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Distribution of Benzene, Toluene, Ethyl Benzene, Xylene (Btex) and Polynuclear Aromatic Hydrocarbons (PAHs) in Diesel Fuel from Independent Marketers and Bunkering Activities in Nigeria

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Abstract In order to check the quality of diesel fuels distributed in Nigeria, a study was carried out *to comparatively assess the distribution of benzene, toluene ethylbenzene and xylene (BTEX) and polyaromatic hydrocarbons (PAHs) in diesel fuels from independent marketers and bunkering activities in Nigeria. Ten diesel fuel samples were collected from each source of the product, extracted and analyzed using gas chromatograph equipped with flame ionization detector. Diesel fuel from independent marketers indicated the presence of benzene , 830.3 ± 11.26 mg/L ; toluene , 1126.2 ± 20.18 mg/L ; ethyl benzene, 14.17 ± 2.11 mg/L; m,p-xylene, 122.7 ± 8.03 mg/L ; o-xylene, 72.28 ± 11.21 mg/L, while diesel fuel from bunkering sources indicated the presence of benzene , 100.6 ± 9.23 mg/L ; toluene , 276.6 ± 11.9 mg/L ; ethyl benzene, 25.78 ± 3.01 mg/L; m,p-xylene, 27.73 ± 5.01 mg/L ; o-xylene, 140.3 ± 12.41 mg/L. . Diesel fuel from independent marketers indicated the presence of PAHs including naphthalene, 377.4 ± 17.2 mg/L ; acenaphthalene, 2337.4 ± 21.9 mg/L ; acenaphthene, 849.5 ± 15.1 mg/L ; fluorene, 428.3 ± 9.11 mg/L ; anthracene, 974.9 ± 12.52 mg/L ; phenanthrene, 575.5 ± 16.12 mg/L ; fluoranthrene, 748.6 ± 21.26 mg/L ; pyrene, 988.3 ± 19.28 mg/L ; benzo(c)fluoranthene, 1983,9 ± 30.16 mg/L ; chrysene, 429.9 ± 12.66 mg/L ; benzo(a)anthracene, 108.7 ± 12.09 mg/L ; benzo(a)pyrene, 193.9 ± 16.22 mg/L ; indeno(1,2,3,c,d)pyrene, 19.16 ± 1.92 mg/L ; dibenzo(a,h)anthracene, 11.52 ± 1.63 mg/L ; benzo(g,h,i)perylene, 34.72 ± 2.71 mg/L , while diesel fuel from bunkering source indicated the presence of naphthalene, 6.587 ± 0.32 mg/L ; acenaphthalene, 2941.6 ± 31.71 mg/L ; acenaphthene, 1029.5 ± 29.22 mg/L ; fluorene, 3375.4 ± 27.39 mg/L ; anthracene, 4507.6 ± 37.69 mg/L ; phenanthrene, 5982.6 ± 41.66 mg/L ; fluoranthrene, 2944.9 ± 39.22 mg/L ; pyrene, 1623.9 ± 37.79 mg/L ; benzo(c)fluoranthene, 5419.5 ± 43.12 mg/L ; chrysene, 1096.8 ± 29.61 mg/L ;benzo(a)anthracene, 647.5 ± 22.16 mg/L ; benzo(a)pyrene, 101.2 ± 9.24 mg/L ; indeno(1,2,3,c,d)pyrene, 17.25 ± 1.73 mg/L ; dibenzo(a,h)anthracene, 68.18 ± 8.23 mg/L ; benzo(g,h,i)perylene, 52.46 ± 7.53 mg/L . Diesel fuel from independent marketers had aromatics contents relatively higher (14.17 – 1126 mg/L) than those from bunkering source (25.78 – 276.0 mg/L), while PAHs contents were relatively higher in bunkering diesel (6.587 – 5982 mg/L) than in diesel fuel from independent marketers (11.52 – 2337 mg/L). Statistical analysis of variance in the contents of aromatics and PAHs at 95% confidence, indicated a significant difference in the diesel fuel quality from the two sources. The study revealed that the diesel fuel quality in use in Nigeria on the bases of PAHs and aromatics content is comparable to the European Union diesel fuel quality specification of a maximum of 4 % m/m PAHs.*

