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SHORT COMMUNICATION

CARCINOGENIC POTENCY OF POLYCYCLIC AROMATIC HYDROCARBONS IN SOIL

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ABSTRACT. Carcinogenic potency of polycyclic aromatic hydrocarbons (PAHs) in soils obtained from seven different sampling locations in Effurun metropolis and its environs of Niger Delta Area of Nigeria were evaluated. The 16 US EPA priority PAHs were determined with GC-MS. The concentrations of individual PAHs observed were used to compute the carcinogenic risk potency of the PAHs relative to benzo(a)pyrene (reference carcinogen). Benzo(a)pyrene equivalent concentration in soils from industrial sites, possess about 22 times carcinogenic potencies than soils from residential areas.

KEY WORDS: Benzo(a)pyrene, Carcinogen, Carcinogenic risk potency, Tumours, Soil

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are very well known for their carcinogenic properties for some time now. They are hydrophobic in nature and their persistence in the environment is mainly due to their low water solubility and electro-chemical stability. Evidence suggest that the lipophilicity, environmental persistence and genotoxicity of PAHs increase as the molecular size of the PAHs increases up to four or five fused benzene rings [1]. PAHs are permanently formed by all sorts of incomplete combustion and hence may be considered to be ubiquitous, which practically makes human and environmental exposure to PAHs to be unavoidable. PAHs have been tested for carcinogenicity in various biological samples by diverse routes of application (oral, intraperitoneal, subcutaneous, epicutaneous, intratracheal and intrapulmonary) and resulted in both benign and malign tumors. Evidence that mixtures of PAHs are carcinogenic to humans comes primarily from occupational studies of workers following inhalation and dermal exposure. No data are available for the oral route of exposures to human. PAHs determined in soils and soil litters [2] were observed to be predominantly from vehicular emissions and forest fires. They also showed in their controlled burn study, that lower molecular weight PAHs, such as phenanthrene and fluorene, which had been deposited to non-detectable levels within two years after burning, but higher molecular weight PAHs such as benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, perylene, and indeno(1,2,3-cd)pyrene were more persistent in litter, decreasing after five years to about 20 % of initial deposition.

Some PAHs are classified as potent carcinogens. The benzo(a)pyrene is referred to as one of the most potent carcinogens known in recent publications. In young rats, a single intraperitoneal injection of 10 mg benzo(a)pyrene per animal caused an immediate, sustained reduction in the growth rate [3]. In mice, a single intraperitoneal injection (dose not specified) resulted in small spleens, marked cellular depletion, prominent haemosiderosis, and follicles with large lymphocytes, leading to death [4]. After a single application of 0.05 mL of a 1 % solution in acetone to the interscapular area of hairless mice (hr/hr strain), the mitotic rate of epidermal

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cells was increased [5]. Death due to myelotoxicity was observed after daily oral administration of benzo(a)pyrene at 120 mg/kg to poor-affinity receptor mice for one to four weeks, whereas high-affinity mice survived with no myelotoxicity for at least six months under these conditions [6].

Rats given 50 or 150 mg/kg per day of benzo(a)pyrene orally for four days showed suppressed carboxylesterase activity in the intestinal mucosa. In Fischer 344/Control rats exposed by inhalation to 7.7 mg/m^3 of benzo(a)pyrene dust for 2 h/day, five days per week for four weeks, no respiratory tract lesions were observed, clearance of tagged particles, and histopathological findings [7]. Most of the studies that have been conducted on PAH were designed to assess their carcinogenicity. Studies on various environmentally relevant matrices such as coal combustion effluents, vehicle exhaust, used motor lubricating oil, and side stream tobacco smoke showed that PAH are the agents predominantly responsible for their carcinogenic potential [8]. Benzo(a)pyrene has been tested in a range of species, including frogs, toads, newts, trout, pigeons, rats, guinea-pigs, rabbits, ferrets, ground squirrels, tree shrews, marmots, marmosets, and rhesus monkeys. Tumours have been observed in all experiments with small animals, and the failure to induce neoplastic responses in large animals has been attributed to lack of information on the appropriate route or dose and the inability to observe the animals for a sufficient time [9]. In studies with other PAH, benzo(a)pyrene was often used as a positive control and therefore administered at only one concentration. The PAH found not to be carcinogenic were anthracene, benzo(g,h,i)perylene, fluorene, benzo(g,h,i)fluoranthene, 1-methylphenanthrene, perylene, and triphenylene. Questionable results were obtained for acenaphthene, benzo(a)fluorene, benzo(b)fluorene, coronene, naphthalene, phenanthrene, and pyrene. The remaining compounds were found to be carcinogenic.

