EMISSION AND FORMATION OF PCDD/DFs AND dlPCBs FROM A DIESEL ENGINE

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Introduction

In the study of dioxins, a lot of research has been performed on the sources, environmental levels, toxicity and formation mechanisms of dioxins (polychlorinated dibenzo-p-dioxins; PCDDs, polychlorinated dibenzofurans; PCDFs, dioxin-like Polychlorinated biphenyls; DLPCBs).

Recently, the motor vehicle has attracted attention as an emission source of PCDDs/DFs and a number of studies have been carried out on the relationship between the engine type and the exhaust gas pollution [1-7]. However, research on the formation mechanism of PCDD/Fs from the vehicles is limited. In addition, an international standard method of sampling vehicle exhaust gas for dioxins does not exist.

In this study, the dioxins emissions of a diesel engine were investigated with the injection of Cl_2 and a fuel additive, and the dioxins levels of the exhaust gas (the outlet gas) were compared with the dioxins levels of the engine room air (the inlet gas).

Materials and Methods

The test methodology of this study is a relatively new approach using a stack sampler, which makes isokinetic sampling possible in engine experiments in accordance with US EPA method 5. Fig. 1 presents the schematic diagram of sampling for the engine experiment.

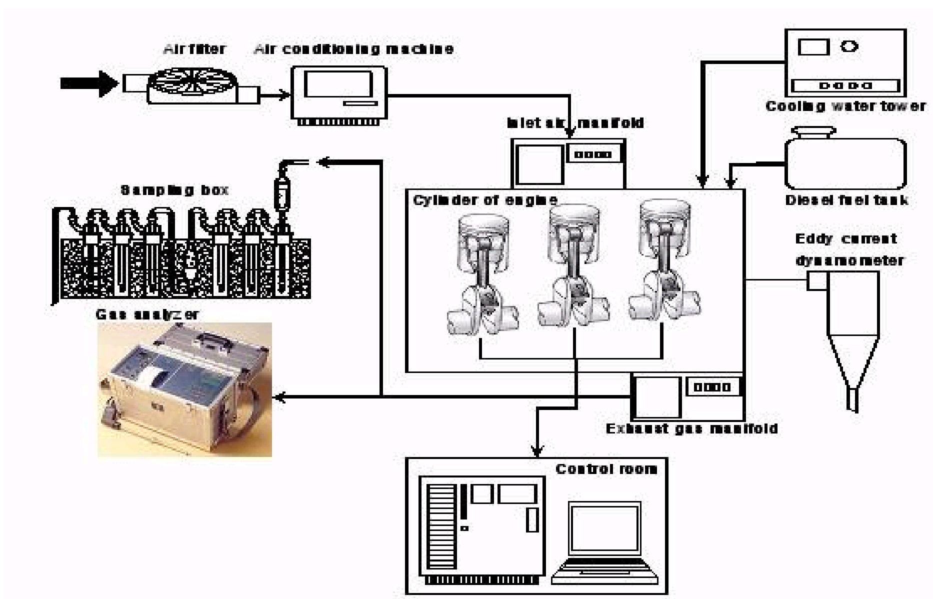

Figure 1. Schematic diagram of sampling for the engine experiment

The sampling of dioxins is carried out with successive test methodology through a probe under constant driving conditions. As the current speed of exhausts varies delicately even during constant driving, a tight combination of a temporary coupling stack with the muffler is conducted in the measurement to maximally prevent the turbulent current of exhausts and to maintain isokinetic sampling.

In this study, the engine used was a direct injection three cylinder F455DN-K engine. Dioxins emissions of this diesel engine were investigated with the emission constant cycles,as the load rate was 2.5 kgf·m (40% road rate) at a constant speed of 1600 rpm. Thus, the isokinetic sampling of the exhaust gas was conducted in the test. Extracted dioxin samples were analyzed according to the Korean Standard Method[8] and dioxins were determined by HRGC/HRMS[9-11].

