

Emissions of PCDD/Fs, PCBs, and PAHs from a Modern Diesel Engine Equipped with Selective Catalytic Reduction Filters

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ABSTRACT

Exhaust emissions of seventeen 2,3,7,8-substituted chlorinated dibenzo-*p*-dioxin/furan (CDD/F) congeners, tetra-octa CDD/F homologues, twelve WHO 2005 chlorinated biphenyls (CB) congeners, mono-nona CB homologues, and nineteen polycyclic aromatic hydrocarbons (PAHs) from a model year 2008 Cummins ISB engine equipped with aftertreatment including a diesel oxidation catalyst (DOC) and wall flow copper or iron urea selective catalytic reduction filter (SCRF) were investigated. These systems differ from a traditional flow through urea selective catalytic reduction (SCR) catalyst because they place copper or iron catalyst sites in close proximity to filter-trapped particulate matter. These conditions could favor de novo synthesis of dioxins and furans. The results were compared to previously published results of modern diesel engines equipped with a DOC, catalyzed diesel particulate filter (CDPF) and flow through urea SCR catalyst. Testing included the use of fuel that contained the maximum expected chlorine concentration of United States' (U.S.) highway diesel fuel. Results indicate there is no risk for an increase in polychlorinated dibenzo-*p*-dioxin/furan and polychlorinated biphenyl emissions from modern diesel engines with wall flow urea SCRF catalysts when compared to flow through urea SCR catalysts for the configurations tested in this program. These results, along with PAH results, compare well with results from other modern diesel engines in the literature.

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INTRODUCTION

Recent changes in the emission standards for oxides of nitrogen (NO_x) and particulate matter (PM) from both highway and non-road diesel engines have for the first time lead to the widespread use of catalyzed exhaust aftertreatment systems to control the emissions from these engines [1, 2, 3]. In addition to the use of diesel oxidation catalysts (DOC), catalyzed diesel particulate filters (CDPF), and urea selective catalytic reduction (SCR) to meet these new emission standards, it is envisioned that a DOC combined with a urea selective catalytic reduction filter (SCRF) will also be used.

Polychlorinated dibenzo-*p*-dioxin/furans (PCDD/Fs) and polychlorinated biphenyls (PCBs) are two of the twelve priority persistent bioaccumulative and toxic compounds for which the U.S. EPA has developed strategies for emission reductions. Air emissions are a significant source of PCDD/Fs to food and the environment. The main source of exposure to humans is through food such as meat and dairy products. PCDD/Fs and PCBs bioaccumulate in fat tissue and remain in the body for years. Thus, any increase in PCDD/F

and PCB emissions is viewed as a serious health risk by the U.S. EPA [4].

Recent studies have shown that emissions of PCDD/Fs, PCBs, and polycyclic aromatic hydrocarbons (PAHs) from modern diesel engines equipped with catalyzed aftertreatment are extremely low with PCDD/F emissions orders of magnitude below that of the U.S. mobile source on-road diesel engine inventory value [5, 6, 7]. These studies have also shown that the introduction of copper zeolite (CuZ) and iron zeolite (FeZ) urea SCR for NO_x control have had no effect on the emissions of PCDD/Fs and PCBs from these engines when compared to engine out levels.

While it is well documented that the presence of organic precursors, carbon, oxygen, and chlorine (Cl) drive the formation of PCDD/Fs via precursor or de novo synthesis routes [8, 9, 10], the exact mechanism of formation in diesel engine exhaust has not been confirmed.

Testing to date on PCDD/F and PCB emissions from modern diesel engines utilizing urea SCR aftertreatment has consisted of urea SCR catalysts of flow through, monolithic design. In this configuration, the exhaust gas enters the inlet channel of the urea SCR catalyst, diffuses to and interacts



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with the catalyst walls, and exits the catalyst by flowing out of the same channel on the outlet side. Use of this catalyst typically incorporates the use of a DOC and CDPF upstream of the urea SCR catalyst, thus PM is filtered and oxidized to CO₂ in the CDPF before having an opportunity to interact with the urea SCR catalyst. Urea SCRF catalysts utilize wall flow substrates similar to CDPFs, however they have the CuZ or FeZ function washcoated onto the surface of the substrate and essentially combine diesel particulate filter and SCR functionality onto a common substrate. A DOC is typically located upstream of the urea SCRF catalyst to facilitate partial oxidation of NO to NO₂, optimizing the NO_x reduction over the SCRF catalyst, and provide NO₂ to promote oxidation of trapped soot. In this application, PM and exhaust gas enter a channel on the inlet side of the catalyst. The outlet side of the channel is plugged. The PM is trapped on and within the channel wall surfaces while the exhaust gas can escape the channel by flowing through the porous wall and exiting via the unplugged outlet of an adjacent channel. Since the PM is trapped in the plugged channel, it is afforded an opportunity to reside in close proximity to the CuZ or FeZ catalysts within the washcoat. This creates conditions which may allow de novo synthesis to occur in the SCRF catalyst.

