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Trace metals and ions in particulates emitted by biodiesel fuelled engine

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HIGHLIGHTS

- Trace metals & inorganic ions in particulate from B20 & diesel exhaust.
- Inorganic ions: nitrates, chlorides, fluorides & sulphates were measured.
- Trace metals & Ions in particulate decreased with increasing load.
- Biodiesel particulate had slightly lower trace metals & inorganic ions.
- Morphological studies showed reduction in particulate with DOC.

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ABSTRACT

Particulates emitted by a transportation diesel engine fuelled with Karanja biodiesel blend (20% v/v biodiesel blended with 80% v/v mineral diesel) were tested for the trace metal content and inorganic ions. These particulate were analyzed and compared with baseline mineral diesel particulate for 9 commonly present trace metals namely Ca, Fe, Cr, Cu, Mn, Pb, Ni, Ba and Cd and inorganic anions such as nitrates, chlorides, fluorides and sulphates. Trace metals in particulate decreased with increasing engine load. Ions analyzed in particulate from diesel and biodiesel also showed decreasing trend with increasing engine load. Biodiesel origin particulate contained slightly lower amount of trace metals and inorganic ions compared to mineral diesel for similar operating conditions except nitrates. Particulate sampled on the quartz filter paper were also analyzed for their morphology and 1000× magnification images were captured using scanning electron microscopy (SEM) in order to visualize bulk particulate emission from Karanja biodiesel exhaust compared to baseline mineral diesel.

1. Introduction

Particulate emissions from vehicles are responsible for harmful health impact on humans and the environment. They adversely impact health and environment because they get ingested into the human body by inhalation, contaminate various environmental media by toxic substances, affect visibility adversely (due to black smoke), and accelerate global climatic change (due to black carbon emissions) [1]. In recent years, diesel particulate matter (DPM) has emerged as the main pollutant, which adversely affects human health, especially in urban settlements, mainly because of increased use of diesel fuelled vehicles. Several studies have been performed for characterization and reduction of DPM [2–5]. DPM consists of elemental carbon (EC), organic carbon (OC), sulphates, nitrates, trace metals, etc. [6]. It is reported that transition metals can penetrate deep into the airways in the human body and can even enter into the cells of the human body. These trace metals then increase the reactive oxygen species (ROS) activity in the cell structures [7–9], which results in elevated oxidative stresses [10,11]. HEI [12] report elaborated that there are mainly four sources of trace metal emissions from the vehicle viz. tailpipe emissions, metals emanating from tyre wear, metals emanating from brake liner wear and re-suspension of road dust in the ambient environment. They performed a study for characterization of trace metal emissions from vehicles by carrying out an extensive tunnel and lab based sampling of vehicular smoke [12]. They analyzed these four sources of trace metals due to vehicular activities and attributed their individual contributions to the total trace metal emission using chemical mass balance (CMB) model. Trace metals are either crustal metals or anthropogenic metals, which may be non-carcinogenic or carcinogenic however trace metals emitted by the engine are considered anthropogenic metals. IARC-1990 and IARC-1993 considered Ni, Cd and Cr as carcinogenic

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metal elements [13,14]. Several scientific studies reported that biodiesel is emerging as an important alternative fuel globally. Studies showed that total particulate mass (TPM) emissions from biodiesel or its blends were lower compared to baseline mineral diesel [15–19]. Studies also showed the production and utilization challenges of biodiesel for use in internal combustion engines [20–22]. With increasing possibility of biodiesel usage on a large scale worldwide, there is a need to comprehensively investigate the chemical composition of diesel and biodiesel origin particulate from environmental and health perspective. Betha et al. characterized the emission of particle bound trace metals from a stationary engine fuelled with ultra-low sulphur diesel (ULSD), waste cooking oil-derived biodiesel (B100) and blend of both (B50), and observed that crustal elements such as Mg, K and Al were found to be in higher concentration in particulates than other constituents [23]. They also estimated the health risks based on exposure and dose-response assessment and reported that exposure to biodiesel (B100) particulate was more toxic compared to ULSD origin particulate [23]. In another study performed by Wang et al. 2003, it was reported that crust metals were in significantly higher concentration compared to anthropogenic metals emitted by a diesel engine operated under transient conditions [24]. Muzyka et al. reported in their study that the trace metals were generally attached to the fine granular matter present in the exhaust [25]. Valavanidis et al. explored the toxic effects of Fe, when it penetrated into the lower airways of human lungs [26]. Sharma et al. characterized diesel particulate for trace metals and other emissions from a 40 kW diesel engine [27]. They reported that the trace metal content decreased in the particulate as the engine load increased from idle to full load. They also reported that the crust elements Fe, Mg, Ca were much higher as compared to other trace metals [27]. Gangwar et al. performed experiments on comparative toxicity of diesel and biodiesel particulate using a modern common rail direct injection (CRDI) transportation engine [28]. They reported that trace metals in the particulate decreased with increasing engine load [28]. Cheung et al. evaluated the emissions of trace metals and organic species from three light-duty passenger vehicles in five different configurations [29]. Their results showed much higher crustal trace metal emissions compared to anthropogenic trace metal emissions [29]. Kothari et al. performed chemical analysis of particulate collected from a engine fuelled with mineral diesel and biodiesel blends for trace metals, benzene soluble organic fraction, etc. [30]. They reported that Ca, Mg, Fe, Zn were in relatively higher concentration in biodiesel particulate, while Cu, Pb, Cr, Ni, Na were in relatively higher concentration in diesel particulate [30]. Dwivedi et al. reported that use of 20% biodiesel blend (derived from rice-bran oil) led to increase in carcinogenic metal element such as Cr and decrease in carcinogenic metal elements such as Cd and Ni [31]. Trace metal concentration in exhaust may also vary depending on type of feedstock oil used for biodiesel production. As evident from the literature, DOC is quite an effective tool for reduction of particulate emissions and their toxicity. However, DOCs are not widely investigated for their effect on trace metal emissions from transport diesel engines. Therefore, there is a need to investigate the effect of DOCs on the trace metals in exhaust emissions from transport diesel engines. In the present study, an attempt has been made to determine the concentrations of trace metals and inorganic ions in Karanja biodiesel blend (KB20) origin particulate vis-à-vis mineral diesel origin particulate, emanating from a medium duty transportation engine.

