The Characteristics and Distribution of Chemical Components in Particulate Matter Emissions from Diesel Locomotives

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Abstract: The use of diesel locomotives in transport is gradually decreasing due to electrification and the introduction of high-speed electric rails. However, in Korea, up to 30% of passenger and cargo transport still relies on diesel locomotives and vehicles. Many studies have shown that the exhaust gas from diesel locomotives poses a threat to human health. This study examined the characteristics of particulate matter (PM) in diesel locomotive engine exhaust. In a previous study, PM emissions were found to increase as the throttle was moved to a higher notch. The use of a portable emission measurement system (PEMS) in this study did not detect the highest emissions at notch 5, as is commonly found in gravimetric analyses. When comparing the mass concentrations, the notch 1 and 5 results were similar. However, at notch 8, there was a large difference between the mass concentrations collected on the filters. Further, to reduce the fine PM emitted from diesel locomotives, the ionic components, which account for the largest proportion of the total materials in fine PM, should be clearly identified. Therefore, in this study, an analysis of the weight, ionic composition, and metal components of fine PM discharged from a diesel locomotive was performed. Based on the results, Na\(^+\) (31%), Ca\(^{2+}\) (27%), NO\(_3\)\(^-\) (24%), and SO\(_4^{2-}\) (13%), were the main ionic components, and the most abundant metal components being Ca (45%) and S (20%). In this study, the chemical components generated in diesel engines of other sources were compared, and as a result, different results were shown depending on the engine load and material ingredients. For the first time, a PEMS was used to measure PM from diesel vehicles, and a comparison was made with the results obtained by a gravimetric method. This is the first report of measuring PM concentrations by connecting a PEMS to a diesel locomotive, and of the distribution and characteristics of ions and heavy metals contained in the particles collected in the filter analyzed. The results indicate the importance of identifying the characteristics of fine PM emitted from a diesel locomotive and establishing an effective reduction measurement.

Keywords: diesel locomotive; portable emission measurement system (PEMS); particulate matter; emission component; PM emission source inventory

1. Introduction

Particulate matter (PM) is a key indicator of the air pollution caused by natural and human activities, with effects on air quality, the regional and global climate, and human health [1–3]. Studies have shown the effects of exposure to PM on mortality, respiratory illness, and heart failure, especially PM with a diameter less than 10 \(\mu\)m (PM10) or 2.5 \(\mu\)m (PM2.5). There has been a significant increase in PM2.5 pollutions, and it was shown that the risk of fatality following its exposure is higher than that following PM10 exposure [4].
Diesel locomotives emit significant amounts of air pollutants, and several studies have demonstrated that air pollutants from diesel locomotives affect human health [3,5–14]. Railway transportation is a source of non-road emissions, and when diesel locomotive engine emissions are not controlled, the exhaust emissions can negatively affect communities and ecosystems [8–14]. As of 2016 in diesel locomotives, the amount of particulate matter emissions was 384 tons (PM10) and 354 tons (PM2.5), and the emission of particulate matter from diesel locomotives is about 2% of the total emission of PM from the non-road sector (Table 1). This is the result of clean Air Policy Support System (CAPSS), and it is based on the air pollutant emission inventory. In addition, this value includes the secondary particles according to nitrogen oxides, sulfur oxides and the like. Diesel locomotives need to be managed as the amount of particulate matter emissions per vehicle is about 850 times (3400 kg) that of diesel locomotive in Korea. However, diesel locomotives, unlike construction machinery and ships, have no emission allowance standards, so management was difficult. Recently, new standards for emission of air pollutants have been established for diesel locomotives in the blind spot of particulate matter management in Korea. A comprehensive countermeasure for particulate matter management was announced in 2017, and an amendment to the enforcement regulations of the air quality conservation act, including the establishment of new diesel engine emission allowance standards, was announced in 2019. Since then, tests and certification notices of newly manufactured and imported diesel locomotive have been established in 2020 in Korea.

Diesel locomotives emit substantial amounts of fine PM. Although their contribution to the total amount of PM is small, the particle number concentration is high. Research has shown that fine PM affects human health [3,15–19]. It is therefore important to investigate the number concentration of fine particle sizes in diesel locomotive particulate emissions. This study analyzed the chemical component of diesel locomotives exhaust particulate matter. Diesel exhaust PM is responsible for different respiratory diseases and the precise understanding of atmospheric dust contains various metal components, organic substances, and sometimes carcinogenic substances, such as heavy metals and polycyclic aromatic hydrocarbons.

The characteristic of diesel exhaust PM is important for health risk assessment of human. These materials can cause significant human health problems and negatively affect the growth of animals and plants. Among the particulate contaminants, PM2.5 has a high rate of penetration through the respiratory tract and can accumulate in the bronchi or lungs [16–19]. Due to the small particle size, the surface area is relatively large for a given particle mass. It is therefore easy for the particles to adsorb various heavy metals and harmful pollutants, thereby increasing their accumulation in the human body. Previous studies [20] have suggested heavy metals such as Pb, Cd, As, Mn, Zn, Ni, and Cr in fine PM are absorbed by the human body and generate free radicals. In the case of diesel engines, organic carbon components account for 69–77% of the total mass, and elemental carbon accounts for about 1.3–3.8%. Compared with the discharged particles by the other sources, ionic components and heavy metal components occupy a relatively small proportion [21].