Key Words: *Diesel fuel; polynuclear aromatic hydrocarbon; aromatics; carcinogenic, air toxics*

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1.0 Introduction

There is a global push for cleaner, more efficient means of transportation, bearing in mind that transport is the most significant contributor to ambient air pollution (Common Wealth of Australia, 2000). Also, there has been noticeable accelerated increase in greenhouse gas emissions from only the transport sector for the past few years, with a corresponding effort by environment, transport and industry agencies, working on direct action to improve the emission performances of the transport fleet.

Motor vehicle emissions are key sources of lead, carbon oxides, nitrogen oxides, photochemical smog, aromatics and polynuclear aromatic hydrocarbons (Common Wealth of Australia, 2000). Heavy diesel fuel vehicles are also a significant sources of nitrogen oxides and particles, contributing up to 80 percent of vehicle produced particles in major cities (National Environment Protection Council, 1988)

Priority air toxics likely to encounter from vehicular emissions in consideration of persistence, toxicity and environmental /human exposure include benzene, toluene, 1,3- butadiene, formaldehyde, polynuclear aromatic hydrocarbons and xylene (Victoria Environment Protection Agency, 1999; National Green House inventory, 1999). Air toxics are pollutants that occur in relatively small volumes, compared with ambient pollutants, but are considered hazardous to health or environment (National Green House inventory, 1999)

Motor vehicle emissions are estimated to make the following contributions to ambient levels of air toxics, benzene 80 percent, toluene 57 percent, 1,3-butadiene 76 percent, formaldehyde 64 percent, polynuclear aromatic hydrocarbon 42 percent, xylene 57 percent (National Green House inventory, 1999).

Diesel fuel is a complex mixture of hydrocarbon chemicals with main groups being paraffins, naphthenes and aromatics, alkyl benzene and polynuclear aromatic hydrocarbons structures. Organic sulphur is also naturally present. Additives are generally added to influence properties such as flow storage and combustion characteristics of diesel fuel (IPCPS, 1996). The actual properties of commercial automotive diesel depend on the refining practices employed and also nature of the crude oils from which the fuel is produced (Standard Australia, 1998). The quality and composition of diesel fuel significantly influence emissions from diesel engines into the environment, with attendant health consequences (Standard Australia, 1998).

Key diesel fuel parameters which are known to have significant effects on emissions have been identified as sulphur, cetane number/index, density, T95 distillation (volatility) and polynuclear aromatic hydrocarbons, ash content and viscosity [(commonwealth of Australia, 2000). Fuel quality specifications established in the European Union (Table 1) have been set with particular attention given to the environmental of the fuel.

Table 1: European Union diesel fuel quality specifications

Fuel Parameter	Euro 2 EN 590 (1993)	Euro 3 2000)	Euro 4 (2005)
Sulphur (ppm}	< 500	< 350	< 50
Cetane Number	>49	>51	>55
Cetane index	>46	> 46	>52
Density @ 15 º C (kg/m^3)	820 860	< 845	< 845
Distillation T95	< 380	< 350	< 340
PAHs (% m/m)	-	< 11	< 4

Source [1]

Table 2: WWFC diesel fuel specification based on category (Cat.)

Fuel Parameter	Cat. 1	Cat. 2	Cat. 3
Sulphur (ppm)	< 5000	< 300	< 30
Cetane Number	>45	>53	>55
Cetane index	>45	>50	>52
Density at 15ºC (kg/m^3)	820 -860	820 - 850	820 - 840
Distillation T95	< 370	< 355	< 340
PAHs (%)	-	<5	<2

The World Wide Fuel Charter (WWFC) which is a proposed American, European and Japanese automotive manufacturer, is a set of fuel specifications for petrol and diesel, intended to facilitate worldwide harmonization of fuel quality.

