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# **RESEARCH ARTICLE**

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# Assessment of toxic potential of primary and secondary particulates/ aerosols from biodiesel vis-à-vis mineral diesel fuelled engine

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#### Abstract

Toxicity of engine out emissions from primary and secondary aerosols has been a major cause of concern for human health and environmental impact. This study aims to evaluate comparative toxicity of nanoparticles emitted from a modern common rail direct injection engine (CRDI) fuelled with biodiesel blend (B20) vis-à-vis mineral diesel. The toxicity and potential health hazards of exhaust particles were assessed using various parameters such as nanoparticle size and number distribution, surface area distribution, elemental and organic carbon content and polycyclic aromatic hydrocarbons adsorbed onto the particle surfaces, followed by toxic equivalent factor assessment. It was found that biodiesel particulate toxicity was considerably lower in comparison to mineral diesel.

#### Keywords

Elemental and organic carbon, nanoparticles, polycyclic aromatic hydrocarbons, secondary aerosols, size and number distribution, toxicity equivalent potential

#### History

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# Introduction

Engine exhaust is considered to be a major source of secondary organic aerosols (SOA) (Robinson et al., 2007), which has adverse effects on human health, climate, and environment (Baltensperger et al., 2008). The current vehicular emission legislations focus solely on the control of primary emissions. Currently, biodiesel is drawing serious attention globally as a part of solution to meet the demand for renewable transport fuels and to reduce greenhouse gas emissions. This calls for a comparative study of the toxic potential, quantity and nature of primary and secondary aerosols generated by a contemporary diesel engine fuelled with biodiesel blend (B20) vis-à-vis baseline mineral diesel.

The increased use of diesel engines due to their fuel economy, durability and power advantage has contributed to large volumes of diesel exhaust emissions. There is a need for clear understanding of the physicochemical nature and fate of these emissions in the environment. Diesel emissions are mainly divided into two categories: regulated emissions (nitrogen oxides, unburnt hydrocarbons, carbon monoxide and particulates) and unregulated emissions (aldehydes, benzene toulene xylene [BTX], polycyclic aromatic hydrocarbons [PAHs], etc.) (Cheung et al., 2009). Present emission regulations are based on the mass concentration of tailpipe emissions alone. However, several studies have linked the

adverse health effects directly to the tiny size and overwhelmingly large number of particulates present in the diesel exhaust (Diaz et al., 2012). Therefore, there is a need to regulate the particle numbers as well in order to avoid the harmful effects of ultra fine particles. Several countries have regulated the particle number emissions in their newest emission regulations and many countries are planning to follow the suit in the near future. In the past decades, diesel emissions have been reduced greatly mainly due to advancements in combustion, engine technology, improved fuel injection systems, such as common rail direct injection (CRDI) systems, and use of exhaust gas after-treatment technologies (Majewaski and Khair, 2006). Although particulate mass emissions have reduced substantially from the modern diesel engines, particle number emissions continue to increase, which will have an important role in future emission regulations (Kittelson, 1998). Bergmann et al. (2009) observed that after-treatment devices like diesel particulate trap in the modern engines significantly decrease the total particulate mass. However, this technology increases the number concentration of nuclei mode particles downstream of filters which in-turn significantly enhances formation of SOA by providing additional surface area for condensation (Bergmann et al., 2009).

Particulate formation in diesel engine exhaust is a complex process. When the engine exhaust, volatile organic species rich in ultra fine particulates comes out of the tailpipe; it gets diluted and exhaust cooling takes place in the atmosphere. Gas-to-particle conversion of low-volatility compounds is aided by the complex free-radicals based photo-oxidation

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reactions as well as aqueous chemical oxidation processes (Kaul et al., 2011). Organic part of the particulates produced by gas-to-particle conversion is known as SOA.

