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EMISSION CHARACTERISTICS OF PCDDs/DFs, DLPCBs AND PAHs FROM DIFFERENT FUELED VEHICLES WITH VARIABLE SPEEDS

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ABSTRACT

Emission characteristics of polychlorinated dibenzo-*para*(*p*)-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) and polycyclic aromatic hydrocarbons (PAHs) from different fueled vehicles were studied with variable speeds. The speed of vehicle is changed from 30 km/hr, 60 km/hr and 80 km/hr at constant load rate. Concentration and phase distribution of PCDD/DFs, DLPCB and PAHs with the isokinetic sampling of exhaust gas is obtained in this study. The averages WHO-TEQ concentrations of exhaust gas from LPG, gasoline and diesel fueled vehicles are 9.89, 3.27 and 1.86 pg-TEQ/Nm3, respectively. PAHs concentrations of exhaust gas from LPG, gasoline and diesel fueled vehicles are 1.47, 669.33 and 2417.74 μg/Nm^3, respectively.
PCDD/DFs, DLPCB and PAHs among the exhaust gas emitted from automobiles are examined by the cluster analysis and the result confirms that gasoline and LPG fueled vehicles of spark ignition engine and diesel fueled vehicle of compression ignition engine form a separate cluster respectively. Also confirmed that PAHs have counter-correlations with PCDDs/DFs, DLPCBs and PAHs in their generation.

Key Words: Diesel, LPG, Gasoline, PCDD/DFs, DLPCBs, PAHs, Exhaust gas

INTRODUCTION

Persistent organic pollutants (POPs) with such characteristics as toxicity, bioaccumulation, persistency and long-range transfer are noted as critical environmental pollutants that have toxic effects on the carcinogenesis, decrease the reproduction and the growth rate, and corrupt the immunity system (UNEP, 2001; Govers et al. 1998).
Ballschmiter(1986) measured PCDD/DFs from the automobile exhaust gas and pointed out them as emission sources. Since then, for the last 10 years, not a few studies in relation to automobiles have been reported (Marklund et al., 1990; Oehme et al., 1991; Geueke et al., 1999; Miyabara et al., 1999; Takasuga et al., 1999; Ryan and Gullet, 2000). Most research related to motor vehicles has been conducted with much attention to diesel and leaded gasoline fueled vehicles and considerable data deviation is concidered due to the differences in experimental conditions such as sampling methods, etc. (Schwind et al., 1991).

Therefore, this study invented a new device, based on US EPA method 5 using a stack sampler, for the sampling of PCDD/DFs, DLPCBs and PAHs among the automobile exhaust gas and made the isokinetic sampling possible in order to take representative samples on speed changes and effects of the turbulent current of exhaust gas. Also, measures and analyses are carried out to grasp emission characteristics of gaseous and particulate phase PCDD/DFs, DLPCBs and PAHs emitted from automobiles of different fuels and velocities.

METERIAL AND METHOD

Sampling

Samples of PCDD/DFs, DLPCBs and PAHs were collected difference condition by fuels (LPG, gasoline, diesel) and speeds (30 km/hr, 60 km/hr, 80 km/hr) of vehicles. Experiments are carried out for 1997 year-type gasoline fueled vehicle (77,951 km mileage) with 1,323 cc engine displacement, 70 ps/3500 rpm maximum power and 12.0 kg·m/3,000rpm maximum torque, 2000 year-type LPG fueled car (64, 351 km mileage) with 1,997 cc engine displacement, 115 ps/5000 rpm maximum power and 18.1 kg·m/4500 rpm maximum torque, and 2002 year-type diesel fueled vehicle (52, 310 km mileage) with 2,874 cc engine displacement, 95 ps/4000 rpm maximum power and 19.6 kg·m/2800rpm maximum torque, with cars fixed to chassis dynamometers.

Sampling apparatus was divided into filter part that sampling particulate phase, absorber I that sampling gaseous phase, XAD resin and absorber II. Before taking samples, cleanup standards (EPA-1613 CSS, Wellington Laboratories, Canada; 68A-CS, Wellington Laboratories, Canada) are spiked on XAD resin. After samplings are classified into gaseous and particulate phase, extraction and analyses are performed. Sampling apparatus is shown in Figure 1.

