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The organic composition of diesel particulate matter, diesel fuel and engine oil of a non-road diesel generator

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Diesel-powered equipment is known to emit significant quantities of fine particulate matter to the atmosphere. Numerous organic compounds can be adsorbed onto the surfaces of these inhalable particles, among which polycyclic aromatic hydrocarbons (PAHs) are considered potential occupational carcinogens. Guidelines have been established by various agencies regarding diesel emissions and various control technologies are under development. The purpose of this study is to identify, quantify and compare the organic compounds in diesel particulate matter (DPM) with the diesel fuel and engine oil used in a non-road diesel generator. Approximately 90 organic compounds were quantified (with molecular weight ranging from 120 to 350), which include alkanes, PAHs, alkylated PAHs, alkylbenzenes and alkanoic acids. The low sulfur diesel fuel contains 61% alkanes and 7.1% of PAHs. The identifiable portion of the engine oil contains mainly the alkanoic and benzoic acids. The composition of DPM suggests that they may be originated from unburned diesel fuel, engine oil evaporation and combustion generated products. Compared with diesel fuel, DPM contains fewer fractions of alkanes and more PAH compounds, with the shift toward higher molecular weight ones. The enrichment of compounds with higher molecular weight in DPM may be combustion related (pyrogenic).

1. Introduction

Non-road diesel equipment has been widely used in various applications, such as construction, power generation, underground mines and agriculture *etc*. However, the emissions of diesel particulate matter (DPM) from non-road sources are significant.[1–3] Studies have indicated that fine particulate matter in underground mines can exceed 1 mg m^{-3}.[4] DPM consists of a large number of organic compounds,[5–7] among which some polycyclic aromatic hydrocarbons (PAHs), such as chrysene and benzo(*a*)pyrene, are known or suspected human carcinogens.[8–13] Studies have indicated that occupational exposure to diesel exhaust may be related to lung cancer for bus garage workers, miners, and forklift workers *etc.*[2,7] It is well established that exposure to PAHs and their derivatives may result in a higher health risk.[14] This is resultant from the small size and toxic composition of DPM, as approximately 90% of the DPM mass is within the inhalable range (<1 μm). Diesel particulate matter is considered as a potential occupational carcinogen by several government agencies, such as the U.S. Environmental Protection Agency (EPA)[15] and the National Institute for Occupational Safety and Health (NIOSH).[16]

In addition to combustion (pyrosynthesis), the organic fractions of DPM may be resultant from unburned diesel fuel and engine oil. The composition of the diesel fuel has been identified and categorized into fractions of fuel input, such as 65–85% saturates, 5–30% aromatics, and 0–5% olefins.[17] The percentage may vary with manufactures, the mining locations, the refining processes and sulfur content. Sjogren *et al.* studied ten diesel fuels from different suppliers, and obtained considerably differed percentages for each category.[5] High sulfur content in the diesel fuels has been associated with more DPM emissions.[18] More stringent regulations have been proposed to reduce sulfur content in the near future to reduce particulate emissions. Engine oil is also believed to be a possible source of DPM. It was reported that some organic compounds in DPM are emitted from the evaporation of engine oil, such as some short-chain alkanoic acids, hopanes and steranes.[19,20]

Despite the progress in DPM sampling and analysis, there are still gaps to fill, especially in the compositional correlations among DPM, diesel fuel and engine oil. The aim of this study is to compare the organic composition of DPM to diesel fuel and engine oil and seek the correlation of DPM from petrogenic (raw materials such as diesel fuel and engine oil) and pyrogenic (combustion) sources.

2. Experimental methods

In this study, a Generac diesel generator (1992, Model SD080, model No. 92A-03040-S) was used as the non-road source of diesel particulate matter. It features direct-injection, turbocharging, and compression-ignition, and is rated at 80 kW, 60 Hz and 1800 rpm. Unlike diesel vehicles, diesel generators run at a fixed rpm and voltage and the amperage it produced can vary with the load.[21] The difference in operating mode can potentially result in different emission characteristics. A high volume sampler with a flow rate of approximately 300 L min^{-1} was used for sampling DPM with a sampling time of 1 h. The DPM was taken at idle mode (0 kW). Quartz filters were dried in a desiccator for 24 h and weighed before and after sampling. The low sulfur diesel fuel (Steve Krebs Oil Company, Inc., sulfur content: 433 ppmw) and engine oil from this generator were diluted with HPLC grade dichloromethane (DCM, Fisher Scientific) to known concentrations for GC/MS analysis.

