Source Identification of Polycyclic Aromatic Hydrocarbons in Water at Point of Effluent dischargfe point into the New Calabar River, Port Harcourt, Rivers State, Nigeria

Abstract

Water samples from effluents discharge points were analyzed for polycyclic aromatic hydrocarbons (PAHs) concentration using chromatographic techniques. The result obtained showed the presence of all the PAHs categories in the water samples. The total concentrations of PAHs in the different location showed that Minipiti station was the highest (44.99 mg/L), which was followed by the values obtained at the Police Post station (36.89 mg/L) and finally, the lowest value was obtained at the Iwofe Jetty station (11.923 mg/L). Diagnostic analysis of the concentrations of the different PAHS concentrations based on the ratio of low molecular weight PAHs to high molecular weight PAHs (LMW/HMW), anthracene / anthracene + phenanthrene {An/(An + Phe)} fluoranthene/ fluoranthene + pyrene {Fl /(Fl + Pyr} and benzo[a] anthracene/ benzo[a]anthracene + chrysene {BaA/ (BaA + Chr)} showed the predominance of pyrogenic PAHs over petrogenic PAHs. Thus indicating more of human input sources than natural. Ring size analysis indicated the predominance of the higher molecular weights (4-6) rings over the lower molecular weights (2-3) rings. The implications of the high level of PAHs within the sampled environment should give warning signals to the user of the water environment'

Keywords: PAHs, diagnosis, effluent discharge, environment, source identification.

Introduction

Increase in Industrial development and expansion have led to radical socio-economic advancement. This result associated with this growth is the issue or problem of environmental disintegration and pollution. This has led to prevalent pollution problems from discharged chemicals or derived products arising from the production processes. Some of the pollutants or contaminants of the environment whose increase in any of the atmospheric media are linked to human influence are polycyclic aromatic compounds (Flowers *et al*., 2002). Polycyclic aromatic hydrocarbons are a large class of persistent organic compounds, which are equally toxic to the environment. They are produced as derivatives of nearly every form of incineration of carbon containing matter of biological organisms (Hien *et al*., 2007). Disposal of various waste materials into rivers, estuaries, and marine waters therefore is not a modern phenomenon since this practice has been used as a preferred disposal option virtually since the beginning of human civilization (Marcus & Edori, 2017)

The contribution of the petroleum industry to the world energy and economic development over the past five to six decades is well known. One of the countries that have immensely benefited from this industry is Nigeria (Ite *et al*., 2016). The accidental releases of petroleum products and other chemicals associated with exploration and exploitation activities is also a common occurrence in the environmental (Ite *et al*., 2013). The global attention given to PAHs is due to their mutagenicity, carcinogenicity, teratogenicity and toxicity to humans (Stabenaut et al., 2006, Nwineewii and Marcus, 2015). The presence of these PAHs in the environment therefore portends danger to the users of the water. It has been established that the higher molecular weight PAHs constitute more danger to the environment, since they are potential carcinogens (Chrysikou et al., 2008).

Particularly, the release of petroleum hydrocarbons into the atmosphere without regard to laid down rules causes atmospheric pollution which has negative effect on climate change (Ana *et al*., 2010; Gorleku *et al*., 2014), pollution of aquatic ecosystem with deleterious effects, changes on aquatic ecology with subsequent antagonistic influences on biota, destructive influence on tourism, fishing and recreational activities (Ite *et al*., 2016; Yakubu, 2017).

Polynuclear aromatic hydrocarbons originated from partial burning of carbon-based materials such as crude oil, timber, fire wood, diesel, fat, compost, forest fire, etc, (Srogi, 2007). Man-made sources of PAHs arise from the burning of fossil fuels in the home environment, discharges from automobiles, discharges from industries and gas flaring, and in the treatment of both solid and liquid wastes (Ana *et al*., 2010).

This study was carried out to investigate the concentrations of polycyclic aromatic hydrocarbons in water and their sources at drainage discharge points into the New Calabar River

Materials and Methods

Water samples were collected from three different locations (effluents discharge points) along the New Calabar River. The samples were collected at a depth of 30 cm below surface water with previously washed and dried glass bottles. They were transferred into ice packs and immediately transported to the laboratory. The sampled points were: Police post, Minipiti and Iwofe jetty discharge points.

