclohexene in SBR and 6.96 min for dipentene in NR. These results were applied to the tire sample and TSP, and vinylcyclohexene and dipentene contained in SBR and NR, respectively, were measured through the substance library of GC/MS and spectrum analysis.

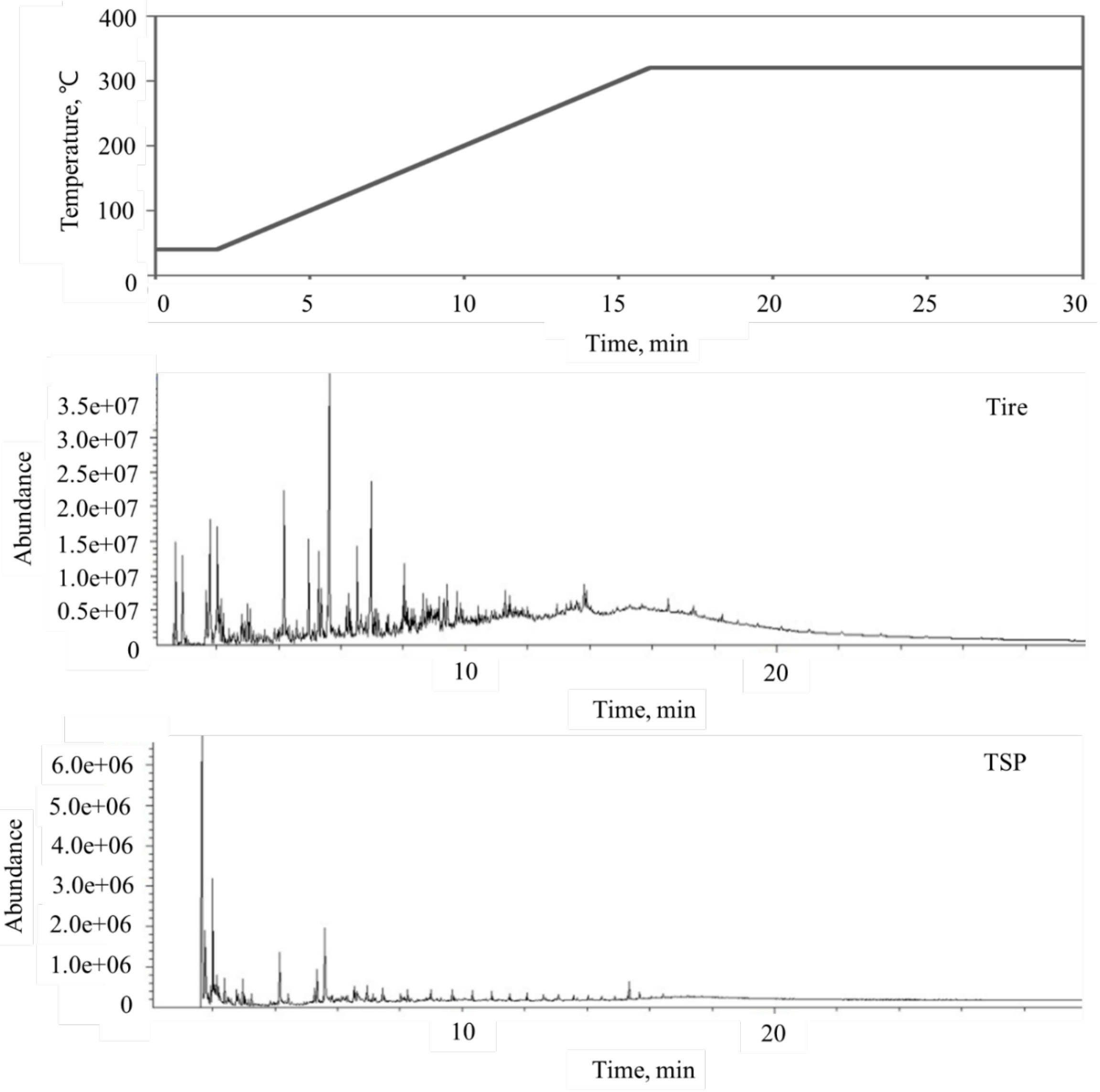

Figure 4. The temperature program and the measured chromatogram for tire tread and TSP with the pyrolysis-GC/MS.