To analyze organic acids in engine oil and DPM, the sample was first derivatized with *N*,*O*-bis[trimethylsilyl]trifluoroacetamide (BSTFA) to convert organic acids to their methyl ester analogues.

The detailed procedures of DPM extraction and instrumental analysis have been published elsewhere[22] and are briefly described here. After desiccation, samples were extracted in DCM with sonication and filtered to remove the insoluble fractions (such as soot). The extraction recovery is between 87–98% and is determined by spiking deuterated internal standards, such as naphthalene-d_8 (Aldrich) and phenanthrene-d_{10} (Aldrich), on sample filters. One fraction of the solution was concentrated to ~1 mL for GC/MS analysis and the other fraction derivatized with BSTFA for the analysis of organic acids.

In this study, gas chromatography/mass spectrometry (GC/MS, Varian, CP-3800 GC, Saturn 2200 MS) equipped with a CP-8400 automatic sampler was used. The column used for the analysis was CP-Sil 8 CB low Bleed/MS (30 m × 0.25 mm × 0.25 μm, equivalent of DB5-ms). The method of selective ion search was used to enhance the identification of the PAH compounds.

The following standards were used for quantification of compounds in DPM, diesel fuel and engine oil: (1) normal alkanes ranging from n-C_{10} to n-C_{25} (Restek, DRO Mix, Cat. No. 31214); (2) branched alkanes: norfarnesane, farnesane, norpristane, pristane and phytane (Chiron); (3) saturated cycloalkanes from C_{13} to C_{25} (Chiron); (4) a suite of 16 priority polycyclic aromatic hydrocarbons recommended by EPA (Aldrich, 16PAHs); (5) 16 alkylated aromatic hydrocarbons (Aldrich); (6) alkylbenzenes from C_1-benzene to C_6-benzene (Fisher Scientific); (7) 13 alkanoic acids from C_6 to C_{18} and benzoic acid (Fisher Scientific).

3. Results and discussion

In this study, the sample was taken at the exit of the exhaust pipe, and natural dilution was used. The DPM mass concentration is approximately 3.7 mg m^{-3}. Compared with other studies, our DPM mass concentration is in the range of the reported results.[18] However, the DPM emissions can vary significantly due to the size and type of diesel machines used, the sampling method, and the load reported. The mass concentration of DPM from a Jeep Bobtail (engine speed: 1700 rpm, engine load: 9–87 kW) reported by Zielinska *et al.* is in the range of 1687–3800 μg m^3.[23] Chan and He reported that the DPM mass concentration from the Ford FSD 425T turbocharged DI diesel engine (four-cylinder, direct injection, 800–4000 rpm, maximum power output 52 kW) was from 0.2 mg m^{-3} to more than a hundred mg m^{-3} at zero load condition.[24] In addition, the DPM emissions from diesel vehicles are often reported as mass per mile, which further complicates the comparison.