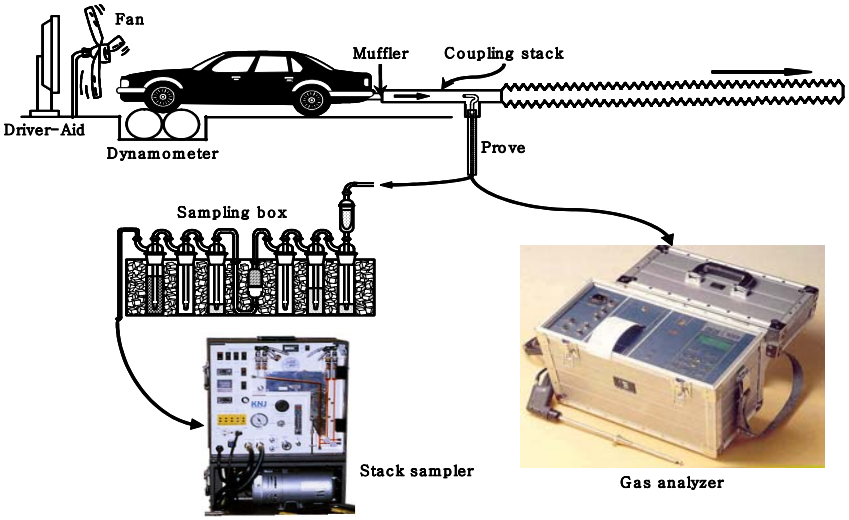

Fig. 1. Schematic diagram of sampling for differently fueled vehicle.

Extraction and analyses

Particulate and gaseous phase of exhaust gas from vehicles were extracted with 350

ml of toluene for 16 h under soxhlet. After extraction, extracts were concentrated to 10 mL in a rotary evaporator. And than, samples were divided 9 mL and 1 mL for Dioxin-like compound and PAHs, respectively.
Reduced extracts were added to 0.5 mL of n-nonane as a keeping solvent and concentrated to <0.3 mL under a gentle purging of nitrogen gas. Solutions were transferred to 10 mL of n-hexane, ensuring the complete removal of toluene, and internal standard solutions of 15 $^{13}C_{12}$-labeled PCDDs/DFs (EPA-1613LCS, Wellington Laboratories, Canada) and 27 labeled DLPCBs (68A-LCS, Wellington Laboratories, Canada) were spiked. Solutions were pre-cleaned up with a multi-layer silica gel column chromatography and cleaned up with an activated alumina column chromatography (Ok et al., 2002).
Samples analyses were carried out using an high resolution gas chromatography (HP-6890, Hewlett Packard, USA) coupled to a high resolution mass spectroscopy (JMS 700D, Jeol, Japan) at a resolution of 10,000 (10% valley) under selected ion monitoring (SIM) mode, and a SP-2331 (60 m length, 0.25 mm inner diameter, 0.25 μm film thickness, Supelco, USA) and a HP-5MS (30 m length, 0.25 mm inner diameter, 0.25 μm film thickness, J&W Scientific, USA) were used for the separation and detection of PCDDs/DFs compounds. For the separation and quantification of DLPCBs, HRGC/HRMS (HP 6890 GC/JMS 700D MS) was operated at a resolution of 10,000. The capillary column used for DLPCBs separation was HT-8 (50 m length, 0.22 mm inner diameter, 0.25 μm film thickness, SGE, Australia) (Ok et al., 2002).
1mL of divided each samples for PAH were transferred to n-hexane and an internal standard labeled standard (ES 4087, CIL, USA) were spiked. The extracted samples were purified using activated silicagel (70-230 mesh, Neutral, Merck) column(300 mm length and 15 mm inner diameter) chromatography with successive elutants of *n*-hexane and 10% methylene dichloride (Pesticide residue analysis, Cica-Merck, Japan) in *n*-hexane. The PAHs fraction was analyzed by gas chromatography (QC 2010, Simadzu, Japan) coupled to mass spectrometry (QP 2010, Simadzu, Japan) (Ok et al., 2002; Kim et al., 2001a; 2001b; 2003a; 2003b).

RESULTS AND DISCUSSION

PCDDs/DFs and DLPCBs

Concentration of gaseous and particulate phase in the automobile exhaust gas does not concider any constant distribution trait as is shown in Table 1 and Figure 2. In LPG fueled vehicle, gaseous concentration is high and in gasoline fueled car, gaseous and particulate phase are similar in concentration level. But, diesel fueled vehicle, concentration of particulate phase higher than gaseous phase.
For emission concentration based on speed, in cases of LPG and gasoline fueled vehicles of spark ignition engine, the concentration is relatively high at 60 km/hr and in diesel fueled car of compression ignition engine, concentration reaches maximum at 30 km/hr. Especially, when LPG vehicle speed at 60 km/hr, the emission concentration is 10 times higher than those at other speeds.
The examination of PCDD/DFs homologue profile pattern indicates that in all the vehicles, HpCDDs and OCDD among PCDD/DFs are high and in diesel fueled vehicle, generation concentration and ratio of PCDFs homologue groups except TCDFs are very low when emitted.