The mass of vinylcyclohexene and dipentene, which are the markers of SBR and NR, respectively, were measured from the tire samples depicted in Figure 5. Note that error bars indicate 95% confidence intervals. As presented, the average mass of vinylcyclohexene was highly detected than that of dipentene, which can be due to the gradual increase of SBR added in the manufacturing process for the tires, compared to NR.

The average mass, standard deviation, and variation for two different tire markers, vinylcyclohexene and dipentene, are summarized in Table 1, which were measured from the tire samples. The average mass for vinylcyclohexene shows a higher value than that for dipentene, 63.51μg for vinylcyclohexene and 5.43μg for dipentene (see Figure 4). For the vinylcyclohexene, the high standard deviation and variation are revealed, 21.07 and 443.74, while it is relatively low for dipentene, 3.30 and 10.86, respectively.

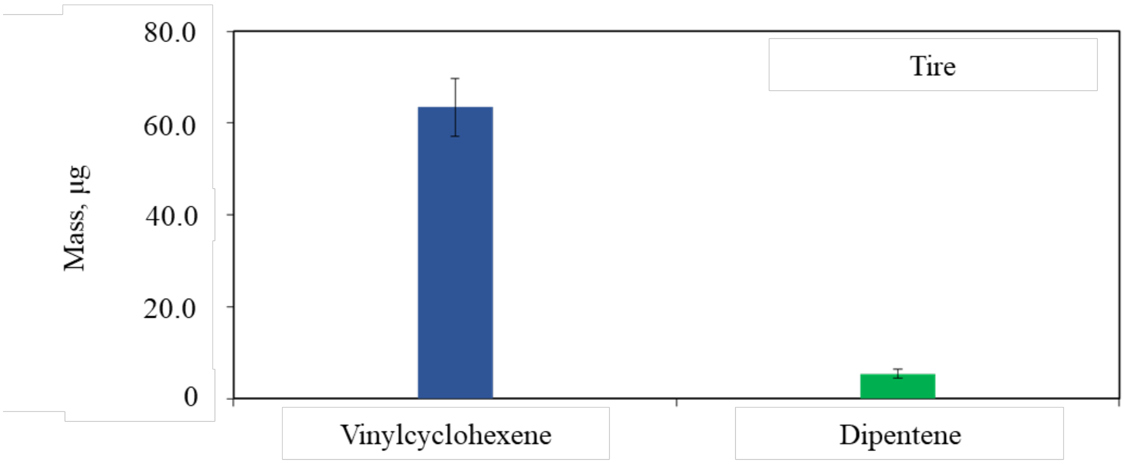

Figure 5. The average mass of vinylcyclohexene and dipentene was measured from the tire samples. Error bars indicate 95% confidence intervals.

Table 1. The average mass, standard deviation, and variation for two different tire markers (vinylcyclohexene, dipentene) measured from the tire samples.

Tire marker	Average	Standard deviation	Variation
Vinylcyclohexene(μg)	63.51	21.07	443.74
Dipentene(μg)	5.43	3.30	10.86

The distribution of vinylcyclohexene and dipentene measured in the TSP sample is depicted in Figure 6. This figure exhibits the higher value in mass for dipentene, 0.48 µg, compared to that for vinylcyclohexene, 0.33 µg. This is different from the tendency in the experiment results for the tire samples (shown in Fig. 4). In general, SBR has a complex structures with bridges, crosslinks, and network structures. In contrast, NR has a general linear structure. Thus, NR appears to wear from tires in the form of lighter particles than SBR, due to the physical and chemical properties of these two substances [34]. Therefore, it can be concluded that more dipentene, a marker of NR, was detected in the high-volume sample than vinylcyclohexene, a marker of SBR.

