

Measurement of Dioxin and Furan Emissions during Transient and Multi-Mode Engine Operation

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ABSTRACT

This study analyzed the impact of transient and multi-mode engine conditions on emissions of dioxins and furans from a variety of diesel aftertreatment configurations. Exhaust aftertreatment systems included combinations of diesel oxidation catalyst, diesel particulate filter, and either Cu/zeolite or Fe/zeolite selective catalytic reduction catalyst. EPA method TO-9A was modified for proportional exhaust gas sampling, whereas EPA method 0023A was modified for raw exhaust gas sampling. Dioxin and furan emissions were first measured with modified method TO-9A during Federal Test Procedure transient cycles, but no toxic dioxins or furans were detected. Measurements were then taken with modified method 0023A during Ramped Mode Cycles-Supplemental Emissions Test experiments. Because more rigorous pre-cleaning and sample extraction procedures were used with this method and lower detection limits were achieved by the analytical laboratory, some dioxin and furan congeners were detected. Results from modified method 0023A showed that there was no statistical difference in dioxin and furan emissions from the same aftertreatment system containing either a Cu/zeolite or Fe/zeolite SCR system. Overall, this study showed that toxic equivalency quotient emissions of dioxins and furans from both aftertreatment configurations under transient and multi-mode cycles were negligible in comparison to EPA mandated emission levels from other sources such as waste incinerators.

INTRODUCTION

Recent advances in diesel aftertreatment technology have enabled engine manufacturers and aftertreatment integrators to meet US 2010 regulations for nitrogen oxides (NO_x) and particulate matter (PM) emissions. These regulations dramatically reduced the permissible levels of pollutants for

heavy-duty diesel engines to 0.013 g/kW*hr (0.01 g/bhp*hr) PM and 0.27 g/kW*hr (0.2 g/bhp*hr) NO_x. However, there are concerns about the formation of toxic contaminants such as polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) from engine exhaust aftertreatment systems. PCDDs and PCDFs, collectively referred to as dioxins in this article, are known carcinogens and mutagens which are included in the Environmental Protection Agency's (EPA) Mobile Source Air Toxics (MSAT) list [1]. Dioxins are emitted by a variety of industrial sources, many of which have been previously regulated due to their historically high levels of dioxin emissions. According to a 2006 EPA study, these regulations have helped reduce annual dioxin emissions from 13,965 grams in 1987 to an estimated 1,400 grams in 2000 [2]. Figure 1 shows estimated annual dioxin emissions from the highest contributors for the years 1987, 1995, and 2000. While municipal waste combustors were the largest contributor to emissions in 1987, regulation has effectively reduced their emissions from 8,905.1 grams dioxin per year in 1987 to 83.8 grams dioxin per year in 2000. However, emissions from on-road diesel fuel combustion have slightly increased over this same period. In fact, the percentage of total dioxin emissions from heavy-duty diesel trucks has increased from 0.2% in 1987 to 4.6% in 2000. Although emissions from heavy-duty diesel trucks account for only a small fraction of total dioxin emissions, it is important to ensure that new aftertreatment technologies-intended to reduce pollution-do not inadvertently catalyze the synthesis of any toxic dioxin congeners.

Diesel aftertreatment systems capable of achieving 2010 compliant emissions levels typically consist of a diesel oxidation catalyst (DOC), a diesel particulate filter (DPF), and a selective catalytic reduction (SCR) catalyst. Recently, a significant amount of research has been conducted to