Results and Discussion

Exhaust gas : In engine exhaust gas experiments, the concentration levels of dioxins (PCDD/DFs, DLPCBs) are 3.345 pg WHO-TEQ/Nm^3 for the fuel without Cl_2 (0 ppb), 10.656 pg WHO-TEQ/Nm^3 for the fuel with Cl_2 of 1ppb (v/v) (1 ppb) and 1.629 pg WHO-TEQ/Nm^3 for the fuel with fuel additive. The total concentrations of PCDD/DFs are 746.156 pg/Nm^3 (0 ppb), 1,128.529 pg/Nm^3 (1 ppb) and 377.288 pg /Nm^3 (fuel additive). PCDD/DF and DLPCB concentration of exhaust gas are shown in Figure 2.

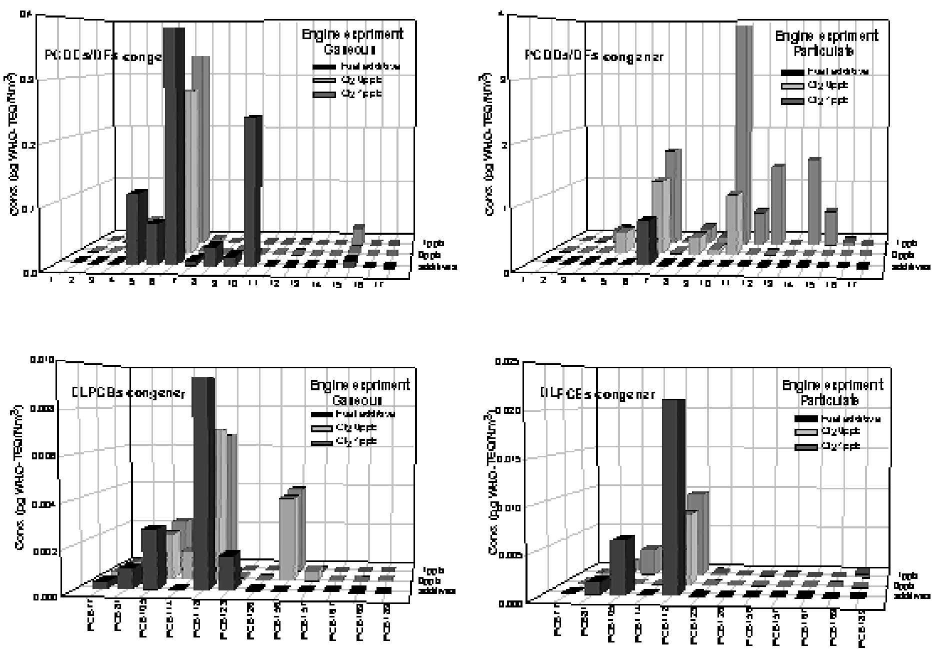

Figure 2. Distribution of gaseous (left) and particulate phase (right) PCDD/DFs (top) and DLPCBs (bottom) concentration in each engine experiment. 1: 2,3,7,8-TCDD, 2: 1,2,3,7,8-PeCDD, 3: 1,2,3,4,7,8-HxCDD, 4: 1,2,3,6,7,8-HxCDD, 5: 1,2,3,7,8,9-HxCDD, 6: 1,2,3,4,6,7,8-HpCDD, 7: OCDD, 8: 2,3,7,8-TCDF, 9: 1,2,3,7,8-PeCDF, 10: 2,3,4,7,8-PeCDF, 11: 1,2,3,4,7,8-HxCDF, 12: 1,2,3,6,7,8-HxCDF, 13: 1,2,3,7,8,9-HxCDF, 14: 2,3,4,6,7,8-HxCDF, 15: 1,2,3,4,6,7,8-HpCDF, 16: 1,2,3,4,7,8,9-HpCDF, 17: OCDF.

In the emission amount of dioxins in accordance with chlorine spiking, Cl_2 1 ppb is higher in concentration level than Cl_2 0 ppb.

