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Effect of biodiesel fuel on "real-world", nonroad heavy duty diesel engine particulate matter emissions, composition and cytotoxicity

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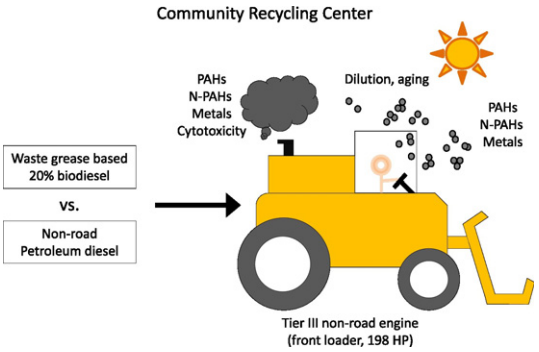
HIGHLIGHTS

- Compared diesel vs. biodiesel PM from "real world" setting utilizing nonroad engines
- Higher total PAHs, Pb, and in vitro cytotoxicity associated with diesel PM
- Higher total N-PAHs, Cu, and Mo associated with waste grease B20 PM
- Notable differences in PAHs and N-PAHs comparing tailpipe vs. "equipment-cabin" PM
- PM from burning diesel in non-road engines may be more harmful to human health

GRAPHICAL ABSTRACT



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ABSTRACT

Biodiesel is regarded by many as a "greener" alternative fuel to petroleum diesel with potentially lower health risk. However, recent studies examining biodiesel particulate matter (PM) characteristics and health effects are contradictive, and typically utilize PM generated by passenger car engines in laboratory settings. There is a critical need to analyze diesel and biodiesel PM generated in a "real-world" setting where heavy duty-diesel (HDD) engines and commercially purchased fuel are utilized. This study compares the mass concentrations, chemical composition and cytotoxicity of real-world PM from combustion of both petroleum diesel and a waste grease 20% biodiesel blend (B20) at a community recycling center operating HDD nonroad equipment. PM was analyzed for metals, elemental/organic carbon (EC/OC), polycyclic aromatic hydrocarbons (PAHs), and nitro-polycyclic aromatic hydrocarbons (N-PAHs). Cytotoxicity in a human lung epithelial cell line (BEAS-2B) following 24 h exposure to the real-world particles was also evaluated. On average, higher concentrations for both EC and OC were measured in diesel PM. B20 PM contained significantly higher levels of Cu and Mo whereas diesel PM contained significantly higher concentrations of Pb. Principal component analysis determined Mo, Cu, and Ni were the metals with the greatest loading factor, suggesting a unique pattern related to the B20 fuel source. Total PAH concentration during diesel fuel use was 1.9 times higher than during B20 operations; however, total N-PAH concentration was 3.3 times higher during B20 use. Diesel PM cytotoxicity was 8.5 times higher than B20 PM ($p < 0.05$) in a BEAS-2B cell line. This study contributes novel data on real-world, nonroad engine sources of metals, PAH and N-PAH species, comparing tailpipe PM vs. PM collected inside the equipment cabin. Results suggest PM

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generated from burning petroleum diesel in nonroad engines may be more harmful to human health, but the links between exposure, composition and toxicity are not straightforward.

1. Introduction

Diesel particulate matter (DPM) exposure is associated with an array of chronic and acute cardiopulmonary health risks, including lung and cardiovascular inflammation, asthma exacerbation, and lung cancer (USEPA, 2002a; HEI 2002; Attfield et al., 2012). U.S. regulatory agencies such as NIOSH and the USEPA have concluded that petroleum diesel exhaust is a "potential occupational carcinogen" (NIOSH, 1988) and "likely to be carcinogenic to humans by inhalation" (USEPA, 2002a). According to Pope et al. (2009), even low-to-moderate levels of fine particulate matter (PM) exposure may result in a linear relationship between exposure to PM and negative health effects, suggesting that there may not be a safe exposure threshold for humans. Reductions in PM emitted by diesel engines may help reduce the impact of PM exposure on public health. One potential method to reduce PM emissions from diesel engines is switching from petroleum diesel to biodiesel fuels.

