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Posted Date: 14 May 2024

doi: 10.20944/preprints202405.0928.v1

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Brake Wear and Airborne Particle Mass Emissions from Passenger Car Brakes in Dynamometer Experiments Based on Worldwide Harmonized Light-Duty Vehicles Test Procedure Brake Cycle

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Abstract: Brake wear particles, as the major component of non-exhaust particulate matter, are known to have different emissions, depending on the type of brake assembly and the specifications of the vehicle. In this study, brake wear and wear particle mass emissions were measured under realistic vehicle driving and full friction braking conditions using current commercial genuine brake assemblies. Although there were no significant differences in either PM_{10} or $PM_{2.5}$ emissions between the different cooling air flow rates, brake wear decreased and ultrafine particle ($PM_{0.12}$) emissions increased with increasing cooling air flow rate. Particle mass measurements were collected on filter media, allowing chemical composition analysis to identify the source of brake wear particle mass emissions. The iron concentration in the brake wear particles indicated that the main contribution was derived from disc wear. Using a systematic approach that measured brake wear and wear particle emissions, this study was able to characterize correlations with elemental compositions in brake friction materials, adding to our understanding of the mechanical phenomena of brake wear and wear particle emissions.

Keywords: brake dust; non-exhaust emission; non-tailpipe emission

1. Introduction

Particulate matter in urban air is of concern in terms of climate change and human health, and emissions from road traffic are known to be an important source. Particulate matter emitted by road traffic includes exhaust particulates from incomplete combustion of fuels and evaporation of lubricating oil components, as well as non-exhaust particulates either emitted by vehicles or resuspended in the air from road surfaces disturbed by moving vehicles [1,2]. Particulate matter associated with brake wear and other non-emission particles accounts for more than half of all vehicle-derived particulate matter in cities, suggesting the importance of non-exhaust emissions in the urban environment [3–5]. In response to the challenge of measuring particle mass emissions related to brake wear particles [3–5], the Working Group on Energy and Pollution (GRPE) organized the particle measurement programme informal working group (PMP-IWG) in 2021 to develop a global technical regulation (GTR24) for the sampling and measurement of brake dust emitted by light duty vehicles up to 3.5 tonnes [6,7]. An industrial standard for measuring the mass emission of brake wear particles in the air by friction brakes for passenger cars was established in Japan by the Society of Automotive Engineers of Japan in 2020 [9]. The EURO7 regulation [8], , recently decided to be introduced in Europe, will limit tire wear amounts and PM_{10} that is particulate matter 10 micrometers or less in diameter missions from brakes due to wear, with the aim of improving air quality by keeping vehicle emissions to the lowest possible level [10]. In accordance with Japan's environmental policy-making process [11], the Japanese Expert Committee on Vehicle Emissions has discussed this issue and is in the process of formulating the "Future Measures to Reduce Vehicle Emissions (15th

 doi:10.20944/preprints202405.0928.v1

Report)". The Japanese Ministry of Environment has stated at the World Forum for Harmonization of Vehicle Regulations (WP.29) that it will actively participate in and contribute to the evaluation of globally harmonized standards to take into account the emission characteristics of brake wear particles, using the knowledge obtained from research on the impact of brake wear particles emissions on air quality [12].

Brake wear is the most important starting point in the emission of brake-related particles. Conventional wear studies measure the mass of a sample used before and after applying a defined amount of friction, which is always done under static conditions, although dynamic friction models that include friction history have been established [13]. The correlation of brake emissions to pad and disc wear factors performed in the World harmonized Light-duty Test Procedure (WLTP) Brake Cycle [14], according to the standard driving conditions of a real vehicle, is the focus of many ongoing research projects. It is known that brake emissions are closely related to the brake wear factors of pads and discs, and research efforts are underway to develop wear-resistant brake pads and discs to minimize emissions from braking systems by modifying the composition of friction and disc materials. Brake pads do not contain a single raw material, but a variety of materials in varying proportions. These materials are classified into four categories based on their functionality: friction modifiers, reinforcing materials, fillers, and binders [15,16]. The effects of various components of brake pads on brake emissions have been studied, focusing on binder resins [17], fillers [18], and other components [19,20]. Low-steel type brake pads tend to cause more brake emissions than non-steel pads because of their high level of aggressiveness toward the corresponding gray iron discs. In addition, brake discs with lower surface hardness have higher brake emissions due to higher disc wear [6,21–29]. On the other hand, there have been reports comparing non-steel and steel pads, where pad and disc wear factors are comparable, but brake emissions are lower for non-steel pads [26,27], so the effect of pad and disc wear factors on brake emissions is complex.

One contributing factor is that the friction film on the pad surface plays an important role in determining the wear resistance and brake emissions of brake pads and discs. Wear particles from the pad and disc aggregate to form a friction film on the pad surface, which serves as a temporary reservoir for wear particles during sliding between the frictions and the counterparts before this film is partially broken down and free particles are released [16,30–33]. Therefore, the cohesion of the friction film, which determines the wear resistance and particle ejection of the brake pad, is strongly influenced by the wear particles produced by the pad and disc. The brake wear factor of the pad and disc are also known to play an important role in determining the friction brake workload (test vehicle mass, tire dynamic load radius, and inertia as related to the kinetic energy provided to the brake), which in turn determines the wear resistance and brake emissions of the brake pad and disc. Despite the fact that previous research has focused on the interaction between brake wear particle emissions and the intended brake assembly (pad/disc combination), a systematic approach to brake emissions and brake friction material characterization for commercial brake assemblies currently in use is lacking.