PAH potencies are used to determine quantitative health risks posed by PAH exposure. The risks posed by a mixture of PAHs are based on an assumption of additivity of the individual risks posed by the PAHs. The IPCS monogram on PAHs [10] describes three approaches used to calculate PAH potencies: 1) toxicity equivalence factors approach which is based on expressing the individual potencies relative to benzo(a)pyrene, 2) comparative potency approach, which does not identify or quantify the individual compounds but determines the potency of the mixture of compounds and 3) benzo(a)pyrene surrogate approach assumes that benzo(a)pyrene is an indicator of all the PAHs. In this study benzo(a)pyrene was used as a reference indicator to determine the carcinogenic potency of the other PAHs. It was also aimed at evaluating the carcinogenic risk potency of PAHs in soils of different activity sites in Effurun metropolis and its environs in Niger Delta area of Nigeria.

EXPERIMENTAL

Sampling was carried out in seven different sampling stations as shown in Figure 1. The details of sampling, handling, treatment as well as analysis procedures have already been discussed [11] and this paper is a discussion on the carcinogenic potency of the PAHs determined in soil matrices obtained from seven sampling locations as described therein. The soil samples were analyzed for 16 EPA priority PAHs using Gas Chromatography Mass Spectrometer HP 6890 series in accordance with method EPA 8100.

RESULTS AND DISCUSSION

Benzo(a)pyrene concentration ranged from 0.001-0.908 µg/g dry weight (dw) in the studied area [11]. Unlike the trend observed in the discussed PAHs constituents [11], the highest value was recorded in samples collected at Enerhen, while the lowest was from Ugboroke. The results at

the various sampling locations in order of magnitude presented in µg/g(dw) are as follows: Enerhen (0.908 ± 0.002 µg/g), Refinery (0.731 ± 0.202 µg/g), Ekpan (0.562 ± 0.000 µg/g), Alegbo (0.441 ± 0.006 µg/g), Effurun Water resources (0.354 ± 0.031 µg/g), Ugborikoko (0.323 ± 0.000 µg/g), and Ugboroke (0.266 ± 0.003 µg/g) [11]. The observed trend is Enerhen > Refinery > Ekpan > Alegbo > Effurun Water resources > Ugborikoko > Ugboroke. The results are comparable to that reported for Birmingham and Brisbane [12].

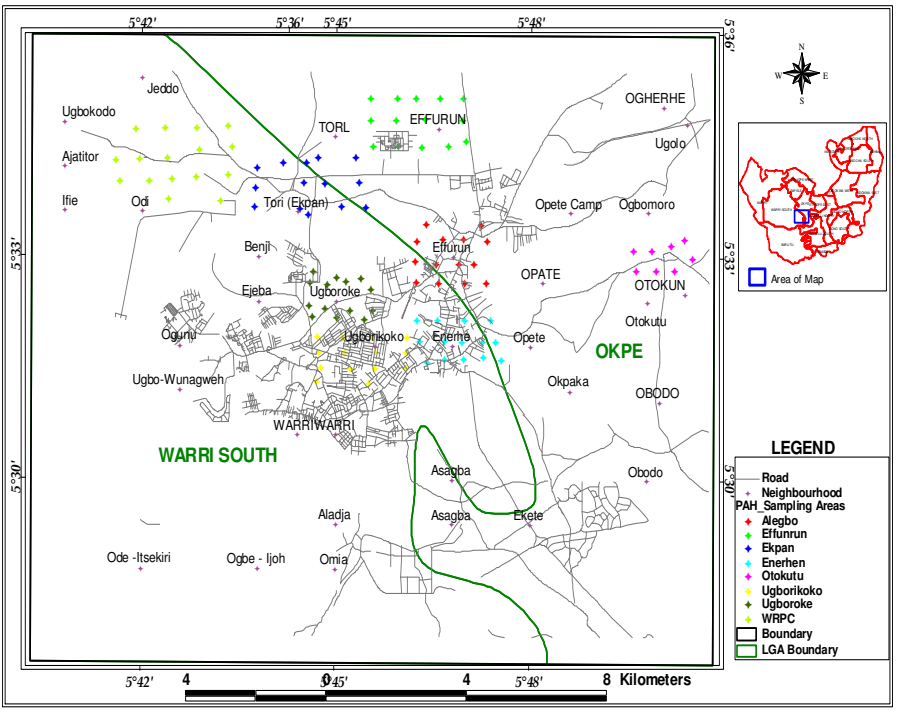

Figure 1. Map of study area, source: designed with ESRI Arc View GIS (version 3.3) software using sampling points coordinates as input.