This is the first report of a portable emission measurement system (PEMS: Pegasor, Tampere, Finland) and a gravimetric measuring device (total suspended particulate (TSP) sampler) being used to measure the concentration of fine PM emitted from diesel locomotives in Korea, with an evaluation of the differences between the two methods. A PEMS is a device that can measure the emission gases in real time while simultaneously calculating the weight. The driving characteristics such as speed and acceleration and the emission gases can be simultaneously measured during operation, and it can be used to conduct on-vehicle emission measurements. The device is small and light enough to be carried inside or moved by a motor vehicle being driven during testing, rather than on the stationary rollers of a dynamometer, which only simulates real-world driving [22]. In particular, in this study, the data measured by PEMS were divided into two. One is the mass concentration detected by the internal sensor of PEMS, and the other is the weight measured by the filter collected by PEMS. Subsequently, an analysis of the PM components
was performed using energy dispersive X-ray fluorescence spectrometry (EDXRF) analysis and ion chromatography (IC).

In particular, there is no separate standard for fuel for diesel locomotives, and diesel locomotives use the same fuel for diesel vehicles in Korea. Since 2009, the fuel used in diesel locomotives has been using a fuel containing less than 30% aromatics with less than 10 ppm sulfur [23]. In addition, the lubricating oil of a diesel locomotives contains zinc, phosphorus, and calcium, which are used as antioxidants and anti-wear agents [24].

Previous studies have focused on the particle size of PM emitted from diesel engines, but this study differed from other studies in that it examined the distribution of the chemical components of the PM and compared it with other sources of diesel engines. This is the first report of using a PEMS to detect PM emissions from diesel locomotives, and a comparison was made with the results obtained by a gravimetric method [2]. These results could be reflected in the construction of the current atmospheric PM emission source inventory.

### Table 1. Non-road air pollutant emissions by source [25].

| Particle Size | Non-Road Pollution Source (Unit:Tons) | Railroad | Ship | Airline | Agricultural Machinery | Construction Equipment |
|---------------|---------------------------------------|----------|------|---------|------------------------|-----------------------|
| PM10          |                                       | 384      | 7589 | 99      | 1342                   | 6173                  |
|               |                                       | (2%)     | (49%)| (1%)    | (9%)                   | (40%)                 |
| PM2.5         |                                       | 354      | 6995 | 91      | 1235                   | 5679                  |
|               |                                       | (2%)     | (49%)| (1%)    | (9%)                   | (40%)                 |

### 2. Materials and Methods

#### 2.1. Engine and Power

The diesel locomotive series 7300 (GT26CW-2), 7400 (GT26CW-2), 7500 (GT26CW, GT26CW-2), and 7600 (PowerHaul PH37ACai) are currently in operation in Korea. In this experiment, one diesel locomotive (7378) was used for PM measurements. To secure the reproducibility and reliability of the study, measurements were repeated twice. The diesel locomotive series 7300 (GT26CW-2) is an electric oversized diesel locomotive employed for passenger and cargo transport and is commonly used in Korea. A diesel locomotive consists of a diesel engine, a main generator, a traction motor, a bogie, and other attached structures. Table 2 lists the characteristics of the series 7300 diesel locomotive engine used in Korea. The locomotive has a two-cycle 16-valve engine and adjustable throttle speeds (notches) ranging from idle to notch 8. The throttle control has eight positions and an idle position. Each of the throttle positions is called a notch. Notch 1 is the slowest speed (revolutions per minute (rpm)) and notch 8 the highest. The diesel locomotive engine operates at 315 rpm when idle, increasing to 900 rpm at notch 8. Diesel engine emissions are presented as pollutants emitted at different brake powers rather than as the distance traveled [7,11], and the pulling capacity is expressed in terms of brake horsepower per hour (bhph). The dimensions of the diesel locomotive are $3150 \times 20,982 \times 4000$ mm ($W \times D \times H$). Table 3 lists the diesel locomotive engine power and fuel consumption [26]. The particulate matter emitted from the 16-645E3 model, which is the 2-cycle engine of this study, can be identified and compared with a 4-cycle engine later.
Table 2. Characteristics of the series 7300 diesel locomotive engine used in this study.

|                  | Electric Motive Division, General Motor Company |
|------------------|------------------------------------------------|
| Maker            | −                                               |
| Model no.        | − 16-645E3                                      |
| Cylinder size (mm)| − 230 × 254                                     |
| Number of cycles | − 2                                             |
| Compression ratio| − 14.5:1                                       |
| Pull capacity (bhp: brake horse power) | − 3000 |
| RPM idle/notch 8 | − (RPM idle) 315                                |
|                  | − (RPM notch 8) 900                             |

Table 3. Characteristics of the diesel locomotive engine power and fuel consumption.

| Notch | Power (bhp) | Rated Power (%) | Fuel Consumption (L/min) |
|-------|-------------|-----------------|--------------------------|
| Idle  | 17          | 0.6             | 0.4                      |
| 1     | 173         | 5.6             | 0.6                      |
| 2     | 426         | 14.4            | 1.4                      |
| 3     | 830         | 28.1            | 2.6                      |
| 4     | 1057        | 35.8            | 3.5                      |
| 5     | 1434        | 48.6            | 4.8                      |
| 6     | 1823        | 61.7            | 6.2                      |
| 7     | 2409        | 81.6            | 8.4                      |
| 8     | 2953        | 100             | 10.4                     |