In this study, our research team measured brake wear particle emissions from current commercial vehicle brake assemblies using different genuine conventional gray iron discs and brake pads. We focused especially on the brake wear factors of pads and discs and on the behavior of airborne particle mass emission factors. Data from 31 test investigations of brake wear particle emissions in our laboratory were compared under various measurement conditions from the public WLTP Brake Cycle to the current state. Brake wear particle emissions were found to correlate with pad and disc wear factors and brake wear particle emissions, but the particle mass emissions to brake wear factor ratios vary for different types of brake assemblies. The characteristics of elements in brake friction materials and brake particle emissions were identified based on the correlation of elemental contents in brake pads to brake wear and brake wear particle emissions.

 doi:10.20944/preprints202405.0928.v1

2. Experimental Methods

2.1. Dynamometer Experiments

Brake wear particles were measured for 31 different types of commercially available original equipment manufacturer conventional gray cast iron disc assemblies (Table A1). The test brake assemblies were commercially available genuine brake assemblies; each consisted of a conventional cast iron ventilated disc, caliper, and brake pads. A single passenger car front brake wheel was used for driving and brake control in accord with the worldwide light vehicle test procedure (WLTP) brake driving profile (WLTP-Brake Cycle) [14] using an electric inertia dynamometer. The conditions required to control the test brake, the tire dynamic load radius and inertia [34], and the nominal wheel load to disc mass ratio (WLn/DM) required to define the brake temperature are given in Table A1. Three enclosure/tunnel types were used (Table A1): Type A, the enclosure/tunnel (inner diameter φ80.7) equivalent to JASO [9] used in previous studies [35,36]; Type B, enclosure type A changed to a height of 700 mm and tunnel type A changed to an inner diameter of φ80.7); and Type C, enclosure type A changed to a depth of 200 mm, and tunnel type A changed to an inner diameter of φ208.3 as in [37]. The brake assembly was fitted to the dynamometer using universal style (L0-U) brake fixings as described in GTR24 [7]. Disc temperature was measured by locating a thermocouple 10 mm radially outward from the center of the friction pad and at a depth of 1.0 ± 0.1 mm from the disc surface for enclosure/tunnel type A or 0.5 ± 0.1 mm for enclosure/tunnel types B and C in some of the experiments.

The sampling of brake wear particles was based on the JASO C 470 test method [9] and previous studies [35,36]; the process consists of an enclosure with a brake assembly inserted downstream of air supplied through a HEPA filter and a constant-flow sampling tunnel (25°C standard for enclosure/tunnel Type A, 20°C standard for enclosure/tunnel types B and C) (Table A1) because the GTR24 test method was not defined at the time of this experiment [7]. The cooling air flows in a right-to-left direction when the brake disc is viewed from the front, whereas the disc rotates in a counter-clockwise (CCW) direction [7] or clockwise (CW) in some of experiments.

The two most important categories used in this study were low-steel (low-metallic) pads (also known as European performance or "ECE"), which are developed and produced primarily for the European market, and non-asbestos organic (NAO) pads, which are designed primarily for the North American and Asian markets [25,38]. These two types of pads can be distinguished, inter alia, by the percentage of metal components in them. Low-steel (low-metallic) pads contain a significant percentage of iron, whereas NAO pads are usually steel-free (non-steel). However, as previous studies have shown [26,27], even NAO could be registered as ECE in electrified vehicles [37], making the chemical definition ambiguous. Therefore, in this study, pads with less than 0.1% Cr (an additive in steel), which are sold in the Japanese market and referred to as NAO, are defined as "non-steel pads", and pads with several percent or more Cr are defined as "low-steel pads". Table B1 summarizes mass percentages of elements in the brake pads and discs used in this study. The elements of brake pads (Table B1) and discs (Table C1) were measured by wavelength-dispersive X-ray fluorescence (WD-XRF) analysis (ZSX Primus II, Rigaku, Corp.) [36].

2.2. Brake Wear and Particle Mass Measurements

Sampling of PM_{10} and $PM_{2.5}$ was conducted with a multi-cascade impactor (MCI) (MCI-20, Tokyo Dylec Corp.) according to the methods reported by [35,36] and JASO test protocol [9] on a Teflon filter (Fluoropore FP-500-100, 47 φ for PM_{10} and $PM_{2.5}$, Sumitomo Electric Fine Polymer Corp.) or a Teflon filter with a support ring (PT47, 47 φ, Measurement Technology Laboratory). Aspiration was from a isokinetic sampling nozzles. In several experiments, PM_{10} and $PM_{2.5}$ were measured using a cyclone for PM_{10} (URG-2000-30ET, URG) and a cyclone for $PM_{2.5}$ ($PM_{2.5}$ Very Sharp Cut Cyclone [VSCC], BGI), respectively [37,39]. Samples were collected by a suction pump with a mass flow controller (MQV0050, Azbil Corp.) at a flow rate of 20.0 L/min according to the MCI design or 16.7 L/min according to the cyclone design and controlled at 20°C standard conditions. Within one hour after the test, in a thermostatic chamber in a clean room (room temperature 22 ± 3°C, relative humidity

 doi:10.20944/preprints202405.0928.v1

45 ± 8%), an electronic balance (XPR2UV, Mettler-Toledo International Inc., resolution 0.1 µg) was used immediately after neutralizing the filter with an ionizer for the filter weighing.

A low-pressure impactor (LPI) (LP-20, Tokyo Dylec Corp.) was used to measure the distribution of mass particle sizes of aerodynamic particles with sizes in the range of 0.05–11 µm. The particles were collected and sampled through the WLTP Brake Cycle three times. Samples were collected by a mass flow controller (MQV0050, Azbil Corp.) at a flow rate of 23.8 L/min at 20°C standard conditions according to the LPI design. The brake wear particles of each 50% cut aerodynamic particle size were controlled at ≤0.05, 0.12, 0.2, 0.3, 0.48, 0.68, 1.2, 2.0, 3.5, 5.1, 7.7, and ≥11 µm of 50% cut aerodynamic particle diameters were collected on a Teflon filter (Fluoropore FP-500-100, 80 φ, Sumitomo Electric Fine Polymer Corp.) by controlling the flow rate, respectively.

Total metals, including the water-soluble and insoluble fractions, were measured via energy dispersive X-ray fluorescence (XRF) (Epsilon 5, Malvern PANalytical) [40].

The experiments were repeated two or three times under full friction brake work conditions after the five bedding cycles in accord with the previous experimental conditions [6] so that the mass loss data could be compared. The mass loss of the friction partners (pads and discs) was determined (mg), and the brake wear amount divided by the total experimental mileage (km) was derived to allow comparison with airborne particle emission factors. Mass loss of the friction partner was measured before and after an experiment in the laboratory at a temperature of 20°C and relative humidity of 50%. For the mass loss measurements, we used an electronic balance for brake pads (XPR404SV, Mettler-Toledo International Inc., resolution 0.0001 g), a mass comparator for brake discs (KA50–2, Mettler-Toledo International Inc., resolution 0.001 g), and a different mass comparator for brake discs over 10 kg (XPR10003SC, Mettler-Toledo International Inc., resolution 0.01 g). The mass loss measurements were taken within 1 hour after the experiment.