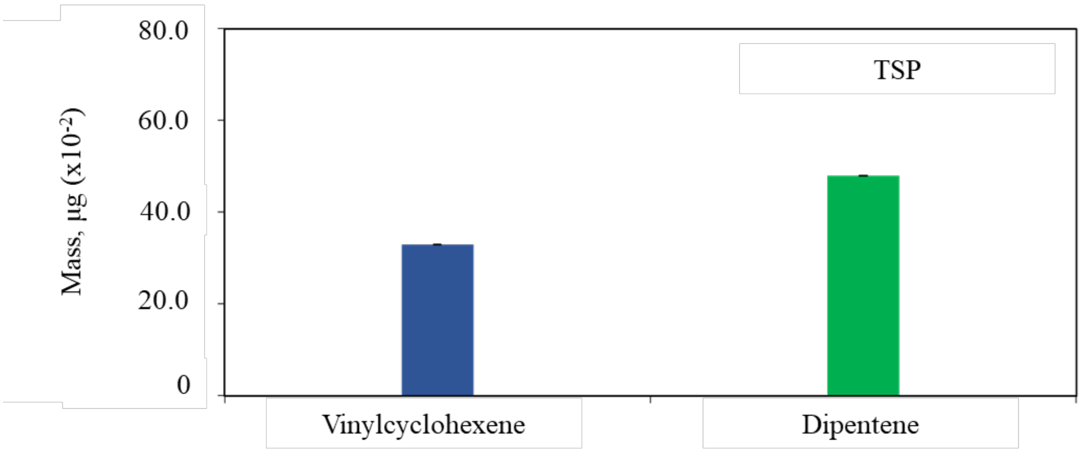

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Figure 6. The average mass of vinylcyclohexene and dipentene was measured from the TSP samples. Error bars indicate 95% confidence intervals.

The average concentration, standard deviation, and variation for TP and TRWP in the air with Equation (9) are provided in Table 2. As shown in this table, in the case of the measurement point close to the roadside, the average concentrations of TP and TRWP in TSP were found to be 1.10 and 2.21 μg/m³, respectively. For TRWP, the high standard deviation and variation were revealed, 0.48 and 0.23, while it was relatively low for TP, 0.24 and 0.06, respectively. The rubber ratio of tire tread is the ratio of the sum of vinylcyclohexene and dipentene to the sample mass of the tire (i.e.,2 mg). The average value for the ratio of polymers in tire tread to the components of tire tread, F_r, was calculated to be 0.52 for the tire samples, and the standard deviation and the variation were 0.12 and 0.02, respectively. The proportion of tire wear particles among the tire and road wear particles was assumed to be 0.5, which is suggested by ISO/TS 20593 [35].

Table 2. The average concentration, standard deviation, and variation for TP and TRWP in the air.

Classification	Average	Standard deviation	Variation
TP(μg/m³)	1.10	0.24	0.06
TRWP(μg/m³)	2.21	0.48	0.23

Figure 7 presents the temperature program for the GC/MS analysis on the particles sampled from a tire and the atmosphere, and the measured chromatograms. To measure, characterize, and monitor polycyclic aromatic hydrocarbons (PAHs), one of the air pollutants that can severely affect health and the environment, evolved from the tire particles in the atmosphere, the further in-depth chemical investigation was performed with the PAHs obtained from the tire samples and TSP. The temperature program consisted of seven different steps. After the temperature was maintained at 50°C for 1 minute, it was increased to 180°C at a rate of 8°C/min, and then to 240°C at a rate of 5°C/min. The temperature ramped to 300°C at a rate of 10°C/min and maintained for 7 minutes. Finally, the temperature was increased to 320°C at a rate of 10°C/min and maintained for 2 minutes. In the GC/MC chromatograms for tire particles and TSP, high-level peaks appeared sporadically over the entire measurement period. As aforementioned, the retention time, RT, for each of the 16 substances composing PAHs was pre-tested with the standard sample of PAHs. These RT values were applied to the tire sample and TSP, and five substances, benzo(g,h,i)perylene, pyrene, fluoranthene, phenanthrene, and naphthalene, were detected, as listed in Table 3.

