STUDY ON THE EFFECT OF CHLORINE IN LUBRICATING OIL ON EMISSIONS OF PCDD/F FROM A DIESEL ENGINE

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Introduction

In 2004 a test programme was initiated to determine whether the chlorine content of lubricating oils had a measurable effect on emissions of PCDD/F and PCB from internal combustion engines. The project is part of a life-cycle assessment on the environmental impacts of lubricants designed to determine what the effect of a restriction on chlorine content in oil would have on the life-cycle impacts.

A review of the literature showed that no detailed study on the effects of chlorine in engine oil on emissions of dioxins had been carried out, although one or two tests had been included in other programmes using different oil formulations. Essers *et al* carried out a series of tests on a number of engines in order to assess emissions of PCDD/F from petrol and diesel vehicles[1]. Results from these tests appeared to show that emissions increased when using low chlorine oil.

An outline of the testing and initial data from this programme was published in the proceedings of the Dioxin 2005 meeting[2]. Results from the first eleven runs indicated that no effect could be seen of chlorine content of the lubricating oils on emissions of PCDD/F or PCB from the engine. This paper covers the extension of testing for conditions with two levels of chlorine in the fuel and for the engine with the diesel oxidation catalyst (DOC) removed as well as results from analysis of the fuel and lubricating oils.

Materials and Methods

Since emissions of dioxins from vehicles tend to be extremely low, a test programme was designed that would provide a real-world condition but would maximise the possibility of detecting effects related to the oil.

The very widely used VW 1.9 TDi engine was selected and the oils were formulated with standard components to give a realistic range of residual chlorine. The engine was run on a computer-controlled dynamometer under steady-state conditions to enable better repeatability. The conditions chosen also ensured reasonably high oil consumption. Single batches of stock reference fuels were used. For tests 18-23 fuel with a chlorine content of 2.52 ppm was used, this was in the middle of the range we measured at fuel supply outlets in Europe, for all other tests fuel with a chlorine content of 0.71 ppm was used, this was at the lower end of the range of diesel samples we analysed.

The engine was flushed three times between runs for each test to ensure that there was minimal cross-contamination of the lubricating oils from one test to the next.

The three oils were used for the tests were derived from a fully formulated lubricant meeting the performance of a 5W-30 ACEA A3/B3/B4/C3, MB229.31. with residual chlorine controlled by the dispersant choice in the range that might be expected in practice (12ppm, 131ppm, 259 ppm).

For the tests 1-27 the engine was fitted with the diesel oxidation catalyst (DOC) that comes as standard. For two tests a diesel particulate filter (DPF) was fitted. For tests 28-40 the DOC was removed, in addition a five-hour conditioning run was introduced based on an autobahn cycle replacing the hour-long conditioning run used previously.

Sampling was by the "filter-condenser" method based on the standard US EPA method 23 and in line with the European standard EN 1948. The apparatus consisted of a heated

titanium probe inserted into the exhaust, a filter (Whatman GF-A) to remove particulate matter held in an oven at under 125ºC, a condenser, resin trap (XAD-2 resin), followed by moisture removal, pump and dry gas meter. Sample extraction and analysis for target congeners and homologue groups was according to EN 1948 by high-resolution gas chromatography and mass spectrometry. All glassware and resin was laboratory prepared for each test and no field clean-up was used.

Results and Discussion

Tests 1-18 and test 26 were conducted with the engine fitted with DOC and using three oils with 12 ppm, 131 ppm and 259 ppm of chlorine and fuel containing 0.71 ppm chlorine. The results from these tests, with emissions of PCDD/F, using the convention of non-detected congeners set to zero and expressed as emission factors, are tabulated in Table 1. Emissions concentrations are extremely low – equating to 0.12-9.0 pg I-TEQ/Nm^3 (dry gas, 11% O_2).

Test number	Chlorine in oil ppm	Chlorine in fuel ppm	After-treatment	Emissions pg-I-TEQ/l fuel
1	259	0.71	DOC	160
2	259	0.71	DOC	61
3	12	0.71	DOC	29
4	12	0.71	DOC	36
5	131	0.71	DOC	47
6	131	0.71	DOC	12
7	259	0.71	DOC	6.0
8	12	0.71	DOC	3.4
9	259	0.71	DOC	42
10	12	0.71	DOC	28
11	131	0.71	DOC	49
12	259	0.71	DOC	8.9
13	131	0.71	DOC	2.5
14	12	0.71	DOC	10
15	131	0.71	DOC	4.2
16	259	0.71	DOC	4.0
17	12	0.71	DOC	8.5
18	259	0.71	DOC	14
26	259	0.71	DOC	3.7

Notes – runs 1,2 possibly some residual contamination in new engine reflected in emissions, 15,16 unable to resolve tetras resulting in some understatement of result

Table 1 Emission factors – engine with DOC, low Cl fuel

Inspection of the data illustrates significant inherent variability. Runs 1 and 2 had the highest measured emissions, which may be related to the engine stabilising from new. There is no relationship detectable between levels of chlorine in the oil and emissions from the engine, confirming the initial findings published previously.

For runs 19-23 we used the second batch of fuel that had a chlorine level of 2.52 ppm. The engine was run under the same test conditions and had the DOC in operation. Results are tabulated in Table 2.