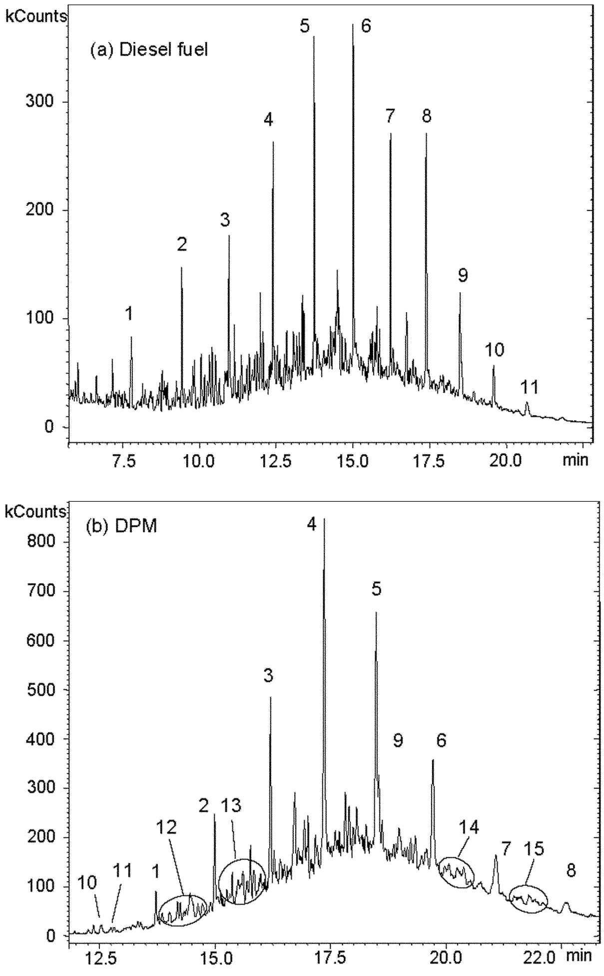


Fig. 1 Total ion chromatogram of diesel fuel and DPM (time in minutes). (a) Diesel fuel. Peaks 1–11: n-alkanes C_{10}–C_{20} (b) DPM. Peaks 1–8: n-alkanes C_{14}–C_{21}; peak 9: Phe; peak 10: 2-MN; peak 11: 1-MN; peak 12: DMN; peak 13: TMN; peak 14: MPh; peak 15: DMPh.

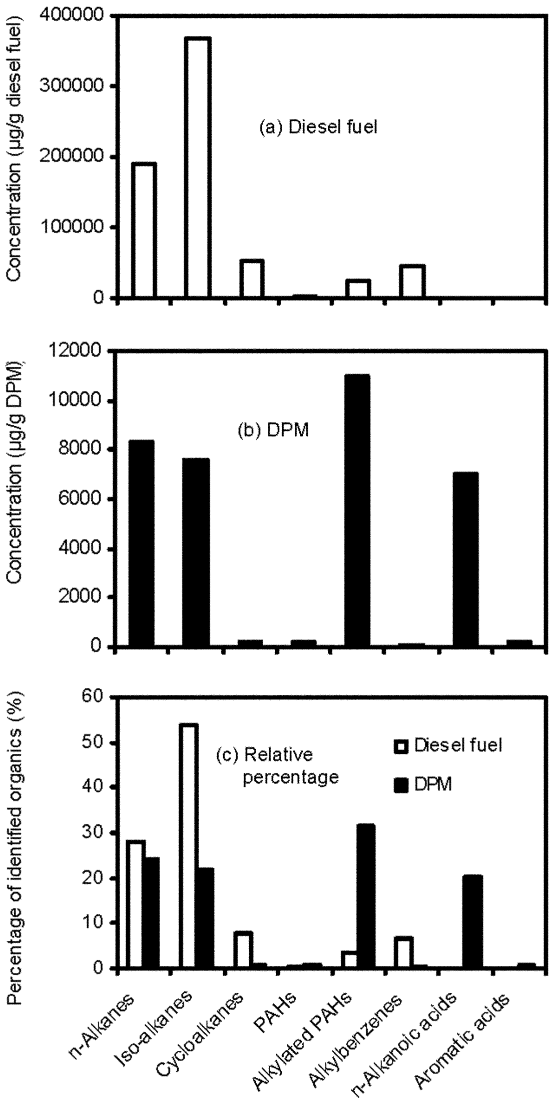


Fig. 2 Categorized organic composition in low sulfur diesel fuel and DPM. (a) and (b) are based on the actual concentrations and (c) is based on the relative percentage of total identified composition.

3.1 Chemical composition

Fig. 1(a) and (b) show the total ion chromatogram (TIC) of diesel fuel and DPM from GC/MS. The chemical composition of low sulfur diesel fuel, DPM and engine oil is listed in Table 1, and the compounds labeled "Nd" (not detected) can be either below the detection limit or not present in the sample. Fig. 2 summed up the compounds by categories, *i.e.* n-alkanes, branched alkanes, saturated cycloalkanes, PAHs, alkylated PAHs, alkylbenzenes, n-alkanoic acids and aromatic acids for the diesel fuel and DPM, and the relative fractions of each

