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Title: PCDD/F EMISSIONS FROM LIGHT-DUTY DIESEL VEHICLES OPERATED UNDER HIGHWAY CONDITIONS AND A DIESEL-ENGINE BASED POWER GENERATOR

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- A new methodology is proposed for sampling the exhaust of small vehicles
- PCDD/F emissions from various diesel vehicles are measured in on-road conditions
- The effect of the engine temperature on the PCDD/F emissions is assessed
- Contribution of power generators to atmospheric pollution is estimated

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PCDD/F EMISSIONS FROM LIGHT-DUTY DIESEL VEHICLES OPERATED UNDER HIGHWAY CONDITIONS AND A DIESEL-ENGINE BASED POWER GENERATOR

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Abstract

PCDD/F emissions from three light-duty diesel vehicles – two vans and a passenger car – have been measured in on-road conditions. We propose a new methodology for small vehicles: a sample of exhaust gas is collected by means of equipment based on United States Environmental Protection Agency (U.S. EPA) method 23A for stationary stack emissions. The concentrations of O_2, CO, CO_2, NO, NO_2 and SO_2 have also been measured.

Six tests were carried out at 90-100 km/h on a route 100 km long. Two additional tests were done during the first 10 minutes and the following 60 minutes of the run to assess the effect of the engine temperature on PCDD/F emissions. The emission factors obtained for the vans varied from 1800 to 8400 pg I-TEQ/Nm^3 for a 2004 model year van and 490-580 pg I-TEQ/Nm^3 for a 2006 model year van. Regarding the passenger car, one run was done in the presence of a catalyst and another without, obtaining emission factors (330-880 pg I-TEQ/Nm^3) comparable to those of the modern van. Two other tests were carried out on a power generator leading to emission factors ranging from 31 to 78 pg I-TEQ/Nm^3. All the results are discussed and compared with literature.

Keywords: PCDD/Fs, emission factor, diesel vehicles, power generator.

1. Introduction

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There is growing concern about compounds and particles emitted by diesel engine exhausts since they contain carcinogenic substances [1]. It is widely known that internal combustion engines are also an important source of nitrogen oxides (NO_x) and particulate matter. These exhausts also contain other pollutants such as polycyclic aromatic hydrocarbons (PAHs), nitro-PAHs, VOCs (benzene, toluene, etc.), oxygenated compounds (formaldehyde, acetaldehyde, etc.) and other compounds which can be formed as a result of incomplete combustion. Already in 1986, Ballschmiter et al. [2] reported emissions of polychlorodibenzodioxins (PCDDs) and polychlorodibenzofurans (PCDFs) from automobile exhaust and compared these emissions with those from a municipal waste incinerator. The combined effect of all these chemical pollutants can raise the potential hazard of the exhaust gases.

Internal combustion engines are widely used in applications ranging from small portable equipment to large stationary and marine engines. Overall, they consume fuel in large amounts and the potential for emissions of PCDD/Fs from these sources has to be carefully assessed.

Power generators producing electricity by means of an internal combustion engine are commonly used when there is a power deficit or when power cuts are a frequent occurrence. The legislation in some countries make it compulsory to install such equipment in places of considerable population density such as hospitals, factories, shopping centres, prisons, official buildings, etc.

It is not easy to quantify emission factors to gauge the incidence of vehicle emissions in dioxin inventories. There are published papers that propose such emission factors, but the range of values is rather wide. Table S1 of the supporting information shows data reported by different authors on PCDD/F emission factors for four groups of engines: leaded gasoline engines (LGE), unleaded gasoline engines (ULGE), heavy-duty diesel engines (HDDE) and light-duty diesel engines (LDDE) [3-30]. The emission factors are expressed in units of pg I-TEQ/Nm^3, pg I-TEQ/km and pg I-TEQ/L fuel. Original data that are quoted directly from references are shown without parentheses. Table S2 of the supporting information shows the conversion factors deduced from the values in the references when there are data presented on

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different basis. These conversion factors have been used to estimate the emission factors in other units, which are presented in Table S1 between parentheses.

From Table S1, it can be noticed that there are three main groups of results:dynamometer tests for vehicles and engines, on-road tests and tunnel studies. There is also another study on a power generator that reports only a single range of values. The emission factors in pg I-TEQ/Nm^3 deduced for dynamometer tests are commonly very low whereas the emission factors reported for tunnel studies are much higher than those obtained by the other procedures. Several other aspects are worth commenting:

a) For LGE, the emission factors vary from 1.4 to 254 pg I-TEQ/Nm^3.

b) For ULGE, these factors range from 0.03 to 301 pg I-TEQ/Nm^3, except for the values of 625 and 650 pg I-TEQ/Nm^3 estimated in two tunnel studies when vehicles circulated upwards.

c) For LDDE, the factors are between 0.06 and 47 pg I-TEQ/Nm^3. The value of 47 pg I-TEQ/Nm^3 was reported from a tunnel study where the contribution from heavy-duty diesel vehicles was also taken into account.

d) For HDDE, the emission factors vary between 0.04 and 121 pg I-TEQ/Nm^3, except for one value of 470 pg I-TEQ/Nm^3 when the diesel particulate filter is catalyzed with a copper-based fuel additive and two tunnel studies in which the emission factor was estimated to be 703 pg I-TEQ/Nm^3.

Monitoring of real-world emissions of road vehicles is important for reviewing the effectiveness of control measures and for taking into account all real-world variables that may affect emissions [31,32]. We found only two papers in literature dealing with on-road procedures involving HDD vehicles that obtained small PCDD/F emission factors varying between 0.6 and 5.1 pg I-TEQ/Nm^3. Only one paper on PCDD/F emissions from a stationary diesel engine has been found with emission factors of 1.5-6.1 pg I-TEQ/Nm^3. No reference works dealing with on-road samplings in passenger vehicles have been found.