Diesel engine exhaust mainly consists of elemental carbon (EC) with adsorbed vapors, a large amount of volatile and semi-volatile organic species, and a large number, and small mass of 10-50 nm diameter particles (mostly sulfate and organic carbon (OC)) formed nearly instantaneously by condensation post-combustion (Maricq, 2007). These particles are rich in many harmful organic species such as PAHs, which are carcinogenic in nature (Karavalakis et al, 2009; Ravindra et al., 2008). He et al. (2010) investigated and characterized the PAHs emissions from diesel engines. They performed the experiments using diesel, biodiesel (B100), and 20% biodiesel blend (B20). Their results showed that there was a significant reduction in PAHs emissions with B100 and B20 vis-à-vis diesel. Their analysis also showed that there was a close relationship between the emissions of PAHs and particulate matter (PM). Borras et al. (2009) conducted a study to investigate the effects of diesel reformulation on engine-operating parameters, with particular focus on PAHs emissions. There is no significant change in percentage in PAHs detection, although they used low-sulfur diesel with varying aromatic content. They concluded that PAHs emissions from the incomplete combustion of diesel greatly depend on the source of fuel and driving cycle.

In the last decade, biodiesel has emerged as an important alternative fuel for diesel engines. Biodiesel emits lesser particulate mass vis-à-vis mineral diesel and is a good alternative renewable fuel for partial replacement of mineral diesel. However, it is essential to investigate the toxicity of biodiesel exhaust particulates in primary and secondary emissions. The toxicity of these particulates largely depends on the organic fraction of the particulates. The main focus of this research is assessment of toxic potential of primary and secondary particulates/aerosols from biodiesel vis-à-vis mineral diesel-fuelled engine.

# **Experimental setup**

Particle number, mass, and surface area distributions with respect to particle size were measured in order to physically characterize primary and secondary emissions at various engine loads (0%, 12.5%, 25%, 37.5%, 50%, 62.5%, 75%, 87.5% and 100%) for rated engine speed (1800 rpm). Chemical characterization of primary and secondary emissions was carried out using real-time EC, OC and total particle-bound PAHs measurements.

For the comparative study of mineral diesel and B20, a modern CRDI diesel engine (Tata; Safari DICOR 3.0L) coupled with an eddy current dynamometer (Dynomerk; ECB 300) were employed. The experimental setup for this study (Figure 1) consists of a custom-built photochemical chamber. A fluorinated ethylene propylene (FEP) membrane was used to construct the chamber walls to avoid contamination and minimize wall losses. The chamber walls were transparent to complete UV spectrum. Additionally, inbetween the UV lamp banks and the photochemical chamber, a 40-µm thick sheet of cellulose acetate was used to filter out UV light with wavelengths below 300 nm (UV-C spectrum). This was done to keep the artificial light spectrum as close as possible to the spectrum of natural sunlight received at earth's surface. A humidity measurement sensor (Testo; 605H1) was used at the outlet of the photochemical chamber for monitoring temperature and humidity inside the chamber. Leak tests were performed in order to avoid any interference from the ambient. FEP membrane was thoroughly cleaned by ethanol and milli-Q water initially. Before starting an experiment, zero air supply was used to flush the photochemical chamber. Zero air supply setup comprised of an external compressor, pressure regulators, chemical scrubbers, a reactor and a temperature controller, all contained in one enclosed unit. Up to 20 LPM Zero grade air can be supplied at 4 bar pressure by the self-contained compressor. This air supply was used to flush the photochemical chamber in order to remove trace pollutants left from the previous experiment. Experimental setup was equipped with EC/OC analyzer (Sunset Laboratory; Semi-continuous field v.4) (Gupta et al., 2011); online PAHs analyzer (EcoChem Labs; PAS 2000) (Bae et al., 2004; Ott & Siegmann, 2006) to measure total particulate bound PAHs; engine exhaust particle sizer spectrometer (TSI; 3090) to measure the number-size distribution of nanoparticles (5.6-560 nm electrical mobility diameters). A partial flow dilution



Figure 1. Schematic of the experimental setup.

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tunnel was employed to dilute the engine exhaust in order to enable completion of particle formation processes mimicking atmospheric conditions (Dwivedi et al., 2006). Average wall losses (approximately 36%) were measured using the penetration of EC through the photochemical chamber in the absence of UV light. All measurements for EC, OC and total particle bound PAHs in the secondary emissions were corrected for chamber wall losses.

