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Emission of Polycyclic Aromatic Hydrocarbon from Vehicles Fueled with Diesel and Compressed Natural Gas using Gas Chromatography-Mass Spectrometry: A Brief Study

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are released into the ambient air as a consequence of incomplete combustion of various types of fuels from vehicles which poses a serious risk to environmental pollution and subsequent health hazards. Dhaka, the capital city of Bangladesh is an overpopulated city with increasing number of vehicles with each passing day. Therefore it is imperative to determine PAHs emission in this city to figure out an alternative to reduce these emissions. In an attempt to do so, a brief study has been performed to evaluate the concentration of PAH in vehicle exhaust samples (specifically, tar and fume) from compressed natural gas (CNG) and diesel driven vehicles driven in Dhaka city. Gas chromatography-Mass spectrometry (GC-MS) was used to identify and quantify PAHs present in collected samples from diesel and compressed natural gas engine vehicles (bus, truck, car, vehicle run by CNG) using dichloromethane (DCM): n-hexane solvent mixture. Four PAH compounds: naphthalene, phenanthrene, anthracene and fluorene (NAPF) was found in varying concentrations. Overall, it has been observed that concentration of PAHs is higher in heavy engine vehicles than light engine vehicles suggesting that most heavy weight vehicles having diesel engine run in Dhaka city are in poor condition contributing to air pollution. This brief study is a starting point study highlighting that CNG conversion of the vehicles offers an inherent advantage in progressively decreasing the emissions released from the vehicles and thus can certainly improve the air quality which must be further validated in future studies using larger samples.

Keywords: Polycyclic Aromatic Hydrocarbon, Fume, Tar.

INTRODUCTION

Road emissions from vehicles are posturing a significant environmental and health impact on urban air quality. The number of motor vehicles are increasing with the rapid growth of urbanization in Bangladesh which calls for an urgent need for environmental protection and increased energy demand. Global organizations and researchers all over the world are searching for low-carbon alternatives to conventional gasoline and diesel engine vehicles in attempt to decrease emission of air pollutants (polycyclic aromatic hydrocarbons, different phenolic compounds, various soluble inorganic organic ions, dust particles) and their effect on the environment.

Polycyclic aromatic hydrocarbons (PAHs) are one kind of semi volatile organic compounds containing two or more fused aromatic rings, which are generated by incomplete combustion of organic substances like wood, coal, fossil fuel, tobacco etc.[1]. They have attracted attention due to their pervasive toxicity, mutagenicity and carcinogenicity[2-4]. When molecular weight of a specific PAH increases, the carcinogenicity of PAHs also increases but acute toxicity reduces [5]. On the basis of this fact, the United States Environmental Protection Agency (U.S.EPA) listed 16 PAHs as priorities pollutants[6].

Both natural and anthropogenic sources contribute to the production of PAHs into the ambient environment[7]. Among anthropogenic sources, vehicles related pollution and biomass combustion are playing the vital role in polluting environment by releasing PAHs into the air[1, 8-10]. According to a recent study, motor vehicles were the fourth key source of atmospheric pollution and contributed approximately 12.8% of the global total annual atmospheric emissions of 16 PAHs in 2007 [11]. Diesel engines are considered as a significant source of releasing PAHs in urban atmosphere [12-13]. PAHs discharged by diesel vehicles are initiated from pyro-synthesis of aromatic compounds, un-burned fuel and lubricant oil [6, 12] ; Correa and Arbilla experimented with heavy-duty diesel engine and high concentrations of phenanthrene and fluorene followed by naphthalene, acenaphthene, acenaphthylene and anthracene were found[14]. Another study by Wada *et al*., showed that diesel vehicles are the main sources of NPAHs in the atmosphere in Nagasaki, Japan[15]. Furthermore, the emission factors of the total PAHs from light-duty diesel trucks was reported to be less than medium-duty diesel trucks and heavy-duty diesel trucks were in Beijing, China. Higher emissions of PAHs were detected on non-highway roads compared to that on highways for light duty and heavy-duty diesel vehicles as well [4].

