Urea-based Selective Catalytic Reduction (SCR) For HDDVs: Chemistry, Physics, And Toxicology of Emissions

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INTRODUCTION
Polycyclic aromatic hydrocarbons (PAHs) and nitro-PAHs include many toxic compounds which may be carcinogenic or mutagenic such as benzo(a)pyrene or 1-nitropyrene. The lighter PAHs (predominantly in vapor phase) are the most abundant in the urban atmosphere and may react with other pollutants to form more toxic derivatives. Motor vehicles are a significant contributor to ambient PAH emissions. The nitrogen PM and NOX diesel emission standards force manufacturers to modify diesel engines and/or retrofit them with advanced emission control devices such as particulate traps and selective catalytic reduction (SCR) technology. These aftertreatment devices have proven effective in reducing PM and NOX but also change the physicochemical properties of diesel exhaust. It is expected that PM 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 ultrafine 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, 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 uncatalyzed, 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 emissions.

METHOD
Teflon coated glass fiber filter in series 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-aromatic analysis, deuterated internal standards 2-nitrophenol-d4 and 1-nitropyrene-d8 were added to the filters, and the filters were then extracted with dichloromethane using the Denog ASPEQ followed by acetonitrile extraction. The extracts were further purified by the solid phase extraction technique and some preparation normal-phase high performance liquid chromatography (HPLC) technique (Waters). The fraction corresponding to nitro- and nitro-PAH was collected and analyzed by negative-ion chemical ionization (NICI) gas chromatography/mass spectrometry (GC/MS) [1].

RESULTS

Figure 1 – Tested Vehicles and Naming Convention

Figure 2 – Test Emissions

Figure 3 – TEM Image of diesel particles from baseline and retrofit collected on fibrous filters

Figure 4 – Individual volatile and particle phase PAHs emissions from Baseline

Figure 5 – Total (volatile + particle phase) PAHs emissions from Baseline and retrofits.

Figure 6 – Selected volatile PAHs emissions.

Figure 7 – Selected nitro-PAHs emissions.

SUMMARY

Retrofit reduce total PAHs (particle and vapor phase) by more than 95%. The particle phase PAH reduction is 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 exhibited lower total PAHs and nitro-PAHs. The engine without retrofits showed the highest total PAHs. The engine with retrofits showed only nitro-PAH. The engine without retrofit in the condition of 1-nitropyrene showed the lower nitro-PAH and catalyzed DPF and catalyzed DPF. The uncatalyzed DPF showed higher emission of 1-nitropyrene than the baseline. The two prototype SCRs did not promote the formation of PAHs. Significant reduction of 1-nitropyrene, a recognized carcinogen, suggests direct benefit of DPF for cancer risk reduction.

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Reference

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