### Physical characterization of particulates

Physical characterization of particulates was done by measurement of nanoparticle numbers, mass and surface distributions for primary and secondary aerosols at different engine loads at rated engine speed of 1800 rpm. In primary diesel exhaust, particle number concentration increased abruptly for 100% rated engine load for nucleation mode particles. For B20, there were significant number of particles less than 10 nm in the primary exhaust and the number-size distribution was relatively flatter compared to mineral diesel. It can also be noted that addition of 20% biodiesel to mineral diesel led to almost two orders of magnitude reduction in particulate size-number distribution. Most of these particles were nucleation mode particles, which usually consists of benzene soluble organic fraction (BSOF), EC and sulfates (Abdulkhalek & Kittelson, 1995). At lower engine loads, the temperature of the combustion chamber was relatively lower, which led to a large fraction of unburned fuel and lubricating oil being pyrolyzed to form a large number of nucleation mode particles (nanoparticles). As the engine load was increased, more fuel was injected in every engine cycle. Combustion takes place at relatively higher cylinder temperatures leading to more effective combustion, and lower amount of unburnt organic species were produced in the cylinder. This led to reduction in BSOF of the particulates and higher exhaust gas temperatures resulted in a phase transition, increasing their concentration in the gas phase. This also led to reduction in total number of particles emitted with increasing engine load as BSOF is critical for growth of soot nuclei. Similarly, sulfur content of the fuel dictates the number of sulfate nuclei formed in the cylinder. This further explains lower number concentration of primary particles from B20 as biodiesel is essentially sulfur free. Biodiesel also contains approximately 10% (w/w) oxygen, which leads to sharp reduction in particle number-size distribution in the primary exhaust.

There was a sharp decrease in particle number concentration in secondary aerosols in comparison to the primary emissions (Figure 2). This might be possibly due to gravitational settling, wall losses, sampling losses and various other chemical reactions occurring inside the photo-chemical chamber (Gupta et al., 2011; Ruiz et al., 2007). Significantly lower particle number concentration in secondary emissions was observed for no load for both the fuels. A large number of smaller particles emitted (particularly at lower engine loads) enter the photochemical chamber, undergo condensational growth and agglomeration. These processes result in lower number concentrations and increase in particle diameters. However, it is interesting to note that very small particles (<10 nm) emitted by B20 were still



Figure 2. Particle number concentration versus mobility diameter for primary and secondary exhaust fuelled with diesel and B20.

prevailing as secondary aerosols. Particles emitted (in primary emissions) at higher engine loads were dominated by relatively larger particles, which shows slightly lower tendency to undergo agglomeration.

A sudden increase in number concentration was observed at 25% engine load for both the fuels. Possibly, the conditions inside the photochemical chamber (37.5 °C and 50% RH) might be the most favorable for SOA formation. Peaks were also observed in the particle number concentration in secondary emissions at smaller particle diameters, which is more clearly visible in secondary emissions from B20. This is a sign of fresh nuclei formation in the photochemical chamber, which is in line with the observations of Robinson et al. (2007). The particles inside the chamber were in a heterogeneous transient phase. This also explains high variability in the aerosol size distribution for the secondary aerosols.

As the engine load increased, the peak of particle number concentration shifted toward larger diameters for primary as well as secondary aerosols for both fuels. The particle number 4 A.K. Agarwal et al.

Figure 3. Integrated particulate matter (PM) mass and surface area concentrations versus engine load for primary and secondary exhaust fuelled with diesel and B20.



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concentration in primary and secondary diesel exhaust was an order of magnitude higher than B20 (Agarwal et al., 2011).

At a constant rated engine speed of 1800 rpm, the total PM mass in primary emissions from diesel increases with engine load (Figure 3). Particle number concentrations at lower engine loads were higher, but particle diameters were smaller. Hence, they cannot contribute significantly to the PM mass. For B20, at lower engine loads, PM mass in the primary emissions increased with engine load, with a maxima at 50% engine load. The PM mass in primary and secondary emissions from diesel was higher than B20 by an order of magnitude. Numerous studies in the literature have indicated similar trends (Agarwal et al., 2011; Cowley et al., 1993; Den Ouden et al., 1994; Kalligeros et al., 2003; Lange, 1991). Oxygen content of B20 favors efficient fuel combustion

resulting in the lower PM mass (Akasaka et al., 1997; American Biofuels Association, 1995; Owen & Coley, 1995).