2.2. Experimental Methods

The experiment was conducted at the Busan Railway vehicle maintenance facility, where a team conducts light and heavy maintenance of diesel locomotives in Korea. Diesel locomotive engine exhaust gases were measured according to SAE procedure J177 (Exhaust gas measurement procedure of diesel engine recommended by SAE International) and ISO 8178F, as follows. The engine was ignited and warmed up for >10 min at a rated speed and load to achieve stable conditions. The engine was then run in each experimental mode for >20 min at its steady state. The engine was stabilized so that the duration of constant discharge of the exhaust material was at least 10 min, and the time required for emission measurement was at least 10 min. The PM characteristics were measured when idling and at notches 1–8, which corresponded to 0.6, 5.6, 14.4, 28.1, 35.8, 48.6, 61.7, 81.6, and 100% of the rated power, respectively (Table 3). The ISO 8178 F mode is a method for measuring non-road emissions that particularly targets locomotives and railcars. It was used for all measurements, taking into account the torque values of the procedures used in the SAE J177 method (Table 4). Measurements were conducted after 10 min, commencing with a warm start, and the engine power was then sequentially raised to notches 1, 5, and 8. As shown in Table 3, ISO 8178F mode should measure 5%, 50%, and 100% of the total load. Because the pull capacity was 3000, notches 1, 5, and 8 (corresponding to 150, 1500, and 3000 bphp) were used for the measurements in this experiment.

Table 4. Method of measuring non-road emission gas (ISO 8178 F mode).

| Mode Number | 1                | 2                | 3                |
|-------------|------------------|------------------|------------------|
| Speed       | Rated speed      | Intermediate speed| Low-idle speed  |
| Torque      | 100              | 50               | 5                |
| Weighting factor | 0.15              | 0.25             | 0.6              |
After installing a smoke chimney for the purpose of discharging, spreading, and diluting exhaust gas in a diesel locomotive, and installing an auxiliary smoke chimney in the smoke chimney, an exhaust gas sampling tube was connected to the auxiliary smoke chimney. In order to collect PM discharged at a constant flow rate by suction at a constant velocity, an auxiliary smoke chimney is installed. In order to prevent the high temperature exhaust gas from condensing depending on the temperature difference with the atmosphere, the measurement probe was insulated with a heat insulating material. It was measured after filtering with a filter through a sample collection tube using a particulate matter collection device. In this study, 2 filters were used. The PEMS was fitted with a 47 mm Polytetrafluoroethylene (PTFE) membrane filter (Toray International Co., Ltd., Shanghai, China), and the gravimetric method was used to measure the mass concentration collected on an 80 mm quartz microfiber filter.

After pre-heating the PEMS, an ambient zero was recorded, and the flow meter was also set to zero. After pre-heating the PEMS, ambient zero was performed and atmospheric air was used. Then, flow meter zeroing was performed at the same time. After ambient zero, it was confirmed that the exhaust flow value changed from 36.5 kg/h to close to zero. According to the PEMS manual, in order to prevent condensation of exhaust gas, in this experiment, when the connection of PEMS was normal, and after the warm-up was completed, the equipment stabilization time of 30 min or more should be taken. To check the completion of pre-heating, the temperature of FID analyzer at 190 °C and 290 °C was checked. After FID ignition and range setting were complete, zero calibration and span calibration were undertaken. At this time, the NOx flow and FEM flow were confirmed, and gas between 1.5 and 2.0 was injected. Waiting time was about 1 min for the gas reading value to stabilize.

Through repeated tests using the PEMS, the PM10 emission trend was determined, and the reliability of the data was confirmed. In this study, PEMS sample probes, PM flow rate and filter collection probes were installed. Particulate matter discharged from the engine was collected using a self-made sampler. The PM sampler can be equipped with a filter. In order to calculate the exact suction flow rate, the flow rate of the sampler was calibrated each time.

After the engine preheating operation was completed, a total of 500 L of exhaust gas was collected with a sampler at engine outputs 1, 5, and 8 notches. As the engine power of the diesel locomotive increased, the exhaust gas temperature increased, and filters were collected for each notch. When collecting particulate matter in the exhaust gas, it withstands a high temperature of about 260 degrees, has no chemical activity, has a low impurity, and uses a PTFE-coated filter suitable for exhaust gas collection (Figure 1). In PEMS, weight concentration and heavy metal analysis were performed using a PTFE membrane filter (47 mm), and 500 L was collected by a gravimetric measuring using a quartz microfiber filter (80 mm).

![Figure 1](image_url)  
**Figure 1.** Photographs of the portable emission measurement system (PEMS) and particulate matter (PM) sampling and measurement.
2.3. Experimental Equipment and Measurement

The PEMS and gravimetric measuring equipment were both used to analyze PM. The PEMS was fitted with a 47 mm PTFE membrane filter (Toray International Co., Ltd., Shanghai, China), and the gravimetric method was used to measure the mass concentration collected on an 80 mm quartz microfiber filter. The filter weight was measured before and after PM collection using an electronic balance that was accurate to 0.0001 mg. The measured mass value was divided by the total flow rate and converted into a mass concentration (Figure 2), and 3 filters were used for each notch.