The analysis of the water samples for the different components of PAHs was first done by extraction with a mixture of *n*-hexane and dichloromethane. The extracts were further concentrated and purified according to the method describe by Nwineewii and Marcus (2015) and the extract analyzed with chromatographic system (HP 6890 Series GC system equipped with FID). The FID was operated at a temperature 325^{o}C.

The results obtained were then analyzed according to the method described by Ilechukwu *et al*., (2016) to determine, predict and apportion the source of the PAHs into the environment.

Results and Discussion

The concentrations of the different PAHs compounds from the various stations is given in Table 1. Table 1: Concentration of polycyclic aromatic hydrocarbons at the different station. The result showed that naphthalene, acanaphthylene and phenanthrene were undetected at the Iwofe Jetty. All the PAHs were detected at the Minipiti station, while at the Police Post station, naphthalene, acanaphthene and Benzo (k) fluoranthene were not detected.

The elevated concentrations of PAHs in the present work possibly originated from fall out from flared gases and waste water from petroleum based industries close to the sample points. Recalling that Rumuolumeni axis of Port Harcourt is replete with plethora of onshore and offshore petroleum activities, deport, illegal oil bunkering and destruction of stolen crude through direct burning. This observation corroborates the findings of Esumang *et al*., (2009), that observed that the entry route of PAHs to the surface water of Accra, Ghana metropolis came from atmospheric fallouts which were either precipitated by gravity or rain into the water, urban-run offs, public and private waste discharges and industrial wastewater.

Exposure to this water which contains all the categories of PAHs at appreciable level can be injurious to pregnant women and infants. It can inflict behavioural disorder, impair intelligent quotient, cause asthmatic breathing, and other health abnormalities in both adults and children (Nwinewii and Ibok, 2014).

PAHs (mg/L)	**Stations**		
	Iwofe Jetty	**Minipiti**	**Police Post**
Napthalene	-	4.25297	-
Acenapthylene	-	3.34848	0.914637
Acenaphthene	0.09024	0.63742	-
Flourene	0.1743	0.94282	2.85662
Phenanthrene	-	0.90227	0.94504
Anthrancene	0.46641	0.75535	1.13056
Fluoranthene	0.13007	0.66517	0.68168
Pyrene	0.38137	0.05029	11.01870
Benzo (a) anthracene	0.567288	7.69750	11.13948
Chrysene	0.62411	0.60233	3.97761
Benzo (b) fluoranthene	1.81437	0.22058	0.229111
Benzo (k) fluoranthene	0.08823	6.12916	-
Benzo (a) pyrene	1.58213	3.92882	0.57
Dibenzo (a,h) anthracene	1.42191	6.2427	0.5304
Benzo (g,h,i) perylene	1.06531	5.09045	2.05952
Indeno (1,2,3-c,d) pyrene	1.09051	0.5246	0.8291

The total concentrations of PAHs from the different sample station showed that Minipiti had the highest concentration of PAHs, which was followed by the values obtained at the Police post station and then the Iwofe Jetty station (Figure 1). The values of PAHs observed in the different stations were higher than the acceptable limit of 10 mg/L stipulated by FMENV, (1992) for drinking water. One would ordinarily expect that the Iwofe Jetty station would have had more concentrations considering the major oil based activities (legal or illegal) take place, but this was not so. The reason might be due to constant flow or movement of the tidal water. The high value recorded at the Minipiti station may probably be due to the proximity of an abattoir where different activities (roasting of cow skin, discharge of the gut content of animals, burning of the discarded bones of animals) take place. Secondly, the effluents from the university (Ignatius Ajuru University of Education) are also discharged through this point and thirdly, the stagnancy of the effluents discharge at this point for a longer time before the tidal water removes them during high tide. The same factors for the Minipiti station (except the university and the abattoir may have contributed to the values of PAHs observed at the Police Post station. However, at the

Police Post station, fallouts from nearby filling stations can also be a contributory factor in PAHs input.