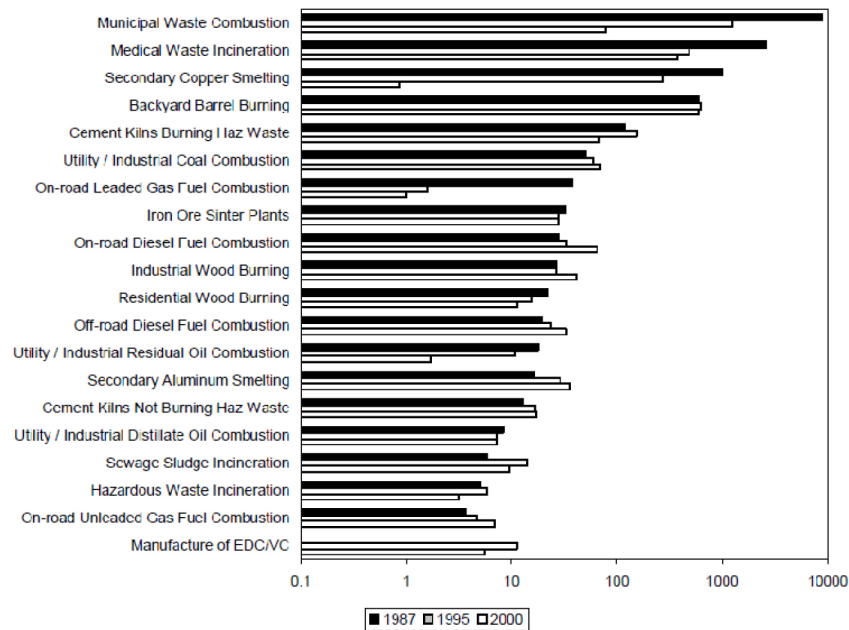


Figure 1. Primary dioxin sources for years 1987, 1995, 2000 (g TEQ-WHO1998/year) [1]

optimize SCR catalyst formulations to meet 2010 emissions standards. As a result, new Cu/zeolite formulations have been developed that have improved low temperature performance, are thermally stable at temperatures above those required for active DPF regeneration, and are less sensitive to NO:NO₂ ratio than Fe/zeolite catalysts [3,4]. However, it is well reported in the literature that copper is an active catalyst for the synthesis of dioxins when in the presence of chlorine and precursor molecules such as chlorophenols [5, 6, 7]. Moreover, Heeb et al. and Mayer et al. have shown that fuel borne copper catalysts in the presence of a high concentration of chlorine can lead to the synthesis of dioxins in diesel exhaust systems [8,9]. To analyze the real-world implications of these results, a number of steady-state studies have recently analyzed the impact of a Cu/zeolite SCR system on dioxin emissions. These steady-state studies found no evidence of dioxin formation in a 2010 aftertreatment system with a Cu/zeolite SCR [10,11]. Still, more data is necessary to determine the impact of transient and multi-mode engine conditions on emissions of dioxins from a Cu/zeolite containing diesel aftertreatment system.

This study will analyze dioxin emissions from a diesel aftertreatment system during transient and multi-mode engine operation. EPA methods TO-9A and 0023A were modified to measure dioxin emissions during Federal Test Procedure (FTP) heavy-duty transient cycles and Ramped Mode Cycles-Supplemental Emissions Test (RMC-SET) experiments, respectively. Exhaust aftertreatment configurations included combinations of DOC, DPF, and either Cu/zeolite or Fe/zeolite SCR. Dioxin emissions were first measured during FTP cycles with modified method TO-9A. Because no toxic congeners were detected in any of the experiments, emissions

from the same aftertreatment configurations were measured during RMC-SET experiments with modified method 0023A. Total equivalency quotient (TEQ) concentrations of dioxin emissions measured with modified method 0023A were used to compare the effect of the aftertreatment configurations on dioxin emissions. The measured TEQ concentrations of dioxins were then compared to emissions from an industrial source to understand their environmental implications.

EXPERIMENTAL

MODIFIED EPA METHODS TO-9A AND 0023A

Modified versions of EPA methods TO-9A and 0023A were used to measure dioxins in this study [12,13]. The modifications made to these EPA methods have been previously described [14], but they are briefly detailed below. Method TO-9A, originally intended for ambient air sampling, was modified by the addition of a full-partial-full source dilution sampling (SDS) system. The SDS system consists of a critical flow venturi-constant volume system (CFV-CVS) for primary dilution, a secondary micro-diluter, and a residence time chamber (RTC) for aging and atmospheric conditioning [15]. Figure 2 shows the modified TO-9A sampling system. The sampling train consists of a high volume sampler that draws diluted exhaust from the RTC and through a dioxin-retaining quartz particulate filter and a polyurethane foam (PUF) cartridge. The sample is then pulled through a rotometer and flow venturi for flow-rate control. Method TO-9A was selected for this testing and modified with the addition of a SDS system in order to simulate atmospheric conditions and to perform proportional