Laroo et al. reported no increase in baseline emissions of PCDD/Fs, PCBs, and PAH from modern diesel engines utilizing just CuZ or FeZ flow through urea SCR catalysts when compared to systems including a DOC, CDPF, and ammonia slip catalyst (ASC), however their testing did not include a condition where soot was trapped in close proximity to the CuZ or FeZ in a wall flow type catalyst substrate [5].

Based on the uncertainty surrounding PCDD/F formation mechanisms in diesel combustion and aftertreatment, the U.S. EPA initiated a test program to determine the emissions of PCDD/F, PCB, and PAH emissions from modern aftertreatment systems incorporating a DOC and either a CuZ or FeZ urea SCRF, given the possibility that this may be an advantageous catalyst configuration for PM and NO_x control in future applications for diesel engine emission control.

The objectives of this program were to (i) determine the seventeen 2,3,7,8-substituted congener and tetra-octa homologue chlorinated dibenzo-*p*-dioxin (CDD/F) profiles including International Toxic Equivalency (I-TEQ), the twelve World Health Organization (WHO) 2005 congener and mono-nona homologue chlorinated biphenyl (CB) profiles including Toxic Equivalency (TEQ), and nineteen PAH emissions from a modern diesel engine utilizing a DOC and either a CuZ or FeZ urea SCRF, (ii) determine how these catalysts' emissions compare to previous reported values for modern diesel engines with and without catalyzed aftertreatment, and (iii) determine whether the use of CuZ or FeZ urea SCRF poses a risk for increased PCDD/F formation when compared to traditional flow through urea SCR catalyst applications.

MATERIALS AND METHODS

Test Configuration

Testing was performed at the U.S. EPA National Vehicle and Fuel Emissions Laboratory (NVFEL) in Ann Arbor, MI using a Schenck AC dynamometer and STARS control system. The engine used to generate exhaust gas was a 280 Hp, turbocharged, 2008 MY 6.7 L Cummins ISB equipped with electronically controlled high pressure common rail fuel injection, high pressure loop EGR, and a DOC/CDPF for PM control. The DOC was well aged and had approximately 1,000 hours operation at the start of testing. The factory CDPF was removed and replaced with one of two SCRF configurations for this testing. The SCRF catalysts were pre-conditioned by operating the engine at high speed, 25% load for 4 hours, followed by peak torque for 4 hours. The SCR urea dosing control system was designed by our lab to represent a production type urea dosing system, targeting an NO:NO₂ ratio of 1:1 at the outlet of the DOC, keeping instantaneous peak ammonia (NH₃) slip below 10 ppm and average NH₃ slip below 4 ppm. The urea dosing system and SCRF was active at all times during testing. The SCRF was regenerated (to remove assumed soot build-up) in a tube furnace, that was open to atmosphere, at 600 °C for 5 hours before each 16 hour test; as the soot trapped in the filter cannot be passively regenerated adequately during testing due to lack of platinum group metals in the SCRF catalyst washcoat.

A fuel survey of pump diesel fuel chlorine content was performed with the fuel analyzed for Cl content using Neutron Activation Analysis (NAA). The survey results and the analysis method have been previously described [5]. We chose to operate the engine on a fuel with a target Cl content of 600 ppb, doping the fuel with 1-chlorohexadecane, chosen for its carbon chain length when compared to that of diesel fuel. Errors in the fuel spiking procedure led to actual fuel Cl levels of 1.2 ppm. The test fuel properties can be found in [Table A1](#) of the appendix. Cl content of our intake air was not performed, but was adequately accounted for based on previous considerations [5].

Transient testing was performed over the Heavy-Duty Diesel Engine Federal Test Procedure (HDDE-FTP) and a profile of engine speed, torque, and urea SCRF catalyst temperature for each of the urea SCRF catalysts tested can be found in [Figures A1](#) and [A2](#) of the appendix. For the transient testing performed here, 2 cold start and 46 hot start HDDE-FTPs were run for each sample taken affording a 1:23 ratio of cold to hot start tests. Testing was performed at this ratio to maximize the number of tests that could be run over a test day due to the high number of test required per module (48 tests total).

SCRFs were supplied by the Manufacturers of Emission Controls Association (MECA) member companies. The DOC used was supplied with the engine and was present for all testing. The urea dosing system was active during all testing



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and the urea used was Cummins Diesel Exhaust Fluid by Fleetguard®. A description of the catalyst properties can be found in [Table A2](#) of the appendix. Undiluted exhaust was proportionally sampled directly from the exhaust system for all testing performed here.

