

EMISSIONS OF PCDD/Fs FROM A POWER GENERATOR

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Introduction

There is increasing concern over the exposure of humans and ecosystems to trace levels of highly toxic organic compounds, in particular polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs). Since internal combustion engines are so widely used in applications ranging from small portable equipment through to large stationary and marine engines, and since the total fuel consumed in these systems is so large, the potential for emissions of PCDD/Fs from these sources has to be carefully assessed¹.

From the pollutant emissions point of view, internal combustion engines using diesel as fuel are an important source of nitrogen oxides (NO_x) and particulate matter (PM)². Their emissions also contain other pollutants such as polycyclic aromatic hydrocarbons (PAHs), nitro-PAHs, VOCs (benzene, toluene, etc.), oxygenated compounds (formaldehyde, acetaldehyde, etc.) and PCDD/Fs. PCDD/Fs can be formed due to an incomplete combustion and the presence of chlorine in fuel or fuel additives³.

A power generator generates electricity by means of an internal combustion engine. It is commonly used when there is a power deficit or when power cuts occur frequently. The legislation of the countries can make compulsory the installation of these equipments in places where there is a considerable population density (hospitals, factories, shopping centers, prisons, official buildings, etc.).

In this work the emissions of a power generator have been studied in order to obtain the amount of dioxins emitted to the atmosphere. Moreover, this work is the beginning of future experiments in which diesel will be replaced with diesel/biodiesel blends in different proportions to evaluate the effect of this substitution in the formation of dioxins.

Materials and methods

The power generator used to carry out the samplings was purchased in Franvicar® and has a KAMA air-cooled diesel engine of 2.5 kW. The fuel used was standard diesel obtained from a commercial source.

PCDD/F samples were collected using the EPA Method 23 sampling train shown in Figure 1⁴. This sampling train consists of different parts through where the gas sample passes. First, there is a glass probe covered by a stainless steel sheath which heats the probe and maintains it at 120°C. The glass probe is connected to a 9 cm glass filter housing containing a 9 cm quartz microfiber filter. The filter was supported in the filter housing by a perforated Teflon disk, sealed with Teflon-coated O-rings. The filter housing was contained in a heated (120°C), insulated enclosure in which the temperature was monitored. Next the hot gas sample passes through a horizontal condenser and a glass module with about 40 g of XAD-2 sorbent resin, both kept cooled so that the gas sample was not hot before entering the sorbent module. Finally, there is a metering/pumping system to control and measure different parameters such as probe temperature, filter temperature, glass flow, etc. Moreover, different parameters such as exhaust gas composition were monitored and measured in real time and continuously using an IM 2800-P portable gas analyzer (IM Environmental Equipment Germany GmbH). Every effort was made to follow EPA Method 23 equipment and operational requirements.

The particulate matter fraction of the sample was collected in the filter whereas the condensable PCDD/Fs were collected in the glass module with XAD-2 sorbent resin.

The total sampling time was one hour and a total of 0.726 m³ was sampled. The sampling took place with the sample probe inlet positioned at the center of the 25 cm internal diameter exhaust pipe, perpendicular to the flow. The sampling was not performed in isokinetic conditions due to the assumption that diesel PM is sufficiently small so that it will tend to follow gas streamlines.

During the sampling a device was connected to the power generator so that the fuel consumption was higher and the exhaust obtained was denser.

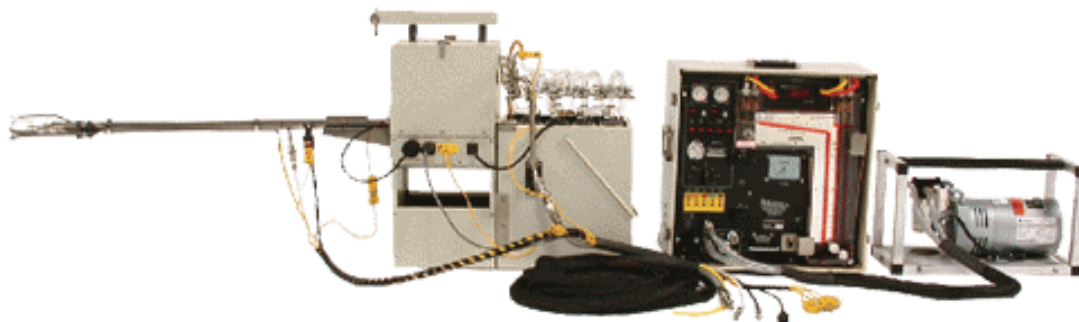


Figure 1. EPA Method 23 sampling train employed

The samples were analyzed by high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS), as described in EPA Method 23, on an Autospec Ultima-NT high resolution mass spectrometer (Micromass, UK) with a positive electron impact (EI+) source and interfaced with a Hewlett–Packard (Palo Alto, CA, USA) 6890 Plus gas chromatograph equipped with a split/splitless injector. An Agilent DB5-MS chromatographic column (60 m x 0.25 mm x 0.25 μm) was used. Filter and XAD-2 resin were extracted with toluene separately using Soxhlet extraction but combined for a single analysis.

Results and discussion

Table 1 shows the mean values obtained with the gas analyzer for the combustion gases emitted in the sampling that was carried out. These values can give an idea of how the combustion was taking place.

Table 1. Combustion gases emitted by the power generator studied

	mg/Nm ³	O ₂ %	CO ₂ %
CO	353.0	11.8	6.4
SO ₂	nd		
NO ₂	79.9		
NO	491.9		

nd: not detected (<2 mg/Nm³)

Table 2 shows the PCDD/Fs obtained in the analysis of the filter, the resin and also the total amount of PCDD/Fs in the emissions of the power generator studied. It is important to note that all the isomers were detected and considerable amounts of the seventeen 2,3,7,8-substituted PCDD/F congeners was found. As far as we are concerned, there are not any published data about PCDD/F emissions in power generators. However, a relation between these equipments and diesel vehicles can be established due to the fact that both are internal combustion engines. The total amount of PCDD/Fs obtained for the power generator was consistent with others found in literature for diesel vehicles³.

