Redox Activity of Soluble Organic Fraction emitted from modern diesel passenger vehicles operated on Biodiesel fuels

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Introduction

It is very well established that particulate matter originating from diesel vehicles (DPM) is connected to various adverse health impacts, such as cardiopulmonary diseases, lung problems and various types of cancers (Laden et al., 2007). Despite the progress in toxicological research in the field of air pollution induced by vehicles, the exact relationship between particle properties (size, surface area and composition) and specific health outcomes is not completely understood. A few mechanisms have been proposed to explain health impacts of DPM, including production of reactive oxygen species (ROS) and consequent generation of oxidative stress (Schafer et al., 2003). On the other hand, DPM is also connected to a wide series of environmental problems, including visibility degradation, global warming and acid rain (Cheung et al., 2009).

The last decade there has been a great effort to better understand how the chemical characteristics of the DPM affect their toxicity in order to produce more effective emission control technologies. The introduction of exhaust aftertreatment devices and particularly diesel particulate filters (DPF) has led to a significant reduction of the particulate matter emitted by modern diesel vehicles. On the other hand, EU's legislation requirement for the use of renewable fuels has led to the extensive use of Fatty Acid Methyl Esters (FAMEs). Many different FAME types are in use throughout Europe and the rest of the world, but Rapeseed Methyl Ester (RME) is currently the most common and was chosen for this study. The aim of this study was to investigate the influence of higher biodiesel levels on soluble organic fraction's (SOF) redox activity measured in the emitted DPM of modern diesel passenger vehicles.

Methods and materials

For the purposes of the present study three modern (Euro 4-compliant) light-duty diesel vehicles were selected. They all were equipped with direct injection, high injection pressure and common rail diesel engines. Additionally they all featured exhaust gas recirculation (EGR), some type of diesel oxidation catalyst (DOC), while vehicles 1 and 3 were equipped with Diesel Particulate Filters (DPF). Before starting the vehicle testing, the DPF regeneration interval for both vehicles was investigated and steps were taken to ensure that no automatic regenerations occurred during measurements.

Four RME fuels were used: a reference diesel fuel (B0) and 3 blends of the B0 with RME at 10% v/v (B10), 30% v/v (B30), and 50% v/v (B50). The base fuel contained less than 10 mg/kg sulphur and complied with the European EN 590 specification. A single batch of European RME which contained 1,000 ppm of a commercial antioxidant additive was used. The RME complied with the European EN 14214 specification and the antioxidant was used to ensure oxidation stability. Finally, a fully-formulated diesel performance additive package that is widely used in Europe was added to all test fuels in order to ensure fuel system cleanliness throughout the vehicle test programme. The main properties of the fuels are given in Table 1. The vehicle testing protocol was statistically designed in order to provide robust results for all emissions, including DPM, over both the regulatory New European Driving Cycle (NEDC) and 'real-world' ARTEMIS Urban driving cycle.

The Dithiothreitol (DTT) assay was applied in order to measure the redox potential of the SOF. DTT assay provides a procedure for measuring the redox activity of a sample based on its ability to catalyze electron transfer between Dithiothreitol and oxygen in a simple chemical system. The rate of DTT consumption under standardized conditions is proportional to the concentration of the catalytically active redox-active species in the sample [Cho et al., 2005]. In

particular the DTT assay determines the redox activity by measuring the PM dependent oxidation of DTT. It measures the formation of reactive oxygen species by a known amount of DTT. During this reaction DTT is consumed. The loss of DTT is followed by its reaction with 5,5-dithiobis-(2-) nitrobenzoic acid (DTNB) to form 2-nitro-5-mercaptobenzoic acid, which is monitored spectrophotometrically at 415nm.

Table 1: Fuels overview

Fuel Property	Units	Test Method	B0	B10	B30	B50
Cetane Number		EN ISO 5165	53.2	53.6	53.8	53.9
Density at 15°C	kg/m^{3}	EN ISO 12185	823.1	829.1	841.0	853.0
Final Boiling Point	°C	EN ISO 3405	326.5	337.3	344.2	352.1
Total Aromatics	% m/m	EN 12916	22.3	18.3	15.0	10.6
Mono-aromatics	% m/m	EN 12916	20.8	17.1	14.1	9.9
Di-aromatics	% m/m	EN 12916	1.4	1.2	0.9	0.7
Tri-aromatics	% m/m	EN 12916	0.1	0.1	<0.1	<0.1
PAHs	% m/m	EN 12916	1.2	1.2	0.9	0.6
FAME	% vol	EN 14078	<0.1	10.7	30.6	50.9
Sulphur	mg/kg	EN ISO 20846	<3	<3	<3	<3

Results and discussion

The mean values of the DTT-redox activity per mass of emitted SOF (nmol/min*µg) are given in table 2. The DPF equipped vehicles exhibited DTT-redox activity that varied from 0.077 to 0.138 nmol/min*µg. This range is within the value of 0.110 nmol/min*µg found for a Euro 3 diesel vehicle operated on neat diesel on Artemis Road (Geller et al., 2006). On the other hand, in V2 the DTT-redox activity per mass of emitted SOF was lower and varied from 0.028 to 0.057 nmol/min*µg. Similar values are also found in the existing literature (Geller et al., 2006; Cheung et al., 2009).