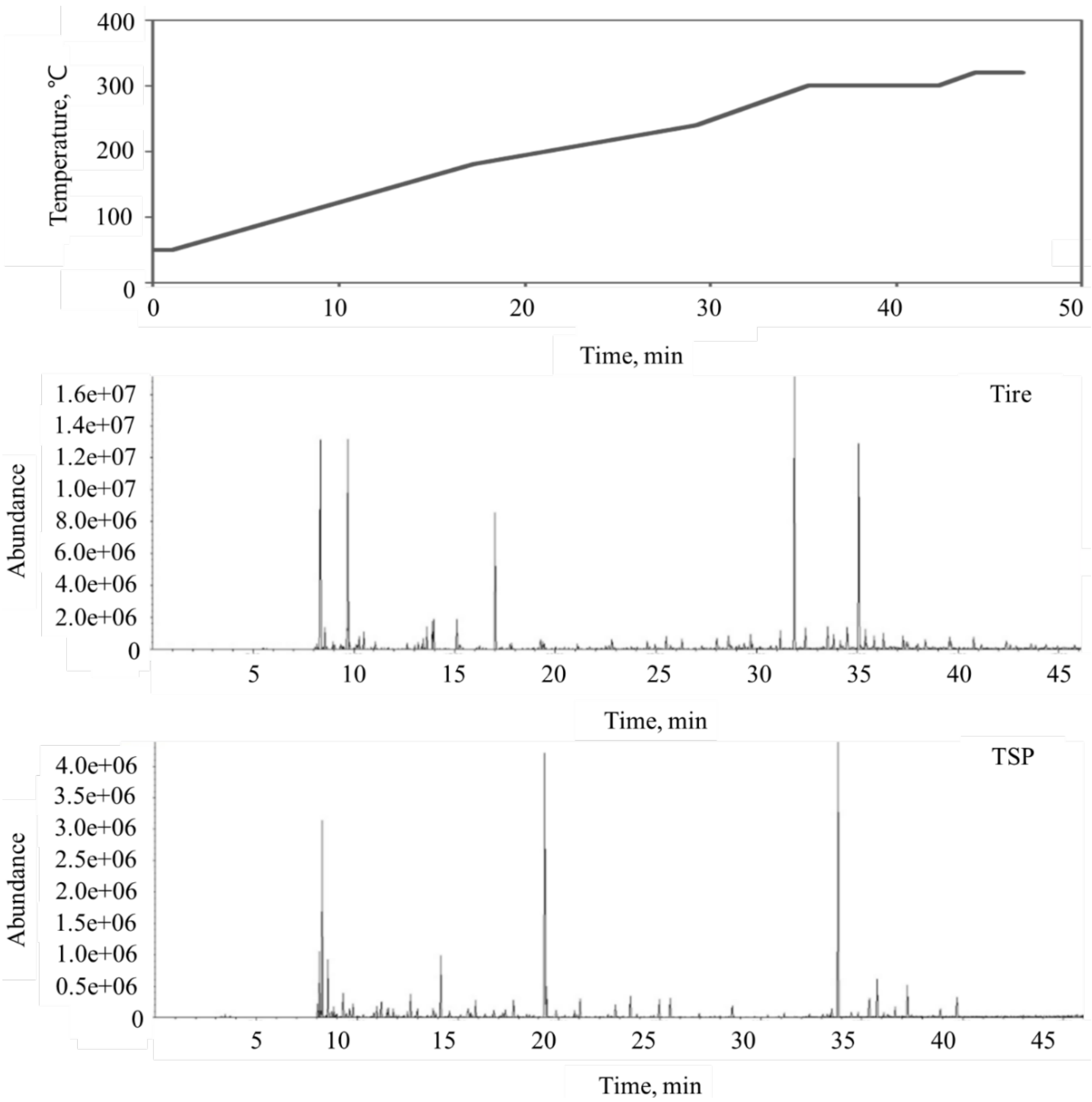

Figure 7. The temperature program and the measured chromatogram for tire tread and TSP with the GC/MS.

Table 3. Five different PAHs compounds were measured in tire samples.

PAHs compounds (ng/ul)	Average	Standard deviation	Variation
Benzo(g,h,i)perylene	0.28	0.14	0.02
Pyrene	0.73	0.09	0.01
Fluoranthene	0.12	0.04	0.00
Phenanthrene	0.04	0.00	0.00
Naphthalene	0.02	0.01	0.00

The distribution of benzo(g,h,i)perylene, pyrene, fluoranthene, phenanthrene, and naphthalene of PAHs measured from the tire samples were represented in Figure 8. The highest concentration of pyrene was exhibited, followed by benzo(g,h,i)perylene, fluoranthene, phenanthrene, and naphthalene in that order. This result can be attributed to the aromatic oil being chemically added to the tire manufacturing process [10,11,17,18,36].