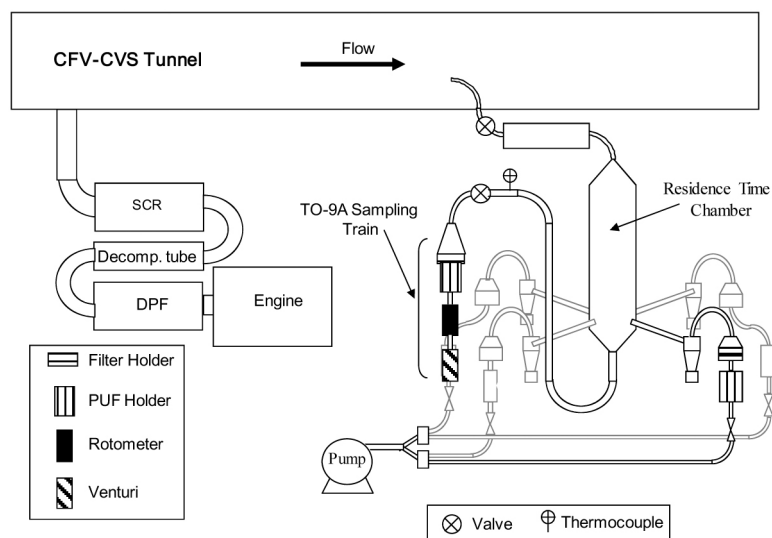


Figure 2. Apparatus for modified method TO-9A.

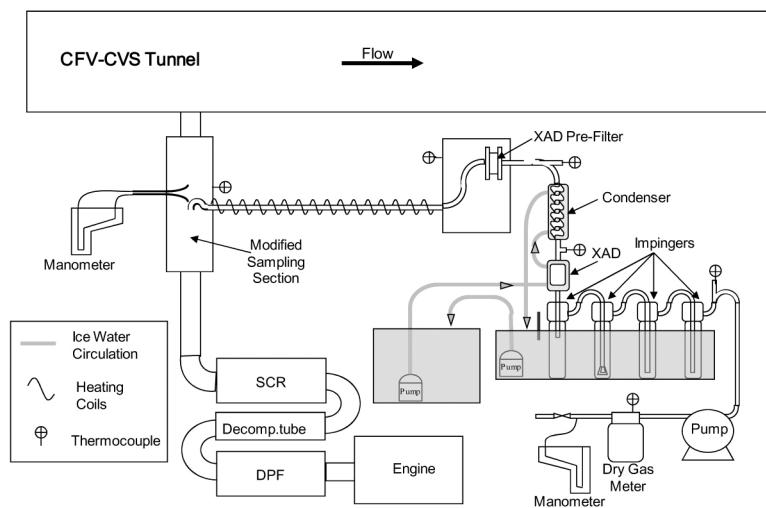


Figure 3. Apparatus for modified method 0023A.

sampling, which enables the calculation of exact exhaust emission levels during transient testing.

Figure 3 shows the modified method 0023A sampling system. Although a borosilicate glass probe is specified for this method, a titanium sampling probe was used due to engine vibrations. Other modifications to this method included remote camera monitoring of critical system components including the cooling system for the XAD resin, as well as external controls on the cooling system. As seen in Figure 3, raw exhaust is isokinetically sampled with a heated probe. The sample then proceeds through a filter heated to $120 \pm 14^\circ\text{C}$ and a condenser before entering the dioxin-retaining XAD trap which is cooled to below 20°C , as specified by EPA method 0023A. The exhaust then flows through a series of impingers which dry the sample and are

used to measure the water vapor concentration. Finally, the exhaust proceeds through a dry gas meter before venting to the atmosphere through a flow orifice. Method 0023A was selected for this testing because of its rigorous sampling procedures which include mandatory temperature limits and a detailed pre-cleaning and extraction procedure for the complete sampling train. However, it is difficult to calculate total dioxin values using modified method 0023A for transient or multi-mode engine raw gas sampling because the instantaneous exhaust flow rate is unknown. Rather, emissions measured with modified method 0023A will only be used to compare the effect of different aftertreatment configurations on dioxin emissions under identical engine operating and sampling conditions.