Determination of Elemental and Ionic Compositions for Diesel Exhaust Particles by Particle Induced X-ray Emission and Ion Chromatography Analysis

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The purpose of this study is to clarify the chemical characterization of PM_{2.5} and PM₁₀ in diesel exhaust particles (DEP). Sampling of PM_{2.5} and PM₁₀ in DEP was carried out in November 1999 using an automobile exhaust testing system at the National Traffic Safety and Environment Laboratory, with a diesel truck (engine type: direct injection, displacement: 7961 cc, carrying weight: 2020 kg, equivalent inertia weight: 5600 kg) placed on a chassis dynamometer. Sampling conditions included idling, constant speed of 40 km/h, M-15 test pattern and 60%-revolution/40%-load of maximum power. Samples were collected on a polycarbonate membrane filter (Nuclepore®, pore size: 0.8 µm) using a MiniVol Portable Air Sampler (Airmetrics Co., Inc.). The concentrations of several elemental and ionic species in the PM_{2.5} and PM₁₀ samples were determined by particle induced X-ray emission (PIXE) and ion chromatography analysis. PIXE analysis of the PM_{2.5} and PM₁₀ samples revealed 15 elements, of which Na, Mg, Si, S, Cl, Ca, Fe and Zn were found to be the major components. Ionic species were Cl⁻, NO₂⁻, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, K⁺ and Ca²⁺. Concentrations of elements and ionic species under the sampling condition of 60%-revolution/40%-load were highest in comparison with those of the other sampling conditions. The elemental and ionic species data were compared for PM_{2.5} and PM₁₀; PM_{2.5} concentrations were 70% or more of PM₁₀ concentrations for the majority of elements, and concentrations of ionic species in PM_{2.5} and PM₁₀ were almost identical.

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Introduction

In megalopolis Japanese cities, severe air pollution due to suspended particulate matter (SPM: particles with diameter less than 10 µm) occurs frequently, and the achievement rate of ambient air quality standards of Japan for SPM is low for long periods.¹ Many reports have suggested that one of the reasons for this SPM pollution is the large quantity of diesel exhaust particles (DEP).²⁻⁴ As DEP are fine grained, they are inhaled deep within the respiratory system and easily adhere to it, and concerns have been pointed out that it may affect respiratory disorders.⁵⁻⁷ Methods for evaluating the proportion that DEP contributes to atmospheric PM_{2.5} and PM₁₀ use as an indicator soot, *i.e.*, elemental carbon (EC), which is generally at the core of DEP,^{4,8} but according to a report⁹ by the Japan Clean Air Program (JCAP), the proportion of EC in DEP ranges from 50% to 85%, although it differs depending on the engine standard, combustion type and the presence or absence of a catalytic converter. Since there is variation in the proportion of EC in DEP, the proportion that DEP contributes to atmospheric PM_{2.5} and PM₁₀ as an indicator of EC may be overestimated or underestimated. According to the report⁹ by the JCAP, soluble

organic fraction (SOF), another main component of DEP, is 15 – 48%. On the other hand, the proportion that DEP contributes to atmospheric PM_{2.5} and PM₁₀ can also be evaluated using the chemical mass balance (CMB) method,¹⁰ but it requires a detailed elemental and ionic composition profile of PM_{2.5} and PM₁₀ in DEP. However, as far as we know there is no such detailed elemental and ionic composition profile of these.

Consequently, we have begun to study a multi-probe chemical characterization and composition profile for PM_{2.5} and PM₁₀ in DEP. Sampling of PM₁₀ and PM_{2.5} in DEP was carried out using an automobile exhaust testing system, with a diesel truck placed on a chassis dynamometer, and samples of the PM_{2.5} and PM₁₀ were collected on a polycarbonate membrane filter. Elemental compositions in the filter samples of PM_{2.5} and PM₁₀ were determined by means of particle induced X-ray emission (PIXE) analysis, which allows analysis of minute samples smaller than a milligram without any complex chemical manipulation. It not only simultaneously detects elements from Na to U in a short time but also detects major-to-ultratrace elements at the concentration levels of ppm to sub-ppb. Ionic species (anion: F⁻, Cl⁻, NO₂⁻, Br⁻, NO₃⁻, PO₄³⁻, SO₄²⁻ and C₂O₄²⁻; cation: Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺) in the filter samples were analyzed by ion chromatography.

