Cod: 8.10019

EMISSIONS OF DIOXINS AND PCBS FROM A DIESEL ENGINE USING USED LUBRICATING OIL AND COCONUT OIL AS DIESEL EXTENDERS.

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Introduction:

The volumes of used oil generated from Pacific island countries, ranging from 5,000 litres per year in the smallest to several million litres per year in the largest, remains a complex and costly issue for most Pacific island nations . A consequence is that used oil is often disposed of inappropriately through dumping or by open burning or incineration, generating unintentional persistent organic pollutants (uPOPs) such as dioxins and furans. The use of used oil as a diesel extender in the generation of electrical power is increasingly being regarded as a viable short-term (5 years) option for the disposal of used oil in the Pacific. It is important that the potential environmental consequences of this disposal option are critically evaluated.

The specific aim of this project was to determine the emission factor of uPOPs from diesel generators used to generate electrical power, and the impact on these emission factors when used oil is added as a diesel extender (1-5% by volume).

Materials and methods:

Selection of fuels and fuel blends

A range of coconut oil and used lubricating oil concentrations in diesel fuel were tested to assess the influence different fuel mixtures have on the emissions. Used lubricating oil used in this project was pre-filtered by diluting 50% with diesel fuel and filtering through a 5 μm fuel filter. Table 1 contains the list of fuel blends used in this project.

Engine specifications and operation

Exhaust emissions were collected from a Cummins ISBe220 31 engine. This engine is a 6 litre, six cylinder, turbocharged after cooled, common rail diesel engine, which is typically used in medium size trucks. The engine was coupled to a water brake dynamometer, and connected to an electronic control unit (ECU). The engine was operated at 1500 rpm (maximum torque speed) at 25% load, to be representative of a power generator. The engine was pre-warmed to a steady state before exhaust sample collection began.

Sample collection

The exhaust gas was collected from a sample port in the exhaust pipe. It was then drawn through a glass filter paper before the exhaust gas was cooled in a condenser, and drawn through an XAD-2 cartridge. Prior to sampling, the XAD-2 cartridge had been spiked with a labelled breakthrough PCDD/F mix to ensure there was not any loss of PCDD/Fs from the XAD-2 cartridge during sampling. Emissions samples for PCDD/Fs were collected over a 2 hour period. The raw exhaust volume collected was between 8 m^3 and 12 m^3 per sample.

Sample extraction and clean up

The XAD-2 and filters were extracted together at 150ºC using toluene in an Accelerated Solvent Extractor (Dionex ASE 350). Extracts were split into two fractions, 10% for future analysis and the remaining 90% for PCDD/F and PCB analysis. The clean-up steps for PCDD/F and PCB analysis consisted of acid washing the sample with concentrated sulfuric acid, adsorption chromatography using a silica column, an aluminum oxide column and finally a carbon column where the sample was eluted

off in two fractions, the first fraction for mono-ortho (MO-) and indicators (I-)PCBs, and the second fraction for co planar (CO-)PCBs and PCDD/Fs.

Instrument details
PCDD/F and PCB analysis was conducted on a Thermo Scientific TRACE 1300 gas chromatograph, coupled to a DFS high resolution mass spectrometer. Experiments were conducted in MID mode at a resolution of 10,000. Separation was achieved on a 60m Agilent J & W DB-5MS column (0.25mm x 0.25μm) for PCDD/Fs and a 30m column for PCBs.

Results and discussion:
Twenty two emissions samples were collected in total, with each diesel blend being run in duplicate with the exception of D100 and D85C10U05 which were run in quadruplet. After extraction and clean up, 19 samples were able to be quantified for PCDD/Fs and 18 samples for PCBs.