Table S3 of the supporting information summarizes some published data concerning the main congeners (without toxicity factors), the congeners that contribute to the total toxicity I-TEQ (taking into account the toxicity factors), and the percentage x 100 of

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PCDFs/(PCDFs+PCDDs) without and with TEF factors [2,3,6,8,15-19,21,22,24,26,27,29-33].

There is no uniform fingerprint but there are some significant aspects:

a) Concerning the congeners in many exhaust samples, OCDD exhibits one of the highest concentrations. Other congeners with relatively high concentration are HpCDD/Fs.

b) 2,3,4,7,8-PeCDF is among the congeners that contribute most to total toxicity I-TEQ.

c) In general, PCDFs occur in higher concentrations than PCDDs, although there are several references that report similar contributions from PCDFs and PCDDs, or where PCDD concentrations exceed those of PCDFs.

The objectives of this paper are to (i) prove a methodology for mobile sampling of PCDD/F emissions from light-duty diesel vehicles; (ii) compare these results with those obtained by other procedures; (iii) evaluate if other aspects such as catalyst, old or dirty exhaust tailpipes, mileage, fuel, automobile brand, etc., can be studied under real driving conditions; (iv) call attention to the pollution from small generators located on streets and in small shops, hospitals, etc. whose emitted pollutant gases can have a marked influence on the air quality of the surrounding areas; and (v) compare the results obtained from a stationary engine to those obtained on-road.

2. Materials and methods

Three diesel vehicles were selected for sampling: a 5-year-old Renault Kangoo van (RK1) (about 125000 km, 1500 cm^3 cylinder, 2004 model year), another 5-year-old Renault Kangoo van (RK2) (about 125000 km, 1500 cm^3 cylinder, 2006 model year) and a 12-year-old VW Golf passenger car (about 200000 km, 1900 cm^3 cylinder, 2000 model year). All three vehicles are equipped only with a diesel oxidation catalyst (DOC) to reduce hydrocarbons (HCs) and carbon monoxide (CO) emissions, but not with a diesel particulate filter (DPF) arranged in series with the DOC to reduce particulate matter. RK1, RK2 and the VW Golf belong to Euro 3, Euro 4 and Euro 2 stages, respectively. At the moment of sampling, the three vehicles were in a roadworthy condition and had passed all previous inspection tests in accordance with legislation.

The driving route selected for carrying out the tests was representative of a highway route, and the driving conditions were kept constant as far as possible during the samplings. The

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testing speed averaged around 95 km/h (2400 rpm) and a total distance of approximately 100 km was driven on an inclined motorway (slope of around 1.5%) between Alicante and Alcoy (Spain). Half the distance was uphill-, the other half downhill driving. A cold condition test, which comprised the first 10 minutes from the engine start, and a warm condition test, which took place from minute ten till the end, were done with the RK1 van to assess the effect of the engine temperature on the PCDD/F emissions.All samplings were performed from the same lot of standard diesel compliant with EN 590 standard. Tables S4-S6 of the supporting information show the results of the analyses carried out to the test diesel.

Figure 1 shows a scheme of the on-road dioxin sampling train; it travelled inside the vehicle during samplings. This system enables measuring the emissions under real and representative driving conditions. Moreover, different parameters such as the exhaust gas composition were monitored and measured in real time and continuously. The exhaust was sampled directly during on-road operation by means of a modified version of the U.S. EPA Method 23 sampling train. Every effort was made to follow U.S. EPA Method 23 equipment and operational requirements. The sampling train consisted of a probe, filter, condenser, organic sorbent trap, flow meter and gas analyzer (pumping/metering system). The probe was designed specifically for these samplings since the one specified in the original method cannot be used under conditions prevalent during driving. It consisted of a stainless steel tube of 8 mm internal diameter starting inside the exhaust pipe and extending outward from it, forming a 90º angle to it further out as shown in Figure 1. A Teflon® tube connected the probe to a 9 cm glass filter housing containing a 9 cm quartz microfiber filter. The filters were supported in the filter housing by a perforated Teflon disk, sealed with Teflon-coated O-rings.

Figure 1

The particulate matter fraction of the sample was collected in the filter whereas the condensable PCDD/Fs were collected in a glass module containing about 40 g of XAD-2 sorbent resin. The two modifications with respect to U.S. EPA Method 23 were: the filter housing was not heated and the sample gases were not cooled before entering the sorbent module. These two modifications were necessary in view of the fact that no power was

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available due to sampling conditions. In any event, the XAD-2 module inlet temperature was measured and was always below 35ºC, which is slightly above the inlet temperature limit specified in Method 23 but is below the temperature at which the resin begins to decompose. Collection of the condensate (1-2 mL) and rinses of the probe were done to minimize PCDD/F losses.

The exhaust was drawn through the sampling system with an IM 2800-P portable gas analyzer (IM Environmental Equipment Germany GmbH), which was also used as the pump. The sample flow rate was 1.6 L/min and the total sampling time was about 75 min. The sampling took place with the sample probe inlet positioned at the center of the 5 cm internal diameter exhaust pipe, and perpendicular to the gas flow. The sampling was not performed under isokinetic conditions because of the assumption that diesel particulate matter is sufficiently small to follow gas streamlines.

The IM 2800-P portable gas analyzer gives information in real time and continuously about the pumped gas in terms of the concentrations of O_2, CO, CO_2, NO, NO_2 and SO_2. The percentage of CO_2 is calculated from that of O_2 by a mass balance depending on the type of fuel used. Prior to each run, the gas analyzer was calibrated.