Sampling Procedure, Sample Preparation, and Sample Analysis

The sampling procedure, sample preparation, and sample analysis were identical to procedures used in our testing of modern diesel engines equipped with catalyzed emission control systems [5].

Briefly, PCDD/F, PCB, and PAH emissions were collected using a transient proportional sampling system based on EPA method 0023A, EPA method 0020, and EN 1948-1 [11, 12, 13]. A functional schematic of the sampling system can be found in [Figure A3](#) of the appendix.

The system differs from Method 23A in that it uses a larger sorbent module design similar to that used by Method 20 to allow up to 50 g of XAD-2 resin; as well as a titanium (Ti) sample probe, filter holder, and condenser along with a nickel (Ni) sample module per EN 1948-1 [11,13]. The larger sorbent module permits a higher sampled exhaust volume to ensure that there is no breakthrough due to the potential for high hydrocarbon concentrations. Ti and Ni sample train components were chosen for their durability and inertness toward catalyzation of PCDD/F formation. All joints were sealed with Teflon gaskets. A peristaltic pump was utilized to collect condensate from the water trap.

Samples were taken from the center of the exhaust pipe without dilution. Proportional sampling was maintained for transient testing according to 40 CFR part 1065.545 [14]. Exhaust flow was calculated from the intake air and fuel flow measurement. Sample flow was calculated by taking the difference between the total flow through the sampler and make-up flow, taking into account the water that condensed and was removed from the sample flow when passing through the condenser. The sampler total flow was controlled with a positive displacement pump while the make-up flow was measured with a laminar flow element and controlled using a proportional valve. Each test required 16 hours of sampling.

Particulate Matter was collected onto a 110 mm Pall Tissuquartz filter (7 mil thickness) supported by a perforated titanium disk. Gaseous phase PCDD/Fs, PCBs, and PAHs were collected on 40 g of XAD-2 located in between 3-inch diameter polyurethane foam (PUF) plugs. A perforated Teflon disk held the downstream PUF plug in place. The module was located downstream of the condenser coil and both were submersed in a water bath controlled to achieve a sample gas temperature of 5 ± 1 °C at the module outlet. Cooling the sample gas allowed collection of higher volatility analytes and minimized the potential for loss from the sorbent module. A leak check was performed between the inlet of the

sample probe and the outlet of the sample flow control hardware before each test. The target sample flow rate through the module at peak exhaust flow was 200 L/min. Target total sample volume was 64 m³, or 1% of the total exhaust volume, which represents a 21 fold increase in total sample volume targeted by Method 0023A.

All sample preparation and analysis were carried out by Analytical Perspectives, Inc. (Wilmington, NC), a NELAC accredited lab. Sample preparation was carried out according to an enhanced version of EPA method 8290a, taking into consideration ARB methods 428 and 429, and has been previously described [5,15, 16, 17]. For all tests the PUF, XAD-2, rinse, and PM filters were extracted together. Isotopic dilution was used throughout the test program and has been previously described [5]. Surrogate standard recoveries were typically in the 70 to 110% range unless otherwise noted.

[Figure 1](#) shows the general molecular structure of PCDD, PCDF, and PCB with position numbering. For this testing total tetra-octa CDD/F homologue and mono-nona CB homologue plus PCB-209 totals were measured. Seventeen individual 2,3,7,8-substituted CDD/F congeners (congeners where Cl is substituted onto any of the carbon atoms at the number 2, 3, 7, and 8 positions) were measured to determine I-TEQ. I-TEQ is determined by applying a toxic equivalency factor (TEF), that equates each congeners' toxicity to that of 2,3,7,8-TCDD (TEF = 1), to the final emission value of each congener and then summing the values of all seventeen congeners. Twelve individual PCB congeners that are considered to be "dioxin-like", referring both to their toxicity and structural features which make them similar to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), were measured to determine WHO 2005 TEQ. These "dioxin-like" PCB congeners have four to seven Cl substituents; with both para (4 and 4'), two or more meta (3, 3', 5, and 5'), and up to one of the ortho (2, 2', 6, and 6') positions chlorinated. WHO 2005 TEQ is determined in a manner similar to that used for ITEQ, using WHO 2005 specific TEFs. The nineteen PAHs measured were a subset of urban Hazardous Air Pollutants (HAPs) incorporating six of seven PAHs that EPA has designated as mobile source air toxics. These seven PAHs are: benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, chrysene, indeno(1,2,3-cd)pyrene, and 7,12-dimethylbenz(a)anthracene (not measured) [18].

The analytical protocols and quality control methodology, including the use of batch control spikes and method blanks, for the analysis of PCDD/Fs have been previously described by Tondeur, et al. [19]. Those used for PCB and PAH analyses are similar to the PCDD/Fs with exceptions that have been previously described [5]. Detection limits were determined based on considerations laid out by Keith et al. [20] and have been described by Liu et al. [7].