3. Results and Discussion

3.1. Brake Wear Factor Measurement

3.1.1. Storage Stability for Wear Weighting

The brake wear factor is an important measurement item because it is the starting point for brake wear particle emissions, and brake wear itself can vary significantly. For example, the results of an interlaboratory study (ILS) of brake wear particle emission showed a 50% variation (brake wear factors 1.8–7.6 mg/km) among 8 laboratories for the Brake1b [6]. In the GTR24 regulation [7], after the brake emission test is completed, the brake components are stored for up to 24 hours in a room with controlled temperature and humidity, cooled below 30 °C, and weighed. We confirmed the storage stability of the pads in experiments 4, 6, 8, 10, and 12. It shows the pad mass differences and the ratio of pad mass differences to mass loss measured within one hour after the test at various storage times. In experiments 4, 6, 8, 10, and 12, the mass difference increased from 0.2048 to 0.5783 g and the ratio of mass difference to mass loss increased from 16.2% to 51.2% at 24 hours. The change in pad mass was suggested to be due to the adsorption of gases and the oxidation and rusting of the pad material because pads generally have a porous structure that is filled with various materials, compressed and formed, and sintered. In order to reproducibly measure the mass loss of the pad, it is recommended that the measurement be performed within one hour after the test and with the brake temperature below 30°C.

3.1.2. Brake Wear Factors

The disc and brake pad wear amount (i.e., mass loss [6,7]) can provide valuable information for the experimental evaluation of the reasonableness of the particulate matter measurements in this study. It shows the wear factor of the pad and disc for each experiment and the percentage contribution of the disc in the wear factor.

Mass loss measurements are known to be highly variable depending on the type of experimental brake. Results of the ILS with six different Low-Steel Pads and a conventional cast iron disc brake assembly showed total brake wear factors ranging from 5.02 to 20.1 mg/km [6]. In a study comparing brake friction materials, the wear factor was 3.06 mg/km for non-steel pads and 5.12 mg/km for low-steel pads, depending on the pad material [7,21–29]. These brake wear factors [mg/km] were calculated by the author as the ratio of PM_{10} to mass loss from ILS data [6]. Other studies using brake assemblies with low-steel pads and conventional cast iron discs, carbon composite discs, and hard-coated discs obtained brake wear factors of 3.23–24.5 mg/km [26]. In this study, we obtained total brake wear factors of 0.6–21.8 mg/km using genuine brake assemblies of commercial vehicles having test vehicle masses of 943–3390 kg, including non-steel and low-steel pads. Brake wear factors per brake were 0.6–10.2 mg/km for non-steel pads and 13.8–21.8 mg/km for low-steel pads. Non-steel pads were developed to optimize comfort (reduction of noise and rim contamination), and this study as well as previous studies [6,21–29] have shown higher emissions with low-steel pads than with non-steel pads.

The above comparison of brake wear factor with each experiment is based on different brake assemblies and masses of test vehicles. Low-steel pads had a higher brake wear factor than non-steel pads in our experiments. Low-Steel Pads are used in Europe, especially in Germany, where the high demands on braking performance and temperature stability of the friction system require somewhat more aggressive brake pads but have, at the same time, correspondingly higher wear [26,27]. Although the results of this study and those of previous studies based on the WLTP Brake Cycle were in the same range, one study has found that the brake wear factors of non-steel and low-steel pads are almost the same [26]. Therefore, additional systematic studies are needed to clarify whether there are significant differences in brake wear factors between non-steel and low-steel pads.

Brake wear particles are generated by pad and disc wear or by evaporation or thermal decomposition of pad components [41]. To understand the emission factors of brake wear particles, we compared the wear coefficients of the pads and discs. About 14.0–74.8% of the wear particles were from the disc, 14.0–64.4% from the non-steel pads, and 55.0–74.8% from the low-steel pads. We found that the disc wear factor and pad wear factor were correlated with the total brake wear factor. Low-steel pads tended to have higher disc wear factors, and non-steel pads tended to have lower disc wear factors. Al-though the disc and pad wear factors are not necessarily constant, assuming that the slopes of the respective linear regression lines represent the statistical mean of our experiments, we found that the disc wear factor and pad wear factor contribute 64.8% and 35.2%, respectively, to the brake wear factor. a typical characteristic of friction pairs of low iron pads and discs is that disc wear is reported to be higher and often accounts for about 60% or more of the total wear [26]. Therefore, the results obtained in this study reflected typical characteristics of the friction pairing of low-steel pads and discs.

3.2. Particle Mass Measurement

3.2.1. Storage Stability for Particle Mass Weighing

It shows the storage stability of PM_{10} and $PM_{2.5}$ collected on filter media during Experiments 13–18; Day 0 was weighed within 1 hour after the test, Day 1 was measured 24 ± 1 hours after the test, and Day 2 was measured 48 ± 1 hours after the test. The samples were stored in a HEPA-filtered electronic balance chamber at 22 ± 2 °C and 45 ± 8% RH before weighing. The GTR24 test regulation [7] allows filters to remain in the test chamber for an extended period of time as long as the filter remains sealed in the filter holder and the conditions in the test chamber are stable within the same temperature and relative humidity conditions noted above. In our experiments, filter media stored in the weighing chamber were observed to vary within 48 hours, with a relative standard deviation (RSD) of 0.11–0.28% for PM_{10} and 0.14–0.32% for $PM_{2.5}$. The RSD tended to increase when the particle mass on the filter media was small. The variability in the emission factor measurements for Experiments 13–18 ranged from an RSD of 1.1–3.2% for PM_{10} to 1.3–7.1% for $PM_{2.5}$, with a tendency for the variability to increase as the emission factor decreased. Compared to the PM_{10} emission factor data from ILS [6], which used the same brake assembly, there was a general trend toward greater emission variability with lower emission factors, although that included between-test variation in the measurement device.

3.2.2. Collection Device for Particle Mass Measurement

It is important to understand the distribution of emitted particle sizes, both from the perspective of emissions to the atmosphere and from the perspective of health effects. In previous investigations, emissions of brake wear particles according to aerodynamic particle size by LPI were distributed between 2 and 3 µm in mode diameter [36,37]. This means that there is uncertainty in the measurement of $PM_{2.5}$ because the separation characteristic curve is sharper when measuring $PM_{2.5}$. In this study, $PM_{2.5}$ was measured using a GTR24-based PM_{10} cyclone and a sharp-cut cyclone with an impactor that is rated as a method equivalent to the WINDS impactor in $PM_{2.5}$ separation characteristics [26,39].