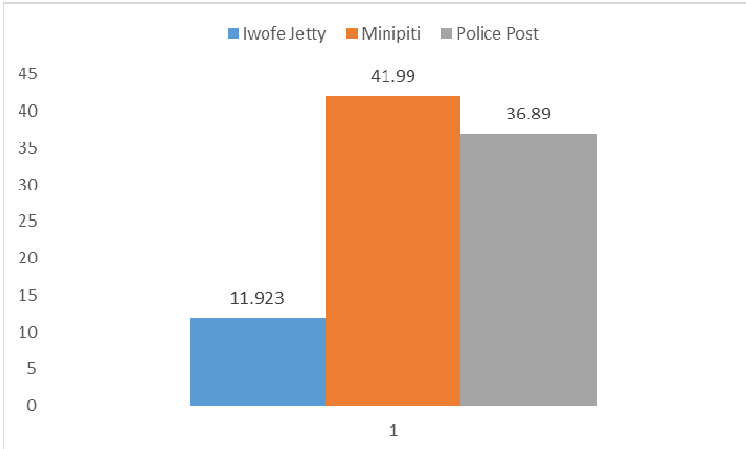

Figure 1: Total polycyclic aromatic hydrocarbon content in the different stations

The result of the diagnostic ratios of the different PAHs combinations is given in Table 2. The present study observed higher values of HMW PAHs as against the LMW PAHs. The ratio between the LMW PAHs/HMW PAHs in the various stations revealed that the PAHs sources were pyrogenic, this is based on the fact that a ratio of less than 1 was obtained in all the stations. Diagnosis using An / An + Phe, gave values of 1, 0.456 and 0.545 at Iwofe jetty, Minipiti and Police Post stations respectively. Values less than 0.1 indicated petrogenic or natural sources while values greater than 0.1 showed pyrogenic or anthropogenic sources. From the values obtained in the various stations, it is evident that the sources were pyrogeniioc. For the higher molecular weight components of PAHs, (4 member rings) Fl / Fl + Pyr, values greater than 0.5 shows pyrogenic origin of PAHs, while values less the 0.4 shows petrogenic or natural origin. The value obtained using this ratio indicated that PAHs in Iwofe Jetty and Police Post were of petrogenic origin, while those of Iwofe orininated from pyrogenic sources. For the 5-6 member rings, the ratio between BaA/ (BaA + Chr) gave values of 0.717, 0.867 and 0.125 for Iwofe Jetty, Minipiti and Police Post stations respectively. When the values from this ratio exceeds or becomes less than 0.2, the origin of the PAHs are from petrogenic sources, while values above 0.35 shows pyrogenic sources of PAHs. The implication of the observation made with respect to BaA/ (BaA + Chr) ratio implies that PAHs from Iwofe Jetty and Minipiti stations originated from pyrogenic sources, while those of Police Post originated from petrogenic sources.

The diagnostic investigation or source identification results indicated diverse sources of PAHs input into the water environment similar to observations of earlier studies in Niger delta environment (Anyakora et al., 2011; Adeyemo and Ubiogoro, 2012; Moses *et al*., 2015), although pyrogenic sources of PAHs origin dominates over petrogenic sources in this present work. This observation is in consonance with the finding of other authors in Niger Delta environments (Inengite *et al*., 2010; Adeyemo and Ubiogoro, 2012; Moses *et al*., 2015). These numerous input sources according to the authors are (oil exploration and exploitation activities, agricultural imputes, forest and agricultural fire, abattoir activities, runoffs, flaring of gases, etc.

Table 2: Diagnostic ratios of PAHs in water from the different sample stations

Stations	∑LMW PAHs	∑HMW PAHs	LMW/HMW	An/(An + Phe)	Fl /(Fl + Pyr	BaA/ (BaA + Chr)
Iwofe Jetty	0.7309	7.700	0.095	1	0.254	0.717
Minipiti	10.839	30.040	0.361	0.456	0.930	0.867
Police Post	5.906	31.036	0.190	0.545	0.058	0.125

