Prediction of Polycyclic Aromatic Hydrocarbons Toxicity Using Equilibrium Partitioning Approach and Narcosis Model

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Abstract The study underscores the use of equilibrium partitioning (EqP) to determine bioavailability and the narcosis theory to estimate toxicity of PAHs to benthic invertebrates. Eight PAHs (anthracene, azuleno(2,1-b)thiophene, benz(a)anthracene, carbazole, dibenzothiophene, benz(a)azulene, dibenzo(a,h)anthracene and phenanthrene) were identified with phenanthrene and carbazole recording the highest (6.29 $\mu\text{g/g}$) and least (0.06 $\mu\text{g/g}$) concentrations at both seasons. Based on EqP and Narcosis model, the sum of PAHs toxic unit ($\sum\text{TU}$), at both sites is $\ll 1$, suggesting no likelihood of PAHs toxicity to benthic invertebrates. The study suggests continuous PAH monitoring especially with aquatic species due to their transfer to human via food chain.

Keywords Sediments · Polycyclic aromatic hydrocarbons · Equilibrium partitioning · Toxicity units

PAHs are among the most widely distributed organic pollutants known to be thermodynamically stable (Chen et al. 2007). Because of their low aqueous solubilities (0.003–0.34 mg/L) and high octanol–water partition coefficient (log K_{ow} = 3.4–7.6), PAH compounds in aquatic

system tend to be associated with sediment and biota with reported cases of toxicity, carcinogenicity and mutagenicity (Koh et al. 2004; Kannan et al. 2005). Very few benchmarks have employed the use of equilibrium partitioning (EqP) theory to predict the biological effects of selected organic chemicals on aquatic organisms (Di Toro et al. 1991). In all these studies, the approach has been created for the protection of both freshwater and marine organisms and is applicable to benthic and water column organisms. It is based on the premise that contaminant distributions are predictable among the different compartments of the sediment matrix based on the physical and chemical properties of the sediment components. This method assumes that there is equilibrium between sediment and interstitial water and that chemicals are partitioned between interstitial water and sediment particles. The partitioning is determined primarily by the organic carbon content of the sediment (for nonionic organics), and the partitioning behavior of each particular chemical.

In a sediment system (Fig. 1), the predominant phases involved in EqP include the sediment organic carbon and dissolved phase (i.e., interstitial water). Based on EqP, if the sediment concentration of PAH and concentration of sediment organic carbon (f_{OC}) are known, the interstitial water concentration of PAH can be predicted. PAH belongs to a class of narcotic toxicants which frequently demonstrates additive toxicity. Generally, the predicted bioavailable PAH concentration by EqP is converted to toxic units based on narcosis theory. The toxic units of individual PAH are summed together. If the sum exceeds a value of 1, toxicity to benthic invertebrates is expected to occur (US EPA 2003). In this report, equilibrium partitioning (EqP) is employed in predicting PAH exposure concentrations, and narcosis theory is applied to determine whether or not sufficient PAHs are present to cause

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Fig. 1 Diagram of Important Sediment Phases Affecting the Bio-availability of PAHs in Sediments

adverse effects. This approach is based heavily upon the recently published EqP Sediment Benchmark (ESB) for PAH mixtures document prepared by the US EPA (2003). Hence, this report should be used in conjunction with US EPA (2003).

Materials and Methods

All chemicals, reagents and standards were, as far as qualitative parameters were concerned, in compliance with the regulations of the standardized and certified analytical methods. The sampling sites (Fig. 2) were divided into two (Ayetoro-Site A and Awoye-Site B). These are areas with reported cases of oil spillage from Shell and Chevron facilities in Ondo State, southwestern part of Nigeria (Ololade and Lajide 2009). At different seasons (dry and wet)

samples of sediments were collected randomly from each site based on APHA standard methods (Aderemi et al. 2003). Samples were collected and rapped inside aluminum foil after proper labeling. The samples were subsequently placed inside coolers containing ice-bag and transferred into the laboratory where they were preserved in the freezer prior to analysis. Organic carbon was determined following modified Walkley and Blacks method as described by Nelson and Sommers (1982).

About 100 g of partially thawed sediment samples were Soxhlet extracted with dichloromethane. After saponification with KOH and partitioned with n-hexane using separating funnel. Internal standard (phenanthrene, anthracene, carbazole and dibenzothiophene) were used. The final evaporation of the extracts was carried out under nitrogen gas and later chromatographed. The final extract was later analysed using GC–MS Hewlett–Packard (HP) 6890/5975 series instrument. The mass spectrometer was operated from 35 to 500 Dalton (SCAN mode). The peaks in the chromatogram were identified by comparison of the retention times and spectra of reference compounds with those in the sample. The peaks were quantified using the flame ionization detector (FID). The recovery and precision of the analytical procedure were tested using mixtures of some PAHs. Four PAHs (phenanthrene, anthracene, carbazole and dibenzothiophene) were employed as surrogate standards. An average of three parallel determinations was carried out for the recovery study. The average percentage recoveries varied from 87% for phenanthrene to 102% for

Fig. 2 Map of the study area (inserted is the area map of Nigeria and Africa showing the geographical location)

Table 1 Precision and recovery of standard PAH mixture

PAH	Retention time (min)	Recovery ^a (%)	Coefficient of variation (%)
Anthracene ^b	30.186	102.30 (0.71)	11.34
Carbazole	46.083	91.23 (0.74)	13.22
Dibenzothiophene	26.351	97.12 (0.93)	10.13
Phenanthrene ^b	30.383	87.24 (0.52)	9.36

^a Recoveries of three parallel determinations; values in parentheses are standard deviation

^b Compounds on the USEPA priority pollutant list

anthracene. The relative standard deviation and coefficient of variation did not exceed 0.93% and 13.22% respectively for any compound (Table 1).