Compressed natural gas (CNG), also called "cleaner" fuel compared to other fossil fuels is used as an alternative fuel in motor vehicles to decrease discharge of air pollutants in environment. The idea of clean fuels has been established by the desire to improve air quality in urban areas [16-17]. Compressed natural gas usage has been increased because of its improved fuel economy and lower emissions compared to diesel engine. Compressed natural gas has been cited as suitable for light duty vehicles [18]. Previously several studies have been done to compare pollutant emissions from diesel and CNG fueled vehicles. Significant reduction of combustive pollutant emission was observed for CNG driven vehicles [19];[20] It has been pointed out that if a diesel-powered vehicle is exchanged with a CNG-fueled vehicle, a significant reduction in total air pollutant emission occurs, resulting in a 21% reduction of volatile organic compounds (VOCs). Another study showed that particulate matter (PM) emissions by CNG engines were significantly lower than diesel engines, with a reduction of 96% [17].

The PAHs concentration in the combustion products discharged by diesel and compressed natural gas vehicles depend on different factors, such as- the fuel composition, the load applied to the engine during the experiment, the use of emission-control system and the vehicle model and year [3, 12-13, 21-23]. PAHs concentrations can be increased due to high engine speed because the short time duration in cylinder at high speed resulting incomplete combustion [24]. Sulphur present in diesel fuel can play a role of nucleation site or adsorption site for PAHs [25]. It is necessary to understand how pollutant like PAHs emission is influenced by fuel composition. Although PAHs are toxic to humans, there is not any Bangladeshi law regarding PAHs emission for vehicles. Therefore, to understand the local emission inventory, experiments on local vehicle emission are required.

For analysis of PAHs present in diesel and compressed natural gas emission, analytical method to concentrate the sample and instruments with low detection limit are important. Because concentration of PAHs emitted from combustion is much lower[6]. The most convenient methods for analysis of PAHs are high-performance liquid chromatography with fluorescence detection (HPLC-FLU) and gas chromatography coupled with mass spectrometry (GC-MS)[6, 21, 26-28]. Though HPLC-FLU has greater sensitivity than GC-MS, usage of single ion monitoring (SIM) in GC-MS provides structural information of compounds[3].

The objective of this work was to propose a methodology to identify and quantify 4PAHs (naphthalene, anthracene, phenanthrene and fluorene) among 16 priority PAHs in samples from diesel and compressed natural gas engine exhaust using GC-MS. Consequently, this method was evaluated in samples collected from diesel and compressed natural gas vehicle exhaust used in Dhaka city.

2. METHODS AND MATERIALS

2.1 Materials

Naphthalene, anthracene, phenanthrene and fluorene standards were obtained from Sigma-Aldrich company with purity of 99.9%. Dichloromethane (BDH, UK) and acetone (Merck, Germany) were of HPLC grade.

2.1.2 Instruments

A gas chromatograph (Varian 3800) coupled with a mass spectrometer (Varian Saturn 2200) with a capillary column was used for determination of concentration of various PAHs.

The carrier gas in GC-MS was helium. Analytical balance (Adventurer^{TM}, OHAUS), electrical oven (model-G-1020, company-Salvis), K-D evaporator were used as major equipment.

2.1.3 Engine operation and sampling

The vehicular emission tests were performed using heavy duty diesel vehicles (3 different buses), light duty compressed natural gas fueled vehicles (3 different cars, 3 different auto rickshaws) and heavy duty compressed natural gas driven vehicles (3 different buses). These vehicles are mainly used in Dhaka city. These experiments were directed with the engine in a steady state condition. This condition is not a characteristic of the engine on the road but allow repeated experiments to be performed for comparison. The exhaust fume was collected by a series of gas collector systems containing four glass containers. The bottom part of the collector containers contained same solvent dichloromethane at different proportion (100 mL, 75 mL, 50 mL, and 25 mL). The tailpipe of the vehicles was connected through to the fume collectors by a polyethylene tube and the fumes generated from the engines were continuously passed through the solvent for 15 minutes.

