Reduction in the Emissions and Toxicity of Polycyclic Aromatic Hydrocarbons from a Heavy-duty Diesel Engine with the Latest Aftertreatment Devices

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Polycyclic aromatic hydrocarbons (PAHs) bound in particles from automobile emissions may cause adverse human health. In this study, a 3L heavy-duty diesel engine with and without the latest aftertreatment devices were characterized for PAH emissions and toxicity using European Transient Cycle (ETC) and the European Stationary Cycle (ESC). The latest combination of aftertreatment devices including a diesel oxidation catalyst (DOC) and a catalyzed diesel particulate filter (c-DPF) were used to remove diesel exhaust particles (DEP). Particle size distribution and number concentrations were measured using a TSI Engine Exhaust Particle Sizer. Eight PAHs [benz(*a*)anthracene, chrysene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*a*)pyrene, indeno(1,2,3-*cd*)pyrene, dibenz(*a,h*)anthracene, and benzo(*ghi*)perylene] within the DEP were analyzed by thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS). Elemental carbon (EC) and organic carbon (OC) were also analyzed with a thermal/optical carbon analyzer. The results indicated that 4-ring PAH emissions are larger than 5 or 6-ring PAH emissions, with and without the aftertreatment devices in place. Number concentrations of particles, PAHs and EC mass emissions in diesel exhaust were dramatically decreased by the aftertreatment devices: > 99%, > 97% and > 99%, respectively. To evaluate the toxicity of PAHs in the DEP, we calculated benzo(*a*)pyrene equivalent (BaPeq) emissions using a toxic equivalency factor (TEF). Total BaPeq emissions of eight PAHs were also substantially decreased by the aftertreatment devices (> 95%). However, the decrease rate of OC was lower than EC (> 72%). We demonstrated that number concentrations of DEP, PAH emissions, EC and BaPeq emissions were similarly and substantially decreased by the latest aftertreatment devices.

Key words — polycyclic aromatic hydrocarbon, diesel exhaust particles, toxicity, toxic equivalency factor

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are generated during incomplete combustion such as wood burning, cooking and road traffic. The composition of the PAH emissions is dependent on a variety of factors, for example, the fuel and its properties, and the combustion technology.¹⁾ PAHs bound in nano and ultrafine particles from automobiles may cause adverse health effects.²⁾ Some PAHs are known to be mutagenic and carcinogenic.^{3,4)} Therefore, PAH emissions from automobiles require anal-

ysis.

In recent years, diesel exhaust particles (DEP) have been reduced to levels close to atmospheric pollution levels by various diesel aftertreatment devices. We used the combination of a diesel oxidation catalyst (DOC) and a catalyzed diesel particulate filter (c-DPF) as the latest aftertreatment devices in this study.

The thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) method is suitable for the analysis of low mass levels of organic compounds, such as PAHs, *n*-alkanes, and *n*-monocarboxylic acids in atmospheric aerosols.^{5–13)} This method does not require an organic solvent extraction process, uses direct sample injection and is highly sensitive.

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Table 1. Specifications of Test Engine, Fuel, Oil and Aftertreatment Devices

Engine	Type	ISUZU DI TCI Diesel
	Cylinder number	4
	Displacement (l)	2.999
	Max power (kW @ rpm)	110 @ 2800
	Max torque (N·m @ rpm)	375 @ 1600
	Injection system	Common rail
Fuel	Air charging system	Inter-cooled turbocharger
	Type	JIS 2
	Cetane index	56.5
	Sulfur content (ppm)	5
	Density (g/cm ³) @ 15°C	0.8313
	Viscosity (mm ² /s) @ 30°C	3.633
Oil	SAE grade	10W-30
Aftertreatment system (DOC)	Material and type	Diesel oxidation catalyst (Precious metal, Pt group)
Aftertreatment system (c-DPF)	Material and type	Cordierite, Wall-flow, Catalyzed (Precious metal, Pt group)

In this study, we used this method to analyze eight PAHs in a small amount of DEP that were collected from a diesel engine fitted with aftertreatment devices. We optimized the conditions for TD-GC/MS combined with a cryogenic-focus trap, selected-ion monitoring (SIM), and a deuterated internal standard for more sensitive analysis and good separation.

