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ESTIMATION OF TOXICITY EQUIVALENT CONCENTRATION (TEQ) OF CARCINOGENIC POLYCYCLIC AROMATIC HYDROCARBONS IN SOILS FROM IDU EKPEYE PLAYGROUND AND UNIVERSITY OF PORT HARCOURT CAR PARKS

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ABSTRACT

This article reported the outcome of investigations of the concentrations of Carcinogenic Polycyclic aromatic hydrocarbons (cPAHs) in soils around playground close to a crude oil flow station at Idu Ekpeye (a town near Port Harcourt) and car parks within University of Port Harcourt and use the data to determine the TEQ of cPAHs in the soils the various sites. All the seven cPAHs investigated were detected in all the sites. Ofrima Car Park (Pk 1) has highest concentration of TcPAHs and TPEC with values of 163.274 mg/kg and 37.522 mg/kg respectively, while Choba mini-park (Pk 2) has the lowest concentrations of TcPAHs and TPEC amongst the three sites with values of 42.474 mg/kg 9.877mg/kg respectively. All the sites exceeded the CAL-EPA BaP risk-based clean-up level of 0.132 mg/kg. Effective soil remediation and detoxification method like Dispersion by chemical reaction technology should be deployed to clean-up sites to avoid soil toxicity due to cPAHs.

Key Words; Tpec, Bap, PAHs, Carcinogens, PAHs, cPAHs,Toxicity, Soil.

INTRODUCTION

Polycyclic aromatic hydrocarbon (PAHs) can be grouped as organic compounds with more than one aromatic rings fused together and are produced mainly as by product of pyrolysis and or incomplete combustion of mostly fossil fuel or organic compounds, hence are naturally present in the environmental matrix. Anthropogenic sources include; tobacco smoking, coke production, processing of crude oil, industrial emissions, incineration, domestic heating and automobile emissions (Hites and Wagrowski, 1997)

Environmental risk assessments are periodically carried out to ascertain the level of risk posed by PAHs in the soil. Seven PAHs have been indicated by USEPA (1993a) as probable human (B2) carcinogens and they are benzo (a) anthracene, benzo (b) fluoranthene, benzo (k) fluoranthene, chrysene, Indeno (1,2,3-cd) pyrene, Dibenzo (a,h)anthracene and benzo(a) pyrene. PAHs could be mutagenic or carcinogenic. Benzo (a) pyrene (BaP) is among the numerous polycyclic aromatic hydrocarbons (PAHs) and it is the most investigated carcinogenic PAHs because of its potency and use as a toxicological symbol for all carcinogenic PAH. The assumption that most PAHs are of comparable toxicity with respect to Bap in most risk evaluation has led to overestimation of cancer and mutagen toxicity and potency of individual PAH as most PAHs are indeed considerably not as potent or toxic as BaP when analyzed using the same method. So many researchers have made serious attempts to ensure a more reliable risk assessment of potential exposures to environmental mixtures of PAHs, which include the Potency Equivalency factor (PEF) and Mutagenicity Equivalency Factor (MEF) (Iwuoha et. al, 2015; Kyung et.al. 2010; Durant et.al. 1996; Nisbet and LaGoy, 1992; Marty et. al. 1994; Wynder and Hoffmann, 1959).

Potency Equivalency Factor (PEF) is an evaluation of the relative potency and toxicity of chemical compound to a reference chemical compound such as BaP. Environmental mixtures of carcinogenic PAHs use Potency Equivalency factor to assess the potency or toxicity as well as the risks of environmental mixtures. PEF protocols are often streamlined to be in line with environmental current realities. In this way, the environmental matrix mixtures of cPAHs are normally considered as a single hazardous unit when estimating and evaluating compliance with clean up and remediation. The use of PEFs values for cPAHs as derived by the California Environmental Protection Agency, (California EPA, 2005) to assess the potency and toxicity of these environmental mixtures in assessing the cross-media matrix impact is very significant. The above agency indicated the PEFs for the minimum required cPAHs under WAC/173-340-708(e) and used 0.133 mg/kg for its risk-based cleanup levels for BaP (Department of Ecology, (2007). Other regulatory risk assessment risk-based clean-up levels for Polycyclic Aromatic Hydrocarbons in an environmental mixture like soils are available, such as MDNR (1993), New Jersey Register, (1992), U.S.E.P.A., (1993b) among others. They use variant derived figures of risk-based baseline cleanup level for BaP values of 0.33mg/kg, 0.66mg/kg and 0.1mg/kg respectively (Iwuoha et. al, 2015; Bradley et al.,1994).