The power generator used to carry out the samplings was purchased from Franvicar® and is powered by a 3.8 kW KAMA air-cooled diesel engine; it was fueled with the same standard diesel as the one used in vehicle samplings. PCDD/F samples were collected following U.S. EPA Method 23. The all-glass sampling train consisted of a probe, a filter stage, a cooler, a condensate separator and an adsorber unit. The probe was covered by a stainless steel sheath and heated at 120ºC. The filter housing containing a 9 cm quartz microfiber filter was kept in a heated (120°C), insulated enclosure whose temperature was monitored. The horizontal condenser and the module containing the XAD-2 sorbent resin were cooled using a submersible pump which provides chilled water to the condenser and sorbent trap water jackets. This ensures that the gas sample was not hot before entering the sorbent module. At the back of the sampling train, there was a metering/pumping system to control and measure various parameters such as probe temperature, filter temperature and the gas flow. As in the vehicle samplings, various parameters such as the exhaust gas composition were monitored and measured using the IM 2800-P portable gas analyzer. The particulate matter fraction of

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the sample was collected in the filter whereas the condensable PCDD/Fs were collected in the XAD-2 sorbent resin. The total sampling time was one hour and about 0.7 Nm^3 was sampled. The sampling took place with the sample probe inlet positioned at the center of the 25 cm internal diameter exhaust pipe and perpendicular to the flow. The sampling was not performed under isokinetic conditions for the reasons mentioned previously. During the sampling a 2000 W electric heater was connected to the power generator to guarantee higher fuel consumption and obtain denser exhaust fumes.

For both the vehicle studies and the power generator study, 40 μL of surrogate PCDD/F standard was added to the XAD-2 sorbent prior to the sampling and 40 μL of internal standard prior to sample extraction. The same set of isotopically labeled PCDD/F standards was also added to the filter prior to sample extraction. For the determination of tetra- through octa- CDDs and CDFs the U.S. EPA 1613 method was used. Every step (sample preparation, extraction and concentration, extract cleanup and HRGC/HRMS analysis) was done following the instructions of methods 0023A and 1613. After extraction was completed, the extracts were concentrated for cleanup. Sample cleanup included liquid-liquid extraction with acid and base, and HPLC using silica, alumina and carbon columns which was performed with a Power-Prep[TM] station from FMS (Fluid Management Systems). The filter and the XAD-2 resin were extracted separately with toluene by Soxhlet extraction and analyzed individually, but combined for a single batch of data. Separation and quantification of PCDD/Fs were achieved by high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) 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. Field blanks, laboratory blanks and the capacity to achieve surrogate and internal standard recovery criteria have been used to validate and qualify PCDD/F data. Quality control and quality assurance also included GC performance and MS sensitivity.

3. Results and discussion

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Tables 1 and 2 show the experimental results for the Renault Kangoo vans and the VW Golf car, respectively, along with data on the combustion gases, driving and sampling conditions, amount of PCDD/Fs in the field blanks, PCDD/F congener concentrations and total pg I-TEQ on a Nm^3, km and L fuel basis. The values of PCDD/F are the result of subtracting the blanks values to the corresponding values of the samples to eliminate any contribution apart from that of the samplings.

Tables 1 and 2

Unexpectedly high emission factors have been obtained for the three vehicles studied. The results vary from 7.9 to 12, 0.71 to 0.78 and 0.46 to 1.3 ng I-TEQ/km for the light duty vans RK1, RK2 and the passenger car, respectively. These values are slightly higher or on the same order of the highest available published data: 1.3-9.5 ng I-TEQ/km [7], 0.72-9.5 ng I-TEQ/km [9], 0.91 ng I-TEQ/km [24] and 1.7 ng I-TEQ/km [26]. Tables S7 and S8 of the supporting information show the congener emissions in terms of pg I-TEQ/Nm^3 and pg I-TEQ/km, respectively.It can be observed that oxygen levels fall within the 10.3-13.4 % range, except in the case of test 3 (cold), where the oxygen and carbon monoxide concentrations are higher than in the other tests; this fact is consistent with the initial period of engine warming. The levels of CO and NO_x are below or close to the emission limits proposed in the European legislation for new vehicles [34] which establish values of 1.0, 0.80 and 0.63 g CO/km in Euro 2, Euro 3 and Euro 4, respectively, and values of 0.65 and 0.33 g NO_x/km in Euro 3 and Euro 4, respectively. The sampled volume is much smaller than that of the emitted exhaust gas but can be considered as representative of the total volume.

As to the concentrations of 2,3,7,8-substituted PCDD/Fs, OCDD, 1,2,3,4,6,7,8-HpCDD/F and 1,2,3,6,7,8-HxCDD, they constitute the four dominant congeners emitted by both RK1 and RK2. For the passenger car operating with the oxidation catalyst, the dominant congeners are OCDD, 1,2,3,4,7,8,9-HpCDF, 1,2,3,4,7,8-HxCDD and 1,2,3,6,7,8-HxCDD. These results are consistent with the data reported in several papers [16,19,22,24,26,33,35], with the exception of the HxCDD congeners mentioned above. Only the study made by the California Air Resources Board (CARB) [3] reported significant concentrations of the HxCDD homologue

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in heavy-duty diesel exhaust. For the passenger car operating without oxidation catalyst, the PCDD/F patterns are dominated by OCDD/F and 1,2,3,4,7,8,9-HpCDF, while there is no prevalence of the HxCDD homologue.

The existing differences in dioxin concentration between tests 1 and 2 (RK1 van) are attributed to dissimilarities in driving conditions considering the difficulty in maintaining driving conditions constant. The same consideration is made for the differences in dioxin concentration between tests 5 and 6 (RK2 van).