Results and Discussion

The concentrations of detectable PAHs in the sediment across the study area are presented in Fig. 3. The trend in the concentrations at both seasons are almost similar but with the PAHs concentrating more during the wet season. Significant positive correlation ($\alpha = 0.01$) were observed between PAHs concentration originating from the two respective sampling sites during both seasons ($r = 0.998$ and 0.923) but without any significant mean difference ($p = 0.077$ and 0.118 , respectively). Though, dry season samples were first collected, it was thought that concentration during the wet season would be less due to the prevailing ecological conditions at that times. However, the increased levels during this period further implicate the continuous release of hydrocarbon residues into the area. It also re-affirms that sediments are capable of

adsorbing organic pollutants such as PAHs (Aderemi et al. 2003; Ololade and Lajide 2009).

However, using the EqP and Narcosis model (Table 2), which are both evaluated with non-alkylated PAHs, four non-alkylated PAHs were identified and consequently used in calculating the toxic units associated with the sediment rather than the recommended 34 by US EPA (2003). Apart from the sediment concentrations and sediment organic carbon (i.e., site data), all other information needed to adopt the EqP approach are obtained from US EPA (2003). This approach is suitable especially when less than the required 34 PAHs have been chemically analyzed as applicable in the present study. The highest and least bio-available concentrations of PAHs ($C_{OC,PAH}$, $\mu\text{g/g}_{OC}$) during the dry season (wet season in brackets) are 48.57 (63.00) and 0.68 (0.30) as recorded in phenanthrene and dibenz(a,h)anthracene respectively (Table 2). These concentrations are more realistic indicator of bioavailable PAHs. Using the values and the organic carbon normalized toxicity value (Table 2, from US EPA 2003), the sum of the toxic units are 0.139 and 0.207 at site A and B, respectively. These values are far less than the 1.0; hence, there is no likelihood that PAH toxicity to benthic organisms will occur. The sediments are therefore predicted not to exhibit chronic toxicity from PAHs (MacDonald and Ingersoll 2000; US EPA 2003). It must however be noted that sediment toxicity to benthic organisms can occur if the sum of toxic units is less than 1.0, but this will most likely be due to the presence of other toxicants including, possibly, unanalyzed PAHs.

Slight variations in PAH concentrations between sites suggests different sources of contamination. Changes in the PAH pattern may reflect changes in the source of PAHs such as coal, oil, gas, and petroleum combustion, and the resulting effect of combustion conditions. Based on the fact

Fig. 3 Mean concentrations of PAH in ($\mu\text{g/g}$)* in sediments from Ondo coast, Nigeria.

* Concentrations are means of triplicate analysis. DS: dry season; WS: wet season, ** compounds on the USEPA priority pollutant list. *** Cancer suspect

Table 2 Calculation of toxic units associated with sediment contaminated with four PAH across the two seasons

PAH	Concentration* ($\mu\text{g/g}$)	COC,PAH** ($\mu\text{g/g}_{\text{OC}}$)	COC,PAH,FCV*** ($\mu\text{g/g}_{\text{OC}}$)	Toxic units
Anthracene	2.190 (4.855)	32.93 (58.71)	594	0.055 (0.099)
Phenanthrene	3.231 (5.211)	48.57 (63.00)	596	0.081 (0.109)
Benz(a)anthracene	0.151 (0.121)	2.26 (1.45)	841	0.0027 (0.0017)
Dibenz(a,h)anthracene	0.045 (0.025)	0.68 (0.30)	1123	0.0006 (0.0003)
			$\Sigma = 0.1393$ (0.2070)	

Values in parentheses are results of site-B. Site-A: TOC = 6.65%; foc = 0.0665(goc/g); Site-B: TOC = 8.27%; foc = 0.0827(goc/g). Toxicity value (TU) = $C_{\text{OC,PAH}}/C_{\text{OC,PAH,FCV}}$ (US EPA 2003)

* Concentrations are mean of both seasons at each site; ** organic carbon normalized PAH concentration = ($\mu\text{g concentration/g}_{\text{DRY WT}} \times 100$) $\div$ % TOC; *** organic carbon normalized toxicity value (Obtained from US 2003)

FCV final chronic value ($\mu\text{g/L}$)

Fig. 4 a Composition pattern of PAH across both seasons by ring size at Site-A.
b Composition pattern of PAH across both seasons by ring size at Site-B

in Fig. 3, the LPAHs (<4rings) are the dominant hydrocarbons constituting about 97.1% and 98.7% at site-A and site-B respectively (Fig. 4a, b).

In the study, the TU did not suggest toxicity of PAH to benthic invertebrates based on narcosis model, however, probability for negative effects is high based on the fact that the concentration of PAHs measured in the sediments are comparable to other contaminated sites in which severe impacts have been observed (Ikenaka et al. 2005; Aderemi et al. 2003; Pavlora and Ivanora 2003). Thus, sediment-dwelling or burrowing organisms such as crabs, periwinkles e.t.c. are at the greatest risk especially during the wet season

because PAHs tend to remain bound to organic sediment (Kannan et al. 2003, 2005; Koh et al. 2004). Aquatic organisms that reside on the sediment surface, restricted to the water column only, are likely to receive less concentration from the sediment-bound PAH, and are therefore at less risk. It is also to be noted that some of the compounds identified (Fig. 3) in this study are those usually found in sediments, some of which have been reported to be carcinogenic and are on the US EPA priority list (Wang et al. 2008). The approach, particularly when used with other contaminated sediment assessment methods, offers risk assessors a useful tool for assessing the risk of PAHs to

benthic invertebrates at hydrocarbon waste sites. Based on the results of the study, continuous PAH monitoring studies are warranted in sediment samples from the study area.

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