PCDD/F EMISSIONS FROM DRAINED LUBRICATING OIL COMBUSTION

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Introduction

The testing reported here is the latest stage in a programme that used life-cycle assessment (LCA) techniques to evaluate the comparative environmental impacts associated with the formulation of additives for vehicle lubricating oils. The programme combined LCA with field and laboratory testing to generate data on environmental burdens associated with elements of the life-cycle where data were crucial, controversial or missing.

Over the past few years Lubrizol (a leading manufacturer of performance additives for lubricants) has been using life-cycle techniques to understand and inform their approach to product formulation and to ensure that full account is taken of environmental impacts of the choices made. Extensive studies of the life-cycle impacts for engine oils, with a particular focus on the impacts of different choices of dispersant, have shown that the life-cycle impacts are dominated by the use-phase[1,2]. This is to be expected since the greatest amounts of fuel and materials are associated with the vehicle use rather than lubricant production or disposal.

Some regulators and oil specifiers have sought to drive a move to lower chlorine lubricating oils assuming that lower chlorine must be "better" environmentally and that lower chlorine would lead to lower PCDD/F. Considerable reductions in residual chlorine in dispersant have been achieved but removal is not straightforward and increases the energy consumption. This life-cycle work was carried out in order to understand the environmental balances thrown up by this trade-off between increased energy consumption and lower chlorine for conventional dispersant and the choice of changing to DA dispersant

Dispersants are a key additive used in lubricating oils acting to keep dirt in suspension avoiding the build up of potentially harmful deposits in the engine. There are two main routes to produce dispersant chemicals for lubricating oils – "conventional" and "DA" - direct alkylation or "thermal" (due to higher energy consumption). The conventional route involves the use of chlorine as a catalyst, the DA process promotes the reaction with thermal energy. Oils formulated with conventional dispersant would typically have residual chlorine levels of up to 150 ppm while those using DA dispersant would have up to 20 ppm chlorine (from components other than the dispersant).

During the course of the life-cycle work it became clear that the issue of PCDD/F was of considerable importance and was also an area where insufficient data were available. In particular there were only inconclusive data on the effect of small changes to the level of chlorine in lubricating oil on emissions from engines. Therefore, a detailed experimental programme was undertaken to find out if the change in chlorine in lubricating oil caused by choice of dispersant would yield a change in emissions of PCDD/F from engines. This work, involving 40 sampling runs, has been reported at Dioxin 2005[3], Dioxin 2006[4] and in Chemosphere[5] and showed that the chlorine flow in the engine was dominated by the chlorine in the fuel (albeit at very low levels), that PCDD/F emissions were not increased by increases in chlorine in oil or fuel and that levels of PCDD/F in exhaust emissions were low. In addition the work demonstrated for the first time that the use of a diesel oxidation catalyst in the exhaust reduced emissions of PCDD/F to about a fifth of their levels with the catalyst removed.

The work reported here focuses on the disposal of used lubricating oils. In many countries a significant proportion of used or waste oils are either burned as received or burned for fuel after relatively little processing. In some instances waste oil may be burned with no controls and in some countries a substantial amount of waste oil is unaccounted for and may either be dumped into the environment or burned in combustion equipment not specifically designed for waste oil since it can be seen as a cheap alternative to purchased fuels.

A study[6] of oil disposal in the European Union (2001) gave an average of 23% being burned or used locally (assumed to be in garage heaters) with data for one country showing that as much as 90% of oil may be burned in simple systems likely to have no pollution controls.

Although lubricating oils used for cars and trucks often make up a substantial proportion of the used oils in a country, mixed waste oil streams may contain components that are quite different to lubricating oils – such as cutting oils and solvents – which can increase levels of chlorine for example. Our testing aimed to isolate and test the effect of chlorine in drained lubricating oils on emissions of PCDD/F.

In order to provide data for the life-cycle assessment and to develop a reasonable worst case testing was carried out on a simple waste oil combustor of the type widely used in garages and workshops for the generation of heat by combustion of waste lubricating oils. The unit has no pollution control devices so emissions are essentially uncontrolled and reflective of simple combustion systems in use. This represented the least controlled case that was believed suitable to achieve the steady state conditions for repeated tests in order to isolate the effects of the oil composition on emissions.