The emissions of brake wear particle masses were determined according to their aerodynamic particle diameters measured with an LPI. Generally, the height of each particle size interval is affected by the width of that interval, and the result is a distortion of the shape of the fraction. We therefore used a histogram, in which the particle mass of each fraction was divided by the width of that fraction (d*M*/dlogDp), and the particle size distribution was normalized by the particle size intervals [42]. However, because the height of each particle size fraction was expressed as the emission factor of the particle mass measured in each fraction, the vertical axis of the graph was used as d*M*. The brake wear particle emissions were distributed in a mode diameter range of 2–4 µm throughout the WLTP Brake Cycle. The ratios of emissions of fine particles ($PM_{2.0}$ based on LPI specifications) and nanoparticles ($PM_{0.12}$ based on LPI specifications) to PM_{11} based on LPI specifications were 31.2% (12.8 to 43.3%, n=21) for non-steel pads of $PM_{2.0}$, 21.3% (11.1 to 28.3%, n=21) for low-steel pads of $PM_{2.0}$, 31.2% (11.1 to 43.3%, n=7) for non-steel pads of $PM_{0.12}$, and 0.4% (0.1 to 0.7%, n=7) for low-steel pads of $PM_{0.12}$. For the brake assemblies investigated in this study, the contribution of fine and nanoparticles to the total PM emissions was small, which is consistent with results from previous studies [29,35–37].

On the other hand, for particle collection using multistage impactors (e.g., 13 stages for the LPI in this study), there have been reported that 14% particles deposited on the walls of the device, and the relative loss has an error of 50%, depending on the production lot of the impactor [43]. It shows the emission factors for PM_{10} and PM_{11} (Experiments 1-28), $PM_{2.5}$ and PM_2 (Experiments 1-28), cyclone and MCI for PM_{10} (Experiments 13–18), and cyclone (Experiments 13–15) and MCI (Experiments 20–22) for $PM_{2.5}$. Previous studies have indicated that the LPI, a multistage impactor, tends to detect lower particle loss [43], and assuming that the slope of the regression line that crosses the origin is the mean value, the loss was estimated to be 22.9% for PM_{10} and 37.4% for $PM_{2.5}$. Due to the slight variation in the 50% cut diameter characteristics for $PM_{2.5}$, we expected a larger error in the measurement of brake particles with mode diameters between 2 and 3 µm for the aerodynamic diameters. For the comparison of MCI by the JASO C470 method and cyclone by the GTR24 method, the difference was 1.9% for PM_{10} and 1.8% for $PM_{2.5}$ (estimated from the regression line). There was no significant difference between these two measurement methods, especially for PM_{10}, which is proposed as a regulation value in Euro 7.

The above findings indicate that the differences in measured PM_{10} emission factors can be considered equivalent unless a multistage impactor is used. PM_{10} and brake wear factors will be discussed in subsequent sections, including comparisons with emission factors and mass loss.

3.2.3. Cooling Air Flow Effect for Particle Mass Emission

The emission factors of PM_{10} and $PM_{2.5}$ were similar with increasing cooling air flow (from 1 m^3/min to 10 m^3/min); the regression lines cross the origin point from the measurement principle (PM_{10}: R^2 = 0.965, r=0.924, p<0.05, n=5; $PM_{2.5}$: R^2 = 0.988, r=0.961, p<0.05, n=5). Because the regression lines cross the origin, R^2 was treated as a similarity index, not as a coefficient of determination. There was no significant difference in the emission factors between the two conditions using the JASO C470 sampling systems (Enclosure/Tunnel Type A) [9]. We estimated the difference due to cooling air flow

 doi:10.20944/preprints202405.0928.v1

to be about 8.1% for PM_{10} based on the slope of the linear regression line, with a similarity R^2 of 0.981 (r = 0.65, p<0.1, n=5) when comparing the two cooling flow rates of 1 m^3/min and 10 m^3/min. In a previous study, there was also no significant difference in the $PM_{2.5}$ to PM_{10} ratio when the cooling flow rate was increased from 15 m^3/min to 20 m^3/min [44]. Therefore, the current results were consistent with those of previous studies, and the PM_{10} and $PM_{2.5}$ emissions were reproduced under very low air flow conditions (1 m^3/min) using the JASO C470 method and under high air flow conditions (10 m^3/min) equivalent to those of the GTR24 method. On the other hand, our observed $PM_{0.12}$ under high air flow conditions (10 m^3/min) tended to be 12.2 times higher than the low air flow conditions (1 m^3/min) (R^2 = 0.965, r=0.065 p<0.5, n=5). There was no significant difference in the ratio of $PM_{2.5}$ to PM_{10} as the flow rate increased, but the ratio of $PM_{0.12}$ to PM_{10} increased by 14.7 times from a flow rate of 1 m^3/min to 10 m^3/min. $PM_{0.12}$ emissions, known as ultrafine particles, contributed only a small fraction of PM_{10} emissions in our study, ranging from 0.1–28% (3% on average, n=28). These small particles (particle size less than 0.12 µm) may be agglomerated into larger coarse particles and emitted less (i.e., ultrafine particles will be counted among coarse particles).

It shows that the increase in cooling air flow rate clearly implies a higher PM_{10} to total wear ratio. The slope of the regression line of the two variables across the origin associated with the measurement principle shows that the brake wear factor increases by a factor of 2.03 for PM_{10}, 1.99 for $PM_{2.5}$, and 23.2 for $PM_{0.12}$ with higher cooling air flow rates. The difference between the PM_{10} (2.03) and $PM_{2.5}$ (1.99) emission factors of the two experiments indicates the uncertainty of the experiments. The decrease in losses in the tunnel by decreasing the Stokes number (increasing collection efficiency, as shown in the PM to brake wear factors) at increasing cooling air flow rate should have a strong impact, indicating the uncertainty of the experiment [44]. The extremely low cooling air flow rate (1 m^3/min) in the JASO C470 method used in this study is a limitation of the structural requirements for future tests using automobiles, and it has been used in previous studies to collect sample air at 0.1–0.3 m^3/min [45], 0.5–1.3 m^3/ min [46], and 1.48 m^3/min [47]. As described above, there is a trade-off between the reproducibility when the sample to be measured is diluted by increasing the cooling air flow rate and the reproducibility when the concentration is lowered, in order to study the health effects and reproducibility of ultrafine particle measurement without mass contribution focusing on ultrafine particles in the future investigation. For reference, Experiments 23 and 27 were compared under high flow (7.7 m^3/min) measurement conditions with different sampling methods using the same brake assembly for Experiments 4 and 12, respectively (but different production lots). The regression lines were generally consistent with the low flow rate (1 m^3/min) and high flow rate (10 m^3/min) using the JASO C470 enclosure, and the plots for Experiments 23 and 27 were observed to be higher than the regression lines for PM_{10} only. The brake wear factor was higher at lower cooling air flow rates (1 m^3/min), while it was 58.3% lower than the slope of the regression line at higher cooling air flow rates, indicating that the increased sampling efficiency resulted in PM_{10} and $PM_{2.5}$ emissions being similar in the GTR24 procedure as a result of improved sampling efficiency. GTR24 defines brake temperature, but the flow rate is not defined at a constant value. Therefore, when designing brakes considering the total brake wear rate, manufacturers should be careful to note that brake wear factor varies with the tunnel flow rate being measured.