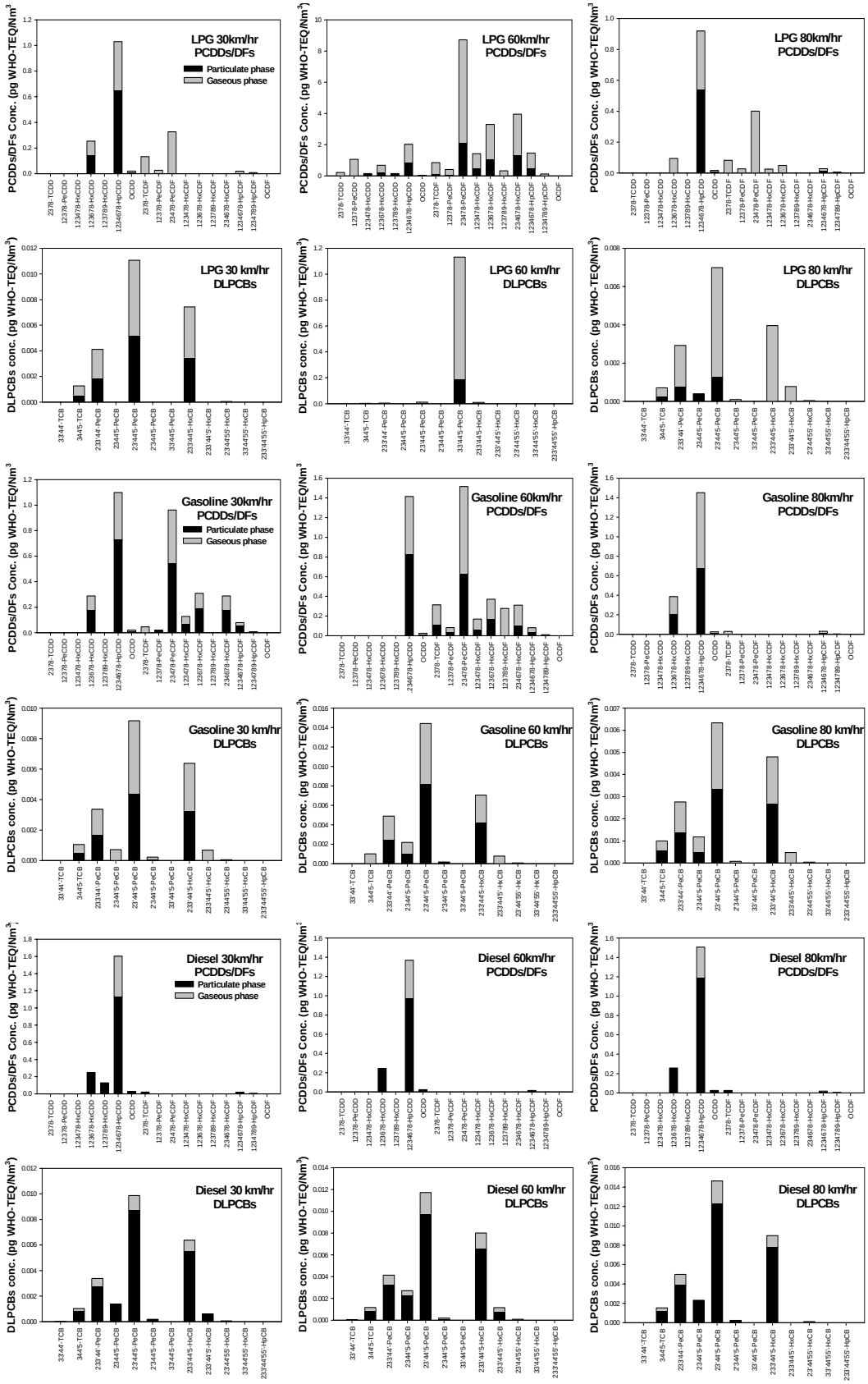

Fig. 2. Concentration of toxic 2,3,7,8 substituted PCDDs/DFs and DLPCBs from different fueled vehicles with variable speeds.