Materials and Methods

For the tests reported here we built on and extended the test series reported previously[7] guided by the following principles:

- Tests should be on commercially available combustion equipment;
- Repeated tests were required at each condition since emissions tend to be variable;
- Steady state conditions should be used to ensure repeatability;
- No artificial doping would be used to control chlorine content – ie the oils would only have components found in real lubricating oils and chlorine content would be driven by choice of dispersant used;
- The drained oils would be from real-world vehicles and after considerable distance.

The drained oils were collected from trucks involved in long-distance heavy-duty truck tests. Typically the lubricants had been in service for between 50 000 and 100 000 km. As trucks reached the end of the tests the lubricants were drained and set aside. Samples were analysed for chlorine content and the drained oils divided into two pools, those with low (<20ppm) chlorine were designated U1 and those with greater than 100 ppm chlorine U2. It was assumed that the chlorine content was driven primarily by the dispersant used, U2 consisted of lubricants with mainly or exclusively "conventional dispersant", U1 lubricants using mainly or exclusively "DA" dispersants.

The Thermobile AT400 waste oil fired air heater was described previously[7]. The unit has an output of hot air and provides 41kW of heat, operating on a relatively simple principle with the oil being fed onto a pan and burned. Units similar to this are being sold in the UK and elsewhere in Europe now and being installed in a garages and workshops to provide space heating during the winter season using drained lubricating oils.

Oil from a tank is pumped into the combustion chamber and from the fuel supply pipe onto a cast iron dish where it vapourizes and is burned with input air from the single forced draught fan. Combustion gases from the cylindrical combustion chamber pass through an air-air heat exchanger and into the flue. In our tests we had a stainless steel flue (supplied with the burner) rising vertically a distance of approximately 6m. The stack was fitted with sample points to facilitate extractive sampling using modified method 23 equipment for PCDD/F. For selected tests PCB were analysed with results being reported for the 12 PCB assigned TEFs by WHO in 1997. In addition combustion gases were extracted and analyzed continuously for CO, CO_2, SOx, NOx, and volatile organic compounds (VOC). Temperatures in the lower stack were measured.

For each run the boiler was lit using paper and 300ml of diesel in the burner dish (as per the instructions) and the unit run for 20 minutes on low fire. Then the unit was switched to high fire and run for 2 hours and monitored to ensure steady conditions were being achieved. After the two hour conditioning run sampling was commenced for PCDD/F. Sampling was by conventional filter – condenser methods, the sample probe was titanium. The principles of EN1948 were followed. Isokinetic sampling was not possible due to the low stack velocities inherent in this type of equipment. Levels of particulate were low and it is not thought that deviation from isokinetic conditions will have affected the samples. A target volume of 10 m^3 of sample was set and this was achieved in about 6 hours.

At the end of the test the unit was allowed to cool, any remaining oil was drained and the tank cleaned. The burner pan, fuel feed pipe and combustion stabilizer were cleaned of any soot or other deposits with wire brushes and a vacuum cleaner.

An initial series of nine runs burning three clean lubricants was reported previously[7]. The testing reported here consisted of six runs measuring emissions of PCDD/F from the drained oil samples, two reference runs for PCDD/F from the lubricants previously used and two runs for measuring metal and particulate emissions.

Results and Discussion

Previous testing had established stable conditions, the unit ran well and the temperature in the base of the flue was around 310 ºC. For these tests using drained lubricating oils combustion was highly effective, the unit operated with no intervention during the test periods and levels of carbon monoxide and VOC were low.

There was a similar build up of residue in the burner pan from each run as seen with the clean oils previously tested. This had a mixed nature with some sooty/char components (possibly arising during final burnout), residue of the paper used to light and mineral matter that came from the oil.