Isokinetic sampling of PM, discharged at a constant flow rate, was conducted by considering the suction nozzle diameter, constant velocity suction coefficient, exhaust gas temperature, flow velocity, dynamic pressure, static pressure, orifice pressure difference, atmospheric pressure, and oxygen concentration. Isokinetic sampling is a technique that ensures uniform sampling of particles and gases in motion within a stack or exhaust system [5,27]. It is particularly important for measuring PM.

ED-XRF (ARL QUANT’X EDXRF Spectrometer, Thermo. Inc., Agawam, MA, USA), Anion IC (IC Metrohm 883, Herisau, Switzerland, A supp 150/4.0 column, 3.7 mM Na2CO3 and 1.0 mM NaHCO3), and Cation IC (IC Metrohm 930, Herisau, Switzerland, Metrosep C4-250/4.0 column, 5 mM HNO3) analyses were performed to measure the heavy metal and ionic components of the PM. In the IC analysis, both anions and cations were determined. Using an automatic injector (Metrohm 858, Herisau, Switzerland), samples were simultaneously injected (250 µL) into anion and cation IC columns, and the respective electrical conductivity detectors were measured. It was quantified with at least 5 anion standard samples (0.25~4 ppm) and cation standard samples (0.25~4 ppm), and the accuracy was confirmed by 10% reanalysis of all samples. Table 5 shows the results of examining method of detection limit (MDL) for determining the reliability of analysis of Anion IC and Cation IC.

| Anion IC | ppm | MDL | Cation IC | ppm | MDL |
|----------|-----|-----|-----------|-----|-----|
| F−       | <0.001 | Na+ | 0.001     |
| Cl−      | 0.001  | NH4+ | 0.004    |
| NO3−     | 0.001  | K+  | 0.002     |
| PO43−    | <0.001 | Mg2+ | 0.002     |
| SO42−    | 0.002  | Ca2+ | 0.002     |

ED-XRF is based on the multi-channel energy dispersive principle and measures all emitted X-rays simultaneously. Accordingly, quantitative analysis of elemental components

![Figure 2. Photographs of the on-site gravimetric measurement.](image-url)
among the particulate matter samples collected from the filter can be accurately calculated. Among the elemental components of particulate matter using ED-XRF, Trace elements exist in traces in the filter, so standard deviations were calculated for the results of the 7 analysis for each filter. As a result of analysis per unit area (cm$^2$) in the filter using ED-XRF, Ca was analyzed to be 8.4 ng/cm$^2$, S 15.4 ng/cm$^2$, and the like (Table 6). This represents a method detection limit (MDL) suitable for analyzing elemental components for particulate matter.

Table 6. The result of Ion and method of detection limit (MDL) using ED-XRF.

| Ion | Ng/cm$^2$ | MDL |
|-----|-----------|-----|
| Na  | 16.53     |     |
| Mg  | 8.09      |     |
| Al  | 12.75     |     |
| Si  | 10.61     |     |
| S   | 15.4      |     |
| Cl  | 6.63      |     |
| K   | 5.53      |     |
| Ca  | 8.4       |     |
| Ti  | 7.13      |     |
| V   | 0.39      |     |
| Cr  | 1.39      |     |

In this experiment, the average value of the co-filters was subtracted from each filter concentration to derive the results. In addition, for tracking the sampling blank, the system background value of the device itself was checked and was not detected.

3. Results and Discussion

3.1. Analysis of the PM Concentration

The PM mass was recorded using the PEMS, and the averages were 1.81 ± 0.64 mg/m$^3$ at notch 1, 10.16 ± 0.76 mg/m$^3$ at notch 5, and 33.52 ± 0.82 mg/m$^3$ at notch 8. The results presented here are the mean values of triplicate measurements (Figure 3a).

The mass of PM was recorded using the gravimetric TSP system and averaged 4.87 ± 2.27 mg/m$^3$ at notch 1, 37.76 ± 8.46 mg/m$^3$ at notch 5, and 45.09 ± 4.81 mg/m$^3$ at notch 8. The results presented here are the mean values of triplicate measurements (Figure 3b).
The fine PM collected on the filter using a PEMS device and the fine PM measured by a gravimetric method displayed the same tendency, with a gradual increase from notch 1 to notch 8. However, there was a difference observed. The reason is that the exhaust gas temperature rises to 800 degrees at notch 8, so it moves to the collector, but the gas temperature cools and condensate is formed. The results obtained gravimetrically increased rapidly up to notch 5 and then slightly increased from notch 5 to notch 8, whereas the results obtained using the PEMS sensor revealed a slight increase up to notch 5 and a rapid increase from notch 5 to notch 8. In Figure 3a, the difference between the two different trends in notch 1 can be seen as an error caused by deriving the average value. The results obtained by the PEMS and gravimetric TSP system are shown in Figure 3a, b, respectively. The reason for the difference in the results was considered to be the difference in the particle size collected on the different filters. As shown in Figure 3, when the output of the diesel locomotive increased, the excess air ratio did not decrease but remained almost constant after notch 6. This was likely because the turbocharger operated at notch 6, which is a characteristic of a diesel locomotive engine, thereby limiting the reduction in the excess air ratio by supplying compressed air above atmospheric pressure. The first measurement was slightly higher than the second and third measurements (Figure 4).