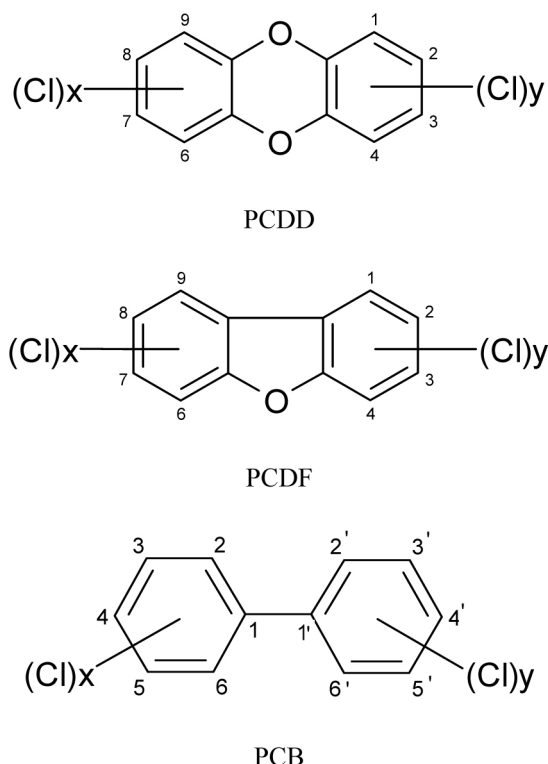


Figure 1. General molecular structure of PCDD, PCDF, and PCB with position numbering.

Field and media blanks were analyzed over the course of testing to determine the contribution of the media and environment to the actual test results. A single media blank consisting of PM filter/PUF/XAD-2 was analyzed for each SCRF tested while a single field blank accompanied the test modules for each SCRF tested, and was analyzed to determine the effects on the module from environmental exposure. Results can be found in [Tables A6](#) and [A10](#) of the appendix and showed negligible contribution from media and field blanks thus no corrections were made for media or environmental contributions to the test results. It should be noted that field blank results show that environmental exposure can contribute to mono-nona CB homologues plus PCB-209 results.

RESULTS AND DISCUSSION

The sampling and engine operation data can be found in [Table 1](#). The information provided is averaged across all of the test runs for a given test configuration. The FTP composite emissions for NO_x, HC, CO, and PM from each DOC and SCRF combination compared to the standard can be found in [Table 2](#). The results indicate that modern diesel emission control technology incorporating a DOC and urea SCRF is very effective at significantly reducing NO_x, NMHC, CO, and PM emissions. It should be noted that the SCRF catalysts were not fully optimized with respect to NO_x reduction in this testing, thus the composite FTP NO_x

emission level is at about 2.5 times the 2010 standard, achieving about a 73% reduction in NO_x emissions from pre-catalyst levels.

Replicate testing was performed to assess measurement variability. In one instance, test number 1 of the CuZ SCRF results for PCDD/Fs was deemed an outlier at the upper 0.1% significance level utilizing a one-sided T-test when the standard deviation is calculated from the same sample, as described in ASTM E178-08 [21]. The outlier value was 16.42 pg I-TEQ/L fuel consumed, where non-detect equals zero (ND=0). The reason for this outlier cannot be confirmed, but we believe that it may be due to sample contamination as the 2,3,7,8-substituted CDD/F congener and tetra-octa CDD/F homologue profiles are dominated by both dioxins and furans in these tests at levels which are not seen in any of the other CuZ SCRF tests. Specifically for this test 1,2,3,7,8-PeCDF, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, and 2,3,4,6,7,8-HxCDF are driving I-TEQ while these congeners are non-detects in all but two cases in the other four tests combined.

Table 1. Sampling and Engine Operation Data for All Test Configurations.

	DOC+CuZ SCRF+urea	DOC+FeZ SCRF+urea
Number of Valid Repeats PCDD/Fs	4	5
Number of Valid Repeats PCBs and PAHs	5	5
Average Total Engine Work (hp-hr)	855	854
Average Brake-specific Fuel Consumption (L/hp-hr)	0.227	0.228
Average Sampler Total Volume (m ³)	64.6	60.4
Average Total Exhaust Volume (m ³)	6,175	6,221

Table 2. FTP Composite Emission Results and 2010 Heavy-Duty Diesel Engine Standard for the Catalyst Configurations Tested.

	DOC+CuZ SCRF+urea	DOC+FeZ SCRF+urea	2010 Emission Standard
NO _x (g/hp-hr)	0.485	0.472	0.2
NMHC (g/hp-hr)	0.014	0.011	0.14
CO (g/hp-hr)	0.112	0.179	15.5
PM (g/hp-hr)	0.003	0.003	0.01

For the results presented here, any estimated maximum possible concentrations (EMPC) are reported in the results. EMPC is used for a result where a peak is detected that does not meet all of the criteria for qualitative determination of the congener (most commonly the ion abundance ratio outside

the allowed theoretical range of $\pm 15\%$). The reported EMPC concentration represents an upper bound on the congener concentration.