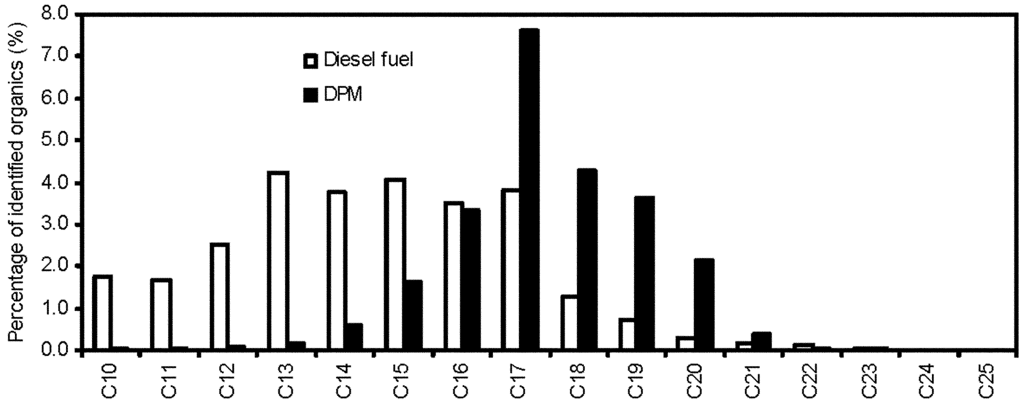
Table 1 Organic compounds present in low sulfur diesel fuel and diesel particulate matter[a]