Bradley et al., in 1994 investigated the background levels of PAHs and selected metals in New England urban soil and were of the view that background data should be integrated in achieving realizable target clean-up levels of PAHs in soils. Kyung et al., in 2010 investigated the benzo(a) pyrene-equivalent carcinogenicity and mutagenicity of residential indoor versus outdoor PAHs exposed to young children in New York city and concluded that during heating seasons, residential exposure to PAHs increases risk of cancer and mutation to young children. Iwuoha et al., in 2015 investigated the total potency equivalent concentration (TPEC) of cPAHs within Sugi-Bodo city and found that TPEC in the crude oil contaminated soils in Bodo areas were significantly higher than the risk-based clean-up levels.

In car parks, countless vehicles are either entering, leaving or are stationary at designated positions with heavy human presence. PAHs from the automobile engines (oil and fuel) can enter the environment through air and soil at these sites. The PAHs particulates in the air are gradually adsorbed on the top soil around the car parks because soil acts as one of PAHs natural sinks (Nadal et. al 1994). Heywood et al., in 2006 noted that the loading of PAHs in top surface soil is directly related to cumulative atmospheric deposition, minus volatized PAHs, its biodegradation and mixing-depth ratio. In urban areas, PAHs concentrate in top soils

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close to its point source with higher amount of organic matter, (Villaverde et al, 2008). The people who found pleasure hanging out at the car parks could be at higher risk of exposure through contact with contaminated soils in the vicinity.

The focus of this article is to estimate the Toxicity Equivalent Concentration (TEQ) of cPAHs in the soils around playground and car parks in the University of Port Harcourt in Port Harcourt province from their PAHs data. The outcome will be informative enough to precipitate the most suitable response from the University Management and would also serve as baseline study for future monitoring.

MATERIAL AND METHODS

Description of Study Area and Sampling

The three sampling sites are located within Port Harcourt province in Rivers State Nigeria. Two of the sampling sites are located in Car parks within the University of Port Harcourt (Uniport) namely; the Ofrima Car Park (Pk 1) where staff park their vehicles and Choba car park (Pk 2), which is a campus public park in Uniport with geographical coordinates of 4^0 47^1North $6^0 59^1$ East. The other site is a playground (Pg) near a crude oil flow station in Idu Ekpeye with geographical coordinates of latitude 5.083 and longitude 6.55.Top soils were collected at various designated locations and stored in different clean dry bottles. The corked bottles with the soil samples were taken to the laboratory of Jawura Environmental Services Port Harcourt for analysis.

Sample Preparation and Analysis of PAHs

The soil sample extract was partitioned into saturated hydrocarbon and polycyclic aromatic hydrocarbons in a column chromatography. The polypropylene column was prepared by parking glass wool at the base of the chromatographic column which support the stationary phase made of baked 10g silica gel packed in the column. The column was filled with eluent and the soil sample extract injected slowly. Slowly 60ml of n-hexane was used to elute the aliphatic saturated hydrocarbon fractions of the soil extract in the column and the eluent collected with a beaker. 40ml of dichloromethane (DCM) was used to elute the PAH fractions. The eluents were collected differently with conical flask and then concentrated with rotary evaporator at 60^0C. The different partitions were later analyzed with Gas Chromatography coupled to a Flame ionization Detector, Agilent 6890 model with Chemstation 32 software. Test method (1997); Method for the determination of EPH (1995).

RESULTS

Table 1: Concentrations (mg/kg) of PAHs in soil samples of Idu Ekpeye playground and parks 1and 2, (i.e. Pk 1 and Pk 2 at Ofrima and Choba parks respectively) in University of Port Harcourt.