The present paper focuses on characterizing the elemental compositions and ionic species of DEP and on examining the changes in element and ionic species concentrations in DEP

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Fig. 1 Elemental concentration rate of $PM_{2.5}$ and PM_{10} . I: idling, C: constant speed of 40 km/h, M: M-15 test pattern, P: 60%-revolution/40%-load.

Table 1 Specification of the tested truck

Vehicle	
Transmission	5 M/T
Passengers	2
Carrying weight	2020 kg
Vehicle weight	3430 kg
Gross vehicle weight	7815 kg
Equivalent inertia weight	5600 kg
Engine	
Displacement	7961 cc
Maximum power	200.0 hp/2900 rpm
Maximum torque	54.0 kgm/1700 rpm
Type	Direct injection

resulting from changes in the traveling conditions of a diesel truck. It also addresses acquiring basic data for a chemical composition profile related to DEP for use with the CMB method.

Experimental

Sampling of $PM_{2.5}$ and PM_{10} in DEP was carried out in November 1999 using an automobile exhaust testing system at the National Traffic Safety and Environment Laboratory, with a diesel truck placed on a chassis dynamometer. Specifications of the tested truck are listed in Table 1. Sampling conditions included idling, constant speed of 40 km/h, M-15 test pattern and 60%-revolution/40%-load of maximum power. Samples were collected on a polycarbonate membrane filter (Nuclepore®, pore size: 0.8 μ m) using a MiniVol Portable Air Sampler (Airmetrics Co., Inc.). Flow-rate was 5 l/min. $PM_{2.5}$ and PM_{10} samples were obtained with the MiniVol Portable Air Sampler by sampling exhaust diluted 8 – 18 fold (idling: 18-fold, constant speed of 40 km/h: 8-fold, M-15 test pattern: 10-fold, 60%-revolution/40%-load of maximum power: 8-fold) using dilution air after introducing exhaust emitted from the engine exhaust pipe into a dilution tunnel attached to the automobile exhaust testing system.

The filter samples were sealed in plastic bags and kept in portable refrigerators during transport back to the laboratory, and they were stored in a freezer (-35°C) until they were analyzed. Elemental concentrations in the samples were determined by PIXE at Nishina Memorial Cyclotron Center, Japan Radioisotope Association. For PIXE analysis, samples

were mounted on a target frame made of Mylar film, and bombarded with 2.9 MeV protons from a baby cyclotron.¹¹ Beam currents, the accumulated charge and the typical measuring time were 33 – 60 nA, 30 – 40 μC and 15 – 20 min, respectively. X-ray spectra were analyzed using the SAPIXE program.¹¹ Quantitative analysis of elements was based on the Nuclepore-Br method.¹² Moreover, blank filters were analyzed with all the techniques, and the concentrations of elements that could be measured in the blank filters were always below the minimum detection limits. Ionic species in the samples were determined by ion chromatography (Dionex, DX-120). For ion chromatography analysis, half of a filter was directly treated with 10 ml of ultra-pure water (made by Milli-Q Labo) for 10 min using an ultrasonic apparatus. As for operating conditions during ion chromatography, the sample injection volume was 50 μl and the conductivity detection response was 10 μS . Blank filters were analyzed with all the techniques, and the concentrations of ionic species that could be measured for the blank filters were always below the minimum determination limits. Ionic species concentrations were determined based on calibration curves generated from analysis of the continuing calibration standard solutions. Wako Pure Chemical Industries, Ltd.'s 1000 mg/l standard was used for the standard solution. The concentration of calibration standard solutions is zero (ultra-pure water), 0.005, 0.01, 0.05, 0.1, 0.5, 1, 2 and 2.5 mg/l. For generation of calibration curves, determination of each concentration was repeated five times.