Biodiesel fuel is biodegradable, made from renewable feedstocks, has high engine lubricity characteristics (USDOE, 2004), and its use results in an overall reduction in greenhouse gas emissions (Hill et al., 2006). Previous studies have demonstrated that replacing diesel fuel with biodiesel fuel can reduce emission of PM, carbon monoxide and total hydrocarbons in tailpipe exhaust (USEPA, 2002b; Lapuerta et al., 2007; Di et al., 2009; McCormick et al., 2006; Robbins et al., 2009; Yanowitz and McCormick, 2009; Agarwal et al., 2015). Less is known about the impact of biodiesel on PM composition (such as polycyclic aromatic hydrocarbons) and associated health effects, but this is an area of active research (Karavalakis et al., 2009; Cheung et al., 2010; Hemmingsen et al., 2011; Fukagawa et al., 2013; Gerlofs-Nijland et al., 2013). In the aforementioned studies and most other diesel emission studies, the predominant method for collecting source or tailpipe PM is to follow standardized testing procedures using passenger car diesel engines (i.e., the Federal Testing Procedure at 40 CFR Part 86). These emissions studies collect particles directly from the tailpipe exhaust under controlled laboratory conditions of air dilution, temperature, humidity, and engine operating mode. While laboratory studies mimic dilution conditions and capture emissions trends, in-use studies of nonroad heavy duty diesel (HDD) equipment operating in occupational or public community settings provide an important complement to engine dynamometer tests. Performing an exposure assessment at an active work site better approximates PM inhalation levels and incorporates real world variations in fuel consumption and engine activity patterns (i.e., equipment moving with a heavy load) that ultimately influence PM characteristics. According to the most recent EPA diesel engine nonroad population estimates, there are over 300,000 large front loaders, 300,000 tractors and 100,000 excavators in use across the U.S. (EPA, 2010). These types of nonroad vehicles are commonplace in commercial, agricultural and construction type settings. Yet, to the best of our knowledge, biodiesel exposure studies in these types of settings are nearly absent from the literature, other than our previous work (Traviss et al., 2010; Traviss et al., 2012; Traviss et al., 2014). Traviss et al. (2012) determined that $PM_{2.5}$ mass concentration significantly decreased during B20 usage (compared to petroleum diesel). Such reductions in PM mass are often linked to biodiesel's increased oxygen content within the fuel (~11% w/w) (Agarwal et al., 2015).

A better understanding of the potential human health impacts related to "real world" biodiesel and diesel PM exposure requires evaluation of the PM mass concentration, chemical composition, and cytotoxicity. Biodiesel feedstocks vary and may include soybean oil, rapeseed oil, waste grease, and animal fats (with varying degrees of saturation/unsaturation) which can impact PM composition and result in differences in metal, polycyclic aromatic hydrocarbon (PAH), nitro-polycyclic aromatic hydrocarbon (N-PAH), and elemental carbon/organic carbon (EC/OC) content between diesel and biodiesel fuels (Karavalakis et al., 2009; Cheung et al., 2010; Ballesteros et al., 2010; Karavalakis et al., 2011). Traviss et al. (2012) reported a significant reduction (up to 76%) in $PM_{2.5}$ mass concentration during B20 use (soy feedstock), despite an associated increase in OC concentration (467% greater than diesel OC concentration). However, during the previous study the OC fraction was not chemically characterized, and toxicological responses were not examined. Polycyclic aromatic hydrocarbons are most likely a component of the overall OC fraction and currently, the EPA lists 16 PAHs as potential carcinogens (US EPA, 2014), each with varying chemical structure and toxicological potential (Ravindra et al., 2008). Agarwal et al. (2013) showed that diesel PM had slightly higher toxic potential than a 20% biodiesel blend due to PAH composition. However, in a study comparing emissions from various biodiesel feedstocks, Karavalakis et al. (2011) found that use of waste grease based biodiesel increased total PAH emissions by 27% (urban drive cycle) compared to the reference diesel fuel. The authors suggest this may be due to the chemical composition of used frying oil, possibly containing already oxidized compounds; burning used frying oil also resulted in higher levels of N-PAH's compared to other biodiesel blends, but reference diesel had the highest overall N-PAH emissions (Karavalakis et al., 2011). Nitration of PAHs, i.e. the formation of N-PAHs, can result from combustion processes as well as exposure of PAHs to the ambient environment (Finlayson-Pitts and Pitts, 1997). Previous studies demonstrate that ambient concentrations of N-PAHs are associated with increased mutagenic activity relative to PAHs (Umbuzeiro et al., 2008), possibly because N-PAH's do not require metabolism to become reactive, genotoxic compounds (Fu and Herreno-Saenz, 1999). Finally, metals composition could also contribute to the negative health impacts associated with diesel and biodiesel PM. Previous studies show that metals, particularly transition metals such as Cu, are a major component of diesel and biodiesel PM (Betha and Balasubramanian, 2011; Traviss et al., 2014; Godoi et al., 2016). The presence of transition metals, and polar and nonpolar organic species in biodiesel and diesel PM can induce production of Reactive Oxygen Species (ROS) in vitro (Verma et al., 2010; Hemmingsen et al., 2011; Fukagawa et al., 2013; Godoi et al., 2016). While ROS is integral to many cellular processes, increased exposure to ROS causes damage to intracellular components like DNA, lipids and proteins (Dröge, 2002). Excessive ROS levels can result in cytotoxic effects.

The goals of this study were to compare the mass concentration, chemical composition, and cytotoxicity of diesel vs. B20 PM collected in a "real world" occupational setting. We performed an exposure assessment at a community recycling facility, where HDD nonroad vehicles were first fueled with commercially purchased nonroad diesel fuel before switching to a B20 biodiesel blend (20% waste grease biodiesel/80% nonroad petrodiesel). Work area and equipment-cabin concentrations of size fractionated PM mass (2.5 μm and <0.25 μm), EC/OC, metals, PAH, and N-PAH were quantified and compared. Bulk PM was collected directly from inside the exhaust tailpipe for each fuel and