Names of PAHs	Pg (mg/kg)	Pk 1 (mg/kg)	Pk 2 (mg/kg)	Total site (mg/kg)
Naphthalene	1.669	-	-	1.669
2-Methyl Naphthalene	-	-	-	-
Acenaphthalene	1.533	-	-	1.533
Acenaphthene	2.080	1.912	-	3.992
Fluorene	2.228	1.796	-	4.024
Phananthrene	2.312	2.050	-	4.362
Anthracene	5.000	5.588	2.572	13.160
Fluoranthene	9.230	8.429	2.144	19.803
Pyrene	15.731	12.790	3.528	32.049
Benzo (a) Anthracene	10.575	23.672	3.237	37.484
Chrysene	7.965	14.309	5.257	27.531
Benzo (b) Fluoranthene	5.675	18.715	4.690	29.080
Benzo (k) Fluoranthene	6.422	16.798	6.835	30.055
Benzo (a) pyrene	6,737	24.980	6.780	38.497
Benzo (g,h,i) Perylene	5.069	20.373	5.055	30.497
Dibenzo (a,h) Anthracene	23.059	38.649	8.851	70.559
Indeno (1,2,3-cd) Pyrene	31.437	26.151	6.824	64.412
Total PAHs	136.725	216.211	55.794	408.730

Table 2: Concentrations (mg/kg) of cPAHs in soil samples collected of Idu Ekpeye playground (Pg) and parks 1and 2, (i.e. Pk 1 and Pk 2 at Ofrima and Choba) respectively in University of Port Harcourt.

Name	Pg (mg/kg)	Pk 1 (mg/kg)	Pk 2 (mg/kg)
Benzo (a) Anthracene	10.575	23.672	3.237
Chrysene	7.965	14.309	5.257
Benzo (b) Fluoranthene	5.675	18.715	4.690
Benzo (k) Fluoranthene	6.422	16.798	6.835
Benzo (a) pyrene	6.737	24.980	6.780
Dibenzo (a,h) Anthracene	23.059	38.649	8.851
Indeno (1,2,3-cd) Pyrene	31.437	26.151	6.824
Total cPAHs	91.87	163.274	42.474

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Table 3: Potency Equivalent Concentrations (PEC) in mg/kg of cPAHs in soil samples of Idu Ekpeye playground Pg and parks 1and 2, (i.e. Pk 1 and Pk 2 at Ofrima and Choba respectively) in the University of Port Harcourt.

cPAHs	(PEC)Pg	(PEC)Pk 1	(PEC)Pk 2
Benzo (a) pyrene	6.737	24.98	6.78
Benzo (a) anthracene	1.058	2.367	0.324
Benzo (b) fluoranthene	0.568	1.872	0.469
Benzo (k) fluoranthene	0.642	1.68	0.684
Chrysene	0.079	0.143	0.053
Dibenzo(a,h) anthracene	2.306	3.865	0.885
Indeno (123cd) pyrene	3.144	2.615	0.682
TEQ/TPEC	14.534	37.522	9.877