Concerning test 3 (cold conditions) and test 4 (warm conditions), which were carried out 2 days apart, it can be observed that the emission of PCDD/Fs was higher in the former than the latter. These results are consistent with the fact that in the cold period the formation of char particles and CO is greater than during the subsequent warm period, indicating that the combustion is not perfect and consequently there can be a parallel formation of intermediate organic compounds that can lead to the formation of many compounds, including PCDD/Fs. Regarding Table 2, it is important to note that the DOC reduces PCDD/F emissions by approximately 65%. Dyke et al. [22] claimed that the DOC had in their testing a major effect of reducing PCDD/F emissions by approximately 80%, from 97 to 23 pg I-TEQ/L of fuel. In all runs, the concentration of PCDDs in exhaust gases exceeds that of PCDFs.

Figure 2 shows the distribution of congeners for the light duty vehicles RK1 and RK2, expressed as pg I-TEQ/Nm^3. The compounds that contribute the most to the total toxicity in the case of the RK1 van are 1,2,3,6,7,8-HxCDD (38-45%) and 1,2,3,7,8,9-HxCDD (18-19%) from among the PCDDs, and 2,3,4,7,8-PeCDF (3.8-5.1%) from among the PCDFs. The pattern changes when it comes to the cold test and the main contributors now are 2,3,7,8-TCDD (25%), 1,2,3,7,8-PeCDD (23%) and 2,3,4,7,8-PeCDF (8.3%). As far as the RK2 van is concerned, the total toxicity is still dominated by PCDDs, 1,2,3,7,8-PeCDD (30-34%), 1,2,3,6,7,8-HxCDD (9.5-21%), 2,3,7,8-TCDD (12-14%) and 2,3,4,7,8-PeCDF (6.3-23%) contributed most. When we compare these results with those reported in the literature and compiled in Table S3, we see that several authors [17,19,24,27] reported 2,3,4,7,8-PeCDF, 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD as the main contributors to toxicity. However, we found

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no papers mentioning the high contributions of 1,2,3,6,7,8-HxCDD and 1,2,3,7,8,9-HxCDD. In all runs, the PCDD contribution to I-TEQ is greater than that of the PCDFs.

Figure 2

The TEQ-weighted congener distribution of the diesel passenger car is shown in Figure 3. The majority of the I-TEQ contribution comes from 2,3,7,8-TCDD (32%), 1,2,3,4,7,8-HxCDD (16%), 1,2,3,6,7,8-HxCDD (13%) and 2,3,4,7,8-PeCDF (9.0%) for the vehicle operating with the diesel oxidation catalyst, and 1,2,3,7,8-PeCDD (23%), 2,3,7,8-TCDD (15%), 2,3,4,7,8-PeCDF (11%) and 1,2,3,7,8,9-HxCDF (8.8%) for the vehicle operating without the catalyst. Figure 3 also shows the effect of the catalyst on the reduction of PCDD/F emissions.

Figure 3

RK2 and the passenger car release PCDD/Fs on a comparable level and reproduce comparable congener patterns. However, the emission strength and the pattern of RK1are quite different. Most remarkable are the differences between both Renault Kangoo. Both vans were 5 years old and about 125000 km at the moment of sampling. However, RK1 is from the year 2004 and RK2 from 2006. It is possible that the engine of RK2 worked more efficiently which results in a better combustion and lower emissions of incomplete combustion products. Moreover, RK2 belongs to Euro 4 whereas RK1 belongs to Euro 3. That means that RK1 is allowed to emit 0.07 g/km of particulate matter whereas RK2 only 0.04 g/km. These two aspects would justify the difference between RK1 and RK2 with respect to the emission strength but not with respect to the pattern. There is no clear explanation about the difference in the patterns but since the pattern of RK1 is the same for the three samplings carried out with this van, it could be thought that some unexplained effect of the DOC could be taking place.

In general, vehicle engines are not very efficient, which is demonstrated by their considerable emissions of incomplete combustion products (CO and HCs). Incomplete combustion in

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engines can increase PCDD/F emissions. There is a temperature gradient from in-cylinder combustion to actual exhaust release at the tailpipe-end: combustion temperatures in diesel engine are about 2000 ºC, diesel engine-out exhaust temperatures range between 200 and 400 ºC and tailpipe exhaust temperatures typically are 180 ºC. PCDD/Fs can be formed in both the engine and exhaust system. Finally, chlorine content is important since chlorine input concentration and dioxin output concentration are related when concentrations of chlorine in the feed are small (less than 1%) and when poor combustion occurs [36]. Wang et al. [37] determined that the formation mechanisms of PCDD/Fs are influenced by whether the chlorine content in fuels and wastes is over or below 0.8-1.1 %. When the chlorine level is below that value, the formation of PCDDs dominates. This conclusion is in agreement with our results.

Therefore, the residence time of the exhaust gas in the temperature range of 200-800 °C, the quantity of available chlorine and the presence of fly ash and metals (which serve as catalysts) affect the formation of dioxins [38].

Ballschmiter et al. [2] and Marklund et al. [5] reported similarities in the congener patterns in the used motor oil and in the car exhausts, and those found in fly ash and stack emissions from municipal waste incinerators. Similarities in the PCDD/F patterns could be a consequence of similarities in the PCDD/F formation mechanisms.