Size distributions and number concentrations of DEP were measured in the size range of 5.6–560 nm using an Engine Exhaust Particle Sizer (EEPS). Elemental carbon (EC) and organic carbon (OC) in the DEP were also analyzed with a thermal/optical carbon analyzer according to the IMPROVE protocol.¹⁴⁾

In addition, we estimated toxicity of the eight PAHs using a toxic equivalency factor (TEF).¹⁵⁾ These values have been used as a way of comparing the carcinogenic potency of the individual PAHs with the carcinogenicity of benzo(a)pyrene (BaP) and were expressed in terms of BaP equivalents (BaPeq).¹⁵⁾ We calculated BaPeq emissions with and without DOC+c-DPF, and evaluated the reduction in their toxicity in the presence of the aftertreatment devices.

We evaluated the distribution of the number concentration of DEP, PAH emissions, EC, OC and BaPeq emissions, with and without the latest aftertreatment devices.

MATERIALS AND METHODS

Engine Specifications and Test Cycles — The specifications of the test engine, fuel, oil, and aftertreatment devices are shown in Table 1. To suit Euro V Regulations, DOC and c-DPF were needed, which are the latest combination in aftertreatment devices for diesel engines. The DOC catalyzed the oxidation of CO and hydrocarbons. The c-DPF is a filter coated with a precious metal catalyst that serves as an active regeneration system. The regeneration frequency of this device changes depending on how it is used, but automatic regeneration occurs generally around every 300 km. However, all experiments were carried out without regeneration occurring in the aftertreatment devices.

A heavy-duty diesel engine with and without DOC+c-DPF was operated for 1800 s for the European Transient Cycle (ETC) and the European Stationary Cycle (ESC). The engine was supplied with the aftertreatment devices already fitted, but these were removed before starting the experiments of without the aftertreatment devices condition. The experiments were carried out with this engine on an engine dynamometer. The loads (%) and speeds (%) of both test cycles are shown in Fig. 1.

The ETC is a transient cycle that covers three parts of urban, rural, and highway driving for the emission certification of heavy-duty diesel engines in Europe. The duration of each part is 600 s. The duration of the entire cycle is 1800 s, with and without the aftertreatment devices. The ESC is steady-state cycle for emission certification of heavy-duty

Fig. 1. Loads (%) and Speeds (%) of the Test Cycles, ETC and ESC

diesel engines in Europe, and the engine is operated over a sequence of 13 modes. The engine must be operated for the prescribed time in each mode. The load and speed changes were completed in the first 20 s. The duration of the entire cycle is 1800 s as well as ETC, with and without the aftertreatment devices. Emissions were measured during each mode and averaged over the cycle using a set of weight factors. As a whole, the load (%) for the ESC is higher than the ETC, as shown in Fig. 1.

Table 2. Physical Properties and the LOD and the LOQ of PAHs

PAH	M.W. ^{a)}	B.P. (°C) ^{a)}	LOD ^{b)}	LOQ ^{c)}
BaA	228.3	437.6	0.004	0.014
CHR	228.3	448	0.002	0.009
BbF	252.3	357	0.003	0.011
BkF	252.3	480	0.002	0.008
BaP	252.3	495	0.005	0.017
IcdP	276.3	536	0.066	0.219
DahA	278.3	524	0.167	0.557
BghiP	276.3	500	0.035	0.116

M.W., molecular weight. B.P., boiling point. ^{a)} Values reported by Ho and Yu (2004).⁹⁾ ^{b)} LOD is defined as 3σ of the peak area ratio of each PAH versus the internal-standard of the lowest concentration of the calibration curve ($n = 30$). ^{c)} LOQ is defined as 10σ of the peak area ratio of each PAH versus the internal-standard of the lowest concentration of the calibration curve ($n = 30$).

Reference Material — For quantification of the PAHs, standard reference material (SRM) 1647e solution was purchased from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, U.S.A.). SRM 1647e solution contains 16 PAHs in acetonitrile. We chose eight PAHs as target compounds that have four, five, or six aromatic rings and molecular weights > 220 and are difficult to volatilize from quartz-fiber filters. The eight PAHs were benz(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-*cd*)pyrene (IcdP), dibenz(a,h)anthracene (DahA), and benzo(ghi)perylene (BghiP). The physical properties, limit of detection (LOD) and limit of quantification (LOQ) of each PAH are shown in Table 2. We diluted with HPLC-grade acetonitrile to prepare calibration curves. The certified concentration of BaA in 1647e solution is 4.09 ± 0.09 mg/l, CHR is 3.60 ± 0.08 mg/l, BbF is 4.19 ± 0.09 mg/l, BkF is 4.69 ± 0.10 mg/l, BaP is 4.87 ± 0.12 mg/l, IcdP is 4.27 ± 0.13 mg/l, DahA is 3.49 ± 0.20 mg/l, BghiP is 3.67 ± 0.13 mg/l. However we did not confirm the linearity of the calibration curve and net recoveries of the other eight PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, and pyrene) in SRM 1647e solution because they may vaporize during the spiking process.