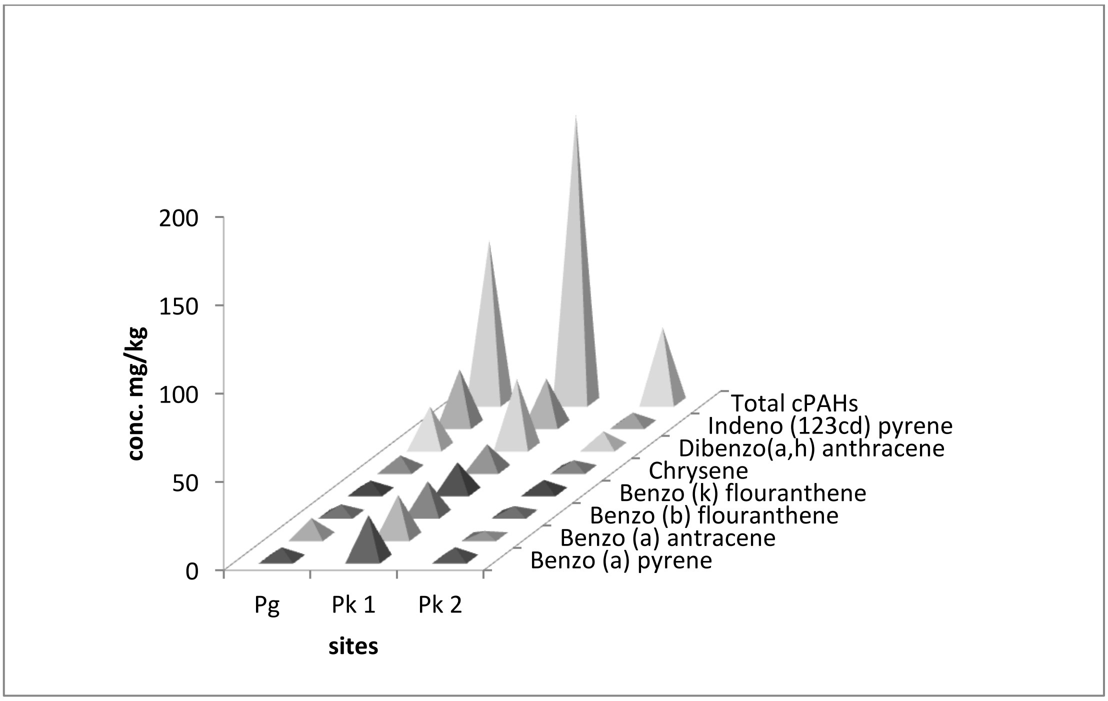

Fig. 1 Graphs of cPAHs and Total cPAHs at Idu Ekpeye playground Pg, Pk1 and Pk2.

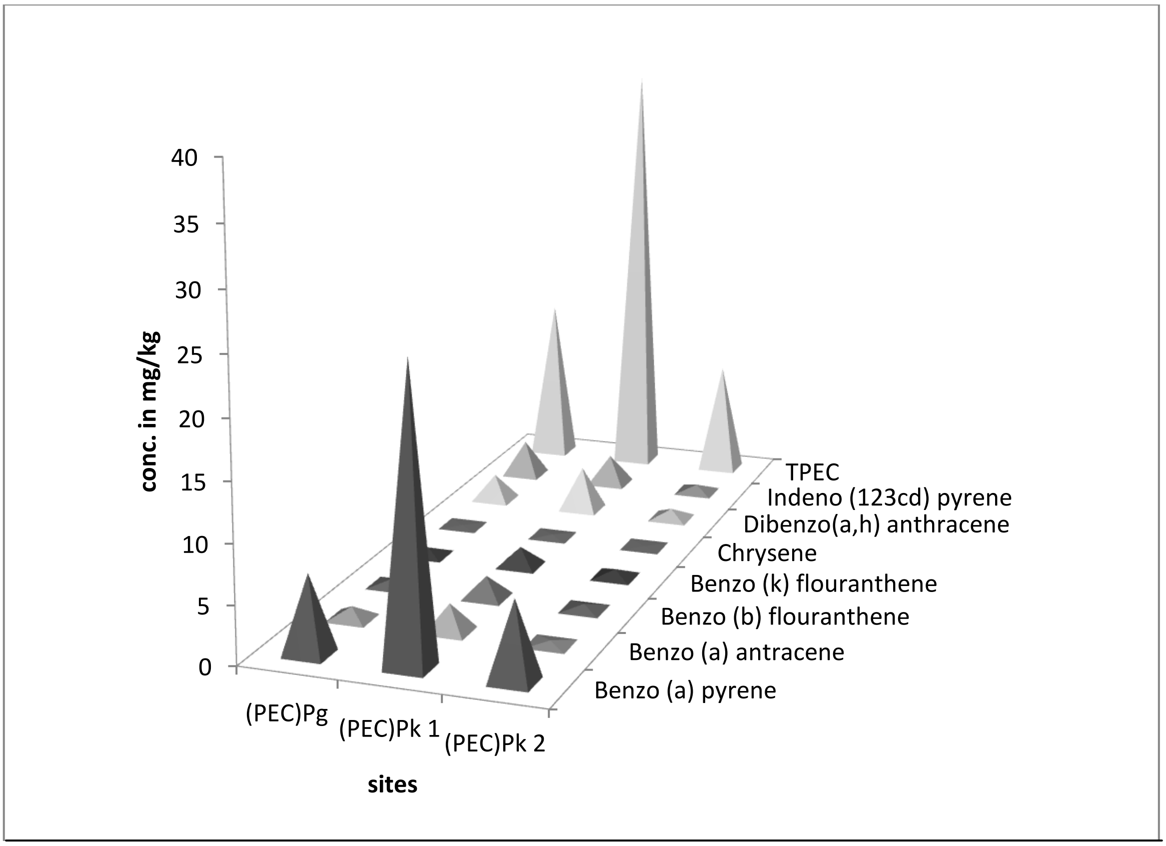

Fig. 2 Graph of (TEQ) TPEC and PEC of cPAHs at the sites of Idu Ekpeye Pg, Pk1 and Pk2 respectively.

