DIOXIN AND FURAN EMISSION EVALUATION IN AUTOMOTIVE DIESEL ENGINES

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Abstract
Dioxins and furans were measured in particulate matter and gases from the exhaust of new heavy-duty diesel engines that comply with the EURO 3 emission limits and are representative of those used to equip new buses and trucks in Brazil at the time of the experiment. The tests were performed in a bench dynamometer using the ESC test. The analyses were performed by HRGC/HRMS in accordance with the USEPA Method 8290. The results indicated emissions generally below or near the detection limit. In one sample it was verified that octachlorodibenzo-p-dioxin (OCDD) was above but near the limit of detection, while in another sample, the same was found for octachlorodibenzofuran (OCDF) and pentachlorodibenzofuran (1,2,3,7,8-PeCDF). The results showed that emission of PCDD/Fs from diesel engines may not be so significant, for the level of technology of the engines tested and composition of the fuel used. The average emission factor obtained in this study (1.95 μg TEQ.t^{-1} of fuel) is higher than the emission factor recommended by UNEP in the Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases 2005 (0.1 μg TEQ.t^{-1} of fuel).

Introduction
The two million heavy-duty vehicles in the Brazilian car fleet play an important role in the transportation system and therefore in the Brazilian economy[1,2]. Diesel vehicles that are used daily for passenger and load transportation in the São Paulo Metropolitan Region, as well as in other metropolitan regions, are important contributors to the deterioration of air quality[3], indicating the need of public regulations to control these pollutants. The hypothesis of this study is that unregulated toxic pollutants such as dioxins and furans may be present in significant amounts in the particulate matter and gases emitted by diesel engines. This hypothesis is strengthened by the high sulfur content of Brazilian diesel fuel, which has a direct influence on the amount and characteristics of the particulate matter generated.

Material and Methods
The emission tests were performed on a dynamometer bench using the steady state cycle (13 points) and new diesel engines that are representative of the vehicles used in the Brazilian market. A mini-dilution tunnel was used to obtain samples of particulate matter. The engines tested (3.9 liter-, 5.9 liter- and 8.3 liter-displacement) are manufactured in Brazil, and produced and sold in accordance with Brazilian emission regulations. The engines used in the tests have the same technology and comply with the EURO 3 emission limits. All engines and their control devices accumulated a sufficient number of working hours to attain stabilization conditions, as recommended by the manufacturer. This study used diesel engines and commercial metropolitan fuel to meet the limits of Brazilian legislation (PROCONVE stage 5).

The fuel used in the tests was provided directly by the distributor, and the fuel characteristics adhered to the National Petroleum Agency (ANP) specification. The chlorine contents in diesel fuel and lube oil new and after use, according to the laboratory analysis abroad (USA), were <1 ppm, 21 ppm and 29 ppm respectively. Measurements of regulated pollutants (NOx, HC, CO, PM) were also performed.

To collect samples of particulate matter and gases for analysis of dioxins and furans, a special device was used. Cartridges of 6 cm x 3.8 cm polyurethane foam (PUF) from Tisch were used to collect the gas phase, in series and after the quartz-fiber filters coated with Teflon (Pallflex Emfab Filters) that were used for the solid phase. Blanks of PUF and quartz filters were used for each set of tests.

Prior sampling, filters and PUF cartridges were cleaned and spiked with 4 ng of $^{13}C_6$1, 2,3,7,8,9-HxCDD (field surrogate). After sampling and filters weighing, the samples and blanks were placed in an original glass container and wrapped with aluminum foil. The PCDD/Fs analyses were carried out in a national certified laboratory according to the US EPA Method 8290[4]. Samples were transported in a refrigerator with dry ice. Each filter and the corresponding PUF were combined and spiked with seventeen $^{13}C_6$PCDD/F internal standards, and then Soxhlet extracted with toluene/hexane for 16 h. Each extract was then cleaned-up in a sulfuric acid-silica gel column using hexane as eluent and a Florisil column using dichloromethane as eluent. The extracts were concentrated to almost dryness and $^{13}C_6$-1, 2,3,4 - TCDD was added in 15 µL of nonane immediately before analysis.

Extracts were analyzed in a Hewlett Packard 6890 model High-Resolution Gas Chromatograph/ VG Autospec Ultima mass spectrometer (HRGC/HRMS) equipped with a Hewlett Packard 7673 auto sampler operating with electron impact ionization energy of 30 eV at a mass resolution of 5000. The GC was fitted with a J&W DB-5 capillary column (60 m x 0.25 mm id. fused silica column coated with 0.25 µm film thickness). The GC oven temperature program used was: 70°C, 4 min, 15°C min-1 to 220°C, 1.5oC min-1 to 240°C, 2 min, 4°C min-1 to 310°C, 10 min. Helium was used as the gas carrier, at a head pressure of 10 psi at constant flow.