Test number	Chlorine in oil ppm	Chlorine in fuel ppm	After-treatment	Emissions pg-I-TEQ/l fuel
19	12	2.52	DOC	11
20	259	2.52	DOC	9.4
21	12	2.52	DOC	2.3
22	259	2.52	DOC	6.1
23	259	2.52	DOC	8.4

Table 2 Emission factors – higher chlorine fuel

Under these conditions emissions remained low and in the range found in the testing with low-chlorine fuel. Two things can be concluded from these results, the chlorine in the oil is not controlling the level of emissions and furthermore the emissions were not affected by a step change in the chlorine in the fuel (which dominates total chlorine input).

Other work has shown that the addition of the diesel particulate filter on otherwise standard tests had no discernible effect on emissions of PCDD/F except in cases where copper was dosed into the fuel[3], we conducted two tests to confirm that this result was replicated here. Results shown in Table 3 illustrate that no effect was observed.

Test number	Chlorine in oil ppm	Chlorine in fuel ppm	After-treatment	Emissions pg-I-TEQ/l fuel
24	259	0.71	DOC/DPF	19
25	259	0.71	DOC/DPF	2.5

Table 3 Emission factors – addition of DPF

The last block of testing was to test whether the DOC was in some way masking any effects of chlorine in the lubricating oil on emissions of PCDD/F. We removed the DOC from the exhaust system. We also changed the conditioning run to a longer five-hour run that had multiple engine conditions rather than the single high load condition, this reduced any chance of cross-over from one test to the next. The engine was hard to stabilise initially and we had to simplify the conditioning run, this was achieved by run 31 (the tests were stable in all cases, we are uncertain as to whether an unstable conditioning run affected results).

Test number	Chlorine in oil ppm	Chlorine in fuel ppm	After-treatment	Emissions pg-I-TEQ/l fuel
27	12	0.71	none	260
28	12	0.71	“”	80
29	12	0.71	“”	150
30	131	0.71	“”	15
31	131	0.71	“”	18
32	259	0.71	“”	8.8
33	259	0.71	“”	31
34	131	0.71	“”	89
35	12	0.71	“”	98
36	259	0.71	“”	61
37	259	0.71	“”	120
38	12	0.71	“”	82
39	131	0.71	“”	94
40	12	0.71	“”	260

Table 4 Emission factors – diesel oxidation catalyst removed

Table 4 presents the results of testing with the DOC removed. The most obvious feature of the data is that results were variable and substantially higher than emissions from the engine with the DOC fitted. Although emissions were higher we could find no relation between emissions and the level of chlorine in the oil.

During the testing we recorded oil and fuel consumption and combustion air flows, combining this information with the measured chlorine content in each stream enabled us to try to relate emissions to total chlorine input to the combustion chamber for each test. However, we could not establish any relationship between total chlorine load to the chamber and the emissions (all results shown in Figure 1).

For completeness we analysed samples of lubricating oils (both fresh oil and after testing) and the fuel. In the past PCDD/F and PCB have been detected in lubricating oils. The laboratory clean-up required significant work in order to achieve adequate recoveries. Once the method was established we got good recoveries and we determined that all our

samples had non-detectable levels of PCDD/F and PCB in them (with the detection limit at approximately 1.5 ng I-TEQ/kg, or 1.5 ppt).

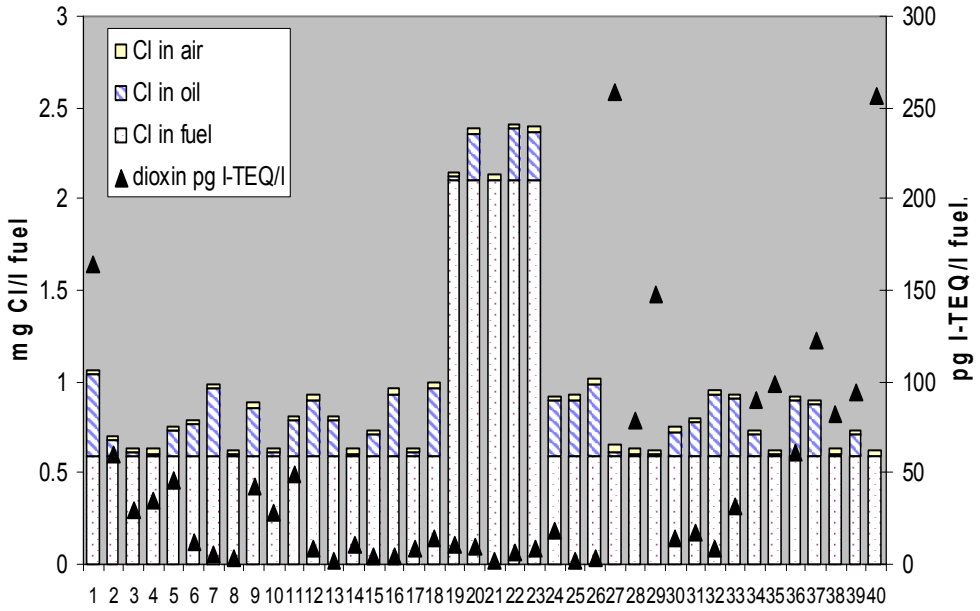

Figure 1 Plot of PCDD/F emission factor and chlorine input via air, fuel and oil, all tests

Conclusions

Emissions of PCDD/F were low from the diesel engine in standard configuration – typically in the range of 5-40 pg I-TEQ/l.

When the diesel oxidation catalyst was removed emissions were significantly higher indicating that the catalyst serves to reduce formation, probably due to reduction of partially burned species.

The emissions were not controlled by the level of chlorine in the oil and no effect of changes in the chlorine level between 12ppm and 259ppm could be detected in the emissions.

The emissions of PCDD/F were also not affected by a change in the chlorine level of the fuel which has a much more significant effect on overall chlorine in the combustion chamber.

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