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On-Road Sampling of Diesel Engine Emissions of Polychlorinated Dibenzo-*p*-Dioxin and Polychlorinated Dibenzofuran

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ABSTRACT

The first known program to sample mobile heavy duty diesel engine emissions for polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofuran ("PCDD/F") during highway and in-city driving routes was conducted. The post-muffler stacks of two diesel tractors hauling loaded trailers were sampled with a modified EPA Method 23 train. Extensive care was taken to ensure high data quality including sampling large volumes, repeat measurements, and high resolution mass spectroscopy. Analytical results from five tests showed significant yields of PCDD/F. The average emission factor obtained from this work was 0.029 nanograms (ng) international toxic equivalency (I-TEQ)/km. The upper limit of the 95% confidence interval provides an estimated emission factor of 0.106 ng I-TEQ/km. Based on these values and 1993 diesel truck travel estimates, the projected U.S. annual emissions from on-road diesel vehicles are 4.4 g I-TEQ/yr with a 95% confidence upper bound of 16.1 g I-TEQ/yr.

INTRODUCTION

The contribution of heavy duty diesel vehicles (HDDVs) to anthropogenic sources of PCDD/F remains relatively uncertain. Some of the first evidence[1)] that PCDD/F might be emitted from vehicular engines suggested that incomplete combustion and the presence of chlorine in fuel or fuel additives led to their formation. Tests[2)] on a light duty (automobile) diesel vehicle in Germany, found 0.024 ng international toxic equivalency (I-TEQ)/L or approximately 0.0024 ng I-TEQ/km. A multi-university study[3)] in Germany reported that emissions from diesel truck engines were approximately 0.070 to 0.081 ng I-TEQ/L. Analysis[4)] of plume emissions from a diesel-fueled bus showed PCDD/F concentrations at 0.010 ng I-TEQ/L. Recent vehicle sampling in Germany[5)] showed that a load-carrying diesel emitted 0.077 ng I-TEQ/L of fuel. At an assumed 5.5 km/L, this results in an emission factor of 0.014 ng I-TEQ/km. Passenger vehicle diesels emitted slightly less at 0.048 ng I-TEQ/L of fuel.

A tunnel study[6)] in Norway estimated that HDDV emissions results were about 9.5 ng TEQ/km in the uphill section (3.5% grade) and about 0.720 ng TEQ/km in the downhill section (values are presented in units of Nordic TEQ which should be within 3-6% of I-TEQ) assuming a fuel economy of 5.5 km/L. From data of Reference 7, an emission factor of 0.065 ng I-TEQ/km

was estimated[8] for road traffic by comparing tunnel sampling with background air sampling outside of the tunnel. This work was conducted in 1991 in Antwerp, Belgium. More recent results[9] derived from a tunnel study sponsored by the American Petroleum Institute (API) indicated an average emission rate of 0.170 ± 0.080 ng I-TEQ/km.

PCDD/F emission data from HDDVs are scarce and are represented by dynamometer sampling results and tunnel air sampling studies. This work provides a third method of emission assessment through direct, on-road sampling. In this work, a HDDV was fitted with a modified EPA Method 23 sampling train. Emissions were sampled during road routes meant to be representative of city and highway driving. This mode of emission assessment provides sampling during actual driving conditions but limits sampling to only a subset of the current vehicle population, geographical factors, and driving-style characteristics. Emission factor assessment for HDDVs will most appropriately be a combination of these three types of sampling programs.

EXPERIMENTAL

The HDDV sampled was a 1991 Freightliner diesel tractor trailer with a 10.3 L, 6-cylinder Caterpillar engine, representative of the first generation of computerized fuel controlled vehicles manufactured in the U.S. The truck used highway diesel fuel for a simulated in-town, delivery route termed "CITY." This route consisted of nonhighway driving with several shopping center stops, incorporating acceleration, shifting, and idling to be representative of urban driving conditions. Highway diesel fuel was also used for the highway route termed "HWY" which consisted of interstate highway driving to represent long-haul conditions. The truck was fully loaded [20.4 Mg (45,000 lb)] during both routes to reflect heavy-load driving conditions. The driving routes were traversed in triplicate and identified as "Freightliner Run #, Route," (example: FL4, CITY). The CITY sampling speeds averaged about 35 km/h, and the HWY sampling speeds averaged about 90 km/h.

The truck was equipped with gas sampling equipment located on the trailer bed and digital monitors for the sampling systems in the truck cabin. Extensive details on the vehicle gas sampling and operating parameter monitoring system can be found elsewhere.[10] PCDD/F samples were collected using a modified Method 23 sampling train. Every effort was made to follow EPA Method 23 equipment requirements with a few exceptions designed to make the system compatible with the on-road sampling environment. The sampling probe was positioned downstream of the exhaust system muffler. The probe inlet was positioned perpendicular to the exhaust flow at the centroid of the 12 cm inner diameter exhaust pipe. Isokinetic sampling was not performed or considered critical based on the assumption that diesel particulate matter (PM) is sufficiently small that it will tend to follow gas streamlines. The sampling flow rate was maintained as constant as possible during testing. Although exhaust flow rate varies with engine speed and load (overall exhaust flow varied by roughly a factor of 4), the mean and median exhaust flow rates were very similar.