3.3. Comparison of Particle Mass Emissions and Brake-Wear Factors

3.3.1. Particle Mass Emissions and Effect of Test Vehicle Mass

Emissions per brake (single axle) ranged from 0.14 to 13.1 mg/km for PM_{10} (non-steel pads: 0.14–4.2 mg/km, low-steel pads: 5.4–13.1 mg/km), from 0.08 to 3.8 mg/km for $PM_{2.5}$ (non-steel pads: 0.08–1.1 mg/km, low-steel pads: 1.1–3.9 mg/km), and from 0.002 to 0.04 mg/km for $PM_{0.12}$ (non-steel pads: 0.002–0.04 mg/km, low-steel pads: 0.007–10 mg/km). A comprehensive literature review of the current status of passenger car brake wear particle emissions showed that for conventional cast iron disc brakes, emissions ranged from 0.1 to 12.4 mg/km for PM_{10} (non-steel pads: 0.1– to 3.9 mg/km, low-steel pads: 1.3– to 12.4 mg/km) and from 0.05 to 6 mg/km for $PM_{2.5}$ (non-steel pads: 0.05– to 2.2 mg/km, low-steel pads: 0.8– to 6 mg/km) [24]. Estimation based on a regression line between vehicle mass and PM_{10} emissions for the 35 cases provided by OICA (Organisation Internationale des Constructeurs d'Automobiles) yielded 3 mg/km per brake per 1000 kg vehicle mass, which is similar to the value obtained from the 62 cases in the literature review on ECE brake assemblies (3.1 mg/km per brake per 1000 kg vehicle) [24]. This study follows the practice in previous studies [e.g., 24] and compares emissions with test vehicle mass. Using the slope of the regression line through the origin between vehicle mass and PM_{10} emissions), low-steel pads (9 cases) had a PM_{10} emission of 3.9 mg/km per brake per 1000 kg of vehicle mass, with a large variance, as was also found in a previous study [24]. Non-steel pads (22 cases) had a PM_{10} emission of 0.4 mg/km per brake per 1000 kg of vehicle mass. The results are in reasonable agreement with those in the literature, and they also vary widely depending on the wear characteristics of the pads.

The brake wear factor for low-steel pads (9 cases) was 7.7 mg/km per brake per 1000 kg vehicle mass with large variability, and that for non-steel pads (22 cases) was 1.7 mg/km per brake per 1000 kg vehicle mass. The $PM_{2.5}$ was 1.2 mg/km per brake per 1000 kg of vehicle mass for low-steel pads (9 cases) and 0.15 mg/km per brake per 1000 kg of vehicle mass for non-steel pads (22 cases). Finally, the $PM_{0.12}$, which has not been previously reported, was 0.012 mg/km per brake per 1000 kg of vehicle mass for low-steel pads (7 cases) and 0.0073 mg/km for non-steel pads (22 cases) (0.0097 mg/km excluding the lower cooling air flow rate of 1 m^3/min).

3.3.2. Particle Mass Emissions Correlated with Brake Wear Factors

The investigation of brake wear factors and wear particle emissions behavior in the WLTP Brake Cycle, as defined by actual vehicle driving, is currently the focus of much research. It is known that there is a large variation in the amount of wear, depending on the environment of each research facility (i.e., the dynamometer); in ILS, the variation of the eight laboratories for Brake1b has been shown to have an RSD of 50% [6]. Therefore, this study compared the correlation between brake wear and the emission factors of wear particles in the WLTP Brake Cycle, as defined by actual vehicle driving, measured at a single laboratory.

As in Section 3.2.3, because the regression lines cross the origin, R^2 is treated as a similarity index rather than as a coefficient of determination. In terms of the average of laboratories using different sampling systems in ILS, the corresponding R^2 values are 0.991 for PM_{10} and 0.977 for $PM_{2.5}$. If we consider the regression lines that cross the origin as the ratio of PM_{10} to the brake wear factor and the ratio of $PM_{2.5}$ to the brake wear factor, respectively, the results are 48.2% for the PM_{10} ratio (as the regression slope) and 43.9% for ILS, and 14.5% for the $PM_{2.5}$ ratio (as the regression slope) and 17.4% for ILS. Therefore, our results are roughly consistent with the ILS, indicating that PM_{10} and $PM_{2.5}$ emissions are generally reproduced, regardless of whether the data include very low air-flow conditions (1 m^3/min) using the JASO C470 method or high air-flow conditions (10 m^3/min) equivalent to the GTR24 method.

However, the systematic error of the measurement method becomes apparent when comparing the effect of cooling air flow rate with non-steel pad experiments, and the results obtained should be interpreted with caution, as the high level of brake wear factor and emission values obtained with ILS are driving the statistics. Previous studies [35–37] have mentioned that not all of the brake wear is emitted as airborne brake wear particles, but a previous study [6] and our present results provide stronger evidence.

It shows a comparison of the brake wear factor and $PM_{0.12}$ (R^2=0.520). Large differences in cooling air flow rates led to large variations in $PM_{0.12}$ emissions, even when the same sampling construction requirements were satisfied (e.g., the enclosure and tunnel based on JASO C470 method in this study). The GTR24 method establishes a brake temperature criterion and adjusts the cooling air flow rate [6], but differences in the cooling flow rate may contribute to the variation in ultrafine particle emissions that do not contribute to mass emissions. Further investigation of the correlation between PN emissions and $PM_{0.12}$, as well as the continued investigation of the effects of PN emissions and wind speeds is needed. For PN emissions, emissions of brake wear particles are low, and no regulation values have been established. In addition, Solid-PN (with volatile particles removed) and Total-PN (including volatile particles) measurement methods were first proposed in GTR24. A comprehensive study with a large number of samples is needed.