2. Experimental setup and methodology

A four-cylinder naturally aspirated water-cooled transportation engine (Tata Motors; Indica 475 IDI) was used for the comparative chemical analysis of mineral diesel and Karanja biodiesel (KB20) origin particulate. The test engine was equipped with a rotary fuel injection pump and a commercial diesel oxidation catalyst (DOC). Engine crankshaft was coupled to an eddy current dynamometer. Fig. 1 shows the schematic of the experimental setup. Test engine and dynamometer specifications are given in Tables 1 and 2.

Diesel and biodiesel particulate were collected from the engine exhaust on a filter paper. Before particulate sampling, blank filter paper sample was taken in order to account for the background concentration of trace metals. Blank values were subtracted from the sample values for this purpose. Sections of this filter paper were analyzed for particulate mass, trace metals, inorganic ions and morphology. For morphological comparison, particulate images were taken at 1000× magnification using a field emission scanning electron microscope (FE-SEM) for all particulate samples collected on the filter paper. FE-SEM features magnification of more than one million times and its resolution is up to 2 nm (Source: Centre of Nano-Sciences, IIT Kanpur, India).

A commercial DOC was fitted in the exhaust pipe of the test engine, and particulate were collected with and without DOC. Sampling probes in the exhaust line were used to divert a fraction of exhaust into a partial flow dilution tunnel, where it mixes with preconditioned and filtered air. Partial flow dilution tunnel is a device in which, a fraction of exhaust mixes with preconditioned and filtered air and a fixed dilution ratio is maintained in this device. Dilution ratio was kept at 16 and conditioned air temperature was maintained at ~52 °C during the experiments. For all operating conditions, the exhaust diluted with conditioned air was passed through a filter paper and the particulate were collected on the preconditioned quartz filter paper placed inside the filter holder assembly of the dilution tunnel. Table 3 provides the details of biodiesel properties measured.

2.1. Procedure

Particulate samples were collected on 47 mm diameter quartz filter papers under different engine operating conditions. Each filter paper was placed in desiccator for 24 h before sampling, in order to remove moisture traces. Particulate sampling was done for 15 min under predetermined conditions and particulate laden filter papers were again kept in desiccator immediately after the sampling. The difference in weights before and after the sampling gives the particulate loading on the filter paper. From these filter papers, two filter paper portions (Circular holes of 16.5 mm diameter) were extracted for ion chromatography and trace metal analysis respectively. These samples were analyzed for trace metal concentration byinductively couple plasma-optical emission spectroscopy (ICP-OES) technique and for ions by using ion chromatography technique. Details on ICP-OES and ion chromatography analyzes can be found in our earlier publication by Chakraborty and Gupta [32]. For comparative morphological investigations, images of particulate laden filter paper with 1000× magnification were taken by placing a 9.5 mm diameter punched portion of filter paper in a scanning electron microscope (SEM). Test matrix for all experiments and analyses in this study is given in Table 4.

3. Results and discussion

Diesel and Karanja biodiesel (B20) particulate were collected on a filter paper, with and without using DOC. PM emissions increased with increasing engine load for diesel and biodiesel both (Fig. 2) for identical sampling duration. Increased fuel quantity injected at higher engine load was the main reason for increased particulate emission from these test fuels. Biodiesel however showed significantly lower PM emissions (approximately 50% lower) compared