POLYCYCLIC AROMATIC HYDROCARBONS IN URBAN SOILS OF KEMAMAN

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Abstract

A study has been carried out to determine the concentration and distribution of polycyclic aromatic hydrocarbons (PAHs) in urban soils of Kemaman, Terengganu. Surface soil samples (< 500 μm) were ultrasonicated using dichloromethane as solvent and the extracts fractionated on silica-alumina column. Detection and quantification of 16 priority PAHs compounds were carried out using GC-FID. With the exception of two stations, results generally indicated that the sum of 16 priority PAHs concentration (total PAHs) in soils ranged from to 6.3 to 176 μg/kg (dry weight); the two stations which exhibited significantly higher levels of total PAHs was at the main road junction located at the heart of the commercial centre of the town (535 μg/kg) and at an industrial estate, adjacent to a sawmill (547 μg/kg). Statistical analysis suggests that there is a significant difference in total PAHs concentration ($p<0.05$) with sampling sites. Most common PAHs compound observed in almost all the soil samples was BgP indicating the importance of vehicular emission as a source of PAHs in these soils. In addition, contribution of biomass burning to the presence of PAHs in these soils was also observed as indicated by a positive correlation between Benzo[a]pyrene with total PAHs.

Abstrak

Satu kajian bagi menentukan kepekatan dan agihan hidrokarbon polisiklik aromatic (PAH) dalam tanah di Bandar Kemanan, Terengganu telah dijalankan. Sampel tanah permukaan (< 500 μm) diekstrak menggunakan kaedah pengekstrakan ultrasonik dengan DCM sebagai pelarut dan hasil ekstrak dipisahkan menggunakan turus silika-alumina. Pengenalpastian dan pengkuantitian 16 sebatian PAH keutamaan dilakukan menggunakan GC-FID. Keputusan secara amnya menunjukkan bahawa jumlah PAH dalam tanah adalah dalam lingkungan 6.3 μg/kg ke 176 μg/kg (berat kering) kecuali pada dua stesen dimana kepekatan adalah jauh lebih tinggi; satu stesen terletak di simpang jalan utama di kawasan pusat Bandar (535 μg/kg) dan satu lagi terletak di kawasan estet perindustrian, berhampiran kilang kayu (547 μg/kg). Analisis statistik menunjukkkan bahawa terdapat perbezaan ketara dalam kepekatan PAH jumlah diantara stesen persampelan. Hampir semua sampel tanah mengandungi BgP dimana kehadirannya sering dikaitkan dengan sumber kenderaan bermotor manakala sumbangan daripada sumber pembakaran biojisim terhadap kandungan PAH dalam tanah juga dikenalpasti berdasarkan korelasi positif antara BaP dan total PAH.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the global environment and soil remains as one of the most important sinks for these compounds. Due to their mutagenic and carcinogenic potentials as well as their persistence, the presence of PAHs in the environment is of great global concern. PAHs are formed from the incomplete combustion of fossil and biomass fuels. Main sources of these compounds in soil include wildfires and biomass burning for agricultural land clearing, municipal incinerators, vehicular emission, residential heating and through the atmospheric deposition as a result of long-range atmospheric transport [1-6]. In this context, knowledge on the PAHs level and its dispersion on regional and national scale are essential. At present in Malaysia, even though studies to determine the concentration, composition and possible sources of PAHs in soils are being reported in the literature [7,8], this type of studies is still limited, particularly in the east coast states of Peninsular Malaysia. In view of this, a study has been initiated to address this gap in knowledge. This paper presents the results of a study to determine the concentrations, composition and possible sources of PAHs in soils of Chukai, the capital of the district of Kemaman, Terengganu, Malaysia.

Experimental

Study area and sampling

Chukai with a population of 45,873 density, lies on the southeast end of the Terengganu state (Fig.1a) and is sandwiched between the booming oil town of Kerteh, Terengganu and the fast growing industrial area of Gebeng, Pahang. It acts as the center for business activities and public agencies for the fastest growing district in the state of Terengganu, largely due to the booming petroleum and related industries in Paka-Kerteh belt. Owing to its strategic location, Chukai also acts as a residential town to those who work in Paka-Kerteh belt as well as Gebeng and Kuantan, the capital of Pahang.