2.1.4 Sample extraction and clean-up procedure

All the solvents were assembled from the collectors and combined. Then Na_2SO_4 was used to dehydrate the solvent and it was filtered. Finally, the filtrate organic solvent was concentrated until the concentration reached 1-2 ml by using K-D evaporator.

Firstly, the cleanup column (ID = 1 cm) was filled with cotton in the bottom. Then an activated silica gel (15gm) soaked with solvent was loaded into the cleanup column (5 cm), which was then topped with 1.5 cm of anhydrous sodium sulphate. To wash the sodium sulphate and the silica gel, 5 ml of solvent was added. Then 1 ml of each sample which were concentrated earlier, then separately transferred into the column and the vessel was dipped twice with 2 ml loaded solvent, which was also added to the column. 60 ml of loaded solvent was added to the column and allowed to flow through at a rate of 3–5 ml/min, and then the eluent was collected. This eluent was re-concentrated to 1 ml by using K-D evaporator. The evaporated samples were then preserved in refrigerator at -20°C for further analysis. The vials were tightly taped to prevent evaporation of the solvents.

2.2 Chemical Analysis

Chemical analysis was performed by using total ion monitoring mode on a Varian 3800 gas chromatograph interfaced to a Varian Saturn 2200 Mass Spectrometer with an ion-trap operating electron impact (EI) as the ionization mode. For the PAHs separation, DB -5 capillary column (30m length, 0.25mm I.D. and 0.25 μm film thickness) was used. The injections were performed using a syringe of 10μL. Injection volume was 0.2μL. Standard solution containing the 5 desired PAHs were used to the development and optimization of the chromatographic method. Helium was used as a carrier gas at a flow rate of 1.0 mL/min. The oven conditions were as follows: an initial temperature of 50^0C held for 1 min, a first heating ramp of 8^0C min $^{-1}$ to 210^0C, and a second heating ramp of 10 ^{0}C min $^{-1}$ to 280 ^{0}C held for 10 min. Total analysis time was 57.75 min. The temperatures of transfer line and ion source were 280°C and 275°C respectively. Calibration curves were constructed using analytical standards in four different concentrations from 0.625 ppm to 5 ppm. The linearity was evaluated through the coefficient of determination (R^2.) The analytical curve parameters were used to determine the identification and quantification limits.

2.3 Identification and quantification

The PAHs compounds were identified and quantified by comparing its retention time and peak area with that of known concentration of standard solution which was also injected into the GC-MS system under the same conditions. The concentration of PAHs was calculated by using the following equation[29]

$$S = \frac{(A_s - A_b) \times C_{std}}{A_{std}}$$

where S is sample strength, A_s and A_{std} represent the peak area of component analyte and standard solutions respectively and A_b represent the peak area of blank sample.

Actual concentration of PAHs was calculated using the following equation

$$ppb = \frac{S \times V}{100mL} \times 1000$$

where S represents sample strength and V represents volume of pre-concentrated sample extract.

3. RESULTS AND DISCUSSIONS

The on-road experiments were carried out at different places of University of Dhaka, Bangladesh. In total, 12 vehicles, which included 3 different types of vehicles of different sizes (high, medium, light) driven by two different fuels (diesel and compressed natural gas) were tested and three vehicles were tested for each size of vehicle.

Calibration for the determination of the 4 PAHs in a standard solution was done. The results proved good linearity over a concentration range of 0.625–5 ppm. In addition, an estimation of the sensitivity of the analytical method that was used in this experiment, was determined to establish the lower limit of detection. In this study, the sensitivity of the GC–MS was a significant parameter to determine individual PAH concentration. It was experimentally established that the lower limit of detection (based on a signal of greater than three times the background noise) of the instrument was 0.002µg/L and the uncertainty of the measurements were ±5%) (Data not shown).