Several authors [39-42] found that dioxin versus furan emissions during the start-up of a municipal waste incineration plant were greater than under steady conditions. Neuer-Etscheidt et al. [39] proposed that the combustion conditions during heat-up combined with residual deposits were sufficient to promote the formation of halogenated products of incomplete combustion. These findings could have a link with the results obtained in this study, in which higher emissions of PCDDs than PCDFs are observed, considering that the time needed for the vehicle engine to reach steady conditions constitutes an important part of the total sampling time. Inside the tailpipe the combination of the combustion conditions during the start-up with the accumulated soot could boost the formation of considerable amounts of PCDD/Fs. Other authors [2,17,27] also reported more PCDDs than PCDFs in exhaust gases. Tejima et al. [41] estimated that around 41% of the total annual emissions of dioxins from MSW incinerators could be attributed to the start-up period. This percentage corresponds to 3

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start-ups per year so the contribution of the start-ups to the total emissions of dioxins is considerable. This fact would also explain the relatively high values obtained in this study since the start-up period represents an important part of the total sampling time, which does not occur in studies conducted by other researchers. Moreover, the vehicles are only equipped with a DOC and not with a DPF arranged in series with the DOC. This has the evident consequence of an exhaust with a higher concentration on particles. The combination of these particles with the diesel engine-out exhaust temperatures (200-400 ºC) can create the perfect atmosphere for an extra formation of PCDD/Fs. The various results obtained thus far suggest that the system described in this study is useful for analysing cases in which there is a considerable level of PCDD/F emissions, as well as for assessing vehicle emissions on short journeys. However, for emission factors of around 50 pg/Nm^3 or lower, the sampling time and/or the sampled volume should be increased by using a portable analyzer of greater pumping capacity or by increasing the distance over which the tests are conducted. The methodology adopted is also useful for determining emission factors under real driving conditions: start/stop, driving uphill/downhill, changing velocity, windy/cold/warm weather conditions, etc.

Table 3 shows PCDD/F emissions, data on the combustion gases, sampling conditions, amount of PCDD/Fs in the field blanks and emission factors in terms of pg I-TEQ/Nm^3 for the power generator. It is important to note that all the isomers from TCDD/Fs to OCDD/Fs were detected although the values are considerably lower than in the case of the vehicles. This can be due to the fact that (i) the distance from the engine to the sampling point in the power generator is very short. This fact together with the fast cooling of the exhaust in the sorbent trap have the consequence that the time spent by the exhaust in the 200-450 ºC temperature region is minimized which results in lower PCDD/F emissions, (ii) power generators are designed so that their engines work with a very poor fuel/air mixture. They do not need to develop power as vehicles do. They just need to produce electricity and that is why their fuel/air mixture is very poor. A lower amount of diesel in the mixture involves a better combustion and a better combustion implicates lower PCDD/F emissions, and (iii) there is no residual carbon deposits in the tube placed after the tailpipe to collect the exhaust gas. Geueke et al. [14] reported emission factors of between 1.5 and 6 pg I-TEQ/Nm^3, which are lower

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than the values obtained in this study: 31-78 pg I-TEQ/Nm^3. The dominant congeners are OCDD/F and 1,2,3,4,6,7,8-HpCDD/F as reported by several authors [6,19,33,35].

Table 3

Figure 4 shows the TEQ-weighted PCDD/F profiles obtained for the emissions from the power generator. As in the case of the vehicles, PCDDs are more prevalent than PCDFs. Among the PCDDs, the congeners that contribute most to the total toxicity are 1,2,3,6,7,8-HxCDD (23-24%), 1,2,3,7,8-PeCDD (14-19%) and 2,3,7,8-TCDD (13-24%) whereas among the PCDFs, 2,3,4,7,8-PeCDF (7-9%) contributes the most. The power generator had neither a particle filter nor an oxidation catalyst and the tube placed after the tailpipe to collect the exhaust gas, in which the sample probe was inserted, was new and soot-free. Thus, the fact that the emission factors are lower than those of vehicles is also consistent with the assumption of possible effects on the formation of PCDD/Fs due to the presence of soot in the tailpipe.

Figure 4

4. Conclusions
An innovative methodology for measuring PCDD/F emissions from light-duty diesel vehicles in on-road conditions has been tested and characterized. This system enables measurements of the emissions under real and representative driving conditions and can be appropriate to estimate emission factors of light-duty diesel vehicles. The vehicles investigated have shown to be an important source of dioxins under the conditions studied. However, vehicles with other diesel engine combustion technology as well as other driving and traffic conditions may lead to considerably different emissions. It is not clear to what extent this limited study is representative of the PCDD/F emissions from the on-road light-duty diesel population. Obtaining reliable estimates of the emission factors of this kind of vehicles would require an extensive sampling program which considered multi-vehicles and multi-routes. The results obtained for the power generator show that these types of equipment should also be

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considered as important contributors to the levels of PCDD/Fs emitted into the atmosphere. Comparing PCDD/F emissions from vehicles and power generators could prove useful for discussing the effects of other parameters such as the type of fuel and the presence of soot in the exhaust tailpipe.

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Figure 4. Emission factors (pg I-TEQ/Nm^3) of the power generator. Tests 9 and 10: cold started sampling.