Soil sampling was carried out around the urban area of Chukai (Table 1 and Fig. 1b). These sites were chosen based on traffic density, residential and industrial activities and were generally diffuse source oriented. Where possible soil samples were collected ca. one metre from the roadside. Twenty sampling sites were ascertained and classified to three zones. Zone A was located in the centre part of this town, where most of the economic activities were found with major road network, Zone B emphasized on residential areas whereas Zone C is located in the industrial zone of the town. Sampling involved the collection of 20 surfacial soil samples (0-10 cm) using metal spades, wrapped in pre-cleaned aluminum foil and transported to the laboratory in an icebox to minimize sample degradation. Once in the laboratory, soil samples were homogenized and sieved through a 500 μm sieve.

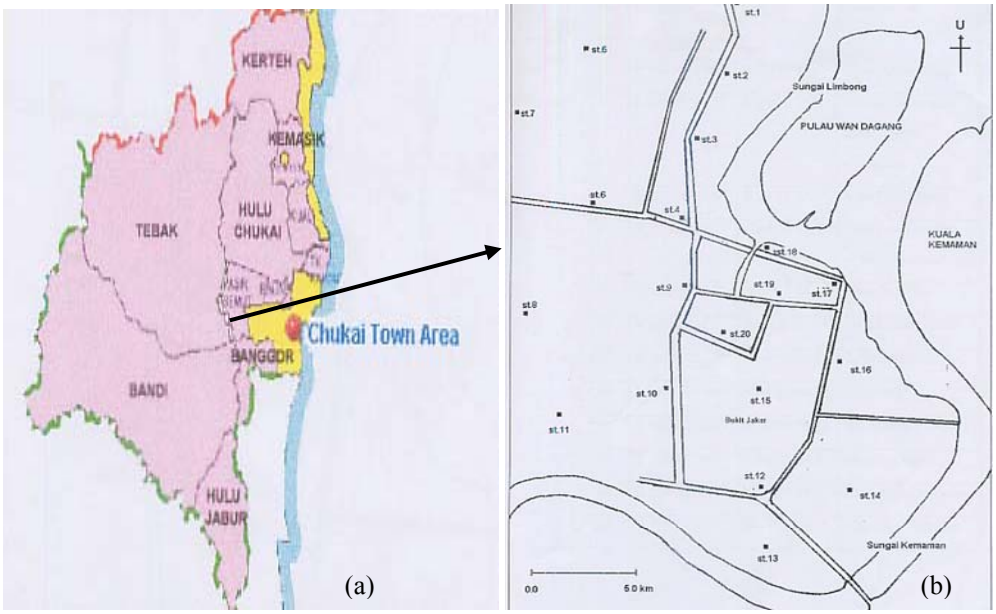

Figure 1. Chukai Town Map (a) and Sampling site map (b)

Table 1 : Longitude and latitude of the sampling site

Zone	Site No	Longitude	Latitude	Sampling Sites
Zone A	1	E 103°25'29.5''	N 04º15'07.4''	Jln Bakau Tinggi
	2	E 103º25'29.5''	N 04º14'50.8''	Sek. Men. Sultan Ismail Kemaman
	3	E 103º25'19.0''	N 04º14'21.4''	Jln Penghiburan
	4	E 103º25'02.5''	N 04º14'21.4''	Center Road Junction of Jln Da Omar
	9	E 103º25'17.3''	N 04º13'56.4''	Jln Da Omar
	10	E 103º25'11.2''	N 04º13'27.0''	Jln Kubang Lurus
	15	E 103º25'25.8''	N 04º13'39.1''	Bukit Jakar
	16	E 103º25'43.5''	N 04º13'49.6''	Jln Jakar
	17	E 103º25'10.1''	N 04º14'09.1''	Bus station
	18	E 103º25'38.8''	N 04º13'54.2''	Jln Sulaimani
	19	E 103º25'33.5''	N 04º13'48.7''	Jln Abd. Rahman
	20	E 103º25'25.8''	N 04º13'39.1''	Jln Mak Donyang
Zone B	5	E 103°24'31.7''	N 04º14'44.8''	Kg Gong Limau
	6	E 103°25'02.5''	N 04º14'10.2''	Jln Air Putih
	7	E 103°23'24.4''	N 04º14'16.0''	Kompleks Quarters Pend. Kemaman
	8	E 103°23'06.0''	N 04º13'31.7''	Kg Mentok
	11	E 103°24'49.6''	N 04º13'32.6''	Jln Pengkalan Lama
Zone C	12	E 103°25'20.8''	N 04º13'10.8''	Jln Jakar (Fire Station)
	13	E 103°25'31.3''	N 04º12'59.6''	Jakar II Industrial Estate (electronic)
	14	E 103°25'48.2''	N 04º13'22.6''	Jakar I Industrial Estate (sawmills)