Results and Discussion

Elemental composition

In PIXE analysis of the $PM_{2.5}$ and PM_{10} samples, 15 elements (Na, Mg, Si, S, Cl, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn and Pb) were determined in total. Errors for the analytical results are mainly from the spectrum fitting, the detection efficiency and the values of X-ray transmission through the absorber. Estimated relative error ($100 \times \text{error}/\text{count}$, in %) was smaller than 10% for four elements (Ca, Cr, Fe and Zn), 10 – 20% for two elements (Si and S) and 20 – 40% for seven elements (Mg, Ti, V, Mn, Ni, Cu and Pb). The accuracy of the PIXE analysis was confirmed by an analysis that used NIST standards.¹³

Table 2 shows the elemental concentrations of $PM_{2.5}$ and PM_{10} in DEP under the sampling conditions. The elemental concentrations shown in Table 2 are the actual values from the truck exhaust calculated based on the dilution ratio, *i.e.*, the emission volumes. Elements detected under all sampling

Table 2 Elemental concentrations ($\mu\text{g}/\text{m}^3$) of the $\text{PM}_{2.5}$ and PM_{10} in DEP under the sampling conditions

Element	$\text{PM}_{2.5}$				PM_{10}			
	Idling	40 km/h	M-15	60%/40%	Idling	40 km/h	M-15	60%/40%
Na	44.1	44.6	65.3	290	61.6	92.8	95.9	312
Mg	ND ^a	ND	ND	139	47.7	51.8	48.4	246
Si	23.8	37.6	28.4	538	23.4	40.4	32.5	634
S	130	81.6	63.0	274	122	92.0	82.5	355
Cl	13.0	16.2	22.2	90.4	13.0	16.7	25.1	118
Ca	2.0	4.2	7.3	54.6	4.9	4.5	13.2	72.9
Ti	ND	ND	ND	1.9	1.4	4.6	1.3	8.2
V	ND	0.2	ND	0.5	ND	1.4	ND	2.5
Cr	0.4	ND	ND	5.3	0.4	ND	ND	0.7
Mn	0.4	0.6	0.8	4.2	0.6	1.0	1.0	4.3
Fe	0.6	0.5	1.1	45.4	0.6	0.8	1.4	95.2
Ni	0.1	0.1	0.2	0.8	0.1	0.1	0.2	2.2
Cu	0.3	0.3	0.6	2.5	0.3	0.5	0.8	4.0
Zn	1.5	2.6	3.4	16.6	1.7	2.5	3.8	27.5
Pb	0.3	0.5	0.8	3.2	1.1	0.5	0.8	3.3

a. Not detectable. 40 km/h: constant speed of 40 km/h, M-15: M-15 test pattern, 60%/40%: 60%-revolution/40%-load.

Table 3 Ionic species concentrations ($\mu\text{g}/\text{m}^3$) of the $\text{PM}_{2.5}$ and PM_{10} in DEP under the sampling conditions

Element	$\text{PM}_{2.5}$				PM_{10}			
	Idling	40 km/h	M-15	60%/40%	Idling	40 km/h	M-15	60%/40%
F^-	ND ^a	ND	ND	ND	ND	ND	ND	ND
Cl^-	ND	ND	ND	174	ND	ND	ND	174
NO_2^-	23.9	42.6	118	291	56.0	64.0	222	291
Br^-	ND	ND	ND	ND	ND	ND	ND	ND
NO_3^-	23.9	21.4	74.1	233	23.9	21.4	163	153
PO_4^{3-}	ND	ND	ND	ND	ND	ND	ND	ND
SO_4^{2-}	200	85.6	74.1	523	134	85.6	88.9	466
$\text{C}_2\text{O}_4^{2-}$	ND	ND	ND	ND	ND	ND	ND	ND
Na^+	ND	ND	14.8	116	ND	ND	14.8	116
NH_4^+	48.1	32.0	29.6	233	40.0	32.0	29.6	233
K^+	ND	10.6	14.8	116	7.9	10.6	14.8	116
Mg^{2+}	ND	ND	ND	ND	ND	ND	ND	ND
Ca^{2+}	7.9	10.6	14.8	58.2	7.9	10.6	14.8	58.2

a. Not detectable. 40 km/h: constant speed of 40 km/h, M-15: M-15 test pattern, 60%/40%: 60%-revolution/40%-load.