PCDD/Fs

PCDD/F emission factor data in pg I-TEQ/L fuel consumed for both configurations tested along with media and field blank results are shown with the 95% confidence interval (student t-test assuming a normal distribution) in Figure 2. Additionally, the average emission results and detection limits with standard deviation for all 2,3,7,8-substituted CDD/F congeners and tetra-octa substituted CDD/F homologues, along with I-TEQ emissions can be found in Tables A3, A4, A5, A6 in the appendix.

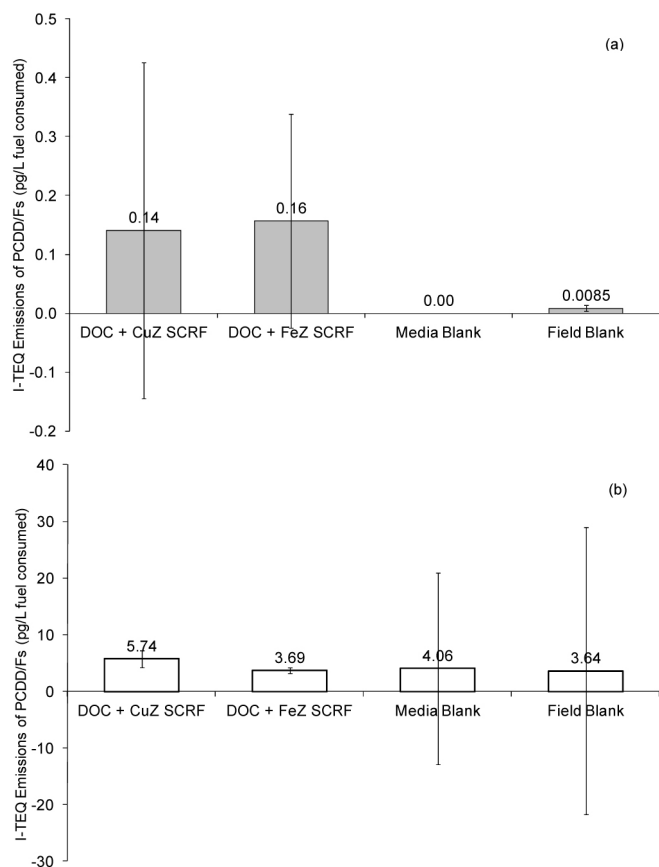


Figure 2. Average PCDD/F I-TEQ emission values with $\pm 95\%$ C.I. ND=0, EMPC=EMPC (a) and ND=DL, EMPC=EMPC (b) for all of the configurations tested, including media and field blank results.

A review of the I-TEQ results across the two configurations tested indicate that the results are not statistically significant where ND=0, but a difference is observed when comparing the results where non-detect equals detection limit (ND=DL). It should be noted that the detection limit, which can be influenced by many factors, varied from about 1 to 2 pg/L fuel consumed for the varying 2,3,7,8-substituted CDD/F congeners and although this is a small range, this uncertainty alone could account for the

apparent reduction in I-TEQ. This is also evident in the media and field blank results.

For 2,3,7,8-substituted CDD/F congeners, 1,2,3,4,6,7,8-HpCDD, OCDD, 2,3,7,8-TCDF, 1,2,3,4,6,7,8-HpCDF, and OCDF emissions are driving the reported I-TEQ for ND=0 for both CuZ and FeZ SCRF configurations, with almost all of the emissions just above the detection limit. The tetra-octa CDD/F homologue totals are at or just above the limit of detection for all homologues and are comparable within a level of chlorination with the exception of tetra CDF homologues, which are an order of magnitude higher than the other homologues.

The results from this test program indicate that PCDD/F emissions for engine and emission control systems that represent 2010 era and later model engines utilizing a DOC and wall flow CuZ or FeZ urea SCRF are at 0.14 pg I-TEQ/L fuel consumed with the upper limit of the 95% confidence interval at 0.43 pg I-TEQ/L fuel consumed (0.03 ± 0.06 pg I-TEQ/hp-hr, 0.0045 ± 0.0092 pg I-TEQ/m³) and 0.16 pg I-TEQ/L fuel consumed with the upper limit of the 95% confidence interval at 0.34 pg I-TEQ/L fuel consumed (0.04 ± 0.04 pg I-TEQ/hp-hr, 0.0049 ± 0.0057 pg I-TEQ/m³) respectively (ND=0) and are 4 orders of magnitude below the historic and U.S. mobile source on-road diesel engine inventory values at the upper limit [22]. This suggests that for a modern diesel engine equipped with a DOC and CuZ or FeZ urea SCRF, PCDD/F emissions are near zero levels.