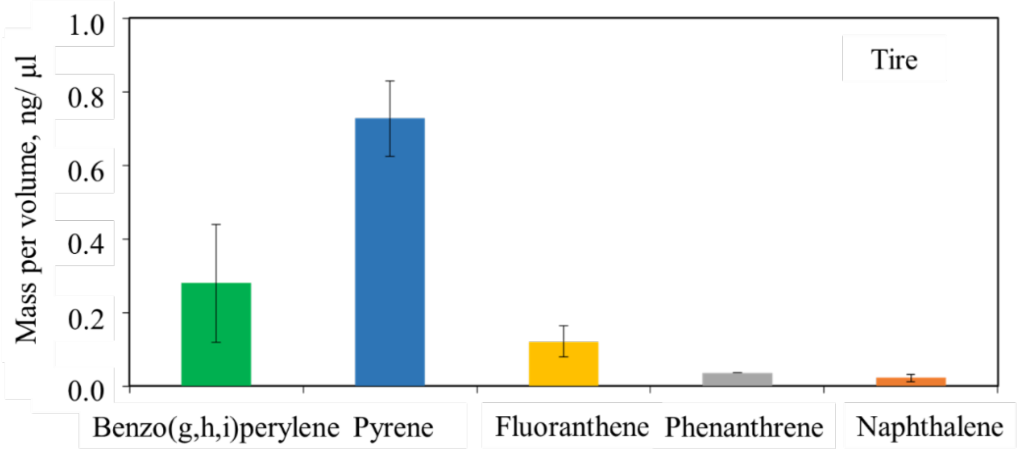

Figure 8. The distribution of benzo(g,h,i)perylene, pyrene, fluoranthene, phenanthrene, and naphthalene of PAHs in the tire samples. Error bars indicate 95% confidence intervals.

The distribution of the chemical components of PM samples in the environment, which was collected at a point 20m and 70 m away from the roadside, respectively, were depicted in Figure 9. For the 20m (solid-pattern bar), benzo(b)fluoranthene showed the highest concentration, followed by fluoranthene, benzo(g,h,i)perylene, pyrene, phenanthrene, and naphthalene in that order. It is generally known that PAHs in the atmosphere are generated mostly through the incomplete combustion of fossil fuels [11,25,26,34,37,38], but it was reported that PAHs are also emitted from TRWP [10,11,16].

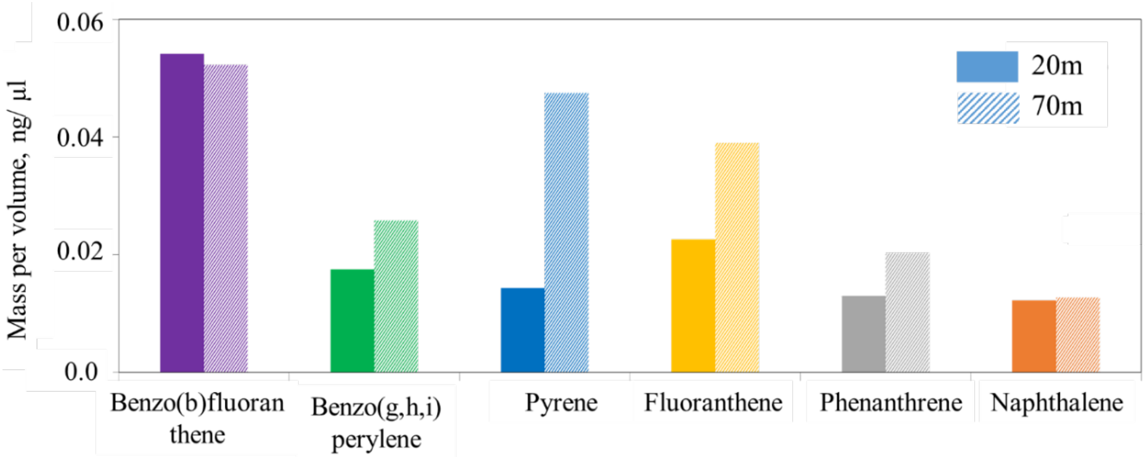

Figure 9. The distribution of chemical components of PM samples in the environment, collected at point 20 m and 70 m away from the roadside, respectively.