Standards (concentration of 5 ppm) of naphthalene, anthracene, phenanthrene and fluorene was run through GC-MS and the retentions times were found to be 10.36, 19.78, 19.81 and 16.98 respectively. Samples were also run through the GC-MS. Figure 1 shows the chromatogram of some of the samples from diesel and CNG driven vehicles. Chromatogram 1 represents standard of naphthalene, anthracene, phenanthrene and fluorene and shows the corresponding retention times. Chromatogram 2 shows that fume sample collected from CNG contains naphthalene as shown by the same retention time of 10.36 minutes. It is evident from figure 1 that the fumes of the CNG driven bus contains all the four PAHs in significant amounts whereas diesel driven bus also contains all the PAHs but in lower amounts. Tar sample from diesel driven truck contains anthracene, phenanthrene and fluorene and on the contrary tar sample from diesel driven bus contains only fluorene.

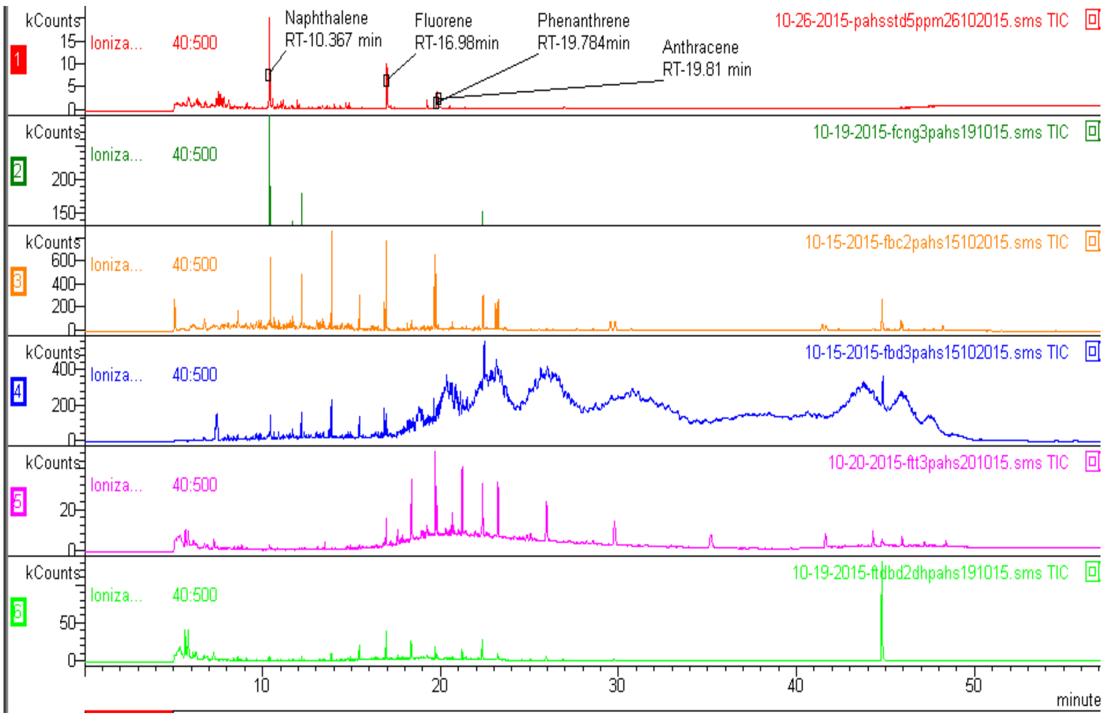

Figure 1: Comparison of retention time of chromatograms of 5 ppm standard solution and samples collected from different vehicles. Numerical Keys:

1: 5ppm standard solution
2: Fume sample collected from CNG autorickshaw 3
3: Fume Sample collected from CNG driven bus 2
4: Fume Sample collected from Diesel driven bus 3
5: Tar sample collected from diesel driven truck 3
6: Tar sample collected from diesel driven bus 2

The study shows the actual concentration of naphthalene, fluorene, phenanthrene and anthracene, predominantly present in the samples collected from different vehicles were analyzed by GC–MS. An appreciable amount of naphthalene, anthracene, phenanthrene and fluorene were obtained in the samples collected from diesel driven vehicles while the constituents were present in a tiny amount in the samples collected from CNG driven vehicles. The results are summarized in Table 1.