Extensive care was taken to ensure high data quality and that the sample gathered was representative of the HDDV's actual on-road emissions (additional details can be found in Reference 11). The samples were analyzed following EPA Method 23 requirements. The filter and XAD-2 sample fractions were extracted separately but combined for a single analysis (earlier work had shown that less than 2% of the total PCDD/F mass was found on the filter associated with the PM). Recoveries of presampling surrogates and internal standards were found to be acceptable per Method 23 criteria. The data quality was validated primarily through the ability to achieve presampling spike recovery criteria. The results from analysis of field and laboratory

blanks and matrix spikes were also used for data quality validation. Also, the mass of analyte present in the sample relative to the amount present in blanks was used as a data validation method. Detection level magnitudes were all considered in the data validation process.

RESULTS

Because the XAD-2 used for the Freightliner tests was prescreened for low contaminants and restricted to a single XAD-2 lot, blank levels had minimal influence on the target analytes. A few of the analytes were recorded as the estimated maximum potential concentration (EMPC) in which the analyte is detected but did not meet all of the Method 23 criteria (e.g., isotopic abundance).

The third CITY test (FL6, CITY) was invalidated because the cooling water line to the XAD-2 module broke during sampling, heating the XAD-2 and resulting in unacceptably low standard recoveries. For some of the target isomers, the concentration ratio to the maximum blank level is greater than 10, although the vast majority are less than 10. Higher ratios ensure greater confidence regarding detectability.

DISCUSSION

The emission factors are shown in Table I. These calculations are made without blank corrections, with target analytes at the detection limits considered as zeros, and using the value of the EMPCs.

The HWY tests resulted in less variability than the two usable CITY tests, and the average emission factor for the HWY tests (0.0151 ng I-TEQ/km) was a factor of 3 below the two CITY TESTS (0.0499 ng I-TEQ/km). However, the two CITY tests were highly variable (0.0030 versus 0.0968 ng I-TEQ/km). One of the two CITY tests was contained within the 95% confidence range of the HWY tests.

This limited data set suggests that HWY yields may be more consistent and may be lower, on average, than CITY yields. Further testing is necessary to support these observations.

It is clear that the five test runs had large variability in emission factors. The ratio of the highest to lowest yields (both CITY runs) is over 30/1. This data variability is also supported by variability in total (mono- to octa-dioxin and -furan) yields. Total yields (not shown) from run to run showed a maximum variation of over 5/1.

In all runs, PCDF was more prevalent than PCDD. The PCDDs are dominated by the tetra-, hepta-, and octa-CDD homologues (TCDD, HpCDD, and OCDD, respectively) while PCDF is dominated by the mono- and di-CDF homologues (MCDF and DCDF, respectively). The PCDD/PCDF (tetra- to octa-homologues) ratio varied between 0.04 and 0.82 which compares well with other work[5)] which had a ratio of 0.1. One apparent distinction between the CITY and HWY results is that the HWY PCDD/PCDF ratios never exceeded 0.29 and the CITY PCDD/PCDF ratios never went below 0.48.

The 2,3,7,8-substituted congener (I-TEQ) profile varies widely across the five samples (data not shown). Even when these values are normalized by the total PCDD or PCDF I-TEQ for each run, the normalized distribution still shows marked variation. For example, in FL4 CITY the 1,2,3,4,6,7,8 HpCDD congener contributes over 60% of the PCDD-related I-TEQ; whereas, none of the other tests exceed a 20% contribution for this congener. This large variation in 2,3,7,8-substituted congener distribution suggests a lack of mechanistic constancy even among similar driving routes.

The HWY- versus CITY-averaged 2,3,7,8-substituted congener distribution (Figure 1)

shows that the majority of the I-TEQ contribution comes from the penta- and hexa-CDF (PeCDF and HxCDF, respectively) homologues, followed closely by the TCDD and penta-CDD (PeCDD) homologues. In all runs, the PCDF contribution to I-TEQ is greater than that of PCDD.

The total tetra- through octa-CDD, CDF values range from 18 to 41 times those of their respective I-TEQ values.