And, in case of the fuel additive, the emission concentration of PCDDs/DFs tends to decline abruptly compared to that before the additive is infused. But, the amount of DLPCBs generation tends to increase conspicuously. It is estimated that this is because elements, including carbon deposited in the engine, are forced to be emitted under the influence of the fuel additive. Therefore, the improvement of combustion efficiency due to the removal of carbon elements in the engine causes the concentration of PCDDs/DFs generation to decline.

Engine room air: Sampling of engine room air was carried out by a high volume air sampler, and measured at the same time as the exhaust gas experiments. Ambient air samples of the engine laboratory are collected at the time conditions of fuel combustion without Cl_2 (0 ppb) and injection Cl_2 (1ppb) that is 1st engine room air and 2nd engine room air, respectively.

For the experiments involving the ambient air in the engine room, the concentration level of dioxins was 43.316 fg WHO-TEQ/Nm^3 for the 1st engine room air, while the concentration level for the 2nd engine room air was 41.533 fg WHO-TEQ/Nm^3. Total concentrations of PCDD/DFs were 3,377.644 fg/Nm^3 and 3,394.944 fg/Nm^3 for 1st and 2nd engine room air, respectively.

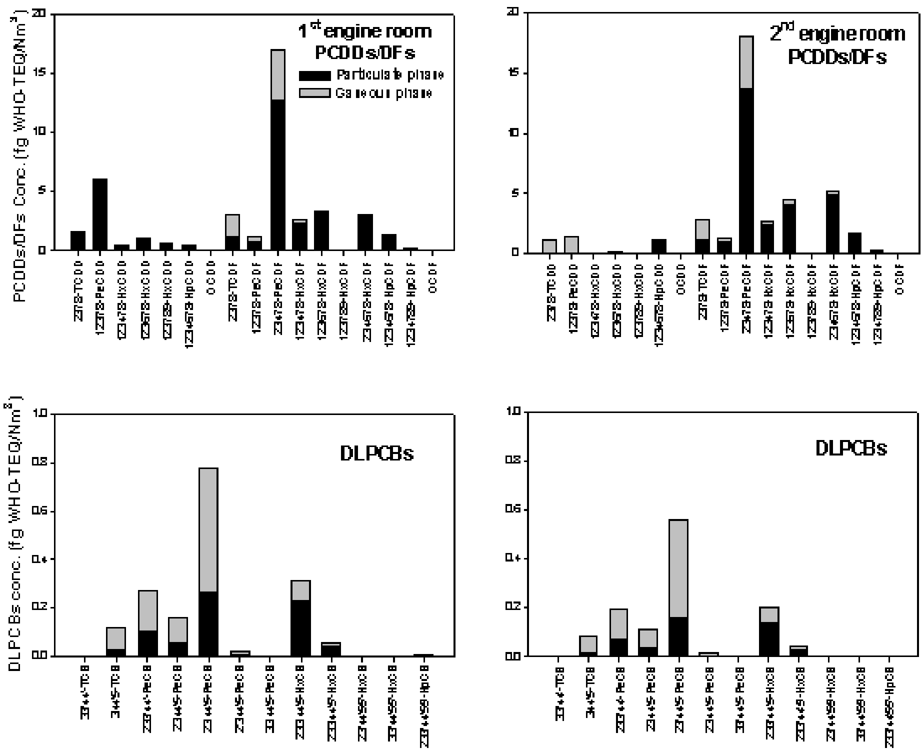

Figure 3. Concentration of toxic 2,3,7,8 substituted PCDDs/DFs (top) and DLPCBs (bottom) in 1st (left) and 2nd (right) engine room air.

The concentration ratio for the particulate phase (77.8%) is higher than that of the gaseous phase (22.2%) in the engine room air. And, dioxins concentration of particulate phase in exhaust gas is about 8.6 times than gaseous phase. As a result, the concentration of the particulate phase is predominated by dioxins concentrations of the engine room air and exhaust gas.

The average dioxins concentration for the outlet air (exhaust gas) from the engine is 165 times higher than that of the inlet air (engine room ambient air) for the same period.

The results of this research present the following points; (1) the motor vehicle engine is one of the emission sources of dioxins; (2) the chlorine amount in fuel is one of main causes of the dioxin generation in the engine.

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