Recently, Laroo et al. reported PCDD/F results for a modern diesel engine equipped with emission control system configurations representing a model year 2007 era emission control system utilizing a DOC and CDPF and a model year 2010 era emission control system utilizing a DOC, CDPF, flow through CuZ urea SCR catalyst, and an ASC. This testing was performed using the same 1:23 cold start to hot start FTP ratio used in this test program. The results yielded PCDD/F emissions (ND=0) of 0.21 pg I-TEQ/L fuel consumed with the upper limit of the 95% confidence interval at 0.51 pg I-TEQ/L fuel consumed for the 2007 era engine and 1.28 pg I-TEQ/L fuel consumed with the upper limit of the 95% confidence interval at 2.89 pg I-TEQ/L fuel consumed for the 2010 era engine [5]. These results are further supported by the work of Hovemann et al. and Liu et al. [6,7].

Overall the results from this test program are comparable to that of Laroo et al. and are not statistically significant when compared to the results of all configurations tested under transient conditions [5]. When comparing the 2,3,7,8 substituted CDD/F congeners that are reported as detects for our results here to that of Laroo et al., I-TEQ results in both cases are due mainly to the emissions of 1,2,3,4,6,7,8-HpCDD, OCDD, 1,2,3,4,6,7,8-HpCDF, and OCDF, with almost all of the emissions just above the detection limit. The differences are that we report emissions of 2,3,7,8-TCDF in this work while Laroo et al. reported emissions of 2,3,4,7,8-PeCDF and 1,2,3,4,7,8-HxCDF [5]. It should be noted that

for both sets of results, emissions of these congeners are just above the detection limit, while they are below the detection limit in the media blanks. When comparing tetra-octa CDD/F homologue totals between the two test programs, the results are at or just above the limit of detection for all homologues and are comparable within a level of chlorination with the exception of tetra CDF homologues, which are on average 1 to 2 orders of magnitude higher for the SCRF test results when compared to those previously reported [5].

The results of this testing support the previously published results of Hovemann et al., Laroo et al., and Liu et al. [5, 6, 7], indicating that if the heterogeneous processes of de novo and precursor formation of PCDD/Fs are occurring as a function of diesel combustion or within these wall flow urea SCRF catalyst systems, they are occurring at an extremely low rate. Further, the placing of Cu into a wall flow diesel particulate filter does not appear to have any effect on PCDD/F formation, indicating that the conditions as they exist are not optimal for either precursor or de novo formation, the latter of which is a concern due to the close proximity of soot trapped in the SCRF to the Cu in the catalyst washcoat. With respect to de novo synthesis, it is in the SCRF where we have the availability of ample precursors in the form of carbon and oxygen (from lean diesel combustion), with Cl being supplied from the fuel. Further, residence time over the catalyst, the availability of Cu sites in the catalyst matrix, and a test cycle that include temperatures that favor PCDD/F formation over Cu (300 °C) should be more than adequate to provide conditions to facilitate formation. The presence of the DOC, which utilizes platinum to facilitate the chemical mechanisms of oxidation, hydrogenolysis, and thermal decomposition, should remove any PCDD/Fs emitted from the engine, as well as any hydrocarbon precursors before the exhaust gas encounters the SCRF. Results from Liu et al. show this reduction across the DOC and CDPF, while results from Laroo et al. show no statistically significant difference when testing with and without a DOC and CDPF present, as all congeners, where detectable, were just above detection limits [5,7].

PCBs

PCB emission factor data in pg WHO 2005 TEQ/L fuel consumed for both configurations tested along with media and field blank results are shown with the 95% confidence interval (student t-test assuming a normal distribution) in Figure 3. Additionally, the average emission results and detection limits with standard deviation for all WHO 2005 CB congeners and mono-nona substituted CB homologues plus PCB-209, along with WHO 2005 TEQ emissions can be found in Tables A7, A8, A9, A10 in the appendix. A review of the WHO 2005 TEQ PCB results across both configurations tested indicate that the results are not statistically significant where ND=0 and ND=DL.

An analysis of the WHO 2005 PCB congeners emitted above the detection limit for both configurations tested indicate that PCB-77, PCB-105, PCB-114, PCB-118,

PCB-123, PCB-156/7, PCB-167, and PCB-189 are driving the reported WHO 2005 TEQ for ND=0 for both CuZ and FeZ urea SCRF configurations. It should be noted that for the FeZ urea SCRF configuration, detects of PCB-81 and PCB-126 were also reported at levels just above the detection limit, while being reported as non-detects in the media and field blanks. Since these two congeners have two of the three highest TEFs (0.0003 and 0.1 respectively) they are the primary reason that the average WHO 2005 TEQ PCB emissions are slightly higher for the FeZ SCRF when compared to the CuZ SCRF. These two congeners were reported above the detection limit in only two of the five FeZ urea SCRF tests for PCB-81 and one of the five tests for PCB-126. In each case the emission was just above the detection limit. The mono-nona CB homologue plus PCB-209 totals are comparable within a level of chlorination for all homologues with the exception of mono CB homologues, which are two orders of magnitude higher than the other homologues for the CuZ SCRF configuration.