Analytical procedure

PAHs were extracted from soils (< 500 μm fraction) with dichloromethane (DCM) as solvent using ultrasonic method. The extracts were then fractionated on partially deactivated (5%) silica-alumina columns. PAHs compounds were eluted using a combination of 20ml of 10% DCM in hexane followed by 20ml of 50% DCM in hexane [9].

Identification and quantification of the 16 priority PAHs compounds were carried out using gas chromatography fitted with flame ionization detector (GC-FID) based on the retention times compared to that of external PAHs standards. These compounds were naphthalene (NAP), acenaphtylene (ACY), acenaphtene (ACE), fluorene (FLU), phenanthrene (PHEN), anthracene (ANT), fluoranthene (FTH), pyrene (PYR), benzo(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenz(a,h)anthracene (DA), benzo(g,h,i)perylene (BgP) and indeno(1,2,3,cd)pyrene (IP). Sums of these 16 compounds were collectively known as total identified PAHs (TIP).

The GC-FID with fused silica column (30 m x 0.25 mm i.d.; 0.25 μm filmed thickness); was set with injection temperature of 290°C using a splitless mode; column temperature was programmed at hold at 50°C for 1 min, first temperature ramp of 50 - 140°C at 5°C min^{-1} followed by the second temperature ramp of 140 - 290°C at 3°C min^{-1} and then maintained at 290°C for 13 min resulting in a total run time of 82 min; helium was used as the carrier gas with a flow rate at 1.2 mL. min^{-1}; detector temperature was set at 300°C.

Total organic carbon (TOC) in soils was analysed using Walkley and Black's rapid titration method [10].

Results and Discussion

Soil Organic Carbon (SOC)

Numerous studies have shown that PAHs are strongly retained by the soil matrix [11, 12]. The partitioning concept of soil sorption of organic contaminants implies that the sorption of hydrophobic organic molecules is determined by the organic carbon content of the substrate [13-14]. The organic matter content is considered to be a very important variable related to PAHs pollution of soils [15]. In this study, the soils exhibited rather low

organic carbon content with values ranging from 0.09% to 0.53% with a mean of 0.27% (Table 2 and Fig. 2). A regression analysis (Fig. 3) showed a negative and weak relationship between the concentrations of the TIP and the amounts of soil organic carbon (SOC, %). Because of the very low SOC in soils, it is probable that this parameter does not play an important role in influencing the concentration of TIP in these soils.