Total surface area of the particles would be directly proportional to the particle's number and inversely proportional to the particle size. Reduction in primary emission particle number concentration and increase in the particle size were observed with increasing engine load for B20. Higher number concentration at lower engine loads (Figure 2) for primary diesel emissions leads to lower PM mass and higher particulate surface area (Figure 3). For B20, the trend of particulate surface area curve is very well correlated to the PM mass curve, with a peak at 50% engine load. At 100% engine load, i.e. rated engine load, the mode of number-size distribution (Figure 2) shifts toward right and the area under the curve is maximum, which results in the maximum particle

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Figure 4. Variation of EC/OC ratio for primary and secondary versus engine load for primary and secondary exhaust fuelled with diesel and B20.

surface area for primary diesel emissions (Figure 3). At all engine loads, the surface area distribution in primary emissions from diesel is an order of magnitude higher than B20.

# Chemical characterization of particulates

Increase in particle number concentration in secondary emissions (Figure 2) with increase in engine load was the main reason for corresponding increase in particulate surface area (Figure 3). The surface area distribution in secondary emissions from diesel was higher by an order of magnitude compared to B20. Larger surface area of particles provided more sites for condensation of toxic organic species (Bruske et al., 2010). Therefore, secondary emissions from diesel would have higher toxic potential compared to B20.

The trend of increase in EC upon increasing engine load matches with the variation of EC with engine load, as observed in a recent study on secondary OC from mineral diesel fuelled CRDI engine (Gupta et al., 2011). At higher engine loads, the fuel-to-air ratio and the temperature of the combustion chamber, both were relatively higher leading to higher EC formation. Moreover, at very high engine loads, relatively higher temperatures caused lubricating oil pyrolysis resulting in even higher EC (Sharma et al., 2005).

OC fraction mainly comprises of unburnt fuel, lubricating oil, and products of incomplete combustion. At lower engine loads, OC increased with an increase in engine load until it attained maxima. From here, it started decreasing with further increase in engine load (Gupta et al., 2011). Higher oxygen content of B20 facilitated more efficient combustion vis-à-vis



Figure 5. Variation of total particle-bound PAHs versus engine load for primary and secondary exhaust fuelled with diesel and B20.

mineral diesel. This brought about a relative reduction in the unburned hydrocarbon content (primarily OC) of B20 particulates therefore a higher EC/OC ratio was observed for primary as well as secondary particles (Figure 4). The EC/ OC ratio was found to be higher for diesel at relatively higher engine loads. This could be possibly because of a more pronounced peak of OC observed at 50% engine load. For B20, EC/OC ratio was relatively lower compared to diesel at higher engine loads.

At a constant engine speed of 1800 rpm, the total particle bound PAHs increase with an increase in engine load (Figure 5) for both fuels. PAHs in secondary emissions were higher than primary emissions at all engine loads for both fuels. At higher engine loads, high cylinder temperature facilitates cyclization of unburned fuel and lubricating oil, leading to formation of PAHs by pyrosynthesis (Ravindra et al., 2008). As a result of cooling and aging processes, large amount of gaseous phase PAHs undergo phase transition and condense onto the particulates. PAHs get adsorbed onto the exhaust particles and somehow persist as a result of incomplete combustion inside the engine (Atal et al., 1997). One interesting observation is that there was a drastic reduction in PM mass for B20 vis-à-vis diesel, whereas particle bound PAHs were comparable for both the fuels. This indicates that the particulates from B20 were relatively highly loaded with PAHs.

# PAHs and nitro-PAHs speciation and determination of toxic equivalent factor

PAHs are categorized as one of the major carcinogenic compounds in the environment, which are formed by incomplete combustion of fuels in combustion systems. PAHs are mainly composed of hydrogen and carbon with traces of oxygen but sometimes may also contain nitrogen, and such species are called nitro-PAHs, which are highly toxic in nature. The toxic properties of PAHs are highly dependent on its molecular structure. Several studies show that some PAHs are highly toxic but on the other hand, some of them are relatively benign (Ravindra et al., 2008). Determination of toxic potential of PAHs can be evaluated for understanding the toxic impacts produced by individual species of PAHs. This can be determined by integrating the individual toxicity of PAHs, which can be obtained by

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Table 1. Total toxic potential calculation of individual PAHs for diesel (primary and secondary emissions).