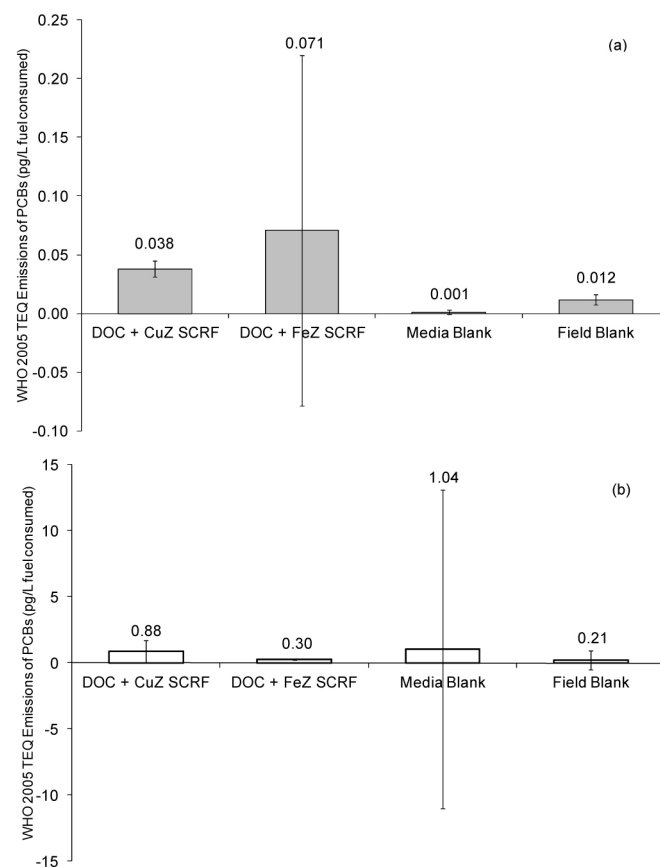


Figure 3. Average PCB WHO 2005 TEQ emission values with ±95% C.I. ND=0, EMPC=EMPC (a) and ND=DL, EMPC=EMPC (b) for all of the configurations tested, including media and field blank results.

Nona CB homologues and PCB-209 emissions were also noticeably lower than mono-octa homologues for both CuZ and FeZ urea SCRF configurations.



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While the PCB data presented here has measurement uncertainty associated with the low levels detected, we believe that the values presented with the upper limit of the 95% confidence interval can be used to provide a worst case estimate of PCB emissions from diesel engines equipped with a DOC and wall flow CuZ or FeZ urea SCRf, 0.038 pg WHO 2005 TEQ/L fuel consumed (upper limit of the 95% confidence interval at 0.045 pg WHO 2005 TEQ/L fuel consumed) for a DOC and CuZ urea SCRf system and 0.071 pg WHO 2005 TEQ/L fuel consumed (upper limit of the 95% confidence interval at 0.22 pg WHO 2005 TEQ/L fuel consumed) for a DOC and FeZ urea SCRf system. Since this testing included the use of a DOC and is similar to conditions tested by Laroo et al., we believe that the mechanisms for the formation and destruction of PCBs in diesel combustion and over the aftertreatment systems tested here should be identical to those previously reported [5]. Overall these results suggest that for a modern diesel engine utilizing a DOC plus either CuZ or FeZ SCRf, PCB emissions are near zero levels.

In addition to reporting results for PCDD/Fs from modern diesel engine equipped with emission control system as discussed above, Laroo et al. reported PCB results as well. The results yielded PCB emissions (ND=0) of 0.01 pg WHO 2005 TEQ/L fuel consumed with the upper limit of the 95% confidence interval at 0.014 pg WHO 2005 TEQ/L fuel consumed for the 2007 era engine (DOC+CDPF) and 0.02 pg WHO 2005 TEQ/L fuel consumed with the upper limit of the 95% confidence interval at 0.03 pg WHO 2005 TEQ/L fuel consumed for the 2010 era engine (DOC+CDPF+CuZ SCR+urea+ASC) [5].