The method detection limits in this study were generally around ~0.5pg m^{-3} for PCDD/Fs congeners and ~10 pg m^{-3} for PCB congeners. These limits of detection would have been sufficient to measure the levels of PCDD/Fs and PCBs reported in diesel emissions from many other studies [1-18]. In this study dioxin-like PCB congeners and 2378 PCDD/F congeners could not be detected with the detection limits, the exception being three samples in which 2378 PCDD/F congeners were detected the levels were between 0.0014 and 1.2 I-TEQ m^{-3} (Figure 1).
Using upper bound values which presents the worst case scenario (non detect = detection limit) gives a range of 0.68-2.2 pg I-TEQ m^{-3}, with two outliers of 4.2 and 8.2 pg I-TEQ m^{-3} (Figure 1). The two outlying results are due to lower recovery during sample clean up pushing the detection limits up in these two samples. Even using this upper bound scenario, overall PCDD/F emission factors were very low.

Non 2378 PCDD/F congeners and non-dioxin-like PCB congeners were detected in all samples in this study. Total PCDD/F emissions ranging from 5.9-129pg m^{-3} and total measured PCB emissions were in the range of 6.7-93ng m^{-3} with a single outlier of 240 ng m^{-3} (Figure 2).

The emissions from diesel and coconut oil and used lubricant oil blends show no significant difference to the observed emissions from the diesel fuel used in this study. In other studies, the use of biofuels as diesel extenders led to a reduction in emissions of 2378 and total PCDD/Fs [12-15]. In studies where a diesel-like fuel was produced from used lubricant and transformer oils, an increase in CO emissions was observed suggesting incomplete or inefficient combustion, which may result in the formation of dioxin precursors [19-21]. It has further been proposed that impurities in fuels such as chlorine [8, 16-18, 22] and metals [16-18] that are possibly present in used lubricant oil will increase formation and subsequent emission of dioxin-like chemicals.

In our study we found relatively low emission factors for PCDD/Fs and PCBs. In fact, despite collection of relatively high sampling volume 2378 substituted PCDD/F concentrations were almost consistently below the LOD and upper bound emission factors were typically less than 2 pg I-TEQ m^{-3}. The addition of either coconut oil or used lubricant oil to the diesel mixture did not lead to emission factors that were sufficiently high for detecting 2378 substituted PCDD/Fs. We could detect selected congeners of the non-2378 substituted PCDD/F congeners and report results for homologue groups and the sum of PCDD/Fs. We also found no real difference in emissions of the ∑PCDD/Fs between experiments using the various fuel compositions. We did however find an increase in particle emission with the use of lubricant oil.

Overall, the findings from this study indicate that emissions of dioxins from diesel engines are likely to be very low, having no measurable increase in PCDD/F emissions when diesel fuels are mixed with used lubricant oil and coconut oil as diesel extenders. Our study suggests that from the point of dioxin and PCB emissions, the use of used lubricating oil alone or, in combination with coconut oil, as diesel extenders for power generation are a sensible approach for the disposal of used lubricating oils. On island nations where other disposal options are currently unavailable due to cost or lack of appropriate recycling regulations this has great advantage.

Acknowledgements:
UNEP and SPREP are thanked for being the funding providers for this study. JFM is funded through an ARC Future Fellowship (FF 120100546).

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Table 1: Fuel blends used in this project (v/v)

Blend Name	Diesel fuel (%)	Coconut oil (%)	Used lubricant oil (%)
D100	100 (Baseline)	0	0
D90C10	90	10	0
D85C15	85	15	0
D80C20	80	20	0
D99U1	99	0	1
D95U5	95	0	5
D89C10U1	89	10	1
D84C15U5	84	15	1
D85C10U5	85	10	5