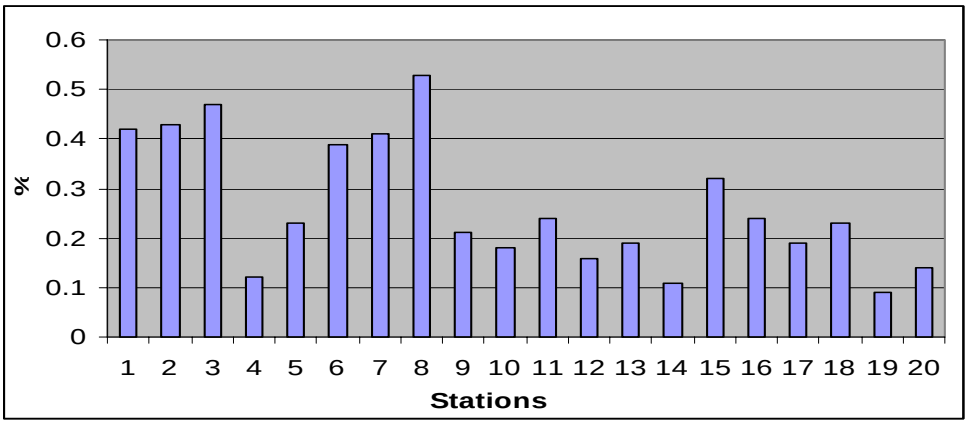

Figure 2: Distribution of SOC in soil samples

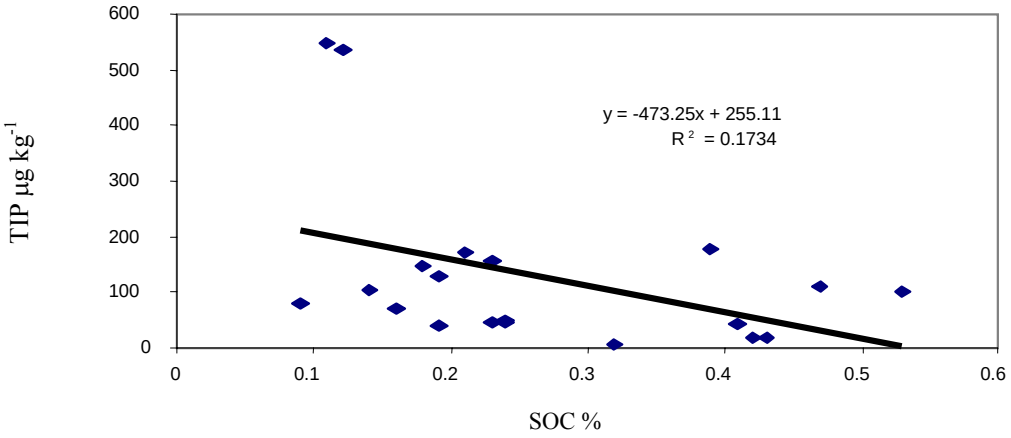

Figure 3: Correlation between TIP and SOC

Total identified Polycyclic Aromatic Hydrocarbon (TIP)

The distribution of TIP obtained in this study is shown in Figure 4. With the exception of two stations (Stations 4 and 14) which exhibited significantly higher TIP than the other remaining stations, the range of TIP values found in this study was between 6.27 µg/kg to 176.3 µg/kg (Table 2); the mean concentration of TIP values obtained for the 20 sites was 129.7 µg/kg whilst the median was 101.4 µg/kg. Statistical analysis showed significant differences ($p<0.05$) of TIP values between the stations monitored. These values are generally in great excess of the reported natural concentration of PAHs in soil (1-10 µg/kg) [16] but within similar range to those reported in soils of Kuala Lumpur [7, 17] and Kuala Terengganu [8]. Comparison between the three sampling zones showed that TIP values in Zone A ranged from 6.27µg/kg to 534.6µg/kg with mean value of 127.2 µg/kg and a median of 106.1µg/kg, Zone B ranged 43.66µg/kg to 176.3µg/kg with mean value of 82.08µg/kg and a median of 44.62µg/kg and Zone C ranging from 71.13µg/kg to 547.3µg/kg with mean value of 219.0 µg/kg and a median of 71.13µg/kg. The stations which recorded exceptionally high TIP values were located in Zone A and Zone C, respectively and it is conceded that their values does exhibit an influence on the mean values calculated for the respective zone, particularly in the case of Zone C where there were only three stations monitored; Station 4 was located at the busiest road junction in Chukai (Zone A) whereas Station 14 is located in the vicinity of a sawmill in Zone C. In addition, as expected, it was also observed that most of the sampling sites located by major roadside generally exhibited relatively higher TIP values (e.g. Stations 3, 4, 8, 9, 10) than sites located in the residential areas (Stations 5, 7, 11, 16).