Test number	Oil type	Oil chlorine content ppm	PCDD/F ng I-TEQ Nm^{-3} @ 11 % O$_{2\ (dry)}$	PCDD/F Emission factor pg I-TEQ l^{-1} of oil	PCB ng WHO TEQ (97) Nm^{3} 11% O$_2$, dry gas	PCB emission factor pg WHO TEQ l^{-1} of oil
18	Low ref (clean)	12	0.00048	9.5	4.3x10^{-5}	0.85
19	U1	117	0.0015	28	4.3x10^{-5}	0.85
20	U1	117	0.0022	42	8.3x10^{-5}	1.6
21	U1	117	0.00032	6.3	4.7x10^{-5}	0.93
22	U2	7	0.0030	59	NM	NM
23	U2	7	0.00062	12	6.7x10^{-5}	1.3
24	U2	7	0.0012	23	5.6x10^{-5}	1.1
27	High ref (clean)	259	0.00024	4.8	8.7x10^{-5}	1.7

ND – set to zero, NM – not measured, concentrations to 2 significant figures

Table 1 Summary results – PCDD/F and PCB emissions

Emissions concentrations of PCDD/F for drained oil tests (summarized in Table 1) were all low in the range 0.3 to 3.0 pg I-TEQ Nm^{-3} (dry gas 11% O$_2$) which can be compared to the widely used emission limit of 100 pg I-TEQ Nm^{-3}. This translates to emission factors of 23 to 59 pg per litre of oil burned (or 26 to 66 pg I-TEQ per kg of oil). Emissions at the beginning and end of the series were tested for reference oils that had been previously used, in this way it was possible to ensure that the unit was still operating as expected and no change had occurred that might be skewing the results. For both the low reference oil (12 ppm Cl) and the high reference oil (259 ppm) results were in the range previously established.

PCB emissions were also low and many of the PCB congeners were below detection limits. The data are included in Table 1 but the reader should be aware that these levels are in the range of the field blank concentrations found.

The results for the drained oil tests are presented graphically in Figure 1, this shows emission factors plotted against oil-chlorine content. The mean emissions for U1 were 26 pg I-TEQ per litre and for U2 31 pg I-TEQ per litre. For each drained oil the range of emissions measured is relatively wide. Based on these six samples there is not a statistically significant change in emissions (at the 95% level) although there is an apparent trend to lower emissions from U2 to U1 even as the chlorine level increased by a factor of more than 16. These results are similar to those found previously where there was a clear, statistically significant, reduction in emissions with increasing chlorine content from 12 to 259 ppm[7].

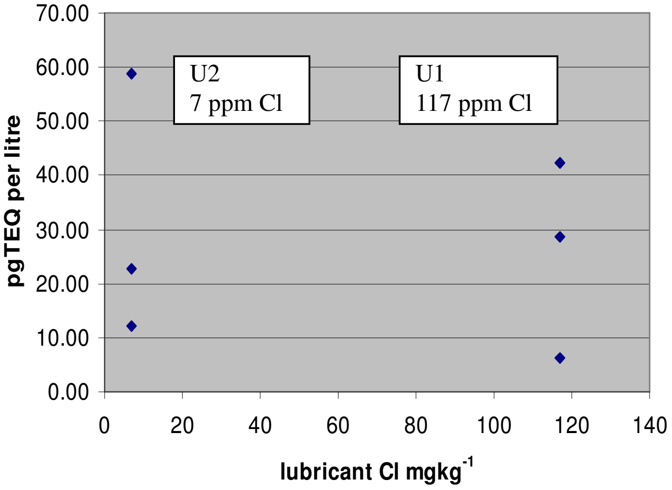

Figure 1 Emission factors and oil-chlorine content

These data show that the emission of PCDD/F from the combustion of these lubricating oils drained from long-term heavy-duty truck tests in readily available combustion equipment (with no pollution controls) were extremely low ranging from 0.3 to 3.0 pg I-TEQ/Nm^3 (11% O_2, dry gas), at least a factor of 30 below the widely used emission limit of 0.1 ng I-TEQ/Nm^3.

Furthermore emissions of PCDD/F for the drained oils did not increase with a substantial increase in chlorine content, which in these tests was related to type of dispersant used. This is consistent with the work carried out on clean (ie unused) lubricants reported previously. In fact a trend to lower emissions with increasing chlorine is observed.

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