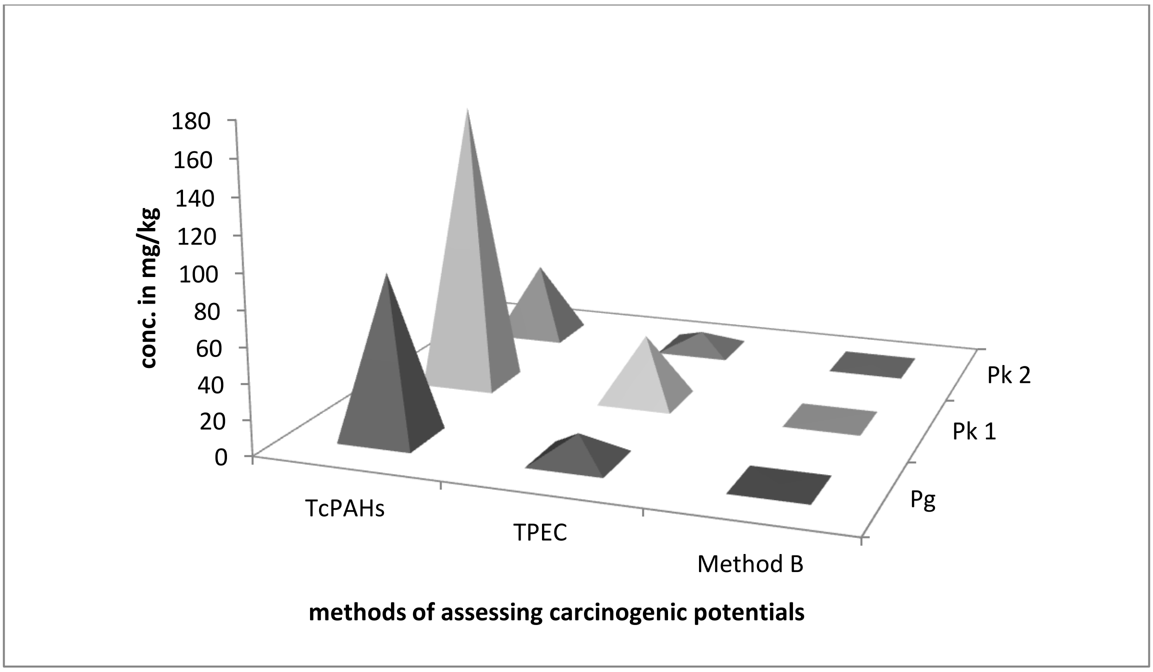

Fig. 3 Graph of TcPAHs, TPEC (TEQ), and Method B at the sites of Idu Ekpeye Pg, Pk1 and Pk2 respectively.

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The results of PAH analyses are presented in Table1. Tables 2 and 3 represent the various concentrations (mg/kg) of cPAHs in soil samples collected at Idu Ekpeye playground (Pg), Ofrima car park (pk1) and Choba park (pk 2) in the University of Port-Harcourt and the result of various concentrations (mg/kg) of potency equivalent concentration of the cPAHs.

The values in Table 1 indicates that Pk 1has the highest overall PAHs concentration followed by Idu Ekpeye playground site Pg and lastly the Choba park site Pk 2. Furthermore the table above shows PAHs with lower molecular weights like anthracene, phenanthrene, fluorine, acenaphthalene, naphthalene, acenaphthene, 2-methyl Naphthalene are much less present in the various soil sites relative higher molecular weight PAHs like Dibenzo (a,h) anthracene, indeno (1,2,3-c-d) pyrene, benzo (a) pyrene etc. This trends is not unconnected to the higher solubility in water and volatility of the lower molecular weight fraction relative their higher molecular weight ones. This implies washing away and the escape into the atmosphere as soon as the lower fraction of PAHs accumulate in the soil sites leaving the higher fractions behind, which are known to be teratogenic, carcinogenic and mutagenic to humans.