Figure 2 shows the PCDD/F profile obtained for the emissions of the power generator studied. As can be observed, PCDDs are more prevalent than PCDFs. This is an aspect that differs from the corresponding published data for a diesel vehicle^{3,5}.

Among the PCDDs, 1,2,3,7,8-PeCDD and 1,2,3,6,7,8-HxCDD are the most prevalent isomers whereas among the PCDFs 2,3,4,7,8-PeCDF is the main one. This fact coincides with the results obtained in the studies of a diesel vehicle.

Table 2. PCDD/Fs obtained in the emissions of the power generator studied

	Filter	Resin	Total
	ng i-TEQ/Nm ³	ng i-TEQ/Nm ³	ng i-TEQ/Nm ³
2378-TCDF	0.0017	0.0020	0.0036
12378-PeCDF	0.0010	0.0006	0.0016
23478-PeCDF	0.0068	0.0059	0.0127
123478-HxCDF	0.0016	0.0015	0.0032
123678-HxCDF	0.0014	0.0013	0.0026
234678-HxCDF	0.0020	0.0024	0.0044
123789-HxCDF	0.0014	0.0010	0.0024
1234678-HpCDF	0.0022	0.0016	0.0038
1234789-HpCDF	0.0003	0.0002	0.0005
OCDF	0.0002	0.0001	0.0004
2378-TCDD	0.0037	0.0112	0.0149
12378-PeCDD	0.0122	0.0114	0.0236
123478-HxCDD	0.0018	0.0008	0.0027
123678-HxCDD	0.0066	0.0155	0.0222
123789-HxCDD	0.0050	0.0085	0.0136
1234678-HpCDD	0.0023	0.0031	0.0054
OCDD	0.0009	0.0008	0.0016
Total	0.0511	0.0678	0.119

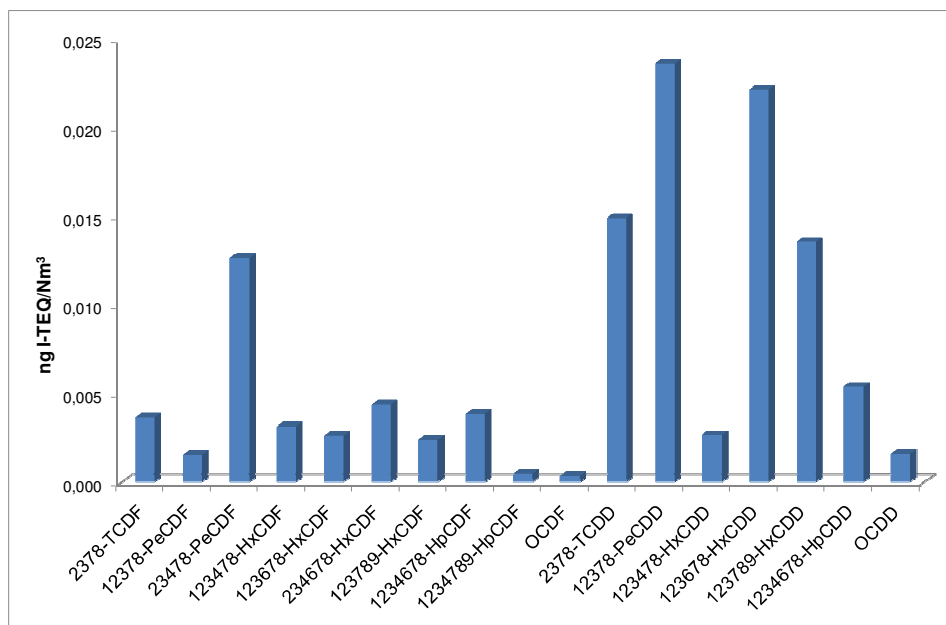


Figure 2. PCDD/F profile obtained for the emissions of the power generator studied

Fundamentally, the conditions that lead to PCDD/F formation in diesel internal combustion engines remain relatively unknown. It has been proved that even chlorine and metals levels below the detection limits can be sufficient for the formation of PCDD/Fs. The temperatures, residence times, and sooting conditions of diesel

engines are consistent with those associated with surface catalyzed formation conditions. Trace levels of chlorine and catalysts such as copper, iron, and nickel have been found to contribute to PCDD/F formation.

We are performing more samplings using diesel as fuel to assess data reproducibility and to obtain more conclusive results about the PCDD/Fs emitted by power generators. Next we will start the experiments with different diesel/biodiesel blends to evaluate the effect of the fuel in the formation of PCDD/Fs in internal combustion engines.

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References

1. Dyke PH, Sutton M, Wood D, Marshall J. (2008); *Chemosphere*. 67: 1275-1286.
2. Karavalakis G, Stournas S, Bakeas E. (2009); *Atmos. Environ.* 43: 1745-1752.
3. Ryan JV, Gullett BK. (2000); *Environ. Sci. Technol.* 34: 4483-4489.
4. EPA Test Method 23, Determination of Polychlorinated Dibenzo-*p*-dioxins and Polychlorinated Dibenzofurans from Stationary Sources. In *Code of Federal Regulations, Title 40, Part 60, Appendix A*; U.S. Government Printing Office: Washington, DC, July 1991.
5. Kim KS, Hong KH, Ko YH, Yoon KD, Kim MG. (2003); *Chemosphere*. 53: 601-607.