conditions were the 11 elements: Na, Si, S, Cl, Ca, Mn, Fe, Ni, Cu, Zn and Pb, in $\text{PM}_{2.5}$ and these plus Mg and Ti in PM_{10} . The major element components of both $\text{PM}_{2.5}$ and PM_{10} were Na, Mg, Si, S, Cl, Ca, Fe and Zn. Elemental concentrations by sampling condition in both $\text{PM}_{2.5}$ and PM_{10} in the order of lowest to highest were idling, constant speed of 40 km/h and/or M-15 test pattern and 60%-revolution/40%-load. However, concentrations of sulfur were higher for idling than for constant speed of 40 km/h or for M-15 test pattern in both $\text{PM}_{2.5}$ and PM_{10} . Concentrations under the sampling condition 60%-revolution/40%-load were several time to several dozen times higher than those under the other sampling conditions. In particular, under the sampling condition 60%-revolution/40%-load, elements that increased dramatically were the major components: Na, Mg, Si, S, Cl, Ca, Fe and Zn, in the cases of both $\text{PM}_{2.5}$ and PM_{10} . Furthermore, Mg and Ti were only detected under the sample condition 60%-revolution/40%-load for $\text{PM}_{2.5}$. Comparing the element data for $\text{PM}_{2.5}$ and PM_{10} , as shown in Fig. 1, one finds that the elemental concentration ratio of $\text{PM}_{2.5}$ and PM_{10} differed according to the sampling condition and one finds no definite tendency, but $\text{PM}_{2.5}$ concentrations were 70% or more of PM_{10} concentrations for the majority of

elements.

Ionic composition

As for ionic species, the anions F^- , Cl^- , NO_2^- , Br^- , NO_3^- , PO_4^{3-} , SO_4^{2-} and $\text{C}_2\text{O}_4^{2-}$ and the cations Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} were analyzed. Cl^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ and Ca^{2+} were determined, of which NO_2^- , NO_3^- , SO_4^{2-} and NH_4^+ were found to be the main components of both PM_{10} and $\text{PM}_{2.5}$. The determination limit is 0.01 mg/l (0.03 – 0.3 $\mu\text{g}/\text{m}^3$) for all the ionic species, and concentrations of F^- , Br^- , PO_4^{3-} , $\text{C}_2\text{O}_4^{2-}$ and Mg^{2+} were smaller than 0.3 $\mu\text{g}/\text{m}^3$ for all the samples.

Table 3 shows the ionic species concentrations of $\text{PM}_{2.5}$ and PM_{10} in DEP under the sampling conditions. The ionic species concentrations shown in Table 3 are the actual values from exhaust calculated based on the dilution ratio, *i.e.*, the emission volumes. Like the elements, the ionic species concentrations in both $\text{PM}_{2.5}$ and PM_{10} in the order of lowest to highest were idling, constant speed of 40 km/h and/or M-15 test pattern and 60%-revolution/40%-load. However, concentrations of SO_4^{2-} and NH_4^+ were higher for idling than for constant speed of 40 km/h or for M-15 test pattern in both $\text{PM}_{2.5}$ and PM_{10} . Concentrations under the sampling condition 60%-

revolution/40%-load were several times to several dozen times higher than those under the other sampling conditions. Furthermore, Cl^- was only detected under the sample condition 60%-revolution/40%-load. Comparing the ionic species data for $\text{PM}_{2.5}$ and PM_{10} , one finds that the concentrations of ionic species in $\text{PM}_{2.5}$ and PM_{10} were almost identical.

Conclusions

The major elements of DEP were Na, Mg, Si, S, Cl, Ca, Fe and Zn, and the main ionic species were Cl^- , NO_2^- , NO_3^- , SO_4^{2-} , Na^+ , K^+ and Ca^{2+} . The concentrations of these rose markedly when the load on the diesel engine was high. Comparing the element and ionic species data for $\text{PM}_{2.5}$ and PM_{10} , one finds that $\text{PM}_{2.5}$ concentrations were 70% or more of PM_{10} concentrations for the majority of elements, and that concentrations of ionic species in $\text{PM}_{2.5}$ and PM_{10} were almost identical.

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