|                       | PAHs                | TEFs           | Engine load (%) |        |         |         |         |         |          |  |
|-----------------------|---------------------|----------------|-----------------|--------|---------|---------|---------|---------|----------|--|
| S No.                 |                     |                | 0               | 20     | 40      | 60      | 75      | 87.5    | 100      |  |
| Toxic po              | tential calculation | for primary er | nissions (dies  | el)    |         |         |         |         |          |  |
| 1                     | B[A]A               | 0.1            | 0.055           | 0.405  | 1.274   | 3.828   | 7.749   | 15.861  | 27.759   |  |
| 2                     | CHR                 | 0.01           | 0.010           | 0.076  | 0.240   | 0.722   | 1.462   | 2.992   | 5.236    |  |
| 3                     | B[B]F               | 0.1            | 0.071           | 0.520  | 1.638   | 4.923   | 9.966   | 20.401  | 35.704   |  |
| 4                     | B[K]F               | 0.1            | 0.065           | 0.479  | 1.509   | 4.534   | 9.178   | 18.788  | 32.882   |  |
| 5                     | B[A]P               | 1              | 0.439           | 3.232  | 10.176  | 30.579  | 61.903  | 126.715 | 221.767  |  |
| 6                     | I[1,2,3]P           | 0.1            | 0.079           | 0.578  | 1.821   | 5.473   | 11.079  | 22.679  | 39.691   |  |
| 7                     | D[A,H]A             | 1.1            | 0.203           | 1.495  | 4.707   | 14.143  | 28.631  | 58.608  | 102.571  |  |
| 8                     | B[G,H,I]P           | 0.01           | 0.008           | 0.061  | 0.191   | 0.573   | 1.159   | 2.373   | 4.153    |  |
|                       | N-PAHs              |                |                 |        |         |         |         |         |          |  |
| 9                     | 1-NPYR              | 0.1            | 0.013           | 0.094  | 0.296   | 0.888   | 1.798   | 3.681   | 6.441    |  |
| 10                    | 6-NCHR              | 10             | 0.067           | 0.492  | 1.548   | 4.652   | 9.418   | 19.279  | 33.740   |  |
| Total toxic potential |                     |                | 1.010           | 7.432  | 23.399  | 70.314  | 142.344 | 291.377 | 509.944  |  |
| Toxic po              | tential calculation | for secondary  | emission (die   | sel)   |         |         |         |         |          |  |
| 1                     | B[A]A               | 0.1            | 0.264           | 1.442  | 6.304   | 16.029  | 23.495  | 50.472  | 84.235   |  |
| 2                     | CHR                 | 0.01           | 0.050           | 0.272  | 1.189   | 3.023   | 4.432   | 9.520   | 15.888   |  |
| 3                     | B[B]F               | 0.1            | 0.339           | 1.854  | 8.108   | 20.616  | 30.219  | 64.917  | 108.342  |  |
| 4                     | BKF                 | 0.1            | 0.312           | 1.708  | 7.467   | 18.987  | 27.831  | 59.786  | 99.779   |  |
| 5                     | B[A]P               | 1              | 2.107           | 11.518 | 50.359  | 128.053 | 187.702 | 403.220 | 672.948  |  |
| 6                     | I[1,2,3]P           | 0.1            | 0.377           | 2.061  | 9.013   | 22.918  | 33.594  | 72.167  | 120.442  |  |
| 7                     | D[A,H]A             | 1.1            | 0.974           | 5.327  | 23.292  | 59.227  | 86.816  | 186.496 | 311.250  |  |
| 8                     | B[G,H,I]P           | 0.01           | 0.039           | 0.216  | 0.943   | 2.398   | 3.515   | 7.551   | 12.603   |  |
|                       | N-PAHs              |                |                 |        |         |         |         |         |          |  |
| 9                     | 1-NPYR              | 0.1            | 0.061           | 0.335  | 1.463   | 3.719   | 5.452   | 11.712  | 19.546   |  |
| 10                    | 6-NCHR              | 10             | 0.321           | 1.752  | 7.662   | 19.482  | 28.558  | 61.347  | 102.385  |  |
| Total toxic potential |                     |                | 4.845           | 26.485 | 115.798 | 294.453 | 431.614 | 927.188 | 1547.418 |  |

Table 2. Total toxic potential calculation of individual PAHs for B20 (primary and secondary emissions).