CHR-*d*₁₂ solution in dichloromethane was purchased from Supelco (Bellefonte, PA, U.S.A.) for use as an internal standard. CHR-*d*₁₂ solution was selected because its analytical behavior is similar to that of the target compounds.¹⁶⁾ To pre-

pare a calibration curve, we spiked diluted standard solution of SRM 1647e on quartz-fiber filters with a microsyringe and added 2 μl of CHR- d_{12} solution diluted 10000 : 1 with dichloromethane (0.4 ng). The calibration curve was obtained from the area ratio PAH/CHR- d_{12} and the concentration ratio PAH/CHR- d_{12} .

Number Concentrations of DEP — The number concentrations of DEP emitted from the engine under the test conditions were measured, with and without the aftertreatment devices, using an EEPS Model 3090 (TSI Inc., Shoreview, MN, U.S.A.). This instrument, which uses electrical mobility technology, measures the size distribution of engine exhaust particles with diameters from 5.6 to 560 nm and has a fast time resolution. It displays measurements in 32 channels (16 channels per decade) and operates at ambient pressure to prevent evaporation of volatile and semi-volatile particles. In this study, the dilution ratio was held constant at 15 : 1. This experiment was separated from the sampling experiment because the dilution conditions were different.

Filter Sampling — We used HORIBA micro tunnel as a partial flow dilution system^{17, 18)} to dilute and cool the exhaust during sampling; the flow rate was set to 80 l/min. The exhaust division ratio of the partial flow dilution tunnel was held constant at 600.

DEP are usually collected on a Teflon-impregnated glass fiber filter, but we selected quartz-fiber filters (2500QAT-UP, Pallflex Products Corp., NY, U.S.A.) because of thermal desorption and carbon analysis. Quartz-fiber filters were conditioned by baking for 2 hr in an electric furnace at 700°C before their initial weighing. In this study, sampling time was the same under all experiments. DEP were collected on a 60-mm-diameter area of a 70-mm-diameter filter. The filters were weighed before and after collection of DEP by means of a microbalance (readability 1 μg , M3P-F, Sartorius AG, Goettingen, Germany) in a chamber in which the temperature and relative humidity were controlled at $25 \pm 5^\circ\text{C}$ and $50 \pm 5\%$, respectively. After sampling, the filters were stored at $-80 \pm 2^\circ\text{C}$ until analysis. Before analysis, an area with a diameter of 10 mm was punched from the filter, and an internal standard solution (2 μl of a 0.2 ng/ μl) was added. The filters were dried under helium gas for about 1.5 min prior to TD-GC/MS analysis. Each filter sample was set into the middle of a TD tube.

Fig. 2. Schematic Diagram of the TD-GC/MS System

TD-GC/MS — The PAHs were analyzed with a T-Dex II TD system (GL Sciences Inc., Tokyo, Japan) installed on a Varian GC-3800 GC with a Varian 300-TQMS (Varian Inc., Lake Forest, CA, U.S.A.). Varian MS Workstation software (ver. 6.9) was used for raw data analysis. The TD instrument was equipped with a TD auto sampler system. The TD tube (Pyrex, 89 mm length, 4 mm Internal Diameter (I.D.), 6 mm Outside Diameter) was automatically placed in the TD area under the injection port of the GC. We did not use glass wool to hold the sample in the TD tube. The cryogenic-focus trap system was located below the TD area in the GC oven and was cooled initially with -100°C liquid nitrogen. A schematic diagram of the TD-GC/MS system is shown in Fig. 2. Use of the cryogenic-focus system permitted effective separation and thus increased peak height. For reuse, the TD tubes were baked for 1 hr at 400°C under flowing helium gas at a flow rate of 100 ml/min. TD analysis of each sample was performed automatically by means of the T-Dex II programming. We selected 350°C as the TD temperature because this temperature does not favor pyrolysis and is effective for desorption of PAHs. Ho and Yu⁹⁾ also reported that the best TD temperature is $> 300^\circ\text{C}$. Fushimi *et al.*¹⁰⁾ showed that desorption is incomplete at temperatures of $> 250^\circ\text{C}$ and that considerable pyrolysis occurs at temperatures of $> 550^\circ\text{C}$. These authors also showed that the peak abundances for ramped desorption to 350°C and to 450°C were equivalent.