3.3.3. Disc Wear Contribution to Particle Mass Emissions

Cast iron discs are composed mainly of iron and tiny amounts of additive metals. Previous studies have shown that when the disc is worn by the pad, wear particles (PM_{10} and $PM_{2.5}$) are emitted [e.g. 36]. They also indicated that the contribution of Fe tends to increase from the pad wear to brake wear particles, and Fe is most abundant in PM_{10} and $PM_{2.5}$ for brake wear particles [35–37]. The emission factor of brake wear Fe particles and the disc wear factor are positively correlated with PM_{10} and $PM_{2.5}$. Hence, we attempted to estimate the proportion of disk wear-derived emission factors by using the Fe brake wear particle emission factors.

The PM originating from disc wear (PM_{disc}) and pad wear (PM_{pad}) can be distinguished from the PMx, where x equals 2.5 or 10, by solving simultaneous Equations (1) and (2), which express the PM and Fe mass balance [35–37,48]:

$$PM_{disc} + PM_{pad} = PMx, \tag{1}$$

$$[Fe]_{disc} \times PM_{disc} + [Fe]_{pad} \times PM_{pad} = [Fe]_{PMx} \times PMx\ , \tag{2}$$

where PMx is PM_{10} or $PM_{2.5}$ emissions, $[Fe]_{disc}$ is the Fe mass concentration (%) in the disc, and $[Fe]_{pad}$ is the Fe mass concentration (%) in the pad.

In previous studies [35–37,48], the Fe mass concentration (%) in the disc was fixed at 100%. In another study, the discs of gray cast iron brakes were measured to be composed of Fe as the dominant element (>95%), with only a few other elements (<1% for individual metals) [49]. However, hand-held energy-dispersive XRF devices cannot measure elements such as C, N, O, and S [49], so we considered that a >95% Fe content was an overestimation based on our WD-XRF measurements, which include C, N, O, and S. Cast iron generally contains iron as the main component, with C, Si, Mn, P, and S as the other major elements, and other trace components as graphitization promoters, graphitization inhibitors, graphite eutectic refinement agents, graphite coarsening agents, and perlite stabilizers [50]. Therefore, in this study, we performed the WD-XRF measurements on the pads and used the respective values of 74.4–81.1% Fe (Table C1). The [Fe] pad results were 0.1–6.6% for non-steel pads and 7.3–10.3% for low-steel pads (Table B1). Although non-steel pads are generally declared to be iron-free [26,51], they may contain iron as a lubricant (as iron sulfide) and/or as an abrasive (iron oxide, chromium oxide) [e.g., 15,16]. For this reason, no iron-free, non-steel pads were detected in the genuine non-steel pads used in the commercial vehicles in this study.

By solving Equations (1) and (2), we determined the contribution of the disc to the PMx (F_{disc} [%]) from Equation (3):

$$F_{disc} = PM_{disc} / PMx\ \times 100 = ([Fe]_{PMx} - [Fe]_{pad}) / ([Fe]_{disc} - [Fe]_{pad}) \times 100. \tag{3}$$

A limitation of using Equations (1)–(3) is that the Fe contained in non-steel and low-steel pads may be transferred to a disc, but there has been no study of whether it can be transferred to materials other than cast iron discs. Further large-scale investigations with many types of pads and discs of different materials would be required to address this question.

It shows a comparison of the disc fraction in PM_{10} and in $PM_{2.5}$ against the disc mass loss fraction. We found that the disc fraction in PM determined from the Fe concentration and Equation (3) were positively correlated with the disc fraction determined from the mass loss measurement. As discussed in previous sections, the R^2 values represent a similarity index, and values closer to 1 indicate greater similarity. The correlation coefficients were 0.953 (n=20) for PM_{10} and 0.837 (n=24) for $PM_{2.5}$, indicating a positive correlation. The population numbers were different for PM_{10} and $PM_{2.5}$ because, in some of the experiments where PM was measured by the MCI sampler, Fe was not measured by XRF because a Teflon-coated glass fiber filter was used. Although not all of the disc wear particles are emitted as PM_{10} or $PM_{2.5}$, these results provide strong evidence that the iron

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concentration in PM measured in this study is comparable to the disc to brake wear ratio measured by mass loss [35–37,48].

3.4. Comparison of Elements in Brake Pad and Particulate Matter Emissions

3.4.1. Correlation between Elements in Brake Pads and Particulate Matter Emissions

The effects of different components of brake pads on brake emissions have been studied, mainly focusing on binder resins, fillers, and other components [15–20]. Low-steel type brake pads tend to produce more brake emissions than non-steel pads [21–23] because of their higher level of aggressiveness against gray iron discs. However, previous studies have either tested small pieces based on the intended material formulation or compared a limited sample of commercially available brake types. In this study, based on actual vehicle specifications for a commercial brake assembly and a medium sample size (31 cases), the mass content of elements in brake pads was correlated with the brake wear coefficient and PM_{10}, $PM_{2.5}$, and $PM_{0.12}$ emissions to investigate the effects of various components in brake pads on brake emissions.

It shows the correlation coefficients between the brake wear factor, disc wear factor, PM_{10}, $PM_{2.5}$, $PM_{0.12}$, and the mass content of each element in the brake pad. The correlation coefficients of the mass content of elements in the pads for the brake wear factor, disc wear factor, PM_{10}, and $PM_{2.5}$ were very similar; C, Mg, Cr, and Fe mainly had high positive correlation coefficients, and O, K, Ti, and Ba mainly had high negative ones. $PM_{0.12}$ had no apparent correlations, and further research would be needed to analyze the detailed the properties of the materials, such as heat resistance.