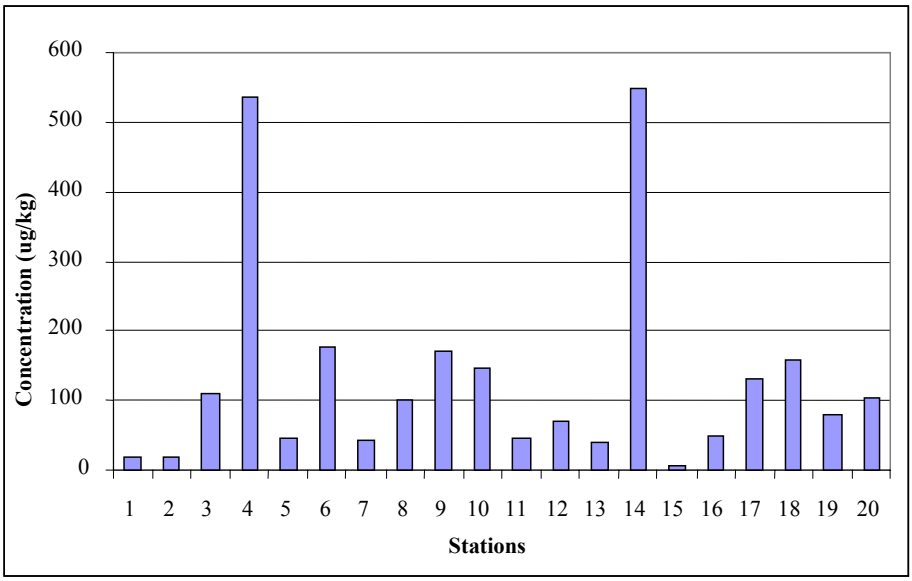

Figure 4: Distribution of TIP in soil samples

The distribution of the 16 PAHs compounds monitored at each sampling site were found to differ with stations, with station 4 showing the presence of all compounds except the very low molecular weight PAHs (with two benzene rings), viz. NAP, ACY and ACE. In fact, NAP was absent from all stations whilst ACY and ACE were found in only few stations at rather low concentrations (< 3 µg/kg). This observation is not surprising as these compounds are generally more volatile compared to the other higher ring number PAHs [18, 19]. Almost all stations exhibited the presence of BgP, the heavy molecular weight PAHs commonly associated with vehicular emissions resulting from internal engine combustion of gasoline [20]; BgP concentration found in this study ranged from 22.08µg/kg to 126.44µg/kg with station 4 exhibiting highest BgP concentration relative to other stations. Other high molecular weight PAHs that were present in almost all stations monitored includes DA and IP. BaP, a high molecular weight PAHs generally taken as a signature of an incomplete burning of biomass or organic matter was also present but only at selected stations with station 14 exhibiting extremely high concentration of this compound (423.5 µg/kg) accounting > 70% of the PAHs recorded for this site. These observations are consistent with the fact that Station 4 is located at the busiest road junction in Chukai whilst Station 14 is located in the vicinity of a sawmill with obvious signs of wood burning activities.

Table 2 : TIP and selected parameters

Site No	TOC %	TIP (µg/g)
1	0.42	19.53
2	0.43	19.32
3	0.47	109.2
4	0.12	534.6
5	0.23	44.47
6	0.39	176.3
7	0.41	43.66
8	0.53	101.4
9	0.21	170.4
10	0.18	146.8
11	0.24	44.62
12	0.16	71.13
13	0.19	38.66
14	0.11	547.3
15	0.32	6.27
16	0.24	49.92
17	0.19	130.1
18	0.23	157.1
19	0.09	80.48
20	0.14	102.9

Phenanthrene to antracene ratio (PHEN/ANT) has often been used to investigate possible sources of PAHs compounds in the environment where a low ratio (PHEN/ANT < 10) is generally considered as indicative of a predominance of pyrolytic sources (i.e. combustion sources) over petrogenic sources (i.e. oil spill) [21-24]. In this study, the PHEN/ANT ratios in soil samples of Chukai ranged from 1.2 to 7.5 suggesting that the PAHs compounds found in these soils were derived from pyrolytic sources.

Differentiating between the two major pyrolytic source, viz. internal engine or biomass combustion require the use of other molecular markers; as indicated above, presence of BaP in the environment is generally indicative of incomplete combustion sources, in particular combustion of organic whilst the association of BgP with vehicular emission has long been established [20]. A linear correlation analysis between TIP and BaP and between TIP and BgP for the 20 stations monitored gave an r-value of 0.68 and 0.58, respectively (Figs.5 and 6) which suggest that both sources contribute to the presence of PAHs in these soils. Station 14 is interesting in that BaP contributes over 70% of the TIP observed at the station, thus to eliminate possible bias, a second linear correlation analysis was calculated between TIP and BaP and between TIP and BgP by excluding this station giving an r value of 0.44 and 0.86. Similarly, since Station 4 is suspected to have a high contribution from vehicular emission, another correlation analysis was carried out by removing the contributions of the two extreme stations; the r value obtained was 0.41 and 0.63 for correlation between TIP and BaP and between TIP and BgP, respectively. The results of the latter two correlation analyses clearly show a stronger correlation exist between BgP and TIP suggesting that vehicular emissions is the more dominant contributor to the PAHs in the soils around Chukai. The contribution from the vehicular emission is expected as samplings were conducted in an urban area with a number of stations located close to major trunk road. The presence of a relatively weaker but positive correlation between BaP and TIP suggests that biomass burning also contributes to the presence of PAHs in these soils. Apart from Station 14, it is most likely that these PAHs were contributed from activities of open burning of rubbish and garden refuse by local residents [17] which are still prevalent in the east coast states particularly in Terengganu and Kelantan.