The PCDD/Fs quantification was done using twelve $^{13}C_6$-labeled internal standards. The labeled PCDD/F internal standards and their response factors were used for quantification of unlabeled PCDD/Fs of homologous groups. Recoveries of $^{13}C_6$-labeled internal standards, determined against external standards, ranged from 51 to 95%. The detection limits of the PCDD/Fs congeners, calculated by signal-to-noise ratio, ranged from 0.003 to 2.5 pg.

Results and Discussion

Results for regulated pollutants measured in accordance with ESC test showed that the emissions of HC and CO complied with the 2004 limits of Brazilian Federal Regulation (Proconve) with clearance. NOx met the emission limit in 80% of the results. With regard to Particulate Matter, measured under the same conditions, results showed compliance in 60% of the tests performed. The 2004 Brazilian emission limits valid at the time of the experiment were similar to Euro 3 limits.

The amount of PCDD/Fs, collected for each sample is shown in Table 1. For the samples A1DF and A4DF with mass of PCDD/Fs above the LD it was calculated the total emission of PCDD/Fs (solid and gaseous phases).

As the levels of dioxins and furans found in the samples A2DF and A3DF were below of the limit of detection, and aiming to reach the detection limit we increased the mass of the sample being examined by increasing the number of tests on samples. So in A4DF and A5DF samples it was changed from the three tests initially planned to six tests in the sample A4DF and ten tests for the sample A5DF. Particulate matter collected increased from 6.25 mg in the sample A3DF to 18.16 mg in the sample A4DF and 26.87 mg in the sample A5DF. The results are shown in Tables 2 and 3 for the samples A1DF and A4DF, respectively since none PCDD/Fs were not detected in sample A5DF.

In Table 4 is a summary of the concentrations of dioxins and furans in the samples A1DF and A4DF in relation to the volume of fuel consumed and in relation to the distance traveled assuming autonomy of 2.5 km/L of fuel obtained in tests performed. Tables 5 and 6 show the results from this work compared to studies performed elsewhere.

Measurements of dioxins and furans from diesel engine exhaust operating under controlled conditions in a dynamometer indicated emissions generally below or near the detection limit of the analytical method. In one of the samples OCDDs were above the limit of detection, while in another sample, the same was found in relation to OCDF and 1,2,3,7,8-PeCDF. The increase in the mass of particulate matter collected in the two samples resulted in values above the limit of detection in only one, the one with the smaller mass of the two. A positive association between PM emission and presence of PCDD/Fs was not valid in this study.

The results of this study shows that the emission of dioxins and furans from internal combustion in diesel engines may not be so significant, for the level of technology of the engines tested, composition of the fuel used and detection limit of the analytical method. The average emission factor obtained in this study (1.95 µg TEQ.t^{-1} of fuel) is higher than the emission factor recommended by UNEP in the Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases 2005 (0.1 µg TEQ.t^{-1} of fuel).

Some hypotheses can be raised to explain non-detected results:

1st hypothesis: The cycle of tests used in the experiment ESC emission test for verification of the formation of dioxins and furans would not be appropriate from the point of view of formation of these compounds.

This hypothesis is not confirmed because the temperature of the formation of dioxins and furans is between 200 °C and 400 °C (USEPA[5]) and in the ESC emission test the engine operates in partial loads, and the temperature of the exhaust gases were between 120 °C and 462 °C, according to tracking done during testing.

2nd hypothesis: Absence of chlorine on possible sources (air, diesel fuel and lube oil), prevented significant formation of PCDD/Fs.

The levels of chlorine in lube oil and diesel fuel in this study, in principle, would not be sufficient for formation of dioxins and furans, which confirms the hypothesis above. The presence of a chlorine donor is a basic condition for the formation of dioxins and furans and international literature available indicates that the source of chlorine donor in the process of combustion engines is not known[6].

3rd hypothesis: Collection of samples was performed improperly (filters, operation)

This hypothesis is not confirmed, because the collection was done following the procedure of testing, filter coated with Teflon, inert, and there is no indication of failure in this process. A critical point is the amount of material collected for analysis due to the low level of D/Fs that can be expected in this type of source.

4th hypothesis: The engines tested do not produce significant amount of PCDD/Fs.

The engines tested are representative of the state of the art of engines for automotive application in the Brazilian market. There is no specific feature in these engines to minimize the formation of PCDD/Fs in the combustion process. However, as they complied with Brazilian emission limits for particulate matter, this could help to reduce the amount of PM formed, because it is known that PCDD/Fs emissions are directly related to particulate matter emitted[7,8].

5th hypothesis: The combustion of diesel is not a relevant emission source of PCDD/Fs.

The contribution of combustion engines to the total of dioxins and furans found in the ambient air is a very controversial issue, and studies on this issue are still very limited and scarce. According to UNEP[8] emission factor for diesel vehicles would be of 0.1 µgTEQ.t^{-1} of fuel, the same emission level of unleaded petrol vehicles without catalyst. So diesel vehicles would not be considered an irrelevant emission source of PCDD/Fs. Measurements done in urban atmospheres where vehicles are on the most significant air pollution source, have shown significant levels of PCDD/Fs[7,9,10].