|                       | PAHs                | TEFs         | Engine load (%) |             |        |         |         |         |         |          |         |
|-----------------------|---------------------|--------------|-----------------|-------------|--------|---------|---------|---------|---------|----------|---------|
| S No.                 |                     |              | 0               | 12.5        | 25     | 37.5    | 50      | 62.5    | 75      | 87.5     | 100     |
| Toxic p               | otential calculati  | ion for prir | nary emissi     | on(B20)     |        |         |         |         |         |          |         |
| 1                     | B[A]A               | 0.1          | 0.077           | 0.211       | 0.602  | 1.115   | 2.761   | 5.516   | 9.108   | 17.703   | 32.770  |
| 2                     | CHR                 | 0.01         | 0.012           | 0.033       | 0.094  | 0.175   | 0.433   | 0.864   | 1.427   | 2.773    | 5.133   |
| 3                     | B[B]F               | 0.1          | 0.067           | 0.184       | 0.527  | 0.975   | 2.414   | 4.823   | 7.964   | 15.479   | 28.653  |
| 4                     | B[K]F               | 0.1          | 0.074           | 0.203       | 0.581  | 1.075   | 2.663   | 5.319   | 8.783   | 17.070   | 31.599  |
| 5                     | B[A]P               | 1            | 0.323           | 0.885       | 2.530  | 4.681   | 11.596  | 23.165  | 38.250  | 74.342   | 137.617 |
| 6                     | I[1,2,3]P           | 0.1          | 0.065           | 0.179       | 0.511  | 0.946   | 2.343   | 4.680   | 7.729   | 15.021   | 27.806  |
| 7                     | D[A,H]A             | 1.1          | 0.226           | 0.619       | 1.771  | 3.276   | 8.117   | 16.215  | 26.775  | 52.040   | 96.332  |
| 8                     | B[G,H,I]P<br>N-PAHs | 0.01         | 0.007           | 0.020       | 0.056  | 0.104   | 0.257   | 0.513   | 0.847   | 1.646    | 3.047   |
| 9                     | 1-NPYR              | 0.1          | 0.025           | 0.069       | 0.197  | 0.364   | 0.901   | 1.800   | 2.973   | 5.777    | 10.695  |
| 10                    | 6-NCHR              | 10           | 0.018           | 0.049       | 0.141  | 0.261   | 0.646   | 1.291   | 2.131   | 4.142    | 7.668   |
| Total toxic potential |                     | 0.895        | 2.452           | 7.010       | 12.969 | 32.132  | 64.186  | 105.987 | 205.994 | 381.320  |         |
| Toxic p               | otential calculati  | ion for seco | ondary emis     | ssion (B20) |        |         |         |         |         |          |         |
| 1                     | B[A]A               | 0.1          | 0.319           | 1.054       | 1.751  | 4.972   | 11.813  | 16.292  | 26.170  | 53.635   | 97.191  |
| 2                     | CHR                 | 0.01         | 0.050           | 0.165       | 0.274  | 0.779   | 1.851   | 2.552   | 4.099   | 8.402    | 15.225  |
| 3                     | B[B]F               | 0.1          | 0.279           | 0.921       | 1.531  | 4.348   | 10.329  | 14.245  | 22.882  | 46.898   | 84.982  |
| 4                     | B[K]F               | 0.1          | 0.308           | 1.016       | 1.688  | 4.795   | 11.391  | 15.710  | 25.235  | 51.720   | 93.720  |
| 5                     | B[A]P               | 1            | 1.340           | 4.426       | 7.353  | 20.881  | 49.610  | 68.418  | 109.900 | 225.241  | 408.155 |
| 6                     | I[1,2,3]P           | 0.1          | 0.271           | 0.894       | 1.486  | 4.219   | 10.024  | 13.824  | 22.206  | 45.511   | 82.469  |
| 7                     | D[A,H]A             | 1.1          | 0.938           | 3.098       | 5.147  | 14.617  | 34.727  | 47.893  | 76.930  | 157.669  | 285.709 |
| 8                     | B[G,H,I]P           | 0.01         | 0.030           | 0.098       | 0.163  | 0.462   | 1.098   | 1.515   | 2.433   | 4.987    | 9.037   |
|                       | N-PAHs              |              |                 |             |        |         |         |         |         |          |         |
| 9                     | 1-NPYR              | 0.1          | 0.104           | 0.344       | 0.571  | 1.623   | 3.855   | 5.317   | 8.541   | 17.504   | 31.719  |
| 10                    | 6-NCHR              | 10           | 0.075           | 0.247       | 0.410  | 1.163   | 2.764   | 3.812   | 6.123   | 12.550   | 22.742  |
| Total toxic potential |                     | 3.714        | 12.263          | 20.375      | 57.859 | 137.464 | 189.578 | 304.520 | 624.116 | 1130.949 |         |