In a previous study [28], as the notch of the diesel engine increased, the PM concentration emitted also increased. PM is produced through the pyrolysis, nucleation, surface growth, coalescence, and agglomeration of diesel fuel. As the engine notch increases, the amount of diesel fuel consumed increases. It was therefore postulated that production of the resulting PM would also increase [29].

Because the amount of diesel fuel consumed increased as the engine notch increased, it was expected that the PM emissions would display the same trend.

The fine PM concentration was measured using the gravimetric measuring equipment for each notch, from 1 to 8; however, for comparison with the PEMS results, only the concentrations for notches 1, 5, and 8 were recorded. The highest PM mass was recorded at notch 6, after which PM emissions decreased with increasing engine power. In the case of a diesel locomotive, the excess air ratio did not decrease when the output increased, and above notch 6, the characteristics remained almost constant. Accordingly, it was concluded that the turbocharger operating at notch 6 supplied compressed air above atmospheric pressure, thereby reducing the extent of the decrease in the excess air ratio [30].
The mass of PM collected using a PTFE filter in the PEMS was defined as Filter PM, and the value converted from the fine PM sensor into the true amount was defined as Pegasor PM; these two values were compared. In addition, the ratio of the two values was defined as Factor K. Figure 4 shows how the ratio differed for each set of measured values.

The mass concentration of PM determined by the internal sensor of the PEMS and the measured weight of the PM in the filter collected by the PEMS were compared. In Figure 4, filter PM is the measurement on the filter collected by the PEMS, and Pegasor PM is the mass concentration detected by the sensor inside the PEMS; both cases represent data measured by the PEMS. Here, Factor K shows the ratio between Pegasor PM and Filter PM. Considering the measurement result of each notch in the PEMS, it was confirmed that the trend was similar only at notch 8. In Figure 4, it can be seen that even in the case of data measured by the PEMS, there was a difference between the values determined by the gravimetric method and the sensor inside the instrument.

The PM measurements using the PEMS (Figure 4) and the gravimetric method only were reviewed comprehensively (Figure 5). When comparing the mass concentrations (i.e., the results obtained using only the gravimetric method with the 47 mm versus 80 mm filter), the notch 1 and 5 results were similar. However, at notch 8, there was a large difference between the mass concentrations collected on the filters. This was due to condensate being formed when the exhaust gas temperature rose above 800 °C at notch 8 and then cooled down in the collector. Therefore, the measurement was not considered as accurate as the PEMS results. However, the results of this study were significant because they represent the first attempt to determine the PM mass concentration emitted from a diesel locomotive at notches 1, 5, and 8 via comparisons between the gravimetric method and a PEMS sensor.

![Figure 5. Comparison of the mass concentration recorded by the PEMS and the gravimetric method (PM10). #Is the place to enter the number per notch.](image)

### 3.2. Ionic Components of the PM

Fine PM is classified as PM10 or PM2.5 according to the particle diameter (PM10 is a diameter less than 10/1000 mm, and PM2.5 is a diameter less than 2.5/1000 mm). Fine PM is discharged as a mixture of solid and liquid particles into the air and is produced chemically [31].

The physicochemical components of the ionic components in PM emitted from diesel locomotives were examined. An IC analysis was used to examine the ionic components of the PM emitted by the diesel locomotive at different notches. It was found that, NO$_3^-$, SO$_2^{2-}$, Na$^+$, and Ca$^{2+}$ were the main ionic components. The abundance of anions followed the order of NO$_3^-$ > SO$_2^{2-}$ > Cl$^-$ > PO$_4^{3-}$ > F$^-$, and the abundance of cations followed...
the order of Na\(^+\) > Ca\(^{2+}\) > Mg\(^{2+}\) > NH\(_4^+\) > K\(^+\) (Table 7; Figure 6). Nitrates (NO\(_3^-\)), sulfates (SO\(_4^{2-}\)), and ammonium salts are the causative agents that produce secondary aerosols of ammonium nitrate and ammonium sulfate [32].

### Table 7. The ionic components of PM (unit: ug/m\(^3\)).

| Notch | F\(^-\) | Cl\(^-\) | NO\(_3^-\) | PO\(_4^{3-}\) | SO\(_4^{2-}\) | Na\(^+\) | NH\(_4^+\) | K\(^+\) | Mg\(^{2+}\) | Ca\(^{2+}\) | Total |
|-------|--------|--------|-----------|-----------|-----------|--------|--------|--------|--------|--------|------|
| Notch 1 | 0.0008 | 0.0217 | 0.0719 | 0.0028 | 0.0500 | 0.2546 | 0.0018 | 0.0000 | 0.0102 | 0.0790 | 0.4926 |
| Notch 5 | 0.0020 | 0.0418 | 0.3822 | 0.0050 | 0.0908 | 0.3207 | 0.0000 | 0.0000 | 0.0127 | 0.2693 | 1.1244 |
| Notch 8 | 0.0032 | 0.0285 | 0.2108 | 0.0042 | 0.2068 | 0.2733 | 0.0000 | 0.0000 | 0.0141 | 0.4086 | 1.1495 |

The NO\(_3^-\) concentration was highest in notch 5 and about five times higher than that in notch 1. The main mechanism of NO\(_3^-\) generation is the reaction between nitrogen oxides and NH\(_3\). Diesel locomotives generate high concentrations of nitrogen oxides. Of the ions, Na\(^+\) was present at the highest concentration in notch 5, while SO\(_4^{2-}\) and Ca\(^{2+}\) were present at the highest concentrations in notch 8. The K\(^+\) concentration was not influenced by the notch.