The average emission factor for the single truck, two-driving-route tests was 0.029 ng I-TEQ/km with the upper limit of the 95% confidence interval at 0.106 ng I-TEQ/km. Based on 152 billion km of U.S. HDDV driving in 1993[12,13)] and the assumption that these values are representative of average national HDDV emission factors, this results in an average emission estimate of 4.4 g I-TEQ/yr with a 95% confidence upper bound of 16.1 g I-TEQ/yr. The 95% confidence range of these emission factors overlaps those of (for example) 0.065 ng I-TEQ/km (Belgium tunnel study[8)]), 0.170 ± 0.080 ng I-TEQ/km (U.S. tunnel study[9)]), 0.014 ng I-TEQ/km (vehicle study[5)], value estimated in this work), and 0.002 ng I-TEQ/km (bus plume,[4)] value estimated in this work). The 1- to 2-order of magnitude variation in these emission factors is not surprising given the wide range of sampling conditions and the variation evidenced within this current work.

It is not clear to what extent this single-truck, two-driving-route sample is representative of the PCDD/F emissions from the on-road, U.S. HDDV population. Clearly there is substantial variation in measurements among the five valid tests of this work. Obtaining high confidence estimates of the U.S. HDDV emission factors would require an extensive multi-vehicle, multi-route sampling program. Sufficient repeats will be required for statistical certainty, as evidenced by our variation in excess of a factor of 30 for the same-truck, same-driving-route emission factor. Alternatively to a large, multivehicle sampling program, identification of potential engine- and/or fuel-specific factors that are critical to the formation mechanism of PCDD/F could limit testing to a subset of relevant engine types or fuels. This would provide emission factors relevant to different categories of the HDDV fleet and provide more accurate emission estimates.

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Table I. On-Road, Heavy Duty Diesel Vehicle PCDD/F Sampling Results.

Test #	Total mono to octa (ng/m^3)	I-TEQ ng/m^3	I-TEQ ng/L	I-TEQ ng/mile	I-TEQ ng/km
FL1, HWY	1.1700	0.0014	0.0293	0.0188	0.0117
FL2, HWY	0.2870	0.0020	0.0477	0.0298	0.0187
FL3, HWY	0.1920	0.0016	0.0347	0.0239	0.0150
AVG, FL HWY	0.5497	0.0017	0.0372	0.0242	0.0151
STD DEV	0.5393	0.0003	0.0095	0.0055	0.0035
Upper 95% Conf. Limit	1.6283	0.0023	0.0562	0.0353	0.0220
FL4, CITY	0.0940	0.0002	0.0051	0.0048	0.0030
FL7, CITY	0.3540	0.0061	0.1736	0.1549	0.0968
AVG, FL CITY	0.2240	0.0032	0.0893	0.0798	0.0499
AVG, FL HWY + CITY	0.4194	0.0023	0.0581	0.0464	0.0290
STD DEV, FL HWY + CITY	0.4309	0.0023	0.0664	0.0613	0.0383
Upper 95% Conf. Limit	1.2813	0.0068	0.1908	0.1691	0.1057

No Blank corrections. Detection limits considered as zeros. EMPCs used as values.

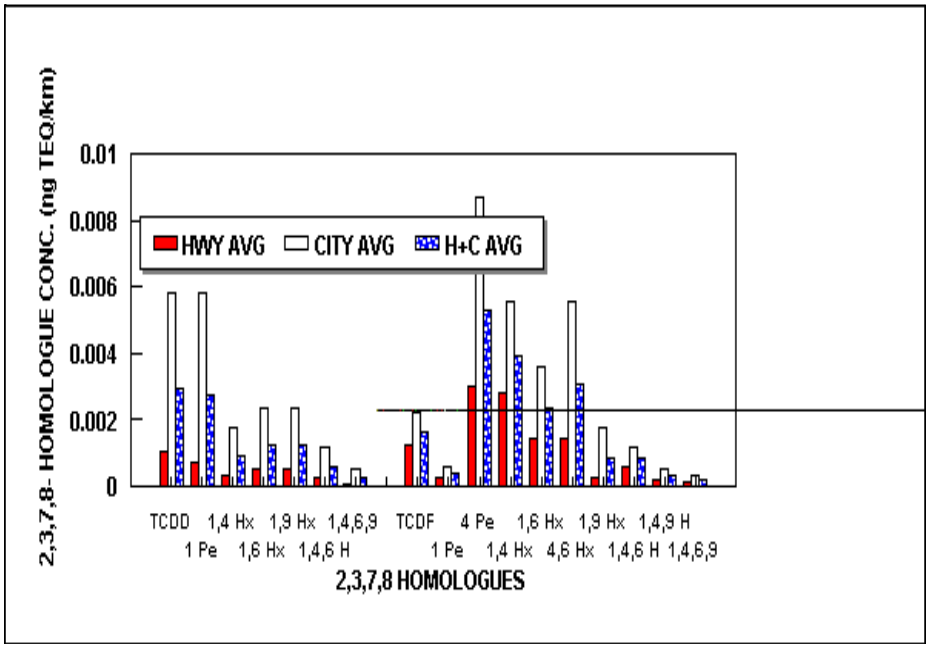

Figure 1. Distribution of I-TEQ among the 2,3,7,8-substituted homologues for averaged HWY and CITY driving routes.