For the 70 m(comb-pattern bar), the mass per volume for benzo(b)fluoranthene noticeably shows highest (0.053ng/µl) than that for the other chemical components consisting of PAHs in TSP, 0.028ng/µl for benzo(g,h,i)perylene, 0.048ng/µl for pyrene, 0.039ng/µl for fluoranthene, 0.019ng/µl for phenanthrene, and 0.01ng/µl for naphthalene, which can be attributed to the incomplete combustion of fossil fuels and tire wear particles. Furthermore, the mass per volume for benzo(g,h,i)peryline, pyrene, fluoranthene, and phenanthrene in the 70m TSP samples were relatively higher than those of 20m, as depicted in Figure 10. This can be, as stated earlier, due to the heavy-duty vehicles used in the industrial complex for cargo transport and various construction machinery in the construction sites, which were placed near the TSP sampling equipment. In general, the environmental condition in which the heavy-duty vehicles drive and construction machinery operate

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would lead to higher PAHs emissions, which can cause to higher chemical components consisting of PAHs.

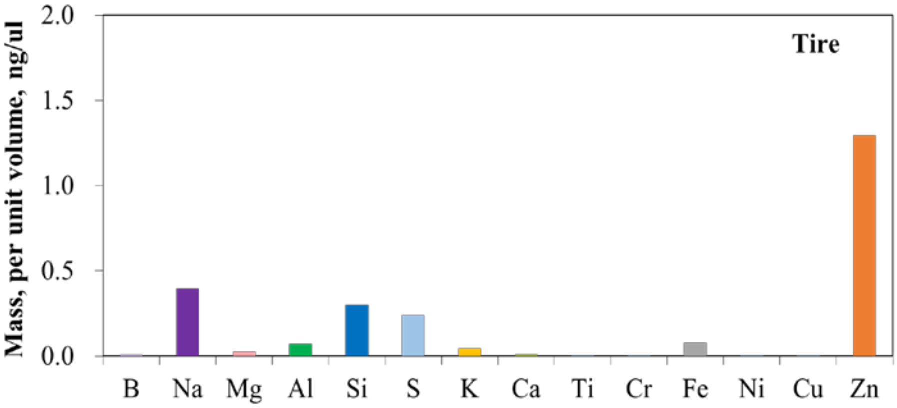


Figure 10. The distribution of metal components in the tire samples.

The distribution of metal components in the tire samples was represented in Figure 10. The metal components in the environment are mainly induced by the additives for fuel and lubricant oil and non-exhaust emissions (i.e., metals used in the tire and brake). The metal components also have a serious impact on human health and the environment, which leads to a comprehensive investigation by measuring, characterizing, and monitoring metal components. As shown in this figure, Zn exhibited the highest concentration among the heavy metals in the tire sample, followed by Na, Si, Al, Mg, Fe, S, and K, in that order. The substances used as accelerators during the vulcanization process in tire manufacturing include Pb, Mg, Zn, sulfur and calcium oxides, and retardants include terpene-resin acid blends. Zn is added by 1% in tire manufacturing [39]. It has also been reported that Zn in tires exists as inorganic matter (ZnS and ZnO) and organic compounds (Zn stearate), and accounts for 0.4–4.3% of tire treads [13,28,39]. Therefore, Zn appears to have exhibited the highest concentration in the tire samples in this study [12,14,17,18].

The list of metals chemically analyzed for the tire samples and the TSP samples are shown in Table 4, Table 5, and Table 6, respectively. For the tire samples, Zinc exhibited the highest concentration of all the tire samples. The other metals showed different tendencies depending on the tire sample. For the total TSP samples and the TSP sample at 20m, Ca is the highest metal component among the metals, followed by Si, Al, Fe, and Na, in that order. In comparison of metal components between both samples, tire samples and TSP samples, S, Cr, and Ni are detected in the tire samples, while these metal components are not shown in the TSP samples. Furthermore, P, Mn, Ba, and Pb are measured in the TSP samples, in contrast, it presents that the tire samples do not include these components.