In accordance with the report of Oehme et al[6] the reasons for the formation of dioxins and furans in diesel engines combustion and the origin of chlorine are not yet very clear. Usually the chlorine present in the diesel fuel is of the order of 1 ppm or less. Dioxins and furans have been found in the lube oil of diesel engines, indicating that they are formed during combustion. Very little work has been done to verify the source of chlorine responsible for the observed emission. The high temperature of combustion of fuels that are poor in hydrogen could perhaps promote the formation of dioxins and furans, though with only traces of chlorine.

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Table 1 List of samples analyzed, in relation to the DL (detection limit) and recovery of extraction in %

Reference	Description of the Sample	Quantity	Extraction Recovery (%)
Blank 1 (Br1DF)	3 blank filters + 1blank PUF	<DL	72-109
Sample 1 (A1DF)	3 filters of particulate matter+ 1 PUF	**>DL**	**72-101**
Sample 2 (A2DF)	3 filters of particulate matter + 1 PUF	<DL	91-109
Blank 2 (Br2DF)	3 blank filters + 1blank PUF	<DL	67-106
Sample 3 (A3DF)	3 filters of particulate matter + 1 PUF	<DL	56-85
Sample 4 (A4DF)	6 filters of particulate matter r+ 1 PUF	**>DL**	**61-109**
Sample 5 (A5DF)	10 filters of particulate matter r+ 1 PUF	<DL	50-99

Table 2 Total mass of PCDD/Fs detected and calculated emission for sample A1DF

Compound	I-TEF	Mass total of PCDD/Fs obtained		Emission total of PCDD/Fs calculated	
		(pg)	(pg TEQ)	(pg/g of MP)	(pg TEQ/g of MP)
OCDD	**0.001**	**11.00**	**0.011**	**1,591**	**1.59**
ΣPCDD		11.00	0.011	**1,591**	**1.59**
ΣPCDF		ND	ND	ND	ND
ΣPCDD/Fs		11.00	0.011	**1,591**	**1.59**

Sample A1 - Mass of MP: 6.91 mg

Table 3 Total mass of PCDD/Fs detected and calculated emission of PCDD/Fs for sample A4DF, according to the compound

Compound	I-TEF	Mass total of PCDD/Fs obtained		Emission total of PCDD/Fs calculated	
		(pg)	(pg TEQ)	(pg/g of MP)	(pg TEQ/g of MP)
OCDD	**0.001**	**64**	**0.064**	**3,524**	**3.52**
ΣPCDD		64	0.064	3,524	3.52
2,3,7,8-TCDF	0.1	ND	ND	ND	ND
1,2,3,7,8-PeCDF	**0.05**	**10**	**0.5**	**550**	**27.5**
ΣPCDF		**10**	**0.5**	**550**	**27.5**
ΣPCDD/Fs		**74**	**0.564**	**4,074**	**31.0**

Sample: A4- Mass of PM:18,16 mg.

Table 4 Emissions of PCDD/Fs in relation to the volume of fuel consumed in the tests on distance traveled (km) estimated for samples A1DF and A4DF

Sample	Fuel consumption in tests (L)	Consumption of fuel equivalent in sample (L)	Distance traveled equivalent * (km)	Emissions of PCDD/Fs (pg TEQ/L)	Emissions of PCDD/Fs (pg TEQ/km)
A1DF	10.93	0.0164	0.041	0.670	0.268
A4DF	45.55	0.0523	0.130	10.7	4.31

* Assuming a rate of 2.5 km/L of fuel

Table 5 Emissions of dioxins and furans, as a function of fuel consumption compared with that of Marklund et al (1990)

Country	Characteristic (Sample)	Year	Level (pg/L)	Reference
Brazil	Diesel Engine (A1)	2006	670	This study
Brazil	Diesel Engine (A2)	2006	ND	This study
Brazil	Diesel Engine (A3)	2006	ND	This study
Brazil	Diesel Engine (A4)	2006	1419	This study
Brazil	Diesel Engine (A5)	2006	ND	This study
Sweden	Diesel Engine	1990	<100	Marklund et al[11]

Table 6 Emission of dioxins and furans in pg-TEQ/km, compared to the available literature.

Country	Characteristic (Sample)	Level (pg-TEQ/Km)	Reference
Brazil	Diesel Engine (A1)	0,268	This study
Brazil	Diesel Engine (A4)	4,311	This study
USA	Diesel Engine	8-23	Gullett and Ryan[12]
USA	Diesel Engine	482	USEPA[5]
Norway	Diesel Engine	38-520	Oehme et al,1991
Germany	Diesel Engine	35	Hagenmaier et al[13]
USA	Diesel Engine	241	CARB[14]