This study performed an analysis of the ionic content of the TSP emitted from a diesel locomotive. Ion components emitted from other diesel engines were compared.

In comparison with the results of this study, the most abundant ionic components in PM emissions from medium-sized diesel engines (2800 cc) were found to be SO\(_4^{2-}\) [21]. However, in the case of large diesel engines (7620 cc) and diesel generators, NO\(_3^-\) accounts for the highest proportion of ionic components [21]. In the case of PM emissions from large diesel engines, the main ions are present in the following order: NO\(_3^-\), SO\(_4^{2-}\), and Cl\(^-\). The concentration and composition of the ionic components of the emitted particles vary depending on the operating conditions of the engine and the additive components of fuel [21]. As a result of this study, the ratio of ionic components of TSP emitted from diesel locomotives was NO\(_3^-\) is 24% and SO\(_4^{2-}\) is 13%, and it was confirmed that the NO\(_3^-\) ratio was high like that of large diesel engine (NO\(_3^-\) is 58%). As with previous studies [21], diesel locomotives can produce results similar to the ionic composition emitted by large diesel engines. Based on the mass per filter presented in Table 7, the relative amount of each ionic components of PM is presented in Figure 6. In addition, as a result of comparison with the total mass collected in the filter for each notch, the ration of the ionic components was found to be 0.001% to 0.006%, which is a very low ratio as in the previous study results [21].

In this study, as a result of examining the ion components for each notch, it was confirmed that Na\(^+\) was 52% in notch 1, which was more than half of the ratio, and that it appeared in the order of Ca\(^{2+}\), NO\(_3^-\) and SO\(_4^{2-}\), and in notch 5, NO\(_3^-\) occupied the highest percentage with 34%, followed by Na\(^+\) and Ca\(^{2+}\). Lastly, it was confirmed that Ca\(^{2+}\) occupied the highest ratio with 36% in notch 8, followed by NA, SO\(_4^{2-}\), and NO\(_3^-\) (Figure 6).

When looking at the all notches, it was found that the ratio of Na\(^+\), Ca\(^{2+}\), and NO\(_3^-\) was high. On the other hand, only in the notch 5, the NO\(_3^-\) ratio was slightly higher than that of Na\(^+\) and Ca\(^{2+}\). Based on the results of this study, it is possible to confirm the difference in the ion components by notch of diesel locomotives (Figures 6 and 7).
that of Na$^+$ and Ca$^{2+}$. Based on the results of this study, it is possible to confirm the difference in the ion components by notch of diesel locomotives (Figures 6 and 7)

Figure 6. The ionic of fine PM emitted from diesel locomotives; (a) NOTCH 1; (b) NOTCH 5; (c) NOTCH 8.
3.3. Elemental Components of PM

EDXRF analysis was used to analyze the metal components of the PM emissions. Fine PM is composed of ionic, metal, and carbon components. Ionic components have a high specific gravity. To establish effective countermeasures for the reduction of fine PM emitted from diesel locomotives, it is necessary to quantitatively analyze the metal components in addition to the mass concentration and to conduct a general chemical analysis. However, no such data have been presented.

In this study, the metal components of fine PM emitted from diesel locomotives at different notches were analyzed using a PEMS. The most abundant metal component was Ca, and the least abundant component was As. It was confirmed that the majority of the metal components were present at a high concentration at notch 8, which had a high rpm (Table 8; Figure 6).

It has been reported that Al, Fe, and Zn are the main heavy metals emitted by all types of diesel engines (i.e., large and medium diesel engines, and diesel generators). These three elements are released by engine wear and are also present in trace amounts in engine oil and fuel [21].

Twenty-one metal components were identified in this study and were present in PM emissions in the following order: Ca > S > Na > Al > Fe > Si > Cl > K > Mg > Zn > Mn > Ba > Ni > Cu > Br > Ti > Cr > Pb > V > Se > As. Ca accounted for 45% of the total metals, with the next most abundant metals being S (20%), Na (9%), and Al (7%). Ca and S accounted for more than half of the metal components measured in the analysis, whereas Se and As were rarely identified. In particular, the Ca component is major additive to the lubricant of diesel locomotives, and is a metal surface protection agent. S can be confirmed to originate from sulfur contained in fuel [23,24].

In a previous study [22], the amount of heavy metals contained in fine PM was determined in a specific area, and a very high concentration of Cr was found, which was concerning because of its carcinogenic properties. As with previous studies [21], it was found that Fe accounted for the majority with 82% of the 2800 cc diesel vehicle, and the large diesel engines, Al is 54% and Fe is 25%. In this study, as a result of measuring the heavy metals in fine PM emitted from diesel engines, the differences in the concentrations of harmful heavy metals may represent the difference between the target and existing environmental conditions.

