Environmental Science & Technology

ARTICLE

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Emissions of PCDD/Fs, PCBs, and PAHs from a Modern Diesel Engine Equipped with Catalyzed Emission Control Systems

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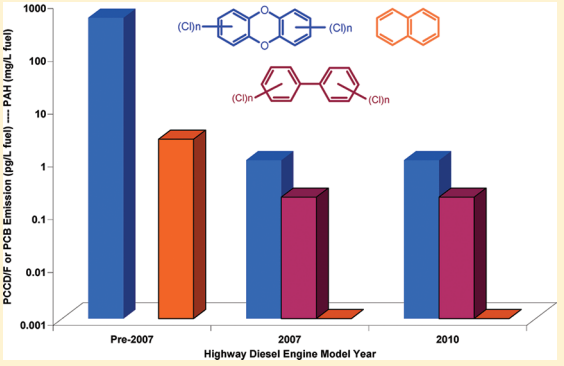
Supporting Information

ABSTRACT: Exhaust emissions of 17 2,3,7,8-substituted chlorinated dibenzo-*p*-dioxin/furan (CDD/F) congeners, tetra−octa CDD/F homologues, 12 2005 WHO chlorinated biphenyls (CB) congeners, mono−nona CB homologues, and 19 polycyclic aromatic hydrocarbons (PAHs) from a model year 2008 Cummins ISB engine were investigated. Testing included configurations composed of different combinations of aftertreatment including a diesel oxidation catalyst (DOC), catalyzed diesel particulate filter (CDPF), copper zeolite urea selective catalytic reduction (SCR), iron zeolite SCR, and ammonia slip catalyst. Results were compared to a baseline engine out configuration. Testing included the use of fuel that contained the maximum expected chlorine (Cl) concentration of U.S. highway diesel fuel and a Cl level 1.5 orders of magnitude above. Results indicate there is no risk for an increase in polychlorinated dibenzo-*p*-dioxin/furan and polychlorinated biphenyl emissions from modern diesel engines with catalyzed aftertreatment when compared to engine out emissions for configurations tested in this program. These results, along with PAH results, compare well with similar results from modern diesel engines in the literature. The results further indicate that polychlorinated dibenzo-*p*-dioxin/furan emissions from modern diesel engines both with and without aftertreatment are below historical values reported in the literature as well as the current inventory value.



INTRODUCTION

Recent changes in the emission standards for oxides of nitrogen (NO_x) and particulate matter (PM) from both highway and nonroad diesel engines have for the first time lead to the widespread use of aftertreatment systems to control the emissions from these engines. Engine manufacturers have employed the use of diesel oxidation catalysts (DOC), catalyzed diesel particulate filters (CDPF), and urea selective catalytic reduction (SCR) to meet these new emission standards.[1−3]

A limited number of dynamometer and tunnel studies have been performed on polychlorinated dibenzo-*p*-dioxin/furan (PCDD/F) emissions from diesel engines generating a wide range of emission results.[4−11] Diesel engines have been generally known to be emitters of hydrocarbons, which include polycyclic aromatic hydrocarbons (PAHs), nitro-polycyclic aromatic hydrocarbons, and PM with a significant fraction of elemental carbon.[12,13] The presence of these pollutants in combination with the availability of chlorine (Cl) primarily from the fuel may drive the formation of PCDD/Fs via either the precursor or de novo synthesis routes.[14] The current inventory value used by the United States Environmental Protection Agency (U.S. EPA) to approximate the PCDD/F emissions from diesel engines is 172 pg international toxic equivalency (I-TEQ)/km or approximately 946 pg I-TEQ/L fuel consumed when using a fuel economy factor of 5.5 km/L.[15,16]

Studies have shown that the use of DOCs and CDPFs for PM control have led to a greater than 90% decrease in hydrocarbons, specifically PAHs.[17] Recently, concern over the potential for increased PCDD/F formation in the catalyst systems of diesel engines was raised due to the introduction of copper zeolite (CuZ) urea SCR for NO_x control. At the time this study commenced, a comprehensive study of the emissions of PCDD/Fs and PCBs from these systems had not been performed. Recently, the results of two test programs similar in nature to the one described here for PCDD/F emissions have been published.[18,19]

Both reactor bench studies and studies involving municipal waste incinerators (MWIs) have shown that dioxin formation increases in the presence of copper (Cu).[20,21] Studies by Mayer and Heeb, et al. showed that the use of Cu fuel additives in the presence of high fuel Cl levels (up to 110 ppm) with an uncatalyzed diesel particulate filter (DPF) increased PCDD/F emission rates by up to 4 orders of magnitude.[22,23] Additional studies on MWIs, equipped with urea SCR utilizing V_2O_5 catalysts to reduce NO_x emissions, have shown that the presence of urea can reduce dioxin emission rates by up to 99.5%.[24,25]

Received: December 22, 2010
Accepted: June 21, 2011
Revised: April 20, 2011
Published: June 30, 2011