In the first step (initial mode), the outside of the TD tube was purged from bottom to top with helium gas at a flow rate of 25 ml/min. In the second step (TD mode), the TD tube was heated from 45°C (held for 1 min) to 350°C (held for 10 min) at a rate of 5°C/s with helium gas at a flow rate of 40 ml/min (in split mode; 5 ml/min for sample and 35 ml/min for split).

Desorbed compounds were collected in the cryogenic-focus trap at -100°C with liquid nitrogen in a cryotube (0.53 mm I.D., inert fused silica capillary column). Trapped compounds were reheated from -100°C (held for 1 min) to 300°C (held for 10 min) at a rate of 50°C/s and then were sent to an analytical capillary column.

The GC was heated from 60°C (held for 3 min) to 200°C at a rate of 15°C/min and then to 325°C (held for 10 min) at a rate of 5°C/min . The compounds were separated on a Factor Four capillary column (model VF-5 ms; $30\text{ m} \times 0.25\text{ mm}$ i.d., $0.25\text{ }\mu\text{m}$ film thickness, lowest guaranteed bleed specification temperature 325°C ; Varian Inc.). The helium carrier gas was supplied at 1.3 ml/min for GC/MS. SIM mode was used for quantitative analysis in this study. The GC injector, ion-source, and transfer-line temperatures were 270 , 230 , and 280°C , respectively.

EC and OC Analysis — EC and OC in the DEP on the quartz-fiber filters were analyzed with a thermal/optical carbon analyzer (DRI model 2001 Carbon Analyzer; Desert Research Institute, Las Vegas, NV, U.S.A.)¹⁴⁾ with the IMPROVE thermal/optical reflectance protocol. A sample (0.503 cm^2 area; 8 mm diameter) punched from a quartz-fiber filter was heated at 120 (OC1), 250 (OC2), 450 (OC3), and 550 (OC4) $^{\circ}\text{C}$ in a helium atmosphere and at 550 (EC1), 700 (EC2), and 800 (EC3) $^{\circ}\text{C}$ in an oxidizing atmosphere (2% oxygen, 98% helium).¹⁹⁾ We calculated PAH/OC and PAH/EC under various test conditions. OC and EC were calculated with a μgC base.

RESULTS AND DISCUSSION

Number Concentrations of DEP

The particle size distributions of DEP in the engine-out exhaust gas, in the exhaust gas of the engine equipped with the DOC alone, and with both devices are shown in Figs. 3 and 4 for the ETC and the ESC, respectively. For both cycles, bimodal distributions were observed; a large peak with a modal diameter of around 50 nm and a small peak with a modal diameter of around 10 nm were observed. For both the ETC and ESC, the number concentrations of DEP were almost the same for the engine-out exhaust and the exhaust of the engine equipped with the DOC alone. The DOC oxidizes CO and hydrocarbons but does not remove diesel soot particles. In contrast, the number concentrations of DEP

Fig. 3. Particle Size Distribution of DEP in the ETC, Obtained by means of EEPs

Fig. 4. Particle Size Distribution of DEP in the ESC, Obtained by means of EEPs

were dramatically decreased ($> 99.9\%$) when both aftertreatment devices were used. This represents the effectiveness of the c-DPF. The decrease rate of the number concentrations did not depend on the diameter of particles between 5.6 nm and 200 nm in either cycle. It was shown that the c-DPF can decrease nano and ultrafine particles, and that has high performance ability for DEP reduction.

TD-GC/MS

The correlation coefficients (R^2) of calibration curves measured at six levels between 0.007 and 2.91 ng were in the range of 0.964 – 0.997 , indicating good linearity. The limits of detection and quantification for the 8 PAHs revealed remarkably low values that were 0.002 – 0.167 ng and 0.008 – 0.557 ng , respectively.