As a result of analyzing detailed metal components for each notch, Fe occupied 20% at 1 notch, showing the highest ratio, and it was identified in the order of Na and Ca, and in notch 5, it was found that Ca occupied the highest percentage with 35%, and it was confirmed in the order of S and Na. Lastly, in notch 8, Ca occupied more than half of the total ration with 60%, and was identified in the order of S and Na, showing a similar tendency of notch 5 (Figure 8).
Table 8. ED-XRF analysis of PM.

| Notch    | Na  | Mg  | Al  | Si   | S    | Cl   | K    | Ca  | Ti  | V   |
|----------|-----|-----|-----|------|------|------|------|-----|-----|-----|
| Notch 1_1| 0.692 ± 0.080 | 0.318 ± 0.026 | 0.409 ± 0.013 | 0.867 ± 0.010 | 0.463 ± 0.006 | 0.241 ± 0.015 | 0.184 ± 0.016 | 0.653 ± 0.020 | 0.024 ± 0.003 | 0.001 ± 0.001 |
| Notch 1_2| 0.592 ± 0.078 | 0.000 ± 0.000 | 0.381 ± 0.012 | 0.206 ± 0.008 | 0.423 ± 0.006 | 0.049 ± 0.013 | 0.047 ± 0.015 | 0.487 ± 0.020 | 0.002 ± 0.002 | 0.002 ± 0.001 |
| Notch 5_1| 0.492 ± 0.075 | 0.000 ± 0.000 | 0.386 ± 0.012 | 0.201 ± 0.008 | 0.639 ± 0.007 | 0.073 ± 0.014 | 0.031 ± 0.016 | 1.195 ± 0.024 | 0.000 ± 0.000 | 0.002 ± 0.001 |
| Notch 5_2| 0.567 ± 0.074 | 0.000 ± 0.000 | 0.351 ± 0.012 | 0.190 ± 0.007 | 0.449 ± 0.006 | 0.076 ± 0.014 | 0.041 ± 0.016 | 0.886 ± 0.023 | 0.001 ± 0.002 | 0.002 ± 0.001 |
| Notch 8_1| 0.441 ± 0.081 | 0.000 ± 0.000 | 0.398 ± 0.013 | 0.373 ± 0.009 | 3.823 ± 0.014 | 0.253 ± 0.017 | 0.083 ± 0.016 | 9.376 ± 0.040 | 0.004 ± 0.002 | 0.003 ± 0.001 |
| Notch 8_2| 0.362 ± 0.075 | 0.000 ± 0.000 | 0.383 ± 0.012 | 0.264 ± 0.008 | 1.373 ± 0.009 | 0.155 ± 0.015 | 0.097 ± 0.016 | 3.297 ± 0.028 | 0.002 ± 0.002 | 0.000 ± 0.001 |

| Cr       | Mn  | Ba  | Fe  | Ni  | Cu  | Zn  | As  | Se  | Br  | Pb  |
|----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 0.000 ± 0.000 | 0.036 ± 0.005 | 0.028 ± 0.004 | 1.269 ± 0.013 | 0.014 ± 0.001 | 0.011 ± 0.001 | 0.108 ± 0.003 | 0.000 ± 0.000 | 0.002 ± 0.004 | 0.007 ± 0.004 | 0.001 ± 0.006 |
| 0.000 ± 0.000 | 0.017 ± 0.005 | 0.005 ± 0.004 | 0.253 ± 0.006 | 0.017 ± 0.001 | 0.011 ± 0.001 | 0.022 ± 0.002 | 0.000 ± 0.000 | 0.000 ± 0.000 | 0.001 ± 0.004 | 0.000 ± 0.000 |
| 0.010 ± 0.003 | 0.005 ± 0.005 | 0.013 ± 0.003 | 0.079 ± 0.004 | 0.013 ± 0.001 | 0.019 ± 0.001 | 0.029 ± 0.003 | 0.000 ± 0.000 | 0.000 ± 0.000 | 0.005 ± 0.004 | 0.000 ± 0.000 |
| 0.000 ± 0.000 | 0.018 ± 0.005 | 0.008 ± 0.004 | 0.164 ± 0.006 | 0.018 ± 0.001 | 0.006 ± 0.001 | 0.022 ± 0.002 | 0.001 ± 0.002 | 0.000 ± 0.004 | 0.001 ± 0.004 | 0.000 ± 0.000 |
| 0.013 ± 0.003 | 0.015 ± 0.005 | 0.030 ± 0.004 | 0.250 ± 0.006 | 0.016 ± 0.001 | 0.032 ± 0.001 | 0.049 ± 0.003 | 0.000 ± 0.000 | 0.005 ± 0.004 | 0.011 ± 0.004 | 0.022 ± 0.008 |
| 0.003 ± 0.003 | 0.076 ± 0.005 | 0.012 ± 0.004 | 0.129 ± 0.005 | 0.017 ± 0.001 | 0.013 ± 0.001 | 0.036 ± 0.003 | 0.000 ± 0.000 | 0.000 ± 0.000 | 0.009 ± 0.004 | 0.000 ± 0.000 |
As a result of analyzing detailed metal components for each notch, Fe occupied 20% at notch 1, showing the highest ratio, and it was identified in the order of Na and Ca. In notch 5, it was found that Ca occupied the highest percentage with 35%, and it was confirmed in the order of S and Na. Lastly, in notch 8, Ca occupied more than half of the total ratio with 60%, and was identified in the order of S and Na, showing a similar tendency of notch 5 (Figure 8).