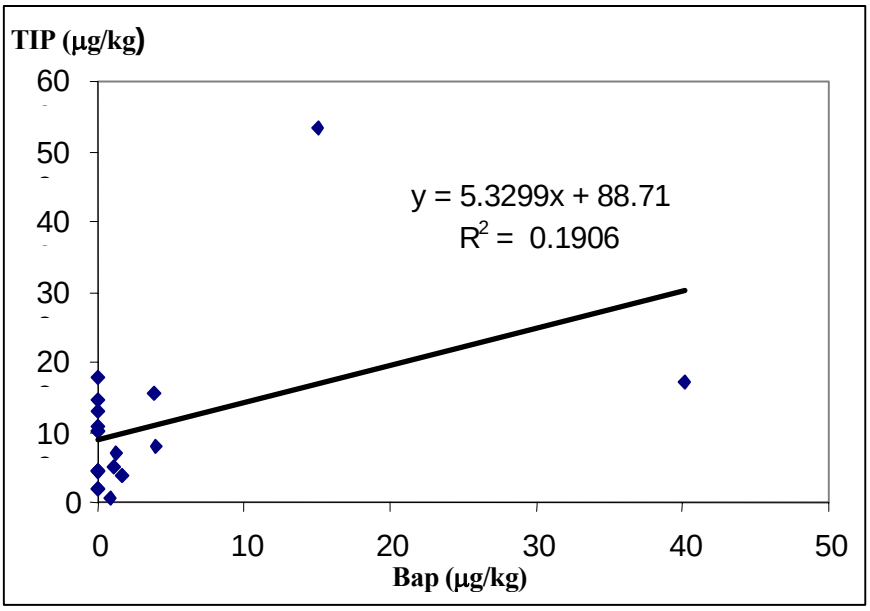

Figure 5: Correlation between TIP and BaP (20 stations)

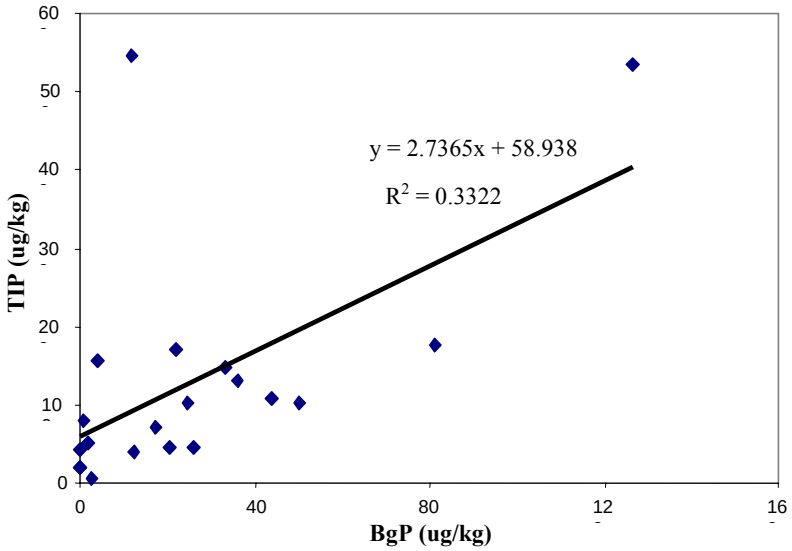

Figure 6: Correlation between TIP and BgP (20 stations)

Conclusion

Total concentration of PAHs found in urban soils of Chukai, Kemaman ranged from 6.27 µg/kg to 547.3 µg/kg with two stations exhibiting exceptionally high TIP values. Almost all stations showed the presence of BgP, a signature PAHs compounds known to be associated with vehicular emissions resulting from gasoline combustion in engines. A strong correlation between BgP and TIP and low PHEN/ANT ratio (< 10) provide further evidence for the importance of vehicular emission sources of PAHs in these soils. In addition, contribution of biomass burning to the presence of PAHs in these soils, through open burning of rubbish and
garden refuse by local residents, was also observed as indicated by a positive albeit a weaker correlation between BaP with TIP relative to the correlation between BgP and TIP.

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