Overall the results from this test program are comparable to that of Laroo et al., although the CuZ SCRf results are statistically significant when compared to the 2007 and 2010 era results tested under transient conditions, with the CuZ SCRf results being higher. It should be noted that although the emission results for this testing are higher on average, they are still well within the same order of magnitude with respect to the results of Laroo et al. on 2007 and 2010 era systems. When comparing the WHO 2005 PCB congeners that are reported as detects for our results here to that of Laroo et al., WHO 2005 TEQ results in both cases are due mainly to the emissions of PCB-77, PCB-105, PCB-114, PCB-118, PCB-123, PCB-156/7, PCB-167, and PCB-189. The overall difference driving the higher WHO 2005 TEQ results from this testing is that reported emission values are higher, but within the same order of magnitude in almost all cases, across all of the congeners. When comparing mono-nona plus PCB-209 CB homologue totals between the two test programs, the results are comparable within a level of chlorination with the exception of mono CB homologues, which are on average 1 to 2 orders of magnitude higher for the CuZ urea SCRf test results when compared to those previously reported [5].

PAHs

Average PAH emission factor data, including standard deviation, in ng/hp-hr for steady-state and transient test configurations are shown in [Table A11](#) of the appendix.

The PAH results for both configurations show consistent results for repeat tests, however results for the CuZ urea SCRf are elevated for some PAHs when compared to the FeZ urea SCRf results and results reported by Laroo et al. [5]. The cause of this difference is unknown, as the same DOC was used for both test configurations and the CuZ tests were performed before the FeZ tests, so loss of oxidative activity over the DOC is not a valid reason for the difference. It should be noted that although some of the CuZ urea SCRf results are elevated, they are nowhere near the high PAH emission levels that have been reported from engines not utilizing catalytic treatment of the exhaust gas. Overall, the data show that generally there is no relative increase in PAH formation when compared to previous results [5]. The results also reaffirm that the presence of platinum group metals in the DOC reduces all of the PAHs measured here when compared to steady-state engine out emissions, which is consistent with previously published results [5,23].

CONCLUSIONS

Overall, the results of our testing show that PCDD/F emissions appear to be unaffected by the use of CuZ and FeZ SCRfs when compared to the results of previous studies [5, 6, 7]. Further, when compared to inventory values, the emission factors suggest a 4 order of magnitude reduction in PCDD/F emissions from diesel engines and suggest that modern diesel engines are a minor contributor to the PCDD/F inventory when compared to stationary sources [22].

The results also indicated that the presence of both Cu and Fe in the form of CuZ and FeZ as a wall flow exhaust aftertreatment, has no adverse effect on PCDD/F formation from modern diesel engines at fuel and ambient air Cl concentrations that represent the maximum level expected to be encountered during normal engine operation. The results from testing here give no indication of an increase in PCDD/F formation from either precursor or de novo synthesis mechanisms.

The PCB results support previous results indicating that modern diesel engines are not a significant source of PCB emissions and that the use of CuZ or FeZ urea SCRf catalysts does not increase the PCB emissions from the engine when compared to previous studies. The results also show that the PAH emissions are unaffected by the presence of CuZ and FeZ as a wall flow exhaust aftertreatment, and that the DOC is highly effective at oxidation of PAHs in the exhaust.

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DEFINITIONS/ABBREVIATIONS

ASC - ammonia slip catalyst
 CB - chlorinated biphenyl
 Cl - chlorine
 CDD/F - chlorinated dibenzo-*p*-dioxin/furan
 CDPF - catalyzed diesel particulate filter
 CuZ - copper zeolite
 DL - detection limit
 DOC - diesel oxidation catalyst
 EPA - Environmental Protection Agency
 EMPC - estimated maximum possible concentration
 FeZ - iron zeolite
 HAP - hazardous air pollutant
 HpCDD - heptachlorodibenzo-*p*-dioxin
 HpCDF - heptachlorodibenzofuran
 HxCDD - hexachlorodibenzo-*p*-dioxin
 HxCDF - hexachlorodibenzofuran
 HDDE-FTP - heavy-duty diesel engine-federal test procedure
 I-TEQ - international toxic equivalency
 MECA - Manufacturers of Emission Controls Association
 NAA - neutron activation analysis
 ND - non-detect
 NH₃ - ammonia
 Ni - nickel
 NO_x - oxides of nitrogen
 OCDD - octachlorodibenzo-*p*-dioxin
 OCDF - octachlorodibenzofuran
 PAH - polycyclic aromatic hydrocarbon
 PCB - polychlorinated biphenyl
 PCDD/F - polychlorinated dibenzo-*p*-dioxin/furan
 PeCDD - pentachlorodibenzo-*p*-dioxin
 PeCDF - pentachlorodibenzofuran
 PM - particulate matter

PUF - polyurethane foam plug
SCR - selective catalytic reduction
SCRF - selective catalytic reduction filter
TCDD - tetrachlorodibenzo-*p*-dioxin
TCDF - tetrachlorodibenzofuran
TEF - toxic equivalency factor
TEQ - toxic equivalency
Ti - titanium
U.S. - United States
WHO - World Health Organization