Table 1. Summary of 2,3,7,8-substituted concentration and homologue of PCDDs/DFs and DLPCBs from different fueled vehicles with variable speeds

Fuel type	Speed (km/hr)	WHO-TEQ concentration (pg WHO-TEQ/Nm^3)		PCDDs/DFs Homologue (pg/Nm^3)	
		Gaseous phase	Particulate phase	Gaseous phase	Particulate phase
LPG	30	1.009	0.832	182.605	240.458
	60	18.652	7.446	1,332.154	980.725
	80	1.092	0.575	159.006	193.584
Gasoline	30	1.250	2.019	155.084	306.643
	60	2.566	2.039	293.044	342.461
	80	1.007	0.937	279.879	253.611
Diesel	30	0.448	1.590	320.710	808.092
	60	0.412	1.271	269.431	657.692
	80	0.329	1.543	214.289	818.558

Table 2. Dioxins concentration from vehicle in other studies

Study and year	Concentration (pg I-TEQ/Nm^3)	Fuel type
This study	1.94–4.60†	gasoline(30, 60, 80 km/h)
This study	1.68–2.08†	diesel(30, 60, 80 km/h)
This study	1.66–26.10†	LPG (30, 60, 80 km/h)
CARB (1987)	218	Diesel-truck, 50 km/hr
Hagenmaier et al. (1990)	9.8	Gasoline unleaded-p. car. No cat , FTP 73 test cycle
Hagenmaier et al. (1990)	0.93	Gasoline unleaded-p. car. with cat
Hagenmaier et al. (1990)	141.5	Gasoline leaded –p.car.
Hagenmaier et al. (1990)	1.20	Diesel-p.car
Miyabara et al. (1999)	3.46–5.33 (mean: 4.18)	Gasoline
Miyabara et al. (1999)	7.13–14.0 (mean: 10.57)	Diesel
Chang et al. (2004)	6.27	Diesel, 40 km/hr
Chang et al. (2004)	41.9	Diesel, Idled

† unit: WHO-TEQ/ Nm^3

The result of this study, the average emission concentration of diesel and gasoline fueled vehicles are 1.86 and 3.27 pg WHO-TEQ/Nm^3 respectively. Compared with the emission concentration of leaded gasoline and diesel fueled vehicles from the other studies, as is shown in Table 2, the concentration level is very low.
From these results, it is judged that concentration deviation varies greatly depending on fuels type, age of vehicle and driving conditions.

PAHs

In case of the concentration of PAHs in the automobile exhaust gas, as is shown in Table 3 and Figure 5, gaseous phase concentration is detected more highly than particulate phase concentration in all kinds of vehicles except diesel at 60 km/hr. But, in carcinogenic PAHs (PAHcarc.), particulate phase concentration is higher than gaseous phase concentration. Among them, LPG fueled vehicle indicates four times higher and diesel fueled vehicle 18 times higher results. The reason is that PAHs

with medium and high molecular weight take relatively higher ratio in particulate phase PAHs presence.

In gaseous phase, concentration ratio declines with PAHs of higher molecular weight and it increases with PAHs of lower molecular weight. But, in case of diesel, it rises unusually in 3 ring-PAHs. In case of PAHs, the highest concentration is concidered in diesel fueled vehicle at 60 km/hr. High concentration is detected from the relatively old gasoline vehicle.

Emission concentration of PAHs according to the vehicle speed, the concentration of LPG and gasoline vehicles turns up in order of 30 km/hr〉 60 km/hr〉 80 km/hr and that of diesel appears in order of 60 km/hr〉 30 km/hr〉 80 km/hr.

Table 3. Summary of PAHs and PAHcarc.(μg/Nm^3) concentration in this study

Fuel type	Speed (km/hr)	16PAHs concentration (μg/Nm^3)		PAHcarc. concentration (μg /Nm^3)	
		Gaseous phase	Particulate phase	Gaseous phase	Particulate phase
LPG	30	2.629	0.020	0.020	0.006
	60	0.381	0.748	0.044	0.297
	80	0.577	0.048	0.015	0.029
Gasoline	30	1,059.683	0.236	0.152	0.126
	60	898.992	0.473	0.642	0.162
	80	47.685	0.925	0.663	0.017
Diesel	30	15.369	175.468	0.015	1.284
	60	6,775.919	131.444	0.136	2.470
	80	13.751	141.271	0.171	1.994