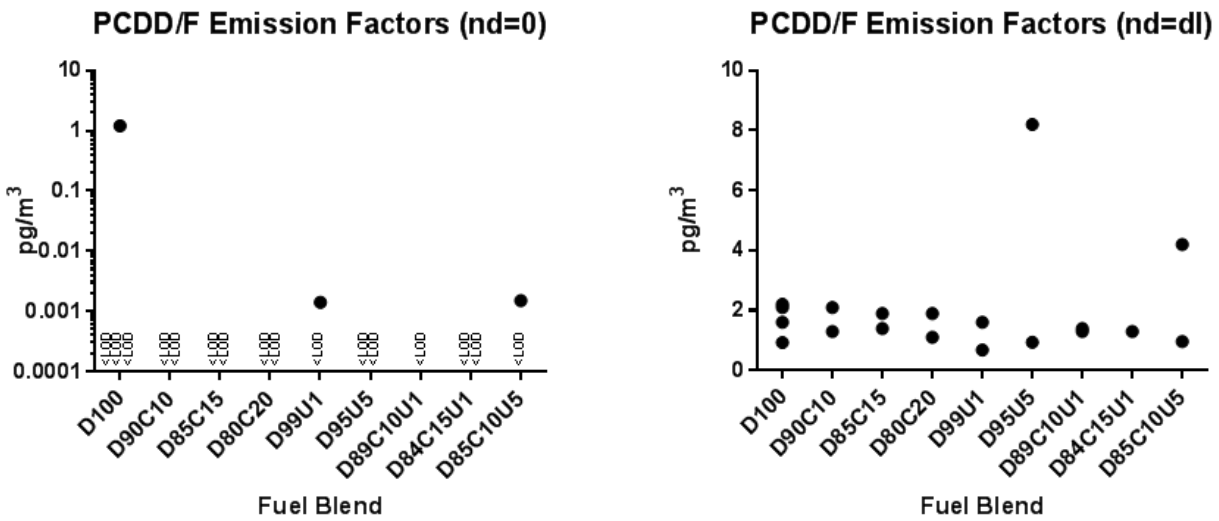

Figure 1. I-TEQ PCDD/F Emissions

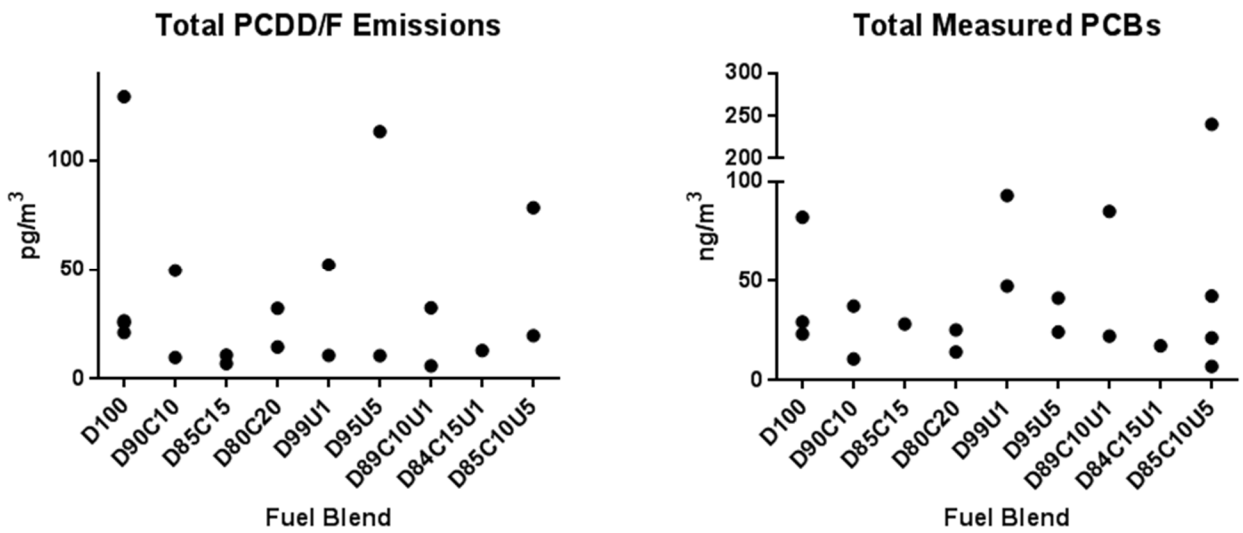

Figure 2. Total PCDD/F and PCB Emissions