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a) RK1

b) RK2

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Table 1

ACCEPTED MANUSCRIPT
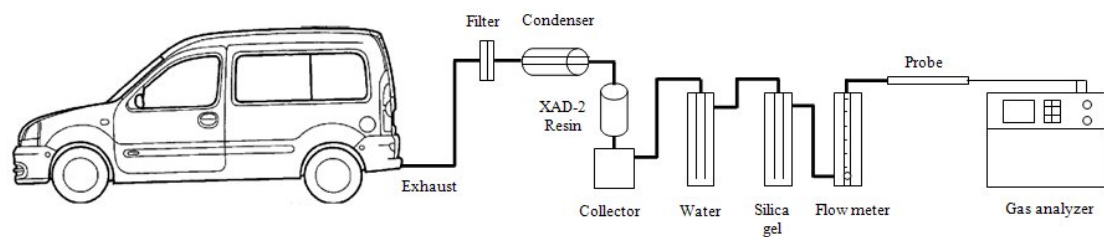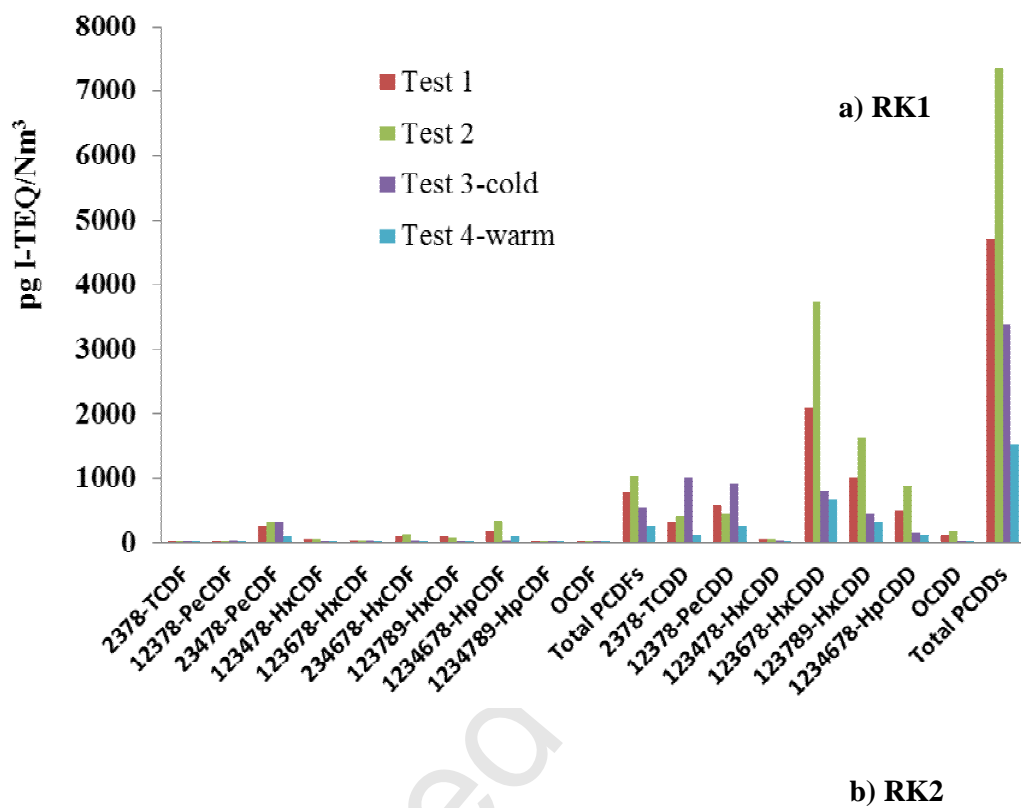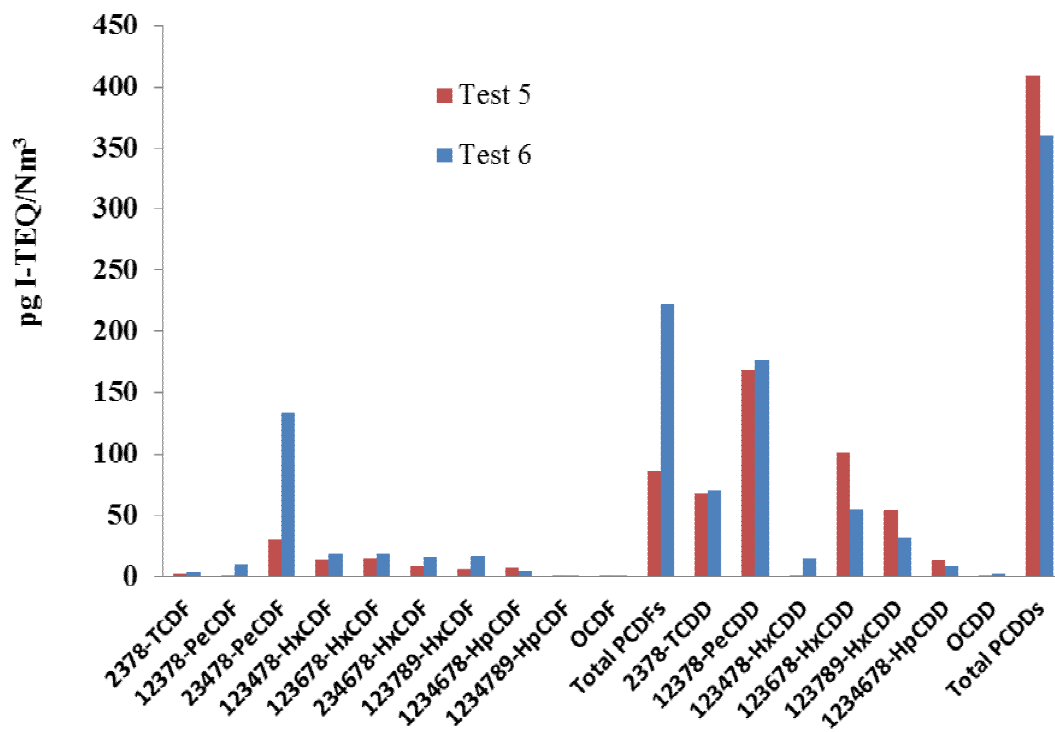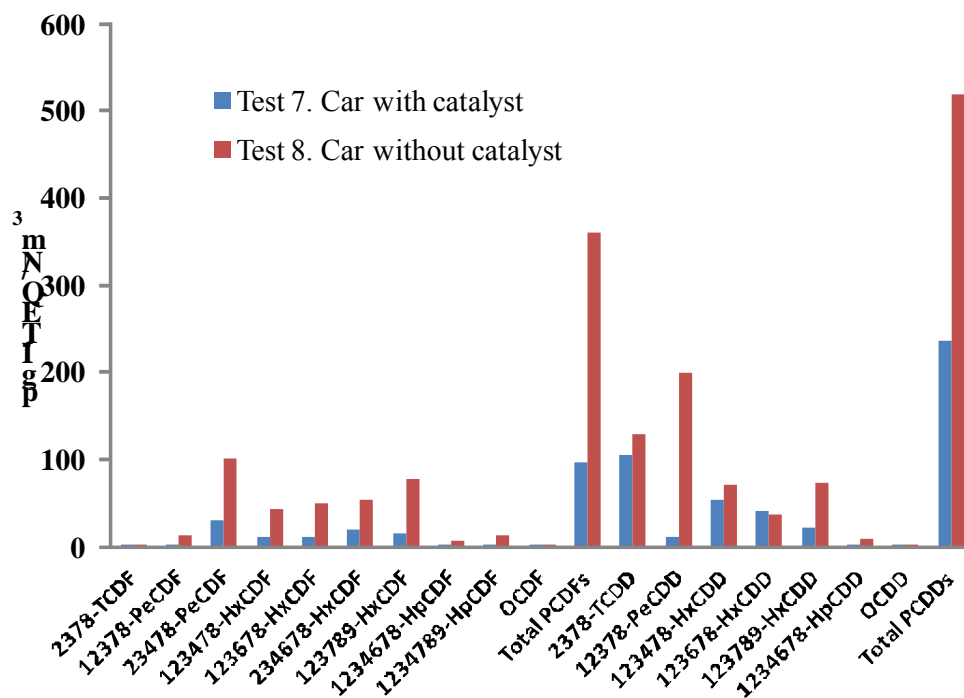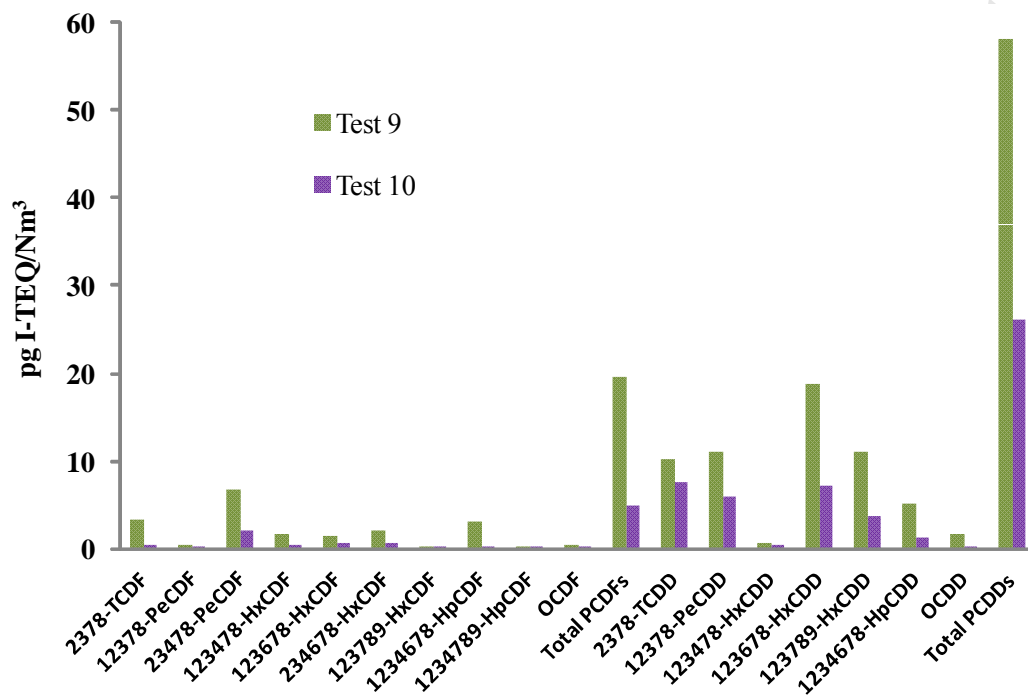
Table 1. Emission factors of the two diesel vans