All the cPAHs namely; benzo (a) anthracene, chrysene, benzo(b) fluoranthene, benzo(k) fluoranthene, benzo (a) pyrene and dibenzo (a, h) anthracene were detected. Ofrima car park (pk 1) had the highest concentration of the cPAHs while Idu Ekpeye playground had the highest individual indeno (1, 2, 3 c-d) pyrene concentration of 31.437 mg/kg, as shown figure 1.

The clean-up levels and risk calculation were done using the Model Toxic Control Acts (MTCA). The MTCA was strictly followed in the estimation of TEQ. The Potency Equivalent Concentration (PEC) in mg/kg for soils at playground (Pg) in Idu Ekpeye for the individual cPAHs i.e., benzo (a) pyrene, benzo (a) anthracene, benzo (b) fluoranthene, benzo (k) fluoranthene, chrysene, dibenzo (a,h) anthracene and indeno (1,2,3-cd) pyrene are 6.737, 1.058, 0.568, 0.642, 0.079, 2.306 and 3.144 respectively. The Potency equivalent concentration (mg/kg) for soils at car park (pk 1) in Ofrima for the individual cPAHs i.e., benzo (a) pyrene, benzo (a) anthracene, benzo (b) fluoranthene, benzo (k) fluoranthene, chrysene, dibenzo (a,h) anthracene and indeno (1,2,3-cd) pyrene are 24.98, 2.367, 1.872, 1.68, 0.143, 3.865, and 2.615 respectively. The Potency equivalent concentration (mg/kg) for soils at Choba park (pk 2) in Uniport for the individual cPAHs i.e., benzo (a) pyrene, benzo (a) anthracene, benzo (b) fluoranthene, benzo (k) fluoranthene, chrysene, dibenzo (a,h) anthracene and indeno (1,2,3-cd) pyrene are 6.78, 0.324, 0.469, 0.684, 0.053, 0.885 and 0.682 respectively.

Individually these PEC values of cPAHs are not enough for expressing the extent of toxicity of the cPAHs and must be examined as a unit hazardous environmental substance to know if the sites require detoxification and remediation. The TEQ or TPEC for the cPAHs at Pg, Pk1 and Pk 2 sites are respectively 14.534, 37.522 and 9.877 mg/kg in these specified soil samples exceeded by far the method B cleanup levels for BaP, i.e. 0.137mg/kg, which is approximately 0.1mg/kg.

All three calculated sites (Pg, Pk 1 and Pk 2) for TPEC exceeded the CAL-EPA, (2005) risk-based Bap clean-up levels of approximately 0.1mg/kg by 145.3, 375.2 and 98.7 times respectively and hence needs massive clean-up and effective remediation strategy.

The various ways of representing the carcinogenic potential of cPAHs in these soils are expressed in figure 3 (across the three sites). The peaks of TcPAHs across three sites are higher than the peaks of TPEC across the three sites respectively because they are additives of the individual cPAHs but do not really reflect on the actual toxicity potential of the cPAHs in the environmental mixture of the sites which the TPEC/TEQ peaks actually did represent. The TPEC peak for soils of Ofrima Park (Pk 1) in figure 3 stood out in all TPEC peaks (peaks at sites Pg, Pk1and Pk2) as the most potent carcinogenic soil amongst the three sites' TPEC even though other sites exceeded baseline clean-up levels. This is due to endless emissions of PAHs in surrounding air and deposition of PAHs in soil from automobiles which eventually settle along soils sandwiched between the concrete pavements at Ofrima Car Park. The design pattern makes soils at Pk 1 reservoir for pollutants like PAHs specifically the higher molecular weight fractions to sink or settle in the soil, whereas at other sites the top soils are easily flushed away by water current during heavy rains.

In conclusion the seven cPAHs investigated were detected in all the sites with high levels of TEQ indicating soil toxicity of cPAHs. Ofrima Car Park (Pk 1) has highest concentration of cPAHs and TEQ while Choba mini-park has the lowest concentrations amongst the three sites. All the sites exceeded the CAL-EPA BaP risk-based clean-up level of 0.132 mg/kg. Effective soil detoxification method such as dispersion by chemical reaction technology could be deployed to clean-up the sites to avoid soil toxicity due to PAHs.

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