All of the notches showed a high Ca, S, and Na ratio, and only notch 1 showed a high Fe ratio. Based on the results of this study, it is possible to confirm the difference in metal components by notch of diesel locomotives (Figures 7 and 8).

4. Conclusions and Discussion

This study analyzed the concentration of PM emitted from diesel locomotives and the main components (ions and heavy metals) of the PM. The emission of particulate matter from diesel locomotives is about 2% of the total emission of PM from the non-road sector in Korea. However, diesel locomotives were found to have about 850 times the amount of particulate matter emissions per vehicle [2]. In conclusion, the reduction of PM emissions

Figure 8. The metal components of fine PM emitted from diesel locomotives; (a) NOTCH 1; (b) NOTCH 5; (c) NOTCH 8.

All of the notches showed a high Ca, S, and Na ratio, and only notch 1 showed a high Fe ratio. Based on the results of this study, it is possible to confirm the difference in metal components by notch of diesel locomotives (Figures 7 and 8).
from diesel locomotives will require ongoing monitoring to minimize the adverse effects on human health. Accordingly, the ministry of environment introduced the enforcement rules of the air quality conservation act to apply emission standards for diesel locomotives to reduce particulate matter. In order to effectively reduce PM, it is necessary to review not only the concentration of PM emitted from, diesel locomotives, which are non-road pollution sources, but also the chemical composition.

The main sources of PM include combustion in the manufacturing industry, non-road pollution sources, and road pollution sources, and the amount of particulate matter emissions continues to increase. In this study, we confirmed ionic, metal, and carbon components of diesel locomotives as the main emission sources of particulate matter in the atmosphere. It was found that Na\(^+\), and Ca\(^{2+}\) were the main ions in diesel locomotive PM emissions. In particular, in previous studies [21], an increase in the concentration of Na\(^+\), Ca\(^{2+}\), NO\(_3^-\), and SO\(_4^{2-}\) was suggested as a factor that increases the risk of cardiovascular death. As a result of investigating the contribution of particulate matter in the PM ion component for each diesel engine, it was found that SO\(_4^{2-}\) accounted for the majority with 74% of the 2800 cc diesel vehicle [21]. As a result of this study, the ratio of ionic components of PM10 emitted from diesel locomotives was NO\(_3^-\) is 24% and SO\(_4^{2-}\) is 13%, and it was confirmed that the NO\(_3^-\) ratio was high like that of large diesel engine (NO\(_3^-\) is 58%) [21]. However, it was possible to derive from the results of this study that the chemical composition of PM emitted by diesel engine type was different.

Furthermore, it found that the metal components in the fine PM emitted from diesel locomotives were mainly Ca and S. It can be seen that the fuel used in the diesel locomotive contains Sulfur and Polycyclic Aromatic Hydrocarbon(PAH) [33], and is also related to the chemical components contained in the fine PM of diesel locomotive. The result of investigating the contribution of particulate matter in the PM metal component for each diesel engine were examined. It was found that the ratio of metal components of PM10 emitted from the 2800 cc diesel vehicle was Fe accounted for the majority with 82% [21]. However, in this study, the ratio of metal components of PM10 emitted from diesel locomotives was Ca is 45% and S is 20%. In the case of large diesel engines [21], Al is 54% and Fe is 25%. It was confirmed that the metal analysis result of the exhaust particles for each engine were different, and it can be seen as the result according to the engine load and material ingredients.

The majority of previous studies [21,34], analyzed the mass, ionic components, and metal components of fine PM contained in the atmosphere. However, this study has significance in that it represents the first application of the use of a PEMS to measure both the concentration of fine PM emissions discharged from diesel locomotives and the ionic components of the fine PM absorbed on the filter. In this study, we compared the mass of dust collected from the PEMS and the fine PM mass using a gravimetric measurement method that can be commonly used. This is meaningful as a method of measuring the PM emitted from a diesel locomotive. In addition, these results are considered to be able to contribute to national policy by reflecting them in inventory construction as a non-road emission source of PM for adapting to climate change.

This is the first report of the use of a PEMS to measure the emissions from diesel locomotives in Korea. The main application of PEMS is to measure the PM concentration from road vehicle emissions, but here the technology was applied to non-road diesel engines for the first time. A PEMS is a device that can measure the emission gases in real time while simultaneously calculating the weight, and the driving characteristics such as speed and acceleration and the emission gases can be simultaneously measured during operation.

In this study, the measurement using PEMS and the standard PM measurement method were compared, and it is considered to be meaningful as a basic study to examine whether it can be applied to diesel locomotives by reflecting the advantages of PEMS. Further studies of specific emission components of non-road contaminants, including diesel locomotives, are necessary.
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