The concentration, predominance and occurrence of the different PAHs rings is shown in figure 2. The result of the concentrations of the different PAHs ring sizes showed that the five member rings and the six member ring were predominant over the lower molecular weights rings in the Iwofe Jetty station. In the Minipiti station, though there was the predominance of the five membered rings over the others, yet they all occurred in appreciable concentrations, with the lowest members (2-3) having the nearest concentration to it. Sediment PAHs in the PolicPost station was dominated by the 4 ringed members, which was followed by the 2-3 ringed members. These observations in the predominant nature of one ring or the other over the rest is not in agreement with the values obtained in Some Creeks of South East Rivers State (Niger Delta) Nigeria (Nwineewii and Marcus, (2015) where no particular ring size dominated the others and those of Okoro, (2008) in in Ekpan Creeks, in Warri Delta state, where the values of the individual PAHs components were within the same concentration range. However, this observation corroborates the findings of Inengite et al., (2010) and Agbozu *et al*., (2017) in Kolo Creek and different environments within Warri respectively.

The ring size possessed by PAHs tend to give the characteristics exhibited by the individual PAHs. The higher ring PAHs are less soluble in water, but the reverse becomes the case with their solubility in fats and oil. Therefore, the higher molecular weights accumulates more in fat tissues of animals and man. Due to the solubility of the lower molecular weights, the have the tendency to be easily absorbed by bio-organisms (Johnsen *et al*., 2005; Agbozu *et al*., 2017) and can easily be assessed or taken in by water consumers. The lower concentrations of the low molecular weights may not be unconnected with their volatility and uptake by plants and animal as against the non-availability of the higher molecular weight PAHs to plants and animals and their non- volatile nature and partial solubility (Haritash and Kaushik, 2009).

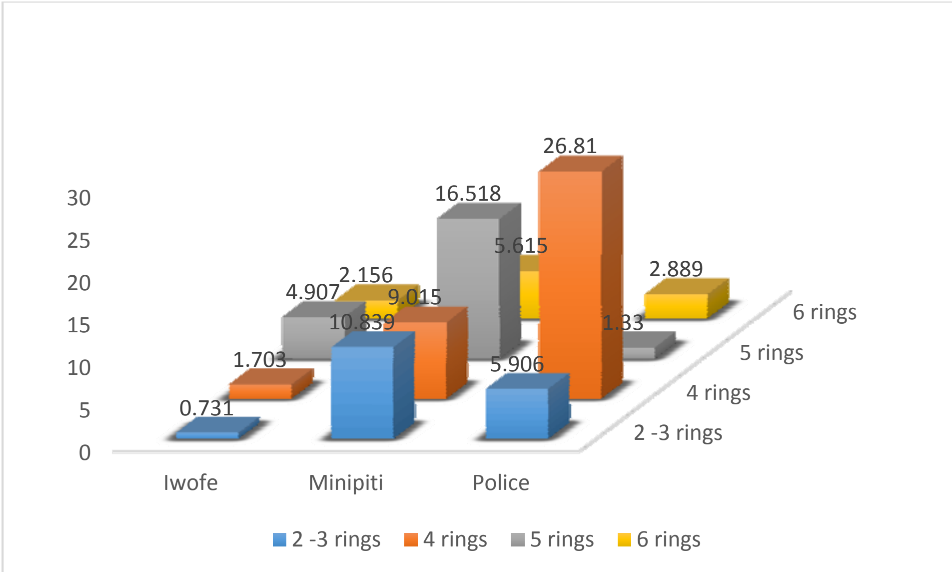

Figure 2: Concentrations (mg/L) of the different PAHs ring categories in water samples from the different sample stations

Conclusion

The concentration of polycyclic aromatic hydrocarbons at the effluents discharge points were higher than required standards for water quality. This could pose negative consequences on the end user. The source determination of the PAHs implicated human activities, although the higher rings were more concentrated. However, knowing the adverse negative effects associated with PAHs, users of the sampled environments should to caution in order to avoid future health challenges. Government should adequately monitor the content of discharged effluents and other pyrogenic activities within the area to cub further increase in concentrations of the PAHs component.

Disclaimer

This paper is based on preliminary dataset. Readers are requested to consider this paper as preliminary research article. Authors are aware that detailed statistical analysis is required to get a scientifically established conclusion. Readers are requested to use the conclusion of this paper judiciously as statistical analysis is absent. Authors also recommend detailed statistical analysis for similar future studies.

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