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CHARACTERIZATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN DIESEL FUEL AND DIESEL EXHAUST EMISSIONS

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Abstract

Concentrations of PAHs were measured by Gas Chromatography in diesel fuel and diesel exhaust emissions emanating from a diesel engine. Exhaust samplings were carried out by a stack sampler on glass fibre thimbles. Diesel fuel was found to contain higher concentrations of low molecular weight PAHs (1.2×10^3 to 2.2×10^3 mg L^{-1}) while the higher molecular weight compounds were generally below detection limit. The mean content of BaP and DbA, the most carcinogenic PAHs were 0.15×10^3 and 0.33×10^3 mg L^{-1} respectively. On the contrary the exhaust emissions were rich in high molecular weight compounds which suggest their origin either from unburned fuel and fuel additives or their pyrosynthesis.

Keywords: Emission factor, Diesel fuel, PAH emissions

Introduction

Polycyic Aromatic Hydrocarbons (PAHs) constitute a class of organic compounds that include potent mutagenic and carcinogenic compound (Nauss, 1995). PAHs are released into the atmosphere as a complex mixture of compounds resulting from incomplete combustion of organic matter (Baek et al, 1991). PAHs are found both the gas and particulate phases, depending on the vapor pressure of the PAH. Smaller PAHs are found predominantly in vapor phase, while PAHs with four or more rings are found mainly in the particle phase.

Motor vehicles are a significant source of PAH emission. Characterization of aerosol in motor vehicle exhaust has indicated that PAH emission profiles are distinct for different vehicle classes. Emission rates of PAH for vehicular exhaust depends on engine type, operating condition and composition of fuel and lubricating oil (Bjorseth et al, 1985). Improved understanding is therefore needed of the relation between fuel composition and particle phase PAH emission from both gasoline and diesel engines. The objectives of this study were to quantify PAH concentrations in commercial diesel fuel samples and in diesel exhaust emissions from a diesel engine. These measurements were made to gain insight into the origin of PAHs in motor vehicle exhaust.

Methodology

Sample collection of Fuel and Engine exhaust

Diesel fuel samples were collected from different service stations in Agra. Samples of exhaust emitted from Diesel engine was collected on desiccated and preweighed Glass fibre thimble using Vayubodhan stack sampler (VSS1). The sampler was operated at a flow rate of 27 LPM for a duration of 4 hour. This sampling was conducted at the Heat Engines Laboratory at Dayalbagh Educational Institute, Agra.

Analysis

Diesel samples were diluted thrice in HPLC grade dichloromethane and cleaned by passing it through a glass column of 19 cm length and 2 cm diameter packed with silica gel. Particulate matter collected on thimbles was extracted with HPLC grade dichloromethane ultrasonically. The extract was filtered, cleaned and concentrated to 1.5 ml with HPLC grade dichloromethane. Concentrated fraction was stored in a Teflon vial at a low temperature until analysis. 16 EPA priority PAH compounds namely; Naphthalene (Nap), Acenapthylene (Acy), Acenapthene (Ace), Fluorene (Flu), Phenanthrene (Phen), Anthracene (Anth), Fluoranthene (Fla), Pyrene (Pyr), Benzo(a)Anthracene (BaA), Chrysene (Chy), Benzo(b)Fluoranthene (BbF), Benzo(k)Fluoranthene (BkF), Benzo(a)Pyrene (BaP), Dibenzoanthracene (DbA), Benzo(ghi)Perylene (BghiP) and Indeno (123-cd) Pyrene (IP) were analysed in both fuel and exhaust samples by Gas Chromatograph (Shimadzu 17AATF) using a temperature gradient program in splitless mode with a FID.

Results and discussion

Fuel PAH concentration

The concentration of measured PAHs in Diesel samples is shown in Table-1. The concentrations of PAH in diesel range from undetectable (0.05×10^3) to 2.2×10^3 mg L^{-1}. The PAHs can be classified on the basis of molecular weight, into the low molecular weight PAHs (MW<168) as, those containing 2 to 3 rings (Nap, Acy, Ace, Flu, Anth, Phen) and middle molecular weight (MW 202-228) containing four rings (Fla, Pyr, BaA, Chy) and high molecular weight PAHs (MW>228) containing 5 to 6 rings (BbF, BkF, BaP, BghiP, IP, DbA).