Table 1: Data of naphthalene, anthracene, phenanthrene and fluorene in Fume and Tar exhaust samples from CNG and Diesel driven vehicles (Keys: MDL: Minimum Detection Limit)

Exhaust Type	Engine Type	Sample Name	Concentration of Naphthalene (in ppb)	Concentration of Phenanthrene (in ppb)	Concentration of Anthracene (in ppb)	Concentration of Fluorene (in ppb)
Fume	Diesel	Bus 1	7.05	12.40	13.26	<MDL
		Bus 2	18.80	35.68	38.22	<MDL
		Bus 3	60.70	53.10	56.84	<MDL
	Compressed Natural Gas	Bus 1	124.00	<MDL	<MDL	<MDL
		Bus 2	98.00	23.94	25.68	5.30
		Bus 3	199.00	21.70	<MDL	4.10
		Car 1	183.00	<MDL	<MDL	<MDL
		Car 2	313.00	<MDL	<MDL	<MDL
		Car 3	<MDL	<MDL	<MDL	<MDL
		CNG autorickshaw 1	42.90	<MDL	<MDL	<MDL
		CNG autorickshaw 2	<MDL	<MDL	<MDL	<MDL
		CNG autorickshaw 3	594.90	<MDL	<MDL	<MDL
Tar	Diesel	Bus 1	0.78	6.04	<MDL	<MDL
		Bus 2	2.86	2.22	2.37	0.32
		Bus 3	1.41	1.99	2.13	<MDL
		Truck 1	4.74	4.76	5.10	<MDL
		Truck 2	0.91	1.59	1.71	<MDL
		Truck 3	2.05	5.19	5.56	0.42
	Compressed Natural Gas	CNG autorickshaw 1	0.51	0.67	0.72	<MDL
		CNG autorickshaw 2	0.06	<MDL	<MDL	<MDL
		CNG autorickshaw 3	0.16	0.17	0.18	<MDL

Emission rate of NAPF depends on the number of rings of these structures. Fluorene is more stable compared to naphthalene, anthracene and phenanthrene as they are 6- membered rings whereas fluorene is a 5-membered ring compound coupled with 2 six membered rings which makes it a rigid structure and makes it more stable. Figure 2 shows the structures of the six and five membered rings present in NAPF. Therefore, this fact explains the reason why concentration of naphthalene, anthracene and phenanthrene were found to be much higher in fumes collected from diesel driven bus compared to fluorene (Table 1).

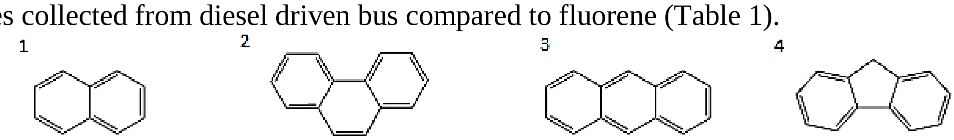

Figure 2. 6 and 5 membered rings present in the molecular structure of NAPF. Keys: 1- naphthalene, 2 - phenanthrene, 3 - anthracene, 4 - fluorene

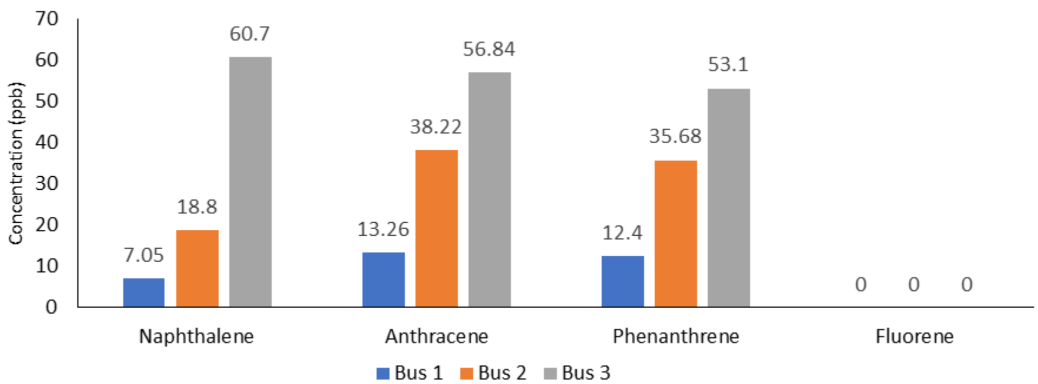

Figure 3. Concentration of NAPF (in ppb) in fume samples collected from diesel driven vehicle (Bus)