Among the seven PAHs classified as probable human carcinogens, benzo(a)pyrene is often used as the reference indicator, because it is thought to be one of the most potent carcinogens [13]. A health investigation level is that critical concentration of a contaminant above which further appropriate investigation and evaluation would be required. In Australia and New Zealand, guidelines for the assessment and management of contaminated sites have been established [14]. The health risk assessment methodology provided the basis for estimation of the health investigation levels. Contaminant levels for a residential location are based on conservative assumptions to protect a young child living at the site. The benzo(a)pyrene levels in soils within the study area were lower than the Australian New Zealand Health Investigation Limits of 1.000 µg/g. This implies that the levels of benzo(a)pyrene in surface soils in Effurun may not pose a major health threat to human, however this could only be ascertained on the evaluation of the carcinogenic potency of the PAHs present.

Evaluation of PAHs carcinogenic risk potency

Among the PAHs, the USEPA [15] has classified seven chemicals are probable human carcinogens. These are benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenzo(a,h)anthracene and indeno(1,2,3-cd)pyrene. The sums of the carcinogenic PAHs (∑PAH carc.) compared to the total PAH are shown in Table 1.

Table 1. Total PAHs and carcinogenic PAHs in soils at the sampling locations.

PAH	Refinery	Ekpan	Enerhen	Effurun Water Res.	Ugborikoko	Ugboroke	Alegbo
∑ 17 PAH	45.9	18.2	13.9	9.0	5.8	3.8	7.8
∑ PAH carc.	13.1	5.5	6.3	3.1	2.4	1.6	3.2

The ratio of ∑17 PAHs to ∑PAH carcinogenic. (∑17 PAHs/∑PAH carc.) in the sampling locations ranged from 2.2 to 3.5. The highest ratio was observed for Refinery location, while the lowest was Enerhen. The ratios of total PAH concentration to the carcinogenic PAHs in samples collected from the refinery vicinity, Ekpan, Water resources were about 3:1, while others were about 2.1, respectively. This suggests the impact of similar emission of PAHs source in the area of study. The graphical presentation of the total PAHs concentration and the carcinogenic PAHs is shown in Figure 2.

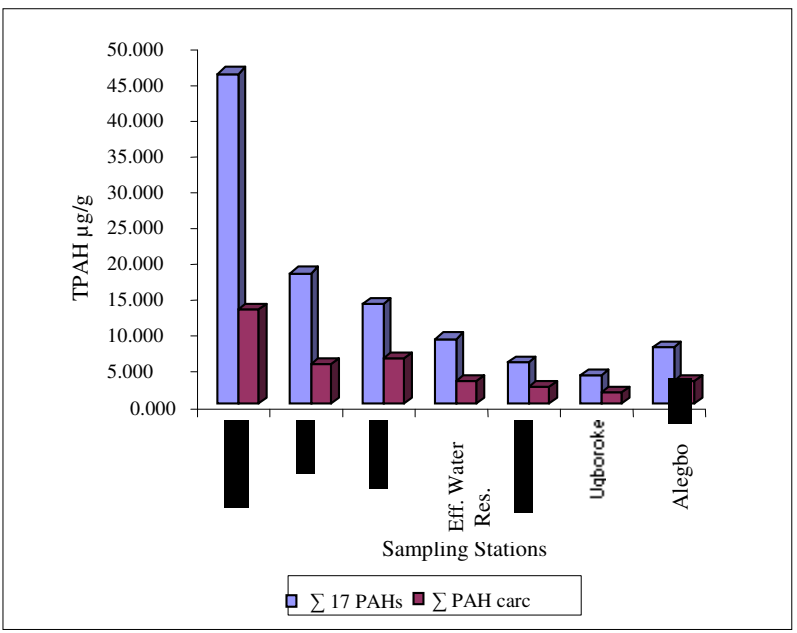

Figure 2. Total PAHs (TPAH) concentration and carcinogenic PAHs along locations.

The closeness in the ratios for Refinery and Ekpan suggest the influence of the same emission source. Similar, close range was observed in the other sampling locations, which appear to be predominantly, influenced by vehicular emissions. The observed trend in the ∑17 PAHs to ∑PAH carcinogen ratio could be attributed to the PAH profiles and constituent

composition which may be source related [16]. The observed marginal difference between the total PAH and total PAH carcinogenic constitute serious health risks for human population in the oil city of Effurun. However, in principle, the carcinogenic potency of a given PAH compound cannot be assessed by its original concentration but on the basis of its benzo(a)pyrene equivalent concentration. Calculation of the benzo(a)pyrene equivalent concentration for a given PAH compound requires the use of its toxic equivalent factor (TEF), which represents the relative carcinogenic potency of the given compound, using benzo(a)pyrene as a reference compound to adjust its original concentration [17].

Toxic equivalent factors have been used as a practical tool for regulatory purposes for a large group of compounds with a common mechanism of action (e.g. dioxin like compounds and PAHs). The concept is based on the following assumptions: that there is reasonably well – characterized reference compound, qualitative similar toxic effects for all members of the class, and the toxic effects of different compounds in a mixture are additive. Only a few proposals for TEFs are available. Among them, the list of TEF completed by Nisbet and LaGoy [18] has been suggested by Petry *et al.* [19], because it reflects the actual knowledge of the toxic potency of each individual PAH compound. The TEF list as completed by Nisbet and LaGoy [18] is shown in Table 2.