Table 4. PAHs concentration from vehicle in other studies

Study and year	Concentration(μg/Nm^3)	Fuel type
This study	47.71–1052.92	gasoline(30, 60, 80 km/h)
This study	155.02–6907.35	diesel(30, 60, 80 km/h)
This study	0.62–2.65	LPG (30, 60, 80 km/h)
Brož et al. (2000)	150–420	leaded gasoline
Mi et al. (1996)	180.4	gasoline
Mi et al. (2000)	318–1,500	diesel(heavy duty diesel): mode 1
Mi et al. (1998)	297	gasoline (fuel additive SA)
Mi et al. (1998)	265	gasoline (fuel additive SB)
Šebor et al. (1994)	46.6	gasoline (Test ECE)
Šebor et al. (1994)	186.0	gasoline (90 km/h)

As is inferred from these results, in gasoline and LPG fueled vehicles, the higher the speed is, the lower the emission concentration becomes. These results are explained as follows. As the temperature of emission gas increases with the speed of vehicle, connecting rings of benzene nucleus involving PAHs are broken into chlorinated compounds and low molecular PAHs. Then, the emission concentration of PAHs declines abruptly (Gullet et al., 2000).

Result of this study, the concentration of PAHs from the diesel fueled vehicle as table 4 is 155.02–6,907.35 μg/Nm^3, higher than 318–1,500 μg/Nm^3 of the other studies level. In case of gasoline, the concentration is higher than the other studies concentration range (46.6–420 μg/Nm^3) (Brož et al., 2000; Mi et al., 1996, 1998, 2000; Šebor et al., 1994). PAHs in the LPG fueled vehicle are 0.62–2.65 μg/Nm^3

indicating very low range of concentration. Therefore, the different concentration levels of PAHs generation are clearly discriminated according to the fuels.

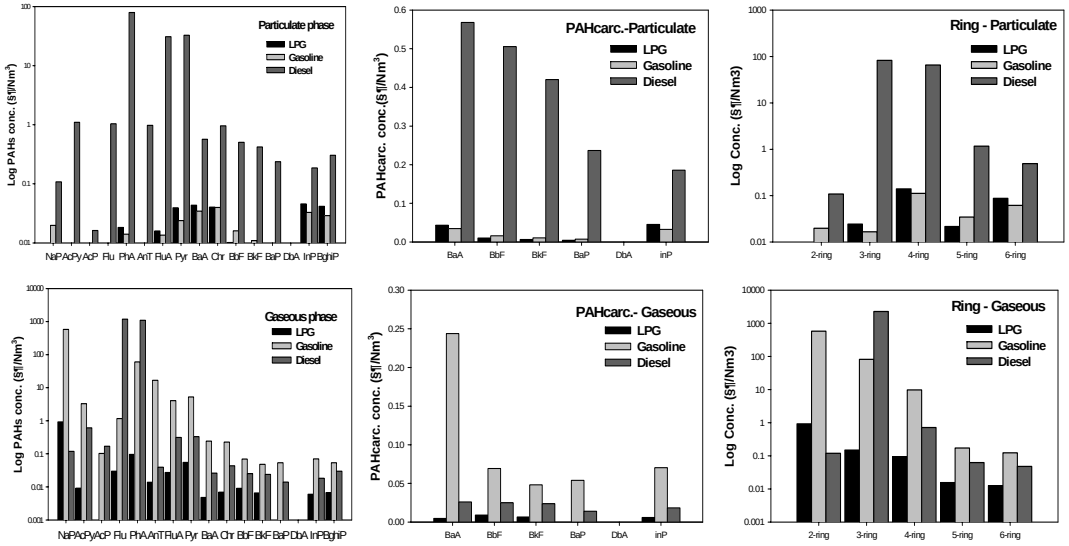

Fig. 3. Distribution of carcinogenic PAHs (upper) and ring-PAHs (under) concentration in differently fueled vehicle experiment.

Data Analyses

PCDDs/DFs, DLPCBs and PAHs among the exhaust gas emitted from automobiles are examined by the cluster analysis and the dendrogram of the analysis is shown in Figure 4. The results from the cluster analysis of PCDDs/DFs, DLPCBs and PAHs are largely grouped into the spark ignition engine of gasoline and diesel, and compression ignition engine of diesel.

But, the result from the cluster analysis of PAHs in the gasoline fueled vehicle shows that the cluster is not dense, unlike the cases of LPG and diesel fueled vehicles, and is dispersed depending on the vehicle speed. Compared to other vehicles, it is considered that the speed of gasoline fueled vehicle affects PAHs emission pattern.