Compounds	Diesel fuel composition/ $\mu g\ g^{-1}$	DPM composition/ $\mu g\ g^{-1}$	Engine oil composition/ $\mu g\ g^{-1}$
n-Alkanes			
n-Decane (C_{10})	12 115	9.71	Nd
n-Undecane (C_{11})	11 271	21.6	Nd
n-Dodecane (C_{12})	17 149	31.3	Nd
n-Tridecane (C_{13})	28 834	57.1	Nd
n-Tetradecane (C_{14})	25 604	204	Nd
n-Pentadecane (C_{15})	27 660	564	Nd
n-Hexadecane (C_{16})	23 965	1164	Nd
n-Heptadecane (C_{17})	26 082	2645	Nd
n-Octadecane (C_{18})	8727	1479	Nd
n-Nonadecane (C_{19})	4988	1257	Nd
n-Eicosane (C_{20})	2193	742	Nd
n-Heneicosane (C_{21})	1092	138	Nd
n-Docosane (C_{22})	756	10.3	Nd
n-Tricosane (C_{23})	220	7.42	Nd
n-Tetracosane (C_{24})	107	5.19	Nd
n-Pentacosane (C_{25})	Nd	3.57	Nd
Sum of *n*-alkanes	19 0763	8339	
Branched alkanes			
Norfarnesane (C_{14})	11 469	12.8	Nd
Farnesane (C_{15})	9719	28.4	Nd
Norpristane (C_{18})	7992	135	Nd
Pristine (C_{19})	5871	147	Nd
Phytane (C_{20})	4775	185	Nd
Other branched alkanes	328 578	7084	Nd
Sum of branched alkanes	368 404	7592	
Saturated cycloalkanes			
Heptylcyclohexane (C_{13})	13 144	11.1	
Octylcyclohexane (C_{14})	11 467	26.8	
Nonylcyclohexane (C_{15})	10 582	28.5	
Decylcyclohexane (C_{16})	9135	43.3	
Undecylcyclohexane (C_{17})	6207	38.8	
Dodecylcyclohexane (C_{18})	2073	60.7	
Tridecylcyclohexane (C_{19})	165	12.3	
Tetradecylcyclohexane (C_{20})	25	9.82	
Pentadecylcyclohexane C_{21})	Nd	6.79	
Hexadecylcyclohexane (C_{22})	Nd	4.29	
Sum of saturated cycloalkanes	52 798	242	
PAHs			
Naphthalene (Nap)	753	4.06	Nd
Acenaphthylene (Acy)	159	2.03	Nd
Acenaphthene (Ace)	85	3.04	Nd
Fluorene (Flu)	100	7.10	Nd
Phenanthrene (Phe)	247	77.1	Nd
Anthracene (Ant)	7.5	4.06	Nd
Fluoranthene (Flt)	Nd	25.4	Nd
Pyrene (Pye)	5.0	67.0	Nd
Benzo(*a*)anthracene (Baa)	Nd	5.07	Nd
Chrysene (Chr)	Nd	5.07	Nd
Benzo(*b*)fluoranthene (Bbf)	Nd	3.04	
Benzo(*k*)fluoranthene (Bkf)	Nd	2.03	
Benzo(*a*)pyrene (Bap)	Nd	4.06	
Indeno[1,2,3-*cd*]pyrene (Ind)	Nd	6.61	
Dibenz(*a*,*h*)anthracene (Dba)	Nd	1.65	
Benzo(*ghi*)perylene (Bgp)	Nd	3.04	
Biphenyl	437	25.9	Nd
Sum of PAHs	1793	246	
Alkylated PAHs			
1-Methylnaphthalene (1-MN)	585	29.8	Nd
2-Methylnaphthalene (2-MN)	2291	86.0	Nd
1,2-Dimethylnaphthalene (1,2-DMN)	373	31.0	Nd
1,3-Dimethylnaphthalene	Nd	235	Nd
1,4-Dimethylnaphthalene	1540	Nd	Nd
1,5-Dimethylnaphthalene	Nd	134	Nd
1,6-Dimethylnaphthalene	1807	61.0	Nd
1,7-Dimethylnaphthalene	2548	24.8	Nd
1,8-Dimethylnaphthalene	Nd	Nd	Nd
2,3-Dimethylnaphthalene	Nd	Nd	Nd
2,6-Dimethylnaphthalene	1224	54.2	Nd
2,7-Dimethylnaphthalene	1837	48.7	Nd
Methylethylnaphthalene	Nd	273	Nd
Trimethylnaphthalene (TMN)	12 327	2641	Nd
1-Methylphenanthrene (1-MPh)	242	1770	Nd
2-Methylphenanthrene (2-MPh)	528	2168	Nd
Dimethylphenanthrene (DMPh)	Nd	3420	Nd
Sum of alkylated PAHs	25302	10977	
Alkylbenzenes			
Toluene	1377	10.7	Nd
C_2-Benzenes	12 932	20.5	Nd
C_3-Benzenes	10 003	14.9	Nd
C_4-Benzenes	9724	15.7	Nd
C_5-Benzenes	5538	6.15	Nd
C_6-Benzenes	5222	3.17	Nd
Sum of alkylbenzenes	44 796	71.1	
n-Alkanoic acids			
Hexanoic acid (C_6)	Nd	Nd	Nd
Heptanoic acid (C_7)	Nd	17.8	37.4
Octanoic acid (C_8)	Nd	39.6	55.9
Nonanoic acid (C_9)	Nd	87.8	98.7
Decanoic acid (C_{10})	Nd	289	120
Undecanoic acid (C_{11})	Nd	354	100
Dodecanoic acid (C_{12})	Nd	591	940
Tridecanoic acid (C_{13})	Nd	444	237
Tetradecanoic acid (C_{14})	Nd	1955	3400
Pentadecanoic acid (C_{15})	Nd	1237	1429
Hexadecanoic acid (C_{16})	Nd	1991	6109
Heptadecanoic acid (C_{17})	Nd	Nd	Nd
Octadecanoic acid (C_{18})	Nd	4.08	Nd
Sum of *n*-alkanoic acids		7012	12 527
Aromatic acids			
Benzoic acid	Nd	226	495

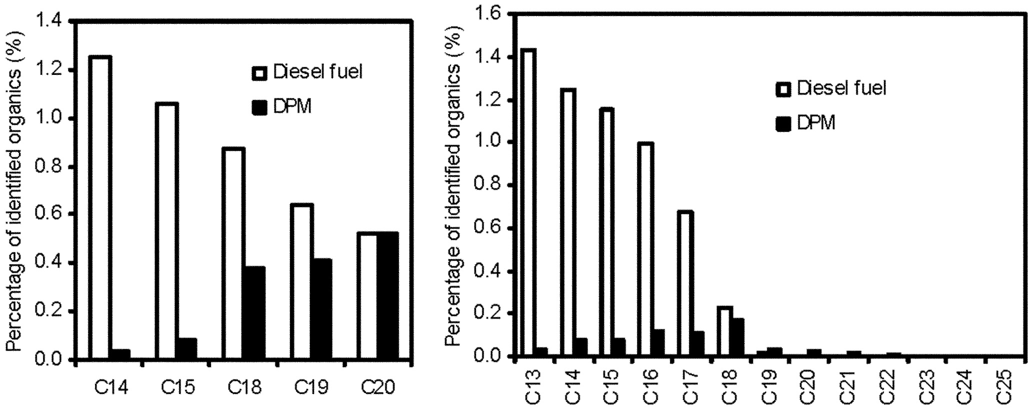
[a] All of the individual concentrations detected were quantified with standard compounds. Nd: not detected, *i.e.* the concentration is lower than detection limit or the compound is not present in the sample.