Figure 6. Values of total toxic equivalent potentials with respect to engine load for primary and secondary exhaust fuelled with diesel and B20.

multiplying the toxic equivalent factors (TEFs) of the individual PAH species with their respective concentrations. TEFs for PAHs were obtained from the study conducted by Nisbet & Lagoy (1992) and are also reported by CAEPA (1993). In this study, a total of eight PAHs and two nitro-PAHs were considered for the evaluation of toxic potential.

Pan et al. (1998) compared the PAHs and nitro-PAHs emissions from diesel, biodiesel (B100; soy methyl ester), and B20. They performed experiment on a Cummins B5.9 engine. The values for PAHs and nitro-PAHs emissions for diesel as well as biodiesel blends were obtained by using gas chromatography and mass spectrometry. In our calculations, the data for percentage distribution of PAHs species from the study of Pan et al. (1998) have been used. Total PAHs data in this study is attributed to individual PAHs based on the above study.

The trend of total toxic equivalent potential (Figure 6) was similar to particle-bound PAHs emissions (Figure 5). Diesel showed slightly higher toxic potential compared to B20 for both primary and secondary particles. Primary particles have lesser total toxic potential compared to secondary particles. When exhaust emanates from the exhaust pipe, a major part of PAHs are present in vapor phase, which remain undetected during primary particle phase PAHs measurement. In this study, secondary measurements were taken after 2 h photochemical chamber residence time. This provided sufficient time for the condensation and transformation of gas phase aged PAHs into particle bound PAHs.

It was observed that TEFs for diesel was higher at 100% engine load for both primary and secondary particles. Overall TEFs were 509.944 and 381.32 for diesel and B20 (primary particles), respectively, at 100% engine load. Similarly, TEFs were 1547.42 and 1130.35 for diesel and B20 (secondary particles), respectively, at 100% engine load. The lower values of TEFs for B20 indicate that it predominantly has individual PAHs with lower toxicity. This signifies that, although B20 originated particulates had significantly higher PAHs loading, their contribution to overall toxicity was far lesser than that of particulates from mineral diesel. Details about TEFs for both fuels (primary and secondary particulates both) are given in tabular form in Tables 1 and 2.

# Conclusions

In this study, particle number emissions, PM mass emissions, EC/OC and PAHs emissions were compared for diesel and B20. Lower BSOF in the exhaust particulates were found at higher engine loads. As the engine load increased, BSOF content of the particulates decreased and there was a phase transition enriching their concentration in the gas phase. This led to reduction in number of particles emitted with increasing engine load because BSOF was critical for particulate growth. Particle number-size distribution peak shifted toward right side on the particle size axis for secondary emissions for both fuels (diesel and B20). Particle number concentration was two orders of magnitude lower for biodiesel blend for primary as well as secondary emissions. The amount of sulfur in the fuel primarily dictates the sulfate nuclei formation. This explains lower number of primary particles in B20 exhaust since biodiesel is essentially sulfur free. Total PM mass was also an order of magnitude lower for B20 exhaust for primary as well as secondary emissions. For B20, EC/OC ratio was relatively lower compared to diesel at higher engine loads. PAHs were significantly higher in secondary emissions for both fuels. The gas-to-particle phase conversion of PAHs in the exhaust leads to higher concentration of PAHs in the secondary emissions. PAHs were higher in case of diesel for both primary and secondary particulates. The particulates emitted by B20 were laden with PAHs to a higher degree. Toxicity was found to be higher for secondary particles compared to primary particles for both the fuels. Toxicity was also found to be lower for B20 in both primary and secondary particles visà-vis mineral diesel. The lower value of total toxicity for B20 indicates that it predominantly has individual PAHs with lower toxicity. This concludes that although B20 originated particulates have significantly higher PAHs loading, their contribution to overall toxicity is far lesser than that of particulates from mineral diesel.

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# **Declaration of interest**

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