3.4.2. Carbon

The mass content of C in brake pads was positively correlated with the brake wear factor, disc wear factor, PM_{10}, and $PM_{2.5}$. C in brake pads is mainly in phenolic resins, silicone modified resin, and epoxy resins commonly used as binders in most braking systems, and the pads in this study contained 24.5–44.6% C. A binder, also known as a binding agent, is any material or substance that adheres or coheres to other materials in a composite system, preventing them from crumbling and ensuring the structural integrity of the brake pad composite. Binder resins are also used to reduce brake squeal and vibration. Their heat resistance is inferior to that of metals; for example, depending on the chemical modification (chemical structure or additives) of phenolic resins, the thermal weight loss at 400°C varies from 8 to 25 mass% [52]. We suggested that the heat resistance varies depending on the structure of the phenolic resin, but the heat resistance of the materials in brake pad may contribute to brake wear and wear particle emissions, some of which are emitted as gaseous substances by mechanochemical reactions [33] and some by metal additives. Aramid fibers are included as C in the pad as a reinforcement that provides strength, thermal stability, and friction properties [15,16]. For reinforcement, the use of steel fibers instead of aramid fibers leads to higher wear due to accelerated plowing of the mating disc surface, while the addition of aramid fibers leads to relatively less wear of the strong transfer film formed on the disc as the aramid fibers wear [30,31]. In general, the greater the amount of aramid fibers, the better the wear resistance properties [30,31] and, consequently, the lower the particle emissions [32]. The addition of graphite particles has also been reported to improve wear properties [53,54]. Various friction phenomena such as adhesive wear, abrasive wear, detachment of ingredients on transfer films, and generation and detachment of tribo-film are caused at the interface of a pad and disk, and the interactions of these phenomena during braking is complicated [30]. The results of this study indicate that the degradation of the organic resin matrix and aramid fibers forms a transfer film that reduces wear. The actual brake wear and particle emissions are caused by the consumption of the organic resin matrix and aramid fibers, which form a transfer film, and by the detachment of the tribo-film due to adhesive wear [55], which is emitted as friction particles. This suggests that the C content in the pad may be correlated with the brake wear coefficient and PM, supporting the assumption [16] that a dynamic equilibrium between the breakdown of the transfer layer due to wear and the formation and restoration of the transfer film by the carbon in the pad occurs during braking.

 doi:10.20944/preprints202405.0928.v1

3.4.3. Magnesium

The mass content of Mg in brake pads was positively correlated with the brake wear factor, disc wear factor, PM_{10}, and $PM_{2.5}$. Mg in the brake pads is in the form of magnesium oxide (MgO), which is mainly contained as filler [56] and abrasives [57,58], and the pads in this study contained 0.2–7.3% Mg. Fillers are used to improve thermal and noise pad properties and to reduce manufacturing costs [59]. Magnesium oxide is added to adjust the coefficient of friction, and its hardness reduces metal wear while properly conducting heat from the friction contact surface. MgO also increases the thermal stability of phenolic resins and the fade resistance of friction materials, and it suppresses low-frequency noise [58]. Its high level of refractoriness contributes to long life in friction applications with high braking temperatures and is helpful in maintaining suitable friction (gripping force). In previous studies, small test pieces with metal oxides added to a phenolic resin-based friction material were tested for wear, and MgO was found to have the lowest wear amount [33,58,60]. In contrast to the above findings, our results showed positive correlations between the Mg content in the pads and the total brake wear rate, disc wear rate, PM_{10}, and $PM_{2.5}$. The previous findings were generally based on the results using test pieces, and tests based on commercial brake pads and actual driving conditions with a wide range of different inertias (as in this study) are more complex. Under these conditions, the Mg-derived material in the pads may have had an unintended abrasive effect.

3.4.4. Iron and Chromium

The mass contents of Fe and Cr in brake pads were positively correlated with the brake wear factor, disc wear factor, PM_{10}, and $PM_{2.5}$. Fe and Cr in brake pads are mainly derived from steel alloys, mainly used as reinforcement [15,16,27]. In the present study, the pads contained 0.1–10.3% Fe and 0–1.5% Cr, respectively. Steel fibers have high strength, modulus of elasticity, and thermal stability, but they are known to increase wear [6,24–26,29] due to accelerated plowing of the counter material (disc) surface [15,16,27]. Primary and secondary contact plateaus are formed at the brake friction interface [4]. The primary contact plateau is composed of wear-resistant components of the pad (e.g., steel fibers and ceramic particles), and it forms the nucleus for the secondary contact plateau, which is formed by the compression of particles that have been stripped in front of the primary contact plateau. The use of steel fibers forms the primary contact plate [61,62], and increasing their content increases contact wear [32,63,64]. Pyrite (iron sulfide, FeS_2) and magnetite (Fe_2O_3) are also present as Fe in the pad, which increases the coefficient of friction, increases brake wear factors, helps remove iron oxides and other undesirable surface coatings from the mating disc surface during braking, improves vehicle braking effectiveness, and acts as an abrasive agent [15,16,27]. Magnetite (Fe_2O_3) acts as a solid lubricant, maintaining the coefficient of friction during braking (especially at high temperatures), protecting the mating disc surface from excessive wear, and reducing vibration and noise [15,16,27]. In metal-to-metal wear, when the oxygen diffusion coefficient of the supplied metal oxide particles was high relative to the oxygen diffusion coefficient, the formation rate of the friction film occurred faster because of the faster sintering rate of the particles, and a negative correlation was observed for the amount of wear [31]. On the other hand, when metal oxide particles were mixed with phenolic resin and worn on the pad and disk, the amount of wear correlated with the oxygen diffusion coefficient [60], and the trends were not consistent. The amount of wear differed greatly between Fe_2O_3 and Fe_3O_4, and the amount of wear was higher when Fe_3O_4 was added, indicating that Fe_3O_4 changes to the "homogeneous metal Fe" when reduced and shows high cohesion with the disc material [33]. This high cohesion between the homogeneous metals significantly increases the wear of the pad material [33]. As the results of previous studies have indicated, the increase in wear and PM emissions with Fe content (positive correlation) cannot be explained in a monolithic manner, but the results of this study suggest that the increase in steel fiber leads to the positive correlation.

3.4.5. Titanium and Potassium

The mass contents of Ti and K in the pad were negatively correlated with the brake wear factor, disc wear factor, PM_{10}, and $PM_{2.5}$. Ti and K in brake pads can be derived mainly from potassium

 doi:10.20944/preprints202405.0928.v1

titanate as friction modifiers [15,16,65]. In this study, the pads contained 0.06–11.6% Ti and 0.2–4.3% K. Potassium titanate has also long been used in non-steel brake pads as a reinforcement in a variety of commercially available brake pads to improve friction stability and wear resistance [65–68]. Another important feature of potassium titanate is its availability in a variety of forms, which allows for control of friction properties. The friction and wear properties of brake friction materials containing potassium titanate in various forms and the shape of potassium titanate play an important role in the formation of friction coatings on the friction surface [67]. It has been suggested that the chemical reaction between titanate and phenolic resin forms char on the pad surface and improves friction stability under burnish conditions [69]. Friction materials with high molecular weight resins and platelet potassium titanate have a greater plateau on the sliding surface at low temperatures before the resin thermally decomposes, thus improving wear resistance properties [68]. It has also been reported that, depending on the blend amount of aramid fiber and potassium titanate, which have low wear resistance, fine spherical wear particles are formed on the surface of the friction material [70]. Consequently, our findings suggest that potassium titanate improves friction stability and wear resistance, leading to a negative correlation with brake wear and disc wear, as well as PM_{10} and $PM_{2.5}$ emissions.