Table 4. Metal components in the tire samples.

Metal compounds (ng/ul)	Average	Standard deviation	Variation
B	0.007	0.004	1.9E-05
Na	0.396	0.222	4.9E-02
Mg	0.027	0.002	5.3E-06
Al	0.074	0.036	1.3E-03
Si	0.300	0.227	5.1E-02
S	0.238	0.109	1.2E-02
K	0.045	0.029	8.4E-04
Ca	0.009	0.007	4.6E-05
Ti	0.001	0.001	1.9E-06
Cr	0.001	0.000	1.2E-07

Fe	0.078	0.091	8.3E-03
Ni	0.002	0.003	7.7E-06
Cu	0.004	0.004	1.6E-05
Zn	1.297	0.216	1.1E-05

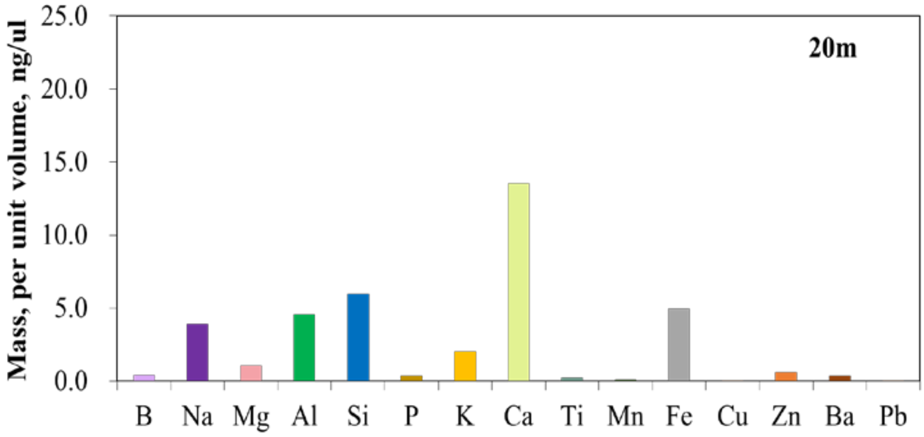
Table 5. Total Metal components in the TSP samples at 20m and 70m.

Metal compounds (ng/ul)	Average	Standard deviation	Variation
B	0.409	0.121	0.015
Na	3.779	1.145	1.311
Mg	1.061	0.704	0.496
Al	4.659	2.015	4.060
Si	5.735	4.678	21.884
P	0.369	0.117	0.014
K	2.125	0.681	0.464
Ca	13.018	4.240	17.975
Ti	0.219	0.167	0.028
Mn	0.112	0.045	0.002
Fe	4.706	2.173	4.723
Cu	0.047	0.026	0.001
Zn	0.604	0.237	0.056
Ba	0.403	0.205	0.042
Pb	0.044	0.013	0.000

Table 6. Metal components in the TSP samples at 20m.

Metal compounds (ng/ul).	Average	Standard deviation	Variation
B	0.421	0.145	0.021
Na	3.926	1.355	1.836
Mg	1.065	0.862	0.743
Al	4.588	2.462	6.060
Si	5.982	5.697	32.458
P	0.393	0.130	0.017
K	2.050	0.814	0.662
Ca	13.564	5.017	25.173
Ti	0.240	0.197	0.039
Mn	0.117	0.053	0.003
Fe	4.963	2.586	6.689
Cu	0.046	0.032	0.001
Zn	0.622	0.287	0.082
Ba	0.378	0.243	0.059
Pb	0.040	0.012	0.000

Figure 11. represents the distribution of metal components in TSP samples at 20 m and 70 m. Ca exhibited the highest concentration among the heavy metals in TSP, followed by Si, Fe, Al, Na, K, Mg, and Zn. This was similar to the result of a previous study in which Ca, Ma, Na, K, Fe, and Al showed high values in the heavy metal analysis results at a roadside measurement point [12]. In particular, Ca, Ma, and K are metal components that occur at high proportions in soil matrices and are reported to be the influence of resuspended dust in soil [12]. In previous studies on the distribution of metals for road dust and vehicle exhaust gas, Al, Fe, and Ca were observed in both road dust and vehicle exhaust gas, but Si, Cu, and Zn were mainly measured in road dust and S, Na, and Mg in the exhaust gas from vehicles [28,40,41]. From the previous studies, it reveals that heavy metals in the atmosphere are affected by various sources such as road dust, tire wear particles, and vehicle exhaust gas.