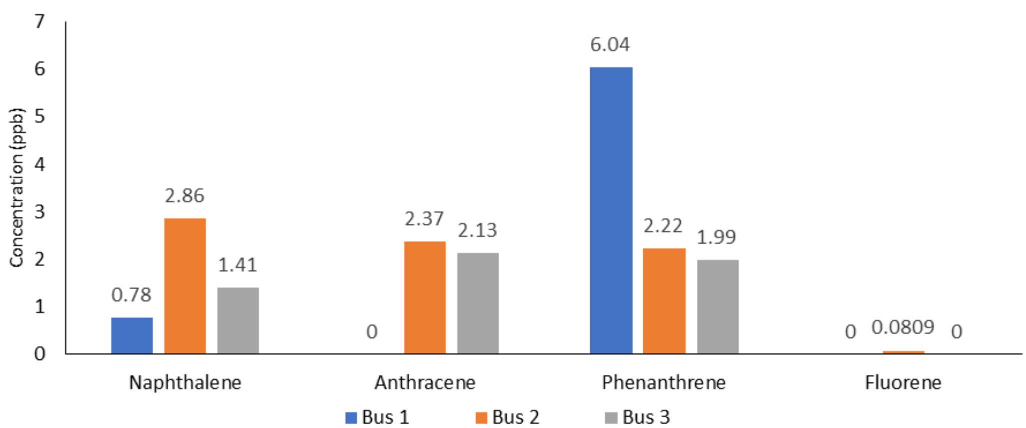

Figure 4. Concentration of NAPF (in ppb) in tar samples collected from diesel driven vehicles (Bus)

PAHs in both tar and fume samples collected from diesel engine heavy vehicles (buses and trucks) are in significant amount (Table 1) as they are heavy engine vehicles and the incomplete combustion rate for this type of vehicle are much higher than light engine vehicles[14]. Figure 3 and 4 shows that the concentration of NAPF in fume and tar samples respectively collected from diesel driven buses (Bus 1, Bus 2, Bus 3). It is evident from these figures that concentration of NAPF is higher in fume samples compared to tar samples in diesel driven bus which accounts for the fact that fume is produced in motor vehicles due to combustion and consequently tar is deposited. It must be noted that the working condition of Bus 1 and Bus 2 is far better than the condition Bus 3 which is the reason for decreased proportion of naphthalene, anthracene and phenanthrene found in fume sample of diesel driven buses (Figure 3). However, contradictory results were seen for tar samples collected from the same diesel driven vehicles in bus 2 for naphthalene and bus 1 for phenanthrene for unknown reasons.