Effectiveness of the Latest Aftertreatment Devices for Reduction of PAH Emissions

DEP were collected on the quartz filter un-

Fig. 5. PAH Emissions in the Engine-out Exhaust Gas in the ETC and the ESC

der engine-out conditions, and these amounted to 3.37 mg in the ETC and 2.2 mg in the ESC. With aftertreatment (DOC + c-DPF), the quantity of DEP collected was 0.20 mg in the ETC and 0.16 mg in the ESC. We calculated the weight of DEP on the punched 10 mm diameter filter. From these, 94 µg was collected from the ETC and 61 µg in the ESC under engine-out conditions, and 5.5 µg in the ETC and 4.4 µg in the ESC under the aftertreatment (DOC + c-DPF) equipped conditions. PAH emissions in the engine-out exhaust gases are shown in Fig. 5 from the ETC and the ESC. The PAH emissions in the ETC were higher than the ESC, but this is thought to be due to the greater mass of DEP collected during the ETC than the ESC. On the whole, the engine load of the ETC is lower than the ESC (Fig. 1). Additionally, exhaust temperature in the ETC is lower than the ESC with and without aftertreatment devices. In particular, at the start of cycle, the inlet temperature of DOC in the ETC is about 100°C, that is lower than active temperature of the catalyst. Therefore, PAH emissions in the ETC is higher than the ESC, because PAH are not oxidized at the start of the ETC, and emit to the engine exhaust.

Total emissions of the eight PAHs following aftertreatment with DOC + c-DPF in the ETC and ESC were remarkably decreased compared to the emissions in the engine-out exhaust gases (Figs. 6–9); the total decrease rates were 98.4% in the ETC and 97.7% in the ESC. For the ETC, the decrease rates for the individual PAHs were as follows: BaA 95.7%, CHR 99.1%, BbF 98.8%, BaP 93.2%, IcdP > 99.8%, and BghiP > 99.9%. The levels of BkF and DahA were below the LOD in the engine-out exhaust, and these compounds were not detected when the engine was

Fig. 6. PAH Emissions with and without DOC + c-DPF in the ETC

N.D., not detected.

Fig. 7. PAH Emissions with and without DOC + c-DPF in the ESC

N.D., not detected.

Fig. 8. Comparison of Distributions of PAH and BaPeq Emissions with and without Aftertreatment in the ETC

equipped with the aftertreatment devices. For the ESC, the decrease rates were as follows: BaA 98.3%, CHR 97.8%, BbF 91.9%, BaP > 99.9%, IcdP 73.3%, and BghiP 77.8%. The level of BkF was < LOD both with and without the aftertreatment devices, and the level of DahA was < LOD in the engine-out exhaust, and the compound was not detected when the engine was

Fig. 9. Comparison of Distributions of PAH and BaPeq Emissions with and without Aftertreatment in the ESC

equipped with the aftertreatment devices. Therefore, the reduction rate for both cycles was the same, but it was slightly higher for the ETC than for the ESC.

Carbonaceous Emissions, PAH/OC and PAH/EC Ratios under Various Test Conditions

The EC and OC emissions are shown in Fig. 10. When the engine was equipped with the aftertreatment devices, the decrease rates of EC in the DEP were 99.6% in the ETC and 99.7% in the ESC, and the decrease rates of OC in the DEP were 72.1% in the ETC and 78.2% in the ESC. The decrease rates in EC in the DEP for both cycles were significantly higher than those for OC. We thought that the large decrease rate for EC was due to the reduction of diesel soot particles by the c-DPF, because the DOC oxidizes CO and hydrocarbons but does not decrease diesel soot particles. Therefore, these results indicated that the aftertreatment devices have high effectiveness for removal of EC but it is thought that OC is not collected completely when the aftertreatment devices fail to reach the active temperature at the start of the ETC and ESC.

The PAH/OC ratios over the ETC and ESC are shown in Fig. 11. All the ratios fell in a range from 1×10^{-2} to 1×10^{-4} in the engine-out exhaust. When the engine was equipped with the aftertreatment devices, all the ratios fell in a range from 1×10^{-3} to 1×10^{-4} . Except in the case of BkF and BghiP in the ESC, the PAH/OC ratios decreased by nearly one order of magnitude under conditions where the aftertreatment devices used. The PAH/EC ratios in the ETC and ESC are shown in Fig. 12. All ratios fell in a range from 1×10^{-2} to 1×10^{-4} in the engine-out exhaust. When the aftertreatment devices were attached, all the PAH/EC ratios fell in a range from

Fig. 10. OC and EC Emissions in DEP in the ETC (a) and in the ESC (b)

1×10^{-1} to 1×10^{-4} , the ratios were greater than in the engine-out condition. Because the EC mass had decreased due to the aftertreatment devices, it was assumed that the PAH/EC ratio had increased.