category were calculated. It is indicated that DPM contains higher fractions of PAHs, alkylated PAHs and *n*-alkanoic acids comparing with the diesel fuel, while the diesel fuel has more fractions of branched alkanes and cycloalkanes.

Approximately 70% (on mass basis) of the diesel fuel has been identified. Among the identified fractions, *n*-alkanes, branched alkanes, saturated cycloalkanes, PAHs, alkylated PAHs and alkylbenzenes account for 27.90%, 53.87%, 7.72%, 0.26%, 3.70% and 6.55%, respectively. This is consistent with several published studies.[5,10,25] For branched and cyclic alkanes, studies have indicated that compounds ranging from C_{10}–C_{20} are the most abundant,[26] and the C_{10}–C_{28} fraction ranges from 65–85%,[17] and 72–96% for the C_8–C_{24} fraction.[5] From Table 1, the aromatic compounds in the low sulfur diesel fuel include naphthalene, fluorene, phenanthrene, and alkylated naphthalenes and phenanthrenes with a total percentage of about 4%. Other studies indicated that volume



(a) n-Alkanes



(b) Branched alkanes

(c) Cycloalkanes

Fig. 3 Relative percentages of alkanes in total identified compounds for diesel fuel and DPM. (a) *n*-Alkanes, (b) branched alkanes (c) cycloalkanes.

fraction of PAHs in diesel fuels varies widely from 5% to 30%, even less than 5% for some high-quality fuels. Some heavy PAHs identified in DPM, such as fluoranthene, benzo(*a*)anthracene, chrysene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*a*)pyrene, indeno[1,2,3-*cd*]pyrene, dibenz(*a*,*h*) anthracene, and benzo(*ghi*)perylene, are not identified in diesel fuel. This is consistent with some other studies where those heavy PAHs are either not present or below detection level in diesel fuel.[5,17,20]

1.3% of engine oil was able to be resolved by GC-MS, which are mainly organic acids. *n*-Alkanoic acids from $C_6H_{12}O_2$ to $C_{18}H_{36}O_2$ are the main components and benzoic acid is the most important aromatic acid in the 1.3% of engine oil that is amenable to identification by GC/MS (Table 1).

84% of DPM can be dissolved in the solvent. This is consistent with the 82–86% of organic fraction obtained from thermal-optical analysis (NIOSH Method 5040, a standard method for organic and elemental carbon (OC/EC) measurement).[27]

The consistency of dissolved fraction with the fraction of organic compounds also indicated the high efficiency of the extraction method. In DPM, the identified organics account for 3.47% of total DPM mass, which falls into the range of other studies.[3,20,28]

Among the identified fractions, *n*-alkanes account for 24.02%, branched alkanes 21.90%, alkylated aromatic hydrocarbons 31.67% and *n*-alkanoic acids 20.23%. This distribution is consistent with the DPM emissions from medium duty diesel trucks.[20]

3.2 Compositional analysis of diesel fuel, DPM and engine oil

3.2.1 Alkanes. As suggested in Fig. 2, alkanes, which include *n*-alkanes, branched alkanes and saturated cycloalkanes, account for a large fraction of the diesel fuel and the identifiable portion of DPM. The relative percentages of *n*-alkanes, branched alkanes and saturated cycloalkanes in both

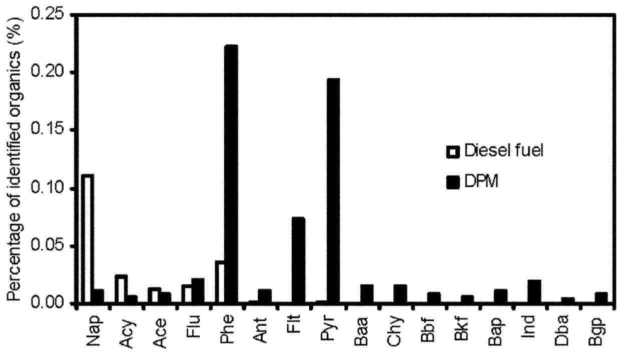


Fig. 4 Relative percentages of PAHs in total identified compounds for diesel fuel and DPM.

