Characterization of Polycyclic Aromatic Hydrocarbons (PAH) and Nitro-PAH Emissions from HDDV with PM and NOx Controls

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) and nitro-PAHs consist of many toxic compounds which could be carcinogenic or mutagenic such as benzo(a)pyrene or 1-nitro-pyrene. The lighter PAHs (predominantly in vapor phase) are the most toxic derivatives. Motor vehicles are a significant contributor to ambient PAH emissions. The stringent PM and NOx diesel emission standards force manufacturers to modify diesel engines and/or retrofit them with advanced emission control devices such as particle traps and selective catalytic reduction (SCR) technology. These aftertreatment devices have proven effective in reducing PM and NOx, and also changes the physicochemical properties of diesel exhaust. It is expected that PAH and nitro-PAH profiles of diesel exhaust could be altered by the aftertreatment devices as well. However, this effect has not yet been fully investigated.

This project is a 4-year collaborative research effort focused on emerging issues relevant to air quality and the protection of health[1]. These issues include: 1) ultrafine emissions from advanced aftertreatment technology, 2) effects on emissions of ultralow and nucleation mode particles by various aftertreatment devices, 3) measurement instrumentation and protocols, and 4) the relative toxicity of PM components as a function of volatility.

In this study, four heavy-duty diesel vehicles (HDDV) of 1998 to 2007 vintage, operating with advanced PM and NOx emissions control retrofits were tested on a heavy-duty chassis dynamometer located at ARB’s Heavy-duty Diesel Emissions Test Laboratory (HDETL) in Los Angeles. The emissions control retrofits included four diesel particulate filters (DPF), catalyzed and un-catalyzed, and two prototype SCR systems. The combination of DPF and SCR technologies are of particular interest because they may represent the future approach for simultaneous control of PM and NOx.

METHOD

Tallied coated glass fiber filter in a marin with XAD adsorbent was used to collect PM and vapor phase pollutants respectively for the analysis of semi-volatile PAHs, volatile PAHs, and nitro-PAHs. One challenge in analyzing PAHs and especially nitro-PAHs is the low mass emissions of these species and the laboratory analytical detection limits. Vapor phase PAHs were analyzed using 5-point calibration curves with the isotope dilution standard method [2]. For nitro- and nitro-PAH analyses, deuterated internal standards 2-nitrophenol and 1-nitrophenol were added to the filters, and the extracts were then extracted with dichloromethane using the 95:5:5 soxhlet acetone extraction. The extracts were then further purified by the solid-phase extraction technique and semi-preparative normal-phase high performance liquid chromatography (HPLC) technique (Waters). The fraction corresponding to nitro- and dinitro-PAH was collected and analyzed by negative ion chemical ionization (NICI) gas chromatography - mass spectrometry - mass spectrometry (GC/MS/MS) (3).

RESULTS

Figure 1 shows the TEM image of diesel particles from baseline and DPF1+SCR1 vehicles collected on fibrous filters. Particles from the baseline are agglomerates. These agglomerates are barely seen in the sample from DPF+SCR1.

Figure 4 shows the volatile and particle phase PAH emissions from the baseline diesel truck without emission controls. The volatile PAHs account for 95% of the total PAHs (volatile + particle phase), and the light molecular weight (MW) PAHs, 2- and 3-ring, dominates the volatile PAHs. Naphthalene accounts for 80% of the volatile PAHs.

Figure 8 shows the sum of the volatile and particulate PAHs from the retrofit during cruise cycle. The retrofit reduces both particulate and vapor phase PAHs by more than 90%. The retrofit reduces particle phase PAHs by more than 95%, independent of the driving cycle and catalytic loadings, which implies that reduction of particle PAHs is due to direct removal in the trap. The un-catalyzed DPF was less efficient in reducing the volatile PAHs compared to the catalyzed DPFs (Figure 6).

Figure 7 shows selected nitro-PAHs from the test vehicles. Results demonstrate that SCR does not promote formation of nitro-PAHs. DPF2 and DPF3 show significant reduction of 1-nitrophenate but slightly increase of 5-nitrophenolate.

SUMMARY

Retrofits reduce total PAHs (particle and vapor phase) by more than 95%. The particle phase PAH reduction are independent of the catalytic surface and driving conditions. However, vapor phase PAHs are highly affected by catalytic loadings and exhaust temperature [1]. With a few exceptions, most of the samples from retrofitted engines do not contain nitro-PAHs. The 1-nitro-phenare the most dominant nitro-PAH. The engine without retrofit show one order of magnitude higher emissions of 1-nitrophenate than the engine with catalyzed DPF and catalyzed DPF. The un-catalyzed DPF shows higher emission of 5-nitrophenolate than the baseline. The two prototypes SCRs do not promote the formation of nitro-PAH, and reduction of 1-nitrophenate, a recognized carcinogen, suggests direct benefit of DPF for cancer risk reduction.

Acknowledgements

The authors are thankful to Dr. Harish Phuleria, Dr. Michael Geller, Dr. Constantinou, Dr. Ning Zhi, Vishal Verma, Dr. Subhasis Bose, Ralph Bodas, George Gatt, and Kechen Sun. We are grateful to the retrofit device makers, JMI, Claire and Engelhard, whose technologies made this investigation possible.

Reference


See also at AAAR

10F.4 Friday 12:00 am The effect of diesel particulate filters and selective catalytic reduction-A predictive framework for ultralow particle formation, toxicity and chemical composition.

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