Table 2. Toxic equivalent factor of individual PAHs.

PAH Components	TEF
Naphthalene	0.001
Acenaphthalene	0.001
Acenaphthene	0.001
Fluorene	0.001
Phenanthrene	0.001
Anthracene	0.01
Fluoranthene	0.001
Pyrene	0.001
Benzo(a)anthracene	0.1
Chrysene	0.01
Benzo(b)fluoranthene	0.1
Benzo(k)fluoranthene	0.1
Benzo(a)pyrene	1.0
Indeno(1,2,3-cd)pyrene	0.1
Dibenzo(a,h)Anthracene	1.0
Benzo(g,h,i)perylene	0.01

On this TEF list, the carcinogenic potency of total PAHs (i.e, total benzo(a)pyrene equivalent concentration) can be assessed by the sum of the benzo(a)pyrene equivalent concentration estimated for each compound with a TEF in the total PAHs. The total PAHs concentration including initial concentration of individual PAH at the different activity sites in this study and their corresponding benzo(a)pyrene equivalent concentrations are shown in Table 3. The results showed that while the initial PAHs concentration in the samples was in the range 0.88 – 44.24 µg/g (dw), the benzo(a)pyrene equivalent concentration was 0.13 – 2.85 µg/g (dw). Thus, there is about 3 – 15 times decrease in concentration. Similar reduction in initial PAHs concentration was reported by Chun-The Li [20] in his study on the emission of PAHs and their carcinogenic potencies from cooking sources to the urban atmosphere.

Benzo(a)pyrene equivalent concentration in soils from industrial sites, possess about 22 times carcinogenic potencies than soils from residential areas. Therefore, efforts should be made to control industrial emissions, with an aim of reducing the exposure of workers to these rather

hazardous chemicals, contamination of ground water, pollution of receiving surface water bodies which otherwise serve as source of drinking water to the neighbouring communities.

Table 3. Total PAH concentration and benzo(a)pyrene, B(a)P, equivalent concentration at the different activity sites.

	Industrial sites		Market site		Road junctions		Road sides		Residential sites	
PAH Component (µg/g-dry wt	Initial conc.	B(a)P equivalent	Initial conc.	B(a)P equiv.	Initial conc.	B(a)P equiv.	Initial conc.	B(a)P equiv.	Initial conc.	B(a)P equivalent
Naphthalene	1.99	0.002	0.044	0.000	0.022	0.000	0.019	0.000	0.012	0.000
2-Methyl naphthalene	2.15	0.000	0.074	0.000	0.049	0.000	0.039	0.000	0.021	0.000
Acenaphthalene	0.93	0.001	0.120	0.000	0.024	0.000	0.050	0.000	0.008	0.000
Acenaphthene	0.88	0.001	0.170	0.000	0.030	0.000	0.044	0.000	0.006	0.000
Florene	0.92	0.001	0.250	0.000	0.160	0.000	0.130	0.000	0.013	0.000
Phenathrene	6.50	0.006	1.120	0.001	0.430	0.000	0.430	0.000	0.120	0.000
Anthracene	0.49	0.005	0.230	0.002	0.031	0.000	0.094	0.001	0.010	0.000
Fluoranthene	6.49	0.006	3.280	0.003	0.870	0.001	0.494	0.000	0.120	0.000
Pyrene	10.40	0.010	2.07	0.002	1.080	0.001	0.640	0.001	0.180	0.000
Benzo(a)anthracene	0.73	0.073	0.81	0.081	0.280	0.023	0.170	0.017	0.012	0.001
Crysene	4.28	0.043	2.43	0.024	0.570	0.006	0.490	0.005	0.071	0.001
Benzo(b)fluoranthrene	1.86	0.190	0.74	0.074	0.380	0.038	0.200	0.020	0.042	0.004
Benzo(k)fluoranthrene	1.97	0.200	0.58	0.058	0.370	0.037	0.200	0.020	0.019	0.002
Benzo(a)pyrene	0.60	0.600	1.12	1.120	0.470	0.470	0.510	0.510	0.025	0.025
Indeno(1,2,3)perylene	0.82	0.082	1.10	0.110	0.300	0.030	0.210	0.021	0.017	0.002
Dibenzo(a,h)anthracene	1.62	1.620	0.30	0.300	1.130	1.130	1.010	1.010	0.090	0.090
Benzo(g,h,i)perylene	1.61	0.016	0.27	0.003	1.360	0.014	1.130	0.011	0.120	0.001
Total PAH	44.24	2.85	14.70	1.78	7.50	1.75	5.87	1.62	0.88	0.13

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