Table 2: Mean (n=5 (B0), n=4 (biodiesel blends)) DTT-redox activity per mass of emitted SOF (nmol/min*µg)

	V1 (NEDC)	V1 (Artemis)	V2 (NEDC)	V2 (Artemis)	V3 (NEDC)	V3 (Artemis)
B0	0.097	0.077	0.042	0.028	0.121	0.114
B10	0.102	0.082	0.045	0.036	0.129	0.117
B30	0.110	0.093	0.049	0.040	0.131	0.122
B50	0.113	0.093	0.057	0.046	0.138	0.133

Figure 1 shows the % average change of the DTT-redox activity per mass of emitted SOF (nmol/min*µg) with the use of biodiesel blends. It appears that both DPF equipped vehicles recorded slightly increased DTT-redox activity with increasing blend. More specifically, V1 exhibited approximately 17% (NEDC) and 21% (Artemis Urban) higher DTT-redox activity with B50 compared to neat diesel. The increase in case of V3 was 14% and 17%, respectively. It seems that the organic species emitted in case of biodiesel contain potentially more reactive oxidative organic compounds which are more likely to involve in the oxidative stress mechanism. The non-DPF equipped vehicle exhibited a statistically significant increase of the DTT-redox activity with B50 which in case of Artemis Urban reached 64%. Despite the increase

of the DTT-redox activity per mass with increasing blend, the DTT-redox activity per km (nmol/min*km) was not found to change significantly, regardless the vehicle tested.

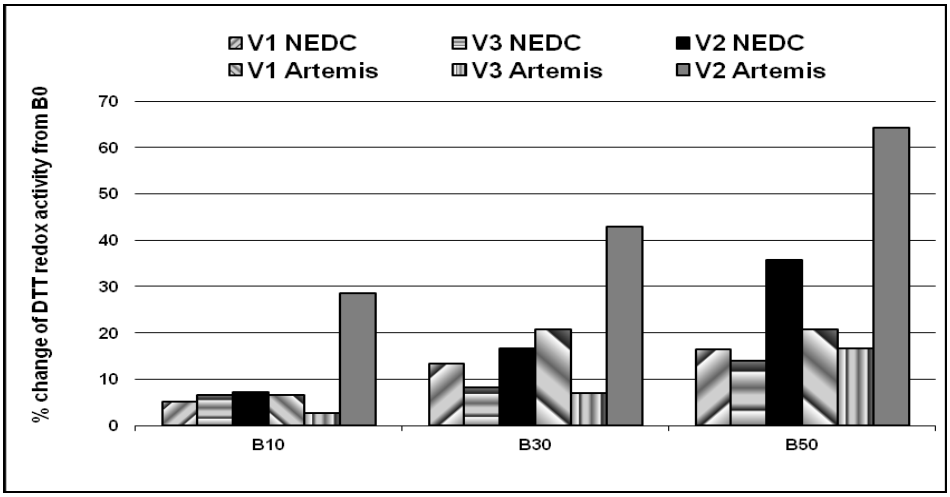

Figure 1: % change of DTT-redox activity from B0 with the use of biodiesel blends.

Figure 2 shows the DTT-redox activity of the emitted SOF per km (nmol/min*km) for all tested vehicles in both driving cycles. As shown in figure 1, both DPF equipped vehicles recorded approximately 2-3 times higher DTT-redox activity per mass of emitted SOF than V2. This observation is in agreement with the existing literature (Geller et al., 2006). Nevertheless, as it appears from figure 2, both DPF equipped vehicles exhibited 3-6 times lower oxidation activity per km than the non-DPF equipped vehicle, regardless the fuel used. This is an indication that a significant amount of potentially more toxic organic compounds are trapped and oxidized in the DPF resulting thus in less oxidative total organic emissions compared to the non-DPF equipped vehicle.

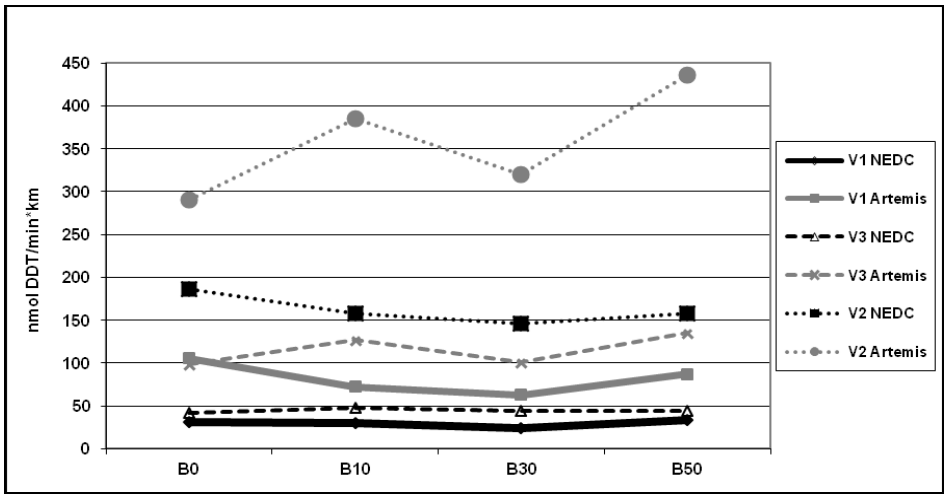

Figure 2: Mean DTT-redox activity of SOF (nmol/min*km) in the DPM emitted by all vehicles in both driving cycles.

In the non-DPF equipped vehicle no statistically significant correlation between n-alkanes emissions (C14-C40) and the DTT-redox activity per mass of emitted SOF was found. This indicates that these species are less likely to be involved in the oxidation stress mechanism which is expected due to their low ability to oxidize DPM. In general, DPM's toxicity has found to

be strongly correlated to organic compounds such as PAHs and their derivatives (Munach et al., 2006).

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