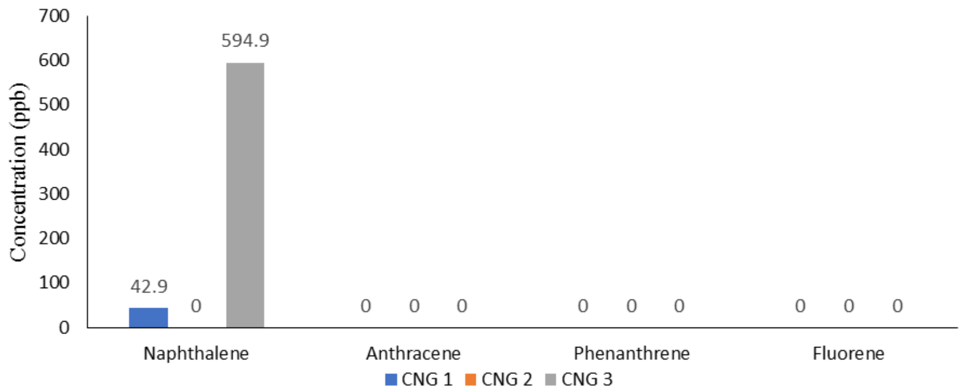

Figure 5. Concentration of (in ppb) NAPF in fume samples collected from CNG

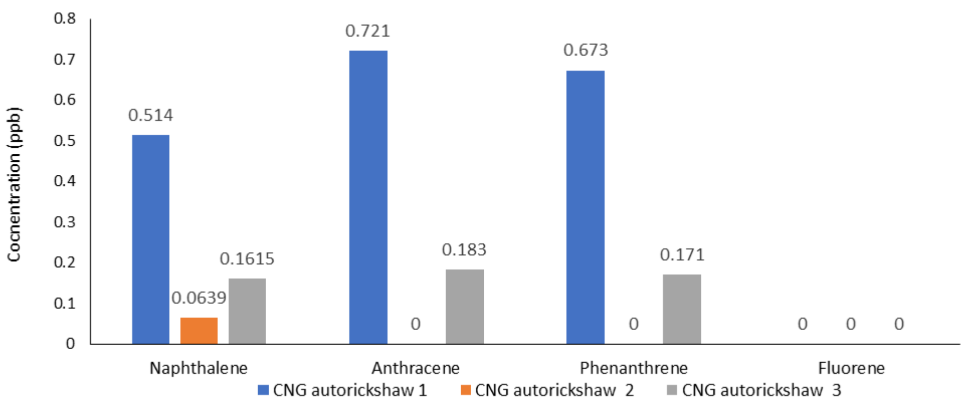

Figure 6. Concentration of PAHs (in ppb) in tar samples collected from CNG driven vehicles (CNG)

Figure 5 and Figure 6 represents NAPF in fume samples and tar samples from CNG driven vehicles respectively. Figure 5 depicts that only naphthalene was extracted from the fumes of CNG driven vehicles (autorickshaw) while no other PAHs were found owing to the fact that compressed natural gas (CNG) has high combustion efficiency and low emissions than the diesel[16]. However, naphthalene, anthracene and phenanthrene were found in tar samples collected from CNG driven vehicles (autorickshaw) but in very low amounts (within the range of 0.06-0.7 ppb) as seen in Figure 6.

From the findings obtained from this research, it can be postulated that the diesel engine is responsible for the emission of polycyclic aromatic hydrocarbons into the air to a great extent. Fume and tar emitted from diesel engine contains more PAHs than CNG engines. Overall, it can be concluded that concentration of PAHs is higher in heavy engine vehicles in contrast to light engine vehicles and therefore CNG can serve as an alternative source of fuel to reduce PAH emissions and environmental pollution. However, it must be noted that for time constraints more samples could not be collected and therefore this study requires further validation with more samples from each vehicle.

CONCLUSION

Dhaka, the capital city of Bangladesh is a densely populated city and traffic is the major source of air pollution, hampering the environment and posing a significant health hazard. Therefore, any reduction in emissions from vehicles is directly related to improvement in the air quality and can prove to be beneficial to the environment. CNG conversion of the vehicles offers an inherent advantage in progressively decreasing the emissions released from the vehicles and thus can significantly improve the air quality which was highlighted in this study. In this study, it has been observed that concentration of PAHs is higher in heavy engine vehicles than light engine vehicles suggesting that most heavy weight vehicles having diesel engine driving in Dhaka city are in poor condition and needs more servicing. Incomplete combustion of fuel in diesel driven buses causes emission of hazardous compounds into the environment. Therefore, heavy transportations such as trucks, buses which are main transportation for general people in Dhaka city should be monitored regularly to check the condition of the engines. It is highly recommended that diesel engines should be converted into compressed natural gas engine as soon as possible to reduce the emission of PAHs in overpopulated cities like Dhaka. However, further investigation to rectify the quality of CNG engines so that they produce less emissions must be carried out.

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