		Diesel RK1						Diesel RK2	
	Field Blank	Test 1	Test 2	Field Blank	Test 3 (cold)	Test 4 (warm)	Field Blank	Test 5	Test 6
O_2 (%)		12.5±2.2	10.3±2.2		15.9±1.9	13.4±2.5		12.9±2.3	12.5±2.0
CO_2 (%)		6.4±1.7	6.2±1.7		3.5±1.4	5.3±1.9		5.8±1.8	5.9±1.5
CO (ppm)		76±180	93±232		163±126	73±149		88±190	114±152
CO (g/km)		0.14	0.17		0.54	0.14		0.16	0.19
SO_2 (ppm)		14±10	3±3		6±3	16±6		166±93	231±76
NO (ppm)		89±58	108±89		32±10	54±16		107±76	130±103
NO_2 (ppm)		3±3	8±8		1±1	3±2		64±18	85±17
NO_x (g/km)		0.18	0.23		0.12	0.12		0.39	0.47
Emitted gas (Nm^3)		136	138		26.5	125		148	129
Sampled volume (Nm^3)		0.123	0.115		0.0109	0.0780		0.104	0.0864
Distance (km)		95	95		10	84		103	95
Time (min)		76	74		8	58		74	65
Velocity (km/h)		95	95		95	100		100	105
	pg	pg/Nm^3		pg	pg/Nm^3		pg	pg/Nm^3	
2378-TCDF	1.2	106	144	1.1	247	94.9	0.65	26.8	28.9