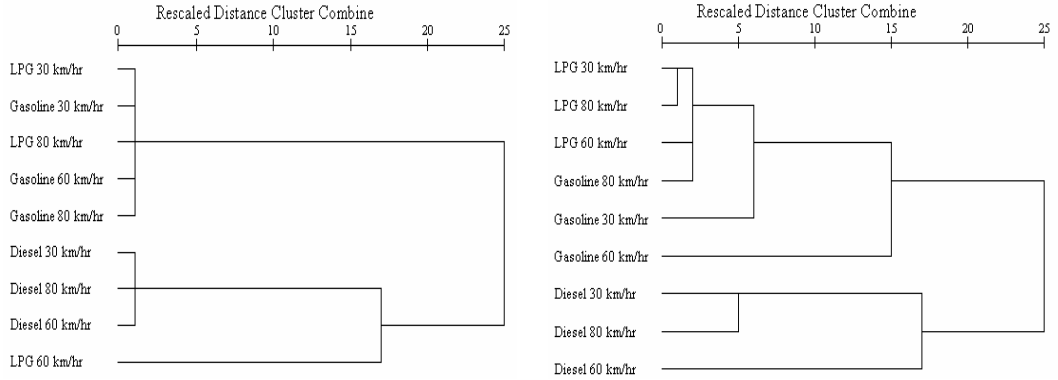

Fig. 4. Dendrogram of PCDDs/DFs, DLPCBs profile (left) and PAHs profile (right) in exhaust gas from different fueled Vehicles with variable speeds.

The correlation between UPOPs generated from the automobile experiment is investigated by the statistical analysis system and the findings show that as a whole,

PAHs mostly have counter-correlations with PCDDs/DFs, DLPCBs and PAHs. As a consequence, it is explained that PAHs is affected by several factors such as combustion temperature, combustion state of fuel, excess air, etc. The basic structure of PAHs, the polycycle is separated in the middle process. This function contributes partly to the generation of PCDD/DFs and partly to the additional reaction of cyclic expansion (Gullet et al., 2000).

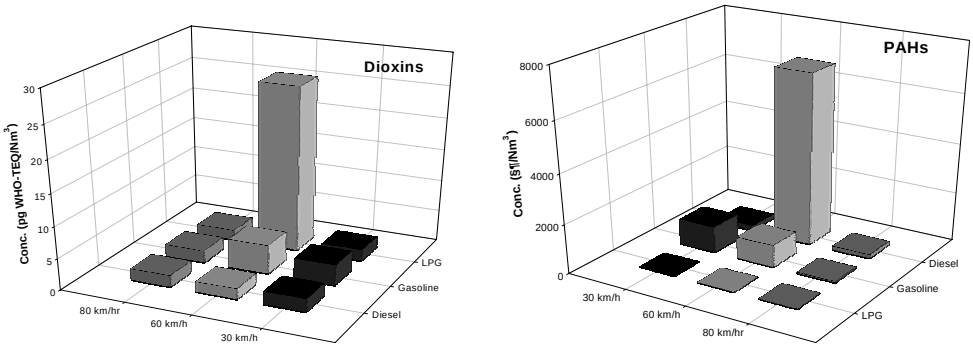

Fig. 5. Distribution of UPOPs (PCDDs/DF and DLPCBs, PAHs, PAHcarc and CBs) concentration in different fueled Vehicles with variable speeds.

CONCLUSION

The results of this study present the following points;
1. For the sampling in this study, coupling stack is air-tightly fixed to the muffler in order to maintain isokinetic sampling and then used for the measures. The ratio of isokinetic factor in the automobile driving experiment shows a range of 95.7–104.7%.
2. Automobile speeds and age of vehicles are proved to be important variables in the generation of PCDDs/DFs, DLPCBs and PAHs.
3. PCDD/DFs, DLPCB and PAHs among the exhaust gas emitted from automobiles are examined by the cluster analysis and the result confirms that gasoline and LPG fueled vehicles of spark ignition engine and diesel fueled vehicle of compression ignition engine form a separate cluster respectively.
4. It is also confirmed that PAHs have counter-correlations with PCDDs/DFs, DLPCBs and PAHs in their generation.
Therefore, in order to illuminate the mechanism of POPs generation in automobiles, experiments should be carried out in a variety of conditions like temperature distribution from the engine to the muffler as well as repeated studies in the same conditions.

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