Research has shown that reducing aromatics in diesel fuel will increase the cetane number , which in turn improves the stability of the engine, thereby decreasing the exhaust smoke opacity during cold start (Egeback, 1991).Diesels higher in aromatics are high in density , but low cetane number , thereby reducing the quality of the fuel (Australian Academy of Technological Sciences and Engineering, 1997).

The regulatory work on fuel quality parameters by the Environment Canada is very specific, fixing the maximum level of benzene in diesel fuel at one percent by 2000, which is limited to reducing exposure to toxic substances or controlling air pollution (Wania, Mackay, 1996}. Higher density of diesel fuel is frequently an indicator of high aromatic contents of the fuel for a given distillation range. Increased aromatic content is known to lead to increased particle emissions (OECD, 1993). Air toxics linked to benzene, formaldehyde, 1,3-butadiene and polynuclear aromatic hydrocarbons (Maliszewska,1999; Agency for Toxic Substances and Diseases Registry, 1995; Kamens, 1998).

This study was burned out of the concern that the bunkering diesel which is produced by local refining may have very little or no quality control in terms of product quality and standardization of the refining process, which ultimately will influence vehicular emission of particles, as compared with the diesel fuel quality parameters [Canadian Fuel Quality Parameters, 2015].

In a case study of Sao Paulo , Brazil ,reported elsewhere , on the impact of diesel emissions on the ambient particles, diesel emissions significantly influence composition and mutagenicity of ambient particles (Cavalho-Oliviera, 2005).

Increased interest in the use of additives to improve the environmental performance of fuels has been accompanied by the development of a wide range of bio-fuels. For the purposes of this discussion these are taken to be fuels containing a significant proportion (>10-15%) of ‘renewable’ hydrocarbon compounds. Typical examples include ethanol and methanol diesel (and petrol) blends and the use of vegetable oils such as canola oil (Commonwealth of Australia, 2000). However, the air quality and greenhouse emissions performance of such fuels are less well understood than those of ‘conventional’ diesel (and petrol).

According to Speight (1991), aromatic hydrocarbons may account for about 1. to 20 percent of the total hydrocarbons in crude oil. Even, BTEX compounds may be at a concentration of several percent in light crude oil, and are typically present at concentrations of 100 to 10,000 mg/kg (Speight, 1991).

The four– ring to six-ring PAH (pyrene/fluoranthene to coronene), are mostly known mammalian carcinogens, usually present at low or trace concentrations in crude oils (Kerr, 1999). Hence, ecosystems and their components vary at time scales ranging from seasons to decades and longer as a result of impacts from anthropogenic activities, mostly oil exploitation activities (The National Academics of Sciences, Engineering and Medicine, 2019).

2.0 Materials and Methods

The diesel fuel samples from Independent Marketers were purchased from some filling stations in Akwa Ibom State, Nigeria, while bunkering diesel fuel were sourced from some bunkering locations where there are illegal local refining activities in the Niger Delta region of the south-south States, Nigeria.

Akwa Ibom State is part of the Niger Delta region which is located in the coastal Southern part of Nigeria, lying between Latitude 4.32 and 5.33 N and Longitude 7.25 E and 8.25 E. Vegetation in the study area is tropical rain forest type and mangrove swamps close to Eastern Obolo, Ibeno and Ikot Abasi LGAs. The study area is sustained by the strong climate characterized by high temperature (annual mean $26\,^{o}$C) and high relative humidity of annual mean of 83 %, and precipitations of 250 mm per year (Igbemi, 2019).

Ten samples of diesel fuel from Independent Marketer sources were collected and pooled into one, while ten samples of diesel fuel from bunkering sources were collected and pooled into one.

Diesel fuel samples were analyzed for PAHs according to Method 6440 of APHA 2018 [17], by Gas Chromatograph, with flame ionization detector and helium gas as the carrier gas, maintained at a pressure of 30 psi (AGILENT 7890 GC).