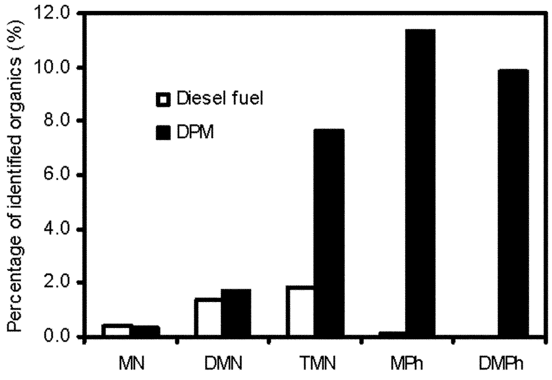


Fig. 5 Relative percentages of alkylated PAHs in total identified compounds for diesel fuel and DPM.

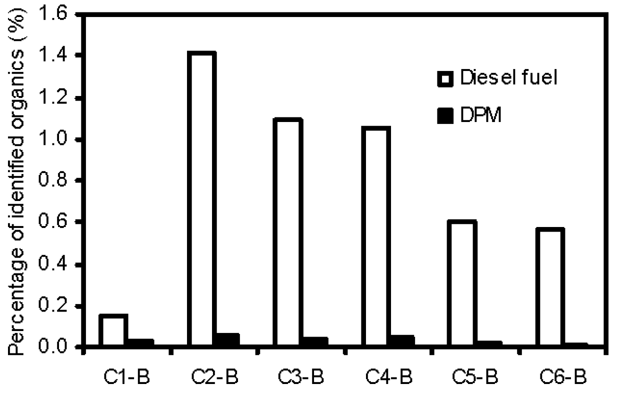


Fig. 6 Relative percentages of alkylbenzenes in total identified compounds for diesel fuel and DPM.

the diesel fuel and DPM were illustrated in Fig. 3(a–c), respectively.

A series of *n*-alkanes from C_{10} to C_{25} have been identified in diesel fuel and DPM. From Table 1, the concentrations of *n*-alkanes in DPM range from several hundred to several thousand μg g^{-1} while in diesel fuel the concentrations can reach as high as tens of thousands μg g^{-1}. Fig. 3(a) suggests that in the identified alkanes the most abundant species are distinct for diesel fuel and DPM. For diesel fuel, the most abundant identified *n*-alkanes are C_{13}–C_{17}, which is consistent with Schauer's results.[20] While for DPM, the distribution represents a bell shape with C_{17} as the most abundant. The relative fractions of C_{17}–C_{21} are much higher in DPM than in diesel fuel while the fractions of C_{10} to C_{16} are much less. The enrichment of aliphatic hydrocarbons with higher carbon number was also reported by Rogge *et al.*[28,29] The shift to heavier *n*-alkanes from diesel fuel to DPM can be the results of combustion synthesis, as shorter-chained alkanes are more likely to undergo complete combustion than the heavier ones.

For branched alkanes, the identifiable compounds are also known as isoprenoids. These compounds are naturally present in crude oil and can be potentially used as tracers for diesel engine emissions.[20] Fig. 3(b) shows the distribution of the isoprenoids from C_{14} through C_{20} in diesel particulate matter compared with diesel fuel used for the generator. As can be seen in the figures, DPM contains a larger fraction of higher molecular weight compounds. Fig. 3(c) shows the similar distributions of saturated cycloalkanes from C_{13} through C_{22} in DPM and diesel fuel. The shift toward higher molecular weight compounds is similar to that of *n*-alkanes.

3.2.2 PAHs and alkylated PAHs. Fig. 4 and 5 illustrate the relative percentages of dominant PAHs and alkylated PAHs in diesel fuel and DPM. It can be seen that compared with diesel fuel, the relative fractions of PAHs and alkylated PAHs are significantly higher in DPM.