12378-PeCDF	7.6	569	224	4.2	667	117	3.7	7.90	196
23478-PeCDF	8.6	540	633	5.2	658	185	4.0	62.1	267
123478-HxCDF	10.8	579	649	6.6	256	153	4.1	138	194
123678-HxCDF	9.4	451	401	4.9	402	132	3.5	149	187
234678-HxCDF	7.9	953	1290	4.1	439	318	3.5	86.7	162
123789-HxCDF	7.1	1050	846	3.9	101	56.4	2.5	67.5	168
1234678-HpCDF	11.2	16800	34900	7.0	3360	8940	4.7	724	416
1234789-HpCDF	5.2	478	355	4.0	64.0	59.0	3.3	20.8	72.0
OCDF	6.1	6910	11200	5.9	3760	1850	5.4	220	101
2378-TCDD	1.6	320	412	1.1	1010	124	1.0	67.8	70.7
12378-PeCDD	8.5	1160	912	5.3	1830	488	4.0	336	353
123478-HxCDD	8.4	681	674	5.0	429	114	4.2	18.1	147
123678-HxCDD	11.1	20900	37400	6.8	8120	6820	4.4	1020	551
123789-HxCDD	8.7	10200	16300	5.5	4490	3180	4.2	542	316
1234678-HpCDD	7.6	51400	87400	4.8	16000	12600	4.4	1370	874
OCDD	11.8	118000	172000	12.2	23100	22600	14.5	1730	2130
TCDFs		3530	5090		6200	1550		608	354
TCDDs		12800	17100		23700	7590		2700	1310
PeCDFs		3640	4600		5380	4280		684	661
PeCDDs		36700	62800		37100	22000		4680	2080

HxCDFs	20900	37800	6500	12800	911	663
HxCDDs	308000	278000	52600	50400	7990	3470
HpCDFs	34300	59900	5380	16000	1130	1110
HpCDDs	110000	200000	14100	25400	3790	2480
Total pg I-TEQ/Nm^3	5500	8380	3950	1790	495	582
Total pg I-TEQ/km	7850	12100	10500	2670	708	783
Total pg I-TEQ/L fuel	123000	191000	101000	41900	11100	12300

Table 2

Table 2. Emission factors of the diesel VW Golf car

	Field Blank	Test 7 Car with catalyst	Test 8 Car without catalyst
O_2 (%)		12.1±2.6	12.9±2.6
CO_2 (%)		6.2±2.0	5.6±2.0
CO (ppm)		353±63	565±66
CO (g/km)		0.60	1.1
SO_2 (ppm)		37±25	54±26
NO (ppm)		272±167	181±132
NO_2 (ppm)		57±20	83±20
NO_x (g/km)		0.66	0.62
Emitted gas (Nm^3)		125	139
Sampled volume (Nm^3)		0.094	0.092
Distance (km)		91	92
Time (min)		66	67
Velocity (km/h)		100	100
	pg	pg/Nm^3	
2378-TCDF	0.68	14.5	12.2
12378-PeCDF	3.6	68.1	252
23478-PeCDF	8.8	60.0	201
123478-HxCDF	3.2	117	438
123678-HxCDF	3.1	109	506
234678-HxCDF	5.2	201	533
123789-HxCDF	4.8	149	778
1234678-HpCDF	10	177	627
1234789-HpCDF	3.7	229	1330
OCDF	7.4	177	1890
2378-TCDD	3.1	106	129
12378-PeCDD	5.3	23.7	399
123478-HxCDD	1.2	539	707
123678-HxCDD	10.2	423	368
123789-HxCDD	5.1	211	727

1234678-HpCDD	6.6	50.8	876
OCDD	9.3	193	1650
TCDFs		14.5	205
TCDDs		106	275
PeCDFs		128	453
PeCDDs		636	996
HxCDFs		577	2260
HxCDDs		1920	1980
HpCDFs		406	2140
HpCDDs		1150	2560
Total pg I-TEQ/Nm^3		332	880
Total pg I-TEQ/km		455	1330
Total pg I-TEQ/L fuel		7150	20900

Table 3

Table 3. Emission factors of the power generator

	Field Blank	Test 9	Test 10
O_2 (%)		11.8±0.3	14.8±0.2
CO_2 (%)		6.4±0.2	3.7±0.1
CO (ppm)		479±24	476±23
SO_2 (ppm)		0±0	4±1
NO (ppm)		623±19	353±11
NO_2 (ppm)		66±2	41±2
Sampled volume (Nm^3)		0.671	0.635
Time (min)		60	60
	pg	pg/Nm^3	
2378-TCDF	0.93	32.7	4.58
12378-PeCDF	3.2	8.78	4.26
23478-PeCDF	4.0	13.5	4.10
123478-HxCDF	5.3	16.1	4.73
123678-HxCDF	3.9	14.0	7.10
234678-HxCDF	4.6	20.4	6.79
123789-HxCDF	3.7	3.27	2.05
1234678-HpCDF	6.8	316	18.0
1234789-HpCDF	3.3	32.4	2.05
OCDF	4.7	337	24.6
2378-TCDD	1.5	10.1	7.58
12378-PeCDD	4.9	21.9	11.7
123478-HxCDD	4.7	5.66	4.10
123678-HxCDD	7.0	189	71.8
123789-HxCDD	5.1	110	37.4
1234678-HpCDD	4.4	515	116
OCDD	7.1	1590	200
TCDFs		623	102
TCDDs		587	175
PeCDFs		226	84.3
PeCDDs		843	337
HxCDFs		362	98.2

HxCDDs	1390	494
HpCDFs	454	20.0
HpCDDs	630	116
Total pg I-TEQ/Nm^3	77.9	31.1