The sample was extracted with dichloromethane as solvent in a separatory funnel and the extract concentrated using a rotary evaporator. One microliter (1ul) of the extract was injected into the column using a micro syringe, and the column maintained at a temperature between 270 to 320 ^{o} C

Diesel fuel samples were analyzed for BTEX by Gas Chromatograph, with flame ionization detector (AGILENT 7890), using the ASTM D5580 – 02. Method for the determination of BTEX in diesel fuel. The Gas Chromatograph was operated according to the manufacturer’s operating manual,

2.0 Results and Discussion

Results of analyses of diesel fuel from Independent Marketers for BTEX are presented in Table 3, while results of analyses of diesel from same sources for PAHs are presented in Table 4.

Results of analyses of diesel fuel from bunkering sources for BTEX are presented in Table 5, while results of analyses of diesel from same sources for PAHs are presented in Table 6.

Table 3: Results of BTEX determination in BD1 and BD 2 samples

BTEX (mg/L)	Ind. Mar. Diesel Fuel (BD 1)	Bunk. Diesel Fuel (BD2)
Benzene	830.3	100.6
Toluene	1126.3	276.1
Ethylbenzene	14.18	25.79
O-xylene	72.28	140.31
M, P -xylene	122.7	27.74
Total	**2165.7**	**570.50**

Diesel fuel from independent marketers indicated the presence of aromatics as follows (Fig.1), benzene , 830.3 ± 11.26 mg/L ; toluene , 1126.2 ± 20.18 mg/L ; ethyl benzene, 14.17 ± 2.11 mg/L; m,p-xylene, 122.7 ± 8.03 mg/L ; o-xylene, 72.28 ± 11.21 mg/L, while diesel fuel from bunkering sources indicated the presence of aromatics as follows (Fig.2) , benzene , 100.6 ± 9.23 mg/L ; toluene , 276.6 ± 11.9 mg/L ; ethyl benzene, 25.78 ± 3.01 mg/L; m,p-xylene, 27.73 ± 5.01 mg/L ; o-xylene, 140.3 ± 12.41 mg/L. . Diesel fuel from independent marketers indicated the presence of PAHs as follows (Fig.3), naphthalene, 377.4 ± 17.2 mg/L ; acenaphthalene, 2337.4 ± 21.9 mg/L ; acenaphthene, 849.5 ± 15.1 mg/L ; fluorene, 428.3 ± 9.11 mg/L ; anthracene, 974.9 ± 12.52 mg/L ; phenanthrene, 575.5 ± 16.12 mg/L ; fluoranthrene, 748.6 ± 21.26 mg/L ; pyrene, 988.3 ± 19.28 mg/L ; benzo(c), fluoranthene, 1983,9 ± 30.16 mg/L ; chrysene, 429.9 ± 12.66 mg/L ; benzo(a)anthracene, 108.7 ± 12.09 mg/L ; benzo(a)pyrene, 193.9 ± 16.22 mg/L ; indeno(1,2,3,c,d)pyrene, 19.16 ± 1.92 mg/L ; dibenzo(a,h)anthracene, 11.52 ± 1.63 mg/L ; benzo(g,h,i)perylene, 34.72 ± 2.71 mg/L Diesel fuel from bunkering source indicated the presence of PAHs as follows (Fig.4): naphthalene, 6.587 ± 0.32 mg/L; acenaphthalene, 2941.6 ± 31.71 mg/L; acenaphthene, 1029.5 ± 29.22 mg/L ; fluorene, 3375.4 ± 27.39 mg/L ; anthracene, 4507.6 ± 37.69 mg/L ; phenanthrene, 5982.6 ± 41.66 mg/L ; fluoranthrene, 2944.9 ± 39.22 mg/L ; pyrene, 1623.9 ± 37.79 mg/L ; benzo(c)fluoranthene, 5419.5 ± 43.12 mg/L ; chrysene, 1096.8 ± 29.61 mg/L ;benzo(a)anthracene, 647.5 ± 22.16 mg/L ; benzo(a)pyrene, 101.2 ± 9.24 mg/L ; indeno(1,2,3,c,d)pyrene, 17.25 ± 1.73 mg/L ; dibenzo(a,h)anthracene, 68.18 ± 8.23 mg/L ; benzo(g,h,i)perylene, 52.46 ± 7.53 mg/L .