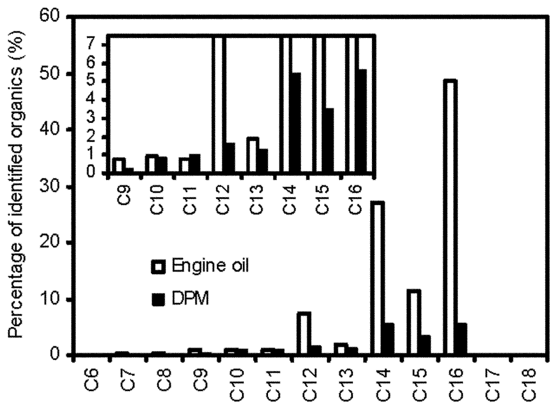


Fig. 7 Relative percentages of *n*-alkanoic acids from $C_6H_{12}O_2$ to $C_{18}H_{36}O_2$ in DPM and engine oil.

Many more PAH species are observed in DPM that are not present in diesel fuel, such as benzo(*a*)anthracene, chrysene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*a*)pyrene, indeno[1,2,3-*cd*]pyrene, dibenz(*a*,*h*)anthracene, and benzo(*ghi*)-perylene, with the mass range of 228–278 u. More phenanthrene and pyrene are identified in DPM than the diesel fuel. This result indicates that many PAH compounds may originate from the combustion process in the diesel engine rather than from direct evaporation of diesel fuel. These pyrogenic PAHs are precursors to soot particle formation and account for 14% of total PAHs identified in DPM. Similar PAH distribution in DPM and diesel fuel was also reported by Dobbins *et al.*[30]

For identified alkylated PAHs, the dominant species are trimethylnaphthalene, methylphenanthrene and dimethylphenanthrene for DPM and dimethylnaphthalene and trimethylnaphthalene for diesel fuel. This also suggests the enrichment of higher molecular weight compounds in DPM. Consistent with Shauer *et al.*[20] and Koziel *et al.*,[31] alkylated PAHs are the most abundant identified species in our study.

3.2.3 Alkylbenzenes. Fig. 6 represents percentages of alkylbenzenes from C_1-benzene to C_6-benzene in low sulfur diesel fuel and DPM. Alkylbenzenes account for 6.55% of the identified fraction in diesel fuel and 0.21% in DPM. It is suggested that alkylbenzenes have been significantly consumed by the combustion processes. The dealkylation from alkylbenzenes and alkylated PAHs and recombination of alkyl groups onto the reactants have altered the relative isomeric distributions of these two categories.[32]

3.2.4 Organic acids. Both benzoic and *n*-alkanoic acids ranging from C_6 to C_{18} have been identified in DPM and engine oil as listed in Table 1. The distributions of *n*-alkanoic acids in DPM and engine oil are also shown in Fig. 7.

In DPM, organic acids account for 20% of the total identified organics with concentrations as high as several thousand μg g^{-1}. *n*-Dodecanoic (C_{12}), *n*-tetradecanoic (C_{14}), *n*-pentadecanoic (C_{15}), and *n*-hexadecanoic acid (C_{16}) are the most abundant species identified. From Fig. 7, similar distribution of *n*-alkanoic acids is observed in engine oil, which indicates that the organic acids from DPM may originate from the evaporation of engine oil.

4. Conclusions

The chemical composition of low sulfur diesel fuel, engine oil and diesel particulate matter emitted from a non-road diesel generator has been investigated. A total of approximately 90 organic compounds are identified and quantified, including a series of *n*-alkanes, branched alkanes, saturated cycloalkanes, PAHs, alkylated PAHs, alkylbenzenes, *n*-alkanoic acids and aromatic acids. It is shown that the organic composition of DPM mainly resulted from three sources: *n*-alkanes in DPM are likely from unburned diesel fuel, the main source of organic acids is from engine oil evaporation, and most PAHs and alkylated PAHs are likely formed during combustion. Compared with diesel fuel, DPM contains fewer fractions of alkanes and more PAH compounds. The enrichment of higher molecular weight alkanes, including *n*-alkanes, branched alkanes and cycloalkanes, is likely resultant from fuel combustion. The pyrogenic process also resulted in the loss of alkylbenzenes and the alteration of isomeric distribution of PAHs and alkylated PAHs.

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