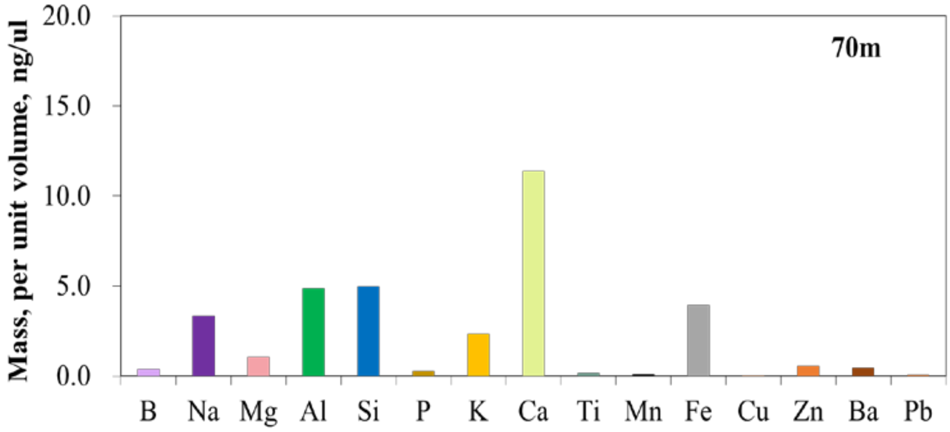


Figure 11. The distribution of metal components in the TSP was sampled at 20m and 70m.

6. Conclusions

In this study, the markers from the rubber used in tires were measured with the pyrolysis-GC/MS analysis, the GC/MS analysis, and the ICP/MS analysis for the tire samples and the particulate matter (PM) samples from the atmosphere. PAHs and heavy metals were analyzed from those samples. The influence of tire wear particles on PM in the atmosphere was investigated by analyzing the measured concentrations of the markers. The results provide accurate experimental data for the distribution of tire markers, PAHs, and metal contents. The data are, however, limited in their applicability for the whole country due to the restrictions imposed by a small sample size and region.

As for the distribution of vinylcyclohexene and dipentene, which are the markers of SBR and NR, measured in tire samples, more vinylcyclohexene was detected than dipentene. This indicates that more SBR is added to tires than NR during the manufacturing process. In TSP samples, more dipentene was detected than vinylcyclohexene. NR appears to wear from tires in the form of lighter particles than SBR due to the physical and chemical properties of these two substances.

In PAH analysis from tire samples, pyrene exhibited the highest concentration, followed by benzo(g,h,i)perylene, fluoranthene, phenanthrene, and naphthalene. This appears to be due to the aromatic oil, which was used during the tire manufacturing process.

In TSP samples, benzo(b)fluoranthene showed the highest concentration, followed by benzo(g,h,i)perylene, fluoranthene, phenanthrene, pyrene, and naphthalene. It appears that the low concentrations of pyrene in the atmosphere originates from tires. This is based on a previous study that reported pyrene detection in tires and in the atmosphere. The other substances appear to have been affected by the exhaust gases emitted from the combustion process.

Zn exhibited the highest concentration for all the tire samples, and metal components, such as Na, Si, Al, Mg, Fe, S, and K, showed different tendencies depending on the tire sample. Zn appears to have exhibited the highest concentration because it is added by 1% during the vulcanization process in tire manufacturing and it reportedly accounts for 0.4 to 4.3% in the tire tread. In TSP samples, Ca showed the highest concentration, followed by Si, Fe, Al, Na, K, Mg, and Zn. Based on the previous studies, it is estimated that heavy metals in the atmosphere are affected by various sources, such as road dust, tire wear particles, and vehicle exhaust gas.

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Data Availability: Not applicable

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

Ethics Statement: This material is the authors' own original work, which has not been previously published elsewhere.

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