The low molecular weight PAHs were the dominant species, corresponding to 49.6% (3.9×10^3 mg L^{-1}) while the middle molecular weight PAHs represented 44.3% of the total PAHs. On the contrary, among the High molecular weight PAH, only BaP and DbA were detectable with concentration ranging between 0.15×10^3 and 0.32×10^3 mg L^{-1} respectively, while other PAHs namely BbF, BkF, BghiP and IP were present below detection limits. The high molecular weight compounds account for only 6% of the total analyzed PAHs. The mean content of BaP and DbA, the most carcinogenic PAHs were 0.15×10^3 and 0.33×10^3 mg L^{-1} respectively. DbA had the highest mean content among the high molecular weight PAHs. Numerous studies have quantified PAH in fuels. Nap, Flu and Phen were found to be the predominant PAH in French diesel fuel (Pointet et al., 1997). Further, analysis of fuel for the PAH profile by Marr et al (1999) and Lin et al (2006) has revealed a greater proportion of low molecular weight PAH in diesel as compared to medium molecular weight and high molecular weight PAH. The results of this study closely agree with the findings of Marr et al., 1999 and Lin et al., 2006.

Characterization of PAH in diesel exhaust emission

PAHs concentration in the Diesel engine exhausts and their emission factors are listed in Table-2. The most significant contributors to the total emission factors of Diesel engine are the 5 and 6 ringed PAHs accounting for 49.3%, which exist predominantly in the particulate phase. BbF, BghiP and IP were not detected in the fuel but did have measurable emission factors. It is possible that they were present in diesel fuel at levels below the limit of detection or that they have sources other than unburned fuel. The presence of these higher molecular weight PAHs in diesel exhaust that are not found in the fuel suggest that these PAHs originate from other sources such as unburned fuel, unburned lubricant, partial oxidation of products of fuel and lubricants, pyrolysis product of lubricants oil, fuel and fuel additives or pyrosynthesis (Rogge et al., 1993). It has indeed been shown previously that pyrosynthesis contributes up to 60% of the exhaust PAHs in heavy duty vehicles (Westerholm and Lin, 1994) and that 80% of total PAHs in exhausts of heavy duty vehicles powered by diesel fuels with 280-470 ppm sulfur contents originate from fuel triatomatic compounds (Mitchell et al., 2000). Similarly, chemical thermodynamic data has been used to show that tri-aromatics, di-aromatics and Nap significantly affect PAHs formation and that the influence of polyaromatics on PAHs formation is enhanced by their synergistic effects with Nap (Tanaka et al, 1998). BkF was not detected in either diesel fuel or diesel exhaust while BbF, IP and BghiP were not detected in the fuel but present in the exhaust emissions.

Table- 1

PAHs concentration in diesel fuel

PAH	**DIESEL (mg L^{-1})**
Naphthalene (Nap)	712
Acenaphthylene (Acy)	903
Acenaphthene (Ace)	962
Fluorene (Flu)	520
Anthracene (Anth)	718
Phenanthrene (Phen)	118
Fluoranthene (Fla)	523
Pyrene (Pyr)	Bdl
Benz[a]anthracene (BaA)	1220
Chrysene (Chy)	2238
Benzo[b]fluoranthene (BbF)	Bdl
Benzo[k]fluoranthene (BkF)	Bdl
Benzo[a]pyrene (BaP)	149
Dibenzo[a,h]anthracene (DbA)	329
Benzo[ghi]perylene (BghiP)	Bdl
Indeno[1,2,3cd]pyrene (IP)	Bdl

Bdl: Below Detection Limit

Table-2 PAH concentration and their emission factors in the engine exhaust

PAH	**Exhaust Concentration (µg m^{-3})**	**Emission factors (µg L^{-1})**
Naphthalene (Nap)	0.033	0.067
Acenaphthylene (Acy)	0.079	0.161
Acenaphthene (Ace)	0.045	0.092
Fluorene (Flu)	0.085	0.174
Anthracene (Anth)	0.015	0.158
Phenanthrene (Phen)	0.056	0.115
Fluoranthene (Fla)	0.066	0.409
Pyrene (Pyr)	0.116	0.014
Benz[a]anthracene (BaA)	0.085	0.173
Chrysene (Chy)	0.247	0.504
Benzo[b]fluoranthene (BbF)	0.097	0.198
Benzo[k]fluoranthene (BkF)	----	-----
Benzo[a]pyrene (BaP)	0.235	0.479
Dibenzo[a,h]anthracene (DbA)	0.337	0.081
Benzo[ghi]perylene (BghiP)	0.418	0.85
Indeno[1,2,3cd]pyrene (IP)	0.105	0.214

Conclusions

PAH were investigated in diesel fuel and diesel exhaust emissions. The present results provide a general picture of diesel fuel and diesel exhaust emissions. Total content of diesel fuel was 7×10^{-3} mg L^{-1}. Diesel fuel was found to contain higher concentrations of two to four ring compounds with low molecular weights while among the higher molecular PAHs only BaP and DbA were detectable while BbF, BkF, BghiP and IP were present below detection limits. In contrast, the higher molecular weight compounds had significant emission factors and low molecular weight compounds had relatively lower emission rates. These results suggest the pyrosynthesis of higher molecular weight PAH compounds during the combustion processes in heat engines.

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