3.4.6. Oxygen

The mass content of O in brake pads was negatively correlated with the brake wear factor, disc wear factor, PM_{10}, and $PM_{2.5}$. In brake pads, O is derived from metal oxide particles (e.g., MgO and Fe_xO_y) and barium sulfate ($BaSO_4$) in fillers; the pads in this study contained 27–35.6% O. The brake friction material including iron oxide consists of reinforcing fibers, friction modifiers, and fillers bonded with a binder resin, and it is used for iron-based disc rotors. The brake friction material contains 1–30% (by volume) iron oxide having a particle size of 0.5 μm or less; it reacts with the iron in the mating material (the disc rotor) when it contacts it in a non-steering state, to produce a protective film of iron oxide on the disc rotor friction surface. As a result, the grinding action of the disc rotor by the grinding component in the brake friction material is suppressed [e.g., 71]. Barium sulfate ($BaSO_4$), which is included as a filler, has a wear-inhibiting effect [18], as is discussed in Section 3.4.7. Thus, we considered that a negative correlation was found between brake wear and emission of brake wear particles because of the formation of an oxide film and the wear-inhibiting effect of oxides, rather than the wear-inhibiting effect of oxygen itself in the pad.

3.4.7. Barium

The mass content of Ba in brake pads was positively correlated with the brake wear factor, disc wear factor, PM_{10}, and $PM_{2.5}$. Ba in brake pads is derived from barium sulfate ($BaSO_4$) in fillers, and the pads in this study contained 0.03–8.4% Ba. Barium sulphate, an inorganic mineral, is the most commonly used space filler because of its high thermal stability and minimal water solubility [15,16,72]. The space filler effect on brake wear particles suggests that proper selection of space fillers can reduce brake wear particles from gray iron discs by preventing direct adhesion with steel fibers [18]. The reduction in metal wear per particle mass suggests that the reduction in the total brake wear factor, PM_{10}, and $PM_{2.5}$ is predominant (negatively correlated with the ratio of Ba mass per pad mass). However, although outside the scope of this study, a comparison of non-steel pads and low-steel pads (ceramic pads) showed that the formation of OH radicals in the aqueous phase increased with increasing Ba concentration in brake wear particles [73]. We suggest that the prevention of direct adhesion with steel fibers by Ba results in a decrease in metal wear per particle mass [18], an increase in organic mass per particle mass, and a predominant formation of OH radicals derived from organic matter. Further investigation is needed to evaluate the reduction of brake wear particles and health effects, as it is suggested that Ba concentration may be negatively correlated with oxidative potential and OH radical formation in the aqueous phase [73], which would be assumed to be in *vivo*, when evaluating health effects based on oxidative potential.

4. Conclusions

 doi:10.20944/preprints202405.0928.v1

In this study, brake wear and brake wear particle emissions were systematically investigated for a commercial friction brake system in a dynamometer test. Different sampling methods and emissions of brake wear particles by particle size (PM_{10}, $PM_{2.5}$, and $PM_{0.12}$) were compared. In addition, elemental analysis in the particles and the correlation of brake wear and brake wear particles to elements in the friction material were investigated to analyze the sources of brake wear particle emissions.

- The ratio of mass difference to mass loss increased from 16.2% to 51.2% after the 24-hour soak required by the GTR24 regulation as compared to the 1-hour soak measurement. Therefore, in our experiments, we measured the mass of the pads and discs within one hour after the test and with the brake temperature below 30°C.
- Based on the mass loss measurements, we found that the disc and pad wear factors accounted for 64.8% and 35.2%, respectively, of the brake wear factor.
- Based on the sampling method required by the JASO C470 method, there were no significant differences between cooling air flow rates for PM_{10}, $PM_{2.5}$, and brake wear particle emissions; however, the total brake wear factor was 58.3% lower at the high flow rate (10 m^3/min) compared to the low flow rate (1 m^3/min). We also observed that $PM_{0.12}$ with high cooling air flow rate conditions tended to be 12.2 times higher than low cooling air flow rate conditions.
- Low-steel pads had a PM_{10} emission of 3.9 mg/km per brake per 1000 kg of vehicle mass, with large variance, similar to the results of previous studies. There was also a large variation in the correlation between inertia and PM_{10} emissions, which was also in agreement with the findings of previous studies.
- For brake wear factors, based on mass loss measurements, 14.0–74.8% of wear particles originated from discs, 14.0–64.4% from non-steel pads, and 55.0–74.8% from low-steel pads. The contribution of disc wear determined from the iron concentration in the brake wear particles was approximately similar to the mass loss measurements, although there was large variation.
- The correlation coefficients of the mass content of elements in the pads for the brake wear factor, disc wear factor, PM_{10}, and $PM_{2.5}$ were very similar; C, Mg, Cr, and Fe mainly had high positive correlation coefficients, and O, K, Ti, and Ba mainly had high negative ones.

Author Contributions: Conceptualization, H.H.; methodology, H.H.; validation, H.H.; investigation, H.H.; resources, H.H.; data curation, H.H.; writing—original draft preparation, H.H.; writing—review and editing, H.H.; visualization, H.H.; supervision, H.H.; project administration, H.H.; funding acquisition, H.H.

Funding: This work was supported by the Japan Society for the Promotion of Science (JSPS) KAKENHI Grant Number JP 22K03895.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All data presented in this study are available on request from the corresponding author. The data are not publicly available due to a confidentiality agreement with the part providers.

Acknowledgments: The author would like to thank co-workers who supported the set-up and operation of the dynamometer and the measurements. In addition, the author would like to thank Dr. Akiyoshi Ito for proofreading support during the preparation of the draft manuscript.

Conflicts of Interest: The author declares no conflict of interest.

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