Effectiveness of the Latest Aftertreatment Devices for Reduction of Toxicity

From the view point of health effects, we calculated the total reduction rate of toxicity for the DEP emitted from a diesel engine fitted with the latest aftertreatment devices. Yang *et al.* (2005)¹⁵⁾ calculated the BaPeq emission factor for individual PAHs by multiplying the emission factor with the corresponding TEF values. The results are shown in Tables 3 and 4, and Figs. 8 and 9. The total reduction rate of BaPeq emissions under ETC and ESC when the aftertreatment devices were fitted was 96.1%

Table 3. Comparison of BaPeqs with and without Aftertreatment Devices for the ETC

PAH	TEF ^{a)}	BaPeq emissions without DOC + c-DPF (ng/kWh)	BaPeq emissions with DOC + c-DPF (ng/kWh)
BaA	0.10	115.1	5.0
CHR	0.01	44.2	0.4
BbF	0.10	52.4	0.6
BkF	0.10	< LOD	< LOD
BaP	1.00	90.1	6.1
IcdP	0.10	4.4	< LOD
DahA	0.10	< LOD	< LOD
BghiP	0.01	0.5	< LOD
Total	—	306.6	12.1
Decrease rate for total BaPeq emissions (%)	—	—	96.1

a) Values reported by Yang *et al.* (2005).¹⁵⁾

Table 4. Comparison of BaPeqs with and without Aftertreatment Devices for the ESC

PAH	TEF ^{a)}	BaPeq emissions without DOC + c-DPF (ng/kWh)	BaPeq emissions with DOC + c-DPF (ng/kWh)
BaA	0.10	29.5	0.5
CHR	0.01	13.0	0.3
BbF	0.10	7.7	0.6
BkF	0.10	< LOD	0.1
BaP	1.00	11.7	< LOD
IcdP	0.10	0.3	0.1
DahA	0.10	< LOD	< LOD
BghiP	0.01	< LOD	< LOD
Total	—	62.2	1.6
Decrease rate for total BaPeq emissions (%)	—	—	97.4

a) Values reported by Yang *et al.* (2005).¹⁵⁾

Fig. 11. Ratio of PAH to OC under Various Test Conditions **Fig. 12.** Ratio of PAH to EC under Various Test Conditions

and 97.4%, respectively.

Thus, the reduction rates for both cycles were almost similar, but the ESC rate was slightly higher than for the ETC. This result shows that the presence of the aftertreatment devices dramatically decreased the toxicity of diesel engine exhaust.

Comparison of the Distributions of PAH and BaPeq Emissions

Figures 8 and 9 show the comparison of the distributions and trends of PAH emissions and BaPeq emissions. Under two different test cycles, the dis-

tributions and trends were very similar with and without the aftertreatment devices.

In conclusion, we have evaluated the reduction efficiency and distribution of PAH emissions and toxicity from a diesel engine equipped with the latest combination of DOC + c-DPF using TD-GC/MS. We analyzed eight target PAHs in very low masses of DEP and determined the quantities of the target PAHs in DEP obtained from the engine operated under representative conditions of the ETC and the ESC. When the aftertreatment devices were fitted to the engine, the overall number concentrations of DEP, total emissions of the eight PAHs and the quantity of EC in the DEP were dramatically decreased to > 99%, > 97% and > 99%, respectively. However the decrease rate of OC was lower than EC (> 72%). The decrease rate of number concentrations did not depend on diameter of particles between 5.6 nm and 200 nm. It was shown that the c-DPF decreases nano and ultrafine particles.

The BaPeq emissions of the eight PAHs were also evaluated using TEF to determine the reduction in carcinogenic potency afforded by the aftertreatment devices, and this analysis revealed that the decrease rate was very high (> 95%). The decrease rate for the ESC was slightly higher than for the ETC.

We demonstrated that number concentrations of DEP, PAH emissions, the quantity of EC and BaPeq emissions decreased similarly and significantly with the latest aftertreatment devices. The effectiveness of the DOC + c-DPF combination was fully demonstrated by means of the TD-GC/MS method and showed that the total emissions of PAHs, number concentrations and the quantity of EC in DEP decreased by two orders of magnitude.

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