Diesel fuel from independent marketers had aromatics contents relatively higher (14.17 – 1126 mg/L) than bunkering diesel fuel (25.78 – 276.0 mg/L) , while PAHs contents were relatively higher in bunkering diesel (6.587 – 5982 mg/L) than in diesel fuel from independent marketers (11.52 – 2337 mg/L), as compared to Department of Petroleum Resources (DPR) Environmental Guidelines

Table 4: Results of PAHs determination in BD1 AND BD 2 samples

PAHs (mg/L)	Ind. Mar. Diesel Fuel (BD 1)	Bunk. Diesel Fuel (BD2)
Naphthalene	377.4	6.587
Acenaphthalene	2337.4	2941.6
Acenaphthene	849.5	1029.6
Fluorene	428.3	3375.4
Anthracene	974.9	4507.6
Phenanthrene	575.5	5982.6
Fluoranthene	748.6	2944.9
Pyrene	988.3	1623.9
Benz[c] fluoranthene	1983.9	5419.5
Chrysene	429.9	1096.8
Benzo [a] anthracene	108.7	647.5
Benzo[a]pyrene	193.9	101.2
Indeno[1,2,3, c,d]pyrene	19.16	17.25
Dibenzo[a,h]anthracene	11.52	68.18
Benzo[g,h,i]perylene	34.72	52.46
Total		

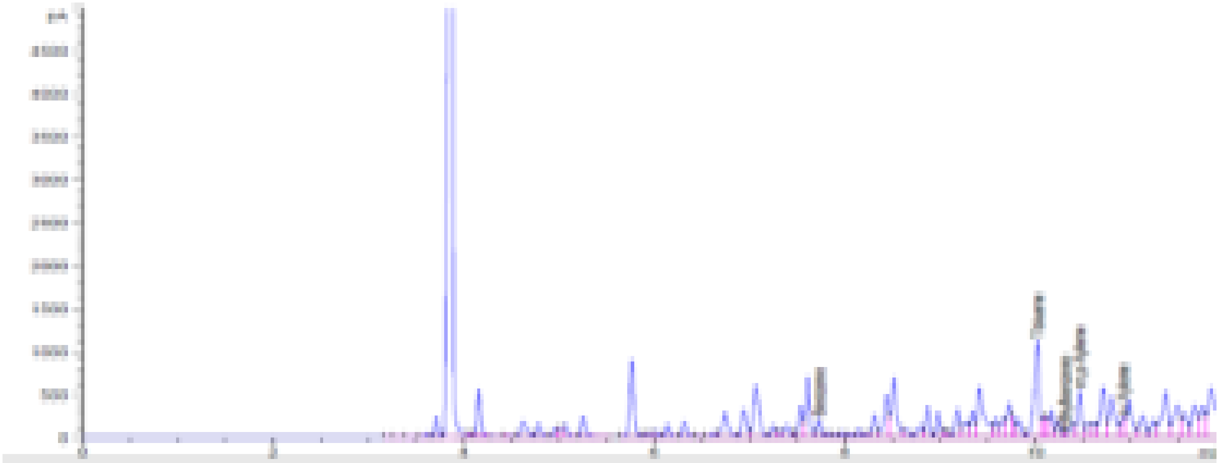

Fig. 1: Spectrum of BTEX in diesel from Independent Marketers source

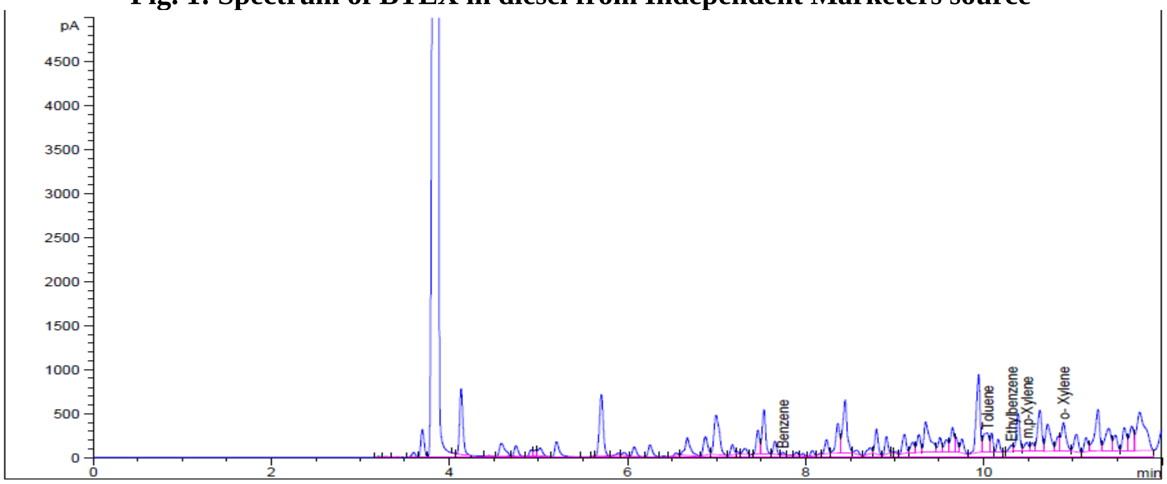

Fig. 2: Spectrum of BTEX in diesel from Bunkering source.

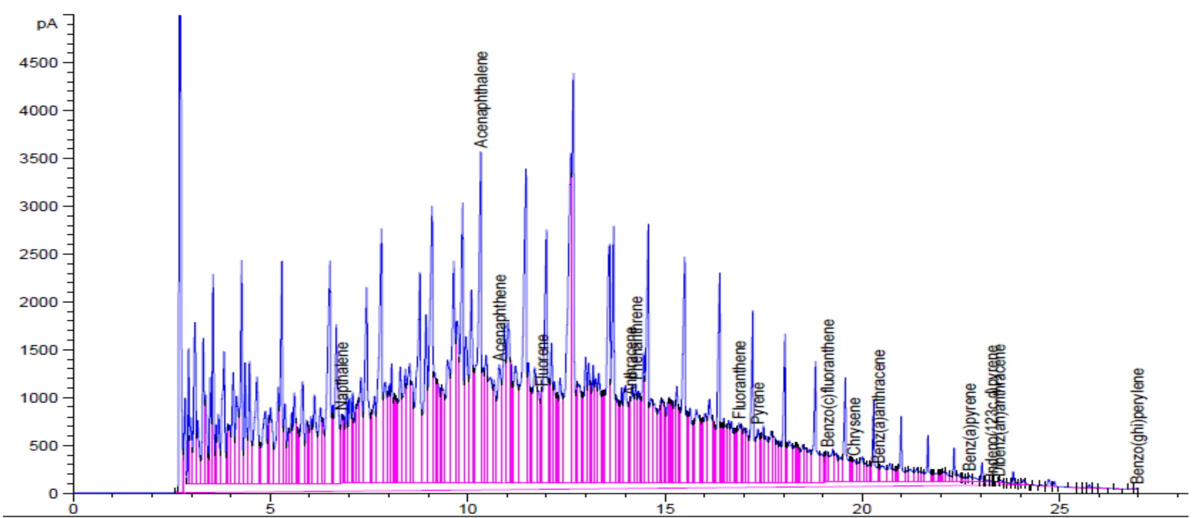

Fig. 3: Spectrum of PAHs in diesel from Independent Marketers Source

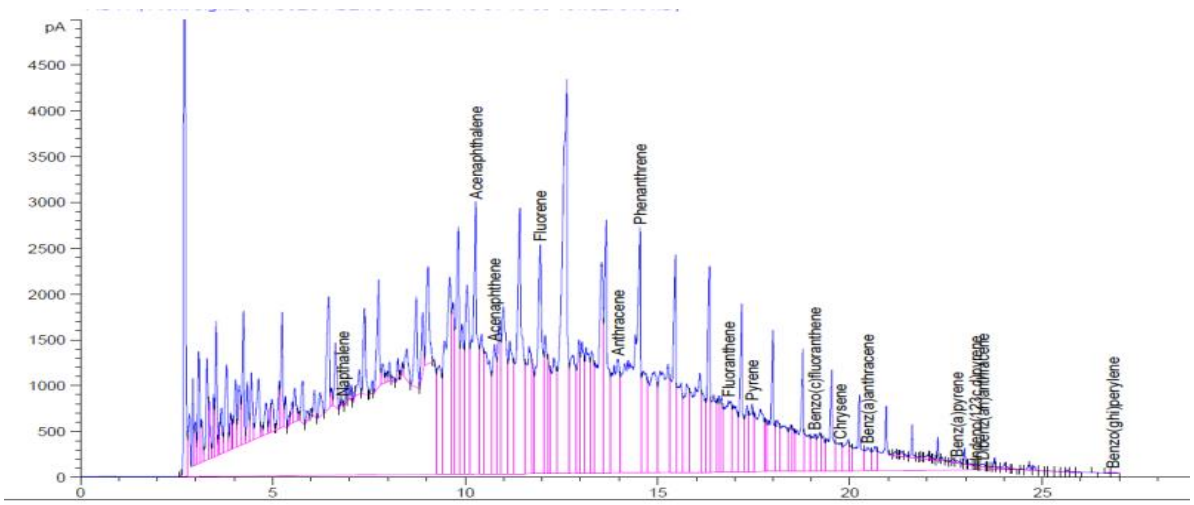

Fig.4: Spectrum of PAHs in diesel from bunkering Source

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Department of Petroleum Resources, 2011. Statistical analysis of variance in the contents of aromatics and PAHs indicated a significant difference in the diesel fuel quality from the two sources.

4.0 Conclusion

Total benzene, toluene, ethylbenzene and xylene (BTEX) concentrations in diesel fuel from independent marketers source was 570.50 mg/L (0.057 percent), which are the more volatile monoaromatic compounds found in crude oil, while, total benzene, toluene, ethylbenzene and xylene (BTEX) concentrations in diesel fuel from bunkering source was 2165.7 mg/L (0.22 percent) . The regulatory work on fuel quality parameters by the Environment Canada specified maximum benzene level at one percent.

Total polyaromatic hydrocarbons (PAHs) concentrations in diesel fuel from independent marketer source was 10,061.7 mg/L (1.01 percent**),** while, total polyaromatic hydrocarbons (PAHs) concentrations in diesel fuel from bunkering source was 29815.077 mg/L (2.98 percent).

By WWFC diesel classification, PAHs contents (1.01 percent) in independent marketer diesel was less than two percent specification, while PAHs content (2.98 percent) in bunkering diesel was greater than two percent specification.

This study revealed that the diesel fuel quality in use in Nigeria on the bases of PAHs and aromatics content is significantly not comparable to the European Union diesel fuel quality specification of a maximum of two percent m/m in PAHs concentrations.

There is a high level of BTEX in bunkering diesel fuel which could be attributed to the crude process of refining of petroleum, without standardization.

Considering the high levels of PAHs in bunkering diesel fuel, the illegal activities of crude production and refining by the locals in the Niger Delta is detrimental to the environment and public health, therefore, should not be encouraged.

The recommendation to be made is that a study of full quality parameters of the diesel fuel from Independent marketers and from bunkering activities should be undertaken, as to